



Faculty of Graduate Studies

Chemistry Department

**Adsorptive Removal of Chromium Metal Ions Using
Pristine Graphene Oxide Nanoparticles**

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Requirements for the Masters Degree in Chemistry, College of
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Pristine Graphene Oxide Nanoparticles**

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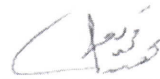
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DEDICATION

I dedicate this work to my beloved mother and father, all my sisters. Their support, encouragement helped me overcome the difficulties and eased the pressure that I faced during my master study and my entire life. To my adorable husband, without his inspiration, assistance, encouragement and support, I would never have gone this far and succeed without his concerns in my study. To my friends, your big hearts and pure souls, thank you from the depths of my hearts only match your encouragement and support.

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LIST OF ABBREVIATIONS:

GO: Graphene oxide.

R_L: Equilibrium parameter (Dimensionless constant of Langmuir isotherm).

ΔG°: Gibbs free energy change.

ΔH°: Enthalpy change.

ΔS°: Entropy change.

AC: Activated carbon.

CNTs: Carbon nanotubes.

WHO: World Health Organization.

US-EPA: US- Environmental Protection Agency.

ATSDR: Agency for Toxic Substances and Disease Registry.

PAC: Poly- aluminium chloride.

ICP-MS: Inductively coupled plasma mass spectrometry.

PWA: Palestinian Water Authority.

q_e: Adsorption capacity (mg/g).

q_{max}: Maximum adsorption capacity.

q_t: Adsorption capacity at time (t).

$q_{e,cal}$: Theoretical values of a dsorption capacity.

R%: Percentage removal efficiency.

CVD: Chemical vapor deposition.

C_i : Initial concentrations.

C_e : Equilibrium concentration of the remaining solute in the solution.

R^2 : linear regression correlation coefficient.

PZC: Point of zero charge.

AAS: Atomic adsorption spectroscopy.

FT-IR: Fourier transform infrared spectrum.

k_1 : Rate constant of pseudo first order adsorption.

k_2 : Rate constant of second –order adsorption.

k_p : Rate constant of intra-particle diffusion.

C: Intercept in intra-particle diffusion curve.

α : Initial adsorption rate.

β : Extent of surface coverage and activated energy.

b: Langmuir constant.

n: Freundlich constant that related to adsorption intensity.

k_f : Freundlich constant that related to adsorption capacity.

$1/n$: Heterogeneity factor.

B_T : constant related to the heat of sorption.

K_T : Temkin isotherm constant.

$^{\circ}C$: Temperature in celcuos.

k : Temperature in Kelvin.

k_c : Equilibrium constant.

R : Universal gas constant ($8.314J \cdot mol^{-1} \cdot K^{-1}$).

Adsorptive Removal of Chromium Metal Ions Using Pristine Graphene Oxide Nanoparticles

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ABSTRACT

Graphene oxide (GO) has recently attracted great attention due to its unique chemical and physical properties like high electrical and thermal conductivities, very high surface area and easily functionalized using biomolecules like polymer, protein, nucleic acids, etc. In the last decades, GO became of great interest in several applications such as adsorption. GO was successfully prepared in our chemical lab to be used as an adsorbent for removal of Hexavalent chromium Cr (VI) from aqueous solution. The Cr(VI) must be removed from water before it is discharged to the environment due to potentially harmful even at 0.05 mg/L concentrations. In this study, pH is an important variable to be taken into account for removing Cr(VI). The Cr(VI) could be better adsorbed by GO at acidic condition. Electrostatic interaction and redox reaction played an important role of adsorption mechanism. Kinetic studies demonstrate that Cr(VI) went fast at beginning but slowed down when the equilibrium was being approached. Further, pseudo- second –order kinetic model explained the adsorption process. The adsorption isotherm was fitted by Langmuir model. The maximum adsorption capacity of the GO was 41.27 mg/g when pH=3 at 25 °C. The equilibrium parameter (R_L) at different concentrations was less than unity indicating the adsorption of Cr(VI) ions onto GO is favorable process. The thermodynamic parameter including gibbs free energy (ΔG°) at 25 °C, enthalpy change (ΔH°), and entropy change (ΔS°) were calculated which are +2.631 KJ/mol.k, +4.3 KJ/mol.k, and +5.59 J/mol.k at 30 mg/L of Cr(VI) solution respectively. The positive value of entropy reflected an increasing

randomness at the solid /solution interface during the adsorption process. The positive value of ΔH° means the adsorption is endothermic process.

Index Words: Graphene oxide; Hexavalent chromium; adsorption process; Kinetic; Isotherm; Mechanis

INTRODUCTION

During the last decades, water pollution is the most environmental issue of the whole world^[1]. This issue started with the industrial revolution, which lead to increase of hazardous organic and inorganic contamination into aquatic system^[2], through various industries such as electroplating, metallurgical and mining activities^[3].

Among of these contaminations, heavy metals is a major toxic compounds for the environmental pollution^[4], due to adverse effect on eco-system and human health^[5]. The major problem in heavy metals pollution is the degradability (not biodegradable) and accumulated in the human body^[3]. From the list of toxic heavy metals like arsenic, cadmium, cobalt, chromium, and lead ^[6], chromium is considered as a common most hazardous contamination^[5].

The chromium in nature has two main forms: hexavalent Cr(VI) and trivalent chromium Cr(III)^[7]. Long term exposure of chromium forms cause many diseases to human health like cancer ^[8].

Several processes have been reported to remove Cr(VI) from aqueous solution, such as chemical precipitation, photocatalysis, ion exchange and adsorption. The adsorption process is considered as the most usefully^[9] process for Cr(VI) removal than others^[9], due to facile preparation and characterization, non-polluting, and low cost^[10].

In literature, many adsorbents reports have been studied for the adsorption of Cr(VI), including activated carbon (AC), clays, zeolite and chitosan^[9]. Nowadays, nano adsorbents have been developed in water treatment because its high reactivity, and specific surface area^[5].

An important example of nano adsorbents is graphene based materials, these materials have unique properties due to high efficiency, strong affinity for various metal ion, and fast kinetic with a large surface area compared to bulk particles^[11].

In this thesis, different issues have been evaluated; the water pollution, hazardous effects of metals, and the technologies of water treatment have been studied in chapter one. Chapter two concentrated on the adsorption methods for water purification from heavy metals like chromium, as well as the aspects related to adsorption such as type of adsorbent, isotherm and kinetic models and experimental effect on these processes were discussed faithfully in chapter three. Finally, chapter four discussed the adsorptive removal of hexavalent chromium metal ions using graphene oxide as adsorbent.



CHAPTER ONE: WATER POLLUTION

1.1 Type of the pollutants in water

1.2 Toxic heavy metals

1.2.1 Chromium

1.2.2 Other metals

1.3 Techniques used for heavy metal treatment

1.4 The Palestinian case toward heavy metals

Water pollution

Water is an essential needs for live, it is used for drinking, house hold needs, and other purposes^[12]. In last decades, the continuous discharge of wastewater into the water bodies that resulted increasing the concentration of contaminations, which cause water pollution^[13]. Approximately two million tons of wastewater flow into the natural water systems every day, involving 70% of domestic sewage and 33% of industrial effluent without pretreatment. So that around 90% of water supply has been contaminated^[14].

Water pollution is an environmental issue of the whole world^[1], which can be defined as the presence of chemical, biological compounds or factors producing a condition of impairment of given water with respect to some beneficial use^[15].

The contamination introduced to water by either naturally sources such as volcanic activates, soil erosion and weathering of rocks and minerals)^[12], or anthropogenic sources, which is pollution arising from human industrial and activities^[15].

The quality of water is determined by the type and quantity of the contamination that present in water^[16]. To prevent the deteriorating water quality, the World Health Organization (WHO) and the US- Environmental Protection Agency (US-EPA) put standards for contaminated species in water^[6], which determined the concentration level of contaminations in drinking water, less than this concentration, there is no valuable or expected risk to health^[15]. However, if the contaminations are higher than permitted limit, they can cause serious diseases and disorders^[10].

Therefore, it is necessary to treat the water systems with low cost efficient techniques^[12] and low energy consumption as well^[17]. Water treatment encompasses

several technologies based on various processes, such as, membrane filtration, chemical precipitation, solvent extraction, oxidation, adsorption and others^[12].

1.1 Type of the contaminates in water

Many of chemical and biological compounds are classified as type of the pollutants in water^[15]. The chemical pollutants are including organic compounds like dyes and polycyclic aromatic hydrocarbon, inorganic compounds like heavy metal ions^[12], dissolved gas like nitrogen, carbon dioxide^[16], and radioactive nuclide such as Uranium, Thallium , etc^[15]. On the other hand, biological compounds including microorganism such as bacteria, algae, and fungi^[16].

Among of these types of the pollutants, the heavy metals are considered as the most toxic to soil and water system, at dosage higher than the permitted WHO limit^[12].

1.2 Toxic heavy metal

Heavy metal is the element which has the atomic weight between 51.0 -200.6, specific gravity higher than 5 and that be in shape either in chemical form or mixed form^[17]. A large number of elements fall into this category, but few of these elements highly toxic^[10], like Cu, Hg, Zn, Cd, Sn, Pb, Fe, Ag, Mn, Co, Cr, As and Ni^[12]. The Heavy metal pollution mainly comes from industry and rapid population growth in world^[18].

Heavy metals unlike the organic pollutants, due to low levels of biodegradability, accumulating in soil, water and food chain at toxic level^[19], chemical stability^[20] and widely dispersed in water^[1].

So that heavy metal ions have serious impact on environmental and human health^[1], the effect on the environmental leads to the end of aqueous life, oxygen insufficiency and algal blooms^[17]. Moreover, it cause dangerous disease and serious cell disorder on

human health^[3], and disrupt the enzymatic process^[17]. Generally, the heavy metals enter the human body through drinking water, aquatic food chains such as fish or aquatic species based product^[10]. Therefore, the mechanism of metal toxicity must be investigated, the oxidative stress is one of the major mechanism, these metals build up large amount of reactive oxygen species, such as super oxide anion (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radical (OH^\cdot), and singlet oxygen (1O_2) have been reported to promote the induction of oxidative stress^[10].

The oxidative stress is responsible for various diseases in human, such as lowering of cerebral and nervous functions, harm the blood contents, lungs, kidney and other organs, bring out weakness, memory loss, increasing of allergies^[17] and cancer^[13].

Among the heavy metal ions, the chromium is a common hazardous contaminant^[5], it's the second abundant metal found in most contaminated site^[7]. Although a certain heavy metals create essential compounds which are required for metabolic activates by living beings in short amount, these metals can cause toxic effect on the human health^[17].

1.2.1 Chromium

The seventh element widely available in the earth is chromium^[17], which is steely – gray, hard and brittle metal^[2], it has an atomic number of 24, atomic weight of 52 g/mole, a specific gravity of 7.2 at 20 C° and melting point of 1857 C°^[7]. This metal is present in many various environmental media including water, soil and air. The chromium metals engage into these media via naturally occurring or anthropogenic source^[7]. The natural resource derived from continual dusts due to weathering, volcanic emission^[14] and soil erosion^[12], However the chief sources of toxic chromium are mostly originated in industrial activates^[7] like electroplating^[20], photography industrial,

fertilizer^[21], leather tanning, dyeing^[22], wood preservation, petroleum refining processes^[9], textile industrial, smelting^[14], cement industrial and steel industrial^[23].

Chromium metal has several oxidation state ranging from -2 to +6^[7], it is presented in water as trivalent chromium Cr(III) and hexavalent Cr(VI) forms^[13]. The relationship between the Cr(VI) and Cr(III) is shown in equation (1)^[24]:



The chromium is influenced by oxidation –reduction (redox) reactions, which alter its physical and chemical properties^[7], the conversion between Cr(III) and Cr(VI) is an important feature^[24].

The dominant Cr(III) species in water include Cr^{+3} , $\text{Cr}(\text{OH})^{+2}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$ and $\text{Cr}(\text{OH})_4^-$. The basic species of Cr(VI) in water is $\text{Cr}_2\text{O}_7^{-2}$, HCrO_4^- , and CrO_4^- ^[25], these species of chromium ions are affected by the pH solution^[25].

Cr(III), once absorbed, it combined with plasma proteins and distributed in the tissue depending on its quantity, on the other hand Cr(VI) absorbed depending on the acidity of media, which favors its reduction to Cr(III)^[24]. Cr(III) is relatively non – reactive in atmosphere under normal conditions, however Cr(VI) reacts in presence of other pollutants to form Cr(III)^[24].

Cr(III) and Cr(VI) have contrasting properties^[7]. Cr(VI) is more soluble than Cr(III)^[26] and the mobility of Cr(VI) is higher than Cr(III), so that most Cr(VI) prevalent in water systems^[20]. However, Cr(III) is an essential trace element for living organisms. It acts an essential micronutrient for carbohydrate and lipid metabolism^[24] and easily removed in neutral or alkaline conditions^[14]. Cr(VI) is more toxic element

and has been classified as group "A" carcinogenic because of its mutagenic, teratogenic, carcinogenic natural^[20] and has a strong oxidation power^[5]. Therefore, the Cr(VI) causes higher level of toxicity toward human's kidney and liver^[4]. It causes gastric damage^[9], creating of ulcer^[17], edema, pulmonary congestion^[23] and skin diseases like allergic dermatitis and eczema through skin^[27]. Mostly it leads to headache, vomiting^[10] and even cause the cancer in digestive system and lungs^[21]. To reduce human exposure to chromium, the WHO and US-EPA organizations have set a guide of 0.05 and 0.1 mg/L for Cr(VI) and total chromium (Cr(VI) and Cr(III)) in drinking water, respectively^[21].

1.2.2 Other metal

The global concern for many years present various type of heavy metal ions in water, which include zinc, arsenic, chromium, mercury, lead, cadmium, Cobalt, and nickel^[28]. Nickel is a silvery-white and very hard metal that is widely used in alloys with other metals. It naturally occurs in the Earth's crust and the Earth's core is composed of 6% nickel. Nickel and its compounds have no characteristic odor or taste^[29]. Nickel is a major constituent in corrosion resistant alloys, like, stainless steel and commonly used as a material of construction of various plants^[30]. The main sources of Ni are metallic ferrous mining, metal finishing industry, electroplating, manures sewage, sludge, alloys and steels^[10]. It is a harmful metal that can cause serious lung and kidney problems, skin dermatitis, gastrointestinal distress, and pulmonary fibrosis. It is also a human carcinogen^[31], so that permissible limit of nickel according World Health Organization (WHO) is 0.02 mg/L^[10].

Cadmium (Cd) is another heavy metal which exhibits carcinogenic effects for humans and it is ranked number seven in the Priority List of Hazardous Substances

released by Agency for Toxic Substances and Disease Registry (ATSDR). Cd has the highest solubility in water compared to other heavy metals. Therefore the rate of Cd propagation in nature is high and it is not an essential element for human life. Due to its water-soluble properties, Cd is taken into biological systems by plants and marine organisms. Cd exhibits long-term persistence in the environment and easily accumulates in vegetables, crustaceans, and mollusks over time. The removal of Cd is extremely difficult when it enters the human body ^[32]. The permissible limit for portable water Cd by the World Health Organization (WHO) is 0.003 mg L⁻¹^[10]. These chemicals (Ni & Cd) improve the performance of the product, but result in enhancement of their concentration in ground water by leaching from the discharged effluent, leading to serious health implications upon consumption of contaminated water. Some common health effects are cancer, kidney and lung disorder, paralysis of nervous system and tissue damage^[30].

On the other hand, Cobalt is an essential nutritional component involved in vitamin B12 formation. It is also a cofactor for enzymes such as dehydrogenases, hydrolases, and transferases. High cobalt concentrations in aquatic environments can cause DNA damage and chromosomal fragmentation. Moreover, cobalt can affect hematological parameters of fish, and cause oxidative stress, and development abnormality ^[33].

The potential health effects, permissible limit for portable water, and source of another various heavy metals are described in table 1 ^[10].

Table 1: The source, permissible limits and health effects of various toxic heavy metals^[10].

Heavy metals	Sources	WHO, permissible limit for portable water (mg L⁻¹)	Potential health effects
As	Electronics, metallurgical industries, manures sewage	0.01	Skin manifestations, visceral cancers, vascular disease
Zn	Metal finishing industry, electroplating, metalliferous mining, agricultural materials, fertilizers	3.0	Depression, lethargy, neurological signs and increased thirst
Cd	Metalliferous mining, agricultural materials, fertilizers, waste disposal, landfill leachate, electronics, metallurgical industries	0.003	Kidney damage, renal disorder, human carcinogen
Hg	Electronics, waste disposal, landfill leachate	0.001	Rheumatoid arthritis, and diseases of the kidneys, circulatory system
Pb	Electronics, metallurgical industries, specialist alloys and steels, waste disposal, landfill leachate	0.01	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system
Cr	Metal finishing industry, electroplating	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic
Cu	Metal finishing industry, electroplating, metalliferous mining	2	Liver damage, Wilson disease, insomnia
Ni	Metalliferous mining, metal finishing industry, electroplating	0.02	Dermatitis, nausea, chronic asthma, coughing, human carcinogen

1.3 Techniques used for heavy metal treatment

Several methods like coagulation –flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical and adsorption have been used for the removal of toxic heavy metals from aqueous solution, especially hexavalent chromium Cr(VI) ^[17].

Coagulation can be defined as a process that relies on the addition of the coagulant (like: ferric chloride and poly-aluminium chloride (PAC)) to aqueous solution containing heavy metals to separate these minerals by forming a precipitate^[17]. In contrast, the ion exchange is a strategy for water treatment in which an ion is replaced by another ion and separated from the aqueous medium^[17]. While membrane filtration which is a separation method that depends on differences in size, pH, solution concentration and applied pressure between ionic metal and the medium^[17]. Chemical precipitation occurs by adding of chemicals to the solution to form the precipitate that cannot dissolve in the solution and may be alter the pH ^[17].

Most of these processes have limitations which hinder their application^[19]. For instance, coagulation –flocculation produces highly sludge production^[10]. Ion exchange process is nonselective, it is highly sensitive to pH of solution^[10], it's limited to low concentration of metal solution. While membrane matrix usually is susceptible to fouling by organic and other solid in water^[19], economically, it is considered as not useful method for ions separation in solution^[27].

Membrane filtration process like reverse osmosis, micro filtration, ultra-filtration and nano filtration have been investigated and showed high operational cost, membrane fouling^[10] and low stability^[27]. The chemical precipitation method is cheap and simplify process ^[19], however the excessive sludge formation requires further treatment and slow metal precipitation considered as the major disadvantages of this process^[10].

On the other hand, adsorption is considered as an efficient technique comparable with other processes that used for heavy metal removal from aqueous solution^[17]. It has been taken into account as non-polluting^[4], ease of operation^[5], low chemicals used^[8], availability of wide range of adsorbent^[19], fast and time constant^[20], high efficiency^[22], economical and low cost^[26] and simplicity of design^[34].

1.4 The Palestinian case toward heavy metals

Palestine is facing an environmental and public health issues like water availability in the region^[35], heavy metals pollution in water, reliable water collection and treatment facilities^[36].

Water availability is obviously one of the most important and highly sensitive issues facing the Palestine in the coming years. Palestine (defined here as the West Bank and the Gaza Strip) is that suffers from water scarcity. The major water resources available to the Palestinians are the Jordan River and the Aquifer, which is located under the West Bank and receives most of its rain. Israel, since its occupation the Palestinian Territories in 1967, has monopolized these water resources to its benefit. Palestinians are not allowed to use more than 15% of their groundwater and are denied access to the Jordan River^[35].

The heavy metal pollution in surface water and groundwater is a global environmental problem^[37]. The problem with pollution is not stop at damaging the water environment only; it also causes great health risk impacts associated with microbial and chemical contaminants^[38].

The heavy metal contamination of water in Palestine was assessed from different studies such as: study applied on 90 Water samples from ten groundwater wells were

taken three different dates of the year (November 2012, March 2013, and April 2013). The results obtained from this study suggest a possible risk to the population of the south West Bank/Palestine given the high concentration of some toxic heavy metals^[39]. Another study showed increasing trends for Cr, Mn, Ni, Cu, Mo, and Al were detected in 100% of the water samples analyzed from five Groundwater wells on North West Bank^[40].

In Gaza, many studies in different cohorts of pregnant women reported high levels of heavy metal contaminants (the remnants of the war and the military attacks on Gaza). These contaminants turn out that affecting on mother metabolic changes, preterm babies, and fetal development newborn health, including increased rates of birth defects^[41]. In Hebron city (south of West Bank /Palestine), rainwater samples harvested for drinking, were analyzed for the content of different toxic heavy metals by inductively coupled plasma mass spectrometry (ICP-MS). A total of 44 water samples were collected in house cisterns used to collect rainwater from the roofs of houses, the results showed that the concentration of five heavy metals (Cr, Mn, Ni, Ag, and Pb) is higher than the WHO limits for these heavy metals in drinking water^[42]. Collectively, the Palestine water system is contaminated with highly heavy metals concentration, which might affect human health.

Palestinian water resources are polluted through many local industries, such as: leather tanning (highly polluted with Cr(III))^[43], surface metal, aluminum powder coating (strongly polluted with Cr(VI))^[43], and galvanization industries (electroplating). There are more than 20 galvanization plants in Palestine that discharge their wastewater into local environment or sewer system without any proper treatment^[44].

Lack of proper treatment for heavy metals wastewater and the mishandling have caused the closure of many tanneries in Palestine by Israeli occupation in prevention of more environmental damage^[45].

The current water treatment plants in Palestine, established during 1970–1980 under the Israeli occupation are overloaded and badly maintained with aging equipment, thus posing serious environmental and public health hazards. So that water treatment sector is manifested by inadequate management due to insufficient infrastructure, unsafe disposal of untreated or partially treated effluent and unplanned use of low water quality^[46].

However, there are few studies in Palestine that dealt with heavy metals pollution of groundwater. So that the Palestinian Water Authority (PWA) oversaw around 300 student researches related to water and sanitation services. Many of these had applied research components, demonstrating potential for new innovations that can solve some of the State of Palestine's problems in the water sector. However, rarely did any of these leave confined lab settings to a widespread use of the Palestinian. These ideas were ready to be recognized, but it did not applied^[47]. It might be due to a reason weakness in Palestinian economy, low income, low level of technical operating expertise and very limited access to the existing advance water treatment technologies^[46]. Finally, the Palestinian Accelerator Lab has identified this issue as a forefront challenge that requires intervention^[47].



CHAPTER TWO: ADSORPTION

- 2.1 Adsorbent: Graphene Oxide
- 2.2 Adsorption isotherm and kinetic models
- 2.3 Experimental parameter that affected on the adsorption process

Adsorption

Adsorption is the surface phenomena where it is accumulated of gas, vapor or liquid particles (called adsorbate) onto the surface of solid material (adsorbent) via physical or chemical force, or both may be involved^[48] as shown in the figure .1.

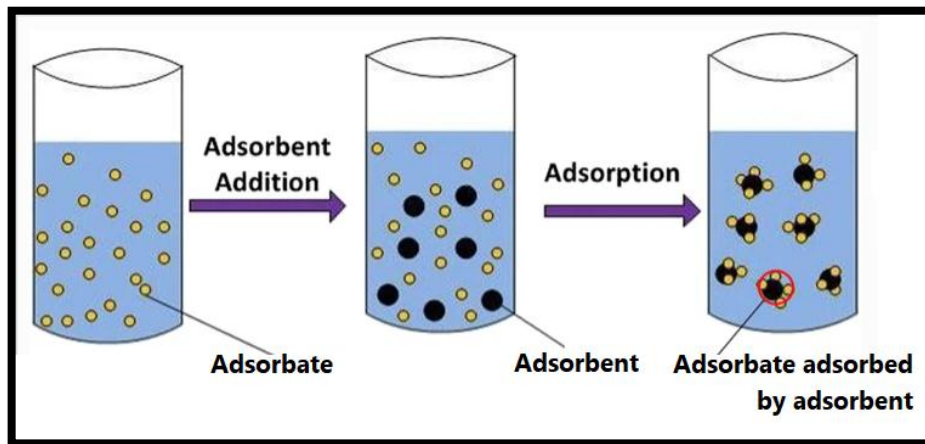


Figure 1: The explanation of adsorption process in aqueous solution.

The physisorption occurred via physical forces like van der Waals force, however, chemisorption is an adsorption via chemical forces (characteristic of covalent) between adsorbent and adsorbate^[10].

This process is reversible reaction (equilibrium reaction) which regenerated of adsorbent by suitable adsorption process^[10], including adsorption and desorption reaction showed in figure 2.

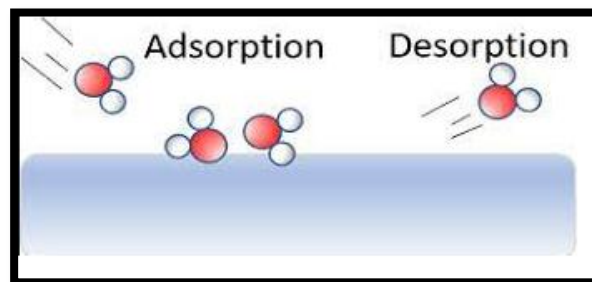


Figure 2: The adsorption and desorption in equilibrium reaction.

That means the adsorption equilibrium is the ratio between the adsorbed amount of the adsorbate with the remaining in the solution ^[49].

The adsorption process that can be expressed through either adsorption capacity q_e (mg/g) or percentage removal efficiency (R). From experimental parameters in this process can be predicted the kinetic and isotherm models which used to examine the controlling mechanism of the adsorption process^[9], and express the surface properties and affinity of the adsorbent^[48].

There are many factors affect the adsorption process of heavy metal ions from aqueous solution, such as type of the adsorbent and its properties ^[50], species of heavy metal ions and experimental conditions^[34].

The type of adsorbent is an important factor that affects the adsorption process. So that ,the adsorbent with low cost and high efficiency ^[6], available with a large quantities^[10], fast separation from the solution^[14], chemical stability under extreme conditions, many adsorption site^[22] and has a high surface area^[26] are considered the best properties for suitable adsorbent used for removal heavy metal ions from aqueous solution .

2.1 Adsorbent: Graphene oxide

Various adsorbents have been reported to removal of heavy metals like chromium hexavalent Cr(VI) from aqueous solution. These adsorbents are classified as natural materials, agriculture and biological waste, industrial materials, polymeric materials or modified forms^[10] and nano adsorbent materials ^[11].

Activated carbon^[3], zelite^[10], sphagnums, saw dust, Neem leaves, sugar bed pulp ^[23], woods, clays ^[51], rice husk ^[52] are considered as natural adsorbents.

Titanium oxide^[10], modified Fe₂O₃^[19], polyaniline, poly ethylene glycol composite^[5], and chitosan^[9] are considered as industrial and polymeric adsorbents. However most of mentioned adsorbents are suffered of low adsorption capacity or unstable under high or low value of pH^[12], therefore its necessary to developed a new adsorbent^[5].

The nano scale materials exhibit unique properties due to their high reactivity^[5], small size, large surface area which enhance the adsorption capacity, rapid adsorption rate^[9], low cost adsorbents, easy to regenerate^[11]. Regeneration of adsorbents (recycling of using adsorbents and recovery of the heavy metals from the desorbing agents) has a different benefits, like: prevent to create another secondary pollution when disposal of used adsorbents containing heavy metals, and success to limited number of adsorption–desorption cycles. Which can be achieved by using various possible regenerating agents such as acids, alkalis and chelating agents (such as ethylene diamine tetraacetic acid)^[53].

The nanomaterials have been considered as an extraordinary adsorbents used for removal of specific contamination in aqueous solution^[9].

Graphene oxide nanoparticles and carbon nanotubes are classified as the major nanomaterials for removal of heavy metals^[6]. Graphene is one layer of graphite material with hexagonal lattice of Sp² hybridization between carbon – carbon bond to form a two dimensional sheet with one atomic thickness^[12].

There are still many problems in the preparation of graphene nanosheets with reliable quantity, it can be prepared by different methods like, chemical vapor deposition (CVD) and exfoliation through physical or chemical routes^[54]. Graphene has a good chemical stability^[22], and a large specific surface area (with a theoretical value of

2630m²/g)^[27], but the low solubility of graphene in water ^[27] and easy to aggregate in the solution make it unbeneficial for adsorption of heavy metal^[22].

To make graphene nanoparticles soluble in water (hydrophilic) and improve its adsorption capacity, some of chemical modifications are needed^[22]. Thus, graphene oxide (GO) which is a derivative of graphene with abundant functional groups such as epoxy, hydroxyl, carbonyl and carboxyl group) on their surface^[27] make it soluble in water and make it as a good adsorbent^[14].

Therefore, the GO is thicker sheet than graphene due to oxygen functionalized groups and Sp³ hybridization^[55]. Figure 3 shows the molecular structure of graphene and graphene oxide.

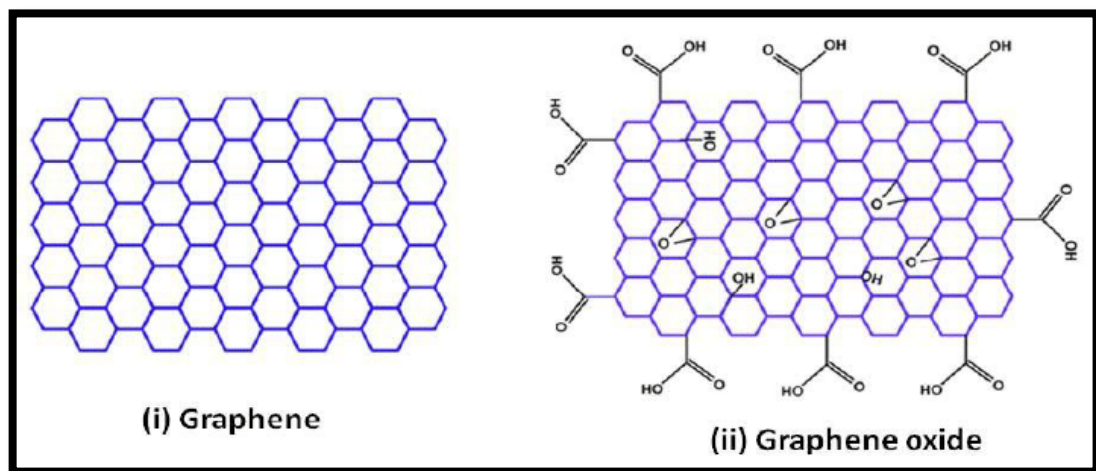


Figure 3: Molecular structure of (i) graphene (ii) graphene oxide ^[56].

Recently, graphene oxide (GO) has a wide applications like sensors^[20], nano-electronics, drug delivery, hydrogen storage ^[21], energy storage, solar cell, coating ^[57], super capacitor, photo catalysis, and adsorption ^[58]. Therefore, recent researchers have indicated that GO has proved to be promising an adsorbent for removal of heavy metal ions ^[21].

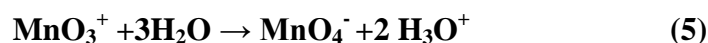
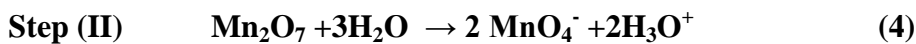
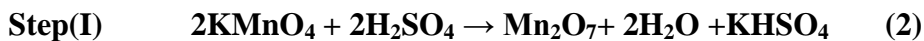
GO conventionally prepared by chemical oxidation and subsequent exfoliation of pristine graphite by either Brodie, Staudenmaier or hummer's methods^[34].

Brodie found the graphite structure could be oxidized to generate graphene oxide (GO) by KClO₃ and concentrated HNO₃ mixture, but Staudenmaier heated the HNO₃, H₂SO₄, and KClO₃ with mixture of graphite and prepared GO. Finally hummer's method required concentrated H₂SO₄ and KMnO₄ for oxidation process^[8]. Brodie and Staudenmaier required long time for preparation comparing with hummer's method (Two hour)^[8]. Therefore, many researchers prefer the hummer's method for preparation of GO.

Hummer's method:

There are various forms of hummer's method due to different sizes of graphite as starting material, the difference in oxidant concentration, the reaction time and temperature^[54].

Hummer's method used KMnO₄ as oxidant material to produce the GO. The KMnO₄ depends on MnO₃⁺ ion for oxidation, the high wettability of graphite with MnO₃⁺ with sulfuric acid, and the oxidant intercalates easily to MnO₄⁻. Thus, the oxidation reaction based on two oxidants (MnO₃⁺ and MnO₄⁻) which occurs in two different steps that explained as shown in equations 2 to 5.



In step (I) the randomly disturbed of oxygen groups distributed on the graphite flakes makes GO available to bind with metal ions^[22], but in step (II) tends to destroy the sp^2 hybridization of graphene layers to create the more carbonyl or carboxyl groups on its surfaces. Further oxidation of epoxide produced in step (I) that hydrolyzed to create additional hydroxyl groups and selectivity of produce oxygen functional group on the edges in step (II)^[54], which makes GO an ideal substrate with various binding points^[14].

The production of GO based on the conditions of oxidation reaction, which influence on the physical and chemical characteristics of GO fabricated^[54]. In general, GO has unique physical and chemical properties, which has low cost^[13] with oxygen groups abundant on the surface of GO, $\pi - \pi$ conjugated structure, easily to fictionalized, and has a large theoretical specific surface area^[14]. The GO nanoparticles are considered as an efficient adsorbent for removal of heavy metals from aqueous solution.

2.2 Adsorption isotherm and kinetic models

The isotherm and kinetic models have been considered as significant models to study the adsorption process^[59]. The adsorption isotherm is an invaluable curve describing the phenomena governing retention or mobility of substance from aqueous media to a solid phase at constant temperature and pH^[49]. Mathematically isotherm is the relationship between the amount of adsorbate per unit mass of adsorbent q_e (mg/g) and the final concentration of adsorbate in solution (C_e)^[58]. Many of equilibrium isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Flory –Huggins isotherm) have been described the equilibrium adsorption^[49].

The adsorption isotherms explain the mechanism of reaction, indicate the affinity of adsorbent^[48] and the qualitative information on the nature of the adsorbate –adsorbent

interaction, as well as the relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surfaces^[20] when the adsorption reach equilibrium^[27].

In this study, three isotherm model applied in the adsorption of Cr(VI) onto GO surface including, Langmuir, Freundlich and Temkin.

Langmuir isotherm model supposed that monolayer adsorption occurs on a uniform surface with binding sites of identical affinity and energy without interaction between adsorbents^[14]. This model indicates the homogeneity of surface^[19]. The most important parameter that obtained from this model is the maximum adsorption capacity (q_{max}), which reflected to a complete monolayer coverage on the surface of adsorbent^[48]. Thus, the model considers the adsorption to be a chemisorption process^[19].

Freundlich isotherm assumes the multilayer adsorption on a nonuniform surface^[14], the adsorbed amount is the total of adsorption on all sites (each having bond energy), with the stronger binding are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption reaction^[49]. Heterogeneous surface is suitable of these model^[19].

Finally, Temkin isotherm model assumes that energy of adsorption of adsorbate decreased linearly with the surface coverage, due to adsorbate –adsorbent interaction, which is characterized by uniform distribution of the bonding energies up to a maximum binding energy^[13].

The kinetic models are used to examine the controlling mechanism of the adsorption^[9], predicated the time to reach equilibrium^[9], the rate of adsorption^[20], and more information about the reaction pathway from these models^[9]. There are many

kinetic models such as Pseudo -first order, Pseudo-second order, Intra-particle diffusion model, and Elovich^[13] have been elucidated in this thesis.

Pseudo-first order describes the removal as a process preceding with diffusion through boundary. The adsorption process is related first order to free site concentration of metal ion charge proportionally with time^[14]. On the other hand, the assumption that adsorption retain second order where the site occupation rate is proportional to the square of unoccupied site amount^[14], and this model assumes the adsorption is a chemical process and occurs through sharing or exchange of electrons between the adsorbent and the adsorbate, and Intra-particle diffusion model was applied to investigate the adsorption mechanism that involve the transportation of ions from aqueous solutions to the adsorbent materials. Finally Elovich kinetic model was used to describe second -order kinetics, in which the adsorbent surfaces are energetically heterogeneous^[13].

The mathematical fitting and the adsorption results of these models were estimated depending on the value of the determination coefficient for the linear regression correlation coefficient (R^2) plotting between the studied parameters^[49].

2.3 Experimental parameters of adsorption process

In general, experimental factors like the pH, adsorbent dosage, contact time, initial concentration, temperature and exist of foreign ions in the solution are important parameter that finally affected on the interaction of heavy metal ions with graphene – based composite and derivatives^[1].

To maximize the removal of heavy metals by adsorbents like graphene oxide, a great knowledge in optimizing the experimental values are important^[3]. In this section, the effect of these parameters on the adsorption process discussed briefly.

2.3.1 pH

The initial pH plays an important parameter on heavy metal adsorption process, the pH variation effects on the kinetic and isotherm characteristics of the adsorption^[27], such as the degree of ionization, speciation of metal ion in solution^[5], binding site of adsorbent^[14] and the surface charge (protonation and de-protonation) of functional groups of adsorbent at different pH values^[1].

The point of zero charge (PZC) is a key point to understand the effect of pH on the adsorption. PZC means the pH of net surface charge of the adsorbent is zero, when pH higher than PZC value, the surface of adsorbent is negative, conversely at pH lower than PZC, the neutralization of surface charge occurs and the adsorption cationic ions will be decreased^[19]. Thereby, the point of zero charge of graphene oxide (GO) adsorbent is below pH = 2, so the GO surface is negatively charge at pH from 2 to 10^[34].

For each metal ion, there is a optimum pH value at which the maximum adsorption of that ion takes place. This pH takes place in basic region for the cationic metals; it takes place as an extraordinary case at the low pH values for the anionic metals^[60].

The optimum pH for different heavy metal ions removal by different adsorbent should be different^[1], due to their difference in metal electronegativity, other constants that related on a standard reduction potential of metal ions and the first associated constant of metal oxide^[34].

2.3.2 Adsorbent dosage

The percentage of heavy metal removal in aqueous solution is mostly based on the amount of adsorbent used^[20]. Adsorbent dosage depends on the adsorption mechanism and other operational parameters^[19].

2.3.3 Contact time

The contact time between heavy metal ions and GO is a vital parameter for adsorption capacity^[34]. It affects the mass transfer rate of heavy metal during the adsorption process. For most metal ion, the adsorption capacity initially increases drastically and then increases slowly until the contact time extends to reaction equilibrium^[1]. The rate of adsorption depends on the initial concentration of heavy metal ions, adsorbent dosage and the adsorption mechanism^[19].

However, the shorter time to reach equilibrium suggests the high efficiency and more economic in water treatment^[1].

2.3.4 Initial concentration

Generally, the increasing of initial concentration of heavy metal will increase the adsorption capacity due to the increasing of concentration gradient between the adsorbent and solution, this is only applicable before the saturation level is reached^[19].

2.3.5 Temperature

Temperature is one of the factors that has a significant impact on the adsorption process^[1]. It depends on either the process is endothermic or exothermic^[19].

Temperature affects the kinetic process by alternating the molecular interaction between the metal with solid surface and solubility^[34]. Increasing temperature might lead either to increase solubility which increase the amount of the available adsorption site on the GO surface or increased in the diffusion rate of heavy metal ions and accelerating the adsorption rate^[34]. On the other hand, the operation at room temperature under ambient conditions is suitable for the pre concentration of metal ions from aqueous solution to GO or GO –based nanomaterials^[1].

2.3.6 Foreign ions

Another factor that impact on adsorption is the presence of foreign ions. These foreign ions that impact on the binding species through affecting the electrical double layers and structure of particles remarkably^[1].

The affinity between the ionic species and the adsorbent effect the binding of metal ion to GO particles, then the foreign ion will complete with metal ion for a finite reactive site on the GO particles, which reduces the adsorption capacity. The concentration of foreign ions affects the electrostatic interaction which would then impact the particle aggregation^[1]. Only, a real sample was used in a few studies addressed the treatment of contaminated water ^[2], but in our study, the absence of foreign ion or other contaminated, because all solutions were prepared in laboratory by distilled water without any impurities.



CHAPTER THREE: EXPERIMENTAL PART

3.1 Aims and Objectives

3.2 Materials and Instrumentation

3.3 Synthesis of Graphene oxide

3.4 Batch Adsorption experiments

1.3 Aims and Objectives

The main goal of this study is removing of chromium hexavalent Cr(VI) from aqueous solution using graphene oxide nanoparticles as an adsorbent with high efficiency .

This goal can be achieved through these objectives:

1. Preparation of graphene oxide nanoparticles with two sizes distribution (450nm and 200nm) by Hummer's method.
2. Study the effect of adsorption experimental parameters to obtain a specific parameters value at which the maximum adsorption of that ion takes place.

Experimental parameters studied:

- A. pH
 - B. Adsorbent dosage
 - C. Contact time
 - D. Initial concentration
 - E. Agitation speed
 - F. Temperature
3. Inference the best kinetic, isotherm models, and mechanism that describe this process.

3.2 Materials and Instrumentation

The natural graphite (average size $< 5\mu\text{m}$), concentrated sulfuric acid (95% H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (30% H_2O_2), potassium dichromate (KCr_2O_7) as source of Cr(VI) ions, 1,5-diphenylcarbazide ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$), sodium chloride (purity > 99.5), acetone, nitric acid (2% HNO_3), HCl and NaOH standard solutions for pH adjustment. All chemicals were purchased from Sigma Aldrich. The Fourier transform infrared spectrum "FTIR" spectra (KBr disc method) were recorded with a Perkin–Elmer BX spectrophotometer. The ultrasonic liquid processor (Model: VCX750) was used to control the size of graphene oxide particles. The pH was measured using HI 2211 pH/ORP Meter (Hanna Instruments). All solutions were shaken in shaking incubator (Dainan Labtech Co -LTD). Atomic absorption spectrometry (AAS) (Perkin Elmer A Analyst 100) and UV-Visible spectrophotometer (Model: 7205) were utilized to measure the absorbance.

3.3 Synthesis of Graphene Oxide

Preparation of graphite oxide

Graphite oxide was produced from natural graphite using modified hummer's method. Typically, a 1.0g graphite was ground with 50.0g of NaCl for 10 min in order to exfoliate the graphite flasks (de- agglomeration) and reduce their dimensions as well. The ground graphite was dissolved in warm water and collected using filter paper by suction filtration ^[61]. The filtrated graphite was mixed with 23 mL H_2SO_4 overnight, the obtained solution was stirred in an ice bath for 45min and slowly added 3g KMnO_4 . After complete addition of KMnO_4 , the mixture was stirred for 30 min at 35 °C, the temperature was raised up to 50 °C for 45 min. After that, 46mL of distilled water was added gradually into the solution and kept the solution with stirring for 45 min at 98 °C.

Subsequently, 140mL distilled water and 10 mL of 3% H₂O₂ were added sequentially to the mixture solution to terminate the reaction. The collected sample was filtered and washed five times with 5% HCl and distilled water to remove any of size products. Finally the graphite oxide powder was obtained after drying in vacuum at 30 °C for 24 h [61].

Synthesis of Nanographene Oxide (GO)

After purification of graphite oxide by centrifugation, the graphene oxide nanoparticles were prepared according to our previous protocol. Substantially, 1.0 mg/ml of graphite oxide was sonicated in an ultra-sonication bath under controlled conditions (power, concentration and time).

3.4 Batch Adsorption experiments

Chromium (VI) stock solution of 1000 ppm was prepared by dissolved 2.8269 g of potassium dichromate (K₂Cr₂O₇) in 1 liter distilled water. Analytical solutions were prepared by dilution from the stock solution. The adsorption experiments were performed in 25 ml flask containing 20 mL of 50 mg/L Cr(VI) solution. The pH of solution was adjusted to 3.0 and **2g/L** of graphene oxide material was added. The mixture was sonicated in ultrasonic bath for few second to homogenize the mixture.

After the **equilibrium time** was reached, the mixture was filtered using syringe filter nylon with pore size (0.45 μm) and stored at 4 °C. After 24 hours, the residual total chromium concentration (Cr(VI)+Cr(III)) was analyzed by atomic adsorption spectroscopy (AAS), while the residual Cr(VI) was analyzed using UV-Visible spectrophotometer which assessed by 1,5-diphenylcarbazide method, the absorbance of

the red-violet colored solution (Cr(VI) with diphenylcarbazide reagent) obtained from the reaction was appeared at 540 nm after 10 min of the reaction^[62].

The adsorption capacity [q_e (mg/g)] and percentage removal efficiency of Cr(VI) were calculated using equation (6) and (7)^[13]:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (6)$$

$$R = \frac{(C_i - C_e)}{C_i} * 100\% \quad (7)$$

Where C_i (mg/L) and C_e (mg/L) are the initial and equilibrium Cr(VI) concentrations respectively, V (L) is the volume of solution, m (g) is the adsorbent weight, and R is the percentage removal of Cr(VI).

Variation parameters

The adsorption process was evaluated at different pH values from 2.0 to 7.0 with increment of 1. The various adsorbent doses of graphene oxide (1, 5, 10, 20, 40, 60, 100 and 140mg) were examined as separated test. The kinetic study was carried out at different time intervals (1, 20, 40, 80, 160, 240 min) in separate experiments for 50 and 100 mg/L of Cr(VI) solution. The variation of initial Cr(VI) concentrations (30, 50, 100, 200, 300, 400 and 500mg/L) and isotherm models were employed in this study. And investigated the reduction of Cr(VI) depended on the initial concentration. And the variation of agitation speeds from 90 r/min to 270 r/min were applied. Finally, the effect of the temperature on the adsorption process was studied at (25°C to 55°C) for different concentration (30, 50, 100, and 200 mg/L) of Cr(VI) solution.



RESULT AND DISCUSSION

CHAPTER FOUR : RESULT AND DISCUSSION

4.1 Characterization of Graphene oxide

4.2 Adsorption results

4.2.1 pH

4.2.2 Adsorbent dosage

4.2.3 Kinetic studies

4.2.4 Initial Cr(VI) concentration

4.2.5 Agitation Speed

4.2.6 Temperature

4.3 Adsorption mechanism

Result and Discussion

In this study, the graphene oxide was used as an adsorbent for Cr(VI) ions removal. Variable parameters were investigated using batch experiment for adjusting the optimum high efficient removal condition. The percentage removal was highly depended on pH, initial Cr(VI) concentration, temperature, shaking speed and adsorbent weight in the solution. The graphite oxide was sonicated to reduce the size of graphene oxide as an adsorbent to 200 nm. The particle size which that affected on the specific surface area, and when the size decrease the surface area increase^[27]. The increase in specific surface area is one of the important reason for the high adsorption capacity of Cr(VI) on the adsorbent^[23]. Then synthesized graphene oxide particles were characterized using Fourier transform infrared spectrum "FT-IR".

4.1 Characterization of Graphene oxide (GO)

FTIR spectrum of synthesized GO

The characteristic FTIR spectrum of GO is depicted in figure 4. As shown in panel a, the figure shows the main functional groups of synthesized GO, which includes O –H stretching vibration at 3365 cm^{-1} . The absorption peak at 1731 cm^{-1} can be assigned to carbonyl group (C=O). The absorption peak at about 1619 cm^{-1} is assigned to the carbon-to-carbon double bonds (C=C stretching vibrations). The peak at 1400 cm^{-1} is attributed to the carboxyl starching vibration. The peak at 1054 cm^{-1} is assigned to the C – O stretching vibrations. The GO particles possess abundant of active functional groups (such as carboxyl, hydroxyl, epoxy), making it an excellent adsorbent for environmental applications^[19].

FTIR spectra of GO – Cr (VI) system

The FTIR spectrum of GO – Cr(VI) nanosystem was performed as shown in figure 4b. The GO – Cr (VI) exhibits three bands at 715, 804 and 890 which assigned to Cr = O and Cr – O – Cr bonds, indicating that Cr(VI) was adsorbed on the surface of GO^[63]. A subtle shifts in the absorption peaks which assigned to the perturbation of energy due to the new coordination between ligands and metal ions, these bands are usually shifted to lower or higher frequency^[3].

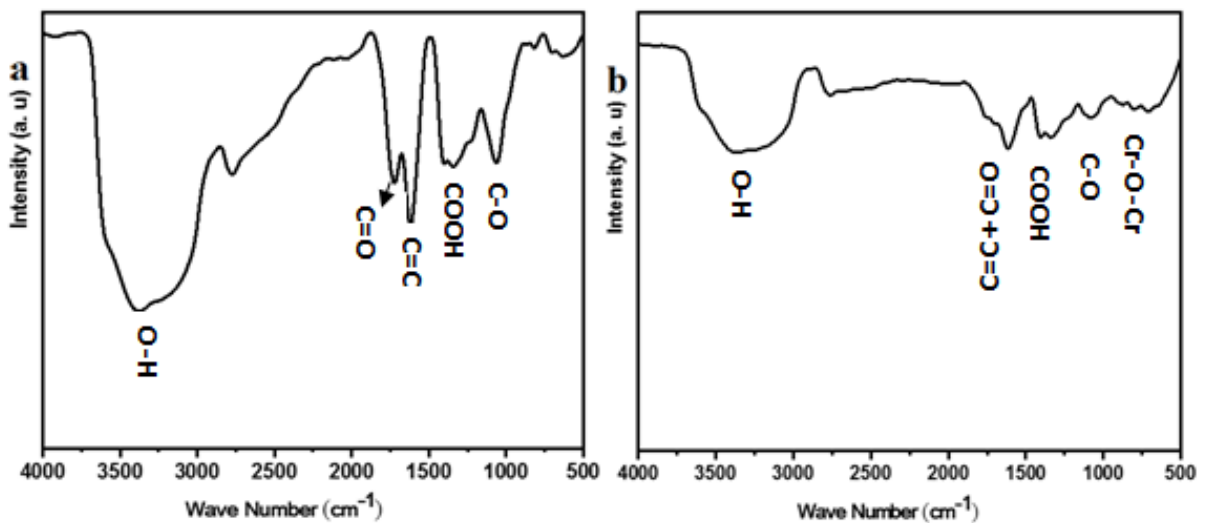


Figure 4: FTIR spectra of (a) Graphene oxide (b) Graphene oxide treated Cr(VI).

4.2 Adsorption results

4.2.1 Effect of pH

The pH is a key parameter controlling the Cr(VI) adsorption process^[21]. It has a significant effect on the surface charge, binding sites of the adsorbent and metal ion speciation^[13]. There are several anionic forms of Cr(VI) existing in solution like (CrO₄⁻²), dichromate (Cr₂O₇⁻²) and hydrogen chromate (HCrO₄⁻). Moreover, the ratio of these ions affected the pH and initial concentration of Cr(VI)^[22]. At $2 \leq \text{pH} \leq 6$, it exists in two equilibrium forms of (Cr₂O₇⁻²) and (HCrO₄⁻) ions, however, it exists predominantly as chromate anion (CrO₄⁻²) in alkaline conditions^[13] as shown in figure 5.

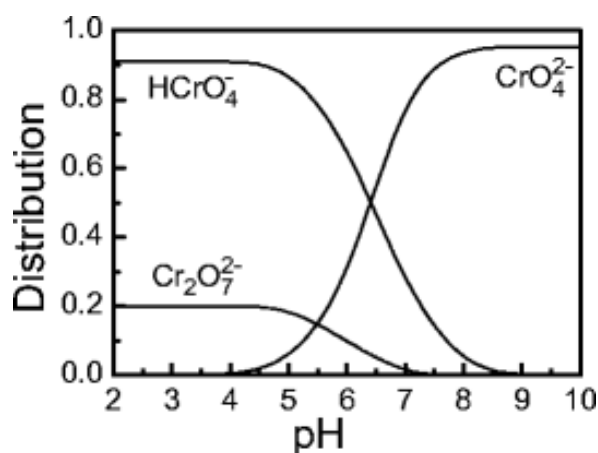
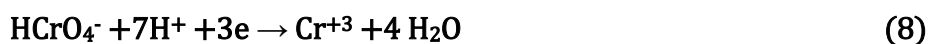


Figure 5: Diagram of species of chromium (VI) as a function of pH^[64]

Figure 6 reveals the percent removal and adsorption capacity (q_e) of Cr(VI) adsorbed onto the basal plane of GO particles as a function of pH. The result indicated that the pH between 3 to 4 has the highest percentage removal at 86.7% and 95.5% respectively. As we discussed above, hexavalent chromium exists in the form of negatively charged anion, as well as GO surfaces have hydroxyl ($-\text{OH}$) or carboxyl ($-\text{COOH}$) groups and other oxygen groups, which can be protonated to ($-\text{OH}_2^+$) and ($-\text{COOH}_2^+$) respectively in acidic conditions. These protonated functional groups have the ability to coordinate with the negatively charged anion Cr(VI) through electrostatic attraction. Meanwhile, the removal of Cr(VI) by GO might still be involved in chemical reduction during adsorption process, Cr(VI) is partially reduced to Cr(III) by reductive surface hydroxyl groups on the surfaces of GO^[22]. This reaction catalyzed by electrons might be applied by π electron on the carbocyclic six membered ring of GO^[63], so that when Cr(VI) ions contact with organic substance or reducing agent (adsorbent), Cr(VI) is easily or spontaneously reduced to Cr(III) in acidic medium due to its high redox potential value^[3]. The redox reaction in the aqueous and solid phase explained in the following reaction^[22].



The resulting Cr(III) is either released back into the solution at lower pH in the form of water –soluble Cr(III) species or precipitated on the surfaces of GO as Cr₂O₃ to achieve the performance of adsorption [22].

The percent removal of Cr(VI) decreases with increasing of pH as depicted in figure 6, this result is due to the higher concentration of OH⁻ ions that compete with Cr(VI) species^[22] and due to deprotonation of oxygen groups on GO surface and decreasing the negative charge densities^[26]. At high pH, the suppression of the hydrolysis of Cr(VI) might be the reason for decreasing the percentage removal of Cr(VI) ions [3]. According to highest percentage removal, the pH=3 was considered in this study.

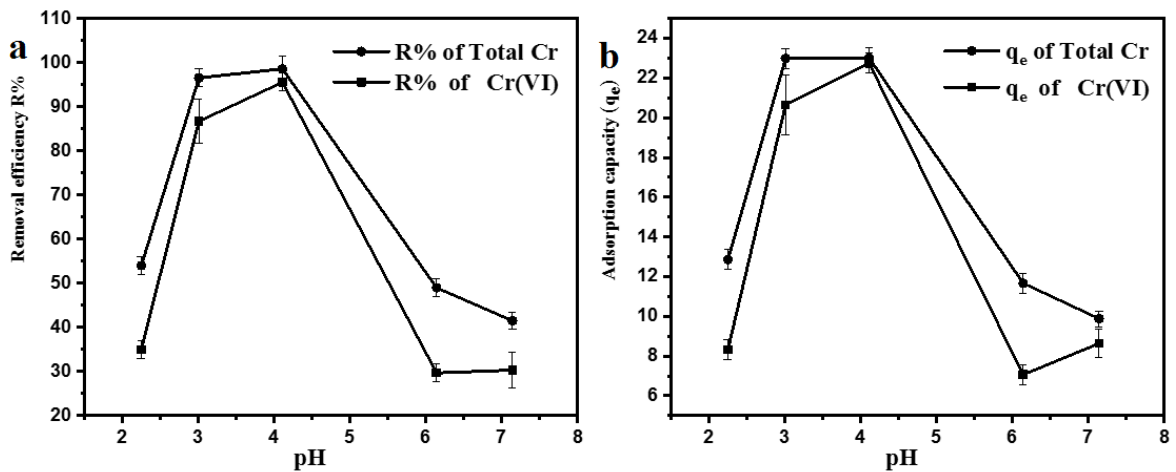


Figure 6: Effect of initially adjusted pH on (a) percentage removal efficiency (R%) of chromium by GO and (b) adsorption capacity(q_e). Initial concentration of Cr(VI)=50mg/L, contact time =2 h, temperature=25±0.2 °C, and adsorbent dosage =2g/L .

Variation of pH during Adsorption

To evaluate the effect of hydrogen ionic concentration on the adsorption, at the end of the adsorption process (equilibrium already reached), the final pH values of the suspension 50 mg/l of Cr(VI) on GO, were measured and reported in table 2.

Table.2 Initial pH and final pH during adsorption of Cr(VI) on GO. Initial concentration of Cr(VI)=50mg/L, contact time =2 h, temperature=25±0.2C°, and adsorbent dosage =2g/L.

Initial pH	Final pH
2	1.93 ± 0.04
3	2.57 ± 0.03
4	3.14 ± 0.04
6	3.9 ± 0.04
7	4.46 ± 0.03

According to the data in table 2, there is decrease in the solution pH after the adsorption process. During the adsorption process, H⁺ ions are released into the solution and lead to decrease in pH value after adsorption. The oxygen containing functional groups on the GO surface could be deprotonated leading to releasing of H⁺ ions during the adsorption process^[13].

4.2.2 Effect of Adsorbent dosage

Figure 7 shows the effect of GO dosage form on the percent removal and adsorption capacity of Cr(VI) in an aqueous solution. It has been detected that, with increasing the GO dose from 0.05 to 2g/l; the removal efficiency increased. From 2 mg to 7 g/l of GO, the percent removal remains constant. So that the optimum adsorbent dosage of GO is 40 mg for 20ml of Cr(VI) solution concentration. The adsorption capacity decreases with increasing dose from 0.05 to 2g/l; after that it shows constant behavior. This behavior attributed to the adsorbent dosage, as the dose increases, more active adsorption sites are available, thereby enhancing the removal of the heavy metal ions. However, when equilibrium is reached, an increase in the adsorbent dosage will not significantly increase the pollutant removal as the number of active sites would exceed the needed sites for the pollutant^[7]. In some instances, an increase in adsorbent dosage might drive to stacking and agglomeration, promoting inter-particles interactions and

reducing the number of active sites for adsorption. On the other hand, an increase in adsorbent dosage has a negative effect on the adsorption capacity since at higher dosage, the ratio of pollutant concentration to adsorbent dosage is low, leading to a decreased unit adsorption^[7].

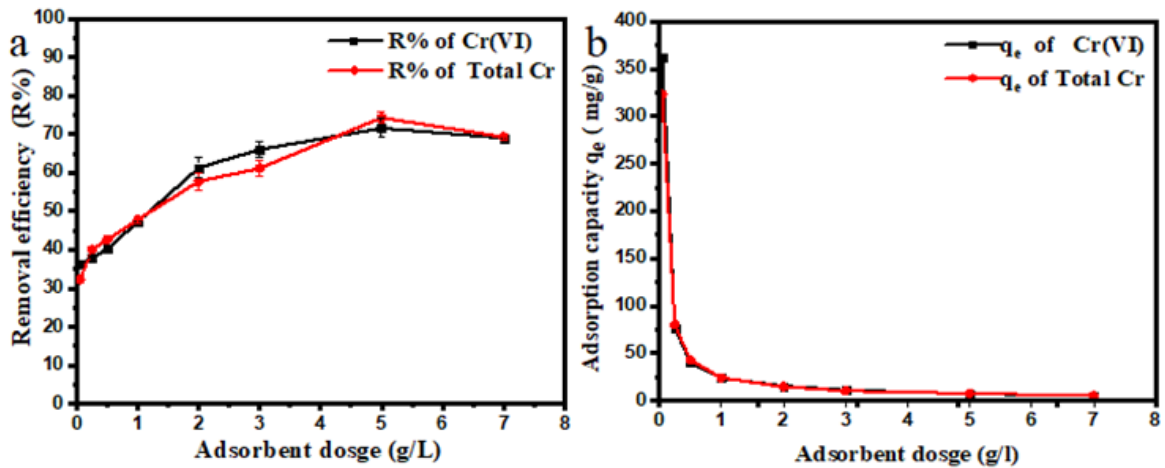


Figure 7: Effect of adsorbent dosage on (a) percentage of chromium removal (R%) by GO and (b) effect on adsorption capacity(q_e). Initial concentration of Cr(VI)=50mg/L, pH=3.0±0.2, agitation speed= 120 rpm, contact time =2 h, and temperature=25±0.2 °C.

4.2.3 Kinetic studies

Contact Time

The contact time is an important parameter that affects the adsorption of heavy metal ions. Generally, removal of metal ions increases with increasing in contact time until the equilibrium is achieved^[19]. Once the equilibrium is reached, the adsorption process of metal ions becomes constant. At the beginning of adsorption process, large active sites are available for the adsorbate and the process proceeded very fast, however, as the active sites are filled up, the adsorption proceeds slowly until the equilibrium is reached^[19]. Figure 8 summarizes the effect of contact time on the percent removal and

adsorption capacity of chromium ions by GO nanoparticles. The percentage removal was increased during the first 80 min, and then reached a plateau at equilibrium.

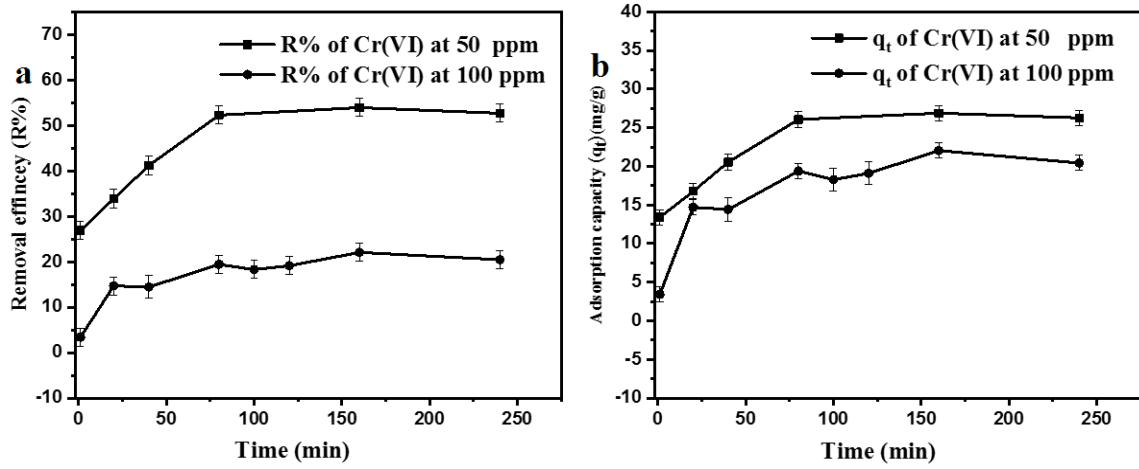


Figure 8: Effect of contact time on (a) percentage removal efficiency (R%) of Cr(VI) by GO and (b) adsorption capacity(q_t) of Cr(VI). Initial concentrations of Cr(VI)=50, 100 mg/L, pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2 °C, and adsorbent dosage=2g/L.

Kinetic models of adsorption:

The Pseudo-first order, pseudo- second order, intra-particle diffusion and Elovich kinetic models have been investigated in this study. These models explain the mechanisms that control the adsorption processes^[13]. The following linear forms expressed the pseudo first order (eq.10)^[13], pseudo second order (eq.11)^[21], Intra-particle diffusion model (eq.12)^[21] and Elovich kinetic model in (eq.13)^[21].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

$$q_t = k_p t^{\frac{1}{2}} + C \quad (12)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (13)$$

Where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time (t) respectively, k_2 is the rate constant of second –order adsorption ($g\ mg^{-1}\ min^{-1}$), k_1 is the pseudo first order rate constant (min^{-1}), k_p is the rate constant of intra-particle diffusion ($mg\ g^{-1}\ min^{-1/2}$), C is the intercept represents the thickness of the boundary layer, α is the initial adsorption rate (mg/min), and β is the extent of surface coverage and activated energy (g/mg).

Figure 9 shows that the pseudo second order model with high linear regression correlation coefficient (R^2) describes the kinetics of Cr(VI) adsorption onto GO nanoparticles. Thus, these results further support the assumption that adsorption is chemisorption and related to valence forces through sharing or exchange of electrons between the GO and Cr(VI)^[13, 21]. The rate constant of the pseudo second order kinetic was found to be decreased with increasing initial Cr(VI) concentration, indicating that the adsorption of Cr(VI) onto GO would be faster at lower initial concentration^[63] as indicated in table 3.

Figure 9b exhibits a linear relation with high correlation coefficient R^2 (0.996 and 0.991) for 50 and 100 ppm respectively, which reflects a very strong correlation between parameters and a good fitting of the experimental data with pseudo second order kinetic model, this is supported by the agreement between the theoretical values of ($q_{e,cal}$) with the experimental values were listed in table 3. Table 3 demonstrates other kinetic models with different correlation coefficients ($R^2 < 0.99$) at 50,100 mg/L.

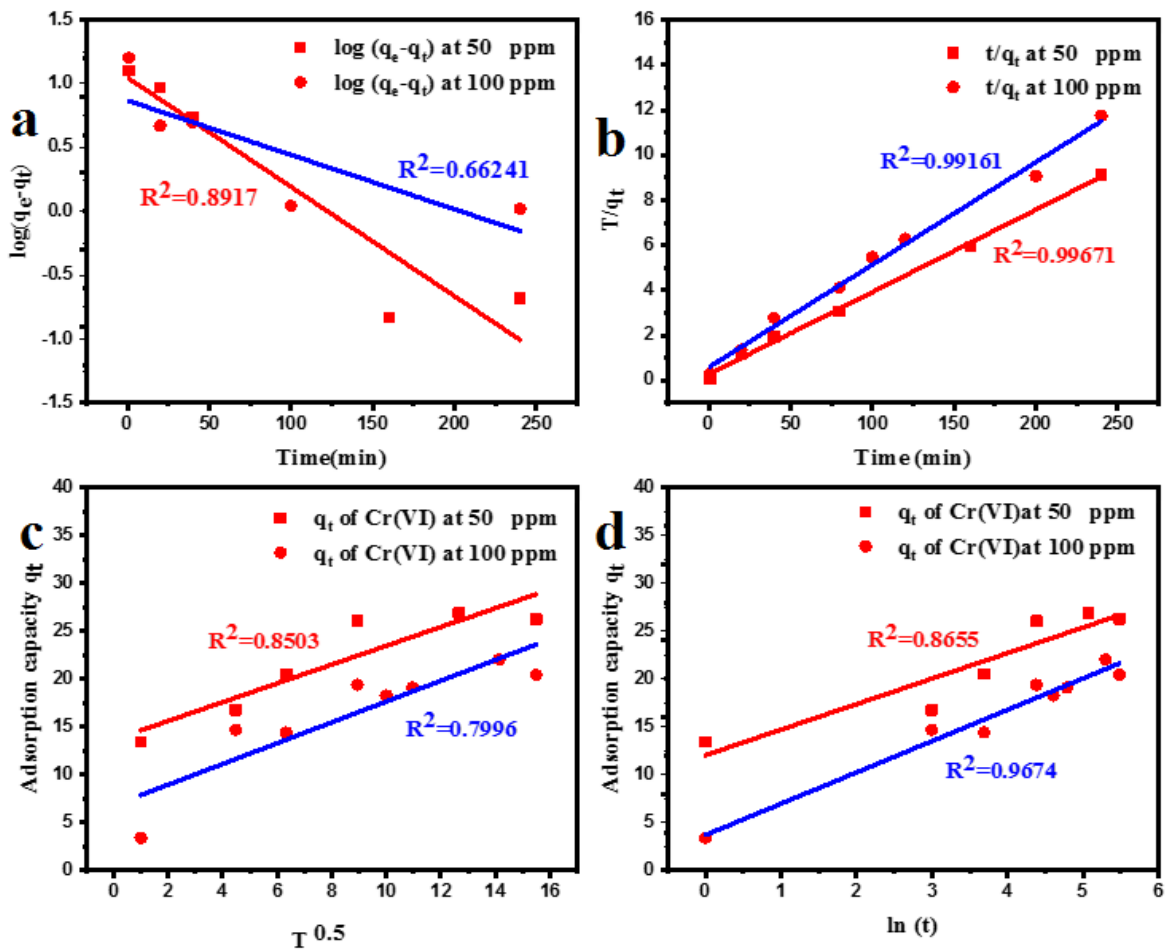


Figure 9: The kinetic models of adsorption Cr(VI) by GO (a) pseudo first order model ,(b) pseudo- second order model, (c) intra-particle diffusion model, and (d) Elovich kinetic model. Initial concentrations of Cr(VI) = 50, 100 mg/L, pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2C°, and adsorbent dosage=2g/L.

Table 3: The kinetic models parameters of adsorption Cr(VI) by GO. Initial concentrations of Cr(VI)=50, 100 mg/L, pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2 °C, and adsorbent dosage=2g/L.

Concentration (mg/L)	Pseudo-second order model			
	R ²	q _e (exp) (mg/g)	q _e (cal) (mg/g)	K ₂ (g/mg min)
50	0.9967	26.06	27.38	4.96*10 ⁻³
100	0.9916	19.39	21.97	3.55*10 ⁻³
Pseudo -first order model				
	R ²	q _e (exp) (mg/g)	q _e (cal) (mg/g)	K ₁
50	0.8917	26.06	11.195	0.0197
100	0.6624	19.39	7.391	0.0098
Intra-particle model				
	R ²	k _p	C	
50	0.8503	0.960	13.66	
100	0.7996	1.086	6.79	
Elovich model				
	R ²	α (mg/g min)	β (g/mg)	
50	0.9674	245.4	0.375	
100	0.8655	10.19	0.308	

4.2.4 The variation of initial concentration Cr(VI) on the adsorption.

The variation of initial concentration Cr(VI).

In order to investigate the possibility of Cr(VI) reduction to Cr(III) upon adsorption onto the graphene oxide at pH=3, the batch experiments were conducted with variation initial concentration ranging between 30-300 mg/l of Cr(VI) at different time intervals. The samples were analyzed for total Cr and Cr(VI), whereas the Cr(III) was determined by subtracting the Cr(VI) from total Cr. Figure 10 exhibits the variation in removal efficiency measured as total Cr, Cr(VI) and the calculated Cr(III). Above the concentration of 300 mg/l, the retention curves of total Cr and Cr(VI) start to advance farther, suggesting that another oxidation state of Cr appeared at these conditions. Presumably, reduction of Cr(VI) to Cr(III) takes place on the adsorbent followed by the release of Cr(III) into the solution leading to an observed deviation of retention

curves^[51]. On the other hand, below the concentration of 300mg/l, no significant release in Cr(III) which means no possible reduction of Cr(VI) ions. So that the equilibrium models were studied at a concentration lower than 300mg/l.

As shown in figure10a, the removal efficiency of Cr(VI) and total Chromium decreased with increasing the initial concentration. In panel b, the adsorption capacity increased with increasing the initial concentration, taking into account the correlation in the oxidation state between Cr(VI) and Cr(III), noted that at lower concentration of Cr(VI) ions, the Cr(VI) ions present in the solution are comparatively lesser as compared to the number of available sites on the GO surface, whereas at higher concentration of Cr(VI) in solution, the available sites for adsorption become lesser, there by the removal percentage of Cr(VI) ions depends on initial concentration^[20].

Generally, adsorption capacity increases with increase in the initial concentration of the heavy metal ions due to the increased remaining concentration ratio to a specific mass of adsorbent^[19].

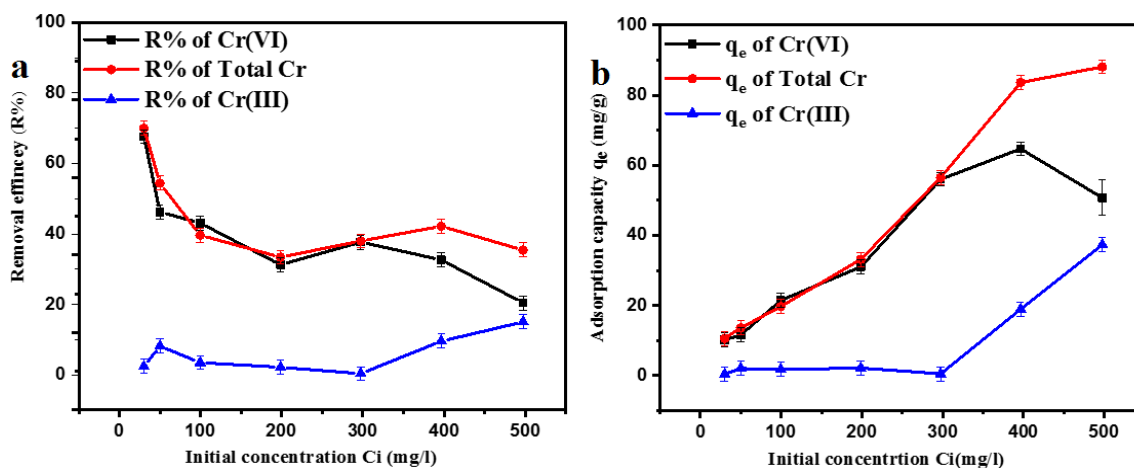


Figure 10: Removal of chromium by GO as total Cr and as Cr(VI). (a) percent of Cr(VI) reduction to Cr(III) is calculated as the difference between total Cr and Cr(VI) percentage. (b) adsorption capacity of chromium. pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2°C, contact time=80 min, adsorbent dosage=2g/L, and initial concentration (30, 50, 100, 200, 300, 400, 500 mg/L).

Adsorption Isotherm Models:

In order to understand the interaction between the metal ions and adsorbent, adsorption isotherms are normally employed^[19]. The adsorption isotherms are based on a relationship between the amount of pollutant adsorbed per unit weight of the adsorbent and the pollutant concentration at a particular temperature, under equilibrium conditions^[19]. Among the various adsorption isotherms, Langmuir, Freundlich and Temkin models were applied in this study to understand the adsorption behavior of Cr(VI) ions from aqueous solution by GO particles, which is observed in figure 11(a-c).

The linear form of the Langmuir model could be expressed as follows in equation (14)^[13]:

$$\frac{C_e}{q_e} = \frac{1}{b Q_{\max}} + \frac{C_e}{Q_{\max}} \quad (14)$$

The linear form of the Freundlich model could be expressed as follows in equation (15)^[49]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (15)$$

The Temkin model could be expressed as follows in equation (16)^[13]:

$$q_e = B_T \ln k_T + B_T \ln C_e \quad (16)$$

Where C_e refers to the equilibrium concentration of the remaining solute in the solution (mg/l), q_e is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g), Q_{\max} is the amount of adsorbate per unit mass of the adsorbent at complete monolayer coverage (mmol/g), b is a Langmuir constant, n and k_f are Freundlich constant that related to adsorption intensity and capacity respectively. $1/n$ is

the heterogeneity factor and $B_T = RT/b$ is constant related to the heat of sorption (j/mol), R is the ideal gas constant, T is absolute temperature (K), b is a constant related to the heat of sorption (j/mol) and K_T is the Temkin isotherm constant (l/g). Figure 11, indicated that the adsorption of Cr(VI) ions by GO is well described by Langmuir isotherm parameters were listed in table.4 . The calculated Q_{max} is 41.27 mg/g for the adsorption by GO.

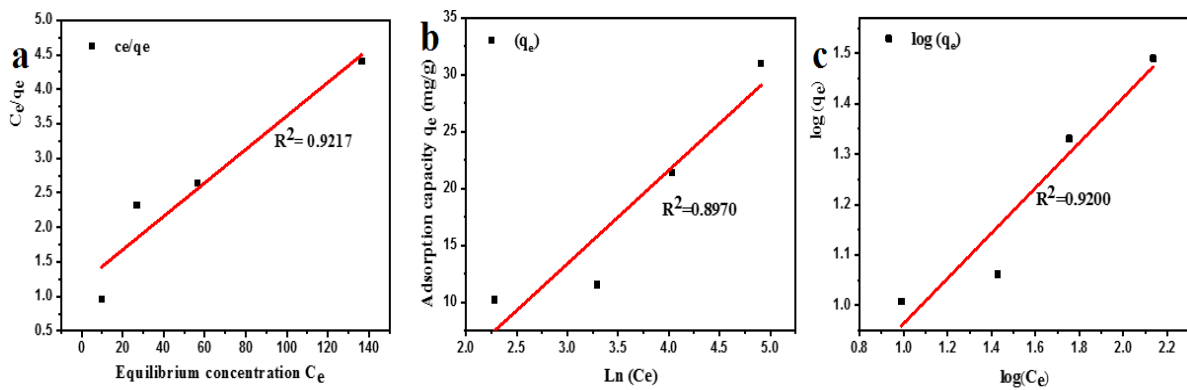


Figure 11: Equilibrium studies of adsorption Cr(VI) by GO, (a) Langmuir isotherm model, (b) Temkin isotherm model, and (c) Freundlich isotherm model. pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2°C, contact time=80 min, and adsorbent dosage=2g/L.

Table 4: Isotherm models parameters for adsorption of Cr(VI) by GO. pH=3.0±0.2, agitation speed= 120 rpm, temperature=25±0.2 °C, contact time=80 min, and adsorbent dosage=2g/L.

Isotherm model	R^2	Parameters	
Langmuir	0.9217	$Q_{max}=41.27$ mg/g	$b=0.02035$ l/mg
Temkin	0.8970	$B_T = 8.226$	$k_T = 0.254$
Freundlich	0.9200	$\frac{1}{n} = 0.449$	$K_f = 3.27$

The nature of the adsorption was addressed depending on the values of the dimensionless constant of Langmuir isotherm the dimensional constant known as the

equilibrium parameter, R_L of Langmuir isotherm and its value were calculated from equation (17):

$$R_L = \frac{1}{1 + bC_i} \quad (17)$$

Where b is a Langmuir constant and C_i is the initial concentration. The values of R_L indicate the nature of the adsorption process. $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, and $R_L = 0$ for unfavorable adsorption, linear adsorption, favorable adsorption, and irreversible adsorption, respectively^[13]. From this data and parameter that shown the R_L values for the removal of Cr(VI) are ranged from 0.197 to 0.620 for GO. These values indicate favorable adsorption process for GO. From Freundlich isotherm model the calculated value for $(1/n)$ of adsorption Cr(VI) using GO are less than unity, this refers to a heterogamous surface with minimum interactions between the adsorbent ions.

Figure 12 shows the best isotherm model is Langmuir model for adsorption of Cr(VI) using GO at different temperatures, a linear relationship between equilibrium concentration per adsorption capacity at equilibrium (C_e/q_e) with equilibrium concentration (C_e) and high correction coefficient ($R^2 = 0.919, 0.981$ and 0.994) for temperatures 298, 318 and 328 k respectively.

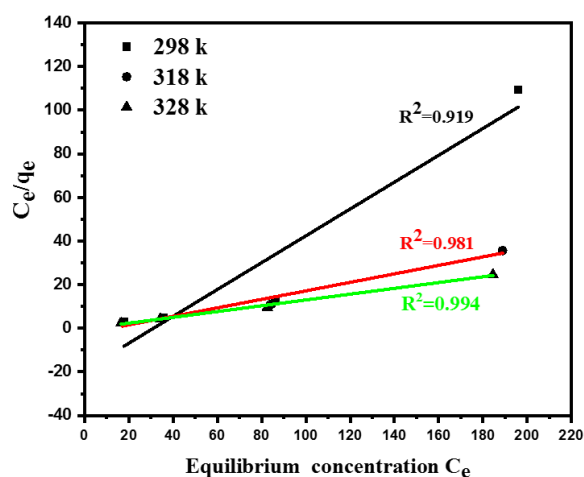


Figure 12: Langmuir isotherm model at different temperature (298-328 k) for adsorption Cr(VI) by GO. pH=3.0±0.2, agitation speed= 120 rpm, contact time=80 min, and adsorbent dosage=2g/L.

In this study, the graphene oxide was used with reduced size of 200 nm to improve their adsorption capacity q_e (mg/g). And GO adsorbent has an adsorption capacity higher than others adsorbent that reported in the literature. But in other literature the graphene oxide can be functionalized to improving qualities of GO, some of functional group that can be increased (for example: Chitosan –CDTA-GO) or decreased (for example: Fe_3O_4 hollow microspheres/graphene oxide) the adsorption capacity comparable with GO. As can be seen from the table 5 below.

Table 5: Comparison of the Cr (VI) adsorption capacity of nanographene oxide with other adsorbents at the same pH range.

Adsorbent	Maximum Adsorption capacity q_{max} (mg/g)	Reference
Amino starch	12.12	[65]
Activated carbon	15.5	[66]
Magnetic nanoparticle ($\gamma - Fe_2O_3$)	19.2	[67]
Polyethylene modified activated carbon	20.05	[68]
Fe_3O_4 hollow microspheres/graphene oxide	32.33	[69]
Nano graphene oxide	41.27	In this study
Chitosan –CDTA-GO	169.49	[26]

4.2.5 Agitation Speed

The effect of agitation speed on adsorption capacity and removal efficiency of Cr(VI) from aqueous solution is shown in figure 13. It has been detected that, with increasing the agitation speed from 90 rpm to 150 rpm the percentage removal of hexavalent chromium and adsorption capacity were decreased, then when increasing speed further than 150 rpm the removal efficiency and adsorption capacity become steady and constant.

At 120 rpm the removal is accessible value, so that another factors are studied at these speed.

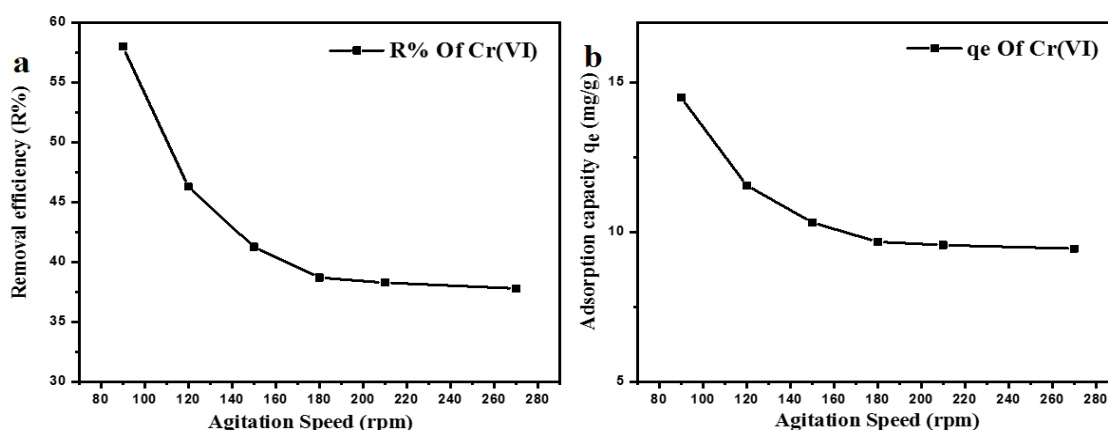


Figure 13: Effect of agitation speed on the adsorption of Cr(VI) onto GO. (a) percentage removal efficiency (R%), (b) adsorption capacity (q_e). Initial concentration =50mg/L, pH=3.0±0.2, temperature=25±0.2 °C, contact time=80 min, and adsorbent dosage=2g/L.

4.2.6 Temperature

The variation of the temperature

The influence of temperature on the percentage removal efficiency is readily seen in figure14.

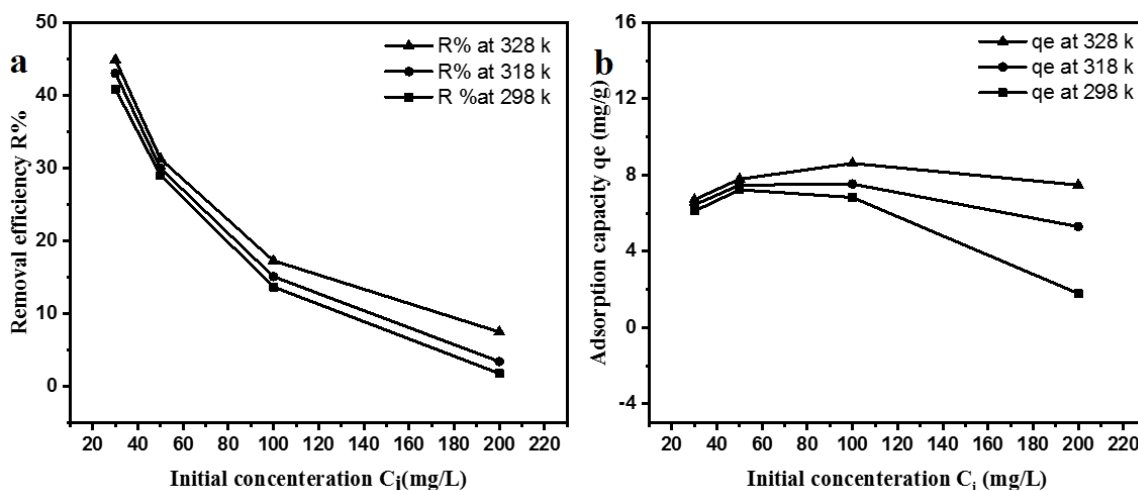


Figure 14: Effect of temperature on the adsorption of Cr(VI) onto GO (a) percentage removal efficiency ($R\%$), and (b) on adsorption capacity(q_e). $pH=3.0\pm 0.2$, agitation speed= 120 rpm, contact time=80 min, and adsorbent dosage=2g/L.

It is clear that when the initial concentration of chromium increases at different temperatures, the percentage removal efficiency decreases gradually. For the same initial concentration, the percentage removal of Cr (VI) increases with increasing temperature from (25-55 °C), this means that the adsorption process is an endothermic process. It's may be due to the enlargement of pore size and activation of adsorbent surface ^[27].

Thermodynamic parameter for adsorption process.

Thermodynamic parameter including Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated for adsorption of Cr(VI) on graphene oxide adsorbent by varying the temperature in the range of 25-55 C° under optimized conditions (table.6).

Table 6: Thermodynamic parameters for the adsorption of Cr(VI) onto GO. Initial concentration =30mg/L, pH=3.0±0.2, contact time=80 min, and adsorbent dosage=2g/L.

T	1/T	k_c	Ln k_c	ΔG (KJ/mol.k)	ΔH (KJ/mol.k)	ΔS (J/mol.k)
298k	3.355*10⁻³	0.345	-1.062	2.631	4.300	5.559
318k	3.144*10⁻³	0.377	-0.973	2.572		
328k	3.048*10⁻³	0.407	-0.898	2.448		

The Gibbs free energy, as well as the enthalpy process were calculated using the following van't Hoff equations (18-20):

$$k_c = \frac{q_e}{c_e} \quad (18)$$

$$\Delta G^\circ = -RT \ln k_c \quad (19)$$

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (20)$$

Where k_c is the equilibrium constant calculated as the surface and solution metal distribution ratio, q_e is the adsorption capacity at equilibrium (mg/g), C_e is the concentration at equilibrium(mg/l), R is the universal gas constant (8.314J·mol⁻¹·K⁻¹), T is the temperature in Kelvin, ΔG° is Gibbs free energy(j/mol.k), ΔH° is enthalpy(j/mol.k), and ΔS° entropy(j/mol.k).

Adsorption enthalpy and entropy were calculated starting from Equation (20) and determine the plot curve of $\ln K_C$ versus $1/T$, the values are presented in Table 6. Positive value of adsorption enthalpy shows that process is endothermic^[60], and its magnitude imply that adsorption of Cr(VI) on GO is a chemical adsorption^[60]. Increase

in equilibrium constant(k_c) when increase the temperature also indicates the increase in the amount of adsorbent metal ion^[60].

Furthermore the positive value of adsorption entropy suggested the 'increased randomness' at the adsorbent- solution interface during the adsorption of Cr(VI) from aqueous solution to the adsorbent^[21]. The Gibbs free energy has a positive value as well, may be due to the enthalpy (ΔH°) has a positive value and entropy (ΔS°) has a small positive value, so that ΔS° multiplied with temperature is smaller value than ΔH° , then the result from these variables when implied in the following equation (21) give a positive free energy:

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \quad (21)$$

Which means the reaction is non-spontaneous, but the reaction occur at optimized condition.

4.3 Probable adsorption mechanism

The proposed mechanism for Cr(VI) removal was discussed in figure 15. The mechanism for the removal of Cr(VI) using GO that includes; adsorption through electrostatic attractions^[19], reduction of Cr(VI) to Cr(III)^[22], and may be coordination between chromium ions and ligands, due to a some shifts in the adsorption peaks in FTIR spectra of graphene oxide before and after adsorption^[3].

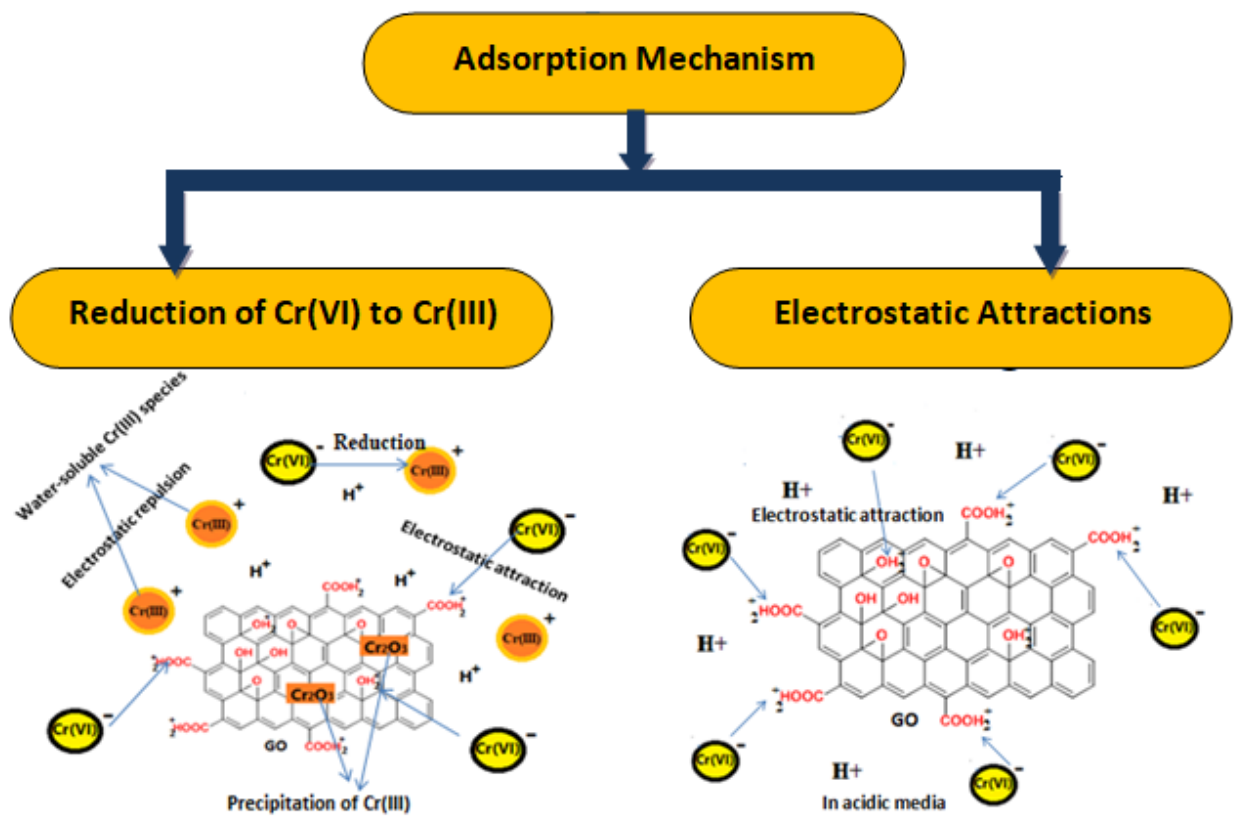


Figure 15: Probable mechanism for Cr(VI) removal by GO in acidic environment

CONCLUSION

In this study, the preparation of GO and their efficient application for the removal of hexavalent chromium ions from aqueous solutions under different experimental conditions such as pH, contact time, initial metal concentration, adsorbent's dosage, and temperature of the system were elucidated. Moreover, GO has been extensively studied as novel adsorbent due to their physicochemical properties like high efficiency and strong affinity for Cr(VI) ions. This process has a good benefit, that is decreased the harm effect of hexavalent to ecosystem and human health from aqueous media.

The FTIR spectroscopy showed oxidation of graphite to GO and confirmed the formation of GO particles. It was used to identify the GO adsorbent and the binding of these particles to Cr(VI). Further, the experimental results showed the pseudo second order model and Langmuir isotherm model well fitted with the adsorption data. The maximum adsorption capacity obtained from Langmuir isotherm model is 41.27 mg/g, which is higher than the other adsorbents. However, the adsorption capacity can be enhanced by functionalization of graphene oxide with good positive functional group which attracts the Cr(VI) anion towards it.

RECOMMENDATIONS

In this study, the removal of chromium hexavalent Cr(VI) from aqueous solution by using graphene oxide nanoparticles (GO) was achieved with maximum adsorption capacity around the 41.27 mg/g . However, can be improvement this adsorption capacity by functionalized the graphene oxide nanoparticles with selective functional groups for binding the anionic species of chromium hexavalent Cr(VI), which give way to increase the adsorption process.

To easy and fast separation of the graphene oxide from aqueous solution and regeneration it, can be prepared graphene oxide with a magnetic particles.

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الخلاصة (ABSTRACT IN ARABIC) :

كيفية حماية البيئة المائية ومصادرها من عنصر الكروم السداسي السام Cr(VI) الذي يشكل خطراً كبيراً على صحة الإنسان والبيئة؟

هذا السؤال الذي سعيت للإجابة عنه في هذا البحث، ولقد تمكنت من إزالته الكروم السداسي السام Cr(VI) من الوسط المائي بواسطة أكسيد الجرافين (Graphene oxide -GO) كمادة مازة (Adsorbent) عن طريق عملية الامتزاز (Adsorption) وكانت أقصى نسبة يمكن تغطيتها من الكروم السداسي Cr(VI) على سطح واحد غرام من أكسيد الجرافين (Adsorption capacity) q_{max} ما يقارب 41.27 mg /g عندما تكون $pH=3$ و درجة الحرارة = 25 °C .

ولقد استخدمت أكسيد الجرافين (GO) لميزاته العديدة من ناحية الكيميائية والفيزيائية الفريدة، ومن أهمها: وجود العديد من مجموعات الأوكسجين الوظيفية المتنوعة و مساحة سطحه الكبيرة، ولهذا الهدف قمت بتصغير حجم جزيئات أكسيد الجرافين إلى ما يقارب 200 نانومتر ليعطي كفاءة (Efficiency) عالية لعملية الامتزاز (Adsorption) وإزالة الكروم من الوسط المائي.

و تم إيجاد أن أفضل وسط لإزالة الكروم السداسي من المياه هو الوسط الحمضي، وعلاوة على ذلك وجد أن تفاعل الامتزاز (Adsorption) يندرج تحت معدل السرعة الحركية

(Kinetic rate) ذات الرتبة الثانيه (pseudo- second –order) وكذلك فإن أفضل نموذج لوصف عملية الامتزاز (Adsorption) من ناحية الديناميكا الحرارية (Thermodynamic) هو نموذج لانجموير (Langmuir model) وحسب هذا فإن عملية الامتزاز تحدث بطريقة الامتزاز الكيميائي (Chemisorptions).

وأخيراً أظهرت المتغيرات الديناميكا الحرارية، أن قيمة الموجبة للمحتوى الحراري (ΔH°) تعني أن عملية الامتزاز ماصة للحرارة وأما قيمه الموجبه لانتروبيا (ΔS°) تعني أن الفوضى والحركة كبيرة ما بين سطح الماز أكسيد الجرافين (GO) (Adsorbent) والمعدن الكروم السداسي الممتز (Cr(VI)) (Adsorbate) مما تزيد من فرصة الالتصاق ما بينهما وتزيد من كفاءة إزالة الكروم من الوسط المائي على سطح أكسيد الجرافين (GO).

وأيضاً بالنتائج العمليه، تم إثبات أن أكسيد الجرافين (GO) يعتبر من أفضل الممتزات (Adsorbents) مقارنة بغيرها حسب الكثير من الدراسات السابقة، على الرغم من أنه إذا تم عمل تعديلات وإضافة مجموعات وظيفية أخرى على سطح أكسيد الجرافين (GO) ستزيد من

الكفاءة (Effeciency) لإزالة الملوثات من الأوساط المائية والتي من أهمها الكروم السداسي السام (Cr(VI)).

”وأخّر دعواتهم أن الحمد لله رب العالمين”

سورة يونس (10)

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ
يٰٓأَيُّهَا الْمُدَّةٰٓرُ
يٰٓأَيُّهَا الْمُدَّةٰٓرُ
يٰٓأَيُّهَا الْمُدَّةٰٓرُ