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Faculty of Graduate Studies

**Synthesis of Functionalized Multiwall Carbon
Nanotube: Application in Removal of
Malathion from Water**

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III

Dedication

Foremost, praise to almighty God, lord of the worlds before and after, This thesis is dedicated to all my family for their unlimited love and encouragement, especially my wonderful mother who created me from nothingness; she was literally willing to do anything for us in the most difficult circumstances, to my only brother "ahmad" and my sisters for their unfailing support, to the souls of everyone who preceded us to God, to my dear grandfather's soul "Younes Massad", my first teacher and inspiration, he would be so glad to see me succeed.

Words would never say how grateful I am to all of you, so I hope my actions will express that one day. Finally, we will never finish the work, and these are just stations in our life while the sky will be the limit.

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أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

Synthesis of Functionalized Multiwall Carbon Nanotube: Application in Removal of Malathion From Water.

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تم الإشارة إليه حيثما ورد، وإن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أي 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 qualifications.

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Table of content

Dedication	III
Acknowledgments	IV
Declaration.....	V
Table of content	VI
List of Figure.....	IX
List of Tables.....	XIII
List of Abbreviations.....	XIV
Abstract	XVI
Chapter One: Introduction	1
1.1 Overview	1
1.2 Novelty	5
1.3 Research Objective	5
Chapter Two: Literature review.....	6
2.1 History.....	6
2.1.1 Ground water.....	6
2.2 Pesticides.....	8
2.2.1 Organophosphorus pesticide	9
2.2.2 Malathion	12
2.3 Water treatment process.....	14
2.3.1 Adsorption techniques	14
2.3.2 Adsorption technique - materials	16
2.4 Carbon nanotubes.....	18
2.5 Adsorption process.....	20
2.5.1 Adsorption Isotherm Models	21
2.5.1.1 Langmuir Adsorption Isotherm	22

2.5.1.2 Freundlich Adsorption Isotherm	24
2.5.2 Adsorption Kinetic Models.....	25
2.5.2.1 Pseudo 1 st Order Kinetics.....	25
2.5.2.2 Pseudo 2 nd Order Kinetics.....	26
2.5.2.3 IPD Kinetic Model	26
2.5.3 Adsorption Thermodynamics.....	27
2.6 Analytical techniques	29
Chapter Three: Experimental part	30
3.1 Chemicals and materials	30
3.2 Analytical method and instrumentation	30
3.3 Preparation of functionalized MWCNT with 2-PEA	31
3.3.1 Preparation of oxidized Multiwall Carbon Nanotube.....	31
3.3.2 Functionalization with 2-phenylethylamine	31
3.4 Dissolved Organic Matter (DOM)	32
3.5 Calibration curve.....	33
3.6 Batch adsorption experiment	34
3.6.1 Effect of contact time	34
3.6.2 Effect of pH.....	35
3.6.3 Effect of temperature	36
3.6.4 Effect of adsorbent dose.....	37
3.6.5 Effect of adsorbate initial concentration.....	38
3.7 Regeneration of adsorbent	38
Chapter Four: Results and discussion	40
4.1 Results of Adsorption	40
4.1.1 Adsorption of Malathion on a non-modified MWCNT.....	41
4.1.1.1 Effect of contact time.....	41
4.1.1.2 Effect of pH.....	42
4.1.1.3 Effect of temperature	44
4.1.1.4 Effect of adsorbent dose.....	45

VIII

4.1.1.5 Effect of adsorbate initial concentration	46
4.1.2 Adsorption of Malathion on MWCNT functionalized with 2-PEA (presence or absence of DOM)	47
4.1.2.1 Effect of contact time	48
4.1.2.2 Effect of pH.....	50
4.1.2.3 Effect of temperature	51
4.1.2.4 Effect of adsorbent dose.....	52
4.1.2.5 Effect of adsorbate initial concentration	54
4.1.3 Summary	55
4.2 Regeneration of adsorbent	57
4.3 Equilibrium Isotherm Models	58
4.3.1 Langmuir adsorption isotherm:	59
4.3.2 Freundlich adsorption isotherm	60
4.4 Adsorption kinetic models	63
4.4.1 Pseudo-1st-order kinetic model	63
4.4.2 Pseudo-2nd-order kinetic model.....	65
4.4.3 IPD kinetic model	66
4.5 Adsorption thermodynamic	70
4.6 Conclusions	72
4.7 Recommendations	74
References	75
الملخص	ب

List of Figure

Figure 1.1: Some Organophosphorus Pesticides (OPPs) structure.....	3
Figure 1.2: The structures of <i>a)</i> MWCNT, <i>b)</i> SWCNT.....	4
Figure 2.1: Ideal ^{13}C - NMR spectrum for Malathion estimated by ChemDraw professional.....	13
Figure 2.2: Advantages and disadvantages of some used wastewater treatment technique.	15
Figure 2.3: General scheme for functionalization of carbon based nanomaterial.	19
Figure 2.4: Different adsorption isotherm models.	21
Figure 3.1: Calibration curve for Malathion standard solution using HPLC instrument.	33
Figure 4.1: Effect of contact time on the removal of Malathion pesticide using MWCNT in the absence of DOM.	41
Figure 4.2: Effect of pH modification on the removal of Malathion pesticide using MWCNT in the absence of DOM.	43
Figure 4.3: Effect of temperature on the removal of Malathion pesticide using MWCNT in the absence of DOM.	44

Figure 4.4: Effect of adsorbent dose on the removal of Malathion pesticide using MWCNT in the absence of DOM.	45
Figure 4.5: Effect of adsorbate dose on the removal of Malathion pesticide using MWCNT in the absence of DOM.	47
Figure 4.6: Effect of contact time on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.....	49
Figure 4.7: Effect of pH on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.	50
Figure 4.8: Effect of temperature on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.....	52
Figure 4.9: Effect of adsorbent dose on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.....	53
Figure 4.10: Effect of adsorbate dose on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.....	54
Figure 4.11: Regeneration of adsorbent (MWCNT, MWCNT-2PEA, and MWCNT-PEA-DOM) for the removal of Malathion pesticide.....	58

Figure 4.12: Langmuir plot for the adsorption of Malathion on MWCNT.....	59
Figure 4.13: Langmuir plot for the adsorption of Malathion on MWCNT-PEA.	59
Figure 4.14: Langmuir plot for the adsorption of Malathion on MWCNT-PEA-DOM.....	60
Figure 4.15: Freundlich plot for the adsorption of Malathion on MWCNT (time = 30 minutes, pH = 12, temperature = 35°C, adsorbent dose = 5 mg, volume = 10 ml).	60
Figure 4.16: Freundlich plot for the adsorption of Malathion on MWCNT-PEA (time = 50 minutes, pH = 7, temperature = 25°C, adsorbent dose = 5 mg, volume = 10 ml).	61
Figure 4.17: Freundlich plot for the adsorption of Malathion on MWCNT-PEA-DOM (time = 10 minutes, pH = 7, temperature = 25°C, adsorbent dose = 7 mg, volume = 10 ml).	61
Figure 4.18: The plot of pseudo-1st-order kinetic model for the adsorption of Malathion on MWCNT.....	63
Figure 4.19: The plot of pseudo-1st-order kinetic model for the adsorption of Malathion on MWCNT-PEA.....	64
Figure 4.20: The plot of pseudo-1st-order kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.	64

Figure 4.21: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT.....	65
Figure 4.22: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT-PEA.....	65
Figure 4.23: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.....	66
Figure 4.24: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT.....	66
Figure 4.25: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT-PEA.....	67
Figure 4.26: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.....	67
Figure 4.27: Van't Hoff plot for the adsorption of Malathion on MWCNT ($C_I = 4$ ppm, pH = 12, time = 30 minutes, adsorbent dose = 5 mg, volume = 10 ml).	70
Figure 4.28: Van't Hoff plot for the adsorption of Malathion on MWCNT-PEA ($C_I = 6$ ppm, pH = 7, time = 50 minutes, adsorbent dose = 5 mg, volume = 10 ml).	71
Figure 4.29: Van't Hoff plot for the adsorption of Malathion on MWCNT-PEA-DOM ($C_I = 2$ ppm, pH = 7, time = 10 minutes, adsorbent dose = 7 mg, volume = 10 ml).	71

List of Tables

Table 2.1: Classification and current status of different pesticides, and its effects on humans and animals.	11
Table 2.2: Some used functionalized MWCNT as adsorbent for removal of aqueous Mercury (Hg^{+2}) with its capacity and optimum pH used.....	18
Table 2.3: Two functionalization method for multi-walled carbon nanotube.	20
Table 2.4: Kinetic and isothermal studies for different adsorbent that used for removal of Malathion pesticide.	25
Table 4.1: Optimum conditions summery for the removal of Malathion pesticide using MWCNT, MWCNT-2PEA, and MWCNT-PEA-DOM. ...	57
Table 4.2: The parameters of Langmuir and Freundlich isotherms for the adsorption of Malathion on MWCNT and MWCNT-PEA or on MWCNT-PEA-DOM.....	62
Table 4.3: the parameters of pseudo-1st-order, pseudo-2nd-order, and IPD kinetic models for the adsorption of Malathion onto MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM.	69
Table 4.4: the thermodynamic parameters for the adsorption of Malathion on MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM	72

List of Abbreviations

Symbol	Abbreviation
$\mu\text{g/L}$	Microgram per liter.
2-PEA	2-PhenylEthylAmine.
A	Arrhenius factor.
AC	Activated carbon.
CAS	Chemical Abstract Number
C_e	Adsorbate concentration at equilibrium (mg/L).
C_o	The initial concentration of the adsorbate (mg/L).
DOM	Dissolve organic matter.
E_a	Arrhenius activation energy (KJ/mol).
EPA	Environmental protection agency.
g	Gram.
HPLC	High performance liquid chromatography.
IDP	Intra particle diffusion
J	Joule.
J/K	Joule per kelvin.
K	Kelvin.
K_1	The rate constant of pseudo 1st-order (min^{-1}).
K_2	The rate constant of pseudo 2nd-order (mg/g.min^{-1}).
K_d	The thermodynamic equilibrium constant (L/g).
K_F	Freundlich Constant (mg/g).
K_{id}	The intra-particle diffusion rate constant ($\text{mg/g.min}^{-1/2}$).
KJ/mol	Kilojoule per mole.
K_L	Langmuir isotherm constant (L/mg).
K_{oc}	Soil Sorption Coefficient
L	Liter
L/g	Liter per gram.
LD_{50}	Lethal Dose that causes death at 50% of the treated animal.
mg	Milligram.
Mg/L	Milligram per liter.
MWCNT	Multi-walled carbon nanotubes.
MWCNT-PEA	Multi-walled carbon nanotubes functionalized with 2-PhenylEthylAmine.
OPPs	Organophosphorus pesticides.
q_e	The amount of adsorbate per unit mass of adsorbent (mg/g).
q_L	The maximum monolayer coverage capacity (mg/g).
q_t	The mass of adsorbate per unit mass of adsorbent at any time (mg/g)

R	The universal gas constant (8.314 J/mol.K).
SWCNT	Single-walled carbon nanotubes.
T	The absolute temperature (K).
t	Time (min).
TEM	Transmission electron microscopy.
USDA	United States Department of Agricultural
US-EPA	United States Environmental Protection Agency.
UV-Vis	Ultraviolet visible spectroscopy.
V	The volume of the solution (L).
W	Mass of adsorbent (g).
WHO	World Health Organization.
WWTP	Waste water treatment plant.
ΔG°	Standard Gibbs free energy (J).
ΔH°	Standard enthalpy change (J).
ΔS°	Standard entropy change (J/K).
rpm	Round per minute.

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Abstract

The aims of the study is to prepare a functionalized multiwall carbon nanotube and use it for the removal of Malathion pesticides from polluted water, the synthesized multiwall carbon nanotube exhibits an excellent chemical, and thermal stability, the analyses were done using a High Performance Liquid Chromatography (HPLC) to measure the remaining amount of substances in the solution after the adsorption process, the obtained results showed that the efficiency for the removals of Malathion were noticeable rose when using a functionalized MWCNT, unfortunately it's decreased to about the half amount (52.74%) with presence of Dissolved Organic Matter, indicating that nonselective adsorbent toward malathion.

However, it took no more than 50 minutes to remove high levels of the dissolved amount depending on the starting laboratory conditions and adsorbent uses, at the optimum removal conditions, the percentage reach (98.34%) of the target pollutant at initial concentration of 6 ppm with neutral pH. Regenerated in three cases showing a little decrease in the adsorbent efficiency, so it can be reusable and efficient materials for removal of malathion pesticide, and use it as specialized filters to capture malathion from polluted groundwater.

Chapter One

Introduction

1.1 Overview

At present days, humans kind fighting for two main challenges in their life which is energy sources and environmental protection issues, to have a clean resources of their essential requirement for life, with the favorable one "water", since ever humans running around sources of clean water which is just around 3% of total amount of water on the planet, with that accelerated population growth, providing a clean water to meet human needs considered great and real challenge for the 21st century, that need a new efficient technological technique for treating and processing to have a clean water for drinking or other human activities [1,2].

In recent years, pharmaceuticals, pesticides and others chemicals such as personal care products have been frequently found in the environmental system, ether in soil or in water bodies, this is due to increasing of demand on these products for modern agriculture or for daily human use [2]. Also these chemicals still in the environment for deferent period of time, since it have varied half time before it decay or degrades to other chemicals, that's a real disaster can affect the hall planet, it can enters our bodes with contaminated drinking water, vegetables and other food sources, so the same science and development that caused this pollution and imbalance of the world must repair it and restore balance again [3].

Among these toxic chemicals are Organophosphorus Pesticides OPPs which are considered as toxic for humans, animals and plant so exposure to these chemicals at a high level could pose significant ecological and public health threats [1,2,4-6]. OPPs compounds are one of the largest and most diverse pesticide groups, accounting for about 40% of pesticides in the world. These pesticides are relatively inexpensive and have high efficiency in the removal of various types of pests [5,7]. Recent studies considered some OPPs as carcinogenic and mutagenic, since some of those OPPs have a behavior similar to organophosphorus nerve species like soman and sarin gases, and thus its reason for irreversible inhibition of the enzyme acetylcholine-esterase which is an enzyme needed to regulates acetylcholine, a neurotransmitter needed for proper nervous system function [4,5,7].

The most famous of these OPPs are Malathion, parathion ($C_{10}H_{14}NO_5PS$) also called parathion-ethyl or diethyl parathion and diazinon [6]. Some of them, like parathion pesticide, cause poisoning in mammals in general, and therefore these pesticides were replaced with lower toxicity pesticides such as Malathion which also still dangerous, with respect to other anthers in their researches it was considered as most toxic kind of pesticide [5,6], figure 1.1 show some commonly used OPPs structures:

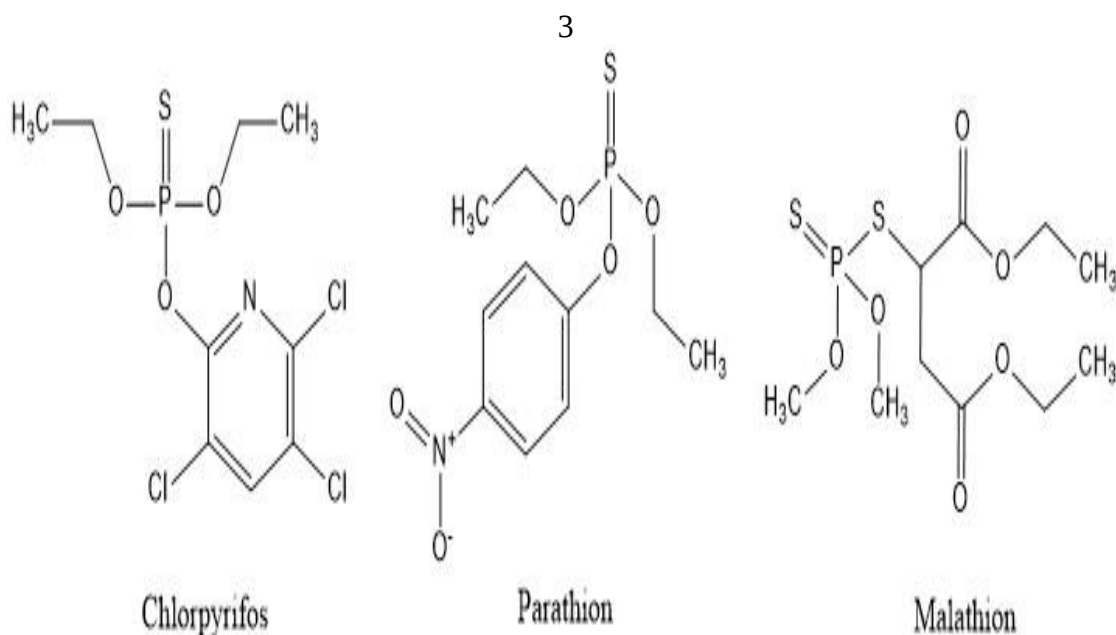


Figure 1.1: Some Organophosphorus Pesticides (OPPs) structure.

The United States Environmental Protection Agency (US-EPA) lists OPPs as either highly or moderately toxic. This is because, under optimum environmental conditions, they tend to degrade to products which are more toxic than the primary pesticide [4,5].

Different adsorbent materials such as activated carbon, polymers, carbon nanotubes and graphene oxide have been used in the removal of pesticides and other pollutant from water [4,5,8], Carbon Nanotubes CNTs have great potential as active adsorbent materials for water treatment due to its large surface area [5,7], CNTs are divided into two main categories, figure 1.2 show the structures of Singlewall Carbon Nanotubes (SWCNTs) and Multiwall Carbon Nanotubes (MWCNTs) [9,10].

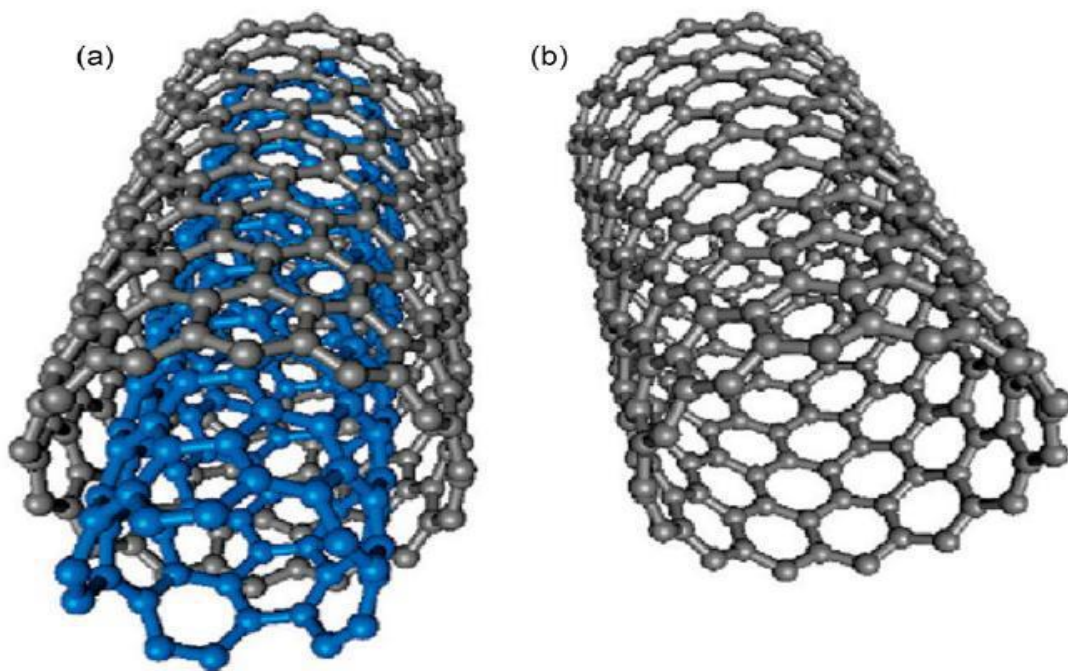


Figure 1.2: The structures of *a*) MWCNT, *b*) SWCNT.

Many studies was done in this field with wide range of decorated carbon nanotubes [11,12], one of these studies was the use of adsorbent carbon nanotubes for the removal of organic substances from the aquatic environment system [13], water purification pass throw several steps starting with a physical separations at macro scale which sometimes considered an easy to do, then finished at a micro scale to treat with a very low pollutant concentration [14].

Adsorption means the buildup of adsorbate "pollutant" on the surface of an adsorbent in a fluid phase (gas or liquid), by either physical or chemical bonds and this process is suitable for the elimination of around 98% natural and synthetic organic pollutants at low concentrations so its consider as a final terminus in water treatment process. The applications and production methods of CNTs have been reviewed recently [15].

1.2 Novelty

The investigation of OPPs adsorption process on a MWCNTs and the generation of isotherm model and kinetic data is very important in the field of water research, unlike previous studies, the impact and effect of Dissolved Organic Matter on the adsorption process by a functionalized MWCNT were taken in account, so we prepared a new functionalized MWCNTs with 2-phenylethylamine [4], and using it as adsorbent for malathion pesticide from water solution either in presence or absence of dissolved organic matter (competition principle) as a comparison [3].

1.3 Research Objective

1. To prepare a functionalized MWCNTs with 2-phenylethylamine, for removal of Malathion pesticide.
2. To study the effect of Dissolved Organic Matter (DOM) that presence in the solution on the adsorption process.
3. To optimize different parameters that impact the adsorption process.
4. To study the kinetic, isotherm, and thermodynamic data for the adsorption of Malathion onto adsorbent in three different cases.

Chapter Two

Literature review

2.1 History

The issues of water considered one of the most ancient conflicts in the world; it was an important to travel by the primitive tribes to catch the water source that was paved the way for the establishment of civilizations and primitive colonies for the agricultural reason, transportation by rivers, and personal use and later in the industrial process. It is clear know that providing a humans need of water is the real challenge facing the humanity at 21st century, such a decrease in clean water resources is due to unorganized used that huge amount of water wasted.

Today water become a clear gold that inter the political warfare, that all countries regulate its sources and territorial waters, this led to the necessity of forming specialized international organization to regulate and take care of all planet water like the international council of water.

2.1.1 Ground water

water is the secret of life, what is that novel molecules nothing can exist without it and it needs no one to exist, water just go throw a cycle starts from evaporating water bodies to the stage of condenses as a clouds in the sky to rain it again, there is some impurities at low quantity enters to the water in the normal case from a living or natural sources and there is no

problem, the main one arise from uncontrolled amount that escape into the water at either stages of its cycle [16].

Groundwater, as one of the major fresh water resources, is a part of the water cycle, and is a decreasing water resource, it makes up approximately 30% of the total worlds freshwater. During the recharge process for groundwater, which is refers to the downward movement of water from the unsaturated zone to the saturated one, rain water take a lots of impurities and pollutant throw this traveling [16], The quality of groundwater in most areas is very good, it usually needs less treatment than surface water in order to make it safe for drinking [17], this is because of flowing of groundwater through the soil and rocks play an important role in the removal of different type of pollutant, here a major source of pollution which occur by ether organics or inorganics or even biological compounds, so these chemical pollutant escape into the surface water at more than allowable specific amount depending on the type and toxicity of that pollutant, this amount called Threshold Limit Value (TLV), which shows the average concentration to which any person with good health may be exposed for seven or eight hours per week for lifetime without showing an adverse health effect [18].

In the last decades, this pollutant spread over as commercial products to meet human needs and a high demands on other essential requirement from agricultural, pharmaceutical and personal care product, because of water is considered a universal solvent; it can easily dissolve many types of

materials, according to the World Health Organization (WHO) guidelines for drinking water at third edition 2008 in Geneva about six hundred chemicals have been listed with threshold limit values ranging from very low concentrations such as 0.001 ppm for mercury to a high value like 1000 ppm for others [19], so in general the pollution of groundwater become larger in the presence of industrial activity.

2.2 Pesticides

The first official scientific report on the removal of pesticides by microorganisms was published in 1985 [20] while with respect to the modern agricultural it does not care about, it would be a great challenge to produce enough food for the growing population (over 20 million a year in India) [21, 22], protect plant, animal, and human health and at the same time conserve the environment, using that technology of green revolution have doubled the yield of rice and wheat, despite this still considerable quantity of food products is destroyed because of pests. Many surveys have indicated that the pesticide residues in the environment increase day by day due to their repeated and continued use. Chronic exposure to small amount of residues through consumption of contaminated foodstuffs may lead to suppression of the immune system, which in turn, may render humans vulnerable to infectious diseases. Laboratory experiments have indicated that some pesticide residues may cause carcinogenicity on long exposure. The pesticide residues also exhibit specific effects on species other than pests for which they are solely intended, it's also known that bodies of water, air, birds, and

aquatic animals are constantly moving and transporting poisons from one region of the globe to another. For example, DDT was used in the field of East Africa, but in a few months, it was found in the water of the Bay of Bengal, that is, at distance of 6000 km away. This threat is considerably greater in developing countries where there is little awareness of the danger of pesticide use and inadequate user protection [23].

2.2.1 Organophosphorus pesticide

Pesticides considered one of the most dangerous pollutants that affect the environmental system due to their stability, mobility, and long-term effects on living organisms. The pesticides can introduced to the source of clean water through agricultural, domestic and industrial activities and causing several effects. When one of these pesticides are introduced into the environment, either through spraying on crops or any other way, some of these chemicals materials stays in either the atmosphere or in the soil then easily can transported to various environmental component such water bodies or still in the sky [24]. Next to that, these pesticides will definitely reach streams or groundwater by different way such as spillage, leaching, and aerial transport then adsorbed by plants and eatable fruits and crops which are the main sources of pesticides exposure in living organisms [25].

In water, these materials may transform to further production of substances that can be greater in toxicity. European Community Drinking Water Directive considered the guideline for allowable pesticides concentration in water for human consumption as 0.1 μg .

Organophosphorus pesticides considered to be highly toxic agricultural chemicals which are widely used in crops inspection. Frequently used organophosphorus pesticides are dimethoate, methylparathion, phosphamidon, fienitrothion, Malathion, monocrotophos and phorate. Between these all pesticides, Malathion is one of the highest toxic and persistent organophosphorus pesticides which produced serious and really environmental problems, classification of some pesticides is shown in Table 2.1 [26].

Table 2.1: Classification and current status of different pesticides, and its effects on humans and animals.

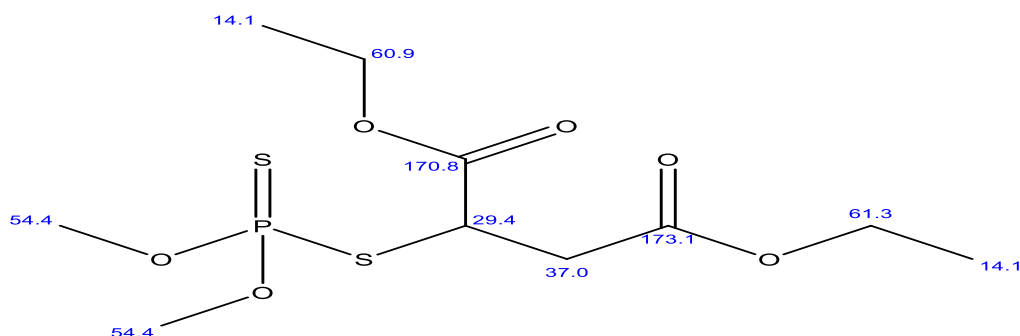
	Activity (current status)	Evidence in humans (cancer sites)	Evidence in animals	Mechanistic evidence	Classification*
Tetrachlorvinphos	Insecticide (restricted in the UE and for most uses in the USA)	Inadequate	Sufficient	..	2B
Parathion	Insecticide (restricted in the USA and UE)	Inadequate	Sufficient	..	2B
Malathion	Insecticide (currently used, high production volume chemical)	Limited (non-Hodgkin Lymphoma, prostate)	Sufficient	Genotoxicity, oxidative stress, inflammation, receptor-mediated effect, and cell proliferation or death	2A†
diazinon	Insecticide (restricted in the USA and EU)	Limited (non-Hodgkin Lymphoma, Leukemia, Lung)	Limited	Genotoxicity and oxidative stress	2A†
glyphosate	Herbicide (currently used: highest global production volume herbicide)	Limited (non-Hodgkin Lymphoma)	Sufficient	Genotoxicity and oxidative stress	2A†

*See the International Agency for Research on Cancer (IARC) preamble for explanation of classification system (amended January, 2006). †The 2A classification of diazinon was based on limited evidence of carcinogenicity in humans and experimental animals, and strong mechanistic evidence; for malathion and glyphosate, the mechanistic evidence provided independent support of the 2A classification based on evidence of carcinogenicity in humans and experimental animals

Humans may be exposed also to pesticides such Malathion if they were near an area affected by Malathion (has been sprayed) or near water polluted with Malathion that transferred from nearby area containing Malathion. A high amount of Malathion Exposure either from air, water and food may lead to difficulty in breathing, vomiting, chest tightness, diarrhea, blurred vision, salivation, watery eyes, dizziness, sweating, headaches, loss of consciousness and even death [25]. Therefore, for environmental issues it is very important to eliminate and decrease these life minatory compounds from environment to prevent its widespread and discharged, their levels in water must be also monitored and checked each time, in drinking water sources mainly. It's really impossible to make a single universal method for the removal of all pesticide enormously since there is wide range of those pesticides. Since that, several methods have been produced either as independent way or in conjunction for this treatment [25,27].

2.2.2 Malathion

Malathion (O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate) has a (CAS) registry number of 121-75-5, since 1956 in the United States it was first registered for use by the United States Department of Agriculture (USDA), now it is controlled by the another official Agency called United States Environmental Protection Agency (U.S. EPA) [28].

ChemNMR ^{13}C Estimation

Estimation quality is indicated by color: **good**, **medium**, **rough**

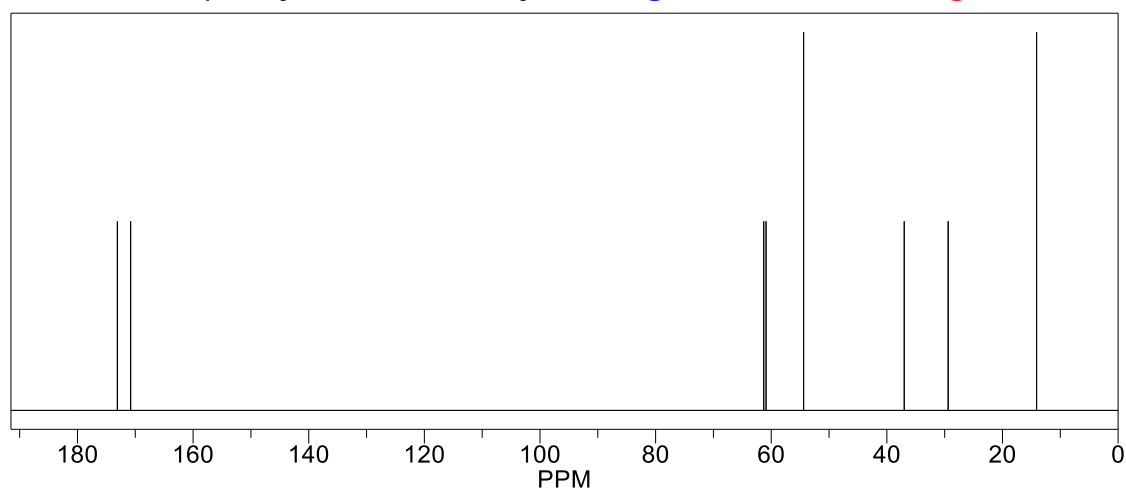


Figure 2.1: Ideal ^{13}C - NMR spectrum for Malathion estimated by ChemDraw professional.

Malathion, 330.4 (g/mole), with a colorless to amber liquid and has a strong odor like skunk or garlic, the vapor pressure of Malathion is 1.78×10^{-4} mmHg at 25 °C [29,30] and its solubility in water is (145 mg/L), Soil Sorption Coefficient (K_{oc}): 30, 93-1800 depending on soil type and environmental conditions, also Henry's constant derived experimentally and equal to $2.0 (\pm 1.2) \times 10^{-7}$ (n = 6 experimental values, dimensionless units) is reported based on a wetted-wall column, concentration/concentration method [31].

Malathion is low in toxicity when ingested with respect to others pesticides. The researchers find a new term to indicate the toxicity of materials which is called acute LD₅₀, its defined as the concentration of material that causes death in 50% of the treated animals that exposure to toxic material single or limited time, researches showed that The acute rat LD₅₀ is 5400 mg/kg in males and 5700 mg/kg in females [28], The low toxicity is due to rapid metabolism by carboxyl esterase enzyme for Malathion pesticide [32].while its ranges in mice from 400-4000 (mg/kg) [33,34].

2.3 Water treatment process

Since pollution of water did not occur by just one type of pollutant, water treatment process must deal with all of these materials in water taking in account the differences in a nature, size, amount that is done by going throw several steps starting with a physical separations at macro scale for larger molecule and heavy material to be filtered and precipitated which is sometimes considered an easy to do, then finished at a micro scale to treat with a very low pollutant concentration, and other biological matter presents in the water, like this pesticide materials amount to get it in the accepted range for human uses [1]

2.3.1 Adsorption techniques

A lots of methods were performed for pesticides treatment including Ozone as chemical oxidation [35], membrane separation, biological

degradation, ion exchange, photo degradation ,chemical precipitation, and adsorption [13,35-39]. Among this, adsorption is the best method since its consider relatively more effective with contrast to other classical methods because of its low operation cost, reusability of the adsorbent, selectivity improvement for some specific adsorbate and also its ability to treat target adsorbate in higher concentrated form [40,41], the following figure shows the main advantages and disadvantages for several main techniques of wastewater treatment.

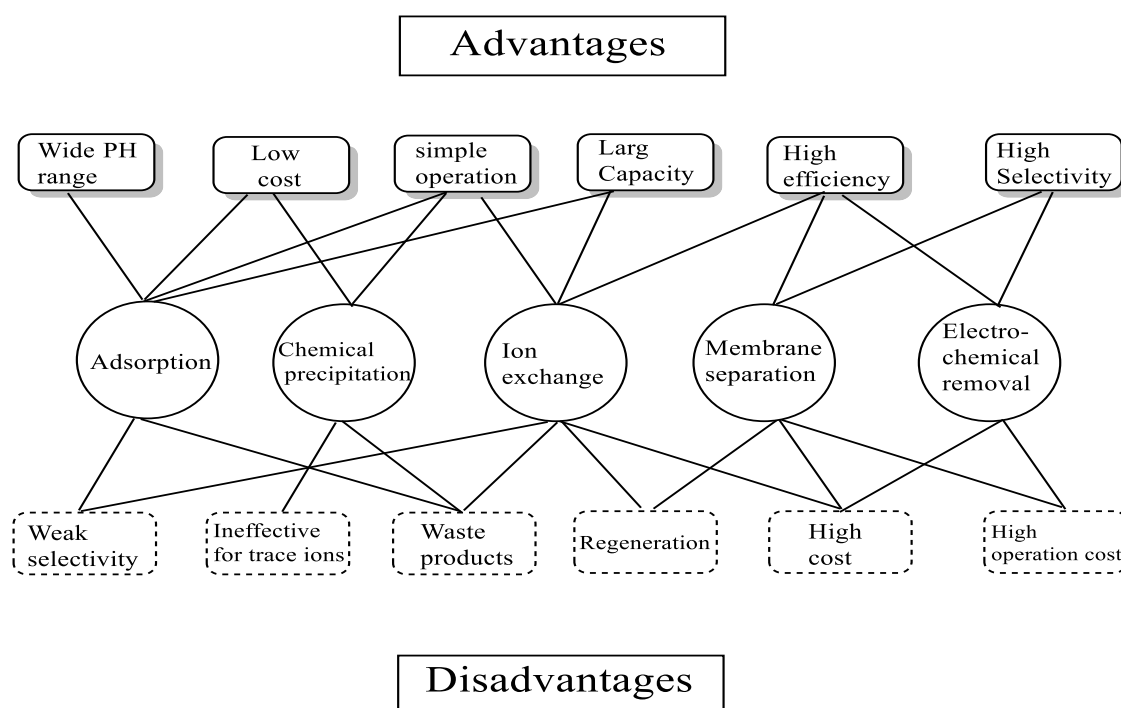


Figure 2.2: Advantages and disadvantages of some used wastewater treatment technique.

several studies have been successfully performed to study different types of cost effective and locally available materials as adsorbent for the removal of several pesticides [42-46].

Despite that, the using of these types of adsorbent associated with some disadvantages including incompatible in operating columns due to non-spherical nature such that resulting in exhausted for industrial columns, adsorption of pesticides at moderately low amount, high cost for the regeneration process and small scale production of carbon materials. furthermore, other methods such as reverse osmosis, Nano filtration and advanced oxidation processes are not desirable because it form undesirable oxidized by products and exposed also to membrane fouling [25]. Despite, prepared resins are moderately more expensive but it may be designed to exhibit more selectivity and adsorption capacity for specific target pollutants than Activated Carbon. Strong potential for the removal of natural organic matter(NOM) and pesticides have been showed by Anion exchange resins [47,48].

2.3.2 Adsorption technique - materials

Separation techniques can classified into two main category depending on the way that adsorption occur that results in batch and continuous adsorption in which analyte are adsorbed on to materials that insoluble in water as it known also as Solid Phase Extraction (SPE) [49,50]. For the materials to be beneficial in it should be synthesized easily, and have a quantitative and reproducible collection to be eluted with minimum efforts exerted in experimental steps. Today, Solid Phase Extraction (SPE) considered as the most used technique in environmental analysis due to it is easy automation and a wide range of materials are available to use for

different domain. Several compounds have been taken as phases in researches as solid phase extracting, such as C18 bonded silica[51,52], polymeric sorbents [53,54], carbonaceous materials [55], zeolites [56] or polyurethane foam [57].

With respect to the mechanism of adsorption it depends on the nature of the adsorbent, adsorbate, and other operation conditions. Adsorption may either done through Van Der Waals forces or hydrophobic interactions, which occur when the solid phase is extremely non-polar. Analyte, sample matrix and technique for final detection should be taken in consideration for predicting of suitable adsorbent to choice, in fact higher enrichment factors can be obtained using adequate experimental conditions (time of contact, adsorbent mass, etc.).

Activated carbon materials was one of the first carbon compounds that applied in SPE; it was and still widely used in eliminate pollutants, as a very good adsorbent for the removal of organic and inorganic pollutants [58,59]. Carbon Nanotubes (CNT) were discovered recently, and this opened new roads to the researches to take place for these carbon materials which based on the flat graphite. CNTs possess many unique electronic, mechanical and chemical properties, high surface and excellent strength. Such material was used widely to eliminate these pollutant from wastewater especially heavy metal and diverge lately for a wide range of organic pollutant. Table 2.2 shows different nanomaterial that used aqueous Mercury (Hg^{+2}) treatment.

Table 2.2: Some used functionalized MWCNT as adsorbent for removal of aqueous Mercury (Hg^{+2}) with its capacity and optimum pH used.

Nanomaterial	pH	Capacity (mg/g)		Ref.
		Exp.	Cal.	
Oxidized MWCNT	7.0	N/A	3.8	[60]
MWCNT-COOH	4.3	81.6	127.6	[61]
MWCNT-OH	4.3	89.4	120.1	[61]
SWCNT-SH	5.0	74.2	131.6	[62]
MWCNT-iodide	6.0	100.0	123.5	[63]

Presently there is so much method used to produce CNTs, for example laser ablation and chemical deposition [64]. Production methods improved in these days to manufactures huge amount of CNTs with high capacity for commercial applications. Carbon nanotubes applications spread widely in last year's research due to their exclusive physical and chemical properties, beside its uses in other field, such as catalyst supports, electronic and optical devices, reinforced materials, storage of hydrogen, and a lots others [65-68].

2.4 Carbon nanotubes

Carbon nanotubes defined as a carbon based materials that can be formed by rolling a sheet of graphite as a cylindrical shape of hexagonal rings, in general it can be classified as either Singlewall (SWCNTs) that have diameters ranging from 0.3 to 3 nm or Multiwall (MWCNTs) structures which composed of many repeated cylinders that arranged and connected to each other, thus can reach up to 100 nm in diameters. Whereas in general the internal holes of the CNTs are large enough to allow small molecules to break throw and migrate into inner layer. Large adsorption surfaces are also

available on the outside and in the interstitial spaces within the nanotube bundles that are held together by Van der Waals force [69].

Carbon Nanotubes (CNTs) are playing really important roles in sensing and separations techniques, such materials considered novel class with varied functionality to facilitate adsorption [1], figure 2.3 represents a general scheme for functionalization of nanomaterial.

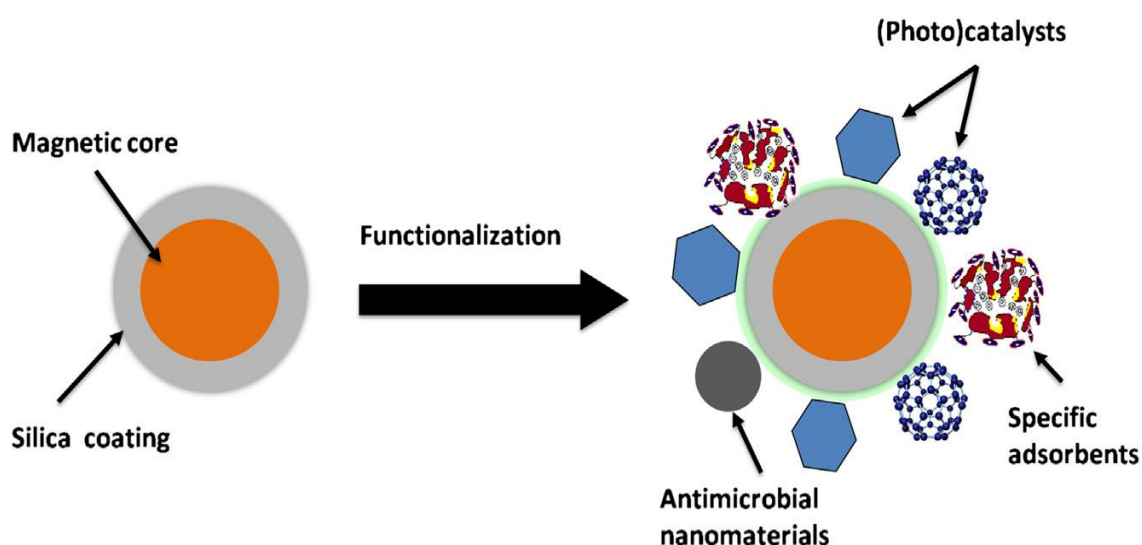


Figure 2.3: General scheme for functionalization of carbon based nanomaterial.

When talking about functionalization of carbon based nanomaterial there are a varied and huge numbers of functional groups that can be used to decorate CNTs making it more efficient in playing its own function, for example, more adsorption site and high surface area can be achieved by functionalized derivatives of CNTs. Functionalization of CNTs or even graphene for different using are often done via chemical methods, that mean chemical processes, like chemical oxidation and deposition, achieving that needed an extended chemical process, for example: electrochemical, sol-gel,

micro emulsion, and hydrothermal methods [70]. Table 2.3 show two functionalization method for MWCNT by using simple chemical methods:

Table 2.3: Two functionalization method for Multiwall Carbon Nanotube.

Nanomaterial	Method	Ref.
Ox- MWCNTs	MWCNT $\xrightarrow[\text{sonicated, 3h, 40}^\circ\text{ C}]{\text{H}_2\text{SO}_4 : \text{HNO}_3 (3:1)}$ $\xrightarrow[\text{dried}]{\text{filtered}}$ oxidized MWCNT	[71]
MWCNT-NH ₂	oxidized MWCNT $\xrightarrow[\text{sonicated, 4h, 40}^\circ\text{ C}]{\text{EDA, N-HATU}}$ $\xrightarrow[\text{dried}]{\text{filtered}}$ MWCNT - NH ₂	[72]

2.5 Adsorption process

Understanding the adsorption process require accurate quantitative method to present the exact process occurs in adsorption and how are these materials behave in considering the isothermal, thermodynamic, and kinetic nature, with respect to isothermal study its meaning the adsorbed amount of a target analyte on the adsorbent as a function of its concentration in the solution at constant temperature. The adsorbed amount is always normalized because of the divided adsorbent mass, that effect allow precise comparison between different situations or compounds [73].

Adsorption equilibrium is confirmed when an adsorbate become in contact with the adsorbent for certain period of time, and in the presence of adsorbate concentration in the bulk solution that allows a dynamic equilibrium with the interface concentration.

In fact there is a wide parameters that influences the adsorption process that is in the solution chemistry like the initial concentration, pH,

contact time, also the temperature can affect the adsorption reaction, a study was done on MWCNTs prove that at the optimized conditions it could be effectively used to remove almost 100% of Malathion pesticide from water [5], another one showed that it could be eliminate up to 96% of Malathion pesticide from the aqueous solutions with an excellent resin material called De-Acidite FF-IP [25].

2.5.1 Adsorption Isotherm Models

It is important to analyze the isotherm data to fit it as an equation that exactly explains the observed behavior.

The most known isotherms which are applied in liquid/solid systems are the theoretical equilibrium isotherm models, including Langmuir, Brunauer, Emmett and Teller (BET), Freundlich and Temkin isotherms, some of these models are shown next [74,75], we were already fitted the data following Langmuir and Freundlich isotherm.

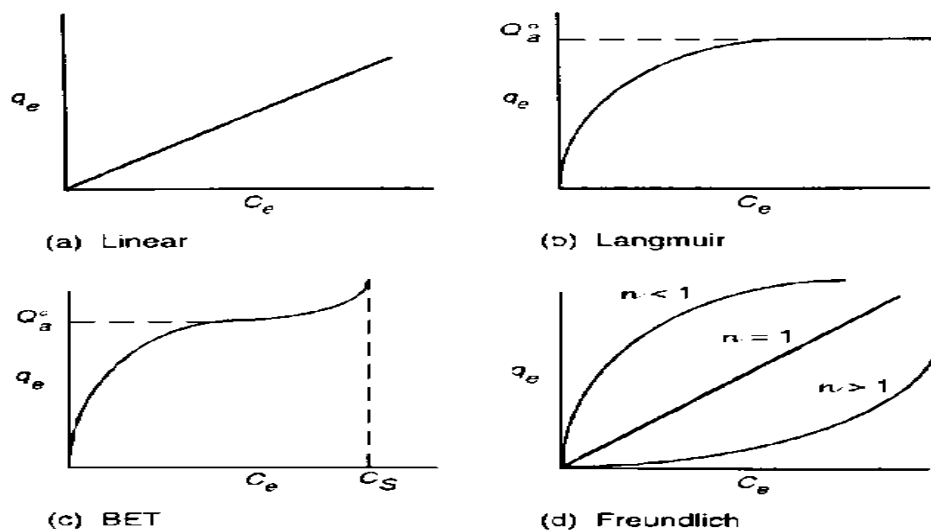


Figure 2.4: Different adsorption isotherm models.

2.5.1.1 Langmuir Adsorption Isotherm

The outer surface of the adsorbent has a maximum capacity for adsorbate, so after the formation of a monolayer on this surface, no more adsorption occurs, so it is called "the ideal localized monolayer model"; such one was developed for representation of chemisorption process. In this adsorption, the process is limited to monolayer coverage, that's mean the adsorbed molecule cannot migrate across the surface into inner structure or interact with neighboring molecules on other sites. Furthermore, the surface of the adsorbent is uniform, and so all the adsorption sites are energy equivalent [75].

The Langmuir principal relates the surrounding of molecules on a solid surface to the medium concentration above the solid surface at a constant known temperature and with a fixed other parameters. This equation can be written as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_e K_L C_e} \quad \text{Eq. 2.1}$$

Where:

C_e = adsorbate concentration at equilibrium (mg/L)

Q_0 = maximum capacity of monolayer coverage (mg/g)

K_L = Langmuir isotherm constant (L/mg).

A q_e is the adsorption amount of adsorbate per adsorbent unit mass (mg/g), and it can be calculated using the following relation:

$$q_e = (C_o - C_e) \frac{V}{m} \quad \text{Eq. 2.2}$$

Where:

C_o is the initial adsorbate concentration in (mg/L).

V is the solution volume in (L).

m is the adsorbent mass in (g).

$(C_o - C_e)$ represents the adsorbed amount (ppm). We can drive the parameters of Langmuir by plot a values of (C_e/q_e) as a function of C_e in a graph, and the slope of such a graph represent $(1/q_0)$, while the y-intercept represent a $(1/K_L Q_0)$ [75].

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

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq. 2.3}$$

Where:

C_0 = initial concentration.

K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the isotherm shape to be unfavorable if $(R_L > 1)$ Linear if $(R_L = 1)$, favorable if $(0 < R_L < 1)$, or irreversible if $(R_L = 0)$.

2.5.1.2 Freundlich Adsorption Isotherm

The adsorption process here depends on different affinities to heterogeneous surfaces. This isotherm model supposes that the bonds with stronger attractions with the surface available sites are occupied first and so on, as a result of increasing the occupied sites, the strength of binding reduced

Related to that articulation, the mass of adsorbate per mass of adsorbent can be calculated by the following equation [4,75,76].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eq. 2.4}$$

Where:

K_F is a constant which indicates the capacity of the sorbent (mg/g).

N is a coefficient that gives an indication of the Favorable way of the adsorption process (g/L)^m if the value of $1/n$ is less than one then the adsorption is normal, and if n is between 1 and 10, the sorption process is favorable [75,77,78].

By plotting a values of $\ln q_e$ as y-axis with $\ln C_e$ as x-axis we can drive a parameters related to this type of isotherm, y-intercept represent $\ln K_F$ and the slope of the curve represent $(1/n)$. Table 2.4 shows a isothermal and kinetic comparison study for some adsorbent uses:

Table 2.4: Kinetic and isothermal studies for different adsorbent that used for removal of Malathion pesticide.

Adsorbent	Optim um pH	Optimum Temp.(°C)	Isotherm	Kinetic	Q max (mg/g)	Refs
Fiber carbon	3	30	Langmuir	Pseudo 1st-order	37.11	[79]
Rice husk (RH)	6	30	Langmuir	Pseudo 2nd-order	4.29	[80]
De-acidity FF-IP resin	6	25	Freundlich	Pseudo 2nd-order	3.5	[25]
Bagasse fly ash	6	30	Langmuir and Freundlich	Pseudo 1st-order	2.08	[81]

2.5.2 Adsorption Kinetic Models

The kinetic energy for the process in physics represents the movement of an objects or in our case "target analyte" molecules from solution matrix to a closer region of the solution in water around the adsorbent surface particle sites throw normal diffusion movement [4,82] this will represent by two way as following:

2.5.2.1 Pseudo 1st Order Kinetics

This was the first model placed to describe kinetics energy for the adsorption reaction.

The rate for pseudo 1st-order kinetic model can be represented by the following equation:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad \text{Eq. 2.5}$$

Where: q_e and q_t are the amounts of target analyte that adsorbed per unit mass of adsorbent at equilibrium, and at time t respectively (mg/g).

k_1 is the pseudo-1st-order rate constant for adsorption (min^{-1}).

The rate constant K_1 and q_e can be calculated by plotting a values of $\text{Ln}(q_e - q_t)$ as y-axis vesus values of t as x-axis.

2.5.2.2 Pseudo 2nd Order Kinetics

This type of kinetic assumes that the chemical adsorption is represent the rate determining step, which involves valence attraction between the adsorbate and the adsorbent by sharing or exchange of electrons.

The final integrated equation for this model type of kinetic is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} = \frac{t}{q_e} \quad \text{Eq. 2.6}$$

Here;

K_2 : adsorption pseudo-2nd-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). By plotting a linear relation between the values of t/q_t as y-axis versus values of t as x-axis, we can drive $(1/ K_2 q_e^2)$ from y-intercept and $(1 /q_e)$ that equals the slope of the graph.

2.5.2.3 IPD Kinetic Model

The final equation of this adsorption kinetic model can be written based on the theory suggested by Weber and Morris, as following:

$$q_t = K_{id} t^{1/2} + Z \quad \text{Eq. 2.7}$$

Whereas;

K_{id} : IPD rate constant ($\text{mg/g} \cdot \text{min}^{1/2}$).

Z : constant gives information about the boundary layer thickness (mg/g).

By plotting a linear relation between the values of q_t as y-axis versus the values of $t^{1/2}$ as x-axis, we can drive the values of Z that equals a y-intercept and K_{id} that equal a slope of the graph.

2.5.3 Adsorption Thermodynamics

Adsorption thermodynamics of a process are necessary to determine the nature of that process and whether the process is favorable or not [84]. The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters as plotted into van 't Hoff equation to determine such parameters as the change in Gibbs free energy (ΔG), that give an information about how this process is favorable or not or how much is the spontaneity of this reactions, that's if the change in Gibbs free energy (ΔG) has a negative sign that mean its spontaneous process, the opposite is not spontaneous when it has a positive sign, also the enthalpy change (ΔH) can be predicted quantitatively, and that indicate the associated energy needed or released by the reaction, there is also the change in entropy (ΔS) indicating

if the direct of the process toward more order or disorder side[85-87]. Here; ΔG and ΔH have a (J) unit while a ΔS has a unit of (J/K).

The general relation which connects between the adsorption parameters will be written as [88]:

$$\Delta G = \Delta H - T \Delta S \quad \text{Eq. 2.8}$$

With respect to ΔG , it can be also calculated using the following relation:

$$\Delta G = -R T \ln K_d \quad \text{Eq. 2.9}$$

Whereas:

R: The Universal gas constant (8.314) J.mol⁻¹.K⁻¹.

K_d : Constant for thermodynamic equilibrium which equals (q_e/C_e) and has a unit of mole or (L/g).

When equals the two equations that previously mentioned, that will result in the following relation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{Eq. 2.10}$$

By plotting a linear relation known as Van't Hoff plot between the values of $\ln K_d$ as y-axis versus the values of (1/T) as x-axis, we can drive the values of ($\Delta S/R$) that equals a y-intercept and ($-\Delta H/R$) that equal a slope of the graph.

2.6 Analytical techniques

Analytical method in general, should be suitable for the target analyte so it can be responded to its concentration at different value, for example in this type of research like in Malathion we could not use UV-VIS spectrophotometer since it difficult to predict this very low concentrations at ppm scale and giving an acetated response sign, using this solid phase extraction, each step were analyzed by High Performance Liquid Chromatography (HPLC) with special analytical method, the adsorbate concentration at equilibrium, q_e (mg /g) is calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{W} V \quad \text{Eq. 2.11}$$

Here C_0 , and C_e (mg/ L) are the adsorbate (Malathion) concentration of initialization, and equilibrium and V (L) and W (g) are solution volume and adsorbent dosage, respectively.

The efficiency of the removal of Malathion was calculated using:

$$\% \text{Removal} = \frac{C(o) - C(e)}{C(o)} * 100 \quad \text{Eq. 2.12}$$

Chapter Three

Experimental part

3.1 Chemicals and materials

MALATHION™ ($\geq 98.0\%$) HPLC AREA % was purchased from SIGMA-ALDRICH chemicals, it's important to say that Malathion pesticide is commercially available in two different concentrations purchased from Sun Tex Investment & Industrial Co, Nablus, Palestine, a 95.1% (w/w) as a primary material for manufacturer to produce the final product for use as 78% (w/w), which is lately diluted further for spraying by farmers and costumers. All other chemicals like 2-phenylethylamine, NaHSO₃, DMF, HCl, ethanol was of the analytical grate and was purchased from SIGMA-ALDRICH chemicals, USA.

3.2 Analytical method and instrumentation

Instruments required in this work were: a bath of water equipped with a shaker (Daihan Labtech, with variable speed 20 rpm to 250 rpm attached to digital speed control), ultrasonic bath, pH scale meter (3510 model, JENWAY), thermometer scale, digital weighing balance (± 0.1 mg) .

High Performance Liquid Chromatography (HPLC) - shimadzu SCL-10A VP, version 5.22 high performance liquid chromatography equipped with a variable length UV/visible detector (SPD 10A VP) using a SUPELCO Discovery reversed phase C18 column, (25 cm x 4.6 mm i.d., particle size 5

μm). The samples were injected manually through a Rheodyne injector. HPLC working conditions were, gradient mobile phase using a previously prepared solvent which was (Acetonitrile: water, 70:30) with 0.8 ml/min flow rate and injection volume (loop size) 20 μL . The wavelength of the UV/visible detector was fixed at 230 nm.

The identification of target pesticide was accomplished on the bases of the retention time of the analyte by searching in the appropriate retention time windows that was 6.8 min, quantification was performed by external calibration, and sample analysis were run in triplicate with relative standard deviations of less than 5% in most of them were achieved.

3.3 Preparation of functionalized MWCNT with 2-PEA

3.3.1 Preparation of oxidized Multiwall Carbon Nanotube

In this step 0.3 g of MWCNT was treated with 300 mL of 69% HNO_3 in flask of 500 ml. The flask was vibrated in ultrasonic bath for 30 min at 25°C. Next, the mixture was diluted with deionized water to reach 400 mL and then filtered through polycarbonate membrane (a 0.22 μm). The same procedure was repeated exactly using H_2O_2 (30% volume/volume) to complete the oxidation process, but in a mild manner. The solid was washed using deionized water and then dried under vacuum for 24 hours to produce the carboxylic acid-functionalized MWNT (MWNT-COOH) [89].

3.3.2 Functionalization with 2-phenylethylamine

MWCNT-PEA was synthesized from the amination of oxidized MWCNT. this was performed in a typical normal synthesis reaction; a 100

mg of oxidized MWCNT was well dispersed in 150 ml water, after that, (12.1 g) of 2-PEA and 10 mmol (2.1 g) Sodium Bisulfite (NaHSO_3) were added to the dispersed MWCNT mixture in the tube and it was kept in oven at 150°C overnight, after cooling to ambient temperature, the resulting material was washed via centrifugation 6000 rpm for 10 min and re-dispersion in fresh water 3 times to remove NaHSO_3 catalyst and non-reacted phenyl ethylamine.

The prepared functionalized MWCNT with 2-PEA is dried by vacuum and can be re-dispersion in water as well as organic solvent such as ethanol and dimethyl formamide for desired applications.

3.4 Dissolved Organic Matter (DOM)

DOM was used in the solution matrix, introduced as a component of the original solvent and it was extracted from soil and organic tree leaves and wastes obtained from the ground of tree garden in the university, that was done by dissolving this materials by mixing 100 g of a homogeneous sample with 1 L of acetonitrile: distilled water 1:1 solvent and shaking (200 rpm) for 12 h. The DOM solution was isolated by centrifugation (10,000 g for 20 min) and subsequent vacuum filtration three times through a $0.45\text{-}\mu\text{m}$ membrane filter to insure removal of larger impurities [91]. The new solvent-DOM then used to dilute Malathion sample into required samples to study the effect of presence of that organic matter on the adsorption process of Malathion

3.5 Calibration curve

In this work, commercial 95.1% Malathion 330.4 (g/mole) was used to prepare 1 L of 1000 ppm stock solution by dissolving exactly 854 μ L using micropipette into 1000 ml volumetric flask completing the volume to the mark with 50/50 acetonitrile: distilled water solvent. Then the stock solution was diluted to prepare a series of several standard solutions of Malathion by using the following relation for dilution calculations ($M_1 \cdot V_1 = M_2 \cdot V_2$). The prepared initial concentration of Malathion was (0.1, 0.5, 1, 2, 4, 6, 8, and 10 ppm). The as prepared standard solutions were used then in our batch experiments to study the effect of different parameters that affecting adsorption process such as time, pH, and temperature and hence to predict the optimum conditions for efficient adsorption reaction for Malathion with MWCNT and MWCNT-PEA.

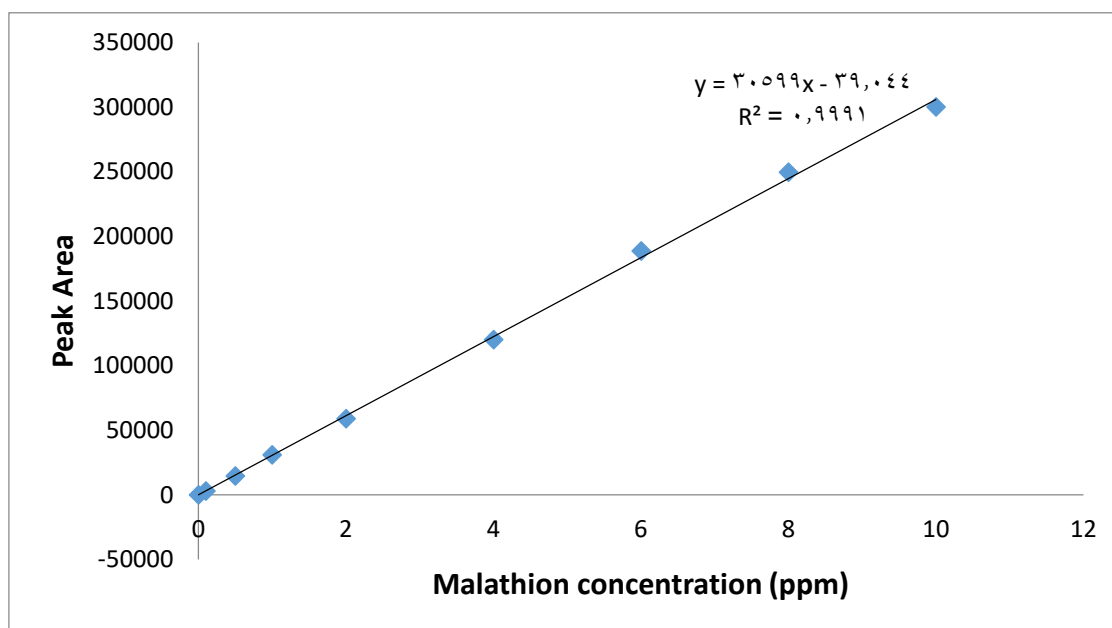


Figure 3.1: Calibration curve for Malathion standard solution using HPLC instrument.

HPLC was used to construct the calibration curve through measuring the area under the peak of Malathion chromatogram. According to Beer-Lambert law, solutions with high concentration absorb more light than solution of lower concentration, since concentration and absorbance are directly proportional. So this law can be used to determine an unknown concentration depending on using the calibration curve of standard solutions of the same material.

3.6 Batch adsorption experiment

This research follows batch experiment procedure that each steps done alone in vials with no flowing of analyte or contaminated water through a constant adsorbent column, whereas the other type of adsorption procedure is the continuous technique in such process the water was polluted by containing adsorbate comes through a column that contains a fixed adsorbent, and the amount of adsorbate enters is highly depends on the flow rate of solution. Here in our batch technique, beside the presence of DOM that highly affect adsorption process several other factors affect the adsorption efficiency, the adsorbate and adsorbent dose, time of shaking, pH value of the solution, and temperature were studied and each optimum parameter was taken in account for next experiment.

3.6.1 Effect of contact time

To reach the equilibrium state in the adsorption process, the time required to fill out the available site on the adsorbent and thus no more

adsorption occur is called contact time, it's very important to predict the optimum time that is exactly needed to reach the reaction equilibrium at the same time not more than needed. The adsorption amount of Malathion pesticide on each adsorbent, either in presence or absence of DOM was studied and instrumentally predicted after time interval in order to predict the optimum required time of shaking for the adsorption process, the experiments were done at room temperature 15°C, where a constant volume of 10 ml (6 ppm) standard solution was shaken with 1 mg of adsorbents MWCNT and MWCNT-PEA in both solutions, and at the end of time interval (5 to 90 min) the concentration of the remained Malathion was measured using HPLC.

3.6.2 Effect of pH

The adsorption process is highly affected by the amount of H_3O^+ and OH^- ion in the solution that's mean the effect of pH value is very important factor to study and control, since these ions can attached on the adsorption site of adsorbent surface changing its behavior and affinity toward the target analyte by either reducing or increasing the adsorbed amount and then get more or less efficient process, so that the effect of pH value on the adsorption reaction was studied over a wide range of pH value ranging from 2 to 12 to predict the value at which the adsorption reaction is more efficient, the percent of removal was plotted as a function of pH. The initial pH for the solutions of Malathion before any modifying was nearly 5 and a roughly prepared concentrations of 0.1 M HCl and 0.1 M NaOH solutions was used

to adjusting the pH value of malathion solutions before the addition of adsorbent.

The adsorbent samples (1 mg of each) were added to 10 ml of the prepared standard solution of constant 6 ppm concentration. The prepared combination solutions were placed in shaking water bath at room temperature (15°C) for a period of optimum contact time that is already measured for each previous adsorption process.

3.6.3 Effect of temperature

The direction of the heat flow between the system and its surrounding is important to predict the type of our reactions or processes if it's either endothermic process (positive enthalpy) or exothermic process (negative enthalpy) so it's very important to prepare a good thermal conditions to have a good percent of removal for analyte, that were done by study the effect of temperature on removal efficiency and also, the obtained data can be used to calculate van 't Hoff parameters to understand the reaction nature of spontaneity and energy needed or released. So that to study the effect of solutions temperature on the adsorption process, 10 ml of 6 ppm standard solution of Malathion was transferred into vials with adjusting its pH to the optimum value that were predicted previously for each one.

The solutions were placed in shaking water bath at desired temperature (the range was 5°C to 55°C), then the adsorbent (1 mg) was added to it for optimum contact time. After the time is over the samples were

filtered and the adsorbate amount was determined by HPLC instrument, the data obtained was a percent removal of Malathion and plotted as a function of temperature.

3.6.4 Effect of adsorbent dose

The affinity of each solute to dissolve in different layer is varied depending on its physical and chemical properties, knowing that adsorbent have a limited adsorption site for interact with solutes, moreover the total amount of adsorption site will increase with increasing the adsorbent dose, any way there is some unabsorbed amount of analyte that will stay soluble in solutions at extremely low quantity (about 1%), however any further addition of adsorbent will be unnecessary and wasted, and it's really important to predict the exact required amount of adsorbent to satisfy a highest % removal at the same time no wasted material.

In order to find out the optimum amount of adsorbent that is required for the adsorption of Malathion pesticide on MWCNT and MWCNT-PEA, a (1, 3, 5, 7, and 10) mg of both adsorbents was added to five vials each containing 10 ml of 6 ppm of Malathion solution. The mixtures were placed in shaking water bath for optimum contact time for each cases at either 35°C or 25°C with pH modifying (pH=7 for MWCNT-PEA) and (pH=12 for MWCNT).

With respect to the case of presence of DOM in solutions, a (1, 3, 5, 7, and 10) mg of MWCNT-PEA was added to another five vials containing

10 ml of 6 ppm of malathion dissolved in saturated solvent with organic matter, the mixture shaken also for optimum time at 25°C with neutral pH.

The concentration of residual Malathion in the filtrate was measured using HPLC.

3.6.5 Effect of adsorbate initial concentration

To find the optimum concentration of Malathion pesticide, the resulting optimum mass of each adsorbent, was added to a number of vials that contain 10 ml of a series of concentrations (2, 4, 6, 8, and 10 ppm), at optimum temperature (25°C or 35°C) at other optimum parameter, for the MWCNT-PEA that adopting Malathion in the presence of DOM, the optimum mass was added to the same concentrations that containing DOM at the same other optimum parameter. After that, the concentration of Malathion pesticide in each filtrate was measured using HPLC.

3.7 Regeneration of adsorbent

After reaching the saturation state for the adsorbent that presented by the equilibrium, a reverse process is the desorption, in such case adsorbate taken off from the adsorbent site were linked in, despite the lower in efficiency of removal it can used for another adsorption process for another times, a mixture of 5 mg adsorbent (MWCNT) and 10 ml of 4 ppm adsorbate at pH=12 was shaken in a water bath for 30 min at 35°C, then HPLC measurements for the filtrate were determined, in the same way for MWCNT-PEA a 5 mg and 7 mg of adsorbent was shaken with adsorbate in

the case of absence and presence of DOM respectively, taking into account all other optimum parameter.

The adsorbent after each adsorption process is washed with 0.1 M HCl solution then with distilled water. After that, each regenerated adsorbent left to dry for 24 hours before second using. The same technique of recovery is then used for each regenerated adsorbent in order to prove that the modified and normal MWCNT can be used for several times with approximately no effect on the percentage removal of Malathion pesticide.

Chapter Four

Results and discussion

4.1 Results of Adsorption

The aims of this research is to prepare a modified Multiwall Carbon Nanotubes for removing Malathion pesticide from contaminated water, these cases were evaluated, is non-modified MWCNT, modified MWCNT, and modified MWCNT in the presence of Dissolved Organic Matter, and hence to make a comparison for the adsorption efficiency and other isothermal and kinetic parameters for these processes, this was done by predicting the remaining concentration amounts at equilibrium, the percentage removal for each adsorption process then was determined. This value meaning the ratio of difference in the adsorbate amounts before and after adsorptions ($C_0 - C_e$), to the initial amount of the target analyte which is Malathion in the aqueous solution (C_0), as shown in the following equation:

$$\% \text{Removal} = \frac{C(o) - C(e)}{C(o)} * 100 \quad \text{Eq. 2.13}$$

The effect of adsorption parameters like temperature, pH, contact time, adsorbent dose, and initial concentration for the adsorption of Malathion on MWCNT and functionalized MWCNT with 2-PEA adsorbent was determined.

4.1.1 Adsorption of Malathion on a non-modified MWCNT

4.1.1.1 Effect of contact time

The time required between adsorbent and adsorbate to allow the direct and dynamic contact for saturation state.

It's important to predict the time of contact that required to achieving optimum removal, that give us an information about the kinetic of the adsorption reaction occur and how fast the process, that was done by dissolving 1 mg of adsorbent in 10 ml of 6 ppm initial concentration of malathion solution with no PH modifying at room temperature then taking a sample to analyzed each period of time (5, 10, 20, 30, 40, 50, 60, 75, 90) min, the measurement were done in triplicate trial on HPLC instrument, Figure 4.1 show the effect of contact time on the removal of Malathion pesticide.

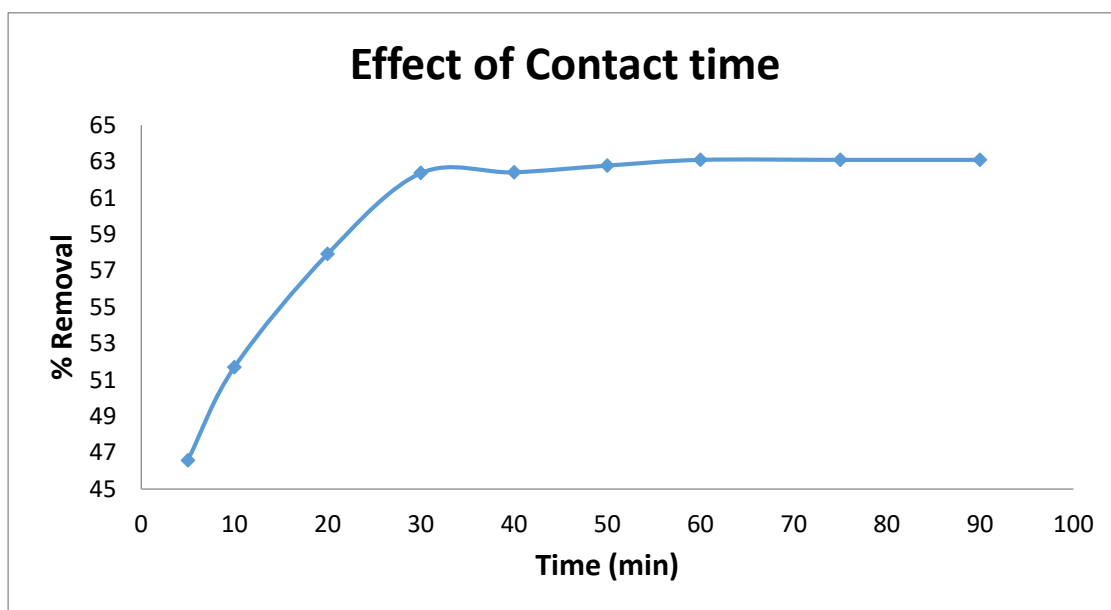


Figure 4.1: Effect of contact time on the removal of Malathion pesticide using MWCNT in the absence of DOM.

The amount of final Malathion concentrations is leveled off at 30 min, so that 30 min was taken as optimum time for removal of malathion pesticide using MWCNT.

The adsorption takes just 30 min to rise up from 46.58% to 62.36% and then no more high effect appears on the concentration of Malathion with extra contact time, it's increased by just 0.73% after 1:30 h of shaking at room temperature.

So this adsorption takes 62.36% of the initial Malathion concentration with just 30 min, so it's considered an optimum contact time and takes its place in the latest experiment.

4.1.1.2 Effect of pH

The pH of the solution highly effected the adsorption process, so it was an important parameter to study, that was done by plotting a %removal of malathion as a function of pH to find at which pH value, the maximum adsorption occur, figure 4.2 show Effect of pH modification on the removal of Malathion pesticide.

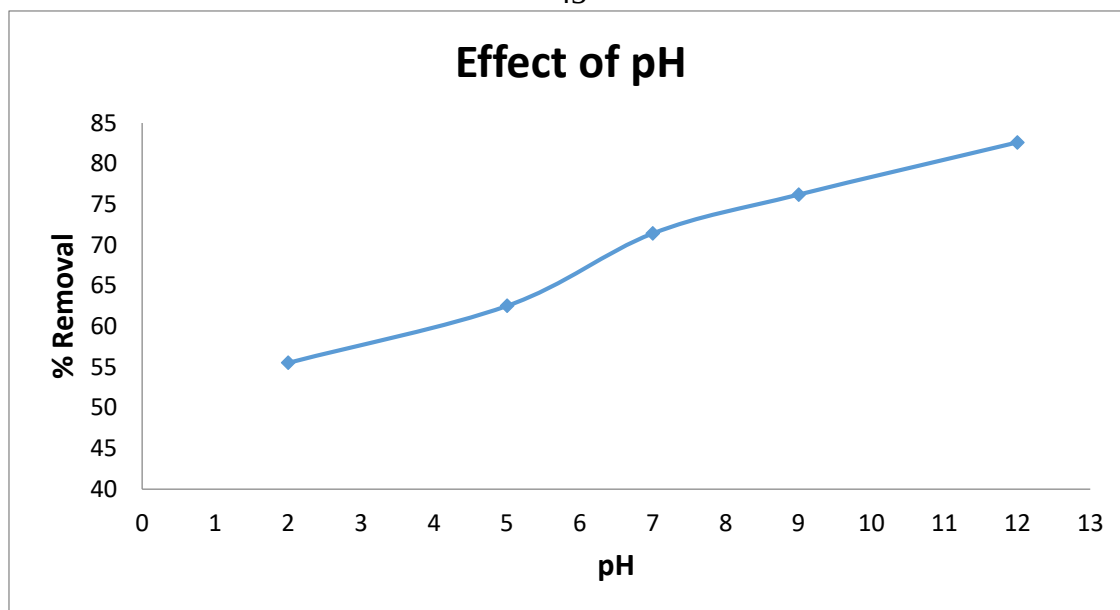


Figure 4.2: Effect of pH modification on the removal of Malathion pesticide using MWCNT in the absence of DOM.

pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions to achieve the required reading.

The adsorption was studied over a wide range of pH (2, 5, 7, 9, 12), by taking 1 mg of adsorbent with 10 ml of 6 ppm of adsorbate initial concentration at room temperature, taking in account the optimum time required. it was clear that the reaction favor the alkaline medium at a high pH value, the % removal was increased sharply between 5 and 7, then its increased further more until it reach pH=12, then no more increasing in pH value to prevent any degradation or side reactions. This adsorption favor the alkaline medium since the % removal was raised up from 55.53% at pH=2 to 82.62% at pH=12, so the pH=12 was taken in account in the later experiments.

4.1.1.3 Effect of temperature

To study the effect of temperature on the removal efficiency of Malathion using multi walled carbon nanotube, the optimum conditions for other parameters was taken in consideration. In general the, the adsorption efficiency becomes higher when increasing temperature values.

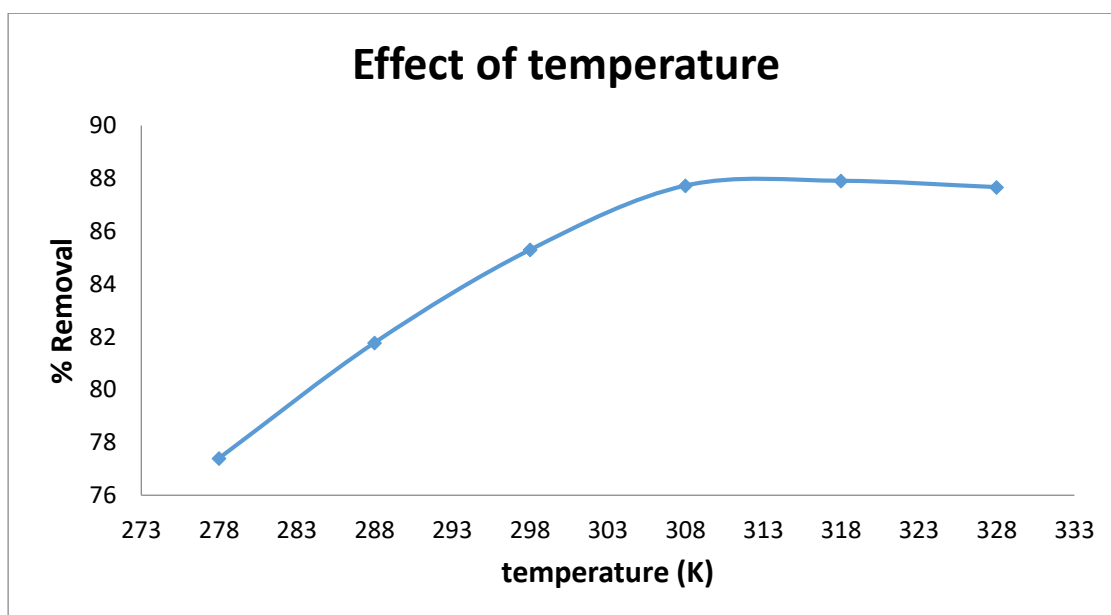


Figure 4.3: Effect of temperature on the removal of Malathion pesticide using MWCNT in the absence of DOM.

As shown in the graph, the adsorption of Malathion pesticide on a MWCNT increased as temperatures rose from 278k to 308k then the efficiency of removal stay constant with farther heating for the solutions, such that the percentage removal of Malathion at the optimum temperature was 87.72%, then still to be nearly constant, the high temperature value of the solutions enhance the complexation ability between malathion and MWCNT, and hence increasing the adsorption efficiency, that indicating endothermic process, while at low temperature values, the adsorption

capacity between the adsorbate and adsorbent is low. 35°C was taken as optimum temperature in further test for adsorption of Malathion on MWCNT.

4.1.1.4 Effect of adsorbent dose

In order to establish an appropriate relation to predict the suitable adsorbent dose for adsorption process of malathion on a non-modified MWCNT, different adsorbent dose (1, 3, 5, 7, 10) mg treated with 10 ml of 6 ppm constant initial concentration of malathion standard solution, after optimum contact time of 30 min at 35°C and pH =12, the amount of target Malathion was measured in triplicate trial using a high performance liquid chromatography and a % removal was calculated as mentioned and plotted as a function of adsorbent dose.

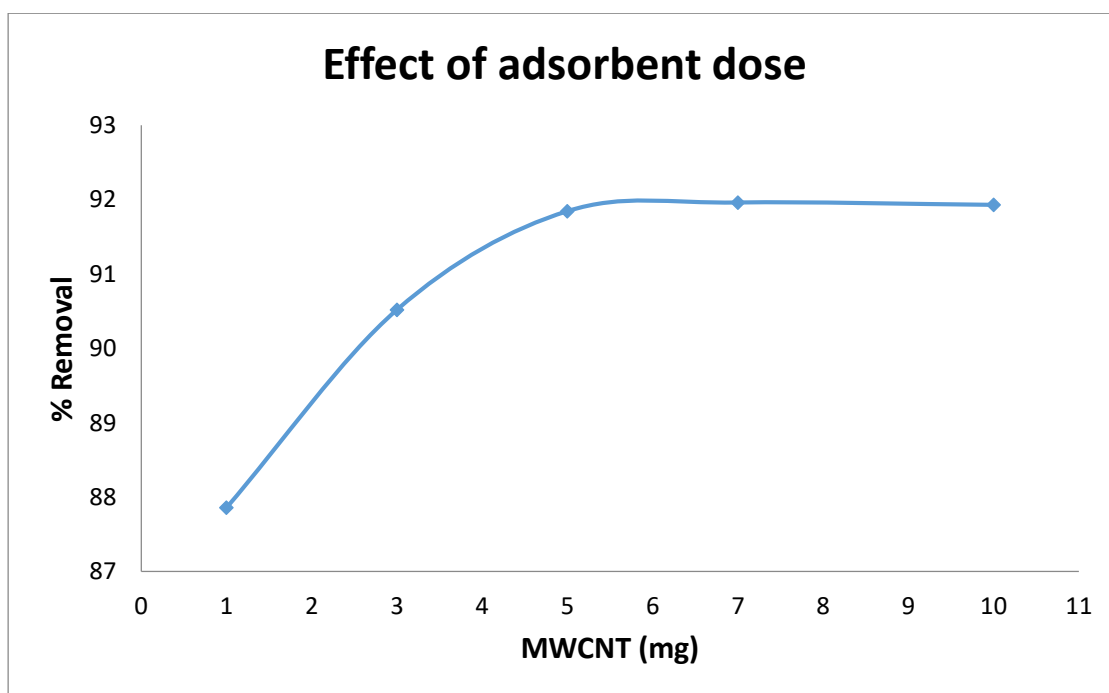


Figure 4.4: Effect of adsorbent dose on the removal of Malathion pesticide using MWCNT in the absence of DOM.

As can be seen from the graph, the maximum removal for Malathion by a MWCNT was at the dosage that can eliminate as much as possible, which was 5 mg of MWCNT, in spite of that increasing the dose of adsorbent higher than 5 mg has no noticeably effect on the concentration, the maximum removal for this amount was 91.84 % at 5 mg of adsorbent while at the double the amount of adsorbent it was 91.93%, so a MWCNT optimum dose was taken as 5 mg for further adsorption tests.

4.1.1.5 Effect of adsorbate initial concentration

The adsorbent has a maximum adsorption amount for the analyte or adsorbate due to its limited adsorption sites on its surface, there is a suitable initial concentration to start with, to achieve the optimum removal as a high % of removal by plotting it as a function of initial concentration of Malathion.

This was done by taking a 10 ml of 5 different initial concentration of Malathion standard solution (2, 4, 6, 8, 10) ppm treated with a constant adsorbent dose of 5 mg for 30 min, at 35°C, (pH for the solution is 5).

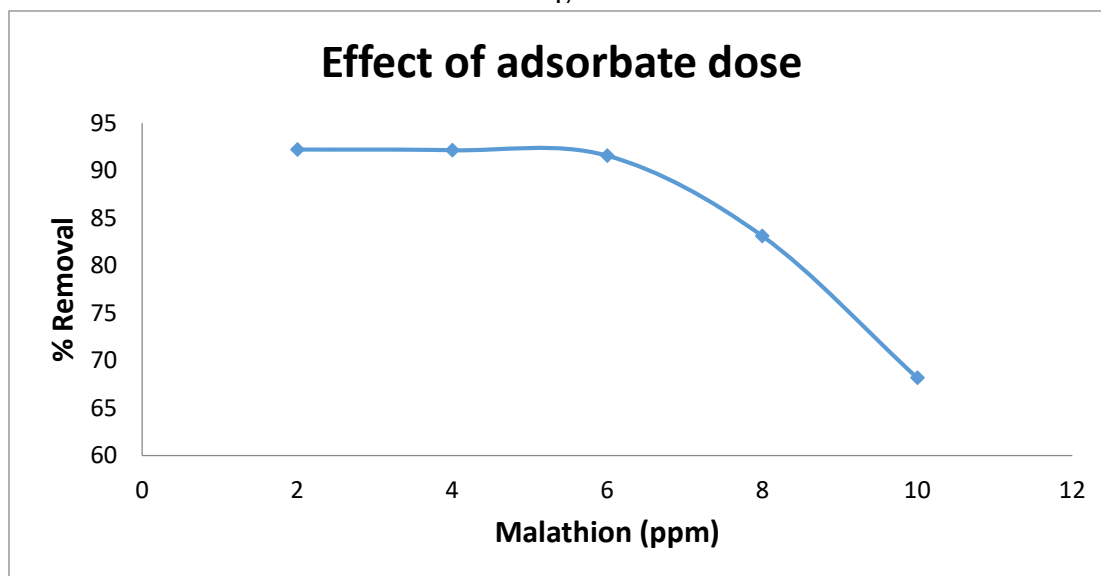


Figure 4.5: Effect of adsorbate dose on the removal of Malathion pesticide using MWCNT in the absence of DOM.

As the initial concentration increased from 2 ppm to 10 ppm the % removal was decreased, strongly when the concentration was higher than 6 ppm.

The maximum removal was taken as 91.56% at the initial concentration of 6 ppm even it was still constant for the lower one concentrations (2 ppm and 4 ppm), while it was just 68.17% for 10 ppm solution.

4.1.2 Adsorption of Malathion on MWCNT functionalized with 2-PEA (presence or absence of DOM)

Adsorption of Malathion on a modified MWCNT shows slight differences in behavior, either in the pH values and in the temperature at which the adsorption occur.

Our purpose in this section of research is to compare between two cases which is the presence or absent of DOM and to try understanding the process of adsorption of our target molecule to attach on a functionalized MWCNT.

A solvent of 50:50 acetonitrile to distilled water was added to the large excess amount of organic natural waste in 1:10 ratio as mentioned previously to insure that is no more matter dissolved and the solution is saturated.

The presence of these materials reduces the solubility of Malathion but compete with the target molecule to occupy the adsorption site on the surface of adsorbent, reducing the removal efficiency for our target material, despite that the total amount of occupied site still the same and the saturation state for adsorbent was reached in both situations due to high amount of pollutant exist in the solutions matrix.

4.1.2.1 Effect of contact time

In order to establish an appropriate contact time between Malathion pesticide and MWCNT functionalized with 2-PEA as an adsorbent in either the presence or absence of DOM, a 1 mg of adsorbent was added to 10 ml of 6 ppm malathion solutions, the concentration of Malathion in a solutions after adsorption process were measured at different contact time (5, 10, 20, 30, 40, 50, 60, 75, 90) min at room temperature and pH=5 value which its already the normal pH of the solution, and a percent of removal were calculated and plotted as a function of contact time. While for DOM it was

added to the solution as a component of the solvent used and in both cases the other parameters kept constant.

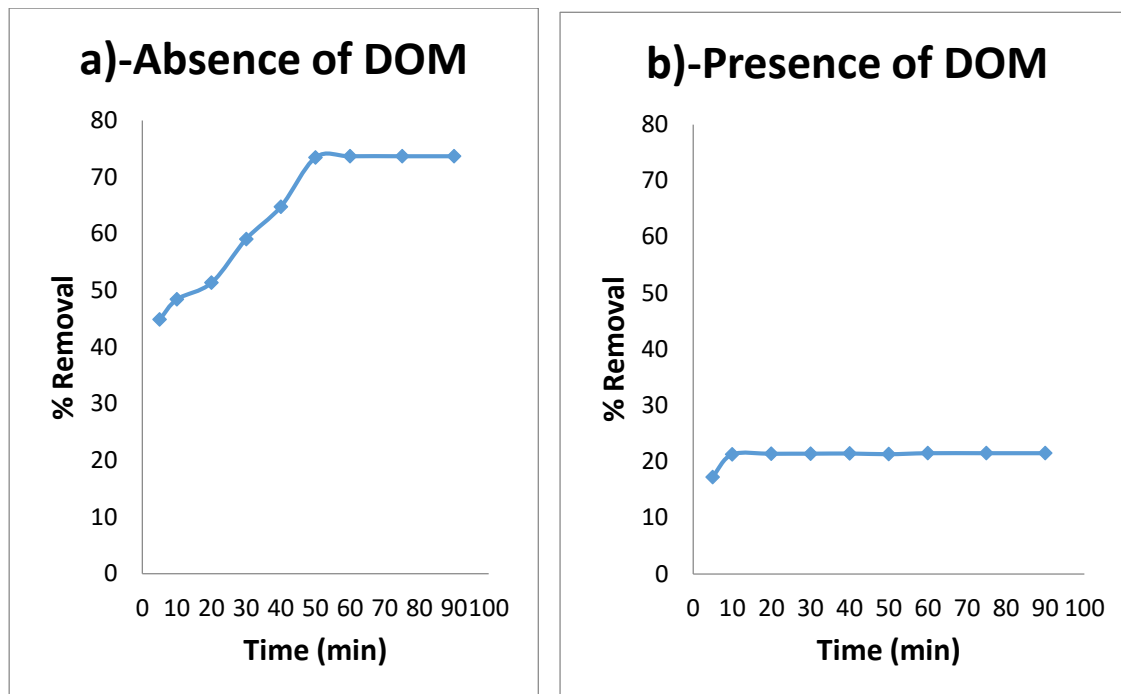


Figure 4.6: Effect of contact time on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.

As shown in the plots, the highest percent of malathion removal was higher in the absence of DOM which it reach 73.48% after 50 min and no further effect on the removal with extra time of adsorption, with respect to Malathion solutions that contain DOM it take less time to reach the maximum removal of target Malathion, the maximum removal was taken to be 21.26% for the time of shaking as 10 min between adsorbate and adsorbent.

It's clear to note that the presence of DOM reduced the time of shaking for that adsorption process due to saturation occur in the solution and high amount of organic matter present in the matrix that making adsorbent to fill the available site so that no more further adsorption attraction for the target analyte.

4.1.2.2 Effect of pH

The effect of pH value on Malathion removal efficiency using a functionalized MWCNT ether in presence or absence of DOM was studied using the same solutions of 0.1 M NaOH and 0.1 M HCl at the optimum contact time that was predicted previously, by added 1 mg of adsorbent to 10 ml of 6 ppm standard malathion solution, the effect of pH value of the solution was studied at a range of pH variation (2, 5, 7, 9, 12) at room temperature and the results is shown next:

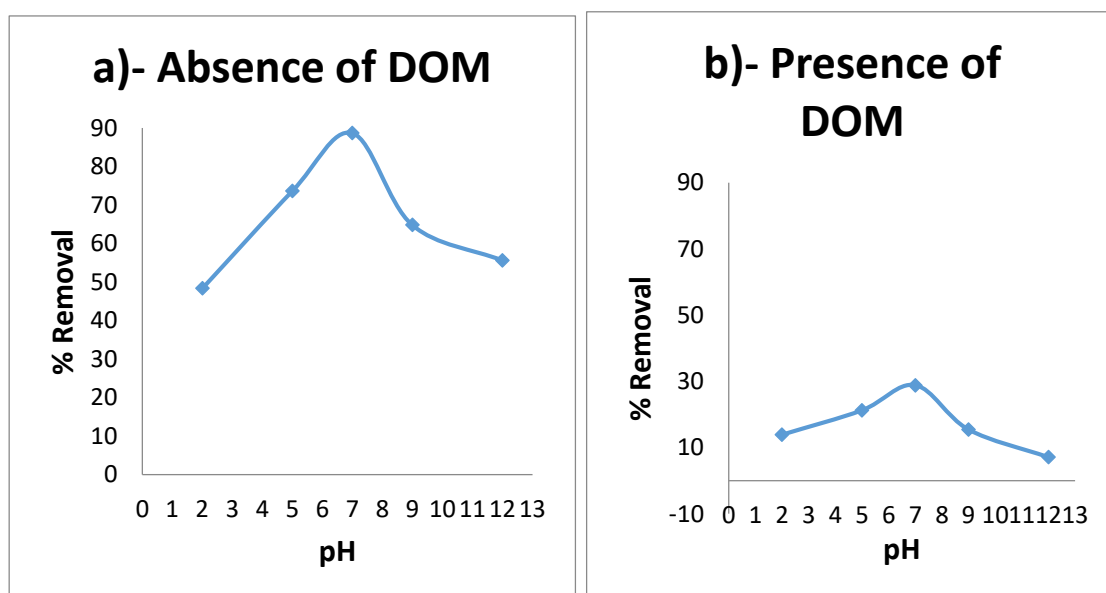


Figure 4.7: Effect of pH on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.

For the solution without DOM, the removal efficiency increased with increasing pH from acidic medium at pH =2 to less acidic at neutral value pH= 7, the percent removal also increased by about double the amount from 48.35% reached 88.69%, the removal efficiency began to decrease sharply again until it reached 55.64% at 12 pH value, but it's still higher than acidic case removal.

With respect to the second type of solutions that contain DOM the effect of pH appear to increase the percent removal when pH value increase until it reach the maximum removal 28.85% at pH value of 7, then start to decrease again during pH raising for the solution until it reach 12 with a minimum removal of 7.12%, this is may be due to increasing the ionic strength of the solution that make more free ions to appear in solution matrix, that ion in a high level compete with adsorption site preventing the target analyte to adsorbed in enough quantity. Here the optimum pH value in both type of solution was taken to be 5 for further

4.1.2.3 Effect of temperature

To study the effect of temperature on the adsorption of Malathion using MWCNT functionalized with 2-PEA, previous parameters were kept at the optimum value that predicted previously, the temperature of the solutions was varied for the same initial concentration.

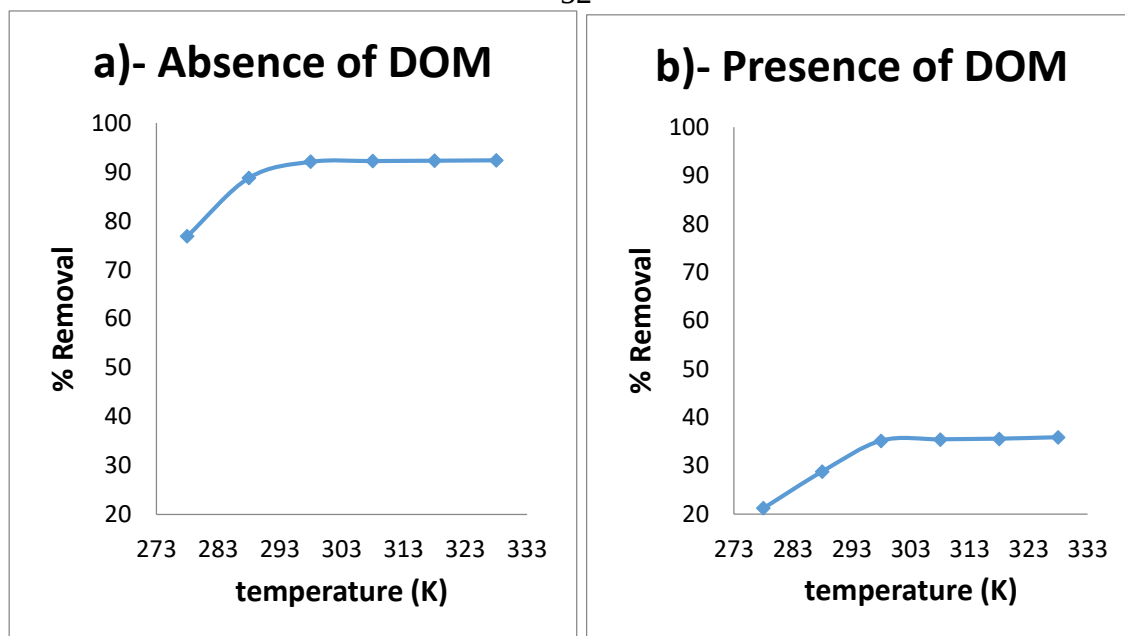


Figure 4.8: Effect of temperature on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.

As shown in the figures, the adsorption of Malathion on the functionalized MWCNT has been found to increase with increasing temperature until reaching the maximum removal, for the absence of DOM it was raising from 76.87% to 92.08% at 298 k (25°C), and still nearly constant at more temperature rise up. The presence of DOM in the solution affects the adsorption process in same manner, since it began to increase sharply until reaching the maximum removal of just 35.19% at (25°C), this is due to increasing the affinity of DOM to dissolved in the solution more and more and decreasing the amount of adsorbed amount at of DOM that occupied the available adsorption site on the surface of adsorbent.

4.1.2.4 Effect of adsorbent dose

The optimum adsorbent dose were determined in the present or absent of DOM by determining the final malathion concentration in the sample after

optimum time of shaking with different doses of adsorbent (1, 3, 5, 7, 10) mg that added to 10 ml of 6 ppm standard initial concentration, taking in consideration that other parameter at optimum amount and to predict the % removal of the target analyte and plot it as a function of adsorbent dose.

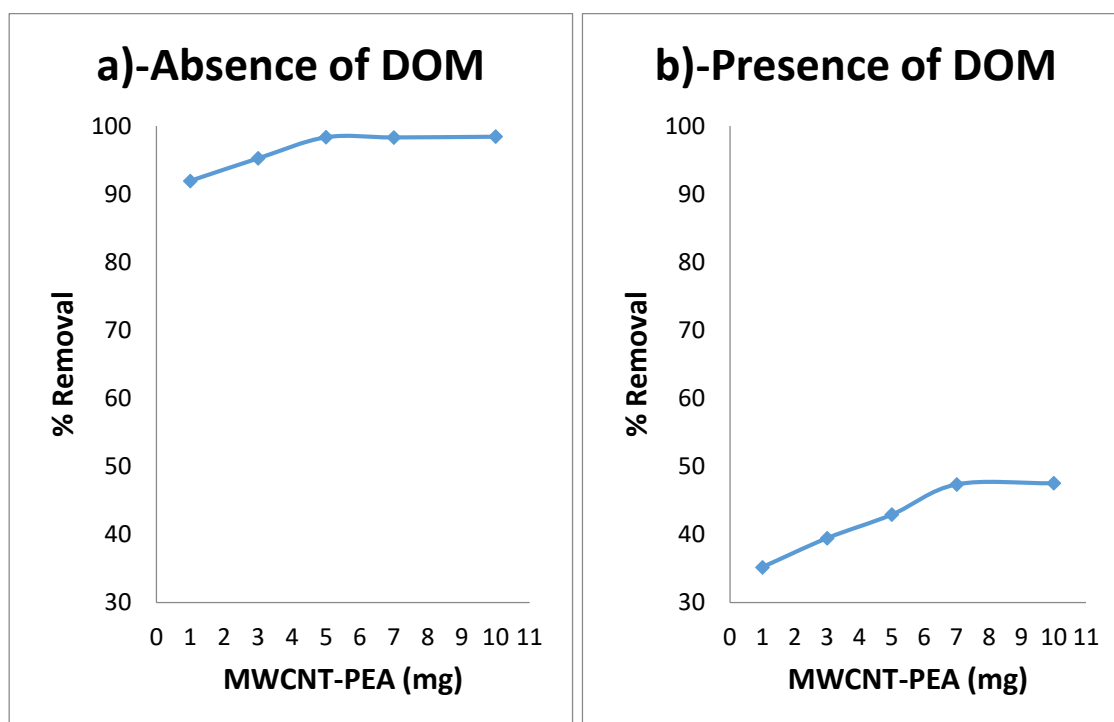


Figure 4.9: Effect of adsorbent dose on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.

The experimental results for the adsorptive removal of Malathion by a functionalized MWCNT that respect to adsorbent dose show the maximum percent of Malathion removal is lower in presence of DOM case, furthermore the optimum adsorbent dose for the DOM case is higher, reaching its optimum removal of about 47.37% at 7 mg of modified adsorbent while the removal percentage is 98.34% when added 5 mg of modified MWCNT to the solutions.

The presence of huge amount of molecules in the solution matrix prevent the target analyte from interacts with an adsorption site on the surface of adsorbent that is a competition principle, taking in account that the adsorption site is already filled and the surface of adsorbent is saturated with molecule.

4.1.2.5 Effect of adsorbate initial concentration

The effect of the initial concentration of Malathion on the percentage removal using functionalized MWCNT either in the presence or absence of DOM is studied throw a series of initial concentration (2, 4, 6, 8, 10, and 15) ppm that treated for optimum contact time with a predicted optimum adsorbent dose for each case at 25°C and pH=7.

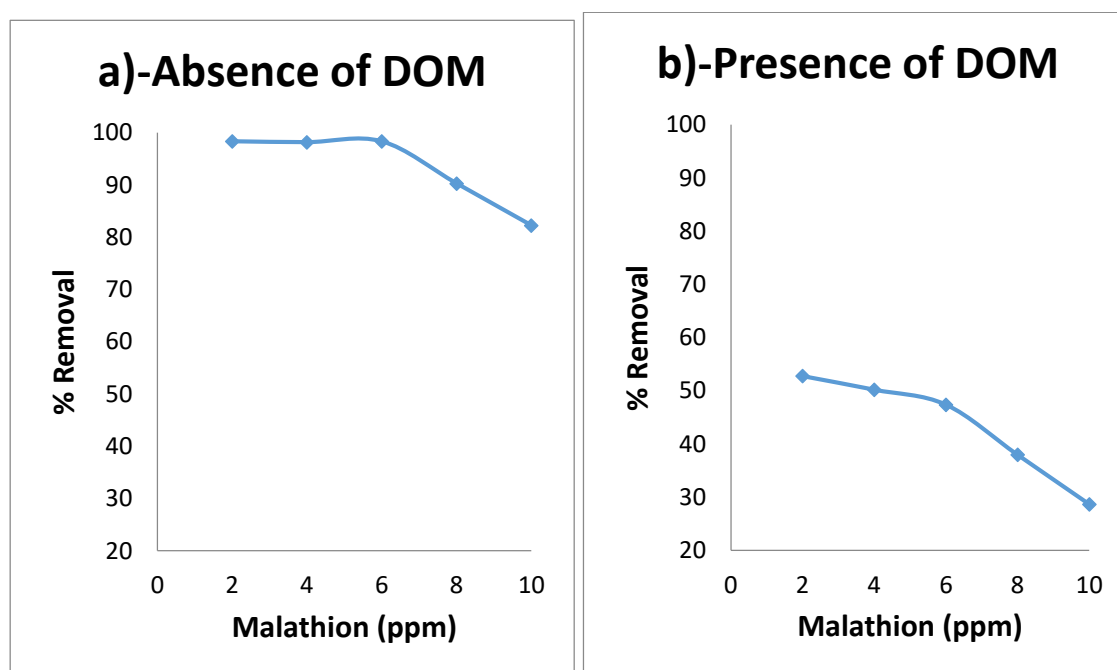


Figure 4.10: Effect of adsorbate dose on the removal of Malathion pesticide using MWCNT functionalized with 2-phenylethylamine in the case of, a) absence of DOM, and b) presence of DOM.

As shown in the plot, for the adsorption of Malathion in clear solution – absence of DOM – the optimum initial concentration of malathion was higher than the case of presence of DOM, the maximum removal was reached 98.34% at 6 ppm of initial malathion concentration, whereas it was just 52.74% at 2 ppm of initial malathion concentration for a DOM solution in the optimum value.

4.1.3 Summary

Up to now the maximum adsorption is already studied for each parameter that effect the adsorption of Malathion pesticide on either MWCNT or MWCNT-PEA and also either in the presence or absence of DOM in the solution, that is for using the optimum conditions in further determinations for isothermal, kinetic and thermodynamic study.

For adsorption of Malathion on MWCNT and MWCNT-PEA the optimum dose in the absence of DOM was 5 mg with a maximum removal (91.85%) and (98.34%) respectively, and for the adsorption of malathion on MWCNT-PEA in the presence of DOM was 7 mg with a maximum removal of (47.37%).

The initial adsorbate concentration was studied also, the results showed that the maximum removal for the removal of malathion by MWCNT and MWCNT-PEA in the absence of DOM was 4 and 6 ppm with a maximum removal of (92.14%) and (98.34%) respectively, and also was 2 ppm in the presence of DOM with a maximum removal of (52.74%), with

respect to the pH value the adsorption of malathion on MWCNT-PEA kept at neutral pH at 7 with no adjustment either in the presence or absence of DOM, and there maximum removal was of about (28.85%) and (88.69%), respectively. The time of shaking that required to reach a maximum adsorption of adsorbate (Malathion) on adsorbent (MWCNT and MWCNT-PEA) is different in three cases, as the contact time required considered a sign for the adsorption speed, it's faster when the contact time become shorter, however it takes 10 and 50 min to reach the optimum removal for the adsorption of malathion on MWCNT-PEA in the presence and absence of DOM, respectively. The temperature of the solution where the adsorption of Malathion on a MWCNT and MWCNT-PEA affect the adsorption efficiency depending on the nature and interaction of each adsorbent and adsorbate, and that is important to predict the essential thermodynamic parameter that helps to understanding the spontaneity of reactions and energy associated with it to classify it as either endothermic or exothermic reaction beside our knowing about how the randomness of the process. Both of adsorbent MWCNT and MWCNT-PEA was also regeneration 2 times for further using of adsorption process for malathion pesticide and the results showed that there is no sharp decrease in removal efficiency after 2nd regeneration and so that it can be used more than just one time, with just a little loss in the efficiency.

Table 4.1: Optimum conditions summery for the removal of Malathion pesticide using MWCNT, MWCNT-2PEA, and MWCNT-PEA-DOM.

Adsorption of malathion		Optimum conditions (% removal)	
Parameter	MWCNT	MWCNT-PEA	MWCNT-PEA (DOM)
Contact time (min)	30 (62.36%)	50 (73.48%)	10 (21.26%)
pH Value	12 (82.62%)	7 (88.69%)	7 (28.85%)
Temperature (K)	35 (87.73%)	25 (92.08%)	25 (35.19%)
Adsorbent dose (mg)	5 (91.84%)	5 (98.34%)	7 (47.37%)
Adsorbate (ppm) concentration	4 (92.14%)	6 (98.34%)	2 (52.74%)

4.2 Regeneration of adsorbent

As shown in Figure 4.2, the effect of adsorbent recovery on adsorption of Malathion pesticide on MWCNT and MWCNT-PEA, either in the presence or absence of DOM was studied, the difference in percent removal between the first and second use of MWCNT adsorbent for removal of Malathion was very small, 1.86% loss of efficiency, and it was also lower by 0.75% for the third use.

With respect to MWCNT-PEA adsorbent it was more loss in efficiency between the 1st and 2nd use by 2.46% in the absence of DOM, while it was 3.22% for the solutions contain DOM, figure 4.11 illustrated removal efficiency for the 1st use and other tow further regenerations:

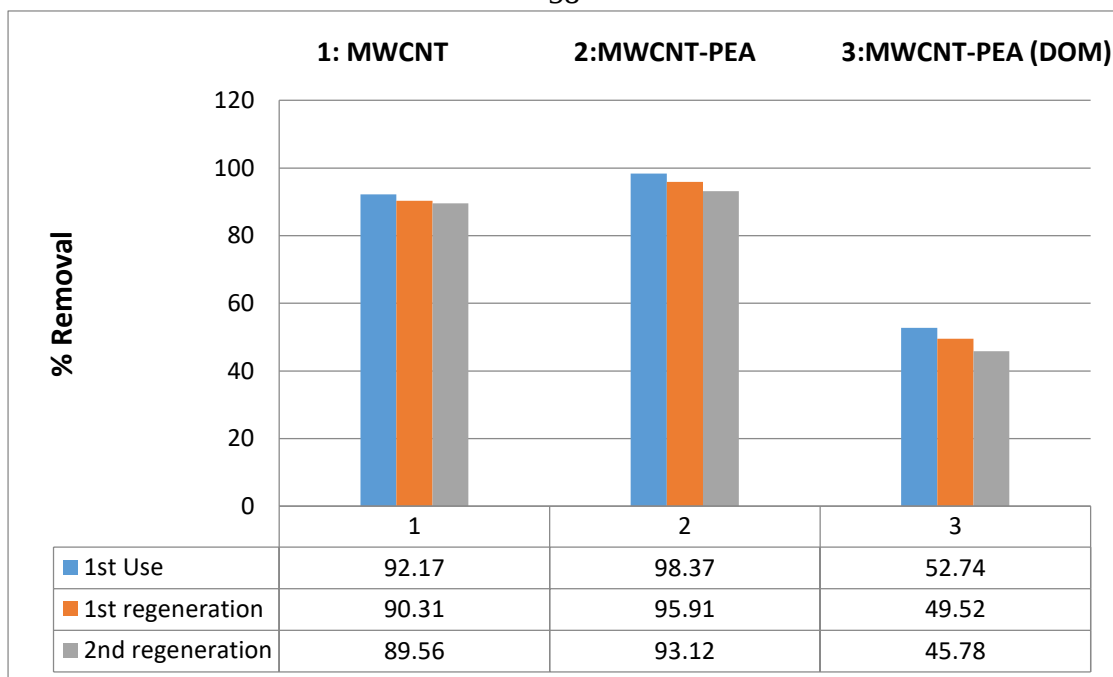


Figure 4.11: Regeneration of adsorbent (MWCNT, MWCNT-2PEA, and MWCNT-PEA-DOM) for the removal of Malathion pesticide.

4.3 Equilibrium Isotherm Models

In order to determine the best adsorption isotherm in either presence or absence of dissolved organic matter for the adsorption of Malathion pesticide onto MWCNT and MWCNT-PE, the suitable isotherm model for this adsorption process can be predicted by choose the higher correlation coefficient that closer to 1 as shown in figures:

4.3.1 Langmuir adsorption isotherm:

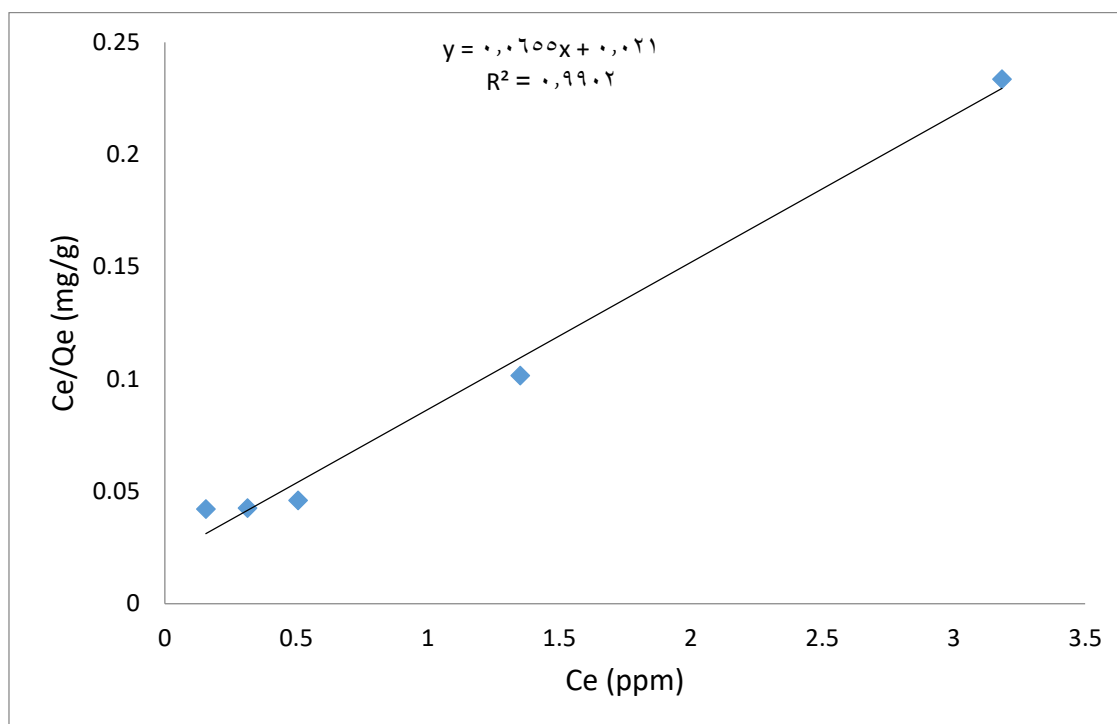


Figure 4.12: Langmuir plot for the adsorption of Malathion on MWCNT.

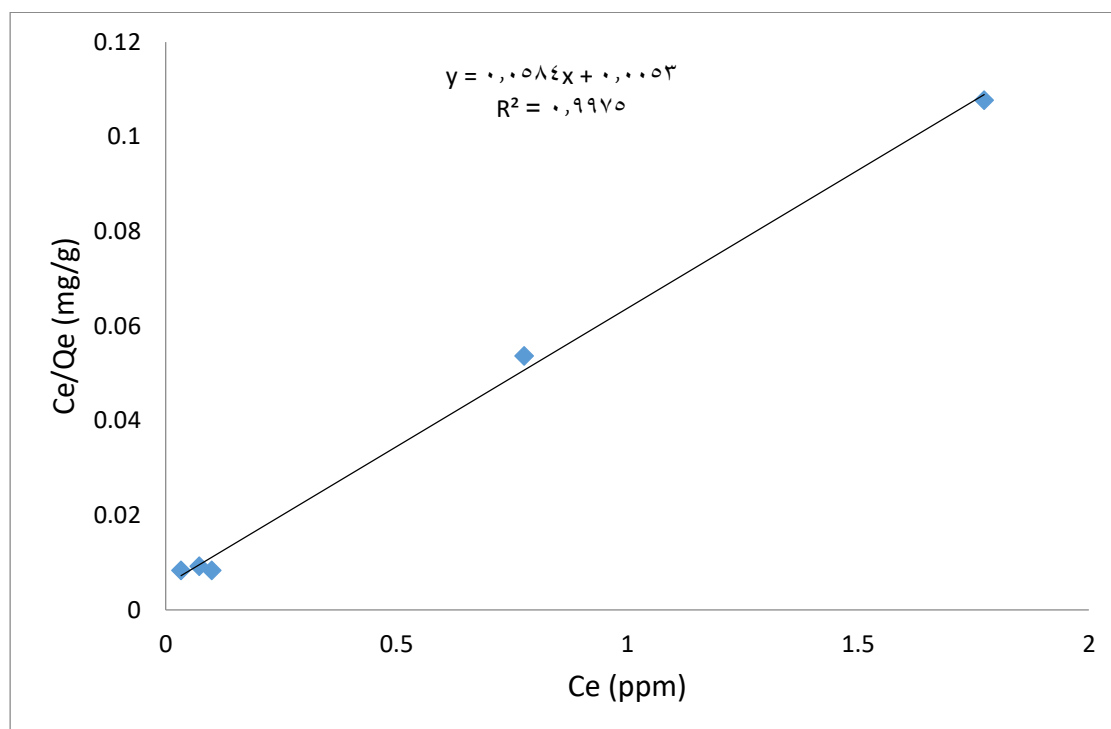


Figure 4.13: Langmuir plot for the adsorption of Malathion on MWCNT-PEA.

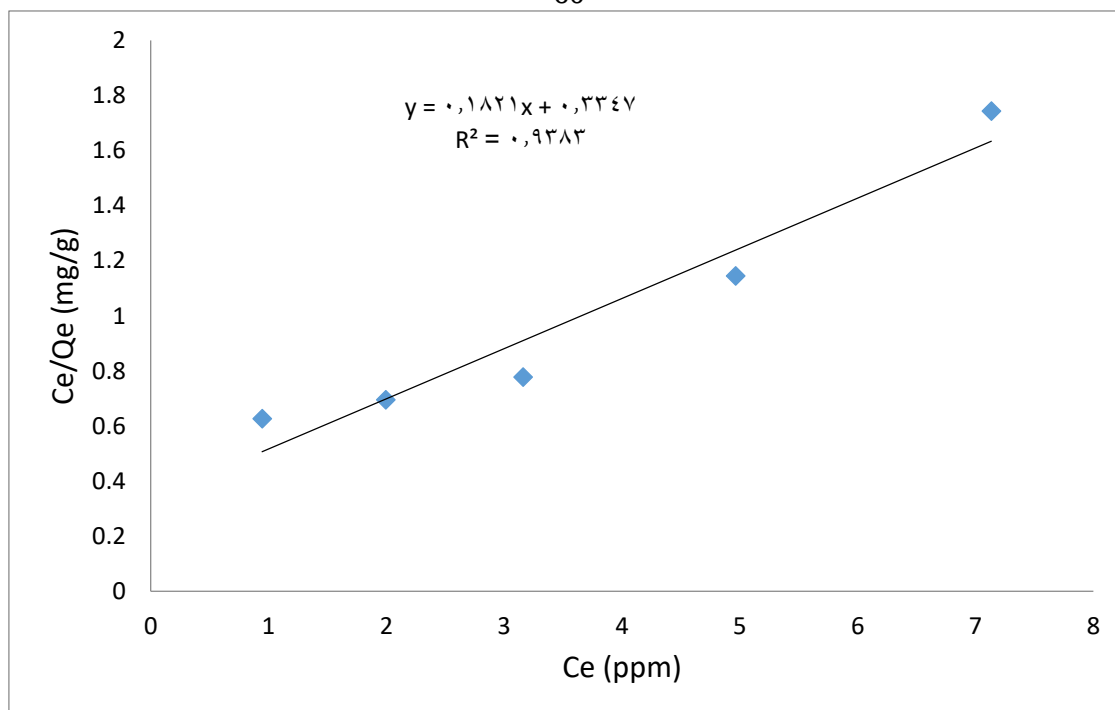


Figure 4.14: Langmuir plot for the adsorption of Malathion on MWCNT-PEA-DOM.

4.3.2 Freundlich adsorption isotherm

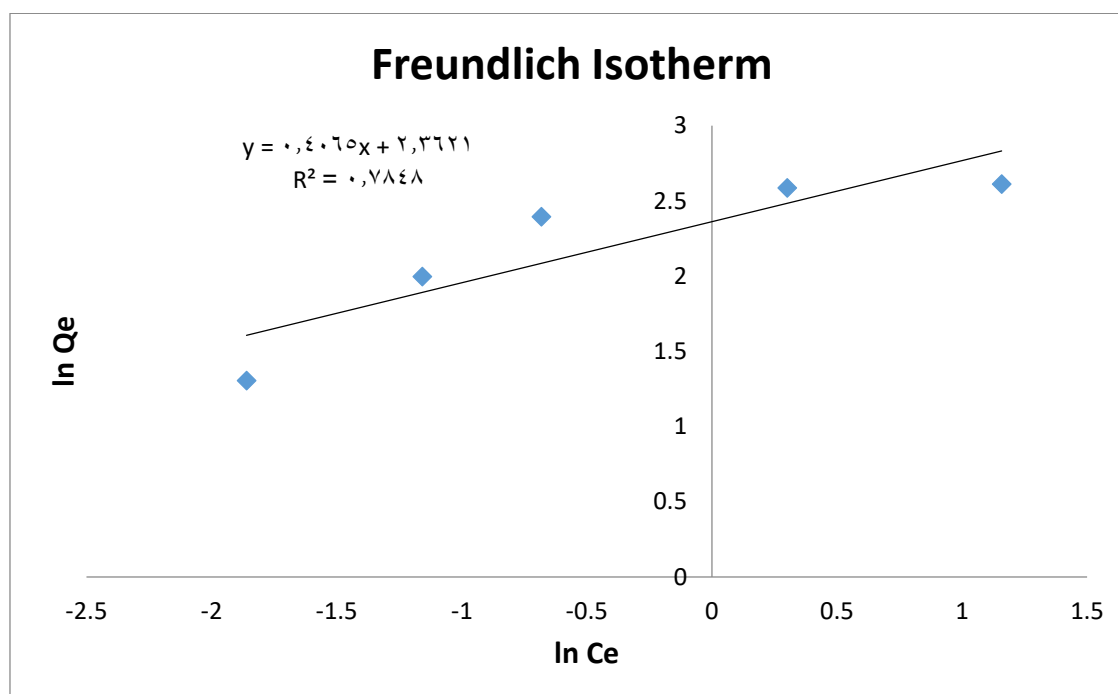


Figure 4.15: Freundlich plot for the adsorption of Malathion on MWCNT (time = 30 minutes, pH = 12, temperature = 35°C, adsorbent dose = 5 mg, volume = 10 ml).

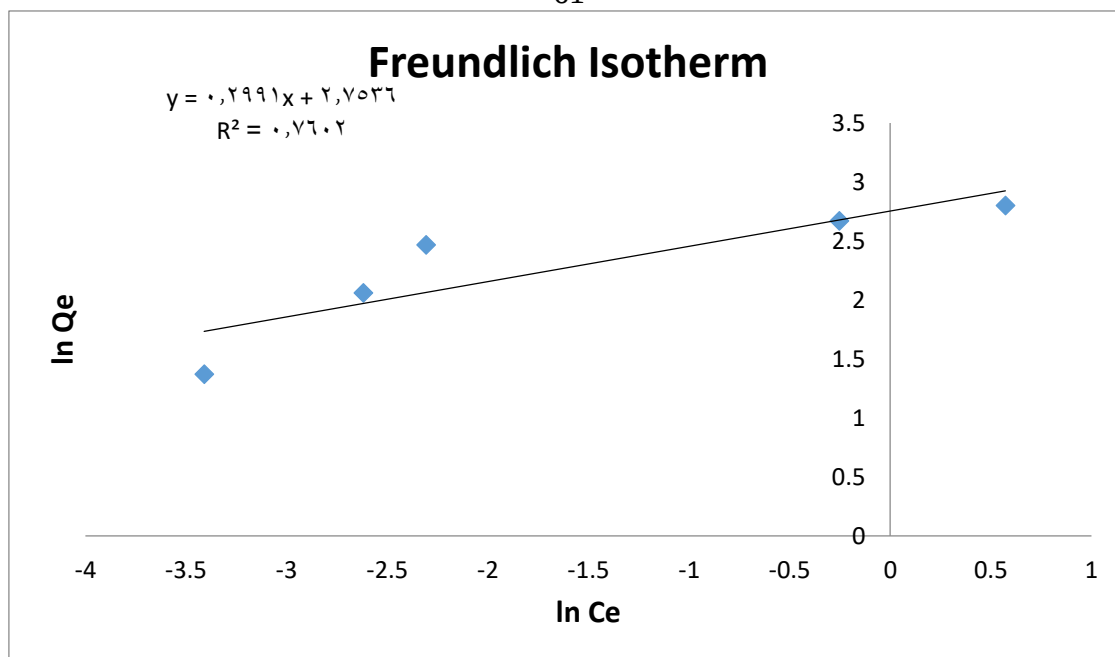


Figure 4.16: Freundlich plot for the adsorption of Malathion on MWCNT-PEA
(time =50 minutes, pH =7, temperature =25°C, adsorbent dose =5 mg, volume =10 ml).

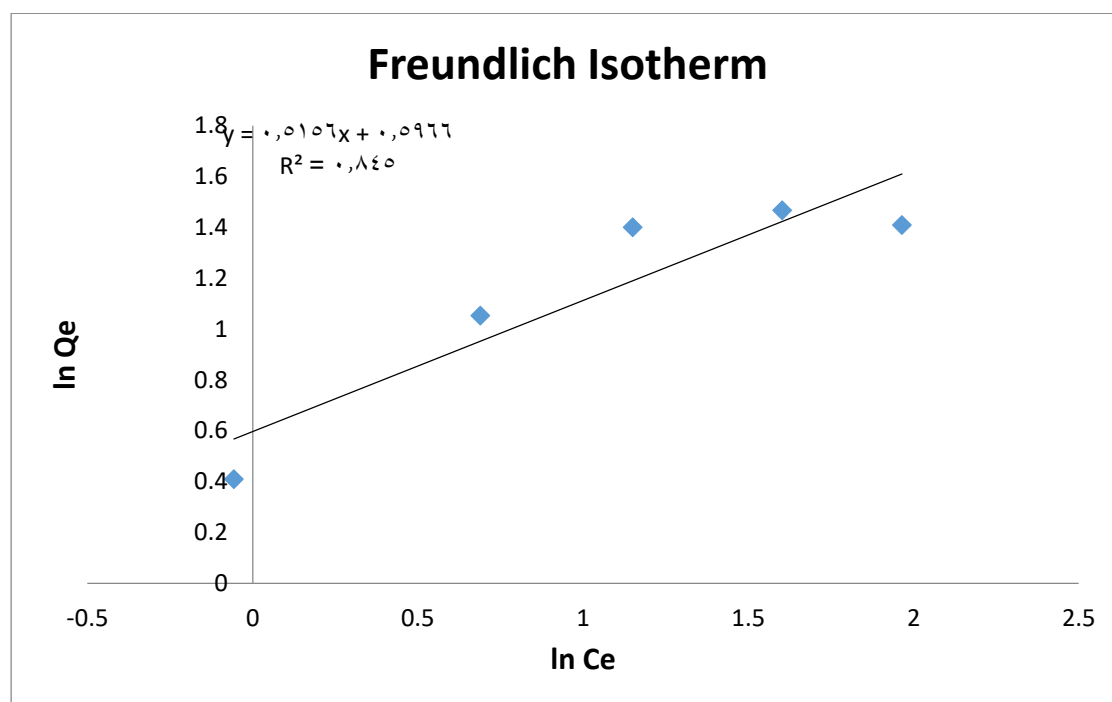


Figure 4.17: Freundlich plot for the adsorption of Malathion on MWCNT-PEA-DOM
(time =10 minutes, pH =7, temperature =25°C, adsorbent dose =7 mg, volume =10 ml).

The R^2 have values of approximately 1 when fitted as Langmuir model indicating that Malathion pesticide adsorption on MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM respect to Langmuir adsorption.

As a result, this means that there are real chemical bonds formed between Malathion and the adsorbent. Furthermore, the values of R_L in all cases for the Langmuir adsorption isotherm was less than one and more than zero, indicating that the process is favorable.

The following table represents the values of Langmuir and Freundlich isotherm parameters for the adsorption of Malathion on MWCNT and MWCNT-PEA in either cases of presence and absence of DOM:

Table 4.2: The parameters of Langmuir and Freundlich isotherms for the adsorption of Malathion on MWCNT and MWCNT-PEA or on MWCNT-PEA-DOM.

Adsorbents	Equilibrium Isotherm Models							
	Langmuir Isotherm				Freundlich Isotherm			
	Q_o (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g)	$1/n$ (L/g)	n (g/L)	R^2
MWCNT	15.27	3.11	0.9902	0.984	10.61	0.41	2.46	0.7848
MWCNT- PEA	17.11	10.99	0.9975	0.947	15.70	0.30	3.34	0.7602
MWCNT- PEA- DOM	5.49	0.54	0.9383	0.996	1.82	0.52	1.94	0.845

4.4 Adsorption kinetic models

The experimental kinetic data for Malathion adsorptions on predicted adsorbents were plotted following pseudo-1st-order and 2nd-order kinetic models and also as IPD model. The R^2 can tell how this process is suitable and follow that type of kinetic and its mechanism. The correlation coefficients and also kinetics parameters can be found from the linear relation for each type that mentioned previously as shown in the next figures:

4.4.1 Pseudo-1st-order kinetic model

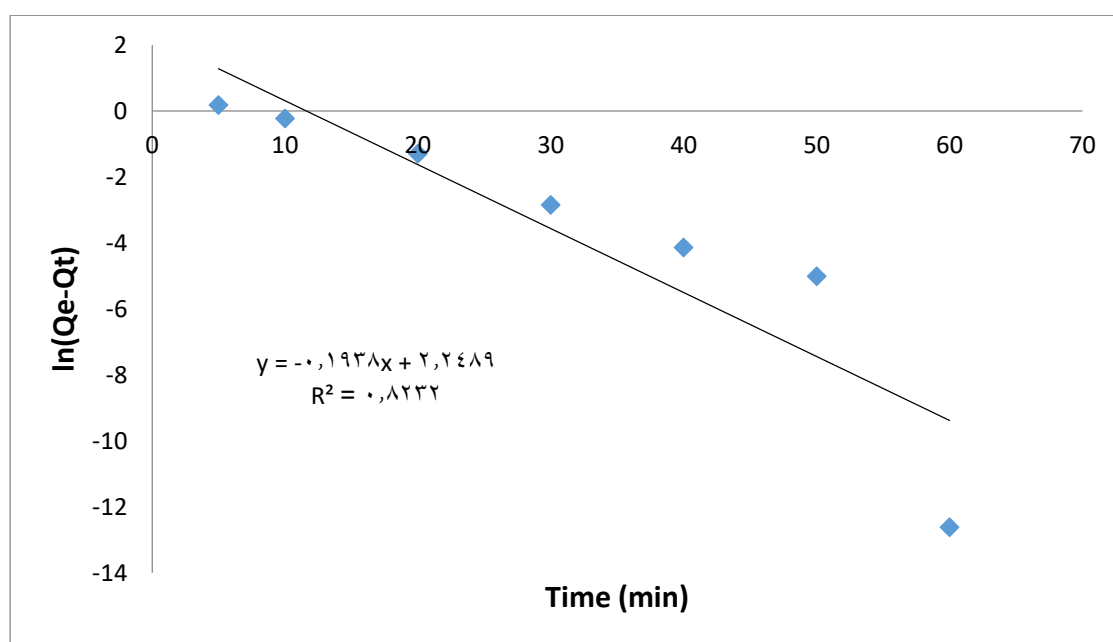


Figure 4.18: The plot of pseudo 1st-order kinetic model for the adsorption of Malathion on MWCNT.

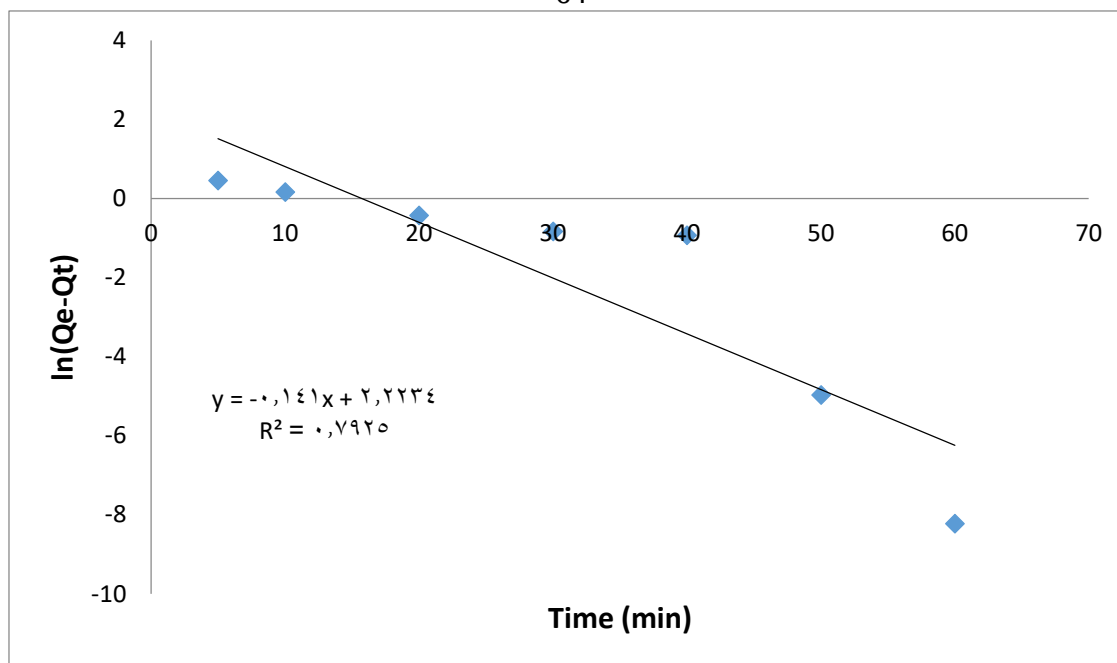


Figure 4.19: The plot of pseudo 1st-order kinetic model for the adsorption of Malathion on MWCNT-PEA.

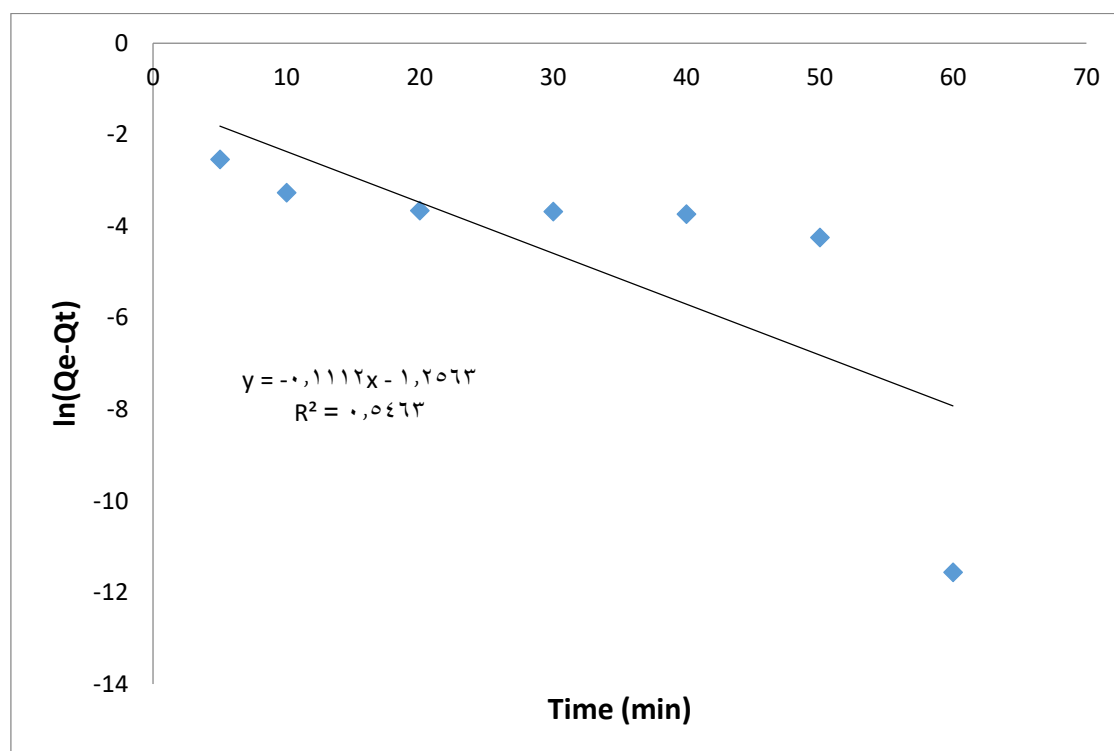


Figure 4.20: The plot of pseudo 1st-order kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.

4.4.2 Pseudo-2nd-order kinetic model

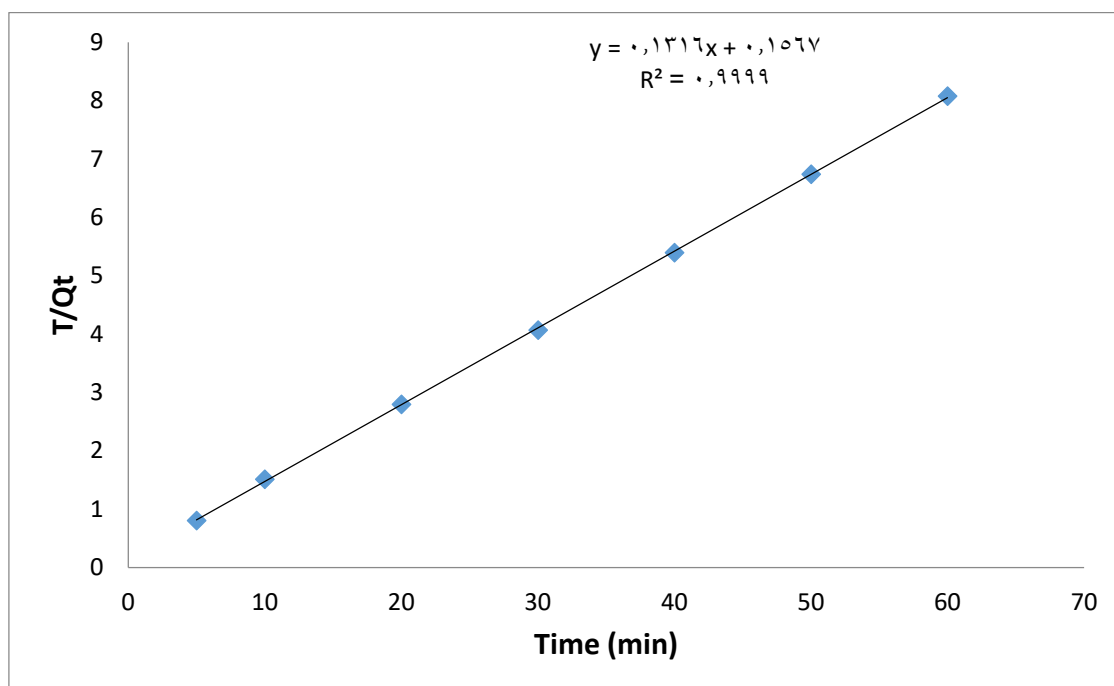


Figure 4.21: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT.

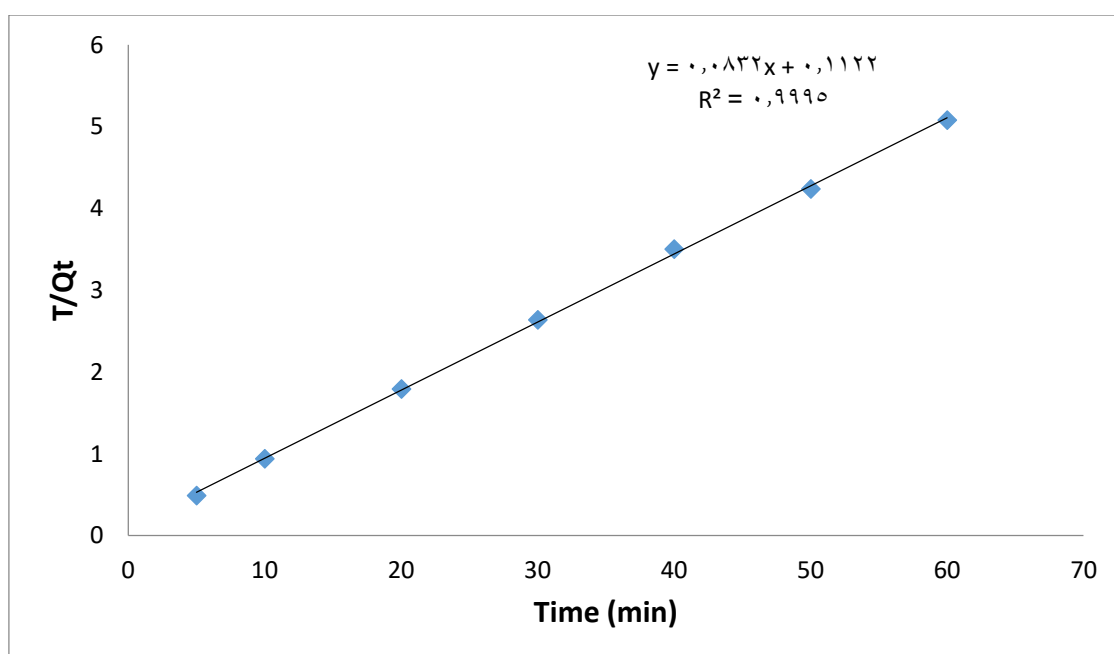


Figure 4.22: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT-PEA.

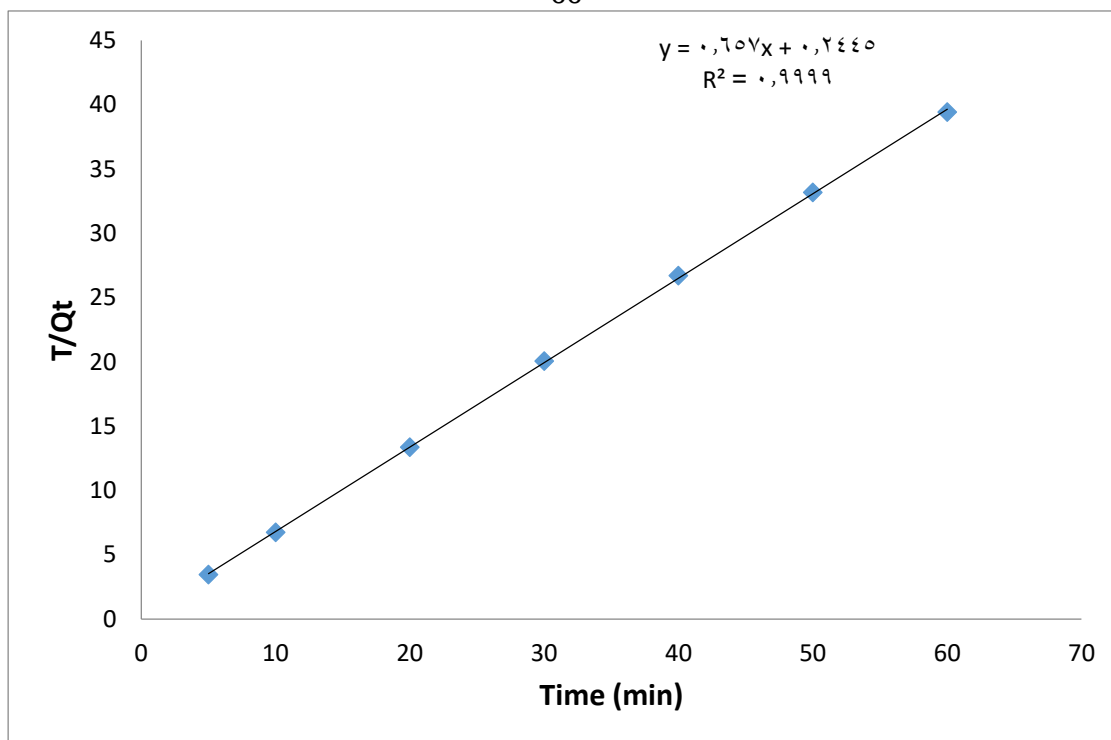


Figure 4.23: The plot of pseudo-2nd-order kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.

4.4.3 IPD kinetic model

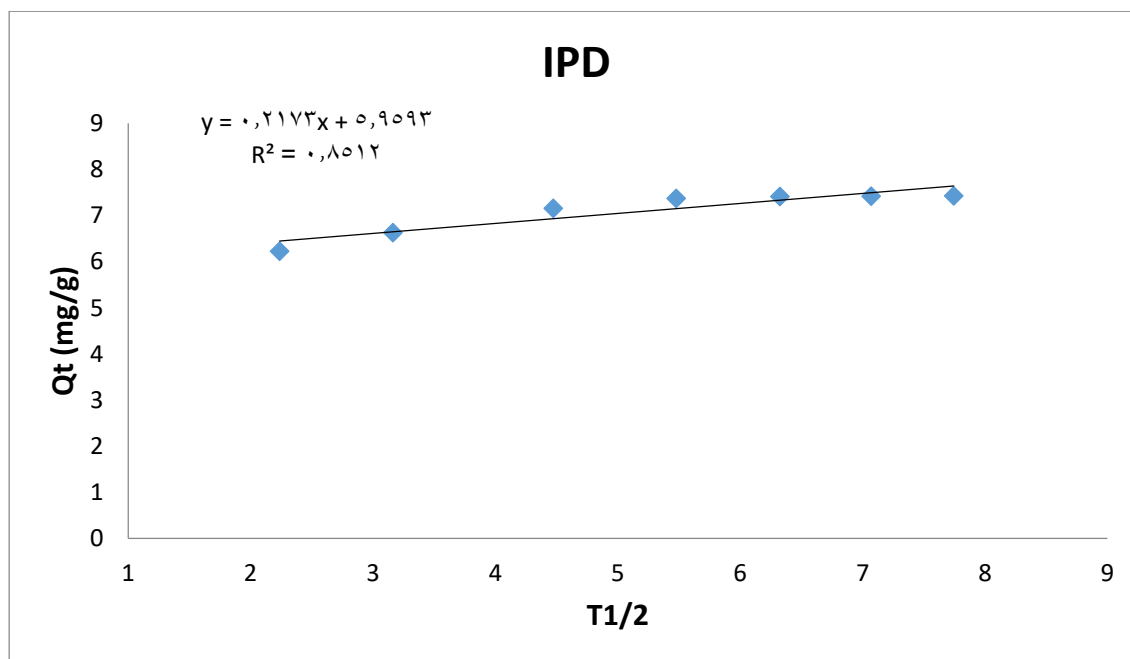


Figure 4.24: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT.

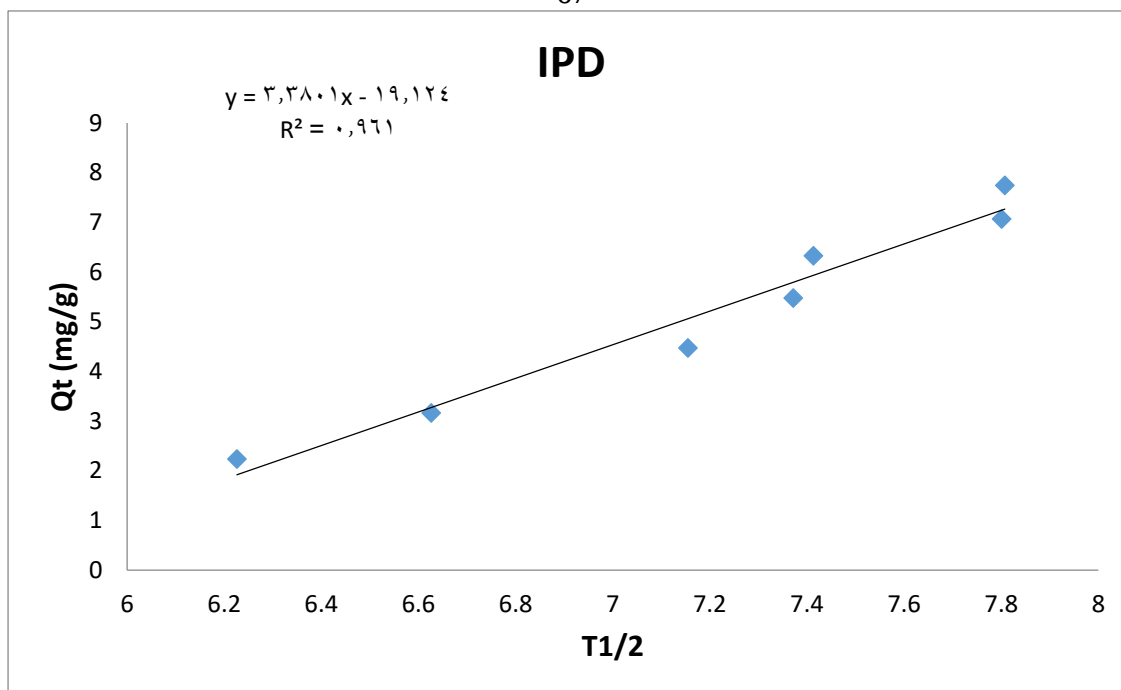


Figure 4.25: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT-PEA.

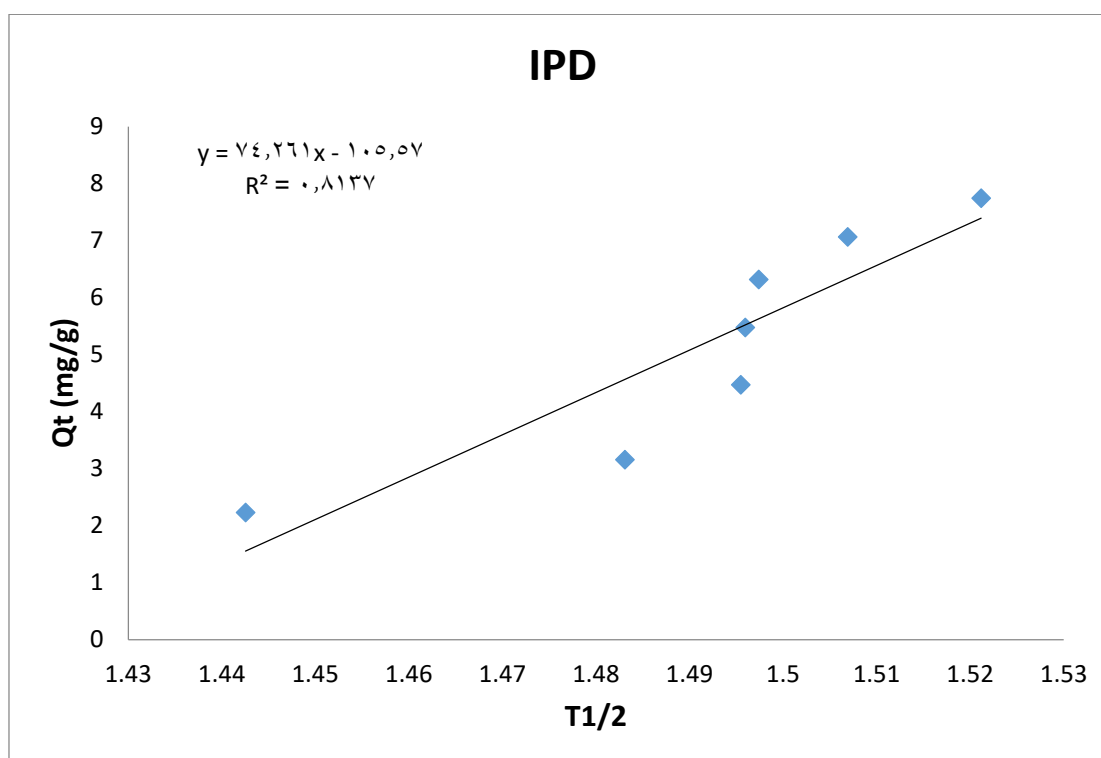


Figure 4.26: The plot of IPD kinetic model for the adsorption of Malathion on MWCNT-PEA-DOM.

With respect to the correlation coefficient values in the previous kinetic models data, it was shown that the adsorption of Malathion on MWCNT and MWCNT-PEA or on MWCNT-PEA-DOM followed the mechanism of pseudo-2nd-order kinetic model, since the values of R^2 in this kinetic model are approximately 1.

The following table shows the kinetic parameters for the pseudo-1st-order, pseudo-2nd-order, and IPD kinetic models for the adsorption of Malathion onto MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM.

Table 4.3: the parameters of pseudo-1st-order, pseudo-2nd-order, and IPD kinetic models for the adsorption of Malathion onto MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM.

Adsorbents	Adsorption kinetic models									
		Pseudo 1 st order			Pseudo 2 nd order			IPD		
	q _e EXP.	q _e (mg/g)	K ₁ (mg.g ⁻¹ .min ^{-0.5})	R ²	q _e (mg/g)	K ₂ (mg.g ⁻¹ .min ⁻¹)	R ²	Z (mg/g)	K _{id} (mg.g ⁻¹ .min ^{-0.5})	R ²
MWCNT	7.429	9.477	0.1938	0.8232	7.6	0.1104	0.9999	5.9593	0.2173	0.8512
MWCNT-PEA	11.808	9.238	0.141	0.7925	12.012	0.0617	0.9995	9.718	0.2843	0.961
MWCNT-PEA -DOM	1.521	0.284	0.1112	0.5463	1.522	1.7659	0.9999	1.4346	0.0109	0.8137

The experimental values of q_e are closer to calculated one in pseudo-2nd-order adsorption model, that's sign this adsorption follow the 2nd-order model mechanism.

4.5 Adsorption thermodynamic

Van't Hoff equation was used to study adsorption thermodynamic; the thermodynamic parameters (ΔH , ΔS , and ΔG) for the adsorption of Malathion pesticide onto MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM can be calculated from the slope and y-intercept of the graph of $\ln K$ versus ($1/T$), as shown in the following figures:

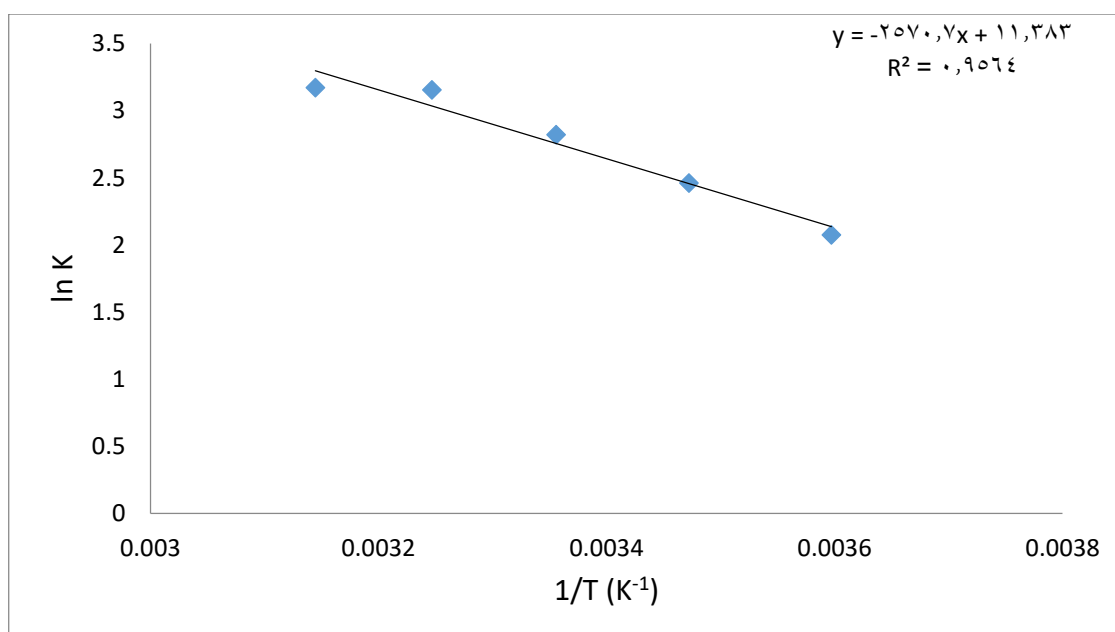


Figure 4.27: Van't Hoff plot for the adsorption of Malathion on MWCNT ($C_I = 4$ ppm, pH = 12, time = 30 minutes, adsorbent dose = 5 mg, volume = 10 ml).

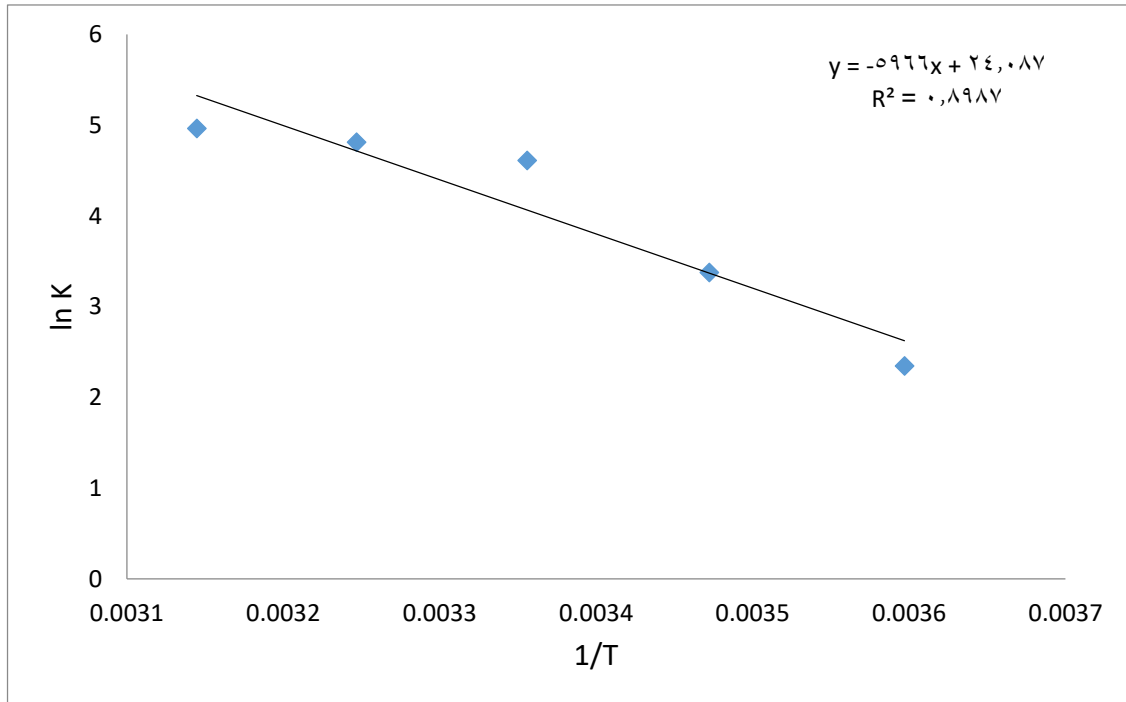


Figure 4.28: Van't Hoff plot for the adsorption of Malathion on MWCNT-PEA (C_i = 6 ppm, pH = 7, time = 50 minutes, adsorbent dose = 5 mg, volume = 10 ml).

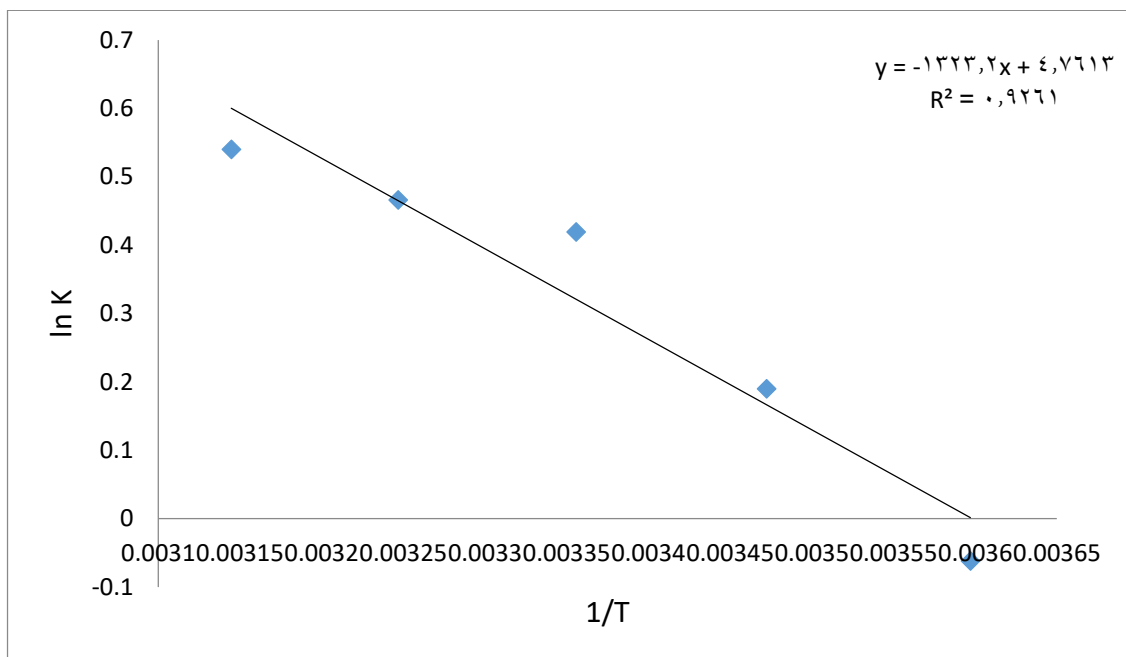


Figure 4.29: Van't Hoff plot for the adsorption of Malathion on MWCNT-PEA-DOM ($C_i = 2$ ppm, pH = 7, time = 10 minutes, adsorbent dose = 7 mg, volume = 10 ml).

The following table represents the values of the thermodynamic parameters (ΔH , ΔS , and ΔG) for the adsorption of Malathion pesticide using MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM.

Table 4.4: the thermodynamic parameters for the adsorption of Malathion on MWCNT, MWCNT-PEA, and MWCNT-PEA-DOM

	Adsorption thermodynamic		
	ΔH (KJ)	ΔS (J/K)	ΔG (15°C) (KJ)
MWCNT	21.372	94.637	-5.882
MWCNT-PEA	49.601	200.26	-8.073
MWCNT-PEA-DOM	11.001	39.585	-0.399

As shown in this table, the adsorption of Malathion on both MWCNT and MWCNT-PEA either in presence or absence of dissolved organic matter is endothermic process ($\Delta H > 0$) giving high % of removal as temperature increased, and also spontaneous ($\Delta G < 0$); furthermore, the all three processes go toward more disorder since the entropy parameter has positive values ($\Delta S > 0$).

4.6 Conclusions

Multi-walled Carbon Nanotube showed a very good result for the adsorption of Malathion pesticide, furthermore, a functionalized Multi-walled Carbon Nanotube have a higher adsorption capacity and the percent of removal at the optimum conditions increased by about 6.2%, both of them showed a very good thermal and chemical stabilities, and hence it can be used as perfect adsorbent to uptake malathion pesticide from wastewater.

The functionalized multi-walled carbon nanotube needs a maximum of 50 minutes to eliminate 98.34% of the original amount of dissolved Malathion without any pH adjustment, while it was 30 minutes to reach the maximum removal of about 92.14% for the non-functionalized one.

The presence of dissolved organic matter as a component of the solvent has a significant effects on the adsorption of target Malathion since the removal efficiency decreased to about just 52.74%, however it has no effect on other physical properties.

The results showed that all adsorption followed Langmuir adsorption isotherm, and all of them are favorable ($1 > R_L > 0$). The mechanism of all reactions followed pseudo-2nd-order kinetic adsorption model.

With respect to thermodynamic, the parameters proved that all processes are endothermic ($\Delta H > 0$), spontaneous ($\Delta G < 0$), and processes go toward disorder state ($\Delta S < 0$).

The regeneration of adsorbent did not highly reduce the removal efficiency, and the regenerated adsorbents showed a good percentage removal after 3rd use for the removal of Malathion pesticide, so it can be used multiples.

4.7 Recommendations

This work aims to remove one of the widespread organophosphorus pesticides (Malathion) by adsorption process onto MWCNT materials, and study the effects of DOM that present in the solution.

1. Survey how much the source of water in Palestine polluted with Malathion, especially in the Jordan valley regions which Malathion used in large amount.
2. Make fusibility study in future researches, and to devote an extra effort in the development of the nanomaterial industry.
3. Try to engineer specialized and commercially available filters using those materials.
4. To use other adsorption materials or other efficient technique for the removal of Malathion pesticide.
5. To increase the level of awareness of farmers about how to properly use pesticides and not to overuse them.

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جامعة النّجاح الوطنيّة

كلية الدراسات العليا

إزالة المبيد الحشري مالاثيون باستخدام مواد معدلة من أنابيب الكربون النانوية المتعددة الطبقات: وتأثير المواد العضوية الذائبة في المحلول

إعداد

يونس ماهر يونس مساد

إشراف

أ. د. شحدة جودة

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية
الدراسات العليا في جامعة النّجاح الوطنيّة في نابلس، فلسطين.

2020م

ب

إزالة المبيد الحشري مالاثيون باستخدام مواد معدلة من أنابيب الكربون النانوية المتعددة الطبقات: وتأثير المواد العضوية الذائبة في المحلول.

إعداد

يونس ماهر يونس مساد

إشراف

أ. د. شحدة جودة

الملخص

تهدف الدراسة إلى إعداد أنابيب متخصصة من النانوي كاربون متعددة الجدران واستخدامه لإزالة أحد أنواع مبيدات الحشرات الملاثيون من مياه الصرف الصحي، ويظهر الأنبوب النانوي الكربوني متعدد الجدران المعدل خواص كيميائية ممتازة واستقرار حراري، بحيث يمكن استخدامه كممتاز جيد، بالمقارنة مع المواد النقية غير المعدلة، فإنه يتمتع أيضًا بسعة امتصاص عالية.

هنا، تمت دراسة سلسلة من التجارب المصممة لإجراء نماذج دراسة السلوك الحراري والتي تمت باستخدام نماذج فريندلخ ولانغمير، كما تم دراسة الديناميكا الحرارية والحركية باستخدام النموذج الحركي الزائف من الدرجة الأولى، والزائف-الدرجة الثانية، ونموذج انتشار الجزيئات الداخلية لعملية إزالة المبيد الحشري الفوسفوري (الملاثيون) باستخدام أنابيب نانوية كربونية متعددة الجدران معدلة بـ (2-فينيل إيثيل أمين)، على عكس الدراسات السابقة، تم الأخذ في الاعتبار أيضًا تأثير المواد العضوية الذائبة في المحلول، لجعلها مثل عينة ملوثة حقيقية حيث لا يوجد تلوث يحدث من مادة واحدة. تم إجراء مقارنة لهذه الحالات الثلاثة من خلال تحديد الكمية الممتصة من الملاثيون (مبدأ المنافسة) بين المواد العضوية الذائبة في المحلول والمبيد الحشري، كما تم دراسة تأثير المعلمات المختلفة التي تؤثر على عملية الامتزاز، مثل درجة الحرارة وتركيز كل من المادة الممتزة والمالاثيون وكذلك وقت التماس بينهما وذلك لأخذ ظروف الإزالة المثلى، تم إجراء التحليلات باستخدام كروماتوغرافيا سائلة عالية الأداء لقياس الكمية المتبقية من المواد في المحلول بعد عملية الامتزاز، أظهرت النتائج التي تم الحصول عليها أن كفاءة إزالة الملاثيون كانت ملحوظة عند استخدام المواد المعدلة، وكان الحد الأقصى لإزالة الملاثيون 98.34% ولكنه خفض إلى حوالي نصف الكمية

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(52.74%) مع وجود مادة عضوية مذابة، مما يشير إلى أن الممتز غير انتقائي تجاه الملاثيون لوحده.

ومع ذلك، لا يستغرق الأمر أكثر من 50 دقيقة لإزالة مستويات عالية من الكمية المذابة اعتمادًا على ظروف المختبر المثلى، تصل النسبة إلى 98.34% من الملوث المستهدف عند التركيز الأولي 6 جزء في المليون على درجة حموضة معتدلة.

كما تم تجديد المواد الممتزة في الحالات الثلاث لإعادة استخدامها مرة أخرى حيث تم تحديد النسبة المئوية للإزالة قبل وبعد استرداد المادة الماصة، وأظهرت انخفاضًا طفيفًا في كفاءة الممتزات، لذلك يمكن أن تكون مواد قابلة لإعادة الاستخدام لإزالة مبيد الملاثيون.