An-Najah National University

Faculty of Graduate Studies

Synthesis of 1-(Pyrrol-2-yl) imine modified silica as a new sorbent for the removal of hexavalent chromium from water

By

Ghadeer "Mohammed Moen" Nemer Hanbali

Supervised
Prof. Shehdeh Jodeh
Co- Supervised
Prof. Ismail Warad

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

2016

Synthesis of 1-(Pyrrol-2-yl) imine modified silica as a new sorbent for the removal of hexavalent chromium from water

By

Ghadeer "Mohammed Moen" Nemer Hanbali

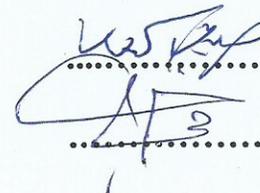**This Thesis was Defended Successfully on 15/6/2016 and approved by:**

Defense Committee Members	Signature
1. Prof. Shehdeh Jodeh /Supervisor	....
2. Prof. Ismail Warad/ Co-Supervisor	....
3. Dr. Subhi Samhan / External Examiner	....
4. Dr. Ibrahim Abu Shqair / Internal Examiner	....

Dedication

To my father and my mother who taught me

how to give

To my beloved husband Motasem

To my brothers and sister

To all my friends who spare no effort to help

To all the martyrs of Palestine

I dedicate this modest work

Acknowledgements

List of Contents

List of Tables

Table	Content	Page
2.1	Physical and chemical properties of Cr.	8
2.2	Comparison between Physisorption and Chemisorption.	24
4.1	Langmuir isotherm model parameters and correlation coefficient for adsorption of Cr(VI) on (Si-NPr).	57
4.2	Freundlich isotherm model parameters and correlation coefficient for adsorption of Cr(VI) on (Si-NPr).	59
4.3	Parameters and correlation coefficient of Langmuir, Freundlich for adsorption of Cr(VI) on (Si-NPr).	59
4.4	The values of calculated thermodynamic parameters of Cr (VI) adsorption.	61
4.5	Pseudo first order and pseudo second order kinetic model parameters for Cr (VI) adsorption on Si-NPr at 25ºC.	65

List of Figures

List of Abbreviation

Symbol	Abbreviation
AAS	Atomic absorption spectroscopy
C_o	Concentration of for Cr(VI) in the sample solution before treatment (mg/L)
C_e	Concentration of for Cr(VI) in the sample solution after treatment (mg/L) at equilibrium
C_i	Initial concentration of for hexavalent chromium in the sample solution (mg/L)
DMSO	Dimethylsulfoxide
EMB	Eosin Methylene Blue Agar
EDX	Energy dispersive X- ray
FT-IR	Fourier Transform Infrared
$G^{(-)}$	Gram-negative bacteria
$G^{(+)}$	Gram-positive bacteria
$\Delta G°$	Standard free Gibbs energy
$\Delta H°$	Standard enthalpy
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)
MAC	Macconkey Agar media
min	minute
m_{sed}	Mass of adsorbent dose
MSA	Mannitol Salt Agar
n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
OPT	Occupied Palestinian territories
PCBS	Palestinian Central Bureau of Statistics
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	Gas constant (8.314 J/mol K)
R^2	Correlation coefficient (regression coefficient)
R_L	Dimensionless constant separation factor

ΔS°	Standard entropy
SEM	Scanning electron microscope
Si-NH$_2$	3-aminopropyl-functionlized silica gel
SiNPr	1-(pyrrol-2-yl)imine-Substituted Silica
SPE	Solid Phase Extraction
t	Time
T	The absolute temperature (^{o}K)
TGA	Thermal gravimetric analysis
UV-visible	ultraviolet-visible
V	Volume of solution
WHO	World Health Organization

Synthesis of 1-(Pyrrol-2-yl) imine modified silica as a new sorbent for the removal of hexavalent chromium from water
By
Ghadeer "Mohammed Moen" Nemer Hanbali
Supervised
Prof. Shehdeh Jodeh
Co- Supervised
Prof. Ismail Warad

Abstract

The water pollution is a big problems faced by the countries of the world, without exception. One of the most important and toxic heavy metals in wastewater is chromium. The major problem here is to detect the concentration of hexavalent chromium and try to remove it by adsorption.

The product 1-(Pyrrol-2-yl) imine modified silica was successfully prepared by immobilizing 1H-pyrrole-2-carbaldhyde on silica gel previously doped with 3-aminopropyltrimethoxysilane. The modified surface shows good thermal stability determined by (TGA). The FTIR and UV results confirmed that the pyrrole-2-carbaldhyde units have been immobilized at the surface of the modified silica gel. SEM images of the modified polysiloxane surface showed tough and porous nature, indicating that the materials present good characteristics to be used as an adsorbent. The synthesized SiNPr was investigated as an adsorbent for removal of Cr (VI). The adsorption experiments were conducted for a wide range of solution pH, adsorbent dosage, temperature, initial concentration and contact time. It was observed that the percentage removal of Cr(VI)

increased with an increase of initial concentration until 20 mg/L, while it decreased with increase in solution pH, contact time, adsorbent dose and temperature. Over 86% removal efficiency of Cr (VI) was achieved after 5 min, at solution pH around 4, 25°C temperature, 0.01 g weight of dose and initial concentration of 20 mg/L Cr(VI) solution.

The adsorption of Cr (VI) on the (Si-NPr) was optimized under acidic conditions and at room temperature. Cr (VI) adsorption using (Si-NPr) can be described using pseudo second order and Freundlich isotherm model.

The amount of Cr(VI) adsorbed per unit mass of (Si-NPr) obtained by pseudo second order model, Q_e calc (2.469) were in consistent with the experimental value, Q_e exp (2.782) indicate the pseudo second order model better represented the adsorption kinetics.

The Langmuir maximum adsorption capacity Q_m is 13.05 mg/g, at 25°C, and pH 4 and 0.03 weight of adsorbent dose. The R_L value (0.48) at 25 °C) indicates that the adsorption of Cr (VI) on (Si-NPr) is favorable. From Freundlich isotherm model parameters, value of $1/n = 0.9863$ while $n = 1.0139$ indicating that the adsorption of Cr (VI) on (Si-NPr) is favorable. The adsorption data suited with Langmuir and Freundlich, but Freundlich adsorption model was found to have the highest regression value and the best suit. The fact

that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the adsorbent surface

The negative $\Delta G°$ values (-4.224 to -1.775 kJ/mol) indicate that the adsorption is favorable and spontaneous at studied temperatures. The negative value of $\Delta H°$ (-26.1 kJ/mol) reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. A negative value of ΔS (-0.075) suggests that the adsorption process involves an associative mechanism. The adsorption leads to order through the formation of an activated complex between the adsorbate and adsorbent. Also a negative value of ΔS reflects that no significant change occurs in the internal structures of the adsorbent during the adsorption process.

The results of the present study exhibit that the prepared compound has a negative biological activity against *Staphylococcus aurous*, *Pseudomonas aeruginosa*, and *Escherichia coli*.

(Si-NPr) is a good effective adsorbent for the removal of Cr (VI) from the wastewater and can be reused for many times.

Chapter One

Introduction

1-1. Overview

The water pollution of the most intractable problems faced by the countries of the world, without exception.The World Health Organization (WHO) reported that a child dies every eight seconds because of contaminated water, and dies about five million people each year from water-related diseases.[1]

The industrial wastewater containing a range of waste and industrial waste with different sources and heterogeneous nature, some of which contain heavy metals and hazardous waste that can accumulate in groundwater and show the results to humans, animals and plants, others contain dyes and remnants of tanneries which contain waste nitrates, lead, cadmium, chromium, organic solvents, petroleum materials, phenolic pollutants and toxic effect of a carcinogen if it exceeds the allowable concentration limits. [2]

Heavy metals can be defined as metals or metalloids have density more than 4 g/cm^3, or 5 times or greater than water. Heavy metals could enter the body system through food, air, water and bio-accumulate over a period of time.

They are introduced and spread into the environment through a number of industrial processes.[1]

Some heavy metals cause toxicity even if the concentrations are very low and this is the main reason behind the price in the interest all over the world, whereas others are biologically essential and become toxic at relatively high concentrations. They combine with body's biomolecules, to form stable biotoxic compounds, thus distortion their structures and hindering them from the bioreactions of their functions.[1]

Heavy metals combine with proteins and form toxic complexes and they can inactivate important enzyme systems.[3]

The term "heavy metal" is not altogether clearly defined, but in the case of water pollution, these are metals such as arsenic, cadmium, iron, cobalt, chromium, copper, manganese, mercury, molybdenum, nickel, lead, selenium, vanadium and zinc. While heavy metals do tend to have a high atomic mass, and so are heavy in that sense, toxicity seems to be a further defining factor as to what constitutes a heavy metal and what does not.[4]

The importance of minimizing heavy metal pollution for industrial organizations extends beyond simple compliance. The impacts of heavy metal pollution on living organisms are very serious. Heavy metals are bio-accumulative, toxic at high concentrations, have neurological impacts, and some are

carcinogenic. They can also interfere with chemical processes by poisoning chemical catalysts and can impact on biochemical processes by interfering with enzyme action. There are hence serious environmental, economic and social impacts associated with heavy metal pollution.[5]

One of the most important and toxic heavy metals in wastewater is chromium. Chromium (VI) is released from different industrial operations, including metallurgy, leather tanning, paint, textile industries, chemical manufacturing, pulp production, ore and petroleum refining, metal corrosion, electroplating and the manufacture of products for corrosion protection. Chromium (VI) has been released to the environment via leakage, poor storage or improper disposal practices .Over the decades, extensive use of chromium in tanning industries have resulted in chromium contaminated soil and ground water at production sites which pose a serious threat to human health, fish and other aquatic biodiversity. Cr(VI) causes skin, lung and throat cancers, infertility, increased incidences of birth and developmental defects among children living around tanneries, leather and chrome industries. According to the World Health Organization (WHO) drinking water guidelines, the maximum recommended limit for total chromium is 0.05 mg/L.[6]

The traditional separation and preconcentration methods for metal ions are liquid-liquid extraction, coprecipitation, and ion exchange. These methods often require large amount of high purity

organic solvents, some of which are harmful to health and cause environmental problems. These difficulties are overcome with Solid-Phase Extraction (SPE). Indeed, SPE has several major advantages such as: (i) higher enrichment factor, (ii) simple operation, (iii) safety witch respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) and the ability to combine with different modern detection techniques. Chemically modified Polysiloxane is one of the most successful adsorbents, because this inorganic polymer support does not swell or shrink like the organic polymeric resin. The modified Polysiloxane may be employed in aqueous and organic solvents media; they present good thermal stability and appropriate accessibility of ions to the adsorbent groups, in addition the organofunctionalized Polysiloxane exhibits higher sorption capacities than polymeric resins, because the number of organic molecules immobilized on the support surface is large, allowing thus more removal of ions from aqueous solution. These systems can be operated indefinitely without loss of the expensive organic molecules. Their potential applications are due essentially to the nature of the grafted ligands. Silica gel compound 1-(pyrrol-2-yl) imine-Substituted Silica (SiNPr) will be synthesized and characterized. This product exhibits good chemical and thermal stability.[7]

The aim of this study is to remove Cr (VI) from wastewater, using this prepared material as an adsorbent for the solid-phase

extraction. The adsorption behaviors of the adsorbent with Cr (VI) will be studied. The effect of pH, temperature, and amount of adsorbent, concentration and the contact time on the adsorption of Cr (VI) will be studied. The adsorption capacity will be investigated using kinetics and pH effects. Equilibrium isotherm studies will be done by varying the following three parameters: initial concentration of Cr (VI) solution, volume of the Cr (VI) solution, and adsorbent dose on the uptake of Cr (VI) from the solution.

1-2. Objectives of this work

1-2-1. General Objectives

1. To prepare a 1-(Pyrrol-2-yl) imine modified silica as sorbent for Cr(VI)

2. To characterize modified polysiloxane (Si-NPr)

3. To specify the optimal conditions for the adsorption.

4. To recover Cr (VI) and reuse the adsorbent.

5. To study the antimicrobial activity of Si-NPr.

1-2-2. Specific objectives

1. To determine if (SiNPr) can be used to clean up Cr (VI) polluted wastewater.

2. To determine the extent that modified silica gel compound can tolerate and adsorb Cr (VI).

3. To study the effect of pH, temperature, amount of adsorbent, concentration and contact time on the adsorption of Cr (VI).

1-2-3. Research question and identified problems

The main questions addressed in this thesis are:

1. Can (SiNPr) be used to clean up Cr (VI) polluted wastewater?

2. To which extent that (SiNPr) can tolerate and adsorb Cr (VI)?

3. What are the optimum condition of pH, temperature, amount of adsorbent, concentration, and contact time for (SiNPr) to adsorb Cr (VI) efficiently?

4. What is the adsorption behavior of the adsorbent with Cr (VI)?

Chapter Two

Background and Literature review

2-1. chromium

2-1-1. Properties of chromium

Chromium is an odorless, steel-gray, hard metal that is lustrous and takes a high polish. It is extremely resistant to corrosive agents. Chromium can exist in water in several different states but under strongly oxidizing conditions, may be converted to the hexavalent state and occurs as chromate anions. Chromium is soluble in dilute hydrochloric acid and sulfuric acid but not nitric and strong alkalies and alkali carbonates.[8]

Chromium is one of the most dangerous inorganic water pollutants. It is constantly released into the aquatic environment by natural processes (mainly by volcanic activity and weathering of rocks) and by anthropic sources, which in the last twenty years have become of leading importance in the worldwide emission balance of these substances .

In aquatic systems, chromium exists primarily in either the trivalent [Cr (III)] or hexavalent [Cr (VI)] states. [9]

Chemical and Physical Properties of chromium is summarized in Table 2-1:

Table 2-1: Physical and chemical properties of Cr

Origin of the name	The name is derived from the Greek 'chroma', meaning colour
Group	6
Period	4
Block	D
Atomic number	24
State at 20°C	Solid
Melting point	1907°C, 3465°F, 2180 K
Density (g cm−3)	7.15
Relative atomic mass	51.99
Discovery date	1798
Discovered by	Nicholas Louis Vauquelin

2-1-2. Hexavalent chromium

Hexavalent chromium, Cr (VI) refers to chemical compounds that contain the element chromium in the +6 oxidation state. Virtually all chromium ore is processed via hexavalent chromium, specifically the salt sodium dichromate. Approximately 136,000 tonnes (300,000,000 lb) of hexavalent chromium were produced in 1985.[10]

Cr (VI) can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. If Cr (VI) is reduced to Cr (III) extracellularly, the toxicity is not observed. Cr (VI) can be reduced intracellularly by hydrogen peroxide, glutathione reductase and ascorbic acid to produce reactive intermediates. Any of these species could attack DNA, proteins and membrane lipids thereby disrupting cellular integrity and functions. Exposure to chromium

(VI) can cause respiratory, renal, hepatic, gastrointestinal, cardiovascular and hematological problems. Also Cr (VI) is considered to be carcinogenic.[11] Cr (VI) is introduced into natural waters by a variety of industrial processes including textile, dyes and pigment production, film and photography, galvanometry, leather tanning, electroplating and metal finishing industries.[12]

2-1-3. Differences between trivalent Chromuim and hexavalent Chromuim

In aqueous solution it most commonly is formed as Cr (VI) or Cr (III). These two oxidation states are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity. Cr (VI) is a highly toxic agent and carcinogenic. Cr (VI) is also known to be carcinogenic and mutagenic to living organisms. It can cause dermatitis, rhinitis, and even lung cancer or naso pharynx cancer. Because of its significant mobility in the subsurface environment, the potential risk of surface water pollution is high. It should be removed from contaminated waters. Cr (III), on the other hand, is less toxic, immobile, and readily precipitates as Cr (OH) $_3$. Cr (III) is also considered to be a trace element essential for the proper functioning of living organisms. Cr (III) is considered as an essential element playing a role in carbohydrate and lipid metabolism.[6]

Water-insoluble Cr (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Cr (VI) have been known for a long time.[13]

Cr (VI) is more important than the Cr (III) because higher capacity for mobility and toxicity of chromium (VI), it attached great importance in the fight against water pollution, WHO declared in a summary guide for drinking water that the maximum permissible limits for hexavalent chromium is (0.05 mg/L), so it is necessary to remove Cr (VI) of sewage disposal.

2-1-4. Industrial uses of hexavalent chromium

Industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to paints, primers, and other surface coatings and chromic acid electroplated onto metal parts to provide a decorative or protective coating. Hexavalent chromium can be formed when performing "hot work" such as welding on stainless steel or melting chromium metal. In these situations, the chromium is not originally hexavalent, but the high temperatures involved in the process result in oxidation that converts the chromium to a hexavalent state.[14]

Chromium is released into the environment from electroplating, anodizing, chromating, metalfinishing, tannery, dying and fertilizer industries. Waste streams from electroplating units

may contain up to 2500 (mg/L) Cr(VI), which according to environmental regulations worldwide must be controlled to an acceptable level before being discharged to the environment.[15]

2-2. Toxicity of hexavalent chromium

Major factors governing the toxicity of chromium compounds are oxidation state and solubility. Cr (VI) compounds, which are powerful oxidizing agents and thus tend to be irritating and corrosive, appear to be much more toxic systemically than Cr (III) compounds, given similar amounts and solubilities. Although mechanisms of biological interaction are uncertain, this variation in toxicity may be related to the ease with which Cr (VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates[16].

2-2-1. Mechanism of Chromium Toxicity

Since Cr (III) is poorly absorbed by any route, the toxicity of chromium is mainly attributable to the Cr (VI) form. It can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin.

The reduction of Cr (VI) is considered to serve as a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effect while reduction of Cr (VI) may serve to activate chromium toxicity if it takes place in or near the

cell nucleus of target organs.[17] If Cr (VI) is reduced to Cr (III) extracellularly, this form of the metal is not readily transported into cells and so toxicity is not observed. The balance that exists between extracellular Cr (VI) and intracellular Cr (III) is what ultimately dictates the amounts and rates at which Cr (VI) can enter cells and impart its toxic effects.[18]

Cr (VI) enters many types of cells and under physiological conditions can be reduced by hydrogen peroxide (H_2O_2), glutathione (GSH) reductase, ascorbic acid, and GSH to produce reactive intermediates, including Cr (V), Cr (IV), thiylradicals, hydroxyl radicals, and ultimately, Cr (III). Any of these species could attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions.[19]

2-2-2. Hexavalent chromium impact on the human body

2-2-2-1. Respiratory Effects

Human occupational experience clearly indicates that, when inhaled, chromium compounds are respiratory tract irritants, resulting in airway irritation, airway obstruction, and lung, nasal, or sinus cancer.[20]

Pulmonary irritant effects following inhalation of chromium dust can include

- asthma,

- chronic bronchitis,

- chronic irritation,

- chronic pharyngitis,

- chronic rhinitis,

- congestion and hyperemia,

- polyps of the upper respiratory tract,

- tracheobronchitis,

- ulceration of the nasal mucosa with possible septal perforation.[15]

Many cases of nasal mucosa injury (inflamed mucosa, ulcerated septum, and perforated septum) have been reported in workers exposed to Cr (VI) in chrome-plating plants and tanneries.[21] In 1983 study of 43 chrome-plating plants in Sweden, where workers were exposed almost exclusively to Cr (VI) acid, revealed that all workers with nasal mucosa ulceration or perforation were periodically exposed to at least 20 micrograms per cubic meter (μg/m³) when working near the plating baths (The newest U.S. permissible exposure level in the workplace for chromates and chromic acid is 5 μg/m³ as a ceiling). The period of exposure for workers experiencing nasal mucosal ulceration varied from 5 months to 10 years. A recent epidemiological study of U.S. workers found that the median time from date first employed to date of first diagnosis of nasal ulceration was less than a month; the median

Cr(VI) concentration was similar to concentrations reported in the Swedish study.[22], [23]

An extensive epidemiological survey was conducted of housewives who lived in an area of Tokyo, Japan, in which contamination from chromium slag at a construction site was discovered in 1973. The exposed population reported a higher incidence of subjective complaints of nasal irritation than the control population in the early years of the study, buy in later years the difference between the two groups became progressively less.[16]

2-2-2-2. Skin Effects

Dermal exposure to chromium has been demonstrated to produce irritant and allergic contact dermatitis.[24] Primary irritant dermatitis is related to the direct cytotoxic properties of chromium, while allergic contact dermatitis is an inflammatory response mediated by the immune system. Allergic contact dermatitis is a cell- mediated immune response that occurs in a two-step process. In the first step (induction), chromium is absorbed into the skin and triggers the next step- an immune response (sensitization). Sensitized individuals will exhibit an allergic dermatitis response when exposed to chromium above a threshold level.[19]

Localized erythematous or vesicular lesions at points of contact or generalized eczematous dermatitis should suggest sensitization.[25]

Chromium allergic dermatitis is characterized by symptoms of

- dryness,
- erythema,
- fissuring,
- papules,
- scaling,
- small vesicles and swelling.[26]

In addition, occupational exposure Cr (VI) compounds has been associated with effects on the skin, nasal septum, and eardrum.[27]

Chromium is one of the most common skin sensitizers and often causes skin sensitizing effect in the general public. A possible source of chromium exposure is waste dumps for chromate-producing plants causing local air or water pollution.

2-2-2-3. Carcinogenic Effects

The mechanism of Cr (VI)-induced carcinogenicity is not completely understood. The toxicity of chromium within the cell may result from damage to cellular components during the hexavalent to trivalent chromium reduction process, by generation of free radicals; including DNA damage[16]. Recent studies indicate a biological relevance of non-oxidative mechanisms in Cr (VI) carcinogenesis.[28]

Studies of workers in the chromium pigment, chrome-plating, and ferrochromium industries showed a statistically significant association between worker exposure to Cr (VI) and lung cancer.[29]

In addition to lung cancer, a number of epidemiological studies of workers in chromate industries also showed significantly increased risk for nasal and sinus cancers.[16]

2-2-2-4. Hepatic Effects

Cr (VI) has been reported to cause severe liver effects in four of five workers exposed to chromium trioxide in the chrome plating industry. The reported liver effects include derangement of the liver cells, necrosis, lymphocytic and histocytic infiltration, and increases in Kupffer cells.[30]

Cases of hepatic effects after oral exposure to Cr (VI) compounds have also been reported. Elevated liver enzyme levels were reported flowing ingestion of 150 mL solution containing (22.5) g potassium dichrome.[31]

Exposure to Cr (III) has not been found to cause any liver effects in workers employed in two factories that produced Cr (III) oxide or Cr (III) sulfate.[32]

2-2-2-5. Gastrointestinal Effects

In a study of 97 workers from a chrome plant exposed to a mixture of insoluble chromites ore containing Cr (III) and soluble Cr (VI) as sodium chromate and dichromate, gastrointestinal radiography revealed that 10 of the workers had ulcer formation, and of these, six had hypertrophic gastritis. Nearly all of the workers breathed through the mouth while at work and swallowed the chromate dust, thereby directly exposing the gastrointestinal mucosa.[33] Most of the previous studies reporting gastrointestinal effects, however, did not compare the workers with appropriate controls.

Cases of gastrointestinal effects after oral exposure to Cr (VI) compounds have also been reported. In one study, a 14-year-old boy who died after ingesting 7.5 mg Cr (VI) /kg as potassium dichromate experienced abdominal pain and vomiting before death. Autopsy revealed gastrointestinal ulceration.[34] In another study, a 44-year-old man died of gastrointestinal hemorrhage after ingesting 4.1 mg Cr (VI) /kg as chromic acid solution.[35]

2-2-2-6. Cardiovascular Effects

Case reports of humans who died after ingesting Cr (VI) compounds have described cardiovascular effects as part of the sequelae leading to death.

A 22-month-old boy who ingested an unknown amount of sodium dichromate died of cardiopulmonary arrest. Autopsy revealed early hypoxic changes in the myocardium.[36] A 35-year-old woman developed cardiovascular collapse and shock within a few hours following ingestion of 50 mL chromic acid.[37] A woman ingested 400 mL of leather tanning solution containing 48 grams of basic chromium sulphate ($Cr(OH)SO_4$).[38]

2-2-2-7. Hematological Effects

Cases of hematological effects have been reported in humans after the ingestion of lethal or sublethal doses of Cr (VI) compounds. In a case of an 18-year-old woman who ingested a few grams of potassium dichromate, decreased hemoglobin content and hematocrit, and increased total white blood cell counts, reticulocyte counts, and plasma hemoglobin were found 4 days after ingestion. These effects were indicative of intravascular hemolysis.[39]

Laboratory analysis of a 35-year-old woman, who died 12 hours after ingesting 50mL of pure chromic acid [25g Cr(VI)], revealed anemia (hemoglobin 56 g/L, hematocrit 17 percent) and thrombocytopenia.[32]

2-2-2-8. Genotoxic and Mutagenic Effects

The mechanism of chromium-induced genotoxicity is not fully understood.

In one experiment, Cr (VI) plus glutathione induced DNA damage in vitro, whereas Cr (III) with or without glutathione did not. Chromium seems to exert its genetic effects by binding directly to DNA. It can produce stable DNA-chromium complexes, DNA strand breaks, DNA-DNA cross links, and DNA-protein cross links. The active species for DNA binding seems to be the trivalent form.[40]

A recent clinical study reported strong DNA oxidative damage from the urinary samples of the patient who ingested 2 to 3 grams of potassium dichromate in a suicide attempt.[33]

Cr (VI) compounds are clearly mutagenic in the majority of experimental situations.[41] It has caused chromosome aberrations in mammalian cells and has been associated with increased frequencies of chromosome aberrations in lymphocytes from chromate production workers. Increases in sister chromatid exchanges were seen in lymphocytes from workers exposed to chromium, cobalt, and nickel dusts.[42]

2-3. Tanneries in Hebron, spread disease and destroy the environment silently

Leather tanning is one of the ancient craft which is famous for the city of Hebron for hundreds of years, to form the only source to provide raw materials to the Palestinian factories such as shoes, garments, leather factories, characterized tanning in the past it was dependent on natural materials friendly to the environment, such as the use of salt and plant ten and pomegranate peel, sumac, but it has become today a source of pollution of soil and the groundwater, especially after the entry of chemicals in the craft, such as the use of "Arsenic" and "Chrome" and "Mercury" and some acids that infect human diseases and the destruction of the Palestinian environment.[43]

There in the city of Hebron more than 12 tanneries use many of the carcinogens arsenic and hexavalent chromium and other chemicals in the processing and tanning. The danger in the presence of tanneries is the production effluents containing toxic chromium hexagon, which is estimated at 2000 m^3 in addition to solid waste, which is estimated at more than three tons per day, which is no less dangerous than the effluent because of the spread of odors updated environmental pollution. Compounding dangerous is the use of contaminated water and toxic substances in the irrigation of crops and thus transmitted to humans.[43]

The chemicals used by tanneries easy to reach the man, whether through food or water or air, causing many disease symptoms may lead to

death in the case of high proportions of these elements in the body, especially mercury, arsenic, chromium elements and these symptoms that infect human as a result of poisoning with these materials: nervous system disorders and atrophy of brain cells and thus imbalance in jobs, genetic and chromosomal disorders, fatigue and headaches in addition to the weakness of sperm production, abortion, fetal abnormalities, and also reduced body's production of white blood cells, red and changes in the skin and the incidence of certain cancers and the induction of lung.[43]

It is necessary to re- straighten put these tanneries by conducting visits in assessing the extent of damage caused by the place , and make recommendations to the competent authorities to look for alternative means as soon as possible of the industry to become the secretariat of the workers and the surroundings of the land and citizens.[43]

2-4. Adsorption

2-4-1. definition of Adsorption

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption. The substance thus adsorbed on the surface is called the adsorbate and the substance on which it is absorbed is known as adsorbent.

Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface

of a solid, and becomes bound by physical and/or chemical interactions. Large surface area leads to high adsorption capacity and surface reactivity.[44]

Adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbate. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.[45]

However, it should be remarked that the distinction between adsorption and absorption vanishes as we go from perfectly crystalline macroscopic materials to porous/structured materials, aggregates and composites made out of increasingly smaller grains, viz., and micron-sized particles to nanoparticles, sub-nano particles and finally molecules (or atoms). In such nano-composites, the internal surface area of particulate matter is very large. Then the adsorption on internal surfaces simply becomes absorption when viewed from the bulk. Then the distinction between adsorption and absorption vanishes. On the other hand, the distinction is clearest between bulk solids without internal structure, but having only

surfaces where only adsorption can occur on the outer surfaces and nanocomposites or aggregates with internal structure where absorption by the host material is simply adsorption on internal surfaces of the host material. As an example, we may consider a crystalline piece of silicon dioxide (quartz) which can absorb water molecules on its surface. However, if the quartz is ground into very fine sand, the pile of sand (an aggregate) has a very large internal surface area. A very large amount of water can be adsorbed by the "internal" surfaces of the grains in the pile of sand, and this absorption is simply "internal adsorption." If water is made to flow through such a pile of sand, ions and toxins in the water may be preferentially adsorbed by the surfaces of the grains of sand, providing a simple, well-known water purification application.

The word "adsorption" was coined in 1881 by German physicist Heinrich Kayser (1853-1940).[46]

2-4-2. Types of Adsorption

Depending upon the nature of forces existing between adsorbate molecules and adsorbent, the adsorption can be classified into two types:

1. Physical adsorption (physisorption): If the force of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption. It is also known as Vander Waal's adsorption. In physical adsorption the force of

attraction between the adsorbate and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure.[47]

2. Chemical adsorption (chemisorption): If the force of attraction existing between adsorbate and adsorbent are almost same strength as chemical bonds, the adsorption is called chemical adsorption. It is also known as Langmuir adsorption. In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed.[47]

Comparison between Physisorption and Chemisorption is summarized in Table 2-2

Table 2-2: Comparison between Physisorption and Chemisorption.[47]

Physisorption	Chemisorption
1. Low heat of adsorption usually in the range of 20-40 kJ mol^{-1}	High heat of adsorption in the range of 40-400 kJ mol^{-1}
2. Force of attraction are Van der Waal's forces	Forces of attraction are chemical bond forces
3. It usually takes place at low temperature and decreases with increasing temperature	It takes place at high temperature
4. It is reversible	It is irreversible
5. It is related to the ease of liquefaction of the gas	The extent of adsorption is generally not related to liquefaction of the gas
6. It is not very specific	It is highly specific
7. It forms multi-molecular layers	It forms monomolecular layers
8. It does not require any activation energy	It requires activation energy

2-4-3. Application of adsorption

The phenomenon of adsorption finds extensive application in field of Industry, laboratory and various other technical processes. A few important applications of adsorption are as under:

1. Manufacture of Gas Masks: Activated charcoal used in gas masks removes all undesirable toxic and poisonous gases while purified air passes through its pores.

2. Removing of Colouring Matter from Sugar Juice & Vegetable Oils: Activated animal charcoal is used as decolourizer in removing colouring matter of sugar solution and other vegetable materials.

3. Dehydration & Purification of Gases: Silica gel and Alumina are used as good adsorbents for removing moisture and for controlling humidities in rooms which store delicate articles.

4. Dyeing of Clothes: Modrants used in dyeing adsorb the colouring matter which does not attach to fabric otherwise.

5. Heterogeneous Catalysis: The action of heterogeneous catalysts like finely divided nickel, finely divided platinum, finely divided iron in hydrogenation of oils, conversion of SO_2 to SO_3 and manufacture of ammonia respectively is based on the phenomenon of adsorption.

6. Ion-Exchange Resins: The organic high polymers containing groups such as $-COOH$, $-SO_3H$ or $-NH_2$ possess the property of selective adsorption of ions from solution. These resins are largely used in Industrial softening of water and separation of rare earths from their mixture.

7. Chromatography: There are a number of chromatographic techniques like adsorption chromatography, paper chromatography and vapour phase chromatography which are based on selective adsorption of different substances of the adsorbent.

8. Drugs: Various drugs get adsorbed on the tissues which then are heated. The germicidal action of medicines is also based on the property of adsorption.[48]

2-4-4. Adsorption as an effective method for removing hexavalent chromium from wastewater

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported. These include reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption. Most of these methods have a lot of disadvantages including high operational cost.[49]

On the other hand, specific sorbents consisting of polymer microspheres containing metal chelating ligands were employed for heavy metal ion removal.[50]

Traditionally, extraction is carried out liquid-liquid extraction, co-precipitation, and ion exchange, these methods have non-economic disadvantages. They often require large amount of high purity organic solvents, some of which are themselves harmful to health and cause environmental problems. Nowadays, several methods are used for pretreatment of the samples. Solid Phase Extraction (SPE) has commonly been used as a technique for pre-concentration/separation of various inorganic and organic species. SPE has several major advantages that include higher enrichment factors, simple operation, safety with respect to hazardous samples, high selectivity, lower cost and less time, the ability to combine it with different modern detection techniques.

A variety of ligands or functional groups are immobilized onto a solid support matrix as a solid phase extractant for the purpose of extraction and enrichment of trace metal ions from environmental samples. Silica gel is of great importance as a solid support because it possesses some definite advantages. The silica support is chosen for its high surface area, high mechanical and thermal stability. In addition, it is easily modified, by reacting with organofuctionalized silanes through its surface silanol groups. These covalently bonded organic groups are highly stable and resistant to removal from the

surface by organic solvents or water. To this end, a great number of organic molecules were immobilized on silica gel surface, xylenol orange,

4_acylpyrazolone,aminothioamidoanthraquinone,oximederivatives,r esacetophenone, diphenyldiketonemonothiosemicarbazone. These systems can be operated indefinitely without loss of the expensive organic molecules. Their potential applications are attributable essentially to the nature of the grafted ligands. Indeed, the most commonly attached molecules have chelating ability due to their donor atoms, such as oxygen, nitrogen and sulphur, which have a large capability to form complexes with a series of metal ions, leading in some cases, to distinguishable selective extraction properties.[51]

2-4-5. Types of adsorbents

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many

waste materials used include fruit wastes, coconut shell, scrap tires, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc.[52]

2-4-6. Adsorption isotherms models

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.[53]

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir-type isotherm remains to be the most widely used for practical application. The Langmuir isotherm for pure component adsorption can be obtained from Equation (2-1):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \qquad (2\text{-}1)$$

Where: C_e is the equilibrium concentration of adsorbate (mg/L), qe is the amount of Cr (VI) adsorbed per gram of the adsorbent (mg/g),

q_m is maximum monolayer coverage capacity (mg/g) ,K_L= Langmuir isotherm constant (L/mg).

Therefore, a plot of C_e/qe versus C_e gives a straight line of the slop $1/q_m$ and intercepts $1/ (q_m K_L)$.[54]

Langmuir isotherm can be characterized by a dimensionless constant called separation factor (R_L). As shown by the following equation (2-2):

$$R_L = \frac{1}{(1 + K_L C_o)} \qquad (2\text{-}2)$$

Where C_o is the highest initial concentration of adsorbate (mg/L), K_L (L/mg) is Langmuir constant.

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).[2]

The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface.[55] The Freundlich isotherm model is describing the adsorption of solutes from an aqueous phase to a solid surface. The Freundlich isotherm assumes several adsorption energies are involved in the adsorption process.

Freundlich adsorption isotherm is the relationship between the amounts adsorbed per unit mass of adsorbent, Q_e, and the concentration of Cr (VI) at equilibrium, C_e. The linear form of logarithmic equation for Freundlich isotherm is written as (2-3):

$$\ln Q_e = \frac{1}{n}\ln C_e + \ln K_F \qquad (2\text{-}3)$$

Where, K_F and n are the Freundlich constants, K_F and n are the indicators of the adsorption capacity and adsorption intensity respectively. In this case, the plot of log (C_e) vs. log (Q_e) was employed to generate the intercept value of K_F and the slope of n.[49]

2-4-7. Adsorption kinetics

The study of adsorption kinetics is significant as it provides valuable insights into the pathways and the mechanism of the process.

Several kinetics models are used to explain the mechanism of the adsorption processes. A simple pseudo-first order equation is given by Lagergren equation (2-4):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \qquad (2\text{-}4)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed

at any time per unit weight of adsorbent (mg/g) and K_1 is first order adsorption rate constant.[56]

On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as equation (2-5):

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2}$$
(2-5)

Where: K_2 is the pseudo-second order rate constant (g/mg. min).

The linear regression correlation coefficient value shows that which model can justify data.[51]

2-4-8. Adsorption Thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change, ΔG^0, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both enthalpy (ΔH^0) and entropy (ΔS^0) factors must be considered in order to determine the Gibb's free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity. The free energy of an adsorption process is related to the equilibrium constant by the following equation (2-6):

$$\Delta G^o = -RT \ln K_D$$
(2-6)

Where, ΔG^0 is the Gibb's free energy change (kJ. mol^{-1}), R is the ideal gas constant (8.314 $J.mol^{-1}K^{-1}$), and T is temperature (K^0) and K_D is the single point or linear sorption distribution coefficient (L g^{-1}).[57]

According to thermodynamics, the Gibbs free energy is the difference between the adsorption enthalpy (ΔH^o) and adsorption entropy (ΔS^o) multiplied by the temperature. In this manner, by applying this concept to Equation (2-6), the thermochemical parameters ΔH^0 and ΔS^o can be determined using Van't Hoff's plot, according to Equation (2-7):[52]

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

(2-7)

2-5. Polysiloxane Immobilized Ligand Systems

2-5-1. Definition of Polysiloxanes

Polysiloxane-immobilized ligand systems, functionalized poly-siloxane sorbents, polyorganosiloxanes, or simply polysiloxanes are intermediates polymers between the pure inorganic silica and organic polymers such as polystyrene.

They are inorganic supports of silica based matrix bearing reactive organic sites which have been the subject of considerable interest. These types are known as functionalized polysiloxanes

which have been prepared either by the low temperature sol-gel process or by modification of pre-prepared polysiloxane.

Flexibility of the siloxane backbone is the main reason of increasing applications of polysiloxanes, this flexibility resulting from the degree of Si–O–Si bond angle of 143° which is much more open than the usual tetrahedral angle of 110°, and the Si–O bond is significantly longer than the C–C bond.

Polysiloxane with chelating groups have a lot of important applications, such as chromatography, extraction and uptake of metal ions from aqueous solutions and encapsulation of organic compounds.[58]

2-5-2. Polysiloxanes Advantages

The advantages of polysiloxane-immobilized ligands are: [58]

1. Negligible swelling in different solutions.

2. Physical rigidity of their structures.

3. Nontoxic.

4. High biodegradation, photochemical and thermal stability.

5. High amount of functionalized groups.

6. Chemical inertness.

7. Uniform distributions of ligand sites within the polymer particles.

8. It can be modified easily by a variety of functional groups.

2-5-3. Preparation of Polysiloxane Immobilized Ligand System

There are two common methods used to prepare these functionalize ligand systems.

1. The first method is the sol-gel process which involves hydrolysis and condensation of $Si(OEt)_4$ with the appropriate silane coupling agent $(RO)_3SiX$ where X represents an organofunctionalized ligand.

2. The second approach is the chemical modification of the pre-prepared functionalized polysiloxane. The second method appears as an interesting alternative mainly on account of substitution of organofunctionalized groups when appropriate chelating silane agents are difficult to prepare.[1]

2-6. Methodology of preparing Polysiloxane surface modified with 1-(pyrrol-2-yl) imine

I. synthesis of 3-aminopropylsilica (Si-NH2)

The first stage in the preparation was the reaction between the silylating agent and silanol groups on the silica surface.

1. Activated silica gel SiO_2 (25g) suspended in 150 mL of dried toluene was refluxed and mechanically stirred under nitrogen atmosphere for 2h.

2. To this suspension, 10 mL of aminopropyltrimethoxysilane was added dropwise and the mixture was kept under reflux for 24h.

3. The solid was filtered, washed with toluene and ethanol.

4. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1/1) for 12h, to remove the silylating reagent residue.

The immobilized silica gel, named $SiNH_2$, was dried in vacuum at room temperature.

II. Synthesis of 1-(pyrrol-2-yl) imine-Substituted Silica (SiNPr) :

1. A mixture of 3-aminopropylsilica ($SiNH_2$) (2.5g) and pyrrol-2-carbaldehyde (1.5 g) in 50 mL of dry diethyl ether was stirred at room temperature for 24 h.

2. After being filtered, the solid product was Soxhlet extracted with acetonitrile, methanol and dichloromethane for 12 h, respectively.

3. The product was then dried over 24 h. (Figure 2-1)

These NH$_2$-groups onto the silica surface were then reacted with Pyrrol-2-carbaldehyde under gentle conditions (room temperature, atmospheric pressure, 12 h), using anhydrous diethyl ether as solvent to form this chelating sorbent SiNPr.
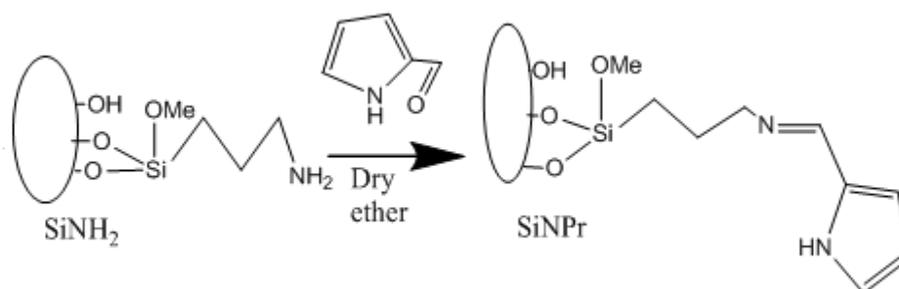
Figure 2-1: The synthesis route of modified polysiloxane.[7]

This work is focused on the synthesis, characterization and applications of adsorbent 1-(pyrrol-2-yl) imine-Substituted Silica (SiNPr) by the chemical modification of the pre-prepared functionalized silica gel for quantitative extraction and elimination of hexavalent chromium from industrial wastewater.

Chapter Three

Experimental Part

3-1. Chemicals and Materials

All solvents and other chemical used in experimental part don't need additional purification. Silica gel (from Sigma-Aldrich, purity more than 98.5%) with particle size in the range of 40-63 µm. The chelating agent $SiNH_2$ (from Sigma-Aldrich, purity more than 99%) was used without purification. The solvent used was Dry diethyl ether. For reflux extraction acetonitrile, methanol and dichloromethane were used. Hexavalent chromium (K_2CrO_4) was used as adsorbate. For pH adjustment nitric acid (0.1M) and potassium hydroxide (0.1M) were used.

The instrument and material used are: glassware, FT-IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific), Atomic absorption spectroscopy (iCE 3300, Thermo Scientific), pH meter (model: 3510, JENWAY), UV-visible spectrophotometer (model: UV-1601, SHIMADZU), shaking water bath (Daihan Labtech, 20 to 250 rpm Digital Speed Control), desiccator.

3-2. Synthesis of 1-(pyrrol-2-yl) imine modified Silicon surface (SiNPr)

To prepare the (SiNPr), a mixture of pyrrol-2-carbaldehyde (1.5 g) and 3-aminopropylsilica ($SiNH_2$) (2.5 g) in 50 mL of dry

diethyl ether was mixed and stirred for 24 h. At room temperature, the solid residue was filtered, acetonitrile, methanol and dichloromethane was used in Soxhlet extraction of the product for 10 h. The desired solid product was dried completely over more 24 h. The synthesis step is shown in Figure 3-1:
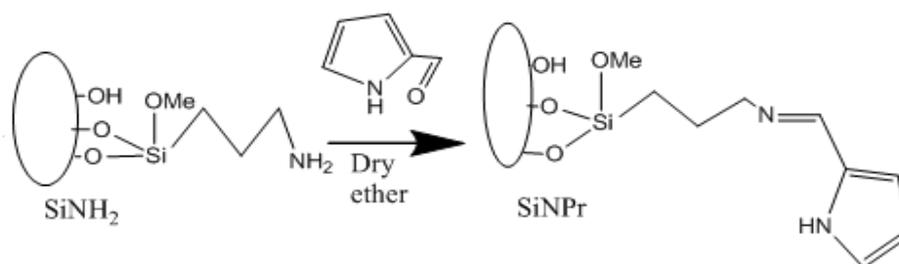
Figure 3-1: The synthesis step of (Si-NPr).[7]

3-3. Characterization of (Si-NPr)

The desired matrix was examined by FT-IR spectroscopy which confirmed that 1H-pyrrole-2-carbaldhyde have been linked onto the surface of gel matrix. A SEM was study to supply information about the morphology of modified polysiloxane surface. UV-visible spectrophotometer was used to confirm that 1H-pyrrole-2-carbaldhyde was effectively linked to the surface of silicon when it was modified by 3-amino-pyltrimethoxysilane. TGA Analysis for Thermal Stability and EDX test for elements present in modified polysiloxane were studied.

3-4. Preparation of Cr(VI) solutions

Exactly 1.868 g of K_2CrO_4 was taken in a 500 mL volumetric flask and diluted up to the mark (we obtained 1000 mg/L Cr (VI) solution). By dilution were prepared 5, 10, 15, 20, 25, 30 mg/L Cr (VI) solutions.

3-5. Calibration Curve

The concentration of several Cr (VI) solutions was analyzed by Atomic absorbtion spectroscopy.

Calibration curve between absorbance and concentration was obtained in the range 5-30 mg/L Cr (VI) solution, as shown in Figure 3-2:
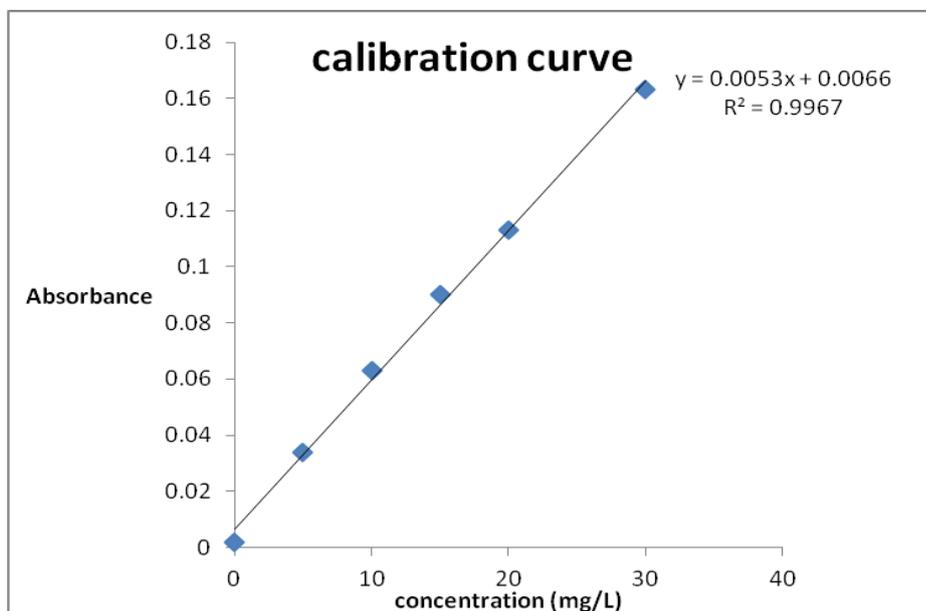
Figure 3-2: calibration curve between absorbance vs. concentration for Cr (VI) concentrations in the range 5-30 mg/L

3-6. Adsorption Experiments

For pH adjustment, nitric acid (0.1M) and potassium hydroxide (0.1M) were used. The efficiency of the absorbtion was estimated by batch experimental studies. The adsorption behavior of the surface with Cr (VI) solutions was studied. The effect of contact time, temperature, pH, dose of adsorbent, and the concentration of Cr (VI) solutions on the adsorption process was studied. Adsorbent was removed by filtration. AAS was served to analyze the filtrate residues of Cr (VI) solutions.

The Cr (VI) removal percentage (R) is calculated using the following equation 3-1:

$$\%Removal = \frac{C_o - C_e}{Co} \times 100 \% \tag{3-1}$$

Where, C_o is the initial Cr (VI) concentration (mg/L) and C_e is the final Cr (VI) concentration in the sample solution after filtration.

The removal capacity (qe, mg/ g) is quantified by equation 3-2:

$$qe = \left[\frac{(C_o - C_e)}{m}\right] \times v \tag{3-2}$$

Where V (L) is the volume of Cr (VI) solution, m (mg) is the mass of the used (SiNPr).[2]

3-6-1. Experiment (1) - Optimization of contact time

A 50 mL of Cr (VI) solution (10 mg/L) was taken and put in 100 mL beaker with 0.1 g of adsorbent. At different time intervals, part of the supernatant was taken using the pipette and residual concentration of Cr (VI) was measured by AAS at normal pH.

For each experiment three samples were taken and the average was reported.

3-6-2. Experiment (2) - Effect of pH value

The effect of pH on adsorption process was measured in range 2.5-10. The pH was adjusted using 0.1M KOH and 0.1M HNO_3. A 15 mL of (10 mg/L) Cr (VI) were added to 0.03 g adsorbent. The sample then put in shaking water bath for 5 min at 25°C. At the end, adsorbent was removed by filtration then filtrate was measured by AAS for the residual concentration of Cr (VI).

3-6-3. Experiment (3) _ Effect of temperature on Cr(VI) adsorption

The effect of temperature on adsorption process was studied in the range 4-60°C. A 15 mL of (10 mg/L) Cr (VI) solutions was added to 0.03 g adsorbent samples at pH 4. Each sample was put in shaking water bath at required temperature for 5 min. Finally, adsorbent was removed by filtration then filtrate was analyzed by AAS.

3-6-4. Experiment (4)- Effect of Cr (VI) initial concentration

The effect of initial concentration of Cr (VI) on adsorption process was investigated. A 15 mL of several concentration of Cr (VI) solution (5-30 mg/L) was added to 0.03 g of adsorbent, under optimized temperature (25°C) and pH 4 for 5 min. The absorbance of filtrate was measured by AAS.

3-6-5. Experiment (5) - Effect of Adsorbent dose

The effect of amount of adsorbent on the adsorption of Cr (VI) was investigated.

 In order to detect optimum dose. A 15 mL of 20 mg/L Cr (VI) solutions were added to 100 mL beakers containing 0.01, 0.03, 0.07, 0.1 and 0.15 g of adsorbent at pH 4. The samples was put in shaking water bath at 25°C for 5 min. Absorbance of the filtrate was measured by AAS.

3-7. Kinetics and Thermodynamics of Adsorption

Pseudo-first order, pseudo-second order kinetic models were investigated from studying contact time effect on Cr (VI) adsorption at Si-NPr. Parameters for Pseudo-first order, pseudo-second order kinetic model for adsorption of Cr(VI) at Si-NPr were determined. The value of both experimental and calculated q_e was compared.

The adsorption behavior of adsorbent with Cr (VI) was studied. In This study we are trying to reach optimum adsorption conditions by studying the effect of:- pH, contact time, adsorbent dose, temperature and initial concentration of Cr (VI). Concentration of Cr (VI) was measured before and after adsorption by using AAS. Langmuir, Freundlich adsorption isotherm equations were studied. The values of corresponding parameters were determined. Thermodynamic parameter like (ΔS^o), (ΔH^o), and (ΔG^o) were evaluated employing Van't Hoff's equation. At different temperatures ranging (4–60°C), the values of K_D and % removal for Cr (VI) were calculated.

Chapter Four

Results and Discussion

4-1. Characterization of Modified Polysiloxane (Si-NPr)

4-1-1. SEM of the Modified Polysiloxane (Si-NPr)

A SEM study was done to provide information about morphology of surface modified with 1H-pyrrole-2-carbaldhyde. SEM micrographs of modified Polysiloxane surface exhibit tough and porous nature, denoting that prepared matrix has good features to be used as an adsorbent. (Figure 4.1)
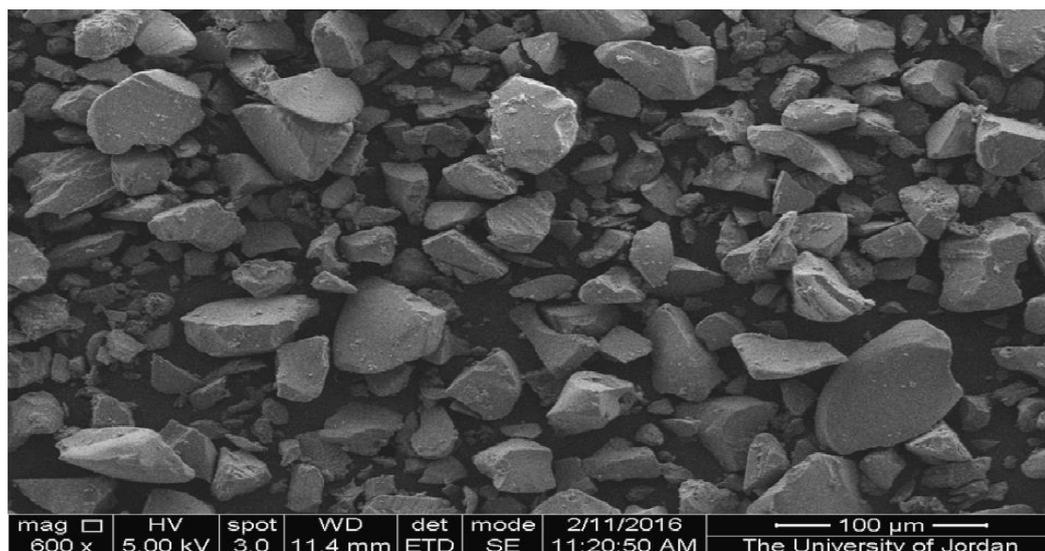
Figure 4-1: SEM of the modified Polysiloxane surface (SiNPr)

4-1-2. FT-IR Characterization

FT-IR spectra for SiNH$_2$, SiNPr were carried out to prove the presence of several functional groups in the prepared matrix. The sharp feature around 1100 cm^{-1} belonged to Si-O-Si stretch vibration. The characterization features of SiNPr compared with

SiNH$_2$ were the recording of new bonds around 1642cm^{-1}, 1425 cm^{-1} due to C=N and C=C vibration formation, respectively, which proves anchoring of 1H-pyrrole-2-carbaldhyde onto the Polysiloxane surface. (Figure 4.2)

Figure 4-2: FT-IR of (a) 3-aminopropyl functionalized silica gel (Si-NH2) (b) and the modified Polysiloxane surface (Si-NPr)

4-1-3. UV-visible spectrophotometry

UV-visible spectrophotometer was used to confirm that 1H-pyrrole-2-carbaldhyde successfully anchored to the surface of silicon matrix during modification with 3-amino-pyl-trimethoxy-silane.(Figure 4-3). 0.01 g of Si-NH$_2$ and SiNPr was dissolved in 10 mL CH$_2$Cl$_2$ and the absorbance was measured by making CH$_2$Cl$_2$ blank solution.

Si-NH$_2$ absorbs UV light at 282 nm, while SiNPr adsorb UV light at 291.5 nm. This difference confirms the supporting of the organic compound onto the surface of silicon matrix.
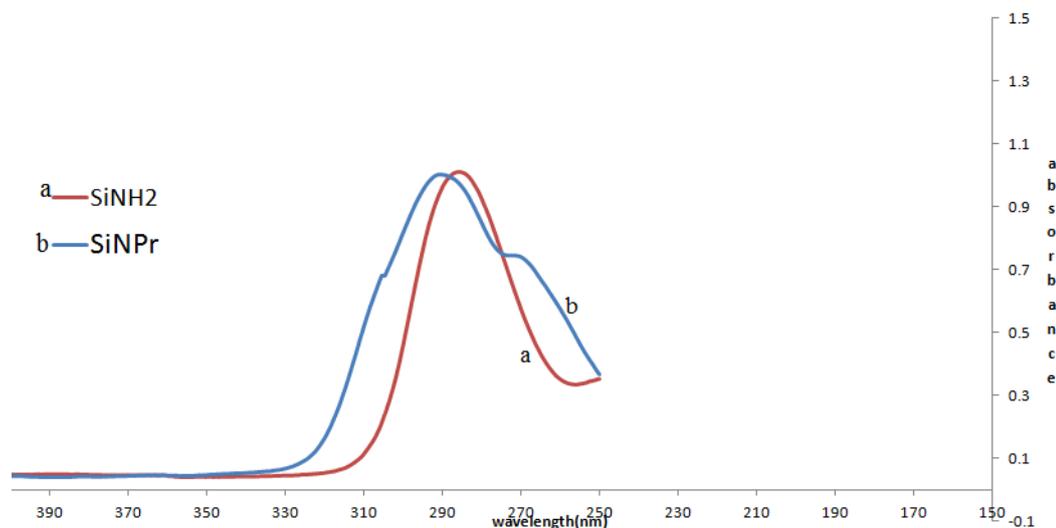
Figure 4-3: UV-visible spectra of (a) 3-aminopropyl-functionalized silica gel (Si-NH2) (b) and the modified Polysiloxane surface (Si-NPr)

4-1-4. Thermal Stability of matrix (TGA)

Thermo stability of (SiNH$_2$), (SiNPr) have been characterized by TGA analysis.

Thermogravimetric curves for (SiNH$_2$) and (SiNPr) indicate a degradation action between 122 – 800 °C that proves expected high thermal stability of Si- matrix.

Two major step of degradation were recorded for SiNH$_2$. The first one, from room temperature to 100°C a small mass loss of 1.56% which refer to the residual water dehydration. The second step, between 208 - 800°C a clear increase of 9.77% in mass loss was observed, which relates to the organic matter attached onto surface through immobilization process.

The modified adsorbent SiNPr showed two obvious step of mass loss. Step 1: From 25-105°C rang, the first mass loss 1.1%

which assigned to adsorbed water. Step 2: between 276- 800°C other mass loss of 14.13% due to the decomposition of pyrrole part immobilized at the surface of silicon matrix. The clear enhance in the mass loss reverberate the higher quantity of organic groups anchored at surface.[7]
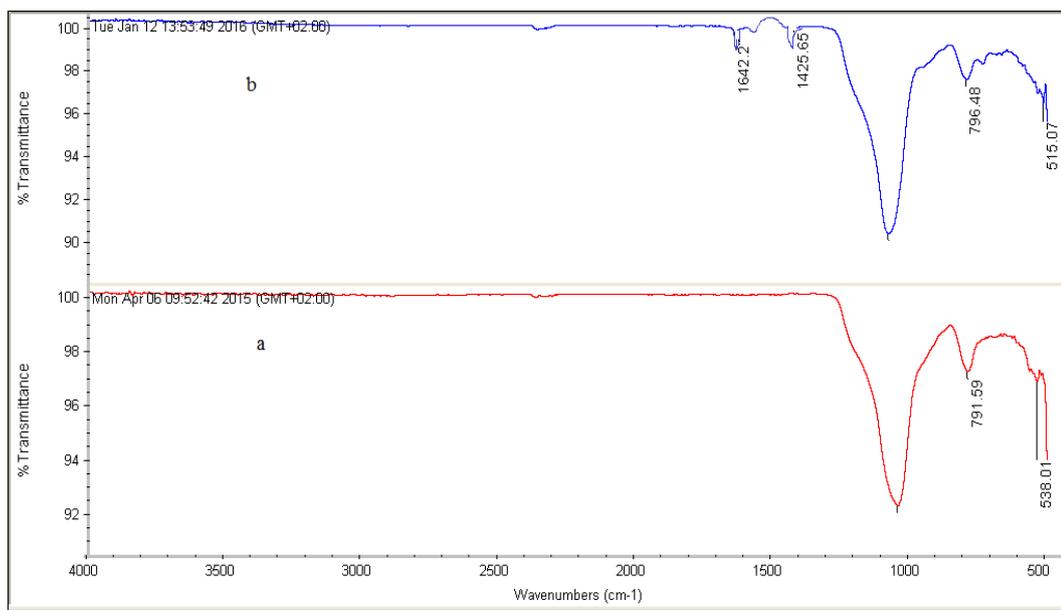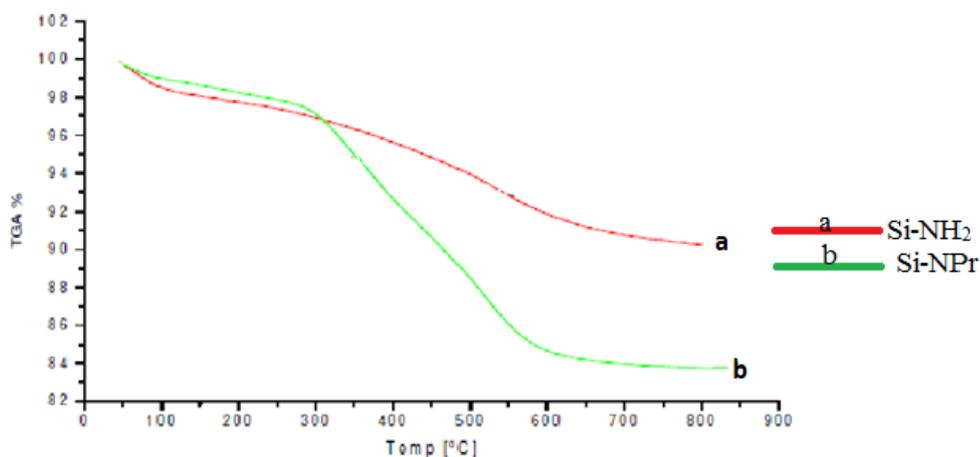

Figure 4-4: TGA curves of (a) 3-aminopropyl functionalized silica gel (Si-NH2) (b) and the modified Polysiloxane surface (Si-NPr) [7]

4-1-5. EDX Characterization

Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. Examination proved the presence of oxygen, nitrogen, silicon and carbon by percentage as shown in (Figure 4-5): 51.67% oxygen, 36.13% silicon, 4.41% nitrogen and 7.79% carbon. These results demonstrate purity of the prepared matrix, where the percentage of purity reaches to 100%.
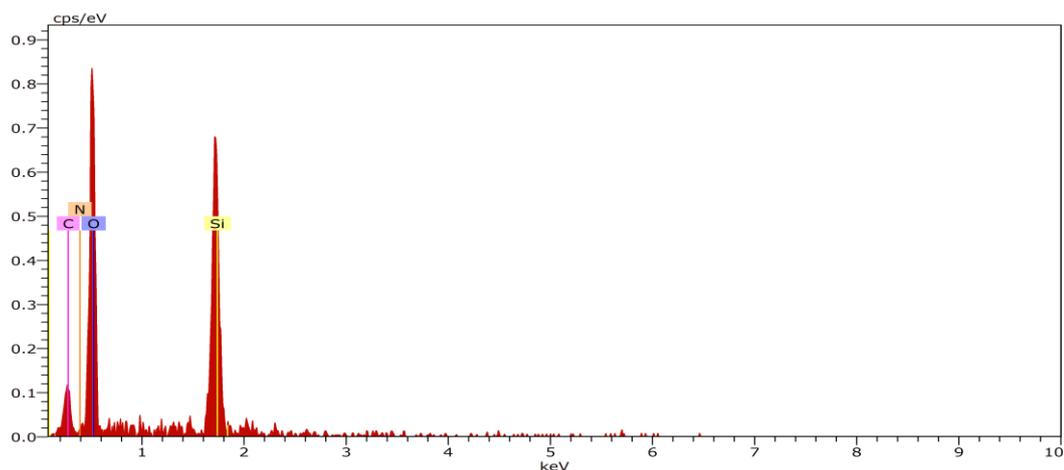
Figure 4-5: EDX of the modified Polysiloxane surface (SiNPr)

4-2. Investigation of adsorption parameters

4-2-1. Contact time effect on Cr (VI) adsorption

Adsorption of Cr (VI) on (Si-NPr) was calculated as a function of contact time to determine the maximum time of adsorption, as shown in Figure 4-6.

During the first 5 min, rapid adsorption of Cr (VI) was detected, which resonated to N and NH donors in the matrix. Indeed, the two donor atoms acting like chelating bidentate donor[7]. At the beginning, all the reacting sites are vacant, for this, the rate of adsorption capacity is high and the adsorbents (SiNPr) have available high surface area for adsorption of Cr (VI). 5 min later the adsorption becomes constant due to consuming of active adsorbing sites.[59]
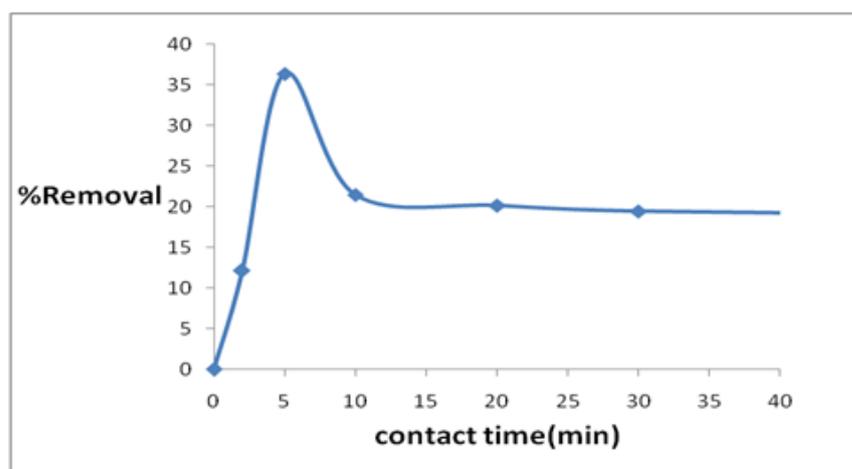
Figure 4-6: Effect of contact time on Cr (VI) adsorption. (dose= 0.1 g, Cr(VI) concentration = 10mg/L, temperature= 25ºC, solution volume= 50 mL.)

4-2-2. pH effect on Cr (VI) adsorption

pH is a critical factor that affects the rate of adsorption process. Cr (III) and Cr (VI), is most oxidation state of Chromium ions, the pH of solution play an important role in such ion form stability. It was assumed at low pH, Cr (VI) reduced to Cr (III) under acidic condition in presence of activated carbon. In H_2O system, at low pH, hydrogen chromate ($HCrO_4^-$) are the dominant ions. In this study at low pH such as 2 to 4 there was increase of the adsorption capacity for Cr (VI). When pH is further enhanced, a sharp decrease in uptake capacity of adsorption was noticed. This is because the sapping of electrostatic forces of attraction between adsorbent and adsorbate. Fig. 4-7, shows that the optimum pH for Cr (VI) adsorption onto SiNPr closes to 4.
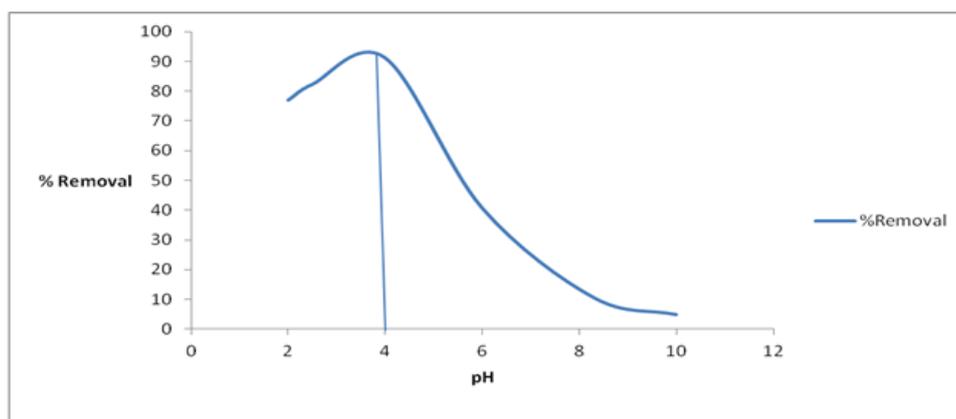
Figure 4-7: Effect of pH on Cr(VI) adsorption. (adsorbent dose= 0.03 g , concentration of Cr(VI)= 10 mg/L, tempreature=25°C, time= 5 min, solution volume= 15 mL).

4-2-3. Temperature effect on Cr (VI) adsorption

Temperature plays a critical role in any kind of adsorption processes. (Si-NPr-Cr (VI)) interaction temp was illustrated in Figure 4.8. This figure shows that increasing the temperature above the room temperature (25°C) has effect on decreasing the adsorption capacity of modified surface. The decrease in removal percentage may because of reduction of the physical forces of attraction between SiNPr and Cr (VI). Results reveled that the removal of chromium is reduced with increase in temperature onto the adsorbent SiNPr which is diffusion-controlled exothermic process (E_a =28.477).[54] Maximum adsorption achieved when room temperature 25°C was applied.
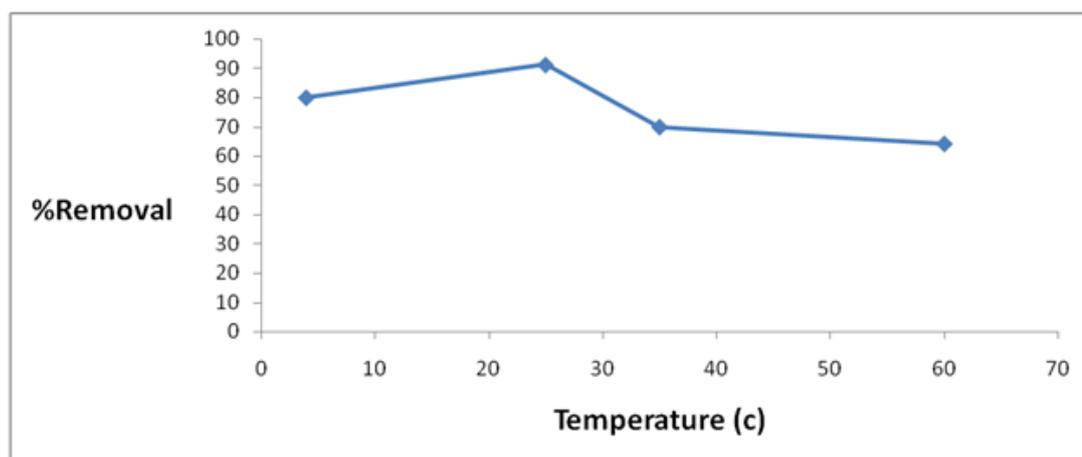
Figure 4-8: Effect of temperature on Cr(VI) adsorption. (concentration of Cr(VI)= 10 mg/L, adsorbent dose= 0.03 g, pH=4, time= 5 min., , solution volume= 15 mL)

4-2-4. Cr (VI) concentrations effects

Effect of initial concentration of Cr (VI) on adsorption processes was investigated with fixing previous conditions like contact time, volume of solution, temperature and pH. The results are shown in Figure 4-9 and in Figure 4-10. In Figure 4.9, the percent removal of Cr (VI) increases with increasing initial concentration of Cr (VI). Figure 4.10 shows that as the metal concentration increases from 5 - 20 mg/L, the adsorption capacity is increasing from 1.18 - 8.30 mg/g. This may be because of gradual increase in the electrostatic attraction between the Cr (VI) and the absorbent desired active sites. In addition, higher initial concentration of Cr (VI) may enhance the affinity of Cr (VI) to the active sites on the adsorbate. Furthermore, this could be interpreted by the logic, more adsorption sites will be enveloped when more ions concentration increase.[60]

Above 20 mg/L initial concentration of Cr (VI), the percentage removal of Cr (VI) ion reduced. This may be because adsorbents active sites become saturated.[61]
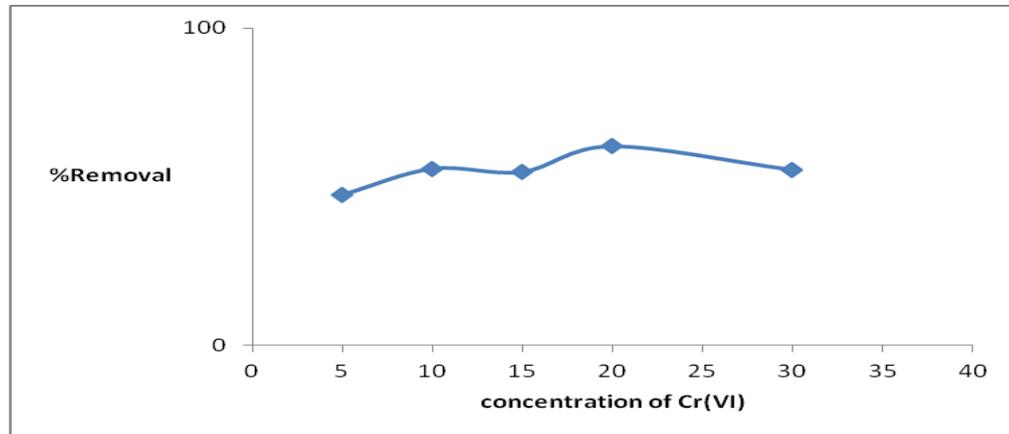
Figure 4-9: Effect of Cr (VI) initial concentration on adsorption. (Adsorbent dose= 0.03 g, time= 5 min, pH= 4, Temperature= 25°C. solution volume= 15 mL)
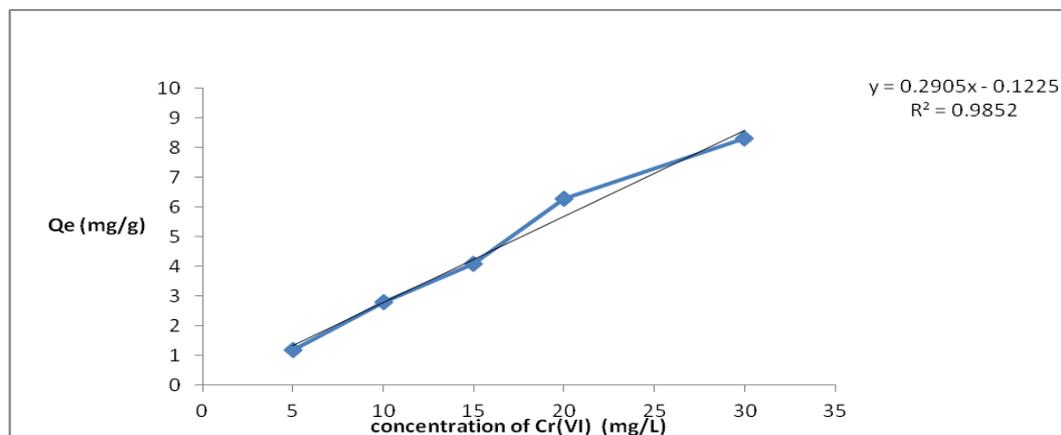
Figure 4-10: Effect of Cr (VI) initial concentration on adsorption capacity. (Adsorbent dose= 0.03 g, time= 5 min, pH= 4, Temperature= 25°C, solution volume= 15 mL)

4-2-5. Adsorbent dose effect

Effect of adsorbents dose on adsorption processes was studied with fixing all previous conditions like contact time (5min) , volume of solution (15mL), temperature (25°C), pH (=4), initial concentration

of Cr(VI) = (20mg/L). Results exhibited in Figure 4.11 shows that removal efficiency was decreased with increasing adsorbent dose. It shows that removal efficiency was 86% when the adsorbent dose was 0.01 g. For 0.03 g, it was 69.80% and 48.90% for 0.07 g. Figure 4.12 shows that Cr (VI) adsorption capacity decreased progressively; adsorption capacity was 25.80 mg/g for 0.01 g adsorbent dosage and 1.09 mg/g for 0.10 g adsorbent. These results may due to overlapping of adsorption sites as a result of adsorbent particles congestion. Furthermore, the high adsorbent dosage may oblige a screening effect on the dense outer layers of the cell, there by shielding the binding sites from metal ion.[62]
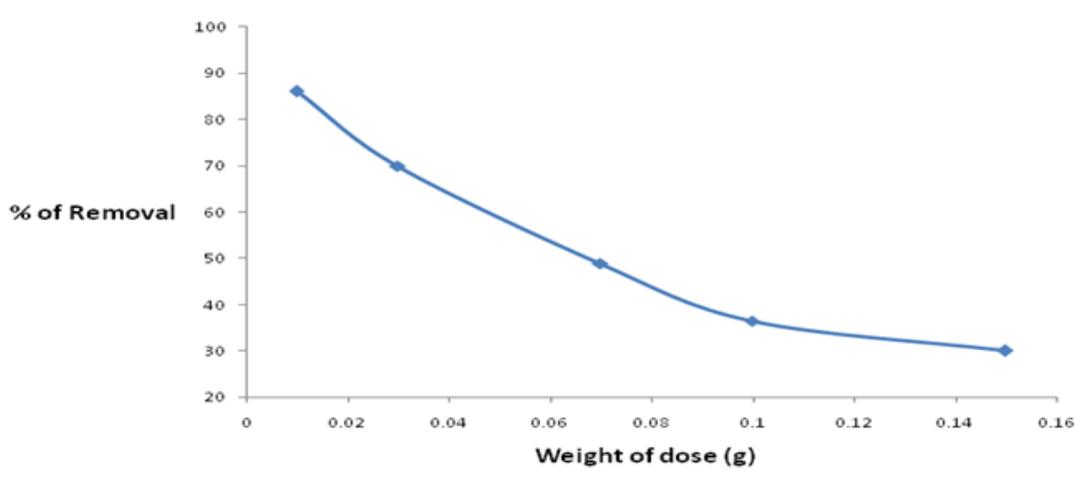
Figure 4-11: Effect of adsorbent dose on the removal of Cr(VI). (time= 5 min., pH= 4, temperature= 25ºC, concentration of Cr(VI) = 20 mg/L, solution volume= 15 mL)
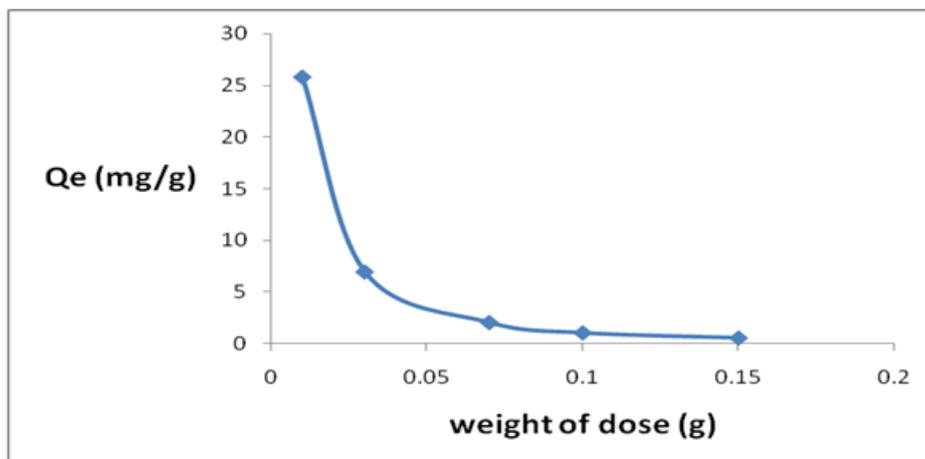
Figure 4-12: Effect of adsorbent dose on adsorption capacity. (time= 5 min., pH= 4, temperature= 25ºC, concentration of Cr(VI) = 20 mg/L, solution volume= 15 mL)

4-3. Adsorption isotherm of Cr(VI)

The most common available isotherm equations to evaluate experimental sorption process parameters are the Langmuir or Freundlich models.[51]

4-3-1. Langmuir Adsorption Isotherm

Langmuir isotherm is based on Hypothesis presence of a limited number of homogeneously distributed active sites above the surface of the desired adsorbent. The active sites have similar affinity for adsorption of a mono- layer molecular model. In Langmuir isotherm model no interaction between the adsorbed molecule.[49]

A Famous linear form of the Langmuir equation can be expressed by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \tag{4-1}$$

Where: q_e is the amount of Cr (VI) adsorbed per gram of the adsorbent (mg/g), q_m is maximum monolayer covering capacity (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_L = Langmuir isotherm constant (L/mg).

A dimensionless constant separation factor R_L, is the essential characteristics of the Langmuir isotherm and can be expressed by the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{4-2}$$

Where C_o: the highest initial concentration of adsorbate (mg/L).

The value of R_L donates the shape of the isotherm. If $(R_L > 1)$ the adsorption process is unfavorable, if $(R_L = 1)$ the adsorption process is linear, if $(0 < R_L < 1)$ the adsorption process is favorable, and if $(R_L = 0)$ the adsorption process is irreversible. The value of R_L was found to be 0.48 at $25°C$ donating that the adsorption of Cr (VI) on (Si-NPr) is favorable.[2, 49]

From Langmuir plot, the values of Q_m, K_L, and R^2 were determined as shown in Figure 4-13. The values of these parameters are shown in Table 4-1.

Figure 4-13: Langmuir plot for Cr (VI) adsorption on (Si-NPr). (contact time= 5min, pH= 4, temperature= 25°C, adsorbent dose= 0.03 g, solution volume= 15 mL.)

Table 4-1: Langmuir isotherm parameters and correlation coefficient for adsorption of Cr(VI) on (Si-NPr)

Langmuir isotherm	Q_m (mg/g)	K_L (L/mg)	R_L	R^2
parameters	13.05	0.03	0.48	0.77

4-3-2. Freundlich Adsorption Isotherm

The Freundlich isotherm is not limited to the formation of a mono-layer as Langmuir isotherm. Freundlich model includes interaction between the adsorbed molecules and applies to adsorption of heterogeneous surface. Such model supposes when adsorbate conc. increases, the conc. of the adsorbate at adsorbent surface should also increases. On the other hand, the sorption energy exponentially decays on completion of the sorption centers of adsorbent. The famous expression for the Freundlich isotherm model is given as in equation:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \qquad (4\text{-}3)$$

Where: K_F, n are Freundlich constants.

K_F is an indicator of adsorption capacity of the adsorbent and 1/n is an indicator of favorability of the adsorption process. If value of (1/n < 1) it donates a normal adsorption. If (10>n>1) this donates a favorable adsorption process[63]. K_F and n constants could be determined from the linear equation of ln (Q_e) versus
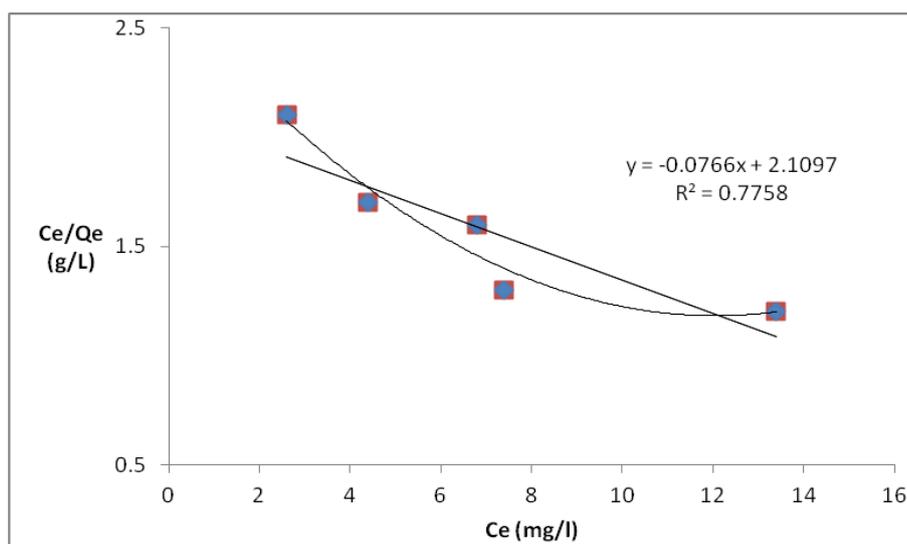
ln (C_e), as shown in Figure 4-14:
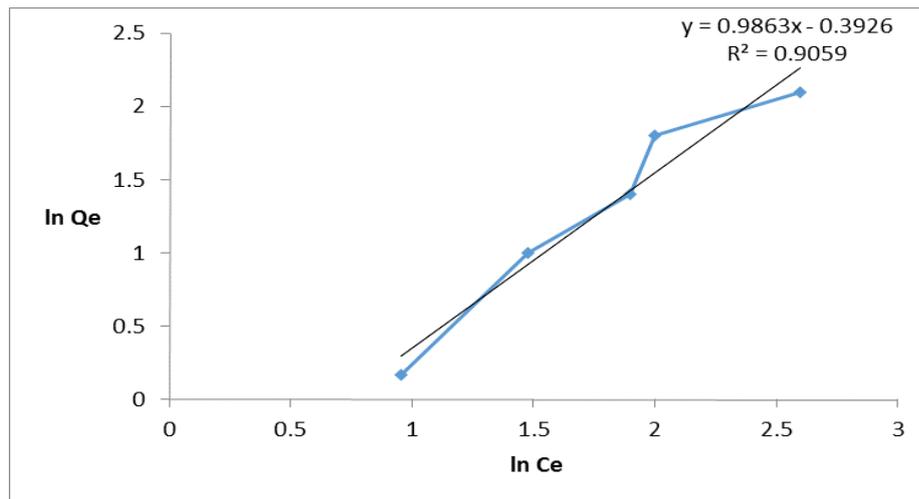
Figure 4-14: Freundlich plot for Cr (VI) adsorption on (Si-NPr). (Contact time= 5 min, pH= 4, temperature= 25°C, adsorbent dose= 0.03 g, solution volume= 15 mL)

Values of freundlich constants n, K_F and regression constant (R^2) are shown in Table 4-2:

Table 4-2: Freundlich isotherm parameters and correlation coefficient for adsorption of Cr(VI) on (Si-NPr)

Freundlich isotherm parameters	n	1/n	K_F	R^2
	1.01	0.98	0.67	0.90

From the data in table 4-2, that value of 1/n= 0.9863 while n=1.0139 denoting that adsorption of Cr (VI) on (Si-NPr) is favorable with R^2= 0.9059.

Table 4-3: correlation coefficient and parameters of Langmuir, Freundlich for adsorption of Cr(VI) on (Si-NPr).

Langmuir isotherm parameters	Q_m (mg/g)	K_L (L/mg)	R_L	R^2
	13.05	0.03	0.48	0.77
Freundlich isotherm parameters	n	1/n	K_F	R^2
	1.01	0.98	0.67	0.90

Freundlich and Langmuir adsorption isotherms were calculated. Adsorption data suited with Langmuir and Freundlich. The value of R_L From Langmuir isotherm data in Table 4-3 was found to be 0.48 at 25 ◦C denoting that adsorption of Cr(VI) at (Si-NPr) is preferred with R^2=0.7758.

From Freundlich isotherm data in table 4-3, the value of 1/n=0.9863 denoting that adsorption of Cr (VI) at (Si-NPr) is preferred with R^2=0.9059. Minimal value of (1/n) denotes stronger interaction relation between the adsorbate and adsorbent. When 1/n approaching to zero the surface heterogeneity becomes more[59]. The

adsorption data suited with Langmuir and Freundlich, but Freundlich adsorption model found to be with highest R^2 and from here the best suit. The Freundlich model fit more with the experimental data of adsorption indicates physical adsorption in addition to heterogeneon mode distribution of adsorbate active sites at the adsorbent surface.[49]

4-4. Adsorption thermodynamics

Thermodynamic parameters using to study adsorption of Cr(VI) by (Si-NPr) were calculated using equations:

$$K_D = q_e/C_e \tag{4-4}$$

$$\Delta G^o = - RT \ln K_D \tag{4-5}$$

$$\ln K_D = (\Delta S^o/R) - (\Delta H^o/RT) \tag{4-6}$$

Where K_D: the distribution coefficient for the adsorption in g/L, ΔG^o: the Gibbs free energy in J/mol, ΔS^o: the entropy change in J/mol.K, R: the universal gas constant in J/mol.K, T: the absolute temperature in K and ΔH^o: the enthalpy change in kJ/mol.

From the intercept and slope of the plot of $\ln K_D$ vs. 1/T, the values belong to entropy change (ΔS^o) and enthalpy change (ΔH^o) was calculated. The values of Gibbs free energy (ΔG^o) were calculated at different temperatures.[64](Figure 4-15)
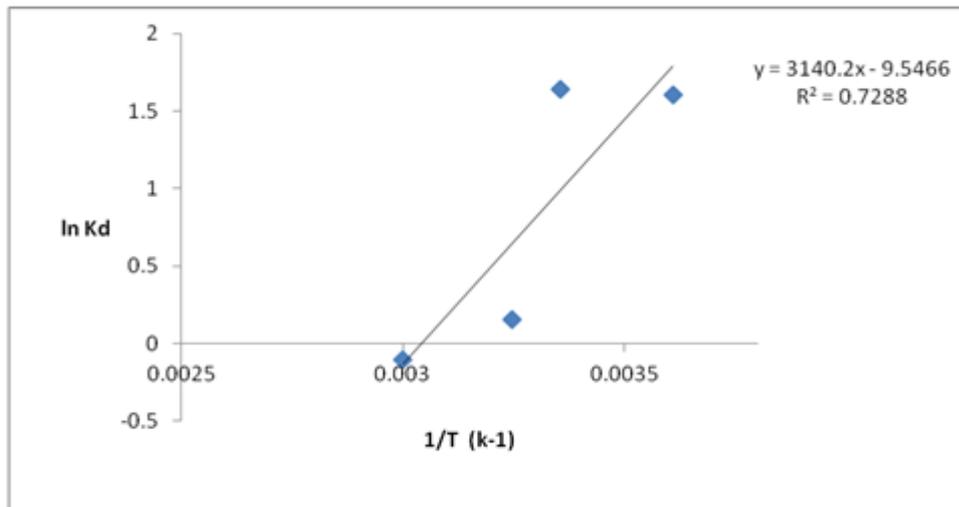
Figure 4-15: Plot of lnKd versus 1/T for Cr(VI) adsorption on (Si-NPr). (contact time = 5 min, pH =4, adsorbent dose = 0.03 g , sol.volume= 15 mL)

The results exhibit that $\triangle S^o$ was - .079 J/ mol K, $\triangle H^O$ was −26.107 kJ /mol. $\triangle G^O$ at different temperatures were calculated from the following equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (4\text{-}7)$$

The calculated thermodynamic parameters are shown in table 4-4:

Table 4-4: **The values of calculated thermodynamic parameters on Cr (VI) adsorption .**

ΔS^o (J/mol.k)	ΔH^o (kJ/mol)	ΔG^o (kJ\mol)			
		277 k^o	298 k^o	308 k^o	333 k^o
-0.07	-26.10	-4.22	-2.56	-1.77	0.20

The negative ΔG^O values denote that the adsorption process is spontaneous. The negative value of ΔH^O indicates to exothermic adsorption and to preferable of the adsorption at low temperature. For physical

adsorption, ΔH^O is commonly smaller than that of chemical adsorption. In general, ΔH^O for physical adsorption ranges from 0-40 KJ/mol and for chemical adsorption ranging from 40-800 KJ/mol. The low negative value of ΔH^O indicates that the adsorption processes of Cr (VI) ions by SiNPr is physical in nature which involve forces of attraction between the adsorbate-adsorbent molecules and adsorption processes was exothermic reactions.[59]

The value and sign of ΔS^O gives an indication if the adsorption process is an associative or dissociative mechanism. A negative value of ΔS^O indicates that the adsorption process involves an associative mechanism. The adsorption process involves the formation of an activated complex between the adsorbent and adsorbate. Furthermore a negative value of ΔS^O denotes that no significant change appear in the internal structure of the adsorbent during the adsorption process.[60]

4-5. Adsorption kinetics of Cr(VI)

Various kinetic models are served to suggest the expected mechanism of the adsorption processes. Lagergren's first-order rate equation represents the adsorption rate process based on the adsorption capacity.

The lagergren equation represents the pseudo-first order: [49, 51]

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \tag{4-8}$$

Where q_e: the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t: the amount of solute adsorbed at any time per unit weight of adsorbent (mg/g) and k_1: first order adsorption rate constant (min^{-1}).

k_1, q_e were calculated from the slope and intersept of linear plot of log (q_e− q_t) Vs time (Figure 4.16). k_1 and q_e values were determined in Table 4-5. Pseudo first order model is suitable to Cr (VI) adsorption on Si-NPr if plot was have good correlation coefficient (correlation coefficient close to 1). The correlation coefficient was calculated from plot in (Figure 4-16) Show that R^2=.0165 so the adsorption process is not pseudo first order process. It was observed the pseudo first order model did not suit. Calculated and experimental q_e values were represented in (Table 4-5) shows that the calculated q_e values are not compatible with the experimental q_e value. This indicates that the adsorption of Cr (VI) does not obey pseudo first-order kinetics.[49]
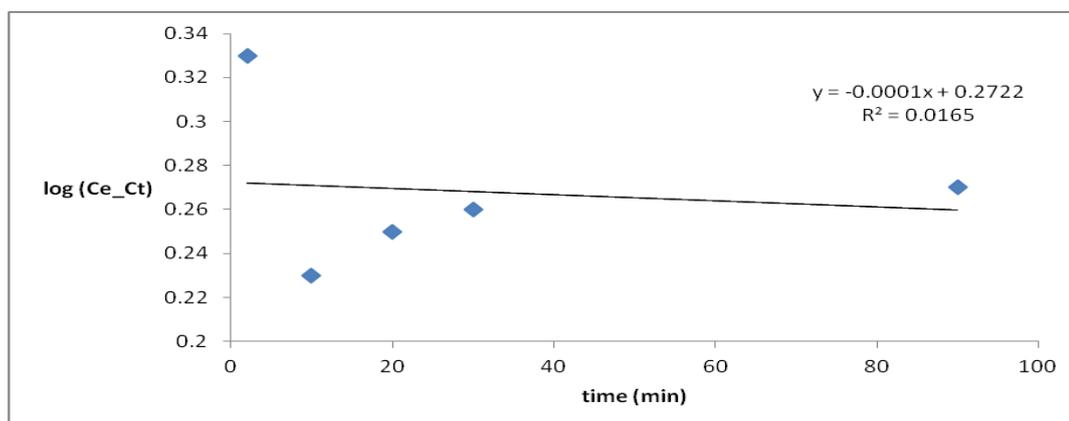
Figure 4-16: Pseudo first order kinetics of Cr (VI) on (Si-NPr). (pH= 4, adsorbent dose= 0.03 g temperature= 25°C, solution volume= 15 mL,)

On the other hand, the pseudo second-order known equation related to equilibrium adsorption as in equation.[49, 51]

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2} \qquad (4\text{-}9)$$

Where k_2: the pseudo-second order rate constant (g/mg. min).
The results show that correlation coefficients are closer to unity (R^2=.9999) so the pseudo second order kinetic model suits completely (Figure 4-17)
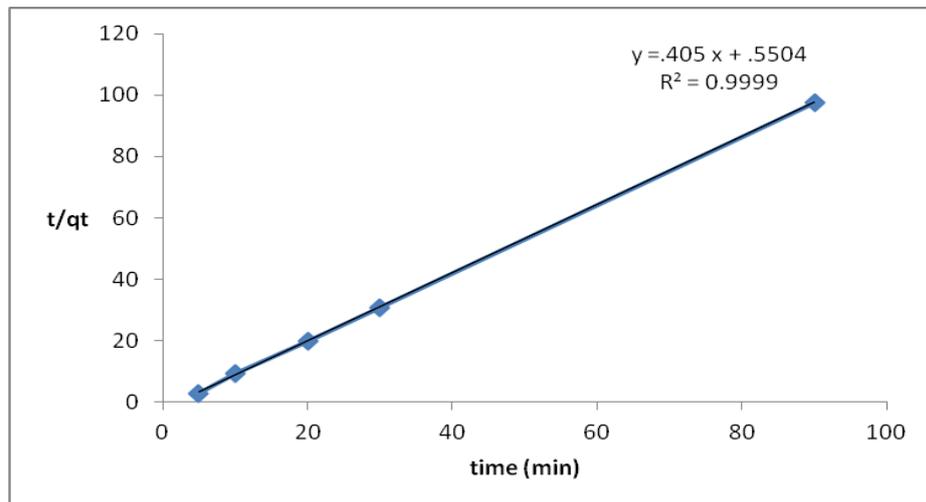
Figure 4-17: Pseudo second order kinetics of Cr (VI) on (Si-NPr). (pH= 4,temperature= 25ºC, adsorbent dose= 0.03 g, solution volume= 15 mL).

Calculated and experimental q_e value were represented in (Table 4-5) shows that q_e calculated value are compatible with q_e experimental value. Furthermore K_2 is greater than k_1. For this, Cr (VI) adsorption does kinetically obey pseudo second-order.

Table 4-5: Pseudo first order and pseudo second order kinetic model parameters for Cr(VI) adsorption on Si-NPr at 25ºC.

Pseudo first order	k_1	q_e (calc)	R^2	q_e (exp)
	-2.30×10^{-3}	1.87	0.01	
Pseudo second order	k_2	q_e (calc)	R^2	2.78
	0.29	2.46	0.99	

4-6. Recovery of Cr(VI) and reusability of Si-NPr

Recovery of Cr (VI) from the Si-NPr was achieved at room temperature. The first step was filtration to collect the adsorbent. The second step was washing the adsorbent with portions of 2M NaOH then washing with deionized water, and finally left the adsorbent to desiccate at room temperature for three days. 0.01g of the regenerated adsorbent was added to a 15 mL of 20 ppm Cr (VI) solution at pH 4 in order to compare the adsorption capability of the regenerated Si-NPr with fresh adsorbent. (Figure 4.18) showed that regenerated adsorbent have good adsorption capability and excellent stability. Results confirmed the possibility of use of adsorbent again without reducing the efficiency of adsorption.[64]
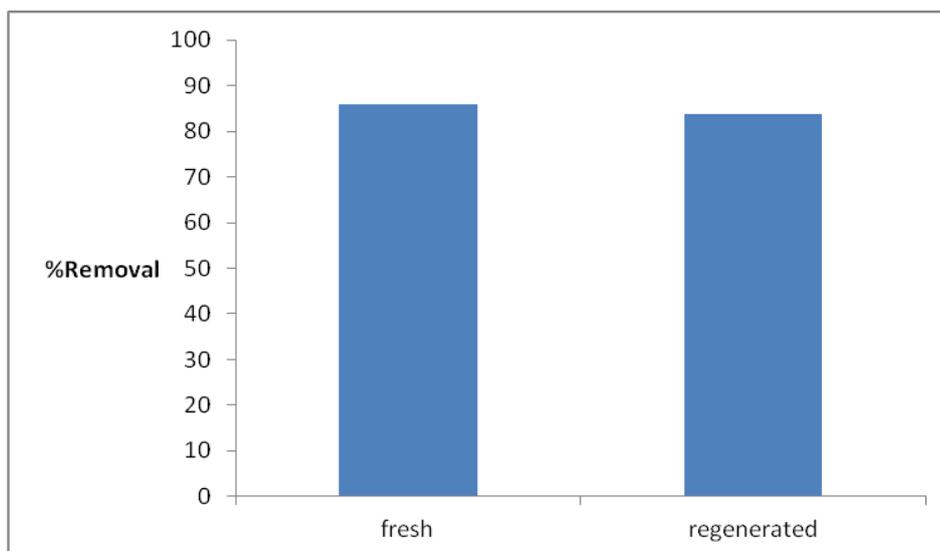
Figure 4-18: Percentage of Cr (VI) removal by recovered adsorbent (contact time= 5 min, pH=
4, temperature= 25ºC, adsorbent dose= 0.01 g, solution volume= 15 mL of 20 ppm Cr (VI) solution.)

4-7. Studying the aantimicrobial activity of Si-NPr matrix

The study was conducted on three types of bacteria such as: *pseudomonas aeruginosa* (G-), *Escherichia coli* (G-) and *Staphylococcus aurous* (G+). Eosin Methylene Blue Agar (EMB), Mannitol Salt Agar (MSA), and MacConkey Agar media (MAC) were prepared for studding antibacterial activity. .01 g of prepared matrix was dissolved in 1 mL of 10% Dimethyl sulfoxide (DMSO). Holes were made by sterilized tips above the entire sterilized agar plates. In one hole 100µl of dissolved Si-NPr matrix was added, the other hole 100µL of DMSO was added and the last hole with positive control. The plates were incubated at 38°C for around 24 hrs. The results were negative in all plates.[65]

The selection of these types of bacteria because of the seriousness and spread quickly in water .
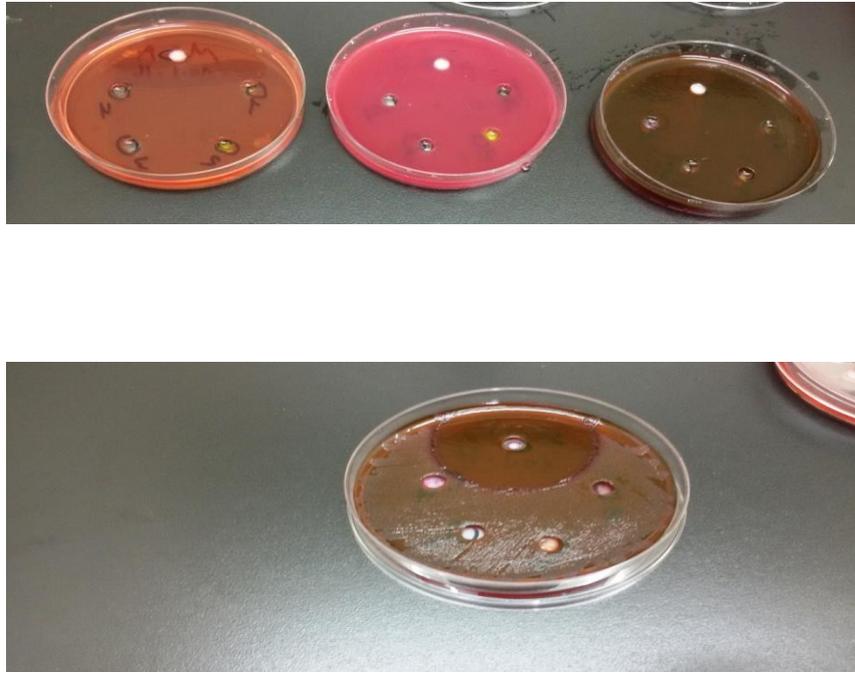
Figure 4-19: Antimicrobial Activity of Si-NPr matrix

Conclusions

1. Over 86% removal efficiency of Cr (VI) was achieved after 5 min. at pH solution around 4 and room temperature, 0.01 g weight of dose and initial concentration of 20 mg/L Cr (VI) solution.

2. It was found that adsorption of Cr (VI) using (Si-NPr) obeyed both Langmuir and Freundlich isotherm models, but mostly fitted with Freundlich model.

3. The amounts of Cr(VI) adsorbed per unit mass of (Si-NPr) followed pseudo second order model, Q_e calc (2.469) was in consistent with the experimental value (Q_e exp 2.782).

4. Thermodynamic parameters of the adsorption of Cr(VI) on (Si-NPr) revealed the following:

• The negative ΔG^o values (-4.224 to -1.775 kJ/mol) indicated that the adsorption is favorable and spontaneous at measured temperatures.

• The negative value of $\Delta H°$ (-26.1 kJ/mol) reflected an exothermic adsorption and indicated low temperature favored adsorption.

• A small negative value of ΔS^o (-0.075) suggested associative mechanism processes.

5. Si-NPr matrix removed Cr (VI) from wastewater and it was recyclable for a promising degree.

6. Low biological activity against *Staphylococcus aurous, Pseudomonas aeruginosa,* and *Escherichia coli* was detected by

Si-NPr matrix.

Recommendations

- Since kinetics is pseudo-second order further investigation is required to study the removal mechanism of Cr (VI).

- The possibility of using this matrix as stationary phase for

  HPLC.

- Studying the effect of presence of metal ions in the aqueous medium on Cr (VI) adsorption.

References

1. Duruibe, J. O. Ogwuegbu, M. O. C., & Egwurugwu, J. N. (2007). *Heavy metal pollution and human biotoxic effects*. **International Journal of Physical Sciences, 2(5), 112-118.**

2. Crini, G. (2005). **Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment**. Progress in polymer science, 30(1), 38-70.

3. El-Ashgar, N. M., & Saadeh, S. M. (2006). **Preparation of Immobilized-Polysiloxane Salicylaldehyde Propylimine and Its Application.** *J. Al-Aqsa Unv*, *10*, 153-161.

4. Förstner, U., & Wittmann, G. T. (2012). **Metal pollution in the aquatic environment.** Springer Science & Business Media.

5. Parikh, J. H. **Some Aspects of Water and Wastewater Treatment**

6. Khatoon, N., Husain Khan, A., Pathak, V., Agnihotri, N., & Rehman, M. (2013). **Removal of hexavalent chromium from synthetic waste water using synthetic nano zero valent iron (NZVI) as adsorbent**. Int. J. Innov. Res. Sci. Eng. Technol, 2, 6140-6149.

7. Radi, S., Tighadouini, S., El Massaoudi, M., Ben Hadda, T., Zaghrioui, M., Bacquet, M., ... & Warad, I. (2014). **Synthesis of 1-(Pyrrol-2-yl) imine modified silica as a new sorbent for the removal of toxic metals from aqueous solutions.** J. Mater. Environ. Sci, 5, 1280-1287.

8. Ashley, K., & Fairfax, R. (2003). **Sampling and analysis of soluble metal compounds.** NIOSH Manual of Analytical Methods, *4*, 167-178.

9. Rad, S. M., Mirbagheri, S. A., & Mohammadi, T. (2009). **Using reverse osmosis membrane for chromium removal from aqueous solution**. *Eng Technol*, *57*, 348-52.

10. Anger, G., Halstenberg, J., Hochgeschwender, K., Scherhag, C., Korallus, U., Knopf, H., ... & Ohlinger, M. (2005). **Chromium compounds**. Ullmann's Encyclopedia of Industrial Chemistry.

11. Baranowska-Dutkiewicz, B. (1981). *Absorption of hexavalent chromium by skin in man.* **Archives of toxicology, 47(1), 47-50.**

12. Kumar, P. A., Ray, M., & Chakraborty, S. (2007*). Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel.* **Journal of Hazardous Materials,** *143*(1), 24-32.

13. Shy, S. L., Hong, C. S., Wu, C. S., Chen, S. J., Wu, H. Y., & Ting, Y. C. (2009, December). **Green binary and phase shifting mask. In** *SPIE Lithography Asia* **(pp. 75202D-75202D**). International Society for Optics and Photonics.

14. Acosta-Rodríguez, I., Arévalo-Rangel, D. L., Cárdenas-González, J. F., de Guadalupe Moctezuma-Zárate, M., & Martínez-Juárez, V. M. (2015). **Hexavalent Chromium (VI) Removal by Penicillium sp**. IA-01.

15. Dermentzis, K., Christoforidis, A., Valsamidou, E., Lazaridou, A., & Kokkinos, N. (2011). **Removal of hexavalent chromium from electroplating wastewater by electrocoagulation with iron electrodes**. *Global Nest J*, *13*(4), 412-418.

16. Gad, S. C. (1989). **Acute and chronic systemic chromium toxicity**. Science of the Total Environment, 86(1), 149-157.

17. Dayan, A. D., & Paine, A. J. (2001). **Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000.** *Human & Experimental Toxicology*, *20*(9), 439-451.

18. Cohen, M. D., Kargacin, B., Klein, C. B., & Costa, M. (1993). **Mechanisms of chromium carcinogenicity and toxicity**. Critical reviews in toxicology, 23(3), 255-281.

19. Mattia, G. D., Bravi, M. C., Laurenti, O., Luca, O. D., Palmeri, A., Sabatucci, A., ... & Ghiselli, A. (2004). *Impairment of cell and plasma redox state in subjects professionally exposed to chromium*. **American journal of industrial medicine, 46(2), 120-125.**

20. Lindberg, E., & Hedenstierna, G. (1983). *Chrome plating: symptoms, findings in the upper airways, and effects on lung function.* **Archives of Environmental Health: An International Journal, 38(6), 367-374**

21. US Department of Health and Human Services. (1999). **Agency for toxic substances and disease registry.** Toxicological Profile for Asbestos. Update. Agency for Toxic Substances and Disease Registry.

22. Gibb, H. J., Lees, P. S., Pinsky, P. F., & Rooney, B. C. (2000). *Clinical findings of irritation among chromium chemical production workers.* American journal of industrial medicine, 38(2), 127-131.

23. Henderson, R. F., Rebar, A. H., & Denicola, D. B. (1979). **Early damage indicators in the lungs. IV. Biochemical and cytologic response**

of the lung to lavage with metal salts. Toxicology and applied pharmacology, 51(1), 129-135.

24. Polak, L. (1983). *Immunology of chromium*. Chromium: Metabolism and toxicity, 51-136.

25. Lewis, R. (1997). **Occupational exposures metals.** Occupational & environmental medicine, LaDou J (Ed.), 416-20.

26. Stern, A. H., Bagdon, R. E., Hazen, R. E., & Marzulli, F. N. (1993). *Risk assessment of the allergic dermatitis potential of environmental exposure to hexavalent chromium*. **Journal of Toxicology and Environmental Health, Part A Current Issues,** *40*(4), 613-641.

27. Gibb, H. J., Lees, P. S., Pinsky, P. F., & Rooney, B. C. (2000). *Lung cancer among workers in chromium chemical production.* **American journal of industrial medicine, 38(2), 115-126..**

28. Zhitkovich, A., Song, Y., Quievryn, G., & Voitkun, V. (2001). **Non-oxidative mechanisms are responsible for the induction of mutagenesis by reduction of Cr (VI) with cysteine: role of ternary DNA adducts in Cr (III)-dependent mutagenesis.** *Biochemistry*, *40*(2), 549-560..

29. Langård, S., & Norseth, T. (1975). *A cohort study of bronchial carcinomas in workers producing chromate pigments*. **British journal of industrial medicine, 32(1), 62-65.**

30. Pascale, L. R., Waldstein, S. S., Engbring, G., Dubin, A., & Szanto, P. B. (1952). *Chromium intoxication: With special reference to hepatic injury*. **Journal of the American Medical Association, 149**(15), 1385-1389.

31. Kołaciński, Z., Kołacinski, Z., Kostrzewski, P., Kruszewska, S., Raźniewska, G., & Mielczarska, J. (1999). *Acute potassium dichromate poisoning: a toxicokinetic case study.* **Journal of Toxicology: Clinical Toxicology,** *37*(6), 785-791.

32. Korallus, U., Ehrlicher, H., & Wustefeld, E. (1974). **Trivalent chromium compounds-the results of a study in the field of industrial medicine. Part I. General; technology; retrospective investigation.** Arbeitsmedizin Sozialmedizin Praventivmedizin, 9(3), 51-4.

33. Mancuso, T. F. (1951). **Occupational cancer and other health hazards in a chromate plant: a medical appraisal. II.** Clinical and toxicologic aspects. *Industrial Medicine and Surgery*, *20*(9), 393-407.

34. Kaufman, D. B., DiNicola, W., & McIntosh, R. (1970). *Acute potassium dichromate poisoning: Treated by peritoneal dialysis*. **American Journal of diseases of children,** *119*(4), 374-376.

35. Saryan, L. A., & Reedy, M. (1988). *Chromium determinations in a case of chromic acid ingestion.* **Journal of analytical toxicology,** *12*(3), 162-164.

36. Ellis, E. N., Brouhard, B. H., Lynch, R. E., Dawson, E. B., Tisdell, R., Nichols, M. M., & Ramirez, F. (1982). *Effects of hemodialysis and dimercaprol in acute dichromate poisoning*. **Journal of Toxicology: Clinical Toxicology,** *19*(3), 249-258.

37. Loubières, Y., Lassence, A. D., Bernier, M., Vieillard-Baron, A., Schmitt, J. M., Page, B., & Jardin, F. (1999). *Acute, fatal, oral chromic*

acid poisoning. **Journal of Toxicology: Clinical Toxicology,** *37*(3), 333-336.

38. Van Heerden, P. V., Jenkins, I. R., Woods, W. P. D., Rossi, E., & Cameron, P. D. (1994). **Death by tanning—a case of fatal basic chromium sulphate poisoning**. *Intensive care medicine*, *20*(2), 145-147.

39. Sharma, B. K., Singhal, P. C., & Chugh, K. S. (1978). *Intravascular haemolysis and acute renal failure following potassium dichromate poisoning.* **Postgraduate medical journal**, *54*(632), 414-415.

40. Cohen, M. D., Kargacin, B., Klein, C. B., & Costa, M. (1993). **Mechanisms of chromium carcinogenicity and toxicity**. *Critical reviews in toxicology*, *23*(3), 255-281.

41. De Flora, S., Badolati, G. S., Serra, D., Picciotto, A., Magnolia, M. R., & Savarino, V. (1987). **Circadian reduction of chromium in the gastric environment.** Mutation Research Letters, *192*(3), 169-174..

42. Jadhav, A. M., & Singare, P. U. (2015). **Studies on water pollution due to toxic metals in Ulhas River flowing along the Dombivli City of Mumbai, India.**

43. Thaer Vqosh, **Electronic monthly magazine published by the Centre for development work, July - August 2012 (46).** http://www.maan-ctr.org/magazine/Archive/Issue46/index.php

44. Hussen, F. M. A. (2013). *Activated carbon from Cyclamen Persicum Tubers for Diclofenac removal from aqueous solution* (Doctoral dissertation, Faculty of Graduate Studies Activated carbon from Cyclamen Persicum Tubers for Diclofenac removal from aqueous solution By Fatima

Mohammed Abdelwahab Hussen Supervisor Dr. Shehdeh Jodeh Co-Supervisor Dr. Nidal Jaradat This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master in Chemistry, Faculty of Graduate Studies, An-Najah National University).

45. Ferrari, L., Kaufmann, J., Winnefeld, F., & Plank, J. (2010). *Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements.* **Journal of Colloid and Interface Science, 347(1), 15-24.**

46. Siminiceanu, I., Lazau, I., Ecsedi, Z., Lupa, L., & Burciag, C. (2008). **Textural characterization of a new iron-based ammonia synthesis catalyst.** *Chem. Bull."POLITEHNICA" Univ*, *53*(67), 1-2.

47. Adamson, A. W., & Gast, A. P. (1967). **Physical chemistry of surfaces.**

48. Somorjai, G. A., & Li, Y. (2010). **Introduction to surface chemistry and catalysis.** John Wiley & Sons.

49. Mahvi, A. H., Naghipour, D., Vaezi, F., & Nazmara, S. (2005). **Teawaste as an adsorbent for heavy metal removal from industrial wastewaters**.

50. Howard, A. G., & Arbab-Zavar, M. H. (1979). **The preconcentration of mercury and methylmercury on dithizone-coated polystyrene beads**. *Talanta*, *26*(9), 895-89.

51. Radi, S., Tighadouini, S., Bacquet, M., Degoutin, S., Cazier, F., Zaghrioui, M., & Mabkhot, Y. N. (2013). **Organically modified silica**

with pyrazole-3-carbaldehyde as a new sorbent for solid-liquid extraction of heavy metals. *Molecules*, *19*(1), 247-262.

52. Rashed, M. N. (2013). **Adsorption technique for the removal of organic pollutants from water and wastewater.** INTECH Open Access Publisher.

53. Vadi, M. (2012). *Adsorption isotherms of celebrex as non-steroidal anti-inflammation on single-walled carbon nanotubes*. **International Journal of Physical Sciences, 7**(8), 1215-1218.

54. Vijayakumar, G., Tamilarasan, R., & Dharmendirakumar, M. (2012). **Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite.** J. Mater. Environ. Sci, 3(1), 157-170.

55. Bhattacharya, A. K., Mandal, S. N., & Das, S. K. (2006). *Removal of Cr (VI) from aqueous solution by adsorption onto low cost non-conventional adsorbents.* **Indian journal of chemical technology**, *13*(6), 576-583.

56. Elmorsi, T. M., Mohamed, Z. H., Shopak, W., & Ismaiel, A. M. (2014). *Kinetic and equilibrium isotherms studies of adsorption of Pb (II) from water onto natural adsorbent*. **Journal of Environmental Protection**, *5*(17), 1667.

57. Saha, P., Chowdhury, S., Gupta, S., & Kumar, I. (2010). *Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin.* **Chemical Engineering Journal,** 165(3), 874-882.

58. El-Nahhal, I. M., & El-Ashgar, N. M. (2007). *A review on polysiloxane-immobilized ligand systems: Synthesis, characterization and applications.* **Journal of Organometallic Chemistry,** *692*(14), 2861-2886.

59. Song, J., Zhang, R., Li, K., Li, B., & Tang, C. (2015). **Adsorption of Copper and Zinc on Activated Carbon Prepared from Typha latifolia L.** *CLEAN–Soil, Air, Water*, *43*(1), 79-85.

60. Tumin, N. D., Chuah, A. L., Zawani, Z., & Rashid, S. A. (2008). *Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon.* **Journal of Engineering Science and Technology**, *3*(2), 180-189.

61. Kavitha, K. , Senthamilselvi, M.M. , and Arivoli.S. (2014). *Removal of hexavalent chromium from aqueous system by low cost adsorbent (AAVNS)*, Journal of Chemical and Pharmaceutical Research, 6(6),6-15..

62. Ossman, Mona E., and Moustapha S. Mansour. "*Removal of Cd (II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies.*" **International Journal of Industrial Chemistry** 4.1 (2013): 1-7.

63. Kumar, P. S., & Kirthika , K. (2009). *Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder.* **Journal of Engineering Science and Technology,** *4*(4), 351-363.

64. Kumar, P. S., & Kirthika, K. (2009). *Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder*. **Journal of Engineering Science and Technology,** *4*(4), 351-363.

65. Al-Rawi, M. S., Hassan, H. A., Hassan, D. F., & Abdullah, R. M. (2013). *Synthesis and anti-bacterial study of novel compounds with bis (four-, five-, and seven-membered) heterocyclic rings*. **International Journal for Sciences and Technology, 8** (2), 48-54.

Appendixs

Data Tables of Experiments

Data of experiment 1: Effect of contact time

Contact time (min)	C_o	C_e	%Removal	Standard deviation
2	10	8.78	12.15%	0.90
5	10	6.36	36.36%	0.99
10	10	7.85	21.48%	1.80
20	10	7.98	20.15%	1.96
30	10	8.05	19.45%	1.08
90	10	8.15	18.46%	1.25

Temperature = 25°C

Concentration of Cr(VI)= 10 mg/L

Solution volume= 50 mL

Adsorbent dose= 0.1 g

Data of experiment 2: Effect of pH

pH	C_o	C_e	%Removal
2	10	2.30	77 %
2.5	10	1.77	82.33 %
4	10	.88	91.19 %
6	10	5.92	40.78 %
8.3	10	8.93	10.72 %
10	10	9.50	5%

c_o= 10 ppm

Temperature=25°C

Time= 5 min.

Adsorbent dose= 0.03 g

Solution volume= 15 mL

Data of experiment 3: Effect of temperature

Temperature (k)	C_o	C_e	%Removal	K_D	$\ln K_d$	$1/T(k^{-1})$ $*10^{-3}$	$\triangle H^o$ Kj/mol	$\triangle S^o$ Kj/mol	$\triangle G^o$ Kj/mol
277	10	2	80%	4.98	1.60	0.0036	-26	-.079	-4.22
298	10	0.88	91.18%	5.17	1.64	0.0033	-26	-.079	-2.565
308	10	3	70.00%	1.16	.154	0.0032	-26	-.079	-1.77
333	10	3.57	64.27%	.89	-.10	0.0030	-26	-.079	.20

C_o= 10 ppm

Time = 5 min.

Adsorbent dose= 0.03 g,

Solution volume= 15 mL

Data of experiment 4: Effect Cr (VI) concentration

concentration of Cr VI (ppm)	C_e	% Removal	Q_e
5	2.63	47.36%	1.18
10	0.88	91.18%	4.56
15	6.80	54.65%	4.09
20	7.45	62.77%	6.27
30	13.39	55.34%	8.30

Temperature = 25°C

Time = 5 min.

PH= 4

Adsorbent dose= 0.03 g

Solution volume= 15 mL

Data of experiment 5: Effect of amount of adsorbent

Weight of dose(g)	C_o	C_e	% Removal	Q_e
0.01	20	2.80	86%	25.80
0.03	20	7.445	62.775%	6.27
0.07	20	10.20	48.95%	2.09
0.1	20	12.70	36.47%	1.09
0.15	20	14	30%	0.60

Temperature= 25°C

Time= 5 min.

pH= 4

Concentration of Cr (VI) = 20 mg/L

Solution volume= 15 mL

Data of experiment 6 : Adsorption isotherm of Cr(VI)

Concentration of Cr (VI) ppm	C_e	Q_e	C_e/Q_e	lnC_e	lnQ_e
5	2.63	1.23	2.1	0.95	0.21
10	0.88	2.58	1.7	1.48	0.95
15	6.80	4.25	1.6	1.92	1.45
20	7.45	5.69	1.3	2	1.73
30	13.39	11.16	1.2	2.59	2.41

Temperature = 25°C

pH = 4

Time = 5min

Solution volume= 15 mL

Adsorbent dose= 0.03 g

Data of experiment 7: Adsorption kinetics of Cr (VI)

Time (min)	Q_t	Q_e-Q_t	$log(Q_e-Q_t)$	t/Q_t
2	0.73	2.14	0.33	2.75
10	1.07	1.69	0.23	9.31
20	1.01	1.78	0.25	19.84
30	0.97	1.82	0.26	30.84
90	0.92	1.86	0.27	97.54

Temperature = 25°C

pH= 4

Solution volume= 15 mL

Adsorbent dose= 0.03 g

Q_e=2.783

Data of experiment 8: Recovery of Cr(VI)

Sample	C_o	C_e	%Removal
fresh	20	2.80	86%
regenerated	20	3.24	83.8%

Temperature = 25°C

pH= 4

Solution volume= 15 mL

Adsorbent dose= 0.01 g

Contact time= 5 min

C_o=20 ppm Cr (VI) solution

جامعة النجاح الوطنية

كلية الدراسات العليا

تحضير البيرول امين المثبت على سطوح السيليكون كممتص لإزالة ايونات الكروم السداسي من الماء

اعداد

غدير "محمد معين" نمر حنبلي

إشراف

أ.د شحدة جودة

أ.د إسماعيل وراد

قدمت هذه الأطروحة استكمالاً لمتطلبات درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2016

تحضير البيرول امين المثبت على سطوح السيليكون كممتص لإزالة ايونات الكروم السداسي من الماء

اعداد

غدير "محمد معين" نمر حنبلي

إشراف

أ.د شحدة جودة

أ.د إسماعيل وراد

الملخص

تلوث المياه من أكثر المشاكل المستعصية التي تواجهها بلدان العالم دون استثناء. مياه الصرف الصناعي تحوي مجموعة من المخلفات والنفايات الصناعية ذات المصادر المختلفة والطبيعة المتباينة، وبعضها يحوي المعادن الثقيلة والنفايات الخطرة التي يمكن أن تتراكم في المياه الجوفية وتظهر نتائجها على الانسان والحيوان والنبات.

والمشكلة الرئيسية هنا هي للكشف عن تركيز واحد من الملوثات وهو الكروم سداسي التكافؤ ومحاولة إزالته عن طريق الامتزاز.

يركز هذا البحث على تعديل سطح البوليسيلوكسين كيميائياً لزيادة قدرته على الامتزاز، وكذلك تشخيص طبيعة سطح البوليسيلوكسين المعدّل واستخدامه في امتزاز الكروم السداسي من مياه الصرف الصناعية.

لقد تم تحضير البوليسيلوكسين المعدل (Si-NPr) وقد أجريت عليه جميع الفحوصات المتاحة لتشخيصه والتعرف على خصائص سطحه، حيث أكدت نتائج تحليلUV و FT-IR أن وحدات pyrrole-2-carbaldhyde قد تم تثبيتها بنجاح على سطح البوليسيلوكسين، كما أظهرت صور المسح الإلكتروني (SEM) أن السطح المعدّل الجديد يتميز بخصائص تجعله قادرا على الامتزاز.

أجريت تجارب عديدة تحت ظروف ومتغيرات مختلفة مثل: درجة الحرارة، درجة الحموضة، تركيز الكروم السداسي، كمية المادة المازة ومدة الاتصال، لتحديد الظروف المثلى لأفضل نسبة امتزاز للكروم السداسي. وقد لوحظ من خلال هذه التجارب أن نسبة إزالة الكروم السداسي من المحاليل

المائية قد ازدادت بزيادة تركيز الكروم السداسي لتركيز 20 ملغم، بينما انخفضت هذه النسبة بزيادة درجة الحرارة وزيادة درجة الحموضة كمية المادة المازة ومدة الاتصال.

كميات الكروم السداسي التي تم امتزازها لكل وحدة كتلة من المادة المازة (Si-NPr) تم حسابها باستخدام نموذج Lagergren ، قيمة (2.78) Qe المحسوبة قد توافقت مع قيمة (2.46) Qe التجريبية، وهذا يؤكد أن عملية الامتزاز للتفاعلات من الدرجة الثانية pseudo second order model.

السعة القصوى للامتزاز Qm حسب نموذج Langmuir كانت 13.05 ملغم/غم على درجة حرارة 25ْم ودرجة حموضة 4 واستخدام 0,03 غم من المادة المازة, وكانت قيمة R_L تساوي 0.48 , هذه النتائج جميعها تشير بإيجابية إلى استخدام هذه المادة (Si-NPr) في امتزاز الكروم السداسي. كما أن قيمة (1/n=0.9863) التي تم حسابه من نموذج Freundlich تؤكد ان امتزاز الكروم السداسي باستخدام (Si-NPr) مناسبة، ولكن في الحقيقه نموذج Freundlich هو مناسباً لبيانات الامتزاز التجريبية التي تشير إلى الامتزاز الفيزيائي فضلاً عن التوزيع غير متجانس من المواقع المفعلة على سطح المازة.

قيم $\Delta G°$ السالبة تشير إلى أن عملية الامتزاز موائمة وتلقائية على درجات الحرارة المحددة، كما أن القيمة السالبة لِ $\Delta H°$ تشير إلى أن عملية الامتزاز طاردة للحرارة ومحبذة على درجات حرارة منخفضة. وكذلك القيمة الصغيره ل $\Delta H°$ تشير إلى الطبيعة الفيزيائية للامتزاز . القيمة القليلة جداً السالبة لِ $\Delta S°$ تعكس أنها عملية ترابطيه وتعكس عدم وجود تغيير كبير يحدث في الهياكل الداخلية للمازة أثناء عملية الامتزاز .

(Si-NPr) قدمت وسيلة عملية لعلاج فعال لمياه الصرف الصحي الملوثة بالكروم السداسي. أجريت تجارب لمعرفة التأثير البيولوجي للمادة (Si-NPr) على السودوموناس الزنجارية، المكورات العنقودية الذهبية والإشريكية القولونية، وقد دلت نتائج التجارب على عدم وجود أي تأثير بيولوجي لهذه المادة على الكائنات الحية الدقيقة موضوع التجربة.

د