

An-Najah National University

Faculty of Graduate Studies

**Efficiency of magnetic chitosan supported on graphene
for removal of perchlorate ions from wastewater**

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**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.**

2018

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Dedication

Every challenging work needs self-efforts as well as encouragements of others especially those who are very close to our heart.

To my father (Allah mercy her soul), and my great mother who sacrificed for our sake. To my wife, my daughter (Eylaf), brothers and sisters whose love and encouragement make me able to get success and honor..

To all of them I dedicate my modest efforts.

Acknowledgements

Beginnings thank Almighty Allah who gave me the ability to complete this work. Then I would like to thank the student of the master's program, and this research was prepared by my professor and supervisor Prof. Dr. Shehdeh Jodeh, who has the merit - after God - for research and researcher since the topic title and idea until it became a message and research. He has all my thanks and appreciation and gratitude. I would like to thank all my professors of the Faculty of Graduate Studies at the Department of Chemistry at An-Najah National University who have spared no effort in guiding me and providing me with books and research papers. And I have to recognize the virtue of my professors of the virtues in this university presidency and Deanship of scientific research, and in the College of Graduate Studies deanship and management to assign them to me throughout the duration of the research and unloading.

Many thanks to Middle East Desalination Research Center (MEDRC) who funded my project through the Palestinian Water Authority whom our thanks go as well to them for their follow up the project.

To all in Chemistry Department at An-Najah National University I offer my honest gratitude, in particular laboratory technician Mr. Nafiz Dweikat. To my colleagues, my supporters, and my friends, I offer my sincere thanks.

الإقرار

انا الموقع ادناه مقدم الرسالة التي تحمل العنوان :

Efficiency of magnetic chitosan supported on graphene for removal of perchlorate ions from wastewater

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يُقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

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Table of contents

No.	Content	Page
	Dedication	III
	Acknowledgement	IV
	Declaration	V
	List of tables	VIII
	List of figures	IX
	List of abbreviations	X
	Abstract	XII
	Chapter One: Introduction	1
1.1	Overview	1
1.2	Objective of this work	4
1.2.1	General objectives	4
1.2.2	Specific objectives	4
1.2.3	Research questions and identified problems	5
	Chapter Two: Background and Literature review	6
2.1	Perchlorate	6
2.1.1	Structure and properties	6
2.1.2	Uses of Perchlorate	7
2.1.2.1	Toxicity of Perchlorate	8
2.2	Industrial wastewater in the Palestinian Territories	9
2.3	Adsorption	10
2.3.1	Adsorption phenomenon Effluents	10
2.3.2	Adsorption Isotherm Models	11
2.3.2.1	Langmuir Adsorption Isotherm	12
2.3.2.2	Freundlich Model Isotherm	13
2.3.2.3	Temkin Model Isotherm	14
2.3.3	Adsorption Thermodynamics	15
2.3.4	Adsorption Kinetics	15
2.3.5	Types of Adsorbents	16
2.3.6	Adsorption as an effective method for removing perchlorate ions from wastewater	17
2.4	Methodology of preparing Cross-Linked Chitosan / Graphene Particles	19
	Chapter Three: Experimental Work	22
3.1	Chemicals and Materials	22
3.2	Preparation of Graphene Oxide	22

3.3	Preparation of cross-linked Magnetic Chitosan with Graphene Oxide	23
3.4	Sample characterization	24
3.5	Batch adsorption studies	25
3.5.1	Effect of pH and co-existing anions	25
3.5.2	Effect of contact time	25
3.5.3	Effect of temperature	25
3.5.4	Regeneration process	26
3.5.5	Analytical Methods	27
	Chapter Four: Results and Discussion	28
4.1	Material Characterization	28
4.1.1	FTIR analysis	28
4.1.2	TEM analysis	29
4.1.3	VSM analysis	30
4.2	Effect of PH on perchlorate adsorption	31
4.3	Effect of co-existing anions	32
4.4	Effect of contact time	33
4.5	Adsorption Kinetics	34
4.6	Adsorption Isotherm	37
4.7	Adsorption Thermodynamics	41
4.8	Regeneration ability	44
	Conclusions	45
	Suggestion for Future Work	46
	References	47
	المخلص	ب

VIII
List of Tables

No	Table	Page
Table 2.1	physical and chemical properties of perchlorate	6
Table 4.1	kinetic model constants and correlation coefficients of perchlorate adsorption onto CM/GO Bs.	35
Table 4.2	Langmuir, Freundlich and Tempkin isotherm models constants and correlation coefficients of perchlorate adsorption onto CM/GO Bs.	39
Table 4.3	Thermodynamic parameters for perchlorate adsorption onto CM/GO Bs.	43

IX
List of Figures

No.	Figur	Page
Figure 2.1	Molecular structure scheme of the perchlorate ion.	7
Figure 2.2	Molecular structure scheme of Chitosan.	18
Figure 2.3	Molecular structure scheme of Graphene	19
Figure 2.4	Methodology scheme of preparation of CM/GO Bs	20
Figure 3.1	Preparation of CM/GO Bs procedure.	24
Figure 4.1	FTIR characterization of CM/GO Bs.	28
Figure 4.2	TEM analysis of CM/GO Bs complex.	29
Figure 4.3	VSM magnetization curves of CM/GO Bs.	30
Figure 4.4	Effect of pH on perchlorate adsorption onto CM/GO Bs complex.	31
Figure 4.5	Effect of co-existing anions on perchlorate adsorption onto CM/GO Bs.	33
Figure 4.6	Effect of contact time on perchlorate uptake by CM/GO Bs complex.	34
Figure 4.7	Frendlich isotherm plot for perchlorate adsorption onto CM/GO Bs.	38
Figure 4.8	Langmuir isotherm plot for perchlorate adsorption onto CM/GO Bs.	38
Figure 4.9	Thermodynamic model for perchlorate adsorption onto CM/GO Bs.	42
Figure 4.10	Adsorption capacity of perchlorate onto CM/GO Bs with five re-adsorption/desorption cycles	44

List of Abbreviation

Symbol	Abbreviation
A°	Angstrom = 1.0×10^{-10} meters
ARIJ	Applied Research Institute Jerusalem
B	Dimensionless Temkin constant
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
C_o	Concentration of perchlorate in the sample solution before treatment (mg/L)
C_e	Concentration of perchlorate in the sample solution after treatment (mg/L) at equilibrium
C_i	Initial concentration of perchlorate in the sample solution (mg/L)
DSC	Differential Scanning Calorimetry
EQA	European Quality Assurance
FT-IR	Fourier Transform Infrared
IQ	Intelligence Quotient
K_1	The pseudo- 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 ($\text{mg/g (L/mg)}^{1/n}$)
K_L	Langmuir isotherm constant (L/mg)
MAC	Minimum alveolar concentration
ClO_4^-	Perchlorate
MAD	Mass of Adsorbent Dose
N	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
OPT	Occupied Palestinian territories
Q_e	The amount of ClO_4^- adsorbed per gram of the adsorbent (mg/g)
Q_m	Maximum monolayer coverage capacity (mg/g)
Q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
R	The gas constant (8.314 J/mol K)

XI

R^2	Correlation coefficient (regression coefficient)
R_L	Dimensionless constant separation factor
SEM	Scanning Electron Microscope
CM/GOBs	Magnetic Chitosan with Graphene Oxide Beads complex
SPE	Solid Phase Extraction
SVR	Systemic Vascular Resistance
T	Time
T	The absolute temperature (K)
TGA	Thermal gravimetric analysis
V	Volume of solution
ΔG°	Stander Gibbs energy
ΔH°	Standard enthalpy
ΔS°	Standard entropy

Efficiency of magnetic chitosan supported on graphene for removal of perchlorate ions from wastewater

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Abstract

One of an emerging trace contaminants is perchlorate that has been detected in surface water, ground water, soil and food globally. Cross linked Magnetic Chitosan / Graphene Oxide Beads (CM/GO Bs) were synthesized and tested to remove perchlorate anions from waste water.

The complex was characterized by transmission electron microscopy, Fourier Transformation Infrared spectroscopy and vibrating sample magnetometry.

The effect of pH, contact time, co-existing anions and temperature on adsorption was investigated. Particles could be recovered easily by external magnetic field because they were super-paramagnetic.

The CM/GO Bs complex could adsorb perchlorate in a wide range of pH from 4 to 10 . Co-existing anions may inhibit the adsorption of perchlorate on CM/GO Bs.

Kinetic data were well fitted to the pseudo-second-order model. The enthalpy and negative gibbs standard free energy show that the adsorption process was exothermic and spontaneous. the exhausted adsorbent can be regenerated well by 0.1% NaCl solution.

Chapter One

Introduction

1.1 Overview

Pollution is the main problem of the environment in the world which is the process of making parts of the environment (land, water and air) dirty and unsafe or unsuitable to use. This occurs through diffusion of pollutants into a natural environment[1].

More than 200 million people worldwide are affected by toxic pollution according to Pure Earth, a non-profit environmental organization. Some places in the world are classified as the worst polluted places, in these places babies are born with birth defects. Children have lost 30 to 40 Intelligence Quotient (IQ) points, and life expectancy may be as low as 45 years due to cancers and other diseases when chemicals runoff, metals like lead or nonmetals such as perchlorate that introduced to water, water pollution will be occurred[2].

The need to maintain a cleaner environment is the main subject of increasing concern to the environment list. There are many agents that may cause pollutants such as heavy metals, dyes and anions[3-5].

Perchlorate ion (ClO_4^-) is an inorganic pollutant that its salts (mostly ammonium sodium and potassium) are mainly used in manufacturing of matches, airbag inflators, e-leomomz tubes, safety flares, electroplating and aluminum relining.

Unfortunately the old unsafe disposal of rocket fired and explosives by chemical industries and the aerospace is the major source of perchlorate contaminants in ground water[6. High dosage of perchlorate may cause eye and skin irritation, vomiting, nausea and cough.

Considering the human health concerns, perchlorate was included into the drinking water pollutant candidate list in 1998 by the US Environmental Protection Agency (USEPA 1998). The USEPA adopted a new drinking water standard of 24.5 ppm for perchlorate in 2005[7] .

Now the main challenge for environmentalists is removal of perchlorate from water especially perchlorate ion which is non-volatile and highly soluble in water[8]. There are many methods to remove perchlorate from drinking water such as adsorption, ion-exchange, biological treatment and chemical catalytic reduction [8-10]. Adsorption is the most suitable one compared with other methods due to its advantages of high treatment efficiency, low cost and easy operation.

Graphene as adsorbent is also used to remove perchlorate from water. However, it needs to be modified by cationic surfactant to improve its adsorption capacity which may cause high cost or second pollutant, so, we may use chitosan which is effective bio-adsorbent because it has good biodegradability and nontoxic and chemical resistance and mechanical properties[11-12].

To avoid problems related to regeneration of chitosan, focusing on magnetic adsorbents in recent years was occurred. The main advantages of magnetic composites include:

1. high efficiency
2. fast adsorption rate
3. their micrometer size and stable structure
4. simple recovery using an external magnetic field
5. their ability to be regenerated easily[13].

The aim of this study is to remove perchlorate ions from wastewater using this new prepared material as an adsorbent for the solid phase's extraction of perchlorate ion. The adsorption behaviors of the new surface with perchlorates ion will be studied.

The effect of pH, contact time, amount of adsorbent and concentration of perchlorate ions will be studied. The adsorption capacity will be investigating using kinetics and pH effects.

Equilibrium isotherm studies will be done by varying the following three parameters, initial concentrations of perchlorate ions, volume of the solution, and adsorbent dose on the uptake of perchlorate from the solution.

1.2 Objectives of this work

1.2.1 General objective

To remove perchlorate ions from wastewater, using this new prepared material (magnetic chitosan with graphene oxide) and to specify the optimal conditions for the adsorption.

1.2.2 Specific objectives

- 1) To study the adsorption behaviors of the new modified material with perchlorate .
- 2) To determine if magnetic chitosan-graphene oxide can be used to remove perchlorate ions from contaminated wastewater.
- 3) To specify perchlorate ions concentration that exists in industrial wastewater.
- 4) To study the effect of pH, temperature, amount of adsorbent, concentration of magnetic chitosan-graphene oxide and contact time on the adsorption of perchlorate.

Beside the major objective of removal of perchlorate ions from industrial wastewater, other objectives will be like screening the wastewater for other pollutants like volatile organic compounds and this will give an idea to different ministries in Palestine like ministries of health, agriculture and water to put some guidelines and restrictions on those industries.

1.2.3 Research question and identified problems

The main questions addressed in this thesis are:

- 1- Can magnetic chitosan-graphene oxide be used to clean up perchlorate ions from contaminated wastewater?
- 2- To which extent magnetic chitosan-graphene oxide can tolerate and adsorb perchlorate?
- 3- What are the optimum conditions of pH, temperature, amount of adsorbent, concentration of magnetic chitosan-graphene oxide, and contact time for magnetic chitosan-graphene oxide to adsorb perchlorate?
- 4- What is the best dosage of magnetic chitosan-graphene oxide needs to adsorb the largest proportion of perchlorate under the optimum conditions?
- 5- Explanation of the adsorption behavior of the new magnetic graphene with perchlorate?

Chapter Two

Back Ground and Literature Review

2.1. Perchlorate Ion

2.1.1. Structure and Properties

Perchlorate ion is an inorganic ion with molecular formula (ClO_4^-), the salts of perchlorate are produced commercially such that they are used for propellants, exploiting properties as powerful oxidizing agent .

Most perchlorates are solids that are soluble in water and colorless. There are four perchlorates produced commercially which are perchloric acid (HClO_4), ammonium perchlorate (NH_4ClO_4), potassium perchlorate (KClO_4) and sodium perchlorate (NaClO_4) [14-15].

Perchlorate is the anion resulting from the dissociation of perchloric acid and its salts. Chemical and physical properties of perchlorate are summarized in table 2.1[16].

Table 2.1: physical and chemical properties of perchlorate

Chemical/Physical property	Values
Solubility in water	Soluble
Molecular Weight	99.451 gmol^{-1}
Chemical Formula	ClO_4^-

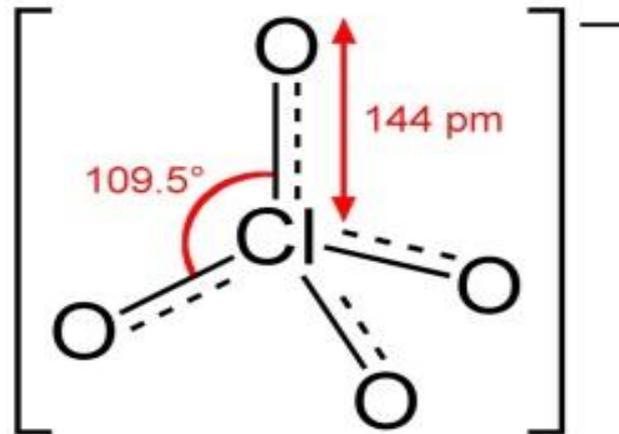


Figure 2.1: Molecular structure scheme of the perchlorate ion.

2.1.2. Uses of Perchlorate

Perchlorates are mostly used as oxidizing agents in propellants for rockets and fireworks of particular value is ammonium perchlorate composite propellant as a component of solid rocket fuel. In a smaller application, perchlorates are used extensively within the pyrotechnics industry and manufacture of matches [17].

Lithium Perchlorate (LiClO_4), which decomposes exothermically to produce oxygen, is useful in oxygen “Candles” on submarines, spacecraft and where oxygen is needed.

Potassium perchlorate (KClO_4) in the past, has been used therapeutically to treat hyperthyroidism resulting from Graves’ disease. It impedes the accumulation of iodide in the thyroid , which results in the blocking of hormone production[18].

2.1.3. Toxicity of Perchlorate

Thyroid gland is the main target of perchlorate toxicity, perchlorate has been shown to partially inhibit the thyroids uptake of iodine.

Synthesis of thyroid hormone requires iodine that is the main building block. Thyroid hormone regulate certain functions of the body after they are released into the blood. Although not demonstrated in humans, but people exposed to excessive amounts of perchlorate for a long time may decrease the production of thyroid hormones.

Hypothyroidism is the medical name of the condition that the lower amounts of thyroid hormones in the blood may cause increasing in pituitary hormones that can lead increasing in the size of the thyroid gland[19].

Many normal body activities are affected by the lower hormone level, because thyroid hormones perform important functions in the body. At one time, perchlorate were given as a drug (more than 400 mg per day, which is many time higher than the doses that people receive from environmental exposure) because perchlorates where known to lower thyroid hormone levels. Some side effects may be seen in a small number of treated patients were skin rashes and vomiting .

Healthy volunteers that took 35mg for 2 weeks of perchlorate daily (equivalence to drinking 2 liters of water that contain 17 ppm of perchlorate every day) or 3mg daily for 6 months (drinking 2 liters of

water that contain 1.5 ppm) of perchlorate every day show signs of abnormal functioning of their thyroid gland [19-20].

By the way, in the study in Nevada found that when body uptake more than 34 mg of perchlorate daily, thyroid, liver, blood and kidney may be affected.

On the other hand, animal studies have shown that perchlorate can alter the thyroid gland in the new born animals. This has generally occurred when perchlorate also affected the thyroid of the mothers.

2.2. Industrial Wastewater in the Palestinian Territories

An inventory of national hazardous waste substances is the essential tool in the management of hazardous waste. No such inventory exists in the Occupied Palestinian Territories (OPT), this absence make it difficult to determine what types of waste are being disposed of or generated.

There are very few estimates of the amounts of hazardous waste generated in the (OPT), this means that OPT does not have adequate facilities for sewage and wastewater treatment and disposal.

In the West Bank, 4 million dollars is the cost of fireworks each year (i.e. fireworks contain ammonium perchlorate (NH_4ClO_4)), this means that the level of perchlorate in west bank is high.

2.3. Adsorption

Adsorption is an important physical phenomenon, which provides bases for understanding such processes as heterogeneous catalysis and chromatographic analysis.

Large number scientists have been working either on adsorption on liquids or gases on different adsorbents directly after discovering adsorption. The property possessed by modified chitosan-graphene of removing perchlorate ions from solutions has been reported and many observations have since been made showing that the modified polymer may be used in water filter production [22].

2.3.1. Adsorption phenomenon

Adsorption is a physical mechanism for organic and inorganic pollutants removal at the surface. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid-solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface.

The solute retained on the solid surface in adsorption process is called adsorbate, whereas, the solid on which it is retained is called an adsorbent.

This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from

that the bulk fluid phase forms the basis of separation by adsorption technology.

Adsorption may be defined as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by chemical and/or physical attraction [23]. Large surface area leads to high adsorption capacity and surface reactivity.

In a bulk material, all the bonds between atoms (covalent, ionic or metallic) are inside the material, so, at the surface, atoms are not wholly surrounded by other adsorbent atoms and therefore can attack the adsorbate.

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.

2.3.2. Adsorption Isotherm Models

The modeled adsorption isotherm describes the adsorption phenomenon at a constant temperature and pH which is an invaluable non-linear curve and the mathematical correlation which is depicted by the modeling analysis that is important for operational design and applicable practice of the adsorption systems[16].

There are many mathematical forms to describe the adsorption isotherm, some of which are based on a simplified physical description of adsorption

and desorption, while others are purely empirical and intended to correlate experimental data.

There are many different equilibrium models, Freundlich, Langmuir, Brunauer-Emmett-Teller, Redlich, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Hill, Flury-Huggins and Radke-Prausnitz isotherm, have been formulated in terms of three fundamental approaches. The first approach is kinetic consideration. Adsorption equilibrium is a dynamic equilibrium at which the adsorption and desorption rates are equal. Whereas, thermodynamics being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models and potential theory as the third approach, usually conveys the main idea in the generation of characteristic curve. However, we may derive the isotherm modeling in more than one approach through the difference in the physical interpretation of the model parameters[17].

2.3.2.1. Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of perchlorate between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

Based upon these assumptions, Langmuir represented by the following equation[28-31].

$$(C_e/Q_e)=(1/Q_m)C_e + 1/(Q_mK_L) \quad (2.1)$$

Where:

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

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

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

K_L = Langmuir isotherm constant (L/mg)

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation

$$R_L = 1/(1+K_L C_o) \quad (2.2)$$

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

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

2.3.2.2. Freundlich Model Isotherm

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. This model is defined by the following equation [28-31]:

$$Q_e = K_F C_e^{1/n} \quad (2.3)$$

The linear form of this equation can be written as:

$$\ln Q_e = (1/n) \ln C_e + \ln K_F \quad (2.4)$$

Where , K_F and n are Freundlich constants. K_F is a rough indicator of the adsorption capacity of the sorbent and n giving an indication of the favorable way of the adsorption process. The magnitude of the exponent, $1/n$, gives an indication of the adsorption favorability. If the value of $1/n$ is less than one this indicates a normal adsorption. If n is between one and ten, it indicates a favorable sorption process.

As the temperature increases, the constants K and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

2.3.2.3. Tempkin Model Isotherm

This isotherm contains a factor reflecting the adsorbent-adsorbate interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer decrease linearly with the coverage. The model is given by the following equation[28-31]:

$$Q_e = B \ln C_e + B \ln A \quad (2.5)$$

Where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature ($^{\circ}\text{K}$).

2.3.3 Adsorption Thermodynamics

We may determine adsorption thermodynamics using the coefficients of the thermodynamic equilibrium obtained at different temperatures and concentrations in order to verify possible adsorption mechanisms. ΔG (Gibbs free energy change) is a term of thermodynamic parameters that used to express the adsorption characteristics of the material, which can be calculated by the following equation :

$$\Delta G = -RT \ln K_d \quad (2.6)$$

Where K_d is the thermodynamic equilibrium constant ($L g^{-1}$). We know in thermodynamics, that Gibbs free energy (ΔG) is the difference between the adsorption enthalpy (ΔH) and adsorption entropy (ΔS) multiplied by the temperature.

Then, we can determine ΔH and ΔS according to equation:

$$\ln K_d = -(\Delta H/RT) + (\Delta S/R) \quad (2.7)$$

2.3.4. Adsorption Kinetics

There is very important issue which is the study of the adsorption kinetics because it gives many insights into the reaction mechanism and path. We may follow the adsorption rate through the study of the contact time up to 6 hours and compared to theoretical models. Pseudo first-order and second-order kinetic models were tested in this study where experimental data obtained for the different contact times were used [32].

Using the pseudo first-order equation (Lagergren equation)(Eq.2.8), the rate constant for the adsorption of adsorbate from the effluent on adsorbent may be determined :

$$\log (Q_e - Q_t) = \log Q_e - (K_1/2.303)t \quad (2.8)$$

Where Q_t is the amount of perchlorate ions adsorped at time (t) (mg/g), Q_e is the adsorption capacity of the adsorbent at equilibrium (mg/g) and K_1 is the first order rate constant (min.^{-1}).

On the other hand, the pseudo second order kinetics can be expressed in a linear form as integrated second order rate law:

$$t/ Q_t = (1/ Q_e)t + (1/K_2 Q_e^2) \quad (2.9)$$

Where K_2 is the constant of the pseudo second order ($\text{g mg}^{-1} \text{min}^{-1}$). If the reaction was pseudo second order, this means that the adsorption depends on the adsorbate and the adsorbent and involves chemisorption process in addition to physisorption. The chemisorption might be the rate limiting step where valence forces are involved via electrons sharing or exchange between the adsorbate and the adsorbent [33].

2.3.5. Types of Adsorbents

There are many different types of adsorbents are classified into synthetic adsorbents and natural adsorbents. Synthetic adsorbents are adsorbents prepared from agricultural products and wastes, house hold wastes, industrial wastes, sewage sludge and polymeric adsorbents. The second type which is natural adsorbent 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 [14].

2.3.6. Adsorption as an effective method for removing perchlorate ions from wastewater.

The big challenge to remove perchlorate ions from wastewater is its high solubility and chemical stability. There are many technologies available for perchlorate contaminated water remediation such as ion-exchange, adsorption, biological treatment and chemical/catalytic reduction.

Adsorption is the most suitable one comparing with other treatment methods because of its advantages of low cost, high treatment efficiency and easy operation.

As the most common adsorbent, the activated carbon is used to remove perchlorate ions from wastewater. But, in order to increase the adsorption capacity it usually needs to be modified by cationic surfactants[11].

Recently, chitosan [Fig. 2.2] has been chosen as an effective bioadsorbent for the removal or recovery of hazardous proteins, dyes and heavy metals due to many properties such as nontoxicity, good biodegradability, excellent chemical resistance and good mechanical property [10].

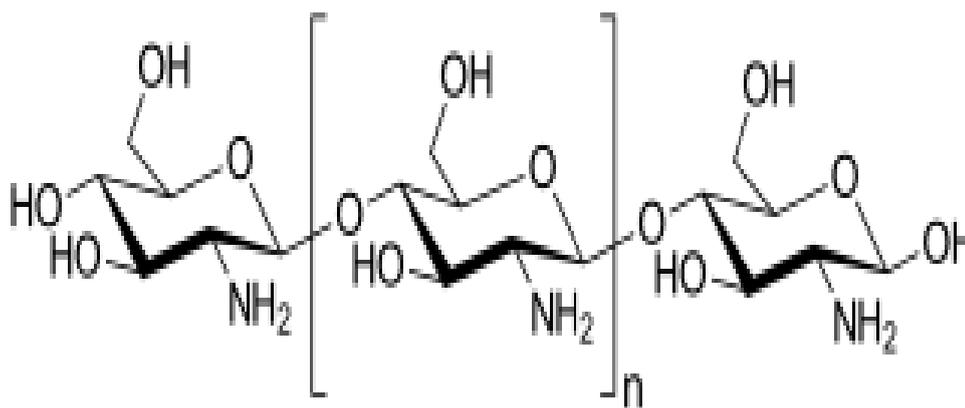


Figure 2.2: Molecular structure scheme of Chitosan.

The protonation of amino group in chitosan easy to occur because of its cationic behavior in acidic media. This protonation exhibit high affinity with perchlorate ions in wastewater.

On the other hand, there is a problem of dissolved chitosan which is difficult to separate from solution after adsorption of the contaminant and needs modification or separation process. To avert this problem related to the ease of separation and regeneration of chitosan sorbents, considerable attention has been focused on magnetic adsorbents in recent years.

The main advantages of magnetic composites are high efficiency even in dilute solution, fast adsorption rate , there micrometer size and stable structure , easily recovering using an external magnetic field and their ability to be regenerated easily.

Chitosan was chosen because it contains many amino (-NH₂) and hydroxyl (-OH) functional groups, that are able to interact with iron. Chitosan can also be modified easily by chemical /physical processes or react with other polymers to prepare chitosan derivatives or form new composites[14-16].

Graphene is an allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is the basic structural element of many other allotropes of carbon, such as graphite, charcoal, carbon nanotube and fullerenes. [Fig. 2.3].



Figure 2.3: Molecular structure scheme of Graphene.

Graphene is nontoxic, good biodegradable and excellent chemical/mechanical properties. Chitosan blended with graphene exhibits good chemical/mechanical properties because of the specific interactions between chitosan and graphene in the blend through hydrophobic side chain aggregation.

2.4. Methodology of preparing Cross-Linked Chitosan / Graphene Particles

As we said that chitosan and graphene will be modified separately before making cross linking as Fig. 2.4 .

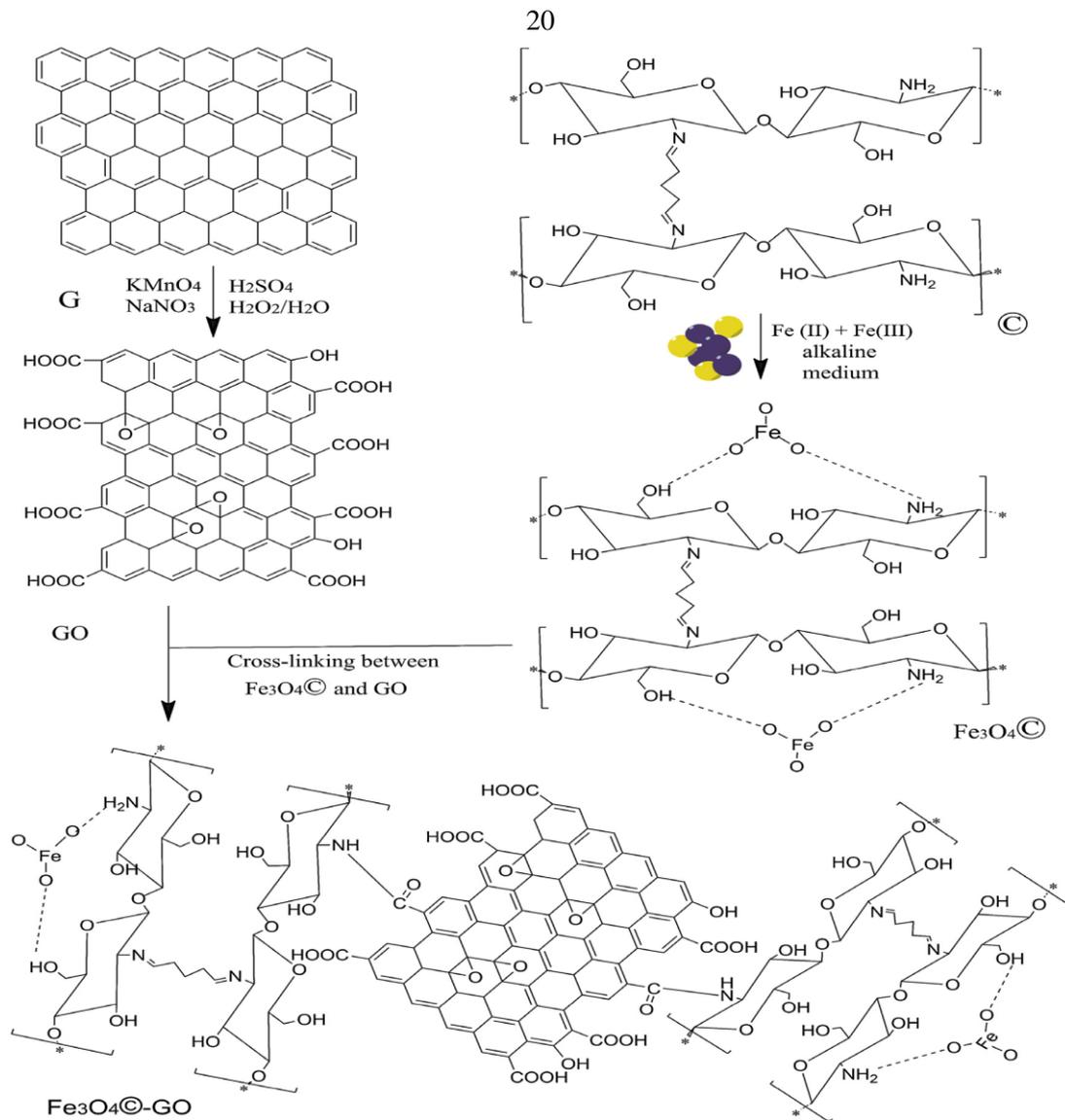


Figure 2.4: Methodology scheme of preparation of CM/GO Bs.

Modifying chitosan and graphene is made by two separately routs, modifying chitosan starts by adding Fe₂O₃ and FeO in alkaline media.

On the other hand, graphene oxidized by adding potassium permanganate (KMnO₄) with sodium nitrite (NaNO₂) and sulfuric acid (H₂SO₄) with hydrogen peroxide (H₂O₂) in water (H₂O).

After that, cross-linking between modified graphene and modified chitosan will be occurred to produce new polymer product (adsorbent) that will be used to remove perchlorate ions from wastewater.

Chapter Three

Experimental Work

3.1. Chemicals and Materials

Fe₃O₄ particles (purity > 99.5% , 20 nm spherical particles), Chitosan powder, Natural graphite, Sulfuric acid (H₂SO₄) (98%) and potassium permanganate (KMnO₄) were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂), sodium nitrate (NaNO₃), tetraethylorthosilicate (TEOS) (Si(OEt)₄) and acetic acid (C₂H₄O₂) (analytical grade) were purchased from Merk-Germany.

3.2. Preparation of Graphene Oxide

In 500 ml beaker, 2 gram of natural graphite powder and 1 gram of (NaNO₃) with 46 ml of (H₂SO₄) were mixed under magnetic stirring for 20 minutes at 25°C. 6 gram of (KMnO₄) were added to the mixture at 20 °C. After 5 minutes of stirring, the mixture was heated to 35 °C for half an hour, then 92 ml of distilled water was added to the mixture while stirring, then, 80 ml of hot water (60 °C) was added to the mixture with (H₂O₂) (3% wt./wt.).

H₂O₂ was added to remove any remaining trace of (KMnO₄) until the absence of bubbles in the solution. In the next step, centrifugation of the mixture at 6500 rpm for 45 minutes was occurred.

To neutralize the pH of the material that was obtained after centrifugation, sodium hydroxide (NaOH) was added again. Finally, the resultant product

was obtained and the final product which is graphene oxide that is dark brown powder.

3.3. Preparation of Cross-linked Magnetic Chitosan With Graphene Oxide

0.1 gram of chitosan was dissolved in 15 ml (CH_3COOH) in 250 ml beaker and the mixture was kept overnight, after that, 1.5 grams of (Fe_3O_4) was added to the mixture. The above mixture was aggitated for 2 hours at 60 °C.

In 5 ml ethanol, 0.05 ml of tetraethylorthosilicate (TEOS) was dissolved and then added drop wise to the above mixture.

Separately, 0.1 gram of graphene oxide was dispersed in 200 ml distilled water, then the mixture was placed in ultrasonic bath in a 400-ml beaker for 1 hour.

Now, both magnetic chitosan solution and graphene oxide dispersion were mixed together at 60 °C. the mixture was stirred for 4 hours until the mixture became thick viscous liquid, then, the mixed solution was placed on plastic plate and dried, the fabricated sheets that were produced have a thickness of about 0.16 nm. See Fig. 3.1 below that show all steps of the preparation.

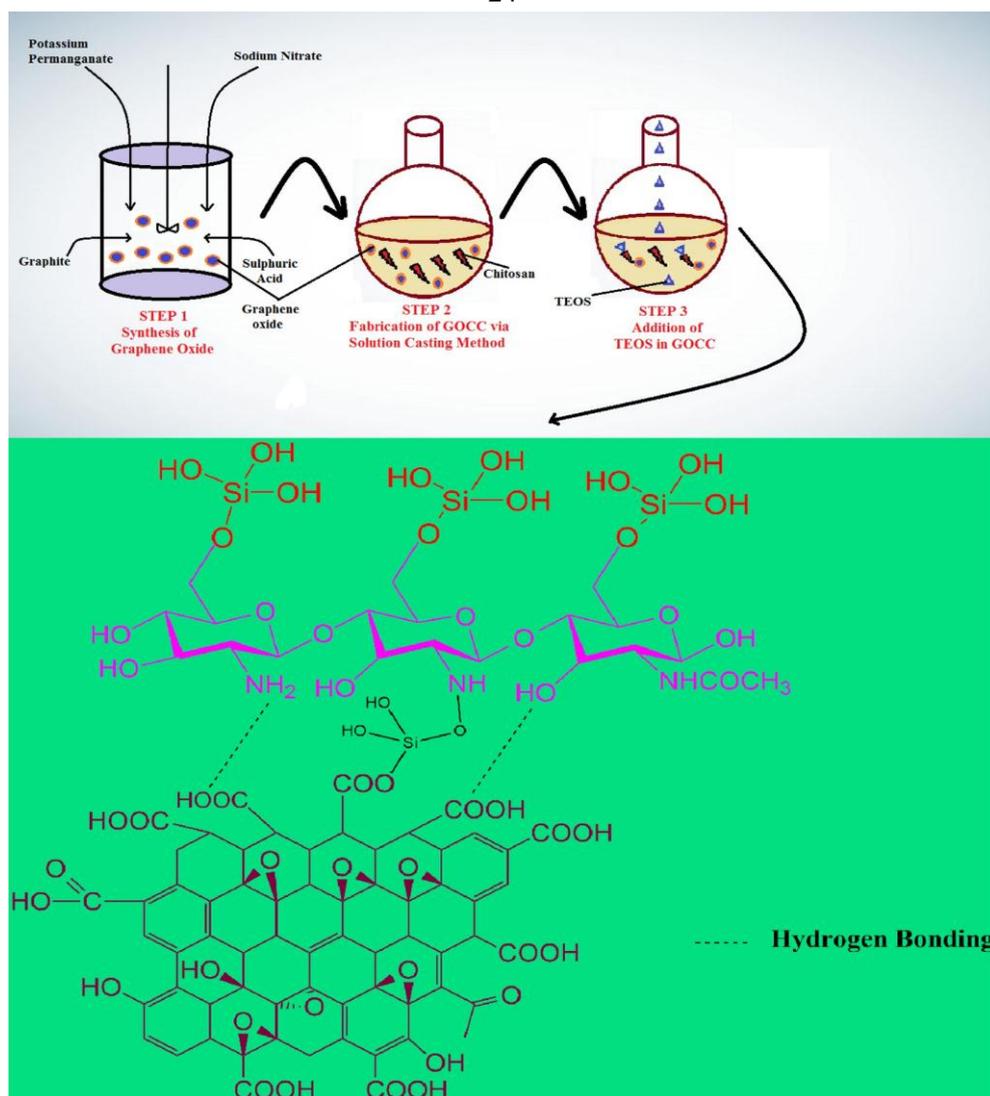


Figure 3.1: Preparation of CM/GO Bs procedure

3.4. Sample characterization

The morphologies of the surface of Cross-linked magnetic chitosan / graphene oxide (CM/GO) were studied by a cold field transmission electron microscope (Inspect F50, Netherlands). To determine the percentage composition of the elements in the complex, EDS(INCA ENERGY 300, England), that used to identify elements from ${}^4\text{Be}$ to ${}_{92}\text{U}$, was used. A vibrating sample magnetometer (Model 155, USA) was used. To determine the magnetic properties of CM/GO Bs at RT, A Fourier

transform infrared spectrometry (Nicolet 6700, Thermo Fisher) was used to obtain (FTIR) spectra. All analysis were occurred at University of Castilla-La Mancha

3.5. Batch Adsorption Studies

3.5.1. pH Effect and Co-existing Anions

The pH effect on adsorption was detected by make PH varied from 2 to 12 using HCl and NaOH solutions. In 50 ml perchlorate solution (15ppm), 1 gram CM/GO Bs is added. After that, the mixture was aggitated at 200 rpm for 4 hours.

The effects of Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- anions, on perchlorate adsorption were determined. The experiments of the study of the effect of co-existing anions were made with the same procedure as the effect of pH described above but with changing the pH.

3.5.2. Effect of Contact Time

To study the kinetics of perchlorate adsorption, many various concentrations (5, 10, 15 and 20 ppm) were taken with constant 1 g/L adsorbent dosage, after that and by shaker, mixtures were shaken at 200 rpm at 303 K.

3.5.3. Effect of temperature

Aliquots of 1 gram each of dry CM/GO Bs were transferred into flasks each contained 50 ml perchlorate solution. The concentration of perchlorate

ranging from 1 to 200 ppm. Each flask was agitated on a shaker at 180 rpm for 4 hours at (303, 313, and 323) K.

After that and when the equilibrium of the adsorption was reached, the solution was filtered and the concentration of perchlorate that remained in the solution was determined. Each experiment was repeated 3 times .

The amount perchlorate that was adsorbed (q_e , mg/g) was calculated by the equation[35] :

$$q_e = V(C_o - C_e)/W \quad (3.1)$$

Where V is the volume of the solution (L), C_o is initial perchlorate concentration (ppm), C_e is perchlorate concentration at equilibrium (ppm), and W is the adsorbent mass (g).

3.5.4. Regeneration process

0.1 gram of CM/GO Bs was added to 50 ml of 10 mg/l perchlorate solution and shaken for 4 hours at 200 rpm. After that and when the equilibrium was reached, the adsorbent was collected by filtration.

The adsorbent was transferred into a flask contained 8 ml of 0.1 % solution of NaCl and stirred at 298 k for one hour. The adsorbent was filtered and collected.

To check the ability of regeneration of the adsorbents, many cycles of re-adsorption/desorption were tested.

3.5.5 Analytical Methods

To determine the perchlorate concentration, ion chromatography (compact IC, Metrohm) was used. The equipment's of IC system were a 250 microliter sample loop, a group of 4x250 mm chromatogram (Metroep A sup 7), a 4 mm suppressor, guard columns, an auto-sampler and electrical conductivity detector in the University of Castilla La-Mancha in Spain.

To detect perchlorate, the eluent that was used is a mixture of 10 Mm (Na_2CO_3) and 45% acetonitrile (v/v) at a flow rate of 0.7 ml/minute. The sample running time was 22 minutes. The perchlorate detection limit was approximately 15 $\mu\text{g/L}$.

Chapter Four

Results and Discussion

4.1: Material Characterization

4.1.1: FTIR Analysis

During modification and process of adsorption, there are many changes in functional groups, so, to show the changes in these functional groups, FTIR spectra were used. In order to note the changing through the modification and adsorption process we took CM/GO Bs loaded with ClO_4^- and then, we will discuss it. The FTIR spectrum for CM/GO Bs is shown in fig.4.1, a strong band from 1400 to 1200 cm^{-1} means the stretching vibrations of epoxide functional groups. The band at 1625 cm^{-1} represents the stretching of $\text{C}=\text{C}$, on the other hand, and at 1720 cm^{-1} there was a good band, that means there are carbonyl groups.

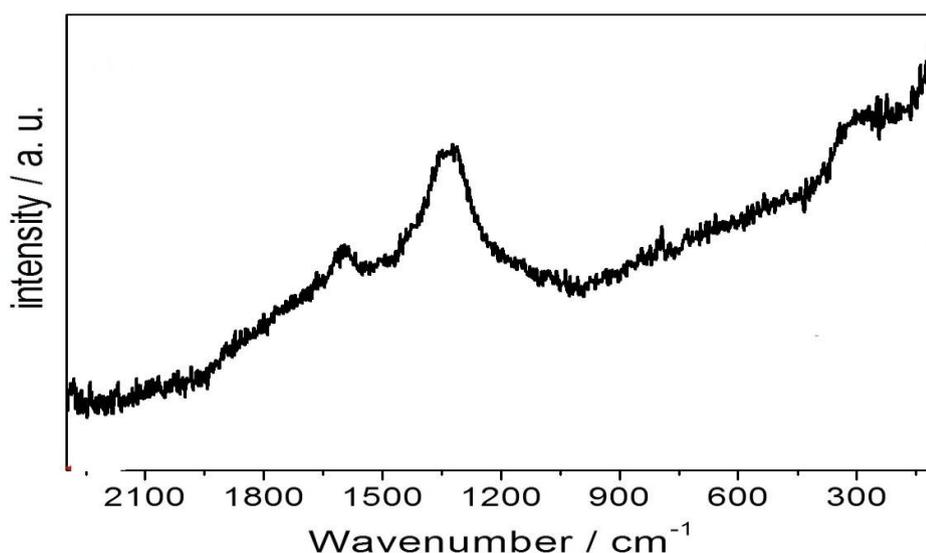


Figure 4.1: FTIR characterization of CM/GO Bs

4.1.2: TEM Analysis

Fig.4.2, shows the TEM micrographs of the complex at the University of Castilla La-Mancha in Spain. It can be seen that CM/GO Bs has a square shape and porous internal structure. On the other hand, the shape of the surface is irregular, that's irregularity in the shape of the surface helps to improve the capability of its adsorption. By optical microscopy, the particle size and size distribution was measured. The particle size was 40-160 nm due to the existing of nano Fe_3O_4 as a frame work. The CM/GO polymer. The average diameter of protonated chitosan was 1.5 μm in last study [27], compared with our complex CM/GO give a larger spectra and lower size surface area that help in the activity of the reaction.

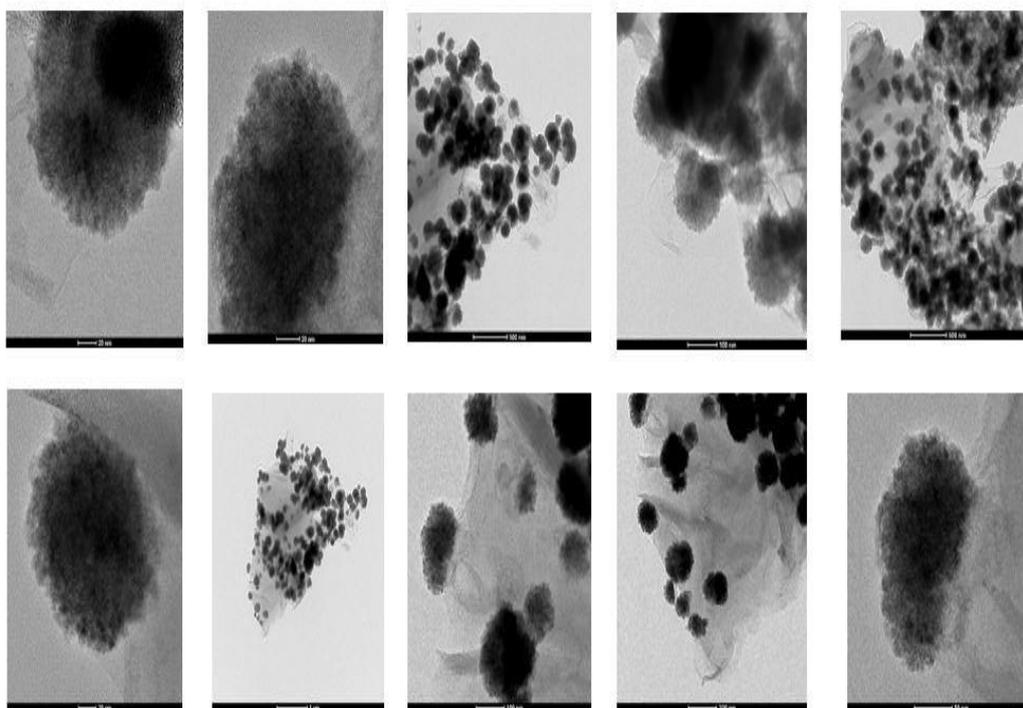


Figure 4.2: TEM analysis of CM/GO Bs complex.

4.1.3: VSM Analysis

Because chitosan was magnetite, we have to measure the properties of the product, this was made by VSM. Fig.4.3(a) shows the hysteresis loops of CM/GO Bs and naked Fe_3O_4 between ± 21.80 Oe of 300 K. The magnetization of CM/GO was about 20.4 emu/g, while naked Fe_3O_4 was about 90.2. The lower in the magnitude of the magnetization between naked Fe_3O_4 and CM/GO polymer is due to interaction of chitosan and graphene. The response to an external magnetic field of the complex was rapid. On the other hand, and through the Fig.4.3(b), CM/GO Bs complex may be attracted quickly to the glass wall of the bottle. Thus good magnetize properties of CM/GO Bs complex may facilitate the magnetize process.

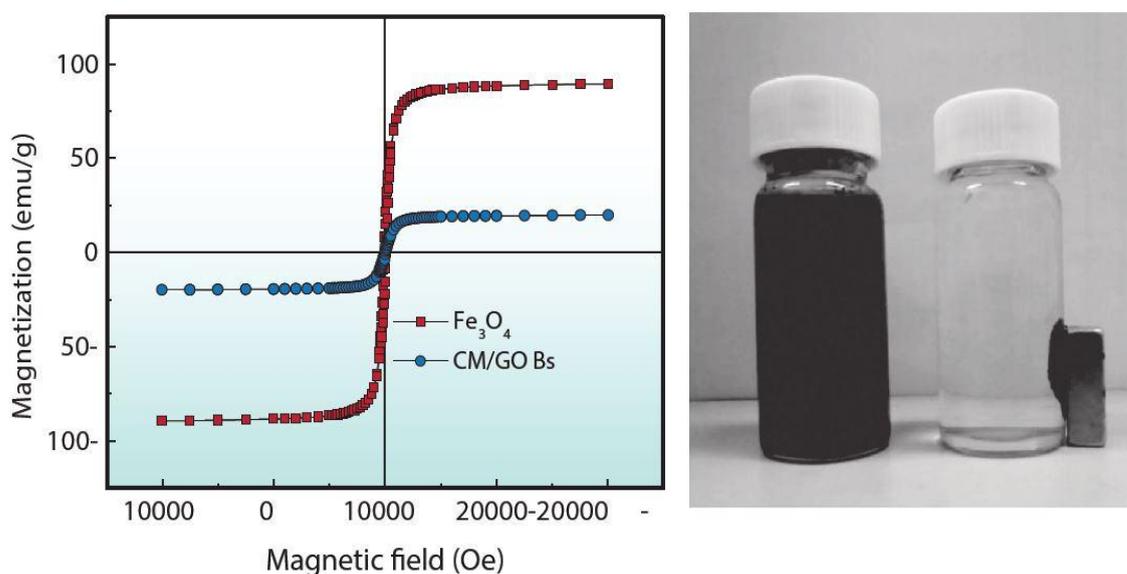


Figure 4.3: (a) VSM magnetization curves. (b) magnetic recovery of CM/GO Bs

4.2: Effect of pH on Perchlorate Adsorption.

The effect of pH was studied in the range 2 to 12. The obtained results are presented in Fig. 4.4. maximum adsorption of perchlorate by CM/GO Bs was obtained in the pH range 5-9.

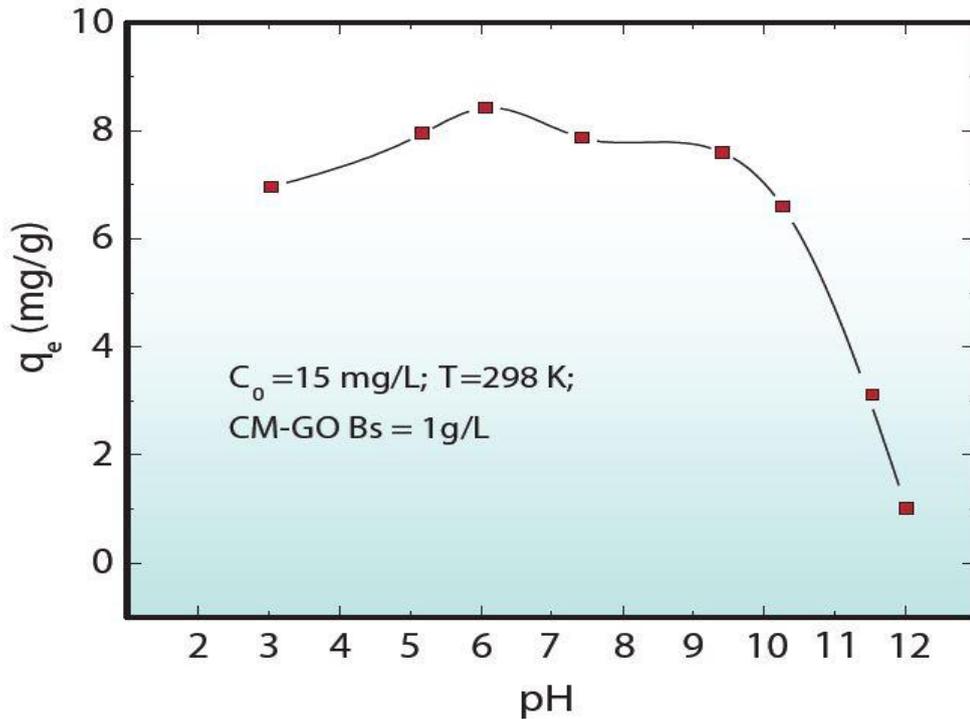


Figure 4.4: Effects of pH on the adsorption of perchlorate by CM/GO Bs complex

Due to the competition that is excessive chloride ions within the pH adjustment, when the pH dropped to 2.0, the capacity of adsorption of the adsorbent declined to 7.02 mg/g. The capacity of the adsorption declined strongly from 7.8mg/g to 1.6 mg/g while the pH increases from 10.0 to 11.5. That is because of alkaline condition that causes a negative change of the surface of the adsorbent. Besides, it creates weak interaction between perchlorate and adsorbent in comparison with protonated cross-linked chitosan that has a range of pH from 4.0 to 10 that can be applied. CM/GO Bs may adsorb over-

widened range of pH from (4-10), this property makes it useful for its adsorption process.

4.3: Effect of Co-existing Anions.

Polluted water usually contains many anions such as ClO_4^- , NO_3^- , Cl^- , SO_4^{2-} and HCO_3^- . The presence of other anions along with perchlorate made the other ions to compete with perchlorate on adsorption on the adsorbent, which caused a decreasing in the capacity adsorption of perchlorate [9].

As shown in Fig.4.5 that studied the consequences of these anions and plotted, this increase in concentration leads to a decline in the adsorption of perchlorate. In addition, SO_4^{2-} anion has the greatest impact on perchlorate that removed. As an increasing in the concentration of SO_4^{2-} from 0 to 28 mg/L, the capacity of perchlorate adsorption by CM/GO Bs complex sharply declined from 7.5 mg/g to 3.3 mg/g. Finally, the inhibitory effects of these anions on perchlorate adsorption by CM/GO was summarized as : $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$, which agrees with last studies [8].

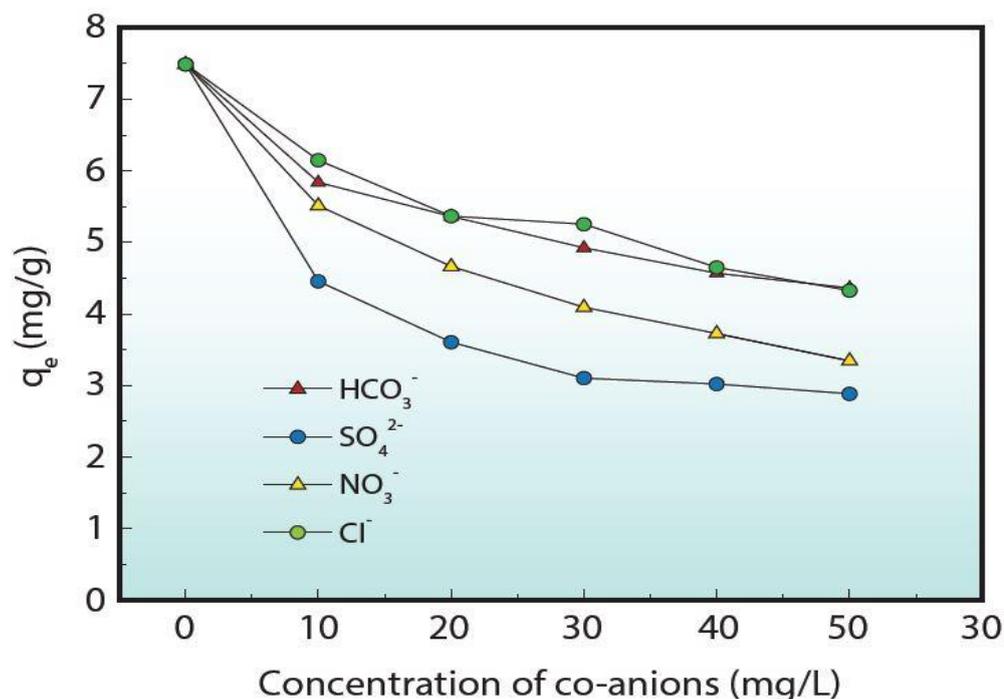


Figure 4.5: Effect of co-existing anions on perchlorate adsorption onto CM/GO Bs.

4.4. Effect of Contact Time

Effect of contact time is very important in treatment of wastewater. To obtain the most suitable contact time of the reaction, many different initial concentration (5, 10, 15 and 20 mg/L) are studied with adjusting other conditions such as dosage of the adsorbent which was 1 g/L, pH which was 6 and temperature that was 303 K. Fig 4.6 shows the effect of contact time on the capacity of perchlorate adsorption.

The adsorption of perchlorate was quick at the first 25 minutes, then the adsorption rate declined and the equilibrium was achieved within 35 minutes. When the initial concentration of the perchlorate was small, the adsorption reached equilibrium within 25 minutes. The residual content of the perchlorate was 0.014 mg/L which agrees with the Drinking Water

Health Advisory level of 15 mg/L that was studied by the United States Environmental Protection Agency in 2008[8].

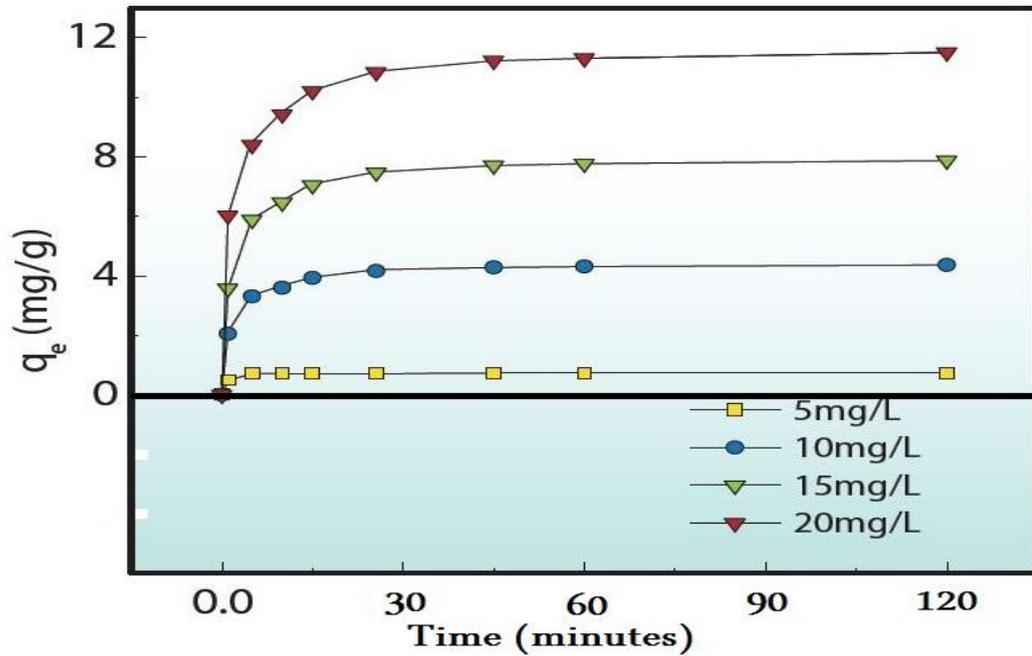


Figure 4.6: Effect of contact time on perchlorate adsorption by CM/GO Bs complex

It can be concluded that the rate of the adsorption of perchlorate by the complex is quick and removing of perchlorate by the complex was efficient at low concentrations.

4.5: Adsorption Kinetics

To obtain the mechanism of the reaction and the rate determining step, results that shown in Fig.4.6 must be analyzed, that's occurred by studding three models of kinetics. We used the pseudo-first-and-second-order models, and described the equations of these models as [32]:

$$1/q_t = k_1/(q_e t) + 1/q_e \quad (4.1)$$

$$t/q_t = 1/(k_2q_e^2) + (1/q_e)t \quad (4.2)$$

while k_1 means the constant of the adsorption rate of the pseudo-first-order (h^{-1}); k_2 stands for the constant of the adsorption rate of the pseudo-second-order ($(g/mg)h$); q_e represents the amount of ion adsorption at equilibrium (mg/g) and q_t shows the amount of ion adsorption amount whenever (mg/g). By the slope of the linear equation, the values of k_1 and k_2 can be calculated. In table 4.1, the rate constants and correlation coefficient (R^2) of the models of kinetic are lodged.

Table 4.1: correlation coefficients and constants of kinetic model of perchlorate adsorption onto CM/GO Bs .

pseudo-											
first-order			second-order			Intra-particle diffusion					
C_0 mg/ L	K_1 h^{-1}	R^2	K_2 g/mgh	R^2	$K_{p,1}$ $\frac{g}{mgh^{1/2}}$	R^2	$K_{p,2}$ $\frac{g}{mgh^{1/2}}$	R^2	$K_{p,3}$ $\frac{g}{mgh^{1/2}}$	R^2	
5	0.991	0.635	269.550	0.999	1.35	0.789	-	-	-	-	
10	0.446	0.607	12.919	0.999	18.60	0.882	0.496	0.971	0.006	0.937	
15	0.448	0.641	8.017	0.999	37.96	0.882	1.177	0.946	0.025	0.973	
20	0.392	0.693	3.780	0.999	45.81	0.932	1.076	0.840	0.055	0.979	

From the data listed in the table 4.1, the correlation coefficient of the pseudo-second-order models were approx. 0.999 at the latter concentrations. This proves that the pseudo-second-order model reflects the experiment data accurately. While the correlation coefficient of the

pseudo-second-order models gave low values between 0.607 and 0.693 which is not appropriate to interact the adsorption mechanism.

Because the pseudo-second-order model is suitable for the mechanism, then the rate determining step may be chemisorption including electron participating or replacing between adsorbent and adsorbate [33] so, chemisorption may be the rate-determining step in the adsorption mechanism, and the obtained result from mass transfer in solution was restricted [34].

To examine the diffusion mechanism, the intra-particle diffusion model was presented. The equation of the model is given as [35]

$$q_t = k_{pi}t^{1/2} + c_i \quad (4.3)$$

Where k_{pi} ($i=1-3$) means the constant of the rate of the intra-particle diffusion ($\text{mg/g h}^{1/2}$) and (i) stands for the number of the levels of the particle such as k_{p1} is the constant in the first level of the external surface adsorption and $k_{p,3}$ is the constant of the rate in the third final equilibrium layer. The constants of the rate are shown in table 4.1.

Within 25 minutes, the adsorption of the external layer was completed. While increasing in initial concentration, the $k_{p,1}$ increased significantly because the increasing in the concentration of gradient force [36]. The rate determining step of adsorption isn't intra-particle diffusion [37.38] because the linearity of the second and the third layers couldn't pass through the origin.

Moreover, $k_{p,2}$ and $k_{p,3}$ are less than $k_{p,1}$ which means that the rate determining step is the external surface adsorption.

4.6: Adsorption Isotherm

The adsorption affinity and surface properties can be expressed by adsorption equilibrium isotherm through certain constants [39]. These isotherms were studied at 303 , 313 and 323 k. To describe the adsorption process, we used Langmuir, Freundlich and Temkin models. The linear relations of these models are given as [37,40] :

$$C_e/q_e = 1/(Q_0b) + C_e/Q_0 \quad (4.4)$$

$$\text{Log } q_e = \text{log } k_f + 1/n \text{ log } C_e \quad (4.5)$$

$$q_e = B \ln A + B \ln C_e \quad (4.6)$$

Where C_e represents the concentration of perchlorate at equilibrium (ppm) , q_e means the amount of perchlorate that adsorbed at equilibrium (mg/g) , Q_0 stands for the amount of adsorbed at complete coverage (mg/g) , b is Langmuir constant reflecting the energy adsorption in (L/mg). K_f represents the constant of Freundlich that relates to the capacity of adsorption and $1/n$ means the intensity of the adsorption.

A is the tempkin constant that represent the maximum energy of bindings and B is the Tempkin constant that represents the changing in the heat of the adsorption.

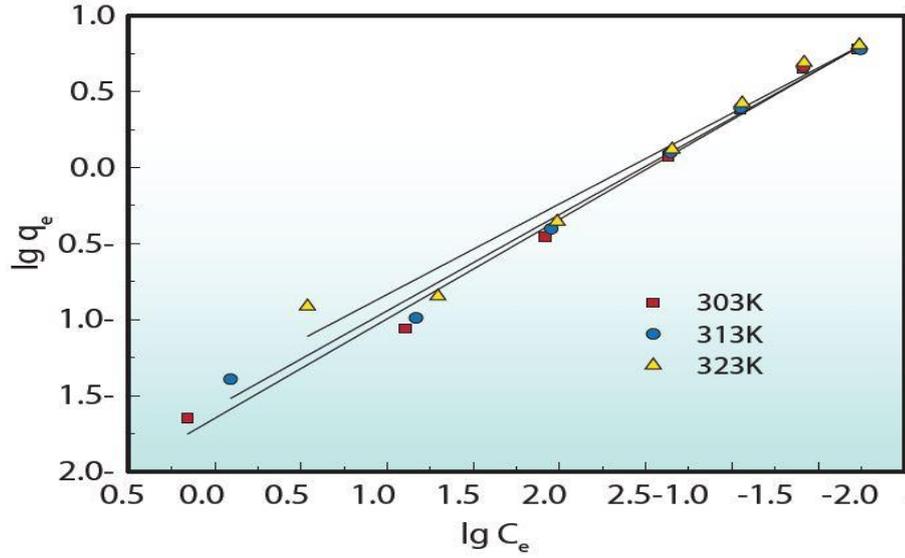


Figure 4.7: Freundlich isotherm plot for perchlorate adsorption onto CM/GO Bs

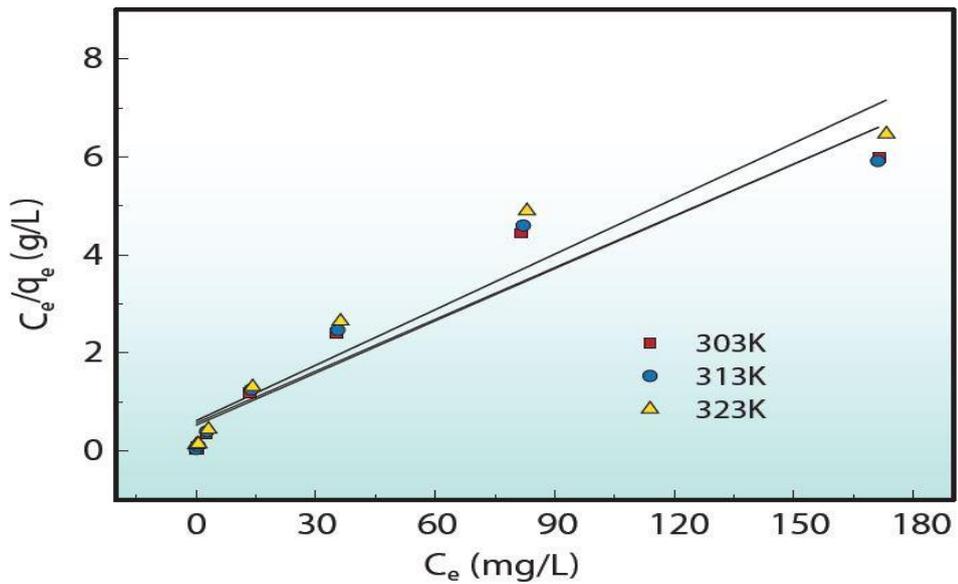


Figure 4.8: Langmuir isotherm plot for perchlorate adsorption onto CM/GO Bs.

Figs.4.7and 4.8 show the equilibrium data for perchlorate adsorption in Freundlich and Langmuir models. From the linear equations of the models , their constants may be determined from the slops and. In table 4.2, the

correlation coefficient (R^2) and theoretical parameters of the models of adsorption isotherm are given.

Table 4.2: parameters and correlation coefficients of the adsorption isotherm models of perchlorate adsorption onto CM/GO Bs.

Langmuir isotherm				Freundlich isotherm			Tempkin isotherm			
T(K)	Q_0 mg/g	B L/mg	R^2	R_L	K_F	1/n	R^2	A	B L/g	R^2
303	28.15 3	0.068	0.913	0.936- 0.068	0.215	0.654	0.991	18.70 7	2.654	0.791
313	28.35 2	0.062	0.897	0.941- 0.074	0.232	0.633	0.985	11.76 6	2.828	0.788
323	26.45 5	0.061	0.910	0.941- 0.075	0.290	0.595	0.962	5.922	3.013	0.844

Through the correlation coefficients (R^2) especially in Langmuir and Freundlich isotherms that have values of (R^2) more than 0.90, while if we look to the value of R^2 in Tempkin that is less than 0.85. In general, and in a previous studies, if Langmuir model data fitted the experiment well this means that the surface is homogenous one and consists of one layer (mono layer) and the process of adsorption is physisorption, on the other hand, if the Freundlich model data fitted well, this means that the surface is heterogeneous and the process will be chemisorption[39].

Through the above results, the process of the adsorption was a complex of homogenous and heterogeneous, whereas the effect of adsorbent interactions on the adsorption was finite. so, both physisorption and chemisorption are important in the process of adsorption.

If we made a comparison between heavy metal adsorption by magnetic adsorbent and perchlorate adsorption by our complex (CM/GO Bs), big difference will be noted in which of the most of the adsorption agreed with chemistry and the main mechanism of perchlorate removal was Langmuir model [13]. In the Freundlich isotherm model, $1/n$ values were ranged from 0.1 to 1, that proves the mechanism of the adsorption was favorable by the model of Langmuir isotherm, the temperature in the adsorption process was insignificant due to the slightly changing in the optimum adsorption capacity with increasing in temperature.

Dimensionless constant term that is the essential property of the Langmuir isotherm can be determined through eq. 4.7. The equilibrium parameter R_L , which is determined as follows [38] :

$$R_L = 1/(1+bC_e) \quad (4.7)$$

Where C_e represents the initial concentration of perchlorate (ppm) and b means the constant of Langmuir isotherm (L/mg). The R_L values indicate the irreversibility, linearity and favorability of the adsorption such as if ($R_L=0$) this means that the adsorption is irreversible, if (R_L larger than 0 and less than 1), this means that the adsorption is favorable or if ($R_L=1$) this means that the adsorption is linear or unfavorable ($R_L>1$). All values of R_L that given in table 4.2 above lead to an impact that the adsorption of perchlorate on CM/GO Bs was favorable at all temperatures that were studied. Through the results, as the initial concentration of perchlorate

increase, the R_L values decrease due to the increasing in concentration of driving force ingredient with increase in initial concentration [11].

4.7: Adsorption Thermodynamics

One of the aims in this work is to determine the parameters of thermodynamics of the adsorption of the perchlorate on CM/GO Bs, the experiments of the adsorption were carried out at 303, 313, 323k. The initial concentration of perchlorate was adjusted at 15mg/L. In order to determine the free energy of the adsorption (ΔG), the equation of the Gibbs free energy is used [41,4]:

$$\Delta G = -RT \ln k_c \quad (4.8)$$

Where R represents the gas constant (8.314 j/mol k), T stands for temperature of the adsorption in Kelvin, and k_c means the constant of the adsorption at equilibrium in (L/g). According to the equation (4.9), The k_c values of equilibrium at any temperature can be calculated as follows:

$$K_c = q_e / C_e \quad (4.9)$$

Where q_e represents the amount of adsorption at equilibrium in (mg/g) and C_e stands for the concentration of perchlorate at equilibrium in (mg/L).

By plotting in $\ln k_c$ vs $1/T$ according to the following equation:

$$\ln k_c = \Delta S/R - \Delta H/RT \quad (4.10)$$

The entropy of adsorption (ΔS) and standard enthalpy (ΔH) can be determined.

The negative value of the slope multiplied (R) represents (ΔH) and the intercept multiplied (R) represents (ΔS) of the adsorption of perchlorate (fig.4.9)

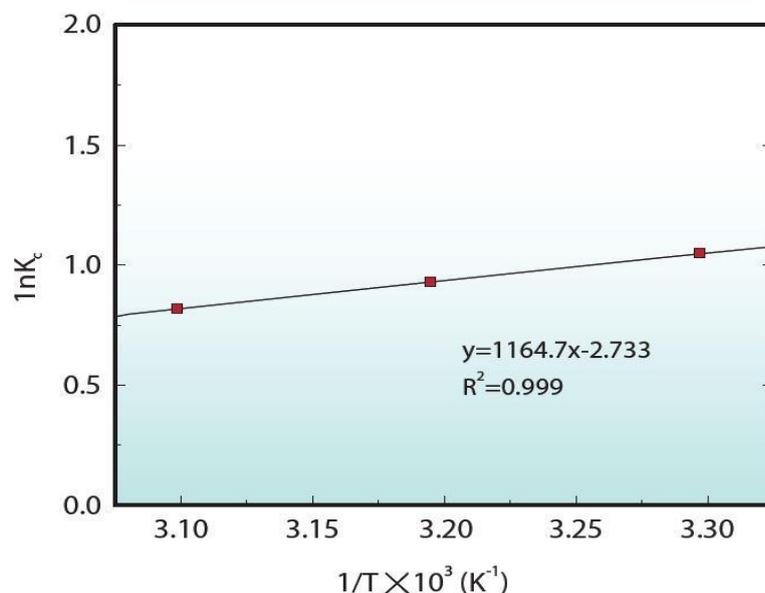


Figure 4.9: Thermodynamic model for perchlorate adsorption onto CM/GO Bs

The three thermodynamics parameters (ΔG and ΔH) are listed in table 4.3. Through the results in the table, the entropy is negative. This means that the random state at the solid/solution interface decreasing. Through the data that are given in table 4.3, the negative values of Gibbs standard free energy at many various temperatures leads the adsorption of perchlorate onto CM/GO Bs process spontaneous. So, the effect of temperature on the process of adsorption was insignificant, because there is no energy input required from the outside of the system of the change in standard free energy that was not affected with increasing temperature. In addition, and due to the negative values of enthalpy, the process of the adsorption was exothermic one. The values of enthalpy were less than 40 kg/mol. This

indicates that the adsorption is physisorption [21]. In addition, theoretically, the changes in energy for physisorption are ranged from 0 to -20 kJ/mol, while those for chemisorption are ranged from -80 to -400 kJ/mol.

Table 4.3: parameters of thermodynamic for adsorption of perchlorate onto CM/GO Bs

T (K)	K_c	G_0 (KJ/mol)	H_0 (KJ/mol)	S_0 J/mol K
303	2.852	-2.683	-9.773	-22.811
313	2.739	-2.455	-9.773	-22.811
323	2.264	-2.231	-9.773	-22.811

The free energy of adsorption ranged from 0 to -2.231 to -2.683 kJ/mol for CM/GO Bs. This suggests that the adsorption likely resulted because of physical sorption. In general, There are different types of interaction according to how pollutants interact with composites of magnetic chitosan including ion exchange, chemical bonding, hydrogen bonding and physisorption [13]. The most important driving force In this study was electrostatic interaction between anion that was perchlorate and cations which were (amin groups)of the adsorbent.

In resultant, according to data that determined in the study of the adsorption kinetics tells us that the adsorption was pseudo-second-order that suggests a chemisorption, while according to adsorption thermodynamics and isotherms, the process was physisorption, such that anions bind to the CM/GO Bs surface by intermolecular interactions [43]. In resultant, the adsorption of perchlorate on CM/GO Bs is a complex physical and chemical adsorption process.

4.8: Regeneration ability

Regeneration of the complex is very important to decrease the costs , to be used another time and to be recycled of useful material, the used adsorbent was eluted using 0.1% sodium chloride.

To check the ability of regeneration of the adsorbents, many cycles of re-adsorption/desorption will be tested, so, in this study , five cycles were tested with adjusted conditions, and the results are shown in fig.4.10.

The capability of the adsorption of the regeneration adsorbent decreased a few amount after five cycles. On the other hand, the capacity of the adsorption changed from 7.8 to 6.2 mg/g due to loss of adsorbent and decrease of the reaction sites on adsorbents.

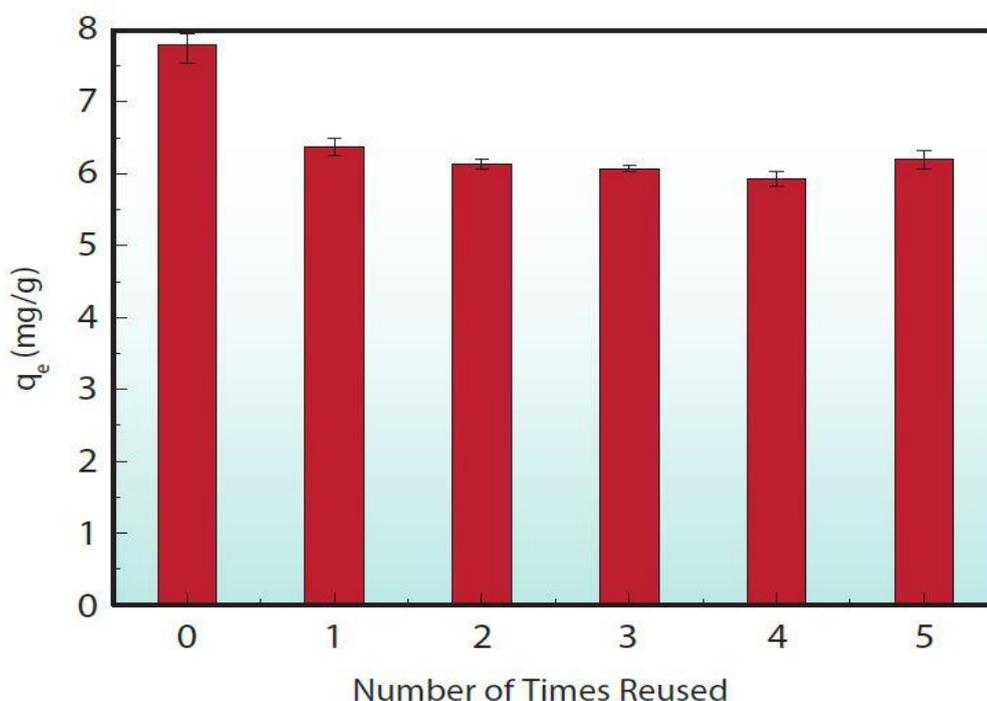


Figure 4.10: Capacity of perchlorate adsorption onto CM/GO Bs with five re-adsorption/desorption cycles

Conclusion

In this study, CM/GO Bs were synthesized and tested for perchlorate removal from wastewater. The magnetization of the CM/GO Bs complex was about 21.8 emu/g, that was sufficient for its high recovery using an external magnetic field .

The CM/GO Bs complex could adsorb perchlorate efficiently at a wider range of pH than raw chitosan which was from 4 to 10.

Co-existing anions, especially SO_4^{2-} , will affect the perchlorate adsorption onto CM/GO Bs.

The rate of adsorption was rapid and almost reach equilibrium within 35 minutes. The adsorption data fitted the pseudo-second-order model. In addition, Langmuir and Freundlich isotherms followed the equilibrium data well. The enthalpy and Gibbs standard free energy showed that the adsorption process was exothermic and spontaneous .

Perchlorate adsorption on CM/GO Bs was a complex chemical and physical adsorption process. The exhausted adsorbent could be regenerated efficiently using NaCl eluent.

CM/GO Bs complex exhibits a good efficiency for removal of perchlorate as an environmentally friendly adsorbent, over a wide pH range and with good regeneration and recovery ability.

Suggestions for Future Work

- Moreover, realization is needed to study the mechanism of removing perchlorate using this adsorbent.
- More study on the economic feasibility of the modified graphene oxide should be carried out .
- Studying the effect of presence of metal ions in the wastewater on perchlorate adsorption should be carried out.
- studying the success of the complex in water filters as a new step should be carried done.

References

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اعداد

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اشراف

أ.د. شحدة جودة

قدّمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء من كلية
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2018

ب

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الملخص

تعدّ البيركلورات واحدة من الملوثات التي تم الكشف عنها في المياه السطحية والمياه الجوفية والترية والغذاء على مستوى العالم. في هذه الدراسة تم تثبيت وربط الشيتوزان المغناطيسي على أكسيد الجرافين الصلب من أجل إزالة أيونات البركلورات من مياه الصرف الصحي.

تم تمييز وفحص وتحليل المعقد الناتج من خلال يتميز المجمع بالمجهر الإلكتروني النافذ والتحليل الطيفي للأشعة تحت الحمراء من فورييه وتهتز مقياس المغناطيسية للعينة.

لقد تم دراسة تأثير العديد من العوامل المؤثرة على عملية ادمصاص المعقد الناتج لأيونات البيركلورات مثل دراسة تأثير درجة الحموضة، زمن التفاعل، درجة الحرارة، كمية المعقد التي تم استخدامها بالإضافة الى دراسة تأثير الأيونات السالبة المرافقة لأيونات البيركلورات في الماء.

من أهم الايجابيات في المعقد الذي تم تحضيره وهي سهولة استخراجها من المياه بعد استخدامه في عملية الادمصاص من خلال مغناطيس خارجي وذلك لان له صفات بارامغناطيسية فائقة. بالإضافة الى ما سبق، فانه من الممكن استخدام هذا المعقد في عملية الادمصاص بمدى كبير من درجة الحموضة يتراوح من 4 الى 10.

من خلال هذه الدراسة تبين لنا أن وجود بعض الأيونات السالبة المرافقة لأيونات البيركلورات يؤثر على عملية ادمصاصه مثل وجود أيونات الكبريتات والتي من شأنها ان تتنافس أيونات البيركلورات في عملية الادمصاص.

ج

من خلال نتائج هذه الدراسة تم التوصل الى ان عملية الادمصاص تتبع تفاعل من الرتبة الثانية وذلك حسب النتائج من الناحية الحركية. أما من الناحية الحرارية فانه تبين من خلال القيم السالبة للمحتوى الحراري ان عملية الادمصاص عملية طاردة للحرارة بالإضافة الى ان العملية تتم بشكل تلقائي نظرا للقيم السالبة لطاقات جيبس الحرة.

اما من ناحية امكانية استخراج هذا المعقد لإعادة استخدامه ثانية فانه تم من خلال قياس مدى قدرة المعقد على ذلك من خلال خمس عمليات من الادمصاص والافتكاك باستخدام محلول ملح كلوريد الصوديوم بتركيز 0.1% .

