

An-Najah National University

Faculty of Graduate Studies

The use of Magnetic Multiwalled Carbon Nanotubes Functionalized with Chitosan for Nitrate Removal from Wastewater

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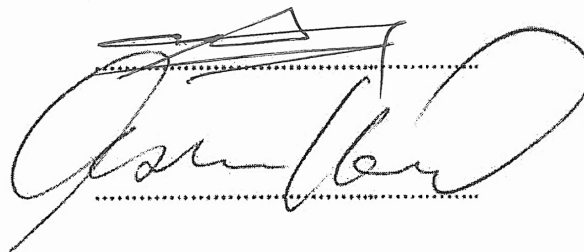
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Dedication

I dedicate this thesis to all who care about the environment and work hard to save it, to all who inspire me by their research in this field also to my dear father and my great mother.

Acknowledgments

Beginnings thank Almighty Allah who gave me the ability to complete this work. I would like to thank my supervisor, Prof. Shehdeh Jodeh for all his directing, supporting and advice in my research work. Also I would like to thank both Palestinian Water Authority and Middle East Desalination Research Center (MEDRC) for their financial funding for my master degree works.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

The use of magnetic multiwalled carbon nanotubes functionalized with chitosan for nitrate removal from wastewater

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص, باستثناء ما تمت الإشارة إليه
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degree or qualification.

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List of Abbreviation

Symbol	Abbreviation
A	the Temkin isotherm constant (L/g)
Å	Angstrom = 1.0×10^{-10} meters
UV	Ultra- Violet
WHO	World Health Organization
MWCNTs	Multi-walled carbon nanotubes
XRD	X-ray diffraction
B	Dimensionless Temkin constant
B	Temkin constant related to heat of sorption (J/mol)
ATR	Attenuated Total Reflectance
CNTs	Carbon nanotubes
C _o	Concentration of nitrate ion in the sample solution before treatment (mg/L)
C _e	Concentration of nitrate ion in the sample solution after treatment (mg/L) at equilibrium
C _i	Initial concentration of nitrate ion in the sample solution (mg/L)
NMR	Nuclear Magnetic Resonance
%DD	Degree of Deacetylation
FDA	Food and Drug Administration
USEPA	US Environmental Protection Agency
MCL	maximum contaminant level
DNA	Deoxyribonucleic acid
MAP	Mitogen-activated protein
K ₁	The Lagergren's first order rate constant
K ₂	The pseudo second order rate constant
K _d	The distribution coefficient
K _F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g (L/mg) ^{1/n})
K _L	Langmuir isotherm constant (L/mg)
TEM	Transmission electron microscopy
PR	Pathogenesis Related
C	Constant that gives an indication of the thickness of the boundary layer (mg/g)
M	The mass of the adsorbent (g)
m _{sed}	Mass of adsorbent dose
N	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
Q _e	The amount of nitrate ion adsorbed per gram of the

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	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	R the gas constant (8.314 J/mol K)
R^2	Correlation coefficient (regression coefficient)
R_L	Dimensionless constant separation factor
K_p	The diffusion rate constant (mg.g ⁻¹ .min ^{0.5})
ΔG	Gibbs free energy change (J)
ΔH	Enthalpy change (J)
ΔS	Entropy change (J/K)
T	Time
T	The absolute temperature (°K)
TGA	Thermal gravimetric analysis
V	Volume of solution
ΔG°	Standard free Gibbs energy
ΔH°	Standard enthalpy
ΔS°	Standard entropy
AC	Activated carbon
CHT	Chitosan

**The use of magnetic multiwalled carbon nanotubes functionalized
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Abstract

This study aims to synthesis magnetic multiwalled carbon nanotubes functionalized with chitosan, and used for removal of nitrate from wastewater. The resulting adsorbent characterized by TEM, ATR, XRD, TGA and Raman analysis. This porous material showed a very good thermal and chemical stability and hence it can be used as perfect adsorbent to uptake nitrate ions from wastewater.

The concentration of the nitrate in the filtrate was determined using UV-visible Spectrophotometer. The results showed that the resulting product has high adsorption efficiency. Also, it showed strong complexation properties with nitrate ions. In order to investigate the adsorption efficiency for the adsorption of nitrate onto magnetic multiwalled carbon nanotubes functionalized with chitosan the effect of solution conditions on each adsorption process were studied. These conditions involve the effect of contact time, pH value, temperature, adsorbent dose and the initial concentration of adsorbate.

The best equilibrium isotherm model for each adsorption process was investigated according to the value of the correlation coefficient of Langmuir and Freundlich isotherm adsorption models. The kinetics of adsorption were also investigated using pseudo first-order, pseudo second-

order and intra-particle diffusion kinetic models. In addition, Van't Hoff plot for the adsorption was investigated in order to determine the values of enthalpy change and entropy change, and hence determining if the adsorption process is spontaneous or not, and if it is exothermic or endothermic one. The results showed that the adsorption followed Frenndlich isotherm and the mechanism of the reaction followed pseudo first-order kinetic adsorption model. The thermodynamic parameters of the adsorption proved that this process is endothermic ($\Delta H > 0$) and spontaneous ($\Delta S > 0$). The synthesized adsorbent was also regenerated, and the percentage removal before and after adsorbent recovery is determined.

Chapter One

Introduction

1.1 Overview

Rising levels of the poisonous materials in the sources of water, air and soil are a dangerous problem to human health, living sources and environmental systems.

In latest years, industrial development, augmenting use of agricultural fertilizers and inappropriate treatment of wastewater have risen poisonous contaminants like metal ions, organic and inorganic ions such as nitrate in water and soil [1].

To decline the level of nitrate in drinking water and set these standards, some operations have been employed and reported. These encompass biological de-nitrification [1,2,3], chemical reduction [1,2,4], reverse osmosis [1,2,3], electrodialysis [2,3], ion exchange [1,2,3] and adsorption operation [1,5]. Somehow, any of these operation has several advantages but they have some disadvantages too. Biological de-nitrification perhaps not practically operable in ground water manipulation, due to it is not being operant on temperatures under 7°C. Furthermore, there could be the possibility of imperfect de-nitrification and post processings could be needed because of microorganisms [1,6]. Hazard of nitrate constitute and eventuality of releasing poisonous composites are disadvantages of chemical operations [2,6]. In reverse osmosis, eluting of concentration and

manipulation of trash streams are perhaps hard and membranes are canted to vitiation. Also, reverse osmosis has elevated processing costs and post manipulation is required [1,3]. Electrodialysis operation can operate without vitiation, scaling, or chemical superinducing and has tall membrane life expectingly, but the treatment could be needed for risen levels of iron, manganese, H_2S , chlorine or hardness [2,3]. In ion exchange operation, the possibility of nitrate climaxing, risen chemical employ (salt), brine tashes removal and final pH exactness are the major disadvantages. In addition to, resins are costly and retain some SO_4 and hydrogen carbonate, that cause of change water content significantly. Also, it causes an augment in the chloride level in water because of substituting chloride instead of nitrate [1,2,3].

Silica gels are perfect materials that can be used to purify water from nitrate because they have low cost with high surface area, high mechanical properties and good chemical and thermal stability [7]. In adsorption operation, nanocarbon tubes (CNTs) are effectual adsorbents to eluting of organic and inorganic pollutants from aqueous solution, due to their comparatively large particular surface area, small size, hollow and their layering structures and risen thermal and chemical stableness [8,9,10].

Adsorption operation is economic, easy and healthy. In this research, magnetic multiwalled nanocarbon tubes (MWCNTs) functionalized with chitosan were synthesized and then employed to elute nitrate ions from wastewater by adsorption technique. The impacts of solution conditions involving pH worth, temperature, contact time, quantity of adsorbent and nitrate ion concentration on the adsorption conduct were determined.

1.2 Nitrate ions

1.2.1 Sources of Nitrate

Nitrate is an example for the common pollutants all over the world, as nitrate is repelled by negatively charged colloids and is highly soluble, its tendency to nominate from soil to water which contaminates drinking water resources particularly ground waters that are the common resource for rural regions [1,12], and when its concentration gets immoderate in water resources it causes many health and ecological threats.

In moderate concentrations nitrate is found in many of the natural waters sources. It eventuates normally because of the deterioration of nitrogen-containing composites from natural resources as organic materials, bedrock and soil [13]. Sulfates and nitrates are major contents of acid rains [14]. Moreover, Nitrate exists as natural constituent of plants. Anyway, the largest cramming of nitrate arises from anthropogenic resources, which outcome from immoderate application of nitrate-based chemical fertilizers in agricultural vitalities [15-19] and from several industrial operations [16-17, 19-20]. The other most major sources of nitrate are overflowing septic tanks [15, 19- 20], the trashes of the outputting of explosives [18], domestic wastes effluents, livestock, herbicides and pesticides that are employed in industrial agriculture [19], disintegration of corrupt organic materials entombed in the ground [20] and the agriculturist of leguminosae crops which fixates atmospheric nitrogen as a form of nitrate [15]. The whole of

these materials can be diverted to nitrate by using biochemical oxidation method.

Nitrification is a series of bacterial reactions collectively which the nitrite ion occurs as intermediate during the biodegradation at this operation. In the nitrification operation bacteria decompose nitrogen containing compounds and release ammonia. Then, some bacteria such as *Nitrosomonas* oxidize the released ammonia to nitrite which is diverted to nitrate by other bacteria which is *Nitrobacter* [13].

1.2.2 Toxicity of Nitrate

Although nitrate in water has no high toxicity, but may be diverted via microbacteria or in vivo reduction methods to nitrites [21-22]. By oxidation of ferrous iron (Fe^{+2}) in hemoglobin to ferric form (Fe^{+3}) nitrites convert hemoglobin to methaemoglobin that inhibit or decrease the capability of blood to transfer oxygen to all cells. This transport is described as methaemoglobinaemia which is dangerous specifically for infants that called blue-baby syndrom [16, 19-20, 22-23]. Moreover, the interaction between nitrite and secondary or tertiary amines perhaps result in the formalization of carcinogenic, mutagenic and teratogenic *N*-nitroso composites (Nnitrosoamines) [16, 20, 22-23] which perhaps cause cancer of the alimentary canal [17]. In adults, risen quantity of nitrate can cause abdominal pain, blood in fece and urine, mental depression, weakness [15], headache, dyspepsia [19], hypertension, vomiting, diabetes, diarrhea, respiratory tract injuries and differences in the immune system [24].

Eutrophication is a phenomenon occurs because of the high concentrations of nitrate in water which leads to high growth of the algae in water which consumes the oxygen gas dissolved in water causing fish death [17, 22-23].

For these reasons, the World Health Organization (WHO) and the European Community have set a maximum contaminant level (MCL) of 50 mg NO_3^- /L which is equal to 11.3 mg NO_3^- N/L (WHO, 2011), whereas the US Environmental Protection Agency (USEPA) have set an MCL of 10 mg NO_3^- N/L (USEPA, 2009). According to international criterions, drinking water should include no further than 50 mg/Litre of nitrate and a guide level of 25 mg/Litre is highly recommended [25].

1.3 Magnetic multi-walled carbon nanotubes

Magnetic adsorption methods are among of several technologies which are modern methods for the eluting of nitrate from industrial wastewaters, because it forms water with high quality and these methods are economically feasible [26].

Magnetic MWCNTs have been vastly used for eluting several pollutants from aqueous solutions because of their large surface area, small size, highly porous hollow structure, light mass density, greater active sites, layered structure and strong interplay between the pollutant particles [27–39]. Moreover, MWCNTs have a good property as high mechanical stability and can be employed as a favorable adsorbent for eluting of contaminants from aqueous solutions [39].

Magnetic nanocarbon tubes are normally prepared employing the chemical deposition of Fe_2O_4 (or $\gamma\text{-Fe}_2\text{O}_3$) nanoparticles onto purified multi-walled

nanocarbon tubes (MWCNTs) [40]. The MWCNTs/Fe₃O₄ nano-composites would react quickly to the permanent magnet, and after sorption, the nanocomposites would be detached from solution readily by an outer magnet [41].

1.4 Chitosan

1.4.1 Structure and Properties

Biopolymers has been earning large attention and being used in several sectors because of their low cost and high components of NH₂ and OH functional groups, that increase the adsorption possibility for disposal of contaminants materials [42, 43].

The most important one of these biopolymers is chitosan. Chitosan is a polysaccharide, cationic biopolymer and has been employed as an opertant chealating agent for metal cation because of it's properties such as biocompatible, biodegradable, nontoxic and the existance of poly functional groups [44, 45]. Also, beacuse of the existance of amino and hydroxyl functional groups as shown in figure 2.1[46].

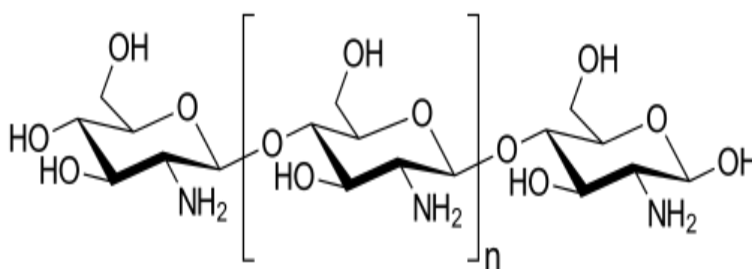


Figure 1.1: Molecular structure scheme of chitosan.

Deacetylation of chitin is the production method of Chitosan, chitin is the skeletal component in the exoskeleton of crustaceans like crabs, shrimp and

cell walls of fungi. The degree of deacetylation (%DD) is calculated by NMR spectroscopy, 60 to 100% is the %DD of commercial chitosans. On the other hand, commercially produced chitosan has a molecular weight that vary from 3800 to 20,000 Daltons.

A major operation of the production of chitosan is the deacetylation of chitin by employing NaOH in augment as an agent and H₂O as a solvent. The interaction occurs in two steps below first-order kinetic model adjudge. Whereas, E_a for the first step is more than E_a in the second step and its equal approximately 48.76 kJ mol⁻¹ under tempereture from 25 to 120°C. The interaction path permit to ward the continue of the deacetylation with yields of the product reach to 98% [46].

The NH₂ group in chitosan has a pKa value roughly 6.5, this value performs to a protonation in acidic media to neutral solution with a charge density predicated on pH value. This makes chitosan soluble in water and has an adhesive property which easily attaches to negatively charged surfaces like mucosal membranes. Although, chitosan is not credited from FDA for drug delivery, but it is improved the transfer of polar drugs via epithelial surfaces, and it has biocompatibility and biodegradability properties. Also, purified amounts of chitosans are affordable for bio-medicine implementations [47, 48].

1.4.2 Uses of Chitosan

1.4.2.1 Agricultural uses

CHT, chemically a linear unbranched polymer of Beta-1,4-D-glucosamin, a co-polymer of N-acetyl-D-glucosamine and D glucosamine constituting the main component of the exoskeleton of arthropods. The agricultural employes of chitosan for defence of plant and rise of yield depends on about how the polymer of glucosamine impact on the biochemical and biological molecular of the plant cell. The cellularly aims are the nuclear chromatin and plasma membrane. Later differences occur in cell membranes, oxidative burst, DNA, MAP Kinase, calcium, reactive oxygen species, chromatin, callose pathologic-related (PR) genes and phytoalexins [49].

Many researchers investigated agricultural applications of CHT-based materials and in several cases these materials resulted able to increase plant productivity. For example, CHT (250–500 ppm), from Sigma-Aldrich (St. Louis, MO, USA), two applications at seven-day intervals, from pre-flowering to post-flowering stage) induces 56% higher fruit production.

1.4.2.2 Biomedical uses

Chitosan's has lately acquired agreeing in the United States (US) and Europe for employ in dressings and another hemostatic reagents because of it's characteristic which lets to rapidly clot blood [50]. Chitosan hemostatic materials have appeared in pretesting fom the U.S. Marine Corps to rapidly ceases bleeding and to reduce blood wastage, also result in 100% survival

of else lethal arterial lacerations in swine [51]. Chitosan hemostatic materials decrease blood wastage in comparative to gauze bandages and rise diseased survival. Chitosan hemostatic materials have been sold out to the U.S. army and are currently employed by the UK army. Both the US and UK have already employed the dressings on the battleground of Iraq and Afghanistan. Chitosan is hypoallergenic and has normal antibacterial characteristics, which more supporting its employ in field dressings. Chitosan's hemostatic characteristics let it to decrease pain by bedeviling nerve endings [52].

Chitosan's characteristics also let it to be employed in transdermal drug delivery; it is mucoadhesive in nature, reactive (so it can be formed in several different shapes), and most important, has a positive charge in acidic media. This positive charge becomes from protonation of its free NH_2 groups. Decreasing of a positive charge implies chitosan is insoluble in neutral and basic media. Anyhow, in acidic media, protonation of the amino groups performs to a rise in solubility. The consequences of this are very significant to bio-medicine implementations. This compound will maintain its structure in a neutral media, but will dissolve and decompose in an acidic media. This performs chitosan can be employed to transfer a drug to an acidic media, where the chitosan packaging will then decompose, releasing the drug to the coveted media. For example of this drug delivery has been the transfer of insulin [53].

1.5 Adsorption

1.5.1 Adsorption Definition

Adsorption has two definitions. Firstly, it is a mass transport operation when a component is converted between the liquid phase and the solid surface then gets destined by physical and/or chemical interplays. As that, the large surface area performs to risen sorption capability and surface interactivity [54].

Secondly, adsorption is a surface phenomenon, which involves the adhesion of the adsorbate on the adsorbent surface. The molecule that adsorbs on the pores of the surface is dubbed the adsorbate, As that, the substance on which adsorption occurs is called the adsorbent. Adsorbate may be gas, liquid, or dissolved solids. whereas, adsorbent may be a liquid or a solid material [55].

Adsorption technique has practical applications in biology, industry, technology and environmental protection so it is an extremely important operation of utilitarian significance. The effectiveness of this treatment method impacted by a number of factors. These are, the nature of adsorbent and adsorbate, the surface area of the adsorbent and its activation. Moreover, it is affected by concentrations of adsorbent and adsorbate, temperature, contact time and pH value [56].

In a bulk substance, every adhesion requisites whether were ionic, covalent, or metallic of the constituent of the substance atoms are heaped by another atoms in the substance. So, adsorption is a result of surface energy.

Anyhow, the atoms of the adsorbent surface are never exact reacquainted by another adsorbent atoms. Thus, the adsorbant can magnetize the adsorbate. The precise normal of the bonding accredits on the minutiae of the types included, but the sorption operation is commonly categorized to physical adsorption that property of weak van der Waals forces and chemical adsorption that property of covalent bonding. Also, It can occur because of electrostatic attractive [57].

The difference between adsorption and absorption disappears when we compare between perfectly crystalline macroscopic substances to perforated or indited substances, entireties and compounds produced of growing smaller cereals, viz., and micron-sized molecules to nanomolecules, sub-nano molecules and finally molecules (or atoms). In such nano-compounds, the inboard surface area of particulate issue is very large. Then the adsorption on inboard surfaces simply gets absorption when looked from the bulk. Then the difference between adsorption and absorption disappears. On the other way, the difference between bulk solids without inboard structure, but having only surfaces where only adsorption can occur on the upper surfaces and nanocompounds or entireties with inboard structure when absorption by the appender substance is simply adsorption on inboard surfaces of the appender substance. For example, we may consider a crystalline segment of silicon dioxide (quartz) that can absorb water molecules onto its surface. Any way, if the quartz is ground into very fine sand, the heap of sand (an entireties) has a very big inboard surface area. A very big quantity of water can be adsorbed by the inboard

surfaces of the cereals in the heap of sand, and this absorption is simply inboard adsorption. When water is made to stream thru such a heap of sand, ions and poisons in the water may be preferentially adsorbed by the surfaces of the cereals of sand, purveying a simple, well-known water scrubbing application. Adsorption was modeled by Heinrich Kayser (German physicist 1853-1940) in 1881 [58].

Adsorption is confirmed to be an economic and operant operation, overgrown technique, cost influence, easy to use, high effectiveness, and constant performance, for the eluting of some pollutants from the water [59, 60]. Moreover, adsorption is a suitable operation on broad range of temperatures and pH values and the used adsorbent will be redecorated by appropriate desorption operation [61].

1.5.2 Types of adsorption

By appropriation on the type of forces finding between particles of adsorbent and adsorbate, the adsorption operation will be categorized to two classes:

1. Physisorption (Physical Adsorption)

This class of adsorption has several characteristics. Which are; weak intermolecular forces of bonding like dipolar interaction. In addition, physical adsorption has low heat of adsorption so it needs a very small or no activation energy at all. Physical adsorption forms multi-molecular layers and it is not very specific. Also, this adsorption class is reversible, as the adsorbate molecule does not stay constant on a certain location on the

adsorbent surface, so it will be free to move from one position to another, and hence making adsorbate recovery probable [62].

Physical adsorption usually takes position at low temperatures and can be readily commutated by increasing temperature or by reducing the pressure [63].

2. Chemisorption (Chemical adsorption)

When the force of attraction finding between adsorbent and adsorbate are roughly equal power as chemical linkages this class of adsorption dubbed chemical adsorption, Langmuir adsorption or chemisorption. In Langmuir adsorption the force of attractive is very powerful, so adsorption cannot be readily commutated [64].

Table 1.1: Comparison between chemical and physical adsorption[64]

Physical adsorption	Chemical adsorption
It has low heat of adsorption normally vary from 20 to 40 kJ mol ⁻¹ .	It has risen heat of adsorption vary from 40 to 400 kJ mol ⁻¹ .
It has Van der Waal's forces Force of attractive .	Forces of attraction are chemical linkage forces .
It normally takes position at low temperature .	It takes position at risen temperature .
Reversible .	Irreversible .
Not very specific .	Very specific .
It constitutes poly molecular layers .	It constitutes single molecular layers.
It doesn't need any activation energy.	It needs some activation energy .
It is appertained to abate of liquefaction of the gas.	The range of adsorption is normally not appertained to liquefaction of the gas.

1.5.3 Types of adsorbents

There are two types of adsorbents :

Natural adsorbents involve charcoal, clays, clay metals, ores, and zeolites. All natural substances featured as not expensive, plentiful and have important potential for alteration and eventually betterment of their adsorption capacities.

Synthetic adsorbents are adsorbents equipped from agricultural materials and trashes, sewage sludge, industrial trashes, house hold dumps and polymeric adsorbents.

Every adsorbent has properties that belongs to it like pores structures and normal of its adsorbing surfaces. Several trash substances employed involve fruit trashes, coconut shell, old tires, bark and another tannin-rich substances, sawdust, rice nutshell, petroleum trashes, fertilizer trashes, fly ash, sugar industry trashes burst furnace slag, chitosan and seafood manipulating trashes, seaweed, algae, clays, red loam, zeolites, precipitates and clod, ore metals, peat moss etc. [65].

1.5.4 Adsorption applications examples

Drugs: several drugs become adsorbed onto the tissues after that are heated. The mulches action of antidotes is also depending on the characteristic of adsorption [66].

Chromatography: some numbers of chromatographic operations such as adsorption chromatography, paper chromatography and vapour phase

chromatography which depend on eclectic adsorption of several materials of the adsorbent.

Eluting of Colouring Materials from Sugar Juice & Vegetable Oils: activated animal charcoal is employed as decolourizer in eluting colouring materials of sugar solution and vegetable substances.

Clothes Dyeing: Modrants employed in tincturing adsorb the colouring material which doesn't bind to callus else.

1.5.5 Adsorption isotherms models

Adsorption operation is normally determined through adsorption isotherm graph. That is the quantity of the adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.

Analysis of the isotherm information is significant to develop an equation, which accurately acts as the observed results. The main isotherms that are applied in solid/liquid systems are the theoretical equilibrium isotherm models, which are Langmuir and Freundlich isotherms [67].

1.5.5.1 Langmuir Adsorption Isotherm

This isotherm is the optimal localized single layer model; it was developed to represent chemisorption so the other name of this isotherm is chemisorption. Langmuir isotherm depends on the subsequent suppositions. Which are, adsorption is stropped to single layer cloaking, for example; the adsorbed particle cannot transfer via a surface or react with neighboring

particles. Moreover, the surface of the adsorbent is uniform. This indicates that all the adsorption positions are equipotent in energy [68].

The Langmuir equation appertains of the cloaking of particles on a surface of solid to the concentration of a medium upper the surface of solid at an invariant temperature. This equation can be represented as:

$$C_e/q_e = (1/b Q_0) + (1/Q_0) C_e$$

While;

C_e assigned to the adsorbate concentration at equilibrium (mg/Litre).

b assigned to the constant of Langmuir affinity (Litre/mg).

Q_0 assigned to the capability of adsorption at equilibrium (mg/g).

q_e assigned to the quantity of adsorbate in mg unit per adsorbent mass in gram, and it can be determined by employing the subsequent equation:

$$q_e = (C_0 - C_e) V/ m$$

When;

C_0 assigned to the initial concentration of the adsorbate (mg/Litre).

V assigned to the solution volume (Litre).

m assigned to the adsorbent mass (gram).

$(C_0 - C_e)$ represents the adsorbed amount (ppm).

A plot of (C_e/q_e) values versus C_e is employed in order to determine the Langmuir parameters. Whereas, $(1/bQ_0)$ is y-intercept and $(1/Q_0)$ is a slope [69].

1.5.5.2 Freundlich Adsorption Isotherm

This isotherm was translated as adsorption to surfaces backing positions of several homeomorphisms or to heterogeneous surfaces. Freundlich isotherm supposed that firmest binding positions are occupied first, like the binding strength reduces with rising degree of position occupation.

According to this statement, the adsorbed mass per mass of adsorbent can be represented by the subsequent equation [70].

$$\log q_e = (1/n) \log C_e + \log K_F$$

While;

K_F assigned to the Freundlich constant appertained to adsorption capability (mg/g).

n assigned to the heterogeneity coefficient that gives a mention of how suitable the adsorption operation (g/L).

A form of $\log q_e$ values versus $\log C_e$ is employed to determine Freundlich parameters. Whereas, $\log K_F$ is y-intercept and $(1/n)$ is a slope.

1.5.5 Adsorption Kinetic Models

The definition of kinetic adsorption is the operation in which adsorbate particles are transfered from bulk solution to a boundary layer of the water vicinity of the adsorbent molecule by molecular diffusion through the stationary layer of water. Like the adsorbate mplecules are transfered into an affordable position. Whereby, an adsorption bond will be configured between the adsorbent and the adsorbate [71, 72].

Many adsorption kinetic models have been created to prescribe adsorption kinetics and rate-limiting step. These exemplars give data about the adsorption system conduct and the rate at any determinant constituent is eluted employing a specific adsorbent. Moreover, they studied when the adsorption operation is a chemical or a physical one, and when exactly the rate determining step occurs. Examples of the adsorption kinetic models involve, external mass transfer model, pseudo first-order and pseudo second-order rate models, Adam–Bohart–Thomas relation, Weber and Morris sorption kinetics, first-order reversible reaction model, first-order equation of Bhattacharya and Venkobachar and Elovich's model [73, 74].

1.5.5.1 Pseudo First–Order Kinetics

This kinetic model is considered as the earliest model sophisticated for describing adsorption kinetics.

The final integrated equation for this model can be represented as:

$$\text{Log}(q_e - q_t) = \text{log}q_e - (K_1/2.303) t$$

While;

q_e and q_t assigned to the adsorbate masses per adsorbent masses at equilibrium, and at time t respectively (mg/g).

k_1 assigned to the rate constant of pseudo first-order adsorption model (mg/g.min).

A form of $\log(q_e - q_t)$ versus t will give a straight line for the pseudo first-order adsorption whereas, $\log q_e$ is y-intercept and $(-k_1/2.303)$ is a slope of the graph [75].

1.5.5.2 Pseudo Second–Order Kinetics

This model of kinetics relies on the supposition that the rate-determining step may be chemical adsorption including valence forces through sharing or exchange of electrons between the adsorbate and the adsorbent.

The rate equation for pseudo second-order kinetic model can be represented as:

$$t/q_t = (1/K_2 q_e^2) + (1/q_e) t$$

While;

k_2 assigned to the equilibrium rate constant of pseudo second-order adsorption (g/mg.min).

The plot of t/q_t versus t should give a linear relationship that helps in the determination of a second-order rate constants, k_2 and q_e [76].

1.5.5.3 Intra-Particle Diffusion Kinetic Model

This model is depends on the theory suggested by Weber and Morris. The equation of this adsorption kinetic model represened as:

$$q_t = K_p t^{1/2} + C$$

While;

K_p assigned to the rate constant of diffusion (mg/g.min^{1/2}).

C assigned to the constant that gives a mention of the thickness of the boundary layer (mg/g) [77].

A plot of qt versus $t^{1/2}$ should give a linear relationship for intra-particle diffusion kinetic model whereas, constant C is a y-intercept and K_p is a slope.

1.5.6 Adsorption Thermodynamics

Thermodynamic reputing of an adsorption operation is important to study when this operation is favorable or unfavorable. This adsorption conduct can appeare employing the thermodynamic factors involving the difference in Gibbs free energy (ΔG), enthalpy change (ΔH) and the difference in entropy (ΔS). Whereas, ΔG and ΔH are in Joule and the unit of ΔS is Joule per Kilogram.

The subsequent equation is the main equation that can be employed to connect between the adsorption factors [78].

$$\Delta G = \Delta H - T\Delta S$$

While;

T assigned to the absolute temperature in Kelvin.

The difference in Gibbs free energy can be also determined by this equation:

$$\Delta G = - R T \ln K_d$$

While;

R assigned to the universal gas constant that equals 8.314 J/mol.K.

K_d assigned to the thermodynamic equilibrium constant that equals (q_e/C_e) with a unit of mol or (L/g).

The combination of the last two equations will give this equation:

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

The plot of $\ln K_d$ versus $(1/T)$ will give a straight line with $(-\Delta H/R)$ as a slope and $(\Delta S/R)$ as an intercept. The resulting graph is known as Van't Hoff plot.

1.6 Multiwalled carbon nanotubes functionalized with chitosan

The surface characterizations of MWCNTs with chitosan are commonly maladjustive with divide condition performing to their congregation in moulding. Lately, COOH-functionalized multiwalled nanocarbon tubes (MWCNTs) have outcropped as a potential solution to this divide trouble. COOH groups can be introduced to the nanocarbon tube surface by oxidation interctions of carbon in strong acid media. The resultant subsances are graspable in water by de-protonation of the acid groups with basic groups of chitosan [39, 44].

1.7 Objectives of this work

1.7.1 General Objectives

1. Purify the water from toxic nitrate ion by employing this new adsorbent of magnetic MWCNTs functionalized with chitosan.
2. To determine the effect of several factors in order to study the extent and the effectiveness of adsorption technique.

1.7.2 Specific objectives

1. To study if magnetic multiwalled carbon nanotubes functionalized with chitosan can be employed to clean wastewater contaminated with nitrate ion.
2. To determine the effect of pH, temperature, amount of adsorbent, concentration and contact time on the adsorption of nitrate.

1.7.3 Research question and identified problems

The main questions addressed in this work are:

1. Can magnetic multiwalled carbon nanotubes functionalized be employed to clean wastewater contaminated with nitrate ion?
2. To which extent that magnetic multiwalled carbon nanotubes functionalized can tolerate and adsorb nitrate ion?
3. What are the optimal condition of pH, temperature, amount of adsorbent, concentration, and contact time for magnetic multiwalled carbon nanotubes functionalized to adsorb nitrate ion efficiently?
4. What is the optimum amount of magnetic multiwalled carbon nanotubes functionalized with chitosan requires for adsorb the largest proportion of nitrate ion below the optimum conditions?

1.7.4 Significance of Thesis

1. Through this work I will try to find out novel technique which is ready to remove nitrate ion from the water to drinkable degree.

2. The stationary phase supported material can be recycled and be used for many times.
3. Small lab station will be established in order to test the method efficiency.

1.7.5 Novelty of the work

As a result of this study someone can find a very good adsorbent (magnetic multiwalled carbon nanotubes functionalized with chitosan) with OH and NH₂ groups like ions in water attached to nitrate, which will make a positive charge on the whole compound. In conclusion, I will be the first to use this process to attract nitrate.

Chapter Two

Experimental Work

2.1 Chemicals and Materials

All reagents in this study are used with no more purification. The wanted chemicals include: multi-walled carbon nanotubes (MWCNTs), chitosan, sulfuric acid (98%), nitric acid (65%), acetic acid solution(1%), glutaraldehyde (0.5%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NH_4OH (25%), NaOH , HCl and potassium nitrate.

2.2 Instrumentations and apparatus

In this research the following instrumentations and apparatus were used: pH meter (model: 3510, JENWAY), thermometer, shaking water bath (Daihan Labtech, 20 to 250 rpm Digital Speed Control), desiccators, UV spectrometry (model: UV-1601, SHIMADZU), glassware, TGA (Q50 V20.10 Build 36 instrument at a heating rate of $50^\circ\text{C}/\text{min}$ and in N_2 gaseous atmosphere and FT-IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific).

2.3 Synthesis of magnetic multi-walled nanocarbon tubes functionalized with chitosan

For the preparation of magnetic MWCNTs nanocomposites, 0.25 g MWCNTs was put with 0.39 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.76 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 70°C under nitrogen atmosphere in 100 ml deionized water with mixing for

1 hour. Subsequently, the pH value of the mixture was acclimatized to 10 by addition of NH_4OH solution (25%) drop by drop. The mixture was held at 70°C for another 4 hour beneath nitrogen atmosphere with mixing then MWCNTs nanoparticles was detached from solution by utilizing a magnet. The final product of nanoparticles adsorbant was laundered with deionied water for two times and dehumidified under 50°C .

To functionalize the magnetic MWCNTs with chitosan, 100 mg of the substance was mixed in a 3:1 [volume:volume] jumble of H_2SO_4 (98%)/ HNO_3 (65%) for 12 hour at 70°C . After that, a 100 mg of the chitosan was dissolved in 10 ml of 1.0% [volume:volume] acetic acid solution to prepared 1.0% chitosan stock solution. A dispersion of 0.5% [mass/volume] functionalized magnetic MWCNTs in 1% [mass/volume] chitosan solution was prepared by adding 10 mg of functionalized magnetic MWCNTs in 2 ml of 1.0% (mass/mass) chitosan solution with mixing, and after that 0.4 ml of 0.5% glutaraldehyde solution was mixed with the prepared solution below vigorous mechanical mixing for three hours. The final prepared solutions was dehumidified at 60°C for four hours[17]. Figure 2.1 shows the mechanism of covalent binding of magnetic nanocarbon tubes employing glutaraldehyde solution and chitosan cross-linking.

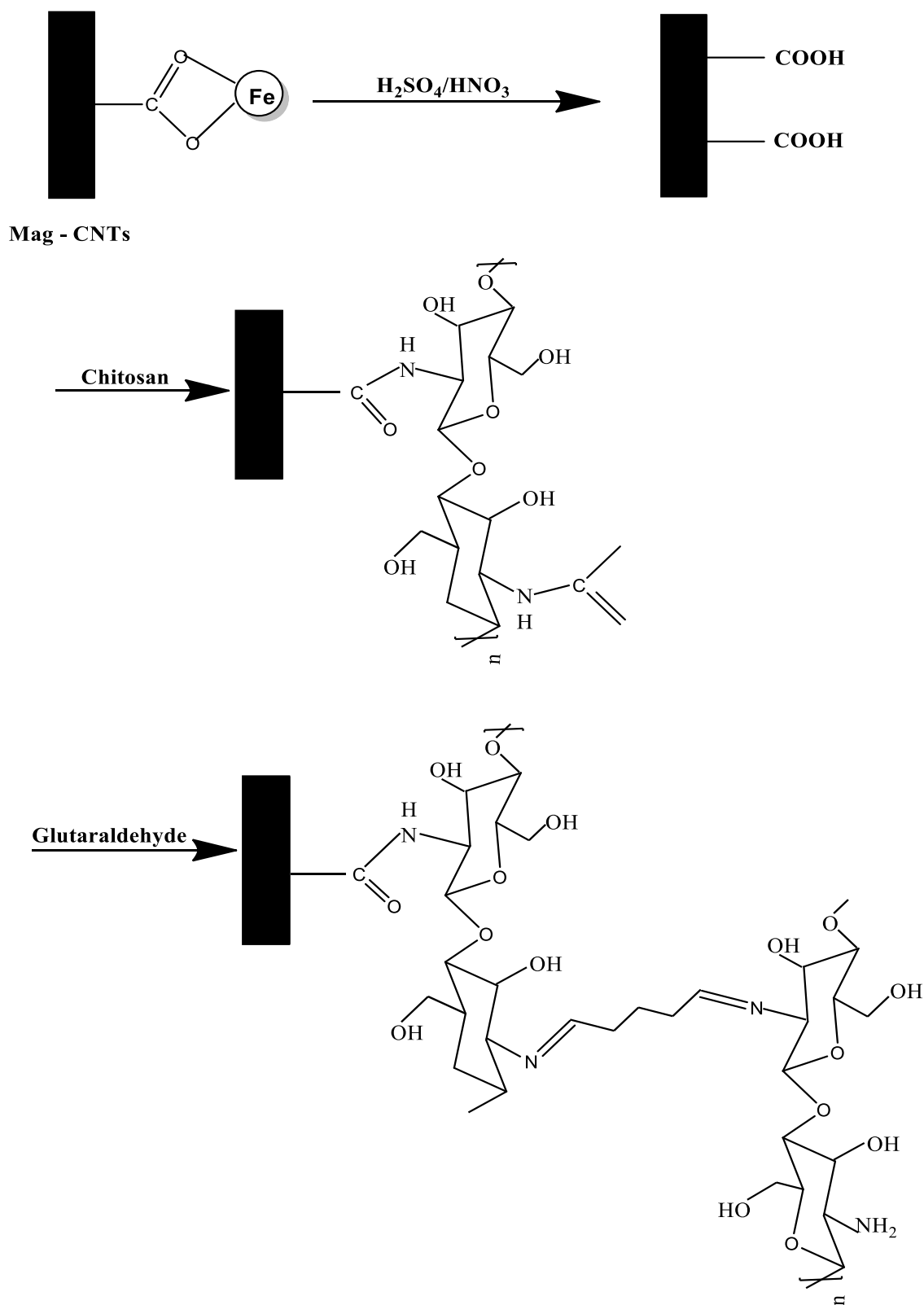


Figure 2.1: The mechanism of the covalent binding of magnetic nanocarbon tubes employing glutaraldehyde solution and chitosan cross-linking.

2.4 Preparation of nitrate solutions

Preparation method of standard solutions of NO_3^- of several initial concentrations with relying on dilution calculations as shown in this equation ($M_1 \cdot V_1 = M_2 \cdot V_2$). Where as potassium nitrate (KNO_3) that has molar mass $318.48192 \text{ g mol}^{-1}$ was employed to make all of standard solutions.

The prepared primary concentrations of nitrate are employed in batch experiments because of determined the impact of several parameters like: time, pH, amount of dosage, temperature on every adsorption operation and concentration of NO_3^- solution. And then determine all of the suboptimal prerequisites for having suitable adsorption of nitrate on magnetic carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent. These standard solutions of calibration are: 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm.

2.5 Calibration Curve

To prepare nitrate solution with 1000 ppm concentration, 1.63 g of KNO_3 was dissolved in about 100 mL water in a small beaker, then transferred into 1 L volumetric flask. Then the flask filled to the mark with distilled water. The flask was shaken several times. Then dilution measurements are employed to compose different solutions with many initial concentrations ranging from 5 to 50 ppm with increasing 5 ppm in each time. The concentration of several NO_3^- solutions was analyzed by UV-visible spectrophotometer.

Plot of absorbance with concentration was acquired in the span from 5 to 50 ppm NO_3^- solution, as shown in calibration curve in Figure 3.2:

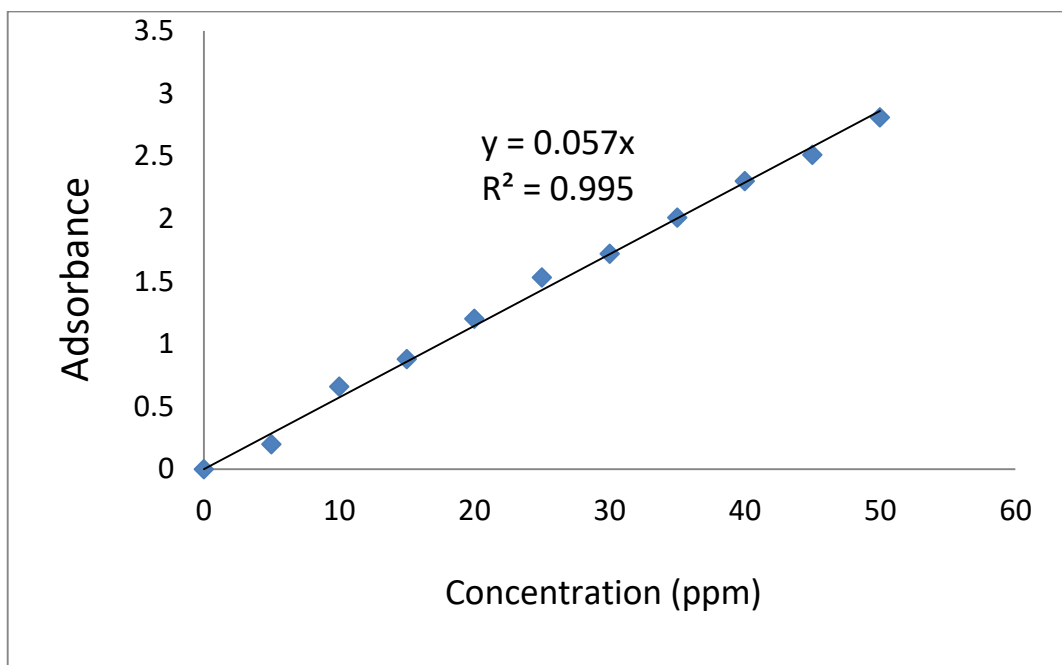


Figure 2.2: Absorbance vs. concentration at calibration curve of NO_3^- concentrations in the range 5-50 mg/L with maximum absorbance at 220 nm.

2.6 Adsorption Experiments

The jumble of 1 mg of magnetic (MWCNTs) functionalized with chitosan and 10 mL sample of wastewater with discerned concentration of nitrate ions was shaken.

The influence of solution conditions involving; contact time, pH value, the quantity of adsorbent, concentration of nitrate ion and the value of temperature were canvassed.

The filtrate jumble of each sample was taken to study the extent of the adsorption efficiency and to evaluate the remained quantity of the nitrate

ion by using UV-visible spectrophotometry with maximum absorbance at 220 nm.

2.6.1 Effect of temperature

A 50 ppm concentration of 10 mL of the standard solution of nitrate ion was added to 1 mg of magnetic (MWCNTs) functionalized with chitosan adsorbent at the optimum worth of pH. In shaking water bath every mixture was put at coveted temperature ranging from 5 to 80°C at optimal contact time. After every sample was percolate, the quantity of any adsorbate was calculated by employing UV-visible spectrophotometer instrument at the end of the time periods. This is was the suitable method to know the impact of temperature on each adsorption operation.

2.6.2 Effect of pH

A 50 ppm concentration of 10 ml of the prepared standard solution of nitrate was added to 1 mg of an adsorbent sample. The prepared mixtures were put at constant temperature 25°C in shaking water bath and taking into consideration the resulting suboptimal time for each quondam adsorption operation. This is was the suitable method to know the impact of pH value on the adsorption operation with using various pH value spanning from 2-12. The pH value was altered by employing 0.1M NaOH and 0.1M HCl.

2.6.3 Effect of the nitrate initial concentration

To determine the optimum concentration of the adsorption operation, 5-50 ppm of 10 ml of several concentrations of NO_3^- solution was added to 1 mg of adsorbent, below optimized temperature 25°C , pH 2 and time 50 min. Finally, the absorbance was determined by employing UV-visible spectrophotometer instrument.

2.6.4 Effect of adsorbent dose

A 7 phials including 50 ppm of 10 mL of nitrate ion standard solutions were added to (0.3, 0.5, 0.8, 1.0, 1.2, 1.4 and 1.6 g) of the adsorbent to know the apogee quantity of adsorbent that is needed for the adsorption of nitrate on adsorbent. In shaking water bath the mixtures were put under the suboptimal temperature 25°C , pH 2 and time 50 min. Lastly, the concentrations of the nitrate ion in the filtrate of sample are studied by employing UV-visible spectrophotometer instrument.

2.6.5 Optimization of contact time

A 1 mg of an adsorbent was shaken with a 50 ppm samples of standard solutions at pH value equalizes 2. The adsorption operation of nitrate ion on every sample of adsorbent was determined as a function of joggling time under 25°C . Every sample was percolate off and the quantity of every adsorbate is measured by employing UV-visible spectrophotometer instument at the end of periods of time ranging from 1 to 200 minute.

2.7 Thermodynamics and Kinetics of Adsorption

The eliminating of nitrate ion from the sample of wastewater was determined by adsorption operation employing the prepared adsorbent of magnetic multiwalled nanocarbon tubes (MWCNTs) functionalized with chitosan. The adsorption technique depended on the suboptimal condition of dose of adsorbent, concentration, contact time, pH and temperature. The concentration of nitrate was studied before and after adsorption process by using UV-spectrophotometer instrument. The eliminating information were constructed by the Freundlich and Langmuir equations of adsorption isotherm. Also, their corresponding factors worths were calculated. Moreover, kinetic models of pseudo second order and pseudo first order were studied in this work when the empirical information acquired for several contact time were employed. Kinetic model parameters of pseudo second order and pseudo first order K , Q_e and R^2 for nitrate adsorption on magnetic multi-walled nanocarbon tubes (MWCNTs) functionalized with chitosan were calculated. Also, calculated and experimental values of Q_e were compared to each other.

By employing Van't Hoff's form relation the thermodynamic factors such as free energy, enthalpy and entropy (ΔG , ΔH and ΔS respectively) were determined for the systems. At several temperatures ranging from 30 to

70°C with periods of 10°C, the worths of % eluting and K_d for dye systems were determined.

These studies were done for a mixture of 10 mL of 50 mg/L of nitrate solution was added to 0.1 g of adsorbent at pH 2. At constant temperature (25°C) the mixture was put in Shaking Water Bath. By examination of the contact time up to 200 min and compared with notional models the adsorption rate was monitored.

Chapter Three

Results and Discussion

3.1 Characterization of Modified magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan

3.1.1 TEM Characterization

Transmission Electron Micrographs of the graphene chitosan, magnetic graphene chitosan and multiwall nanocarbon tubes showed that magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan can be vigorously used as suitable adsorbents for eluting toxic ions. This adsorbent expounds a risen porous and rough nature as shown in figures (3.1-3.3).

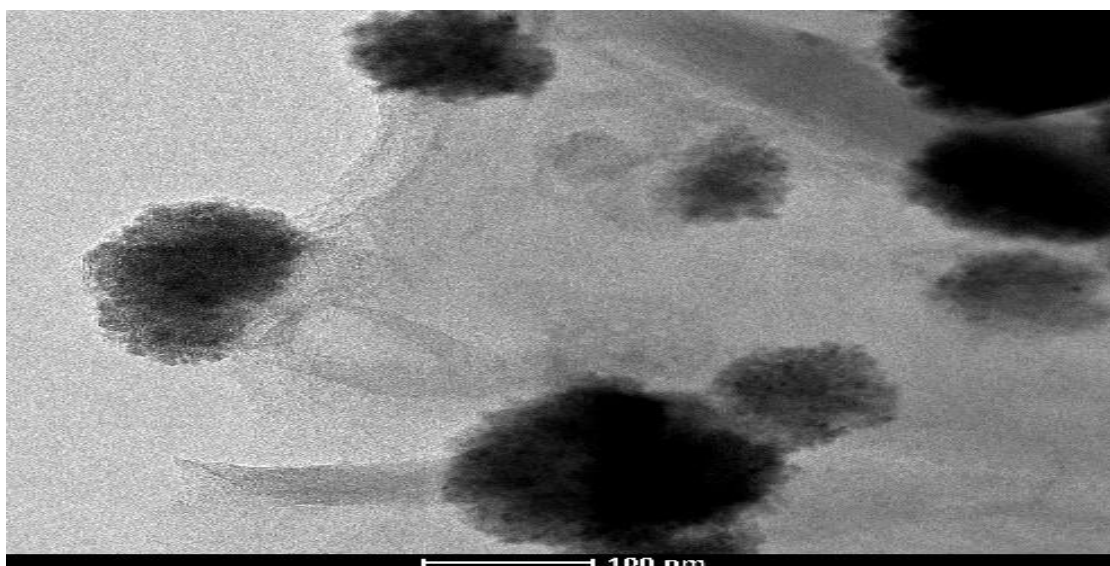


Figure 3.1: TEM photograph of graphene chitosan

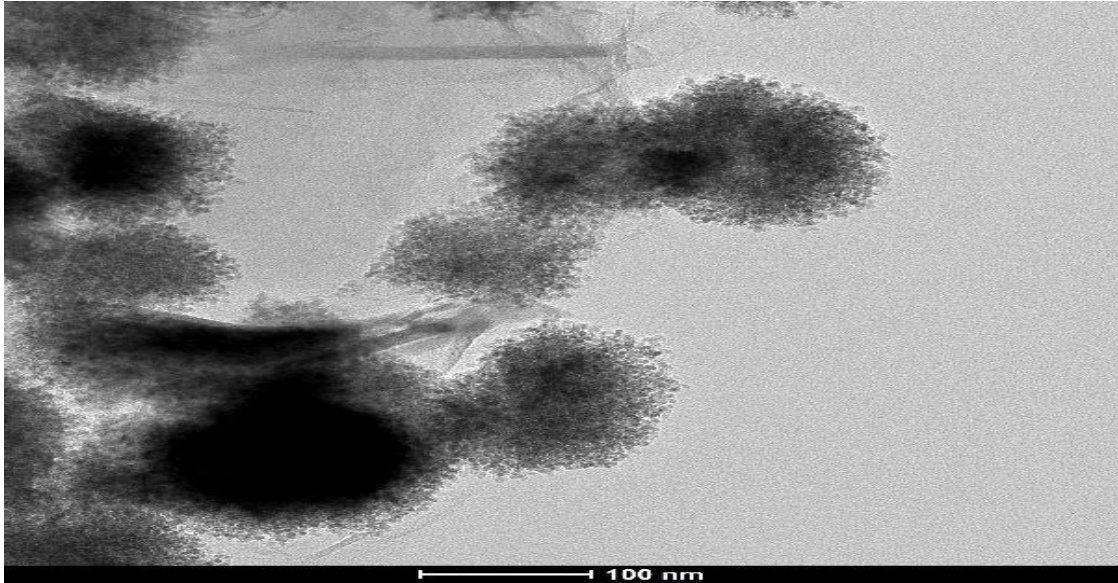


Figure 3.2: TEM photograph of magnetic graphene chitosan

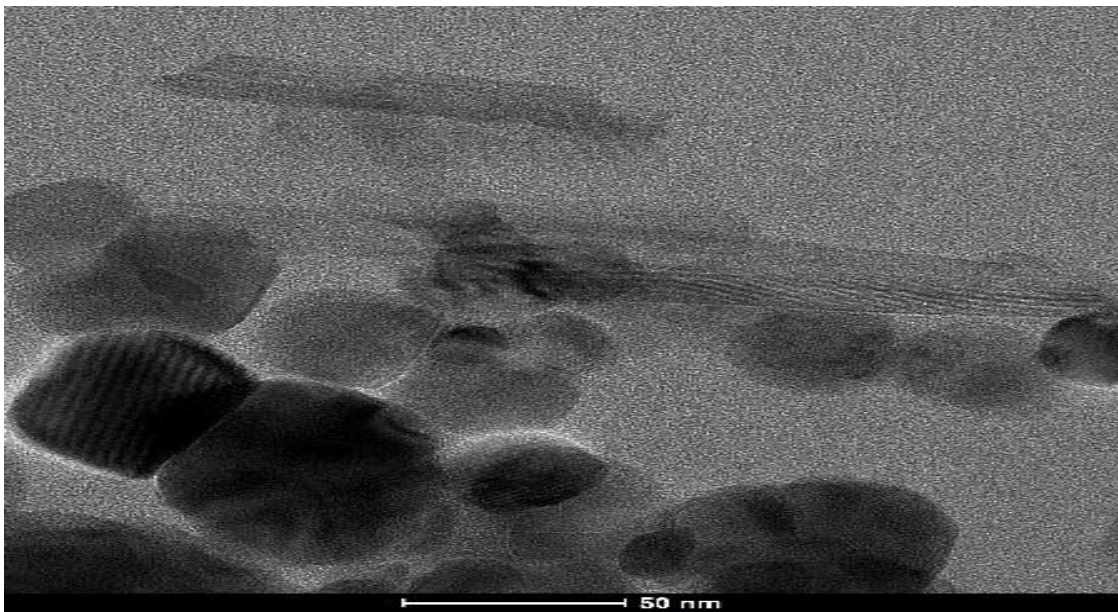


Figure 3.3: TEM photograph of multiwalled carbon nanotubes

3.1.2 XRD Characterization

For the graphene chitosan sample, the characteristic diffraction peak at 11.37° was appeared due to the amorphous character of chitosan. In the magnetic graphene chitosan sample, the peakes observed at 30.2° (220),

35.6° (311), 43.2° (400), 57.1° (511) and 62.7° (440) show the cubic inverse structure of Fe_3O_4 [79].

The peak between 20°-30° in the XRD spectra of CNT graphene magnetic sample was appeared due to presence of carbon.

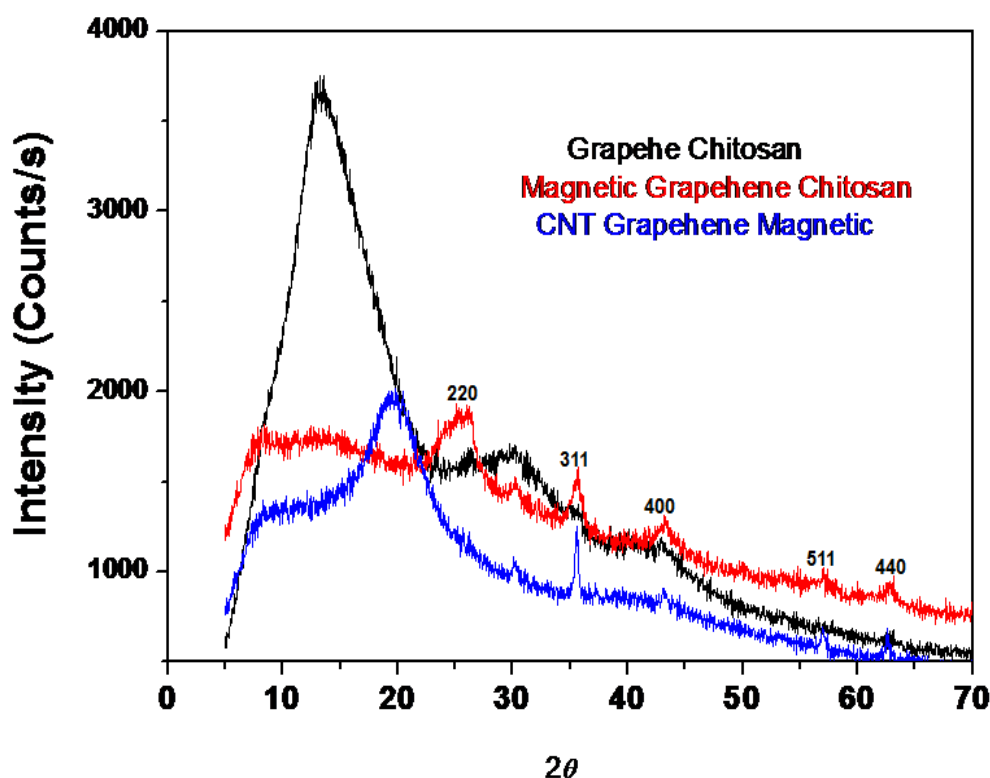


Figure 3.4: XRD spectrum of graphene chitosan, magnetic graphene chitosan and carbon nanotubes graphene magnetic.

3.1.3 Thermal Analysis

To investigate the thermal stability as well as the formation and purity of materials, thermogravimetric analysis (TGA) superinducing with the weight loss derivative curve (DTG) are used. It is a potent method to quantitatively appraise of the graphene chitosan and the multiwall

nanocarbon tubes samples. In figure 3.5 there is two major steps of degradation that were recorded for graphene chitosan. Firstly, from the room temperature to 250°C with mass loss of 9%. Secondly, between 300 – 700 °C a clear increase of 70% in mass. Furthermore, a small peak in the derivative curve at 275°C with the greatest rate of decomposition occurs at 460°C.

The multiwall nanocarbon tubes showed two clear steps of mass loss. Step 1: From 25-250°C rang and step 2: from 250-800°C rang. The greatest rate of decomposition occurs at 403°C.

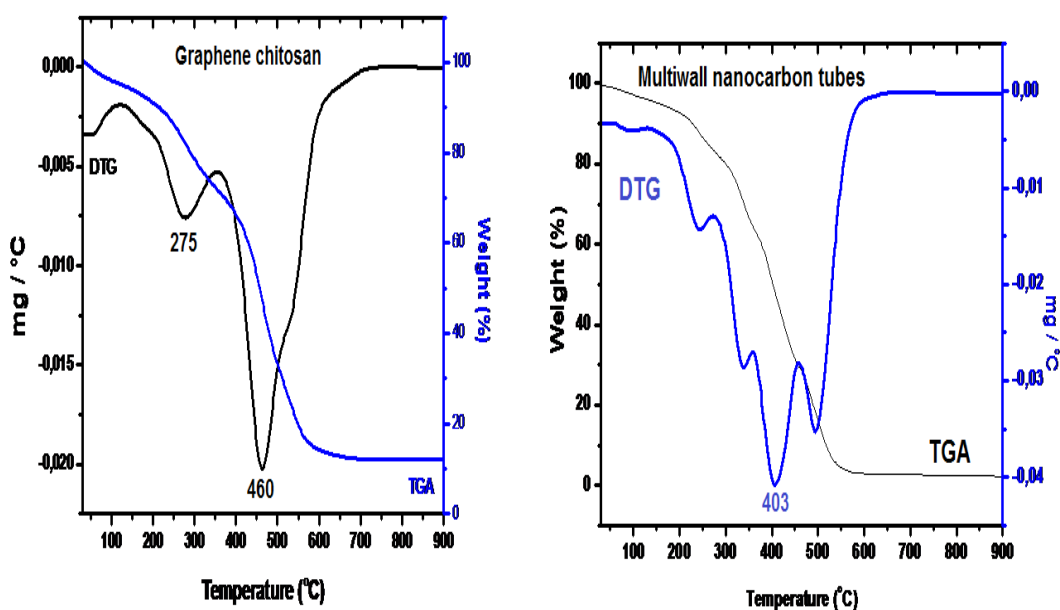


Figure 3.5: TGA and DTG curves of graphene chitosan and multiwall nanocarbon tubes samples.

3.1.4 FTIR Analysis

The graphene chitosan and multiwall nanocarbon tubes samples were checked up on FT-IR analysis. Figure 3.6 shows the broad band from 3000-3440 cm^{-1} in the FTIR spectrum of graphene chitosan (sample 1) was assigned to -NH bond. The absorption peak at 1710 cm^{-1} was because of C=O bond. The peak at 1310 cm^{-1} was because of C=C stretching vibration and at 1590 cm^{-1} was indicated to NH_2 . Moreover, C-O bond was obtained at 1035 cm^{-1} . In the FTIR spectrum of multiwall nanocarbon tubes (sample 2) the broad band from 3100-3450 cm^{-1} , peaks at 2850 cm^{-1} and 2935 cm^{-1} were indicated to O-H and C-H stretching vibration, consecutively. The absorption peak at 1710 cm^{-1} was because of C=O bond, the peak at 1590 cm^{-1} was indicated to C=C stretching vibration. Also, at 1242 cm^{-1} C-O stretching vibration was acquired.

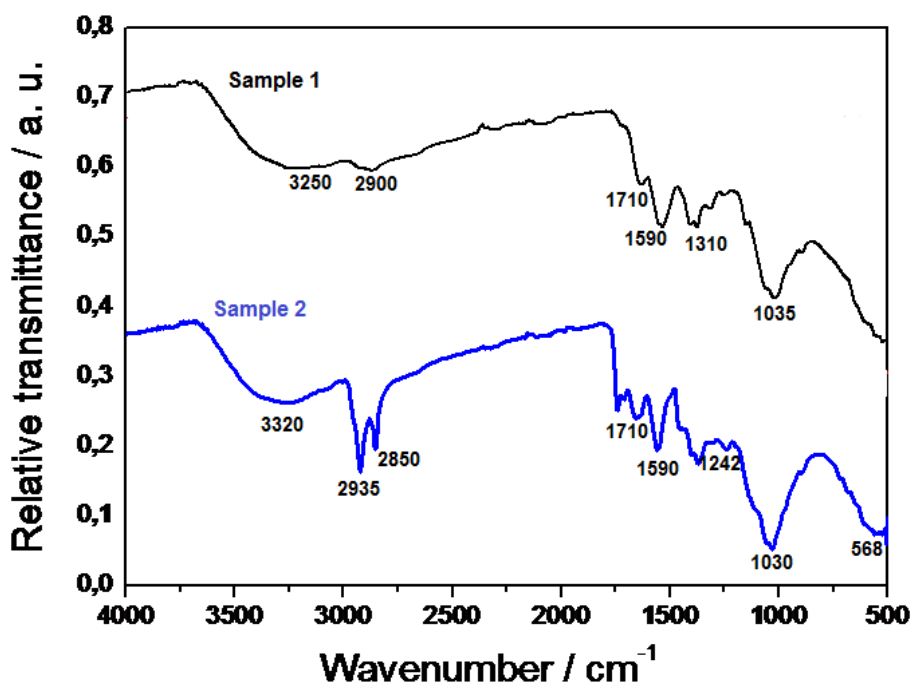


Figure 3.6: FTIR spectra of (sample 1) graphene chitosan and (sample 2) multiwall nanocarbon tubes.

3.1.5 Raman- Analysis

Raman spectroscopy is a widely used tool to characterize the structures of graphene chitosan (sample 1) and magnetic graphene chitosan (sample 2) as shown in Figure 4.7. Raman spectra of these samples shows a peak at 1335 cm^{-1} (D band) and peak at 1620 cm^{-1} (G band). The G and D bands correspond to sp^2 hybridized disordered carbon and sp^3 hybridized carbon respectively [80]. The relative intensities of the D and G bands ($I_D/I_G = 1.2$).

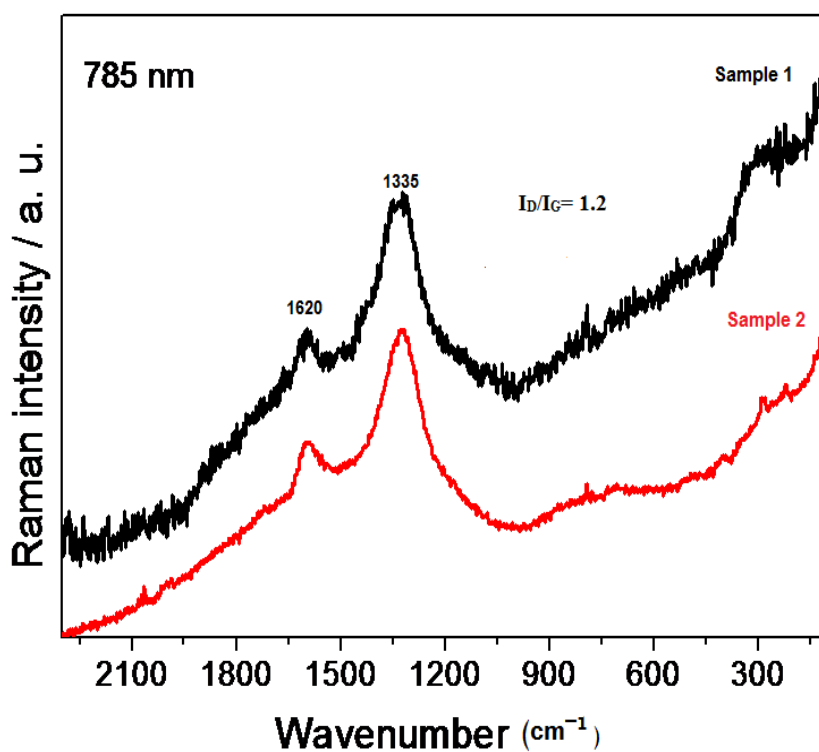


Figure 3.7: Raman spectrum of graphene chitosan and magnetic graphene chitosan samples.

3.2 Investigation of adsorption parameters

3.2.1 Effect of the pH Value

One of the more numerous significant parameters that is dominating the removal of nitrate ions from wastewater is pH value. The impact of pH value on NO_3^- eliminating effectively from wastewater samples shows in Figure 4.8. These tests were streamed at suboptimal contact times for magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent with diverging pH value of the solution.

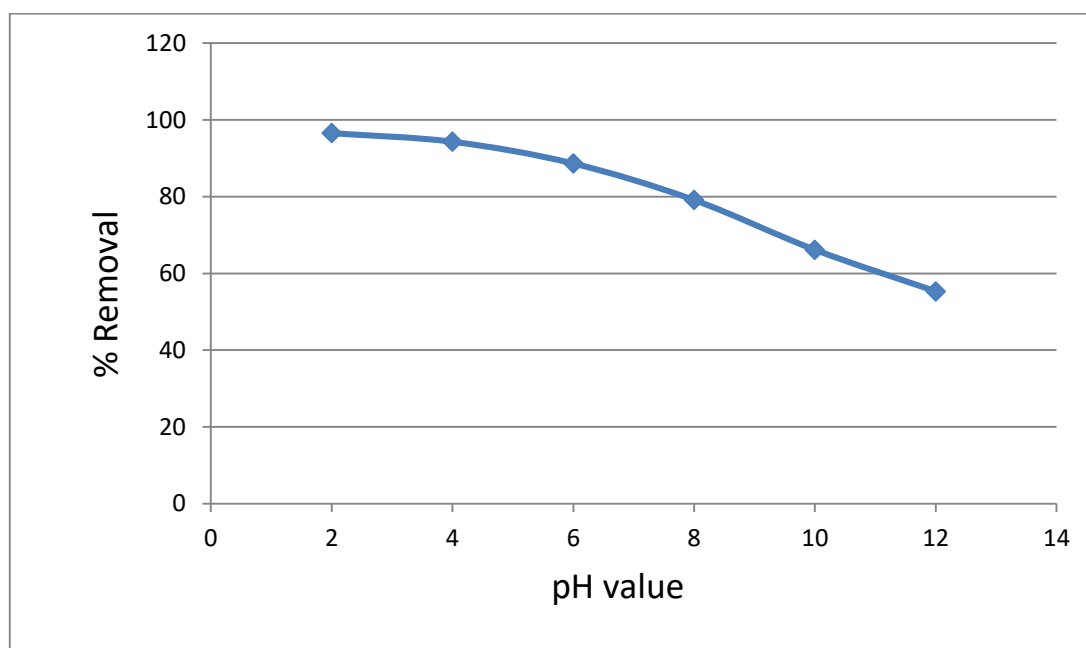


Figure 3.8: Impact of pH value on the adsorption operation of nitrate on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent (CI = 50 ppm, contact time = 50 min., volume of wastewater = 10 mL, temperature = 25°C and adsorbent dose = 1 mg).

In this study at low pH there was rise of the adsorption capability for NO_3^- . The adsorbent of magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan has the maximum amount of NO_3^- removal that is 96.54% at the maximum pH = 2. This behavior is due to the excess of protons in solution at this value of pH. This increases the number of positively freighted sites on adsorbent surface, which favor the adsorption of the nitrate anions onto the adsorbent surface due to electrostatic attraction to each other. The acid-base interaction between base nitrate and acid on the surface of the adsorbent also favors adsorption. While in other studies the percentage of nitrate removal was 79.5% at optimum pH = 5 by employing modified granular activated carbon at 25°C [81]. Also, the percentage of nitrate removal was 87% at pH = 7 by employing functionalized carbon nanotube sheets at 25°C [82].

3.2.2 Effect of temperature on nitrate adsorption

Temperature acts a critical parameter in every type of adsorption operations. Adsorbent and nitrate interplay temperature was appeared in Figure 3.9. This figure shows that rising in temperature above to the room temperature (25°C) has impact on reducing the adsorption capability of adsorbent surface. Reduce in eluting percentage maybe due to reduction of the physical forces of attraction between the adsorbent and nitrate ion.

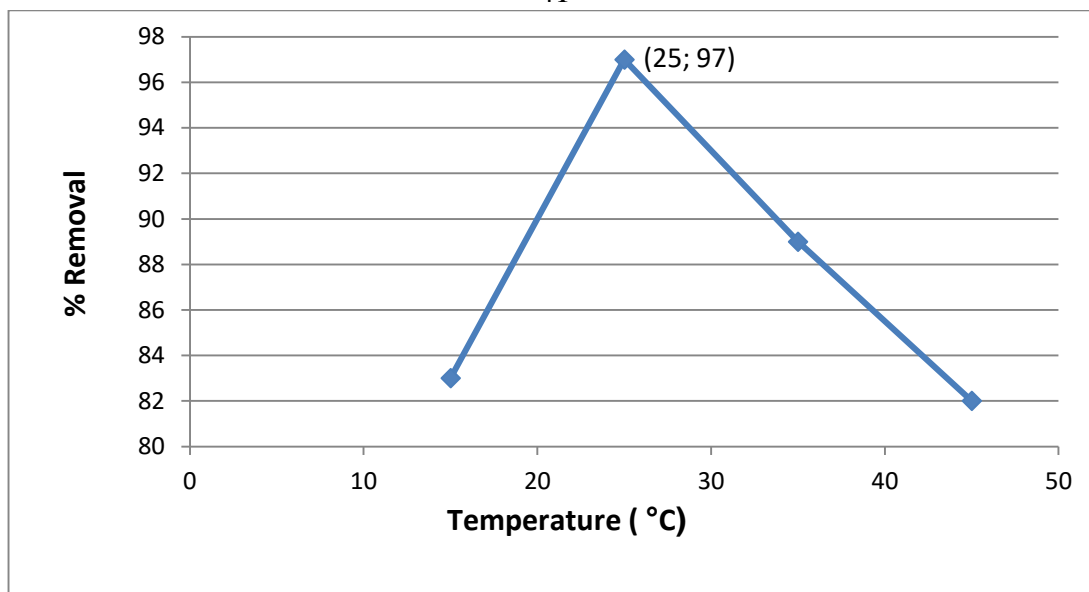


Figure 3.9: Impact of the value of temperature on the adsorption operation of nitrate on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent (Concentration of NO_3^- = 50 ppm, contact time = 50 min., volume of wastewater = 10 mL, pH = 2 and adsorbent dose = 1 mg).

3.2.3 Effect of the concentration of nitrate

The impact of the concentration of nitrate on adsorption capability was studied over wide range of nitrate concentration with conserving other factors like quantity of adsorbent, volume of solution, adsorbent size, and solution pH as constant. Figure 3.10 shows that as the NO_3^- concentration increases from 30-260 mg/L, the adsorption capability is rising from 9-68 mg/g. This may be due to gradual rise in the electrostatic attraction between nitrate ions and the absorbent desired active sites. While in the study of nitrate removal by employing powder activated carbon and carbon nanotubes at optimum pH = 5, contact time = 60 min and temperature =

25°C the adsorption capacity of AC was 10 mmol/g and the adsorption capacity of CNT was 25 mmol/g [83].

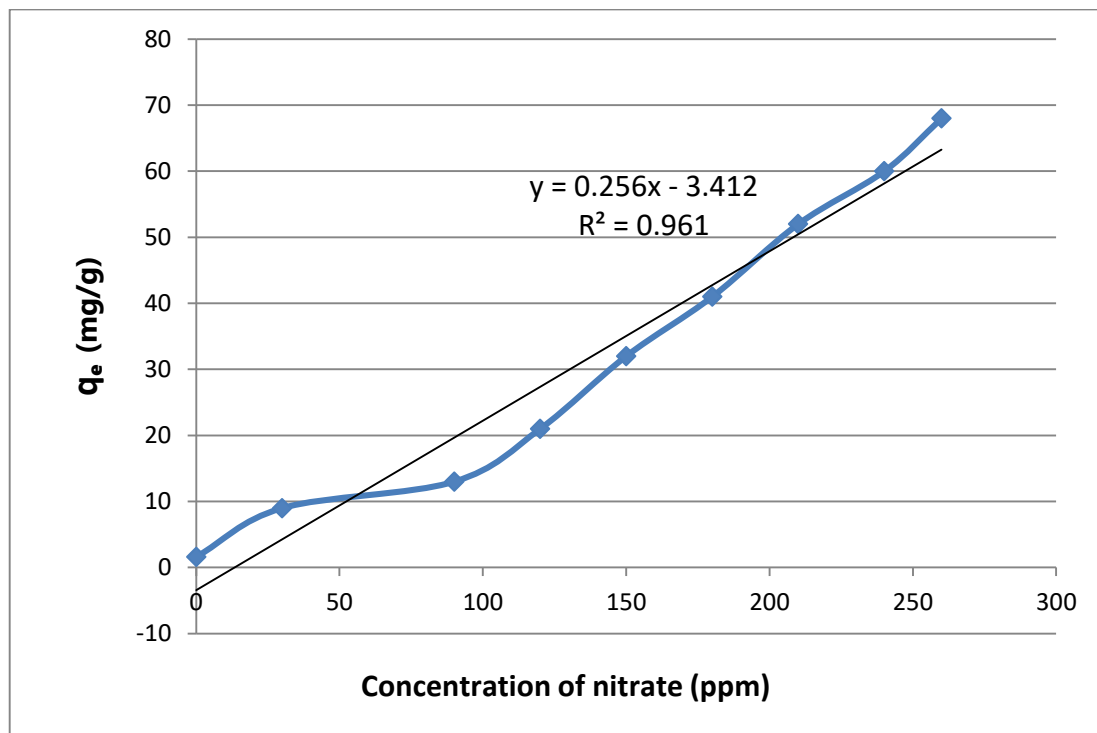


Figure 3.10: Impact of the concentration of nitrate on adsorption capacity of nitrate ion on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent. (Temperature = 25°C, time = 50 min., pH = 2, sol. Volume = 10 mL, adsorbent dose = 1 mg).

3.2.4 Effect of the amount of the adsorbent dosage

Impact of the quantity of adsorbent on the eluting of nitrate ion were studied whereas, the initial concentration of nitrate solution was conserved constant at 50 ppm also, volume of wastewater sample was 10 mL, pH was 2 and temperature was kept at 25°C. The consequences were appeared in Figure 3.11 that shows the eluting effectivity of nitrate ion was risen with rising amount of adsorbent untill 250 mg. After that, the eluting effectivity

was not changed noticeably with rising amount of adsorbent. It shows that eliminating effectively was 97.25% at 250 mg of dosage. While for 300 mg was 98.7%, 99.1% for 400 mg and 99.2 for 500 mg. The adsorption efficiency was increased because of the risen in the number of adsorption sites [84]. Consequently, %removal of nitrate ion accessed in equilibrium with quantity of 250 mg of adsorbent.

The eluting effectiveness of nitrate ion was determined by employing this equation:

$$\text{Eluting effectively (\%Removal)} = \left[\frac{(C_o - C_e)}{C_o} \right] \times 100$$

While, C_o assigned to concentration of nitrate ion in the sample solution of wastewater before treatment and C_e assigned to concentration of nitrate ion in the sample solution of wastewater after treatment. Eluting effectively also can be determined by employing of the absorbance of amount of the nitrate ion in the solution sample of wastewater ahead of tackling A_o and absorbance of the amount of the nitrate ion in the solution sample of wastewater later of tackling A_e rather than C_o and C_e consecutively.

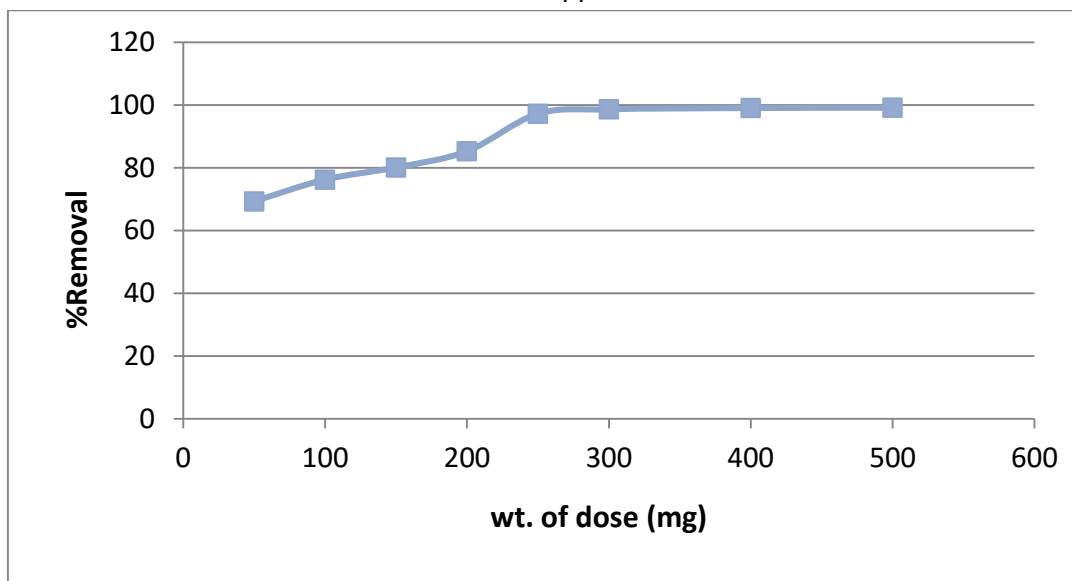


Figure 3.11: Impact of amount of magnetic multiwalled nanocarbon tubes (MWCNTs) functionalized with chitosan adsorbent on the removal of nitrate ion in wastewater sample. (Temp. = 25°C, time = 50 min., pH = 2, conc. Of nitrate solution = 50 mg/L, sol. Volume = 10 mL and contact time = 50 min.).

3.2.5 Effect of contact time

Adsorption capacity of NO_3^- on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan was determined as a function of contact time to determine the optimum time of adsorption at constant pH, concentration of nitrate ion, amount of dosage and temperature as shown in Figure 3.12.

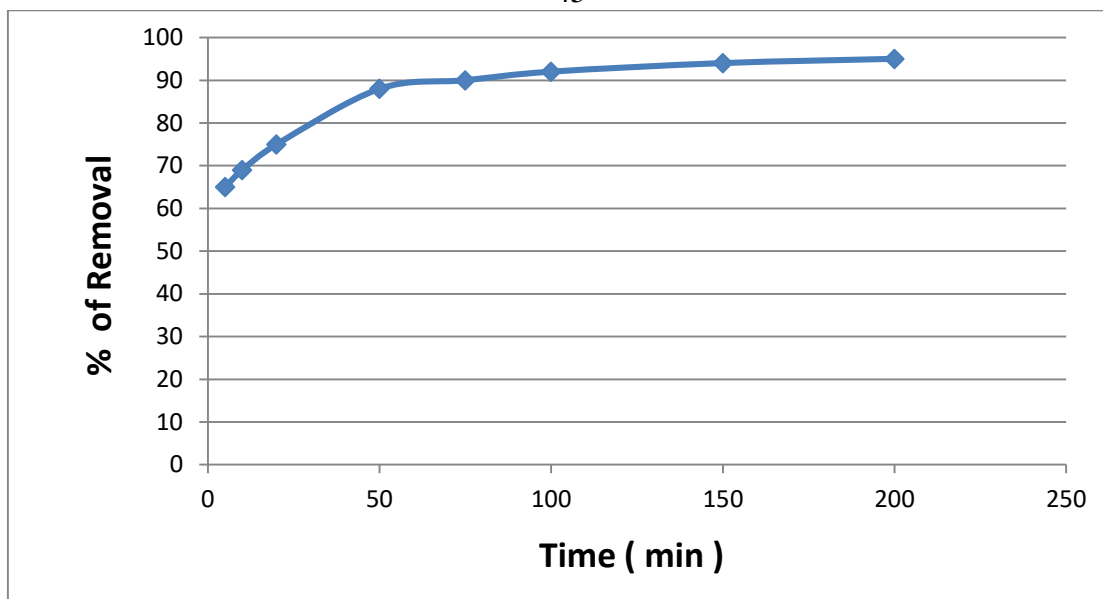


Figure 3.12: Impact of the contact time on the adsorption of NO_3^- on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan (CI = 50 ppm, temperature = 25°C , volume of wastewater = 10 mL, pH = 2, adsorbent dose = 1 mg).

The removal of NO_3^- from wastewater on magnetic multiwalled nanocarbon tubes (MWCNTs) functionalized with chitosan was 88% at the optimum of contact time 50 minutes. Moreover, the residual concentration of the nitrate ion after suboptimal contact time become roughly constant and the rise percent of NO_3^- removal was because of the rise availability of vacant positions on the adsorbent surface.

3.3 Adsorption isotherm of nitrate

Techniques of the adsorption isotherm are discriminated by some constant worths, that determine the characteristics and attraction of the adsorbent surface and can be employed to lookup the optimum adsorption capability. By using commonly known adsorption models the equilibrium data can be analyzed. The main suitable isotherm models to determine empirical

adsorption operation factors are the Langmuir, Freundlich and Temkin models [85].

3.3.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm prescribes quantitatively data for a single layer of adsorbate on the adsorbent upper surface without more adsorption takes position. Moreover, this isotherm is benefit for single layer adsorption upper the surface includes a limitable number of congruous positions and the model supposes standardized energies of adsorption upper the surface with no relocation of adsorbate in the surface plane. A common linear plot of the Langmuir model equation can be determined by the subsequent equation:

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

While, C_e assigned to the concentration of nitrate ion at equilibrium (ppm), q_e assigned to the quantity of nitrate adsorbed in mg per mass of the adsorbent in gram (mg/g), q_m assigned to the optimum single layer coverage capability (mg/g) and K_L is the constant of Langmuir adsorption isotherm model (Litre/mg).

The worths of q_m and K_L were calculated from C_e/q_e versus C_e plot where, slope = $1/q_m$ and intercept = $1/q_m K_L$ as shown in figure 3.13, quantity adsorbed for single layer data (q_m), constant of Langmuir adsorption-desorption at equilibrium (K_L) and regression constant (R^2) were determined and values are shown in Table 3.1.

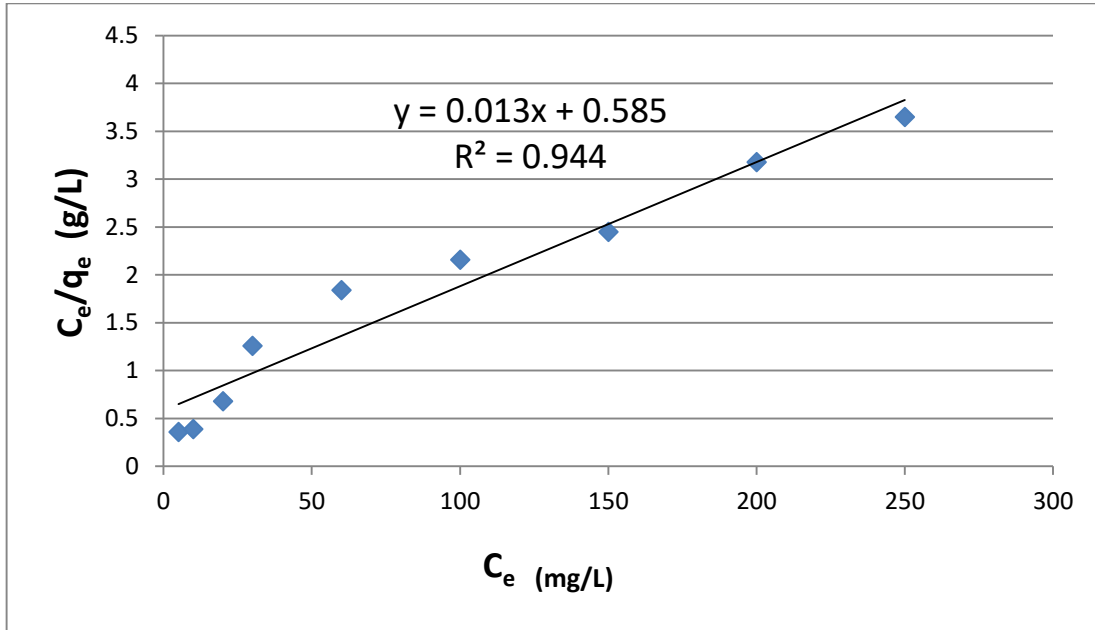


Figure 3.13: Langmuir plot for nitrate adsorption on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan. (Solution volume = 10 mL, quantity of adsorbent = 250 mg, time = 50 min, Temperature = 25°C, pH = 2).

Table 3.1: Langmuir adsorption isotherm model correlation coefficient and parameters for adsorption operation of nitrate onto magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent .

parameters of Langmuir isotherm model				
Adsorbant	Parameters			
	q_m [mg/g]	K_L [L/mg]	R_L	R^2
Magnetic (MWCNTs) functionalized with chitosan	76.9	0.02	0.47	0.944

The Langmuir isotherm characteristics can be determined by the proportion constant separation parameter R_L that is shown in this subsequent equation:

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

While, C_o assigned to the maximal inchoate concentration of nitrate ion adsorbate (mg/Litre).

The value of R_L assigned to the form of the isotherm. The adsorption operation is unfavorable when R_L more than one whereas, the adsorption operation is linear when R_L equals one, while favorable adsorption operation at ($0 < R_L < 1$) and irreversible adsorption operation if R_L equals zero. When R_L value ranging from 0 to 1 that refers to suitable adsorption. However, value of R_L was determined to be 0.47 at 25°C showing that the adsorption of NO_3^- is favorable.

3.3.2 Freundlich model Isotherm

This model isotherm equation used to prescribe heterogeneous systems. The parameters of this model were determined by the subsequent equation:

$$Q_e = K_F C_e^{1/n}$$

This equation can be written as the linear shape by the subsequent equation:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F$$

Constants K_F and n are Freundlich invariables while K_F is assigned to the adsorption capability of the adsorbent, n giving a mention to favorability of the adsorption operation and $1/n$ magnitude of the exponent gives a mention to the preference of adsorption too. When value of $1/n$ is smaller than one it beckons to the natural adsorption operation. Where n locates from one to ten, this beckons to the favorable sorption operation [86]. The

constants K_F and n could be determined from the linear plot of the equation may be employed to forming a graph of $\log Q_e$ versus $\log C_e$ as appeared in Figure 3.14:

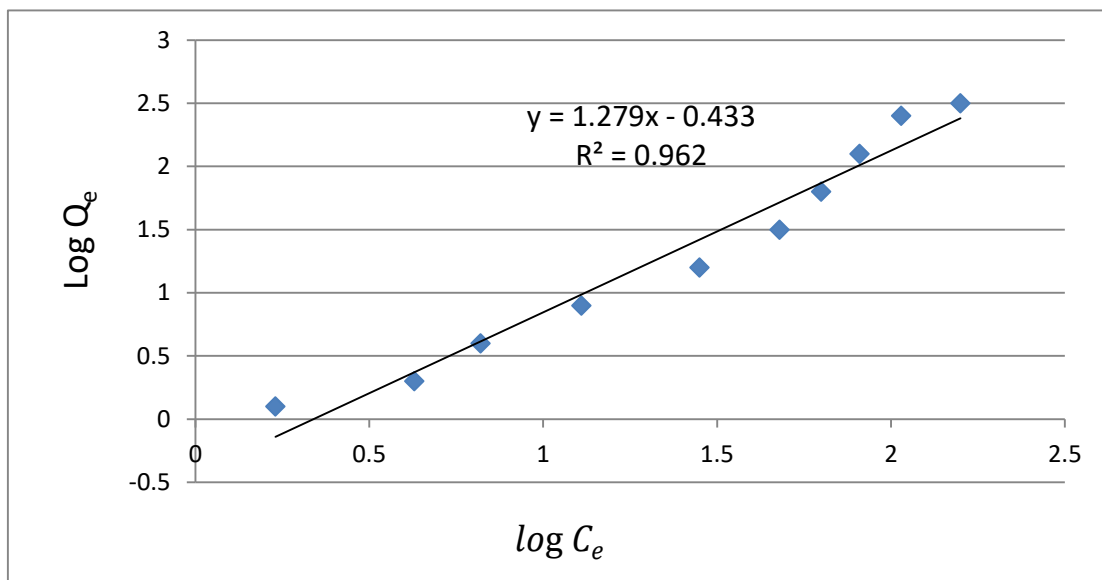


Figure 3.14: Freundlich plot for nitrate adsorption operation on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan. (Solution volume = 10 mL, adsorbent dose = 250 mg, time = 50 min., Temperature = 25°C, pH = 2).

Freundlich constants K_F , n value and regression constant (R^2) were measured and the worths are appeared in Table 3.2:

Table 3.2: Freundlich isotherm model correlation coefficient and parameters for adsorption operation of nitrate on magenatic (MWCNTs) functionalized with chitosan.

Parameters of Freundlich isotherm model				
Adsorbant	Parameters			
	1/n	n	K_F [mg/g (L/mg) ^{1/n}]	R^2
Magnetic (MWCNTs) functionalized with chitosan	1.279	0.78	0.37	0.962

The constants n and K change to reflect the experiential noting that the amount of the adsorbed increases more lingeringly and higher pressures are needed to saturate the surface when the temperature increases [80]. Table 3.2 shows that $1/n$ value = 1.279 while $n = 0.78$ adverting that the sorption of nitrate on magnetic (MWCNTs) functionalized with chitosan adsorbant is suitable and the R^2 value is 0.962.

Table 3.3: Freundlich and Langmuir isotherm models correlation coefficients and parameters for adsorption operation of nitrate on magenatic (MWCNTs) functionalized with chitosan.

parameters of Langmuir isotherm model				
Adsorbant	Parameters			
	q_m [mg/g]	K_L [L/mg]	R_L	R^2
Magnetic (MWCNTs) functionalized with chitosan	76.9	0.02	0.47	0.944
parameters of Freundlich isotherm model				
adsorbant	Parameters			
	n	$1/n$	K_F [mg/g (L/mg)^{1/n}]	R^2
Magnetic (MWCNTs) functionalized with chitosan	0.78	1.279	0.37	0.962

The adsorption information were calculated by Freundlich and Langmuir adsorption isotherms. The value of R_L determined by Langmuir isotherm information in Table 3.3 was 0.47 at 25°C while $n = 78$ denoting that adsorption of nitrate at magnetic MWCNTs functionalized with chitosan is preferred with $R^2 = 0.944$.

From Freundlich isotherm information in table 3.3, the value of $1/n = 1.279$ showing that adsorption of nitrate at magnetic MWCNTs functionalized with chitosan is preferred with $R^2 = 0.962$. Lower limit value of $1/n$ shows stronger interact relationship between the adsorbate and adsorbent. Where $1/n$ come close to zero the surface discrepancy gets more [87]. The adsorption information apposite with Freundlich and Langmuir, but Freundlich adsorption model determined to be with high one worth of R^2 that mean this modle more opposite. Moreover, the Freundlich model suit further with the empirical information of adsorption assigned to physical adsorption also heterogeneon mode dispensation of adsorbate active sites at the adsorbent surface [88].

2.4 Adsorption Thermodynamics

Using the thermodynamic equilibrium coefficients acquired at several concentrations and temperatures in order to underscore possible adsorption thermodynamics mechanisms. Thermodynamic parameters using to study adsorption of NO_3^- by magenatic (MWCNTs) functionalized with chitosan such as ΔG (Gibbs free energy change) were evaluated using this equations:

$$\Delta G = -RT \ln K_d$$

While, K_d assigned to the distribution coefficient of adsorption in gram per litre unit. Gibbs free energy (ΔG) equals the teams between the adsorption enthalpy (ΔH) and adsorption entropy (ΔS) multiplied by the

temperature (T) according to thermodynamics. Therefore, the parameters of thermochemical reaction ΔH and ΔS can be calculated by employing Van't Hoff's form (Figure 3.15):

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

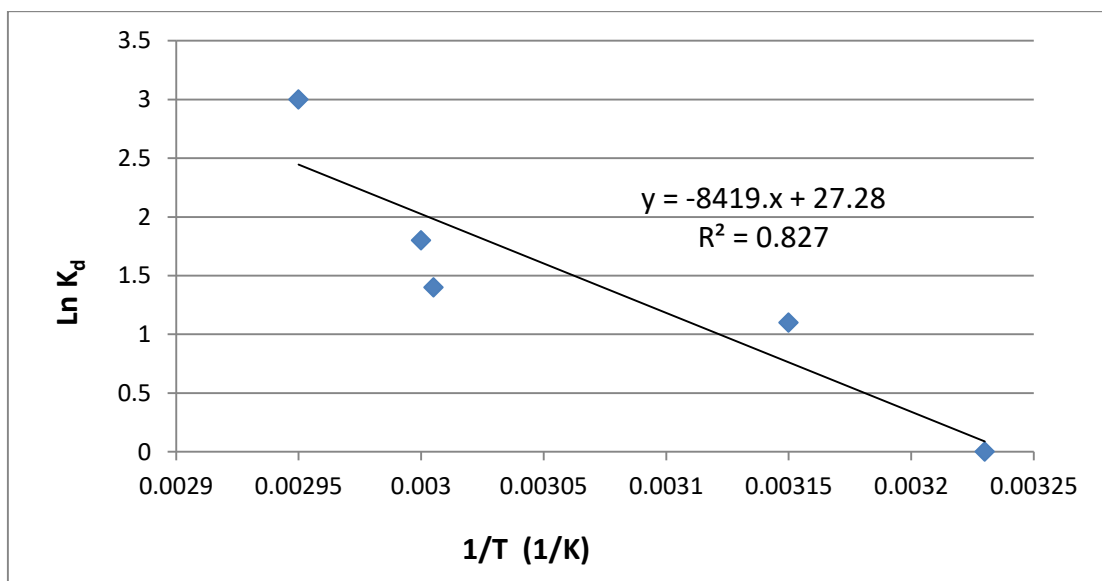


Figure 3.15: Plot of Van't Hoff's by $\ln K_d$ versus $1/T$ for nitrate adsorption onto magnetic (MWCNTs) functionalized with chitosan. (Temp. = 25°C, adsorbent dose = 250 mg, time = 50 min., sol. Volume = 10 mL, pH = 2).

From the $\ln K_d$ versus $1/T$ linear plot ΔH° and ΔS° were evaluated whereas, the slope = $-\Delta H^\circ/R$ and the intercept = $\Delta S^\circ/R$. The results assigned to the enthalpy of adsorption ΔH° was 69.995 kJ/mol while ΔS° was 227 J/mol K. Also, ΔG° was determined at several temperatures by this subsequent equation:

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

The earned thermodynamic values are shown in Table 3.5.

Table 4.5: Thermodynamic values of nitrate adsorption onto magenatic (MWCNTs) functionalized with chitosan at several temperatures.

ΔH° [KJ/mol]	ΔS° [J/mol.K]	ΔG° [KJ/mol]				
		303[K]	313 [K]	323 [K]	333[K]	343 [K]
69.995	227	1.214	-1.056	-3.326	-5.596	-7.866

ΔG° negative values denoted to the adsorption operation is spontaneous under previous temperatures. The value of $\Delta H^\circ > 0$ commutates an endothermic adsorption and denoted to the sorption process is preferred under room temperature. The enthalpy difference value ΔH for chemical adsorption is commonly higher than physical adsorption one. Exemplarly, ΔH for chemical adsorption ranging from 40 to 800 KJ mol⁻¹ compared with physical adsorption vary from 0 to 40 KJ mol⁻¹. The value of ΔH was larger than those comparably with physical adsorption. That means the adsorption operation is chemical. The positive value of entropy ΔS° means that the wantonness at the solid/liquid interface in the adsorption system rises during the operation of adsorption and some structural differences occur on the adsorbent [89].

3.5 Adsorption kinetics of Nitrate

Adsorption kinetics model study is significant as it retrofits assess foresights into the reaction mechanism and the reaction path ways. The rate of adsorption was proctored by threshing the contact time get to two hours and comparable with theoretical models. Pseudo second order, pseudo first

order and Intra-Particle Diffusion adsorption kinetic models were assayed in this work where the empirical information earned for several contact time were employed.

Rate constant for the adsorption of nitrate from wastewater onto magnetic (MWCNTs) functionalized with chitosan adsorbant was determined employing the Lagergren equation (pseudo first order equation) represents as:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t$$

While, Q_e assigned to the quantity of NO_3^- adsorbed at equilibrium in mg unit per weight of adsorbent in gram, Q_t assigned to the quantity of NO_3^- adsorbed in every time in mg unit per weight of adsorbent in gram and K_1 assigned to the rate constant of the Lagergren equation (min^{-1}).

A linear form of the Lagergren equation between $\log (Q_e - Q_t)$ Vs time helps to access the rate constant Figure 4.16. Lagergren's equation is suitable to nitrate adsorption on (MWCNTs) functionalized with chitosan adsorbant if the graph was found to be linear with suitable correlation coefficient. Therefore, the adsorption operation undergo by the pseudo first order operation. The rate constant K_1 and Q_e of the Lagergren's first order calculated from the model are showed in Table 3.5 with the corresponding correlation coefficients.

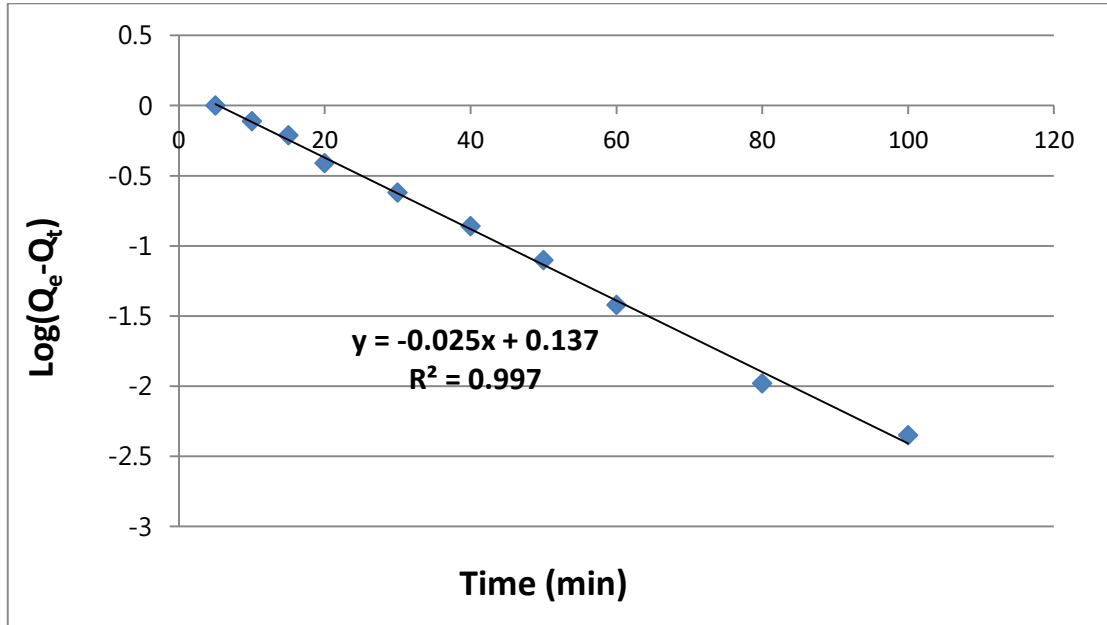


Figure 3.16: Scheme of pseudo first order adsorption kinetics model of nitrate on magenatic (MWCNTs) functionalized with chitosan. (Temp. = 25°C, adsorbent dose = 250 mg, sol. Volume = 10 mL, pH = 2).

A linear form of pseudo second order kinetics could be showed in an integrated second order rate law:

$$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{K_2 Q_e^2}$$

Where, K_2 assigned to the rate constant of the pseudo second order ($\text{g mg}^{-1} \text{min}^{-1}$). The consequences appear that the pseudo second order adsorption kinetic model is never ideally to the empirical information with linear regression coefficients 0.982 as shown in Figure 3.17.

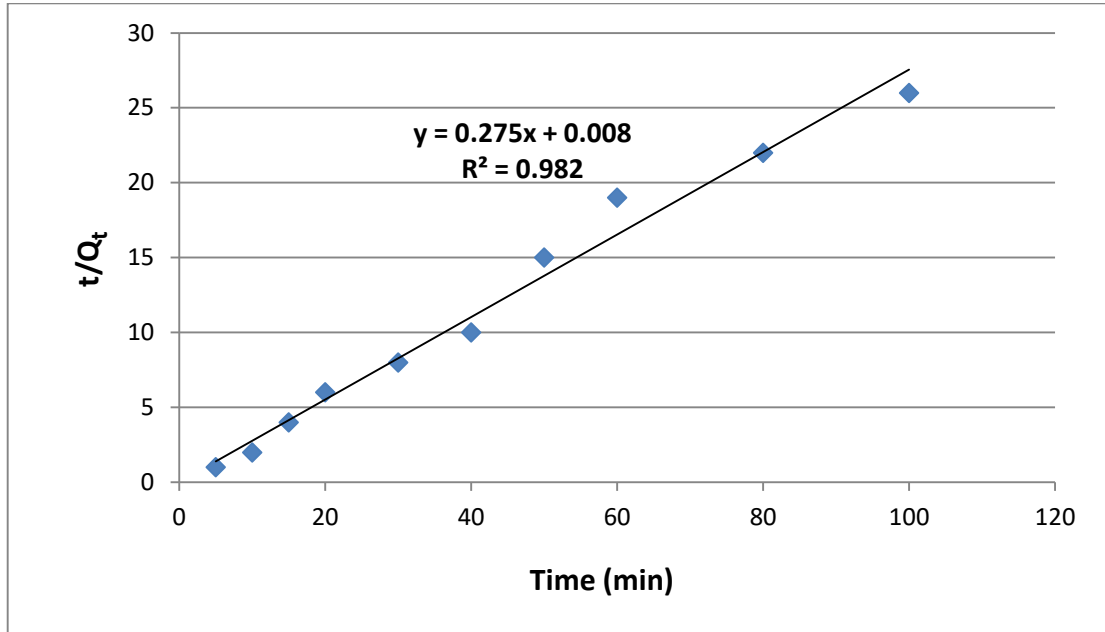


Figure 3.17: Scheme of pseudo second order adsorption kinetics of nitrate on magnetic (MWCNTs) functionalized with chitosan. (Temp. = 25°C, conc. Of NO_3^- = 50 ppm, sol. Volume = 10 mL, adsorbent dose = 250 mg and pH = 2).

Figure 3.18 shows intra-particle diffusion kinetic model acting by this equation:

$$q_t = K_p t^{1/2} + C$$

Where, K_p assigned to the diffusion rate constant that equal 0.25 $\text{mg/g.min}^{1/2}$ and C equal 1.857 mg/g .

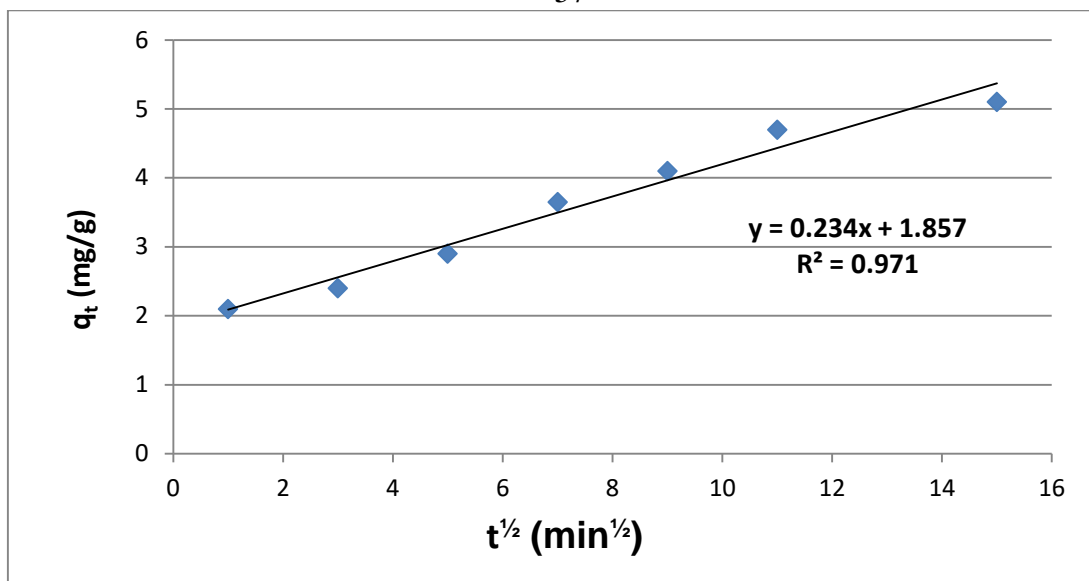


Figure 3.18: Scheme of Intra-particle diffusion kinetic model for the adsorption of nitrate on magnetic (MWCNTs) functionalized with chitosan, (volume = 10 mL, adsorbent dose = 250 mg, temperature = 25°C, pH = 2 and Conc. Of NO_3^- = 50 ppm).

According to the values of the correlation coefficient employing in the last kinetic models, the sorption of nitrate subordinated to the model of pseudo first-order kinetic because the worth of R^2 in this kinetic model is roughly one. Furthermore, the calculation value of Q_e in the first-order kinetic model closed to the experimental value (1.7 mg/g).

Table 3.5: Intra-particle diffusion, pseudo second order and pseudo first order kinetic model parameters for nitrate sorption on magnetic (MWCNTs) functionalized with chitosan.

Intra-particle diffusion			Pseudo second order			Pseudo first order		
C [mg/g]	K _p [mg/g. min ^{1/2}]	R ²	K ₂ [g/mg min]	Q _{e(calc)} [mg/g]	R ²	K ₁ [min ⁻¹]	Q _{e(calc)} [mg/g]	R ²
1.857	0.234	0.971	9.43	3.64	0.982	0.057	1.37	0.997

3.6 Recovery of nitrate and reusability of the adsorbent

Recovery of nitrate from the adsorbent was achieved at room temperature. The first step was filtration to collect the adsorbent. The second step was washing the adsorbent with 6M of HCl then washing with deionized water, and finally left the adsorbent to desiccate at room temperature for three days. 100 mg of the regenerated adsorbent was added to a 10 mL of 50 ppm of nitrate solution at pH 2 in order to compare the adsorption capability of the regenerated adsorbent with fresh adsorbent. Figure 3.19 shows small variations between the amount of nitrate ion eluting after the first to the six regeneration of adsorbent as shown in this plot. This is strong evidence that the magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan adsorbent can be used for several times.

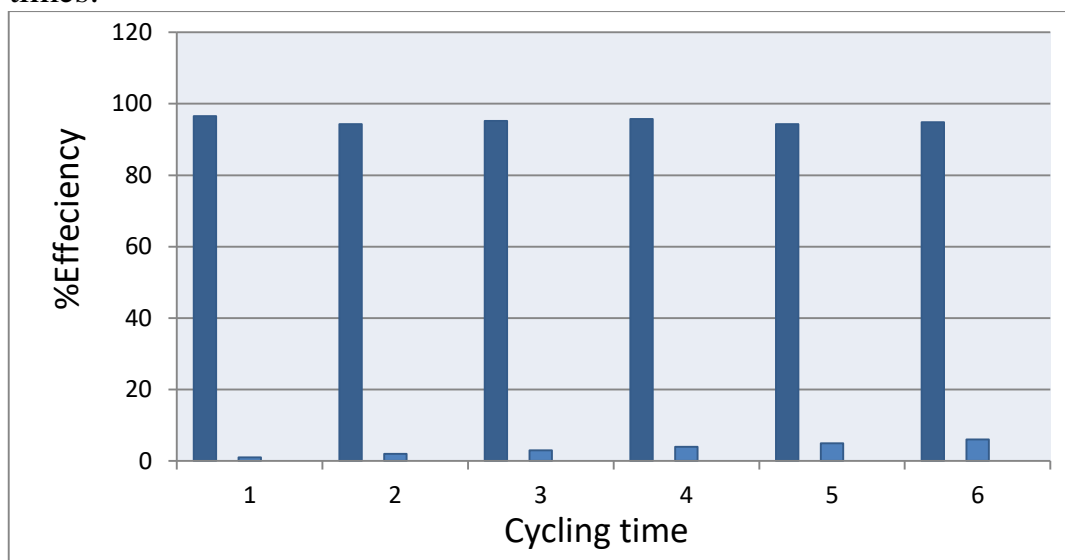


Figure 3.19: The impact of the adsorbent recycle on the adsorption process of the nitrate ion on magnetic multiwalled carbon nanotubes (MWCNTs) functionalized with chitosan (contact time = 5 min, temperature = 25°C, volume of wastewater = 10 mL, pH = 2, adsorbent dose = 100 mg and Conc. Of NO_3^- = 50 ppm).

Conclusions

1. Magnetic MWCNTs functionalized with chitosan removed successfully NO_3^- from wastewater and it was recyclable for a promising degree.
2. By Lagergren pseudo first order model the values quantity of nitrate adsorbed per unit mass of adsorbent are determined, $Q_e(\text{calc.})$ closed to the empirical value, $Q_e(\text{exp.})$ indicating that the chemical adsorption might be the rate limiting step where valence forces are included via electrons subscribing or interchange between the adsorbent and the nitrate ion.
3. By Freundlich isotherm model adsorption conduct of adsorbent is described, and the results assigned to single layer type exothermic adsorption operation includes in the system. Also, Freundlich adsorption model was determined to have the high one regression value (0.962) and hence the best suit. Freundlich isotherm consists a parameter that is taking into account of adsorbent–adsorbate interacts which assigned to exist this interact. Whereas, value of $1/n = 1.279$ and $n = 0.78$ assigned to the sorption of nitrate is favorable.
4. The negative ΔG° values (1.214 to $-7.866 \text{ KJ mol}^{-1}$) assigned to the adsorption is suitable and spontaneous under selected temperatures.
5. The positive value of ΔH° ($69.995 \text{ KJ mol}^{-1}$) indicates to an endothermic adsorption reaction and assigned to the adsorption is suitable under room temperature. The value of ΔH in chemical adsorption was more than those corresponding to physical adsorption.

This means that the adsorption operation is chemical process in normal.

6. ΔS° positive value ($0.227 \text{ J mol}^{-1} \text{ K}^{-1}$) assigned to some structural differences occur onto the adsorbent and the wantonness in the solid/liquid interface of the adsorption system increases during the adsorption operation.
7. Over 97.25% removal efficiency of NO_3^- was achieved after 50 min. at $\text{pH} = 2$ and temperature 25°C , 250 mg weight of dose and initial concentration of 50 mg/L Cr (VI) solution.

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Appendix

Data Tables of Experiments

Effect of temperature

Temp. (°C)	%Removal
15	83
25	97
35	89
45	82

Effect of pH

pH	%Removal
2	96.54
4	94.32
6	88.65
8	79.13
10	66.15
12	55.32

Effect of contact time

Time (min.)	% Removal
5	65
10	69
20	75
50	88

75	90
100	92
150	94
200	95

Effect of amount of adsorbent

Dosage (g)	%Removal
0.3	72
0.5	78
0.8	85
1.0	87
1.2	93
1.4	93.5
1.6	93.7

Effect NO_3^- concentration

C_e (mg/L)	Q_e (mg/g)
0	1.6
30	9
90	13
120	21
150	32
180	41
210	52
240	60

260	68
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Adsorption isotherm of NO_3^-

C_e (mg/L)	C_e/q_e (g/L)	$\text{Log}C_e$	$\text{Log}q_e$
5	0.36	0.1	0.23
10	0.39	0.3	0.63
20	0.68	0.6	0.82
30	1.26	0.9	1.11
60	1.84	1.2	1.45
100	2.16	1.5	1.68
150	2.45	1.8	1.80
200	3.18	2.1	1.91
250	3.65	2.4	2.03

Adsorption kinetics

t (min)	$\text{Log}(q_e - q_t)$
5	0.0
10	- 0.11
15	- 0.21
20	- 0.41
30	- 0.62
40	- 0.86
50	- 1.1
60	- 1.42
80	- 1.98
100	- 2.35

t (min)	t/q _t (min. g/mg)
5	1
10	2
15	4
20	6
30	8
40	10
60	19
80	22
100	26

t ^{1/2} (min) ^{1/2}	Q _t (mg/g)
1	2.1
3	2.4
5	2.9
7	3.65
9	4.1
11	4.7
15	5.1

Recovery of adsorbent

Recycle time	%Removal
First use	96.5
First regeneration	94.3
Second regeneration	95.2
Third regeneration	95.7
Fourth regeneration	94.3
Fifth regeneration	94.8

جامعة النجاح الوطنية

كلية الدراسات العليا

**إستخدام الأنايبب النانويه المغناطيسيه الكربونيه متعددة
الجران والمدعمه بماده الشيتوزان في إزالة النترات
من مياه الصرف الصحي**

إعداد

إيناس إبراهيم محمود بشارت

إشراف

أ.د. شحدة جودة

قُدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء من كلية
الدراسات العليا في جامعة النجاح الوطنية، نابلس- فلسطين
2018م

ب
إستخدام الأنابيب النانوية المغناطيسية الكربونية متعددة الجدران والمدعمة بمادة الشيتوزان في
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الملخص

في السنوات الأخيرة، أدى النشاط الصناعي، وزيادة استخدام الأسمدة الزراعية والمعالجة غير الملائمة للمياه المستعملة إلى زيادة الملوثات السامة في البيئة مثل أيونات المعادن، والأيونات العضوية وغير العضوية، ويؤدي هذا إلى حدوث مشاكل صحية خطيرة لدى الإنسان والكائنات الحية الأخرى.

المشكلة الرئيسية هنا هي الكشف عن تركيز أحد هذه الملوثات وهو النترات ومحاولة إزالته والتخلص منه عن طريق الإمتزاز.

النترات هي واحدة من أكبر الملوثات في جميع أنحاء العالم بسبب ميلها إلى الرشح من خلال التربة مما يؤدي إلى تلوث المياه وخاصة المياه الجوفية التي تعد المصدر الرئيسي للشرب. ومن المعروف جيداً أنّ زيادة تركيز النترات في مياه الشرب هو السبب الأساسي للإصابة بمتلازمة الطفل الأزرق.

في هذه الدراسة، تم إستخدام الأنابيب النانوية الكربونية المغناطيسية متعددة الطبقات و المدعمة بالشيتوزان لإزالة أيونات النترات من مياه الصرف الصحي.

لقد تم تحضير الأنابيب النانوية الكربونية المغناطيسية متعددة الجدران المدعمة بالشيتوزان، وقد أجريت عليها جميع الفحوصات المتاحة لتشخيصها والتعرف على خصائص سطحها، حيث أكدت نتائج تحليل FT-IR أن مادة الشيتوزان قد تم تثبيتها بنجاح على سطح الأنابيب النانوية الكربونية المغناطيسية متعددة الجدران، كما أظهرت صور المسح الإلكتروني (TEM) أن السطح المعدل الجديد يتميز بخصائص تجعله قادراً على الإمتزاز.

أُجريت تجارب عديدة تحت ظروف ومتغيرات مختلفة مثل: درجة الحرارة، درجة الحموضة، تركيز أيونات النترات، كمية المادة المازة ومدة الإتصال، لتحديد الظروف المثلى لأفضل نسبة

ج

إمتزاز لأيونات النترات. وقد لوحظ من خلال هذه التجارب أنّ نسبة إزالة أيونات النترات من المحاليل المائية قد انخفضت مع زيادة درجة الحموضة, بينما ازدادت هذه النسبة بزيادة كمية المادة المازة ومدة الإتصال وزيادة درجة الحرارة.

أجريت تجربة على 10 مليلتر من محلول النترات بتركيز 50 ملغم/لتر, حيث تم إزالة أكثر من 65% منه خلال 5 دقائق الأولى باستخدام المادة المازة ثم إرتفعت نسبة الإزاله إلى 88% بعد 50 دقيقه من زمن الإتصال. كمية النترات التي تم إمتزازها لكل وحدة كتلة من المادة المازة تم حسابها باستخدام نموذج Freundlich ، قيمة R^2 المحسوبة في نموذج pseudo first order model تؤكد أن عملية الإمتزاز للتفاعلات من الدرجة الأولى.

قيم ΔG° السالبة تشير إلى أن عملية الامتزاز موائمة وتلقائية على درجات الحرارة المحددة, كما أنّ القيمه الموجبه لـ ΔH° تشير إلى أنّ عملية الإمتزاز ماصه للحراره ومحبه على درجات حراره مرتفعه نسبياً. القيمه الموجبه لـ ΔS° تدل على أنّ تفاعل الإمتزاز تفاعل يحدث بشكل تلقائي.