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OPTIMIZING THE REMEDIATION OF ORGANOPHOSPHORUS PESTICIDE PROFENOFOS FROM WATER USING ACTIVATED DATE PITS: MECHANISTIC STUDIES

BY

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ABSTRACT

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Title: Optimizing the Remediation of Organophosphorus Pesticide Profenofos from Water Using Activated Date Pits: Mechanistic Studies

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The aim of the study was to examine the efficiency of date pits as an adsorbent to remove the organophosphate pesticide profenofos from wastewater. Various adsorption isotherms models namely Langmuir isotherm, Freundlich isotherm, Dubinin-Radushkevich isotherm and Temkin isotherm models were examined in order to understand the interactions between the adsorbate (profenofos pesticide) and the prepared adsorbents. In addition, thermodynamic adsorption was carried out to determine the homogeneity and spontaneous of the adsorbents. In the first phase of the study, three types of adsorbents namely roasted date pits, activated date pits and nano-activated date pits were prepared from the date pits collected from different sources. Different physical and chemical characterizations were studied such as scanning electron microscopy (SEM), Fourier transform infrared (FTIR), BET surface area, pore radius and pore volume.

The surface area of the nano-activated date pit was the highest 485.441 m^2/g. Moreover, the pore volume and pore radius were also the highest for the nano-activated date pits with values 0.338 cm^3/g and 17.8 Å, respectively. Therefore, nano-activated date pits have resulted in high removal percentage and removal capacity of profenofos from aqueous solution. Based on adsorption isotherm model, the values of R^2 was the highest for the nano-activated date pits. The adsorption maximum capacity (qm) increased with temperature and was maximum for the nano-activated date pit following Langmuir adsorption isotherm model. In the case of roasted date pit and activated date pit, the adsorption fitted the Freundlich model. Thermodynamic parameters showed a negative ΔG for all three adsorbents and the value increased with temperature. The ΔH value was positive for the three adsorbents and was the highest for roasted date pit (23.59 $KJmol^{-1}$); resulting in an endothermic reaction. Whereas, the value of ΔS was negative for the three adsorbents and was the highest for nano-activated date pits (-83.5 $Jmol^{-1}$).

DEDICATION

This thesis is dedicated to my beloved parents & siblings for their love, endless support, encouragement and sacrifices. They have given me invaluable educational opportunities. This is especially dedicated to the memory of my father; he is my source of strength and encouragement to be who I am today.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1: INTRODUCTION

1.1 Introduction

Clean water is one of the most important source for all living organisms to sustain life. In Middle East, countries including Qatar do not face problems in clean water; however, in Qatar it has scarce natural water sources and depends mainly on desalinated seawater (Tiwari & Sen, 2015).

Water paucity is a serious problem for millions of people in the world and is considered as “key to achieve sustainable development in 2030”. In Qatar, due to the rapid economic and population growth and infrastructure development in lieu of FIFA World Cup 2022, water resources of the country are under stress. According to the literature, the availability of freshwater in Qatar is less than 1%; therefore, it is categorized as one of the water poorest areas in the world (Al-Ghouti et al., 2017).

The Qatar National Vision 2030 (QNV 2030) is a development plan to serve as a clear roadmap for Qatar’s future. The vision aims to transfer Qatar towards an advanced society capable of achieving sustainable development by 2030 that ensures economic growth but not on the cost of environment and natural resources.

Due to increases in population, agricultural and industrialization, water contamination has increased globally including Qatar. Water can be contaminated by the disposal of toxic metals from industries, pesticides used by agriculture and by other pathogens.

Moreover, recent increase in agricultural activities in the country due to blockade and rapid industrialization to ensure self-sufficiency, the quality of water resources are under serious threat. These pollutants are dangerous for all living beings and they can cause negative effects on the ecosystem (Gupta & Pradeep, 2013). Hence, there is a need to focus research on the preservation of water quality in Qatar.

Hence, due to the increase of industrialization and agricultural activity there have been large demand on pesticide, insecticide and herbicide use that causes accumulation of these toxic chemicals and can reach to water-resources and result in environmental pollution (Mahmood et al., 2016). The contaminated water with pesticides occurs by industrial wastewater discharge, surface run-off and through leaching (Salman et al., 2011).

Organophosphorus pesticides (OP) are considered an important group of pesticides due to their common use. They are widely used in many developing countries in agricultural to control insect pests (Darko & Akoto, 2008). In the last years, OP was used in Qatar farms and it was found, due to the mishandling of pesticide by the workers to have caused negative health outcomes, such as frequent headaches, joint stiffness and excessive sweating (Shomar et al., 2014). Therefore, in order to protect the environment and living organisms including human, the level of pesticides must be controlled. Certain levels are allowed to use the pesticides and it is controlled legislatively through setting maximum residue levels (MRLs).

Moreover, Qatar being an arid country it is facing challenges in water scarcity due to a high rate of water consumption. One of the solutions to overcome this challenge is the expansion of treated wastewater reuse to improve Qatar's water security (Phondani et al., 2016). In Qatar, water is produced mainly using distillation to contribute to the sustainable development goals. The desalination technologies used in Qatar are: reverse osmosis (RO), multi-effect distillation (MED) and multi-stage flash distillation (MSF)

(Mannan et al., 2018). However, the RO technology is widely used all over the world due to its energy efficiency and can be continuously function in less price (Maliva & Missimer, 2010). In Qatar, the most commonly used technology is multi-stage flash distillation (MSF). Based on literature the MSF technology have proved to be suitable in arid region such as in Qatar. The MSF has the ability to treat variation in seawater temperature especially when there is high turbidity (Mannan et al., 2018).

The Qatar National Vision (QNV 2030) aims to transfer Qatar towards an advanced society capable of achieving sustainable development by 2030 that ensures economic growth but not at the cost of damaging the environment and natural resources. Therefore, the Qatari Government is in support of treating wastewater that can be further used in agricultural activities. Other countries that are engaged in recycling wastewater to achieve the high water demand include Singapore where 30% of water comes from treating wastewater and aiming to increase the supply by 55% in 2060 (Bennett, 2015). Other countries such as Tunisia where they use 30 million m^3 of treated wastewater in irrigation (Jasim et al., 2016). In Egypt they use 2400 million m^3/year of treated water for agricultural activity and have planned to increase up to 90,000 million m^3/year (Jasim et al., 2016). In advanced Asian countries, such as Japan, they use 257.5 million m^3/year for agricultural activity and mainly for non-potable urban (Angelakis and Salgot 2016). Whereas in Europe such as in Spain, the majority of the wastewater is used for irrigation followed by urban green areas (Navarro 2018).

In Qatar, treated sewage water or treated sewage effluent (TSE) is used in agricultural activities and industrial sectors. This method helps to minimize the high demand of desalination treatment and helps to achieve sustainability in recycling of water. Around

39% of TSE production is used in agricultural and it is estimated by Ashgahl that by 2020, 17% of the treated water is used in industries (Ashghal, 2014). Other applications of using TSE water is in cooling systems, fire-fighting training exercise and in the construction sectors.

Nevertheless, treating wastewater from agricultural activity or from greywater might contain infectious bacteria and other pollutants that will cause negative impacts to public health, living organisms and environment. Therefore, the wastewater must be treated to ensure safe treated water (Jasim et al., 2016). The technology of treating wastewater such as greywater that comes from showers, laundry and household is been practiced in some countries. The advantage of treating greywater is that it does not contain a highly toxic pollutants and it contains large volume of water (Pradhan et al., 2018).

However, treated greywater is not acceptable; there is a cultural influence where people are not ready to accept the use to treated wastewater. Lambert & Lee, 2018 have done a survey in Qatar to evaluate the people (Qatari's and expatriates) opinion for the use of treated greywater. Among the questions, majority of the people accepted to use treated greywater for gardening, toilet flashing and car washing. The least acceptance was using the treated water as drinking resource. Nevertheless, treating wastewater from agricultural activity or from greywater might contain infectious bacteria and other pollutants that will cause negative impacts to public health, living organisms and environment. Therefore, the wastewater must be treated to ensure safe treated water. (Jasim et al., 2016).

Hence, water treatment is any process that purifies water and makes it accessible to be used for any purpose. Various technologies to treat water to remove contamination can be used. These treatments include reverse osmosis, chemical precipitation, ion exchange, adsorption, membrane filtration methods, etc. Adsorption technique is the best technique considered in water treatment due to the efficiency in removing targeted pollution available in water on a large scale and due to its economic benefit (Singh et al., 2018) .

In the last few decades, the applications of adsorption has shown an interest in the development of new sorbents. As a result, the efficiency of adsorption from aqueous solutions for different types of sorbents were studied (Awwad et al., 2013). In many environmental remediation applications activated carbons are extensively used as adsorbents and this is due to their surface area and pore size (Belhachemi et al., 2009).

In recent studies the use of natural materials in nano-carbon synthesis have been developed. (Yallappa et al., 2017).

Activated carbons are mostly produced from agricultural byproducts such as nut shells, wheat straw, and others, and this technique is considered as green environmental chemistry and serves the environment by converting the unwanted leftover agricultural wastes to beneficial adsorbents. Moreover, activated carbons are widely used in water treatment for removing pollutants such as, pesticides, heavy metals and other organic chemicals causing serious environmental pollution (Belhachemi et al., 2009 and Awwad et al., 2013).

Therefore, this study has focused on preparing low cost and environment friendly adsorbents from natural by-products such as date pits. Dates are very popular food in arid and semiarid regions such as in Qatar. There are huge amounts of date pit waste suitable for preparing activated carbon due to its unique natural physical structure and low ash content (Belhachemi et al., 2009). Additionally, date pits are considered suitable adsorbents due to their macrostructure, physical and chemical properties such as, insolubility in water, high mechanical strength, chemical stability and economic viability (Al-Ghouti et al., 2010 ; Awwad et al., 2013). Therefore, in this research, date pits were selected as the adsorbent to treat water contaminated with profenofos pesticide, and the removal efficiency of the adsorbents will be determined. In this study, different modifications were investigated namely roasted date pit (RODP), activated carbon date pit (ACDP) and nano-activated carbon date pit (NACDP).

1.2 Aim and Objective

The aim of the study is to prepare low cost and environment friendly adsorbents from date pits. Batch experiments of variable profenofos pesticide concentrations were conducted to determine the adsorption efficiency of three prepared date pits. The following specific activity activities have been carried out:

i. Prepare roasted date pits, activated date pits and nano-activated roasted date pits.

ii. Perform physical and chemical characterization for the prepared adsorbents such as pH in solution, Fourier transform infrared (FTIR) analysis, and surface area characteristics using scanning electron microscopy (SEM) and Brunauer, Emmett and Teller (BET) analysis.

iii. Perform isotherm remediation studies for the removal of pesticides (organophosphorus- profenofos) using the prepared adsorbents.

iv. Apply different isotherm remediation models such as Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models in order to understand the interactions between the adsorbate (profenofos pesticide) and the adsorbents.

v. Perform statistical analysis.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to Pesticides

Pesticides are chemical compounds used to kill pests such as insects, fungi and unwanted plants (weeds) to increase and improve the yield of food supply (Popp et al., 2013). The role of pesticides should have a direct effect on the targeted pests and not on the non-targeted species including human; unfortunately, this is not the case (Kaur & Garg, 2014). Some pesticides causes environmental issues such as effecting the water security, soil microorganisms and affecting the human health. The effects of pesticides on human health is either direct or indirect ways, the direct ways are mainly due to the improper personal equipment (PPE) among the agricultures, and the indirect way is the consumption of aquatic species such as fish in which the pesticides get accumulated in the fish tissues (Srivastava et al., 2016).

Eventually pesticides are classified into different classes based on the uses of each pest directed towards. Carbamates fall in the herbicide category, insecticides include; Organophosphates, Organochlorines, Carbamates and Pyrethroids. The Fungicides include Dithiocarbamates (Yadav & Devi, 2017). Hence, according to the global pesticide market the pesticides are classified as follows: 42.48% herbicides, 25.57% insecticides, 24.19% fungicides, and 7.76% other types of pesticides (Bernardes et al., 2015).

The use of pesticides can also interfere in the food web of the organisms in the ecosystem, in a way that it can cause a loss of a keystone species, which will result in elimination of other species essential to the functioning of an entire community. Moreover, the studies and literature of pest control have created a further dependence on pesticides resulting in the development of new species when their natural dominate enemies are been killed by pesticides (El Atrache et al., 2013 ; Aktar et al., 2009).

The regular use of pesticides can cause both biological and economic effects due to their effects on some natural pollinators such as butterflies and honeybees. Therefore, there will be loss in these species due to their sensitivity to the pesticides. Hence, loss of these species that are used for plant pollination will cause reduction in seed and fruit production (Aktar et al., 2009).

Due to the existence of pesticides and their metabolites at very low concentrations, highly sensitive procedures with a pre-concentration step are needed for their detection. The most common pre-concentration methods are Liquid-Liquid Extraction (LLE) and Solid Phase Extraction (SPE). However, the SPE are considered important extraction method due to their high enrichment factors, simple design, and environmental friendly (El Atrache et al. 2013).These pretreatment steps undergo analytical methods to extract the pesticides and the most common are liquid chromatography-mass spectrometry (LC-MS) and Gas chromatography- mass spectrometry (GC-MS) (Zenilda et al., 2012).

2.2 Pesticides Classification

Pesticides are classified into number of categories, based on their toxicity, their environmental stability, pathways by which they target the organisms and the purpose of their applications, which may be divided into several types including fungicides, insecticides, and herbicides (Yadav and Devi 2017).

2.2.1 Classification of pesticides based on chemical composition

Organic pesticides are classified based on their structures into four major classes:

i. Organochlorine pesticides: are chlorinated hydrocarbons which have been used extensively from 1940’s to 1960’s for agricultural pest control (Jayaraj, Megha, &

Sreedev, 2016). Later on, most of these pesticides (such as Dichloro-diphenyl-trichloroethane (DDT), aldrin, chlordane, and benzene hexachloride) were banned because they were discovered to be persistent and hence accumulate in soils, fruits, and human tissues causing serious health and environmental problems (Singh, 2017).

ii. Pyrethroid pesticides: Pyrethroids are synthesized from pyrethrins. Toxic effect to human is low compared to organophosphate and carbamates. It is effected by sun and results in degradation, therefore it is limited in agricultural use (Tang et al., 2018). Moreover, there are negative side effects when exposed to pyrethroids; it causes serious effects such as brain tumors in children. Hence, it is important to detect samples such as water to determine the presences of the pesticide. For detection, the instrumental analysis used for detection of Pyrethroids pesticides are; gas chromatography and high-performance liquid chromatography (HPLC) (X. Li et al., 2019).

iii. Carbamate pesticides: These pesticides consists of carbamate backbone ($R_1OCONR_2R_3$) and derived from carbamic acid (Struger et al., 2016) . They can be of different uses including insecticides, fungicides and herbicides. Carbamate insecticides kills insects by affecting the nervous system, by causing a disturbance to the release of enzyme that regulates acetylcholine (a neurotransmitter) resulting of paralysis and death of insects. These pesticides, if not used properly, may cause serious acute toxicity, but they break down faster than organochlorines. Common carbamate pesticides include Ethienocrab, Oxamyl and methomyl (Lambropoulou & Albanis, 2007).

iv. Organophosphorus (OP) pesticides: are considered an important group of pesticides due to their common use. They are widely used in many developing countries in agricultural to control insect pests (Darko & Akoto, 2008). They are widely used in many developing countries in agricultural to control insect pests OP pesticides are produced by the reaction of esters and phosphoric acids. These compounds are reactive towards nucleophiles and undergo hydrolysis in presence of base, and are hydrolyzed by acids (Kulshreshtha & Shinde, 2012).

Organophosphorus (OP) pesticides was developed during the early 19th century and some of them were used as nerve agents during the World War II. The OP pesticides such as azinphos methyl is responsible for neurotoxic effects, it can affect the vertebrates by inhibiting the cholinesterase enzyme activity (Songa & Okonkwo, 2016). OP pesticide can cause effects on the environment and on Human health if not handled properly.

OP pesticides are produced by the reaction of esters and phosphoric acids. The general formula of pesticides is shown in figure 1a. The two R groups R1 and R2 are usually methyl or ethyl groups. Therefore, the R groups determine the type OP pesticides and hence determine the range of physicochemical properties. From the structure, the electronegativity of phosphorous is comparable with the hydrogen (Chao et al., 2016). Therefore, the O-P bond is expected to have a similar polarity to the O-H. Therefore, most OP are polar and hence water-soluble. Moreover, the organophosphate structure have bonds P=O can P=S as seen in figure 1b, 1c and 1d, therefore, on the basis of the structure organophosphate pesticides are subdivided into phosphoramidates, phosphates, phosphonate, and phosphorothioates as shown in figure 1b, 1c and 1d (Bernardes et al., 2015). Hence, the structural difference among these compounds results in different organophosphate metabolism and toxicity.

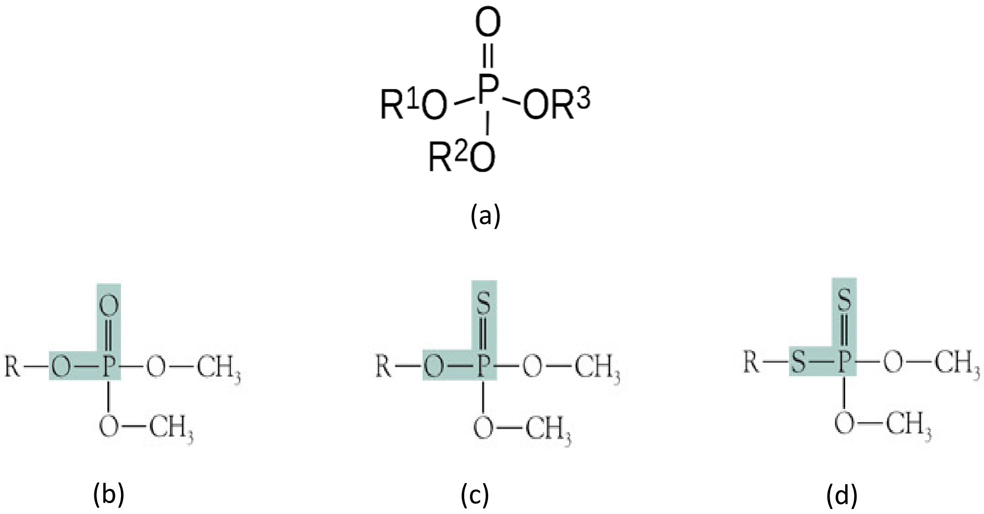


Figure 1. Organophosphorus Pesticides, Divided Into Three Types According To Their Backbones.

2.2.1.1 Profenofos-Organophosphorus

Profenofos is an organophosphate pesticide. Figure 2 shows the molecular structure of profenofos. The molecular formula of profenofos is $C_{11}H_{15}BrClO_3PS$ with molecular weight 373.63 g/mol. Table 1 shows the physicochemical properties of profenofos. Profenofos is highly used in cotton to get rid of cotton bollworm, plant bug and armyworm. It is also used in rice, vegetables, fruits and other crops.

Profenofos is considered to be on the highly poisonous organophosphorus pesticides having high toxicity that have negative effects on the environment and health. Therefore, small residues of it can cause serious health effects to human such as effecting the nervous system by inhibiting cholinesterase hence causing dizziness and nausa, and cause problems in respiratory such as paralysis and eventually result in death (Greish et al., 2011; Al-nahari 2015).

The path route of profenofos in the environment is through waste streams, it can also be released to the air. The vapor pressure of profenofos is 1.2 x 10^{-4} Pa (25^{o}C) (Reddy and Rao 2008). The LD50 stands for the lethal dose of a substance expressed in mg/kg, it is the amount of an ingested substance that kills 50 percent of a test sample such as a pesticides that kills one-half of the animals tested under a certain conditions (McDaniel et al., 2004). Usually the LD50 is calculated for rats and is estimated to be the same for human by multiplying by 70 kg, which is the average weight mass of human. Therefore, it was noted that the LD50 of profenofos for rat is 358 mg/kg of body weight (Fishel 2014). Hence, in order to protect human health, there are certain levels that are allowed to use the pesticides and it is controlled legislatively through setting maximum residue levels (MRLs). Hence, Maximum Residue Level (MRL) for residues of pesticide is defined as the maximum concertation of residue (mg/kg) that is permitted by law in specific foodstuff (MacLachlan and Hamilton 2010).

There are monitoring limits for pesticide residues in water. These limits must have a number of characteristics if they are to be useful and undergo legal challenges. Hence, the pesticide residues in water must undergo certain regulations that include the following characteristics: the type of the water and defining the residue. Based EPA modeling to determine the concentration on profenofos in water. Concentrations of profenofos pesticide in surface water should not exceed 6 ppb to 0.1 ppb profenofos concentration.

These values determine the exposure toxicity, where 0.1 ppb profenofos concentration determines a chronic exposure, whereas 6 ppb profenofos concentration determines an acute exposure (Tolerance, 2006).

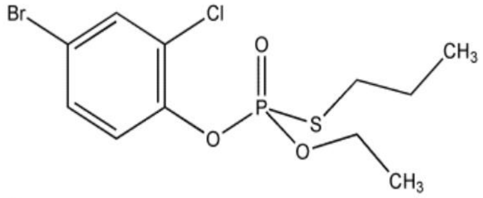


Figure 2. Molecular structure of profenofos.

Table 1. Physicochemical properties of Profenofos

Common name	Profenofos
Trade name	Curacron
Pesticide group	Organophosphorus
IUPAC name	O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate
Molecular formula	$C_{11}H_{15}BrClO_3PS$
Molecular weight	373.63 g/mol
Solubility in water	28 mg/L
Log Kow	4.4
Vapor pressure	1.2×10^{-4} Pa (25^{o}C)

Stability	Relatively stable under neutral & slightly acidic conditions. Unstable under alkaline conditions.
Toxicity	Class II
Acute oral LD50 for rats	358 mg/kg
Flash point	124 °C

2.2.2 Classification of pesticides on mode of action

Pesticides based on their effects and use are classified as non- systemic and systemic pesticides. The non-systemic pesticide will only effect the desired target pest, example of no-systemic pesticides are paraquat. Whereas, the systemic pesticide have the ability to enter the plant tissues and have the ability to transport to the plant vascular system therefore, this type of pesticides effect the human health by causing stomach poison after being eaten, some example of systemic pesticides are glyphosate (Tano, 2011).

2.3 Impacts of using Pesticides

Pesticides consists of a mixture of substances used for combating pests that damage crops and cause diseases; and hence use of pesticides increase the production of the agricultural products and prevent diseases. If not handled properly, however, pesticides when sprayed can distribute through the air and may eventually have harmful effects on the environment such as in water or soil (Borgesen et al., 2015; Aktar et al., 2009). The presences of pesticides in air is due to their physical characteristic in which some pesticide compounds are semi-volatile compounds (Tano, 2011).

The environment is divided into four major components, namely, air, soil, water and biota. Therefore, it is important to know the chemo dynamics of pesticides to know how the pesticides have an influence on the environment (Tano, 2011). Hence, there are certain factors that determine the availability and effectiveness of pesticides in the environment such as the vapor pressure and solubility of the pesticides in air and water. However, if the pesticides have a low vapor pressure it cannot stay in the air, therefore it accumulates in the water (Goodarzi et al.,2016). Since most pesticides are organic compounds, water-soluble serious effects can be observed in the aquatic organisms. Whereas, the major process that controls the behavior of pesticides in soil matrix are adsorption and leaching-diffusion (Borgesen et al., 2015).

Hence, the behavior of pesticides exhibiting in environment and its fate depends on its physical and chemical characteristic; additionally the improper management practice of pesticides also effects the environment (Jayaraj et al., 2016). The solubility of the pesticides is also important since it determines its ability to transport in surface runoff water and leaching to ground water. Therefore, some pesticides such as organophosphate pesticides are mostly soluble in water therefore, these pesticides are carried and in surface runoff and leached to groundwater and other pesticides such as organochlorine are difficult to undergo degradation therefore accumulate mainly for long period in the environment (Bernardes et al., 2015).

2.3.1 Impact of pesticides on Human

The role of pesticides should have a direct effect on the targeted pests and not on the non-targeted species including human, unfortunately, this is not the case (Mahmood et al., 2016). Some studies shows how these chemicals have a negative effect to human and other species and causes a potential risk to the environment. People in developing country are exposed to high risk to pesticides and are effected; these people mostly include production workers and agricultural farm workers (Aktar et al., 2009).

Some of the effects are due to the mishandling of pesticides and due to the lack of knowledge of agricultural farm works since they are not been trained with the basics of personal protection equipment's. A studied performed in Qatar was done to determine the exposure of the farmers to organophosphate (OP) pesticides if it causes any negative health outcomes. The study was performed in different farms in Qatar determining the duration of workers in the field and exposed to the pesticides. It was found that the most common of the self-reported symptoms were joint stiffness, frequent headache, and excessive sweating (Shomar et al., 2014). Hence, the study concluded by proving a mishandling of pesticides with limited knowledge of safe work and how the pesticides can cause health effects and in some cases fatal. Organochlorine (OC) pesticides also cause serious effects on human health. Most of the OC pesticides such as DDT (Dichlorodiphenyltrichloroethane) are responsible to cardiovascular disorders. OC pesticides also interferes with function and circuitry of the endocrine system, hence acts as endocrine disrupting chemicals (EDCs) (Jayaraj et al., 2016).

2.3.2 Impact of pesticides on Environment

The improper and mishandling of pesticides with the great use of it to have a high agricultural production have caused environmental pollution in soil, water and air. The physical and chemical behavior of pesticides, such as water solubility, bioaccumulation, mobility and long life have increased the contamination in the environment. Hence, affecting non-targeted terrestrial and aquatic species (Jayaraj et al., 2016).

2.3.3 Impact of pesticides on Soil

The major process that controls the behavior of pesticides in soil matrix are adsorption and leaching-diffusion (Haque et al. 1974). The mobility of the pesticides and persistence are determined by the interaction of the pesticides with soil, such as water solubility, half-life in soil and the ability of the soil to adsorb the pesticides (Aktar et al., 2009). However, pesticides are further grouped into two groups:

i. Bioaccumulation, Persistent and Hydrophobic: The persistence of pesticide is expressed in terms of half-life. The half-life is further divided into three categories (Kerle et al., 2007) including OC pesticides such as DDT and endosulfan, even though they are banned but their residues are still present.

ii. Polar pesticides: The ability of the pesticides to retain in the soil to different degrees to cause either positive or negative effects depends on the interaction between soil and pesticides, moreover depends on the organic matter content in the soil. If the availability of organic matter in soil is large, the pesticides can be adsorbed and even undergo biodegradation greatly. The negative effects of pesticides are also on the beneficial microorganism species in soil such as bacteria and fungi that might cause decline in their population in soil, which might result in soil degradation. Pesticides also effects the soil organisms that hold beneficial nutrients for plants such as Rhizobia Bacteria that transform atmospheric nitrogen into nitrates (Kanekar et al. 2004).

2.3.4 Impact of pesticides on surface water

In the air, the pesticides can be determined by its vapor pressure, however, if the pesticides have a low vapor pressure it cannot stay in the air. Therefore, it accumulates in the water (Tano, 2011). Since most pesticides are organic compounds water-soluble such as organophosphate pesticides, their solubility in water causes a serious effects that can be observed in the aquatic organisms.

The mobility of some pesticides can reach the surface water through runoff from treated soil and plants, therefore, effecting aquatic species. The residue of pesticides not only affects the aquatic and fauna species, but also effects the fresh water ecosystem (Lea et al., 2017). Depending on the pesticide properties, it can have direct or indirect effects on the species. For example, pesticides indirectly affect fauna species such as fish eating birds and causes decline in bird species (Jayaraj et al., 2016).

2.4 Water treatment

The intensive use of pesticides at high concentration will result in accumulation of toxicity in the food chain by affecting the quality and safety of food products. Therefore, the scientists are in concern to develop simple, selective and sensitive methodologies that will help in remediating pesticides at a very low level. Therefore, various techniques have been used such as membrane filtration, adsorption technique or using biological degradation to remediate pesticide (Rawtani et al., 2018).

2.4.1 Membrane Filtration

A membrane is a thin layer of semi-permeable material when a driving force is applied to separate the material wastes across the membrane. The membranes filtration differs based on the pore size. Therefore, there are different types of membrane such as ultrafiltration (UF), nanofiltration (NF), microfiltration (MF), membrane cartridge filtration (MCF) and Reverse Osmosis.

The membranes remove natural organic material, bacteria, microorganisms and particulate. The first development of reverse osmosis membrane for the desalination of seawater was in 1970’s (Maliva & Missimer, 2010). Later, the development of other membranes such as ultrafiltration, nanofiltration and microfiltration were developed. Each membrane filtration has a specific target pf pollutants, such as ultrafiltration is used in the removal of viruses and microfiltration is used for removing suspended solids (Shuttle, 2006). Reverse osmosis is one of membrane filtration technique having a semipermeable membrane surface; it works on the process of applying pressure on the membrane to remove the water contaminants. However, this method costs a lot due to the higher pressure needed to reverse the movement of the water.

2.4.2 Ion-Exchange

Ion exchange also known as water softener is a cation exchange water purification system. It removes ions such as nitrates, fluorides, calcium and magnesium compounds. Ion exchange works by passing contaminated water through resin beads, where the cation exchange is coated with positively charged sodium ions and replaces with calcium, magnesium and other hard ions in water. In addition, the anion exchange column the resin beads are coated with negatively charged chloride or to exchange the nitrate or fluoride in water (Patel, 2016).

2.4.3 UV radiation

This method uses mercury lamp to kill bacteria’s and viruses in water. This method only works to kill the pathogens contaminating water; it does not have any effects on the removal of other impurities such as heavy metals or salts. Moreover, the water should be pre-filtered before using the UV radiation treatment. It is considered a safe treatment since no chemicals are used. A more advanced UV radiation treatment is ultraviolet light-emitting diode (UV-LED) which has a positive advantage by replacing UV-mercury lamps and by having environmental protection (with no mercury) and also gives diversity in wavelengths (Nyangaresi et al., 2018).

2.4.4 Other Treatments

In the soil, organic pesticides are remediated by soil remediation technology using chemical, physical or biological processes. Selection of an appropriate technology is determined by certain factors, such as, concentration and type of the pesticide to be treated and to have a site characteristics and contamination (Morillo & Villaverde, 2017). Phytoremediation is one of the common biological techniques that are facilitated by using plants to remediate soil contaminated with pesticides. This technique is considered cost-effective and will have less negative impact on the environment (Chang et al., 2018). Another technique is chemical dehalogenation, which is a chemical technique used to remediate pesticides containing halogen mainly chlorine (Correa et al., 2016). Another technology is using optical sensors with high sensitivity for detecting of pesticides by using fluorometer, colorimetric and Surface Enhanced Raman Scattering (SERS), surface plasmon resonance (SPR) and chemiluminescent strategies (Yan et al., 2018).

2.5 Adsorption in water treatment

Adsorption is one of the techniques used for the purification of water. It is considered the most effective method in water treatment compared to other treatments. It can be used in small scale (laboratory) or in industrial scale (Bouhamed et al., 2012).

The phenomenon of adsorption is an adsorption on solid surface. The material that is adsorbed on the surface is called sorbate, and the material on which the adsorption occurs is called sorbent. The mechanism is affected by certain factors such as temperature, pH, surface area and nature of the adsorbed material. The mechanism of adsorption on the surface is either by diffusion or by molecular interaction of the sorbate by forming single or multilayers on the surface (Bushra & Shahadat, 2017). The surface area of the adsorbent is characterized by the pore size, surface area, surface roughness and the homogeneity of the surface. It is important to prepare a suitable adsorbent environmental friendly, having high efficiency in the removal of pollutants from the environment. Commonly used adsorbents: silica, activated charcoal, alumina, bentonite clay, zeolites, bagasse (Bushra & Shahadat, 2017).

The characteristics of the adsorbent are the pore size, pore volume and surface area. Moreover, it is more favorable to prepare an adsorbent that has mesoporous that will be suitable in adsorption than micropores and macropores (Fonseca et al., 2016). Therefore, as the surface area increases, adsorption capacity is high (Wu, Wu, Tseng, & Juang, 2010).

The forces of attraction between the adsorbent and adsorbate are either weak force-van der Waal forces or strong attraction force-chemical bond. Based on the force of attraction, there are two types of adsorption: physical (physisorption) and chemical (chemisorption) adsorption (Chiou, 2003):

i. Physisorption: Adsorption between the adsorbate and adsorbent is physical attraction based on weak bonding-van der Waals force.
ii. Chemisorption: the attraction force between the adsorbent and adsorbate is chemical force-chemical bonding. Unlike physisorption, a monolayer is formed of adsorbent and adsorbate.

2.5.1 Activated carbon as adsorbent in water treatment

Activated carbon are carbonaceous material that play a major role in remediation of pollutants. Ability of formation of high surface area and large porous makes it suitable adsorbent that are widely used in many applications such as water treatment, air pollution control, solvent recovery, catalyst support, and others (Belhachemi et al., 2009). Activated carbon is widely used as an effective treatment to remove and separate unwanted materials. Adsorbents that are activated are characterized by their high surface area, physicochemical stability, mechanical strength and pore volume (Demiral et al., 2010).

In the last few decades, activated carbon materials have gained attention in the adsorption treatment mechanism to wastewater treatment (Sekirifa et al., 2013). Activated carbon materials are black solid material that are amorphous and microcrystalline that come in two variations Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC) (Adib Yahya et al., 2015).

Activated carbon are prepared by physical or chemical activation. The physical activation is based on thermal activation of carbonaceous sample; the sample is heated at high temperature range with flow of inert gas in the absences of oxygen. Carbon dioxide or steam are the active reagents (Pallarés et al., 2018). The samples are activated using tubular cylindrical furnace by setting the temperature and the flow rate of the gas. The liquid by-products are collected in a flask leaving behind the ash formed (Bouchelta et al., 2008).

Several studies have shown that the activated carbon is more effective in removing organic compounds from water than other treatments such as biological treatments (Ioannidou, Zabaniotou, Stavropoulos, Islam, & Albanis, 2010).

Activation by chemical treatment is done by using phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH) and zinc chloride ($ZnCl_2$). Chemical activation uses less temperature range compared to physical treatment. However, among these chemical agents, in literature review, it is reported that using KOH in chemical activation treatment is more suitable for coal materials (Wu et al., 2010). Moreover, H_3PO_4 compared to $ZnCl_2$ is environmental friendly not causing any negative impact to the environment and can be recovered. It is also reported that H_3PO_4 as chemical agent for chemical activation treatment is more suitable for lignocellulosic material (Suresh et al., 2012). Hence, H_3PO_4 as active agent is considered as time and energy consuming since it forms activation in single step heat treatment and producing more yield, (Girgis and El-Hendawy 2002).

Most of the studies use either physical or chemical treatment in preparation of activated carbon. However, both treatments can be used simultaneously-physiochemical activation treatment to produce better mesoporous surface area, but this method is not widely used due to the high cost (Din et al., 2009). Moreover, the concertation of the active agent plays a role in adsorption efficiency. Yalçın & Sevinç, 2000 prepared chemical activation from rice husk using different concentration of $ZnCl_2$ ranging from (0-30%). The highest surface area (480 m^2/g) was observed by the adsorbent prepared by 10% concentration $ZnCl_2$ active agent. Hence, the chemical and physical activation has an effect on the surface area and pore volume, hence having different adsorption efficiency.

Therefore, activated carbons are increasingly used in water treatment for removing organic chemicals and metals causing serious environmental pollution (Awwad et al., 2013). However in the last few years, many studies are conducted to produce economic and environmental friendly adsorbents. Different agricultural waste, such as nutshells, wheat straw, date pits are used as activated carbon. Lignocellulose biomass are widely used as activated carbon due to high porous formation and abundance of carbon and hydrogen bonds (Ioannidou et al., 2010). In the literature, a number of studies have used agricultural waste as adsorbents in wastewater treatment to remediate dyes, phenols, heavy metals and pesticides.

2.5.2 Agricultural wastes as adsorbents

Adsorbents using agricultural wastes have advantages in low costs. Moreover, their porous structure and availability of carboxyl and hydroxyl make them suitable in water treatment (Gao et al., 2018). Agricultural wastes or byproducts are used as activated carbon such as olive stone, apricot stone, nutshell, coconut shell, almond shell, and date stone (Ahmad et al., 2012). Activated carbons from agricultural waste products have showed promising effects in water treatments for removal of organic and inorganic pollutants.

Other application of agricultural wastes are in fertilizers. By using, fertilizing waste technology increases the organic content in the soil and overcome the use of pesticides. One of environmental friendly application using raw material from agricultural waste, is the manufacturing of papers. Majority of the agricultural wastes coming from agricultural production and household life causes environmental issues without being disposed and effectively treating the waste. Therefore, it is more beneficial using these wastes as treatments for environmental remediation (Omo-Okoro et al., 2018).

Over the last few years, many studies are conducted to produce economic and environmental friendly adsorbents. Different agricultural wastes, such as nutshells, wheat straw, date pits are used as activated carbon. Therefore, there is a growing demand to find a suitable adsorbents from the unwanted biomass leftover agricultural waste as adsorbents that are relatively efficient, inexpensive and easily available for the adsorption of pollutants (Cara & Jităreanu, 2015). The activated carbon for the formation of porous is prepared either from lignocellulosic material such as date pits or from coal. In some literature review mentioned that hard material agricultural biomass waste such as date pits, coconut shells and almond shells are suitable to activated by physical treatment due to their physical strength (Suresh et al., 2012).

2.5.2.1 Types of activated agricultural wastes used as adsorbent

Different types of agricultural wastes are used for water treatment for removal of organic and inorganic pollutants (Rashed, 2018). Most of the agricultural wastes undergo modification to increase their efficiency of pollutant uptake. Some of the common modification methods are- activation of raw waste, nano-sized, carbonization and grafting. Bouchelta et al. (2008) studied the physical and chemical characterization of date stone physically activated with steam at different pyrolysis temperature (500-800)^{o}C at a different time. The results have showed the yield was highest at temperature at 500^{o}C. The decrease in the yield is mostly due to the decomposition of the polymers such as cellulose, hemicellulose and lignin present in the date pits (Wu et al., 2018).

However, Bouchelta et al. 2008 showed that the optimum temperature is at 700^{o}C at hold time 1 hour due to the high pore formation at higher temperature.

Some of the materials used as activated carbon their porosity and adsorption using phosphoric acid as active agent in chemical activation is influenced by the thermal activation and concertation of H_3PO_4. It is reported that thermal activation at 450^{o}C using chemical activation as H_3PO_4 as chemical agent is suitable for pore formation in agricultural materials. However, in case of the date pits some literature review have reported at temperature 500-700^{o}C high porosity is formed and this might be due to the material of the date pits that contains high lignocellulose materials having porosity that always the penetration of the of H_3PO_4 (Girgis and El-Hendawy 2002).

Yakout and Sharaf El-Deen 2016 studied activation of olive stones by chemical treatment using H_3PO_4 as chemical agent. This study have supported previous literature reviews on using H_3PO_4 as chemical agent considered to be environmental friendly more than $ZnCl_2$, however, the yield of activated carbon produced by using $ZnCl_2$ is more than H_3PO_4 for the carbon material used.

Another study was done by chemical activation of coconut husk for dye adsorption. The procedure was done by pyrolysis physical treatment at temperature 700^{o}C followed by chemical treatment using potassium hydroxide as chemical reagent. High surface are and large pore volume was achieved to have high effective adsorption of the dye (Tan et al., 2008).

Sirry et al. (2018) have used other chemical activation treatment by using combination of petroleum ether (PE) and hydrochloric acid (HCl) and another combination between PE and sodium carbonate (Na_2CO_3). This combination was used to increase the surface area of the date pits and uptake of the pollutants. Another study was done to prepare activated date pits by chemical treatment using zinc chloride ($ZnCl_2$) and ferric chloride ($FeCl_2$). It was shown the activation by $FeCl_2$ showed higher and this was suggested due to the ability of ZnCl2 to remove more volatile (Ahmed, 2016).

Kumar & Mohan Jena, (2017) supported previous studies in preparation of activated fox nutshell with H_3PO_4 to achieve efficiency removal due to the formation of high surface area. Another study done by Kumar & Mohan Jena, (2016) have studied chemically activated fox nutshell with $ZnCl_2$ to be used in biotechnology treatment to remediate methylene blue and phenols from aqueous medium by using batch and fixed bed column. High surface area and pore volume was developed by increasing the efficiency removal of the pollutants. Moreover, the concertation of the active agent plays a role in adsorption efficiency. Yalçın & Sevinç, 2000 prepared chemical activation from rice husk using different concentration of $ZnCl_2$ ranging from (0-30%). The highest surface area (480 m^2/g) was observed by the adsorbent prepared by 10% concentration $ZnCl_2$ active agent. In recent researchers have been focusing on developing adsorbents that are safe to treat heavy metals polluting water. Heavy metals are disposed to water mostly from industries. Due to their toxic effects on human's and other living organisms, and their ability to not easily biodegrade, hence heavy metals require efficient methods to be treated from the environment (Hegazi, 2013). Different agricultural wastes have shown the ability to remove heavy metals from wastewater. Lead (Pb) is one of the toxic heavy metals that causes environmental issues even at lower concentrations. Lead enters the environment through the effluents from industries. The presences of Lead in groundwater and soil is mostly through leaching, therefore, safe adsorption techniques must be used to remediate

Lead. One of the techniques is using agricultural waste as adsorbents. Two studies have shown removal of lead (II) ion Pb (II) using rice husk. Amer et al., (2017) have shown rice husk proved an efficient adsorbent of Pb (II) from wastewater using surface complexation and physical adsorption mechanism. Other studies have shown that when rice husk is modified by tartaric acid, it shows high removal of lead from aqueous solution. The studied showed that high adsorption capacity was due to the presences of carboxylic groups on the surface of modified rice husk (Wong et al., 2003).

2.5.2.1.1 Removal of organic pesticides

This section shows different types of agricultural wastes adsorption used to remediate pesticides from environment. Organic pollutants such as pesticides and chemical fertilizer reaches the ground water and water stream through leaching. Memon et al. (2008) have used watermelon peels (WMP) as adsorption for the removal of methyl parathion, which is an organophosphate pesticide from the aqueous solution. The removal of the pesticides from aqueous solution were performed in certain parameters such as pH, initial concentration, amount of adsorbent and contact time under agitation using adsorption isotherm to determine the maximum adsorption efficiency. The results have showed removal of methyl parathion is higher in acidic pH, chemically and thermally modified watermelon peels showed effective adsorbent of the pesticide. Based on adsorption isotherm, the results have shown that Freundlich adsorption isotherm showed high adsorption efficiency at lower concentrations compared to Langmuir adsorption isotherm that showed high adsorption efficiency at higher concentrations. Memon et al. (2008) have further carried desorption process of methyl parathion pesticide from the watermelon peel and it was found that methanol was best solvent used.

A study was perfomed by Njoku et al. (2014) to determine the efficiency of sky fruit husk activated carbon (SFHAC) as adsorbent for the removal of herbicide bentazone. The study showed that the SFHAC is a very promising adsorbent having a high surface area (1211.57 m^2/g) in removal of the herbicide bentazon. Rojas et al., (2014) studied the adsorption of four pesticides (atrazine, alachlor, endosulfan sulfate and trifluralin) contaminated in aqueous solution by using different agricultural adsorbents (sunflower seed shells, rice husk). Among the four adsorbents, rice husk have showed maximum removal efficiency. Moreover, the solubility and the hydrophobicity of the pesticides affected the adsorption capacity. It was found that that adsorption of the pesticide for the four adsorbent decreased with their water solubility and increased with their hydrophobicity. Mohammad, (2013) used activated apricot stone to adsorb ethoprophos an organophosphorus pesticide. The activated carbon was done using (H_3PO_4) as chemical active agent. The results showed adsorption capacity of 20.04 mg/g by using Langmuir equation. The SEM images have shown the formation of porous, whereas, the BET surface area (566 m^2/g) indicated high surface area of the activated apricot. Therefore, indicating the apricot stone can be used to remediate ethoprophos pesticide.

2.5.3 Date pits as adsorbent in water treatment

Date pits or date stone have shown a promising removal of pollutants from water treatment. Due to the abundantly availability of the date palm and its chemical structure, the date pits are used as adsorbent in water treatment (Wakkel et al. 2019). Date pits have shown a promising high efficiency in removal of organic and inorganic pollutant. Moreover, due to the presences of lignocellulosic composition and its structure that is suitable in high temperature, makes it suitable to be activated carbon (Krishnamoorthy et al., 2018). Date pits are used in many applications such as removal of heavy metals, pesticides, removal of dye.

2.5.3.1 Removal of Heavy Metals

Activated, non-activated and raw date pits have shown effects on removal of heavy metals from wastewater. El-Hendawy (2009) have proved the efficiency of activated date pits to be used in water treatments. The experiment was carried by differentiating the removal capacity between activated carbon date pits and HNO_3-oxidized date pits to remove lead (Pb) and cadmium (Cd) from aqueous solutions. The activated carbon date pits was prepared using different activation methods. The results obtained showed that the steam-activation of date pits improves the adsorption of Pb (II) ions. Another activated method used was chemical activation with H_3PO_4 to produce H_3PO_4 activated carbon date pits. In this method, the adsorption of Pb (II) ions increased with increasing temperature. Overall, the results have shown lead ions are removed more than cadmium due to its low solubility that enhances its removal. Banat et al., (2002) reported removal of zinc (Zn) and copper (Cu) ion using activated and non-activated date pits. The adsorption was followed by Freundlich isotherm model. The experimental results have showed that non-activated date pits than the activated date pits removed the uptake of both heavy metal ions Zn (II) and Cu (II) ions more efficiently. Both the adsorption of both ions depended on pH, temperature and initial concentration of metal ion. Therefore, with high pH and initial concentration, the adsorption of the ions increases. However, the uptake of Cu (II) ion was more than Zn (II) ion performed under the same conditions. Banat et al., (2002) proved that using date pits as adsorbent without any physical or chemical modification can be used in water treatments to adsorb heavy metal ions such as zinc and copper.

2.5.3.2 Removal of Dyes

The presences of dyes in water is toxic to many aquatic species. The presences of dyes in water is usually discharged from industries such as textiles, plastics, food and cosmetics (Ahmed, 2011). The adsorption of dye from aqueous solution depends on morphology of the dye such as, it's structure and type (Fatiha and Belkacem 2016).

A number of studies were performed to determine the removal of methylene blue (MB) using date pits as adsorbent. Banat et al., (2002) reported the use of date pits as adsorbents to remove MB from aqueous medium. The experiment used raw and activated date pits that was activated at different temperatures (500 ^{o}C and 900^{o}C) physically. Further, the adsorption was performed kinetically and using adsorption isotherm model. The adsorption was studied under the parameters pH, temperature and salinity of the solution on MB dye. The results showed that raw date pits had higher adsorption capacity than the physically activated date pits performed at both temperatures. This unexpected adsorption result can be explained that the functional groups at the surface were effected by high activation temperature. Additionally, the removal of MB dye using raw date pits increased with increasing the pH and decreased by increasing the temperature of the solution. Based on the adsorption kinetics and adsorption isotherm model, the results followed pseudo-second order kinetic model and the experimental equilibrium followed Langmuir model respectively. Al-Ghouti et al., (2010) reported the use of raw date pits to adsorb MB dye and heavy metals ions copper and cadmium ions from aqueous solutions. The results have shown hydrogen bonding was formed between the nitrogen present in the MB chemical structure and the functional groups present at the surface area. The adsorption orientation of MB on the surface of the raw date pit was mentioned. It was found that there are three possible orientations. The first two possibilities is due to the aromatic ring that can for either horizontal or perpendicular attachments to the surface of the raw date pits. moreover, Al-Ghouti et al., (2010) further explained the other orientation is the bond formation between one amino group and the raw date surface, therefore, this results in localization of the charge which was observed from FTIR characterization that there was difference in bands before and after adsorption.

2.5.3.3 Removal of Pesticides

Different researchers have used date pits as adsorbents in the removal of pesticide from the aqueous solution. Hameed et al., (2009) studied the adsorption isotherm mechanism in removal of 2, 4 dichlorophenoxyacetic acid (2, 4-D) on activated carbon derived from date pits. The date pits were activated by both methods physical and chemical activation. First, it was physically activated at 700^{o}C under the flow of nitrogen gas, followed by chemical activation using potassium hydroxide (KOH). The physical characteristics of the adsorbent was observed using BET and scan electron microscopy (SEM). The BET results have shown high surface area (763.40 m^2/g). Whereas, the SEM results have showed homogenized surface with well-developed pores allowing a good adsorption of the pesticide. The size of porosity is important to study depending on the molecular size of the pesticides. Salman et al., (2011) studied the adsorption of the pesticides Bentazon and carbofuran on activated date pits. The activated date pits were carried in two steps, first physical carbonization of the raw date pits followed by activation soaked with KOH. The activation was carried at temperature 850^{o}C. The activated date pits showed surface area from BET 880.18 m^2/g higher than the previous study mentioned. The experiment was studied under optimum conditions pH 5.5, temperature of 30°C and the concentration of the pesticides ranged between 25–250 mg/L. The experimental results have showed the date pits resulted in good efficiency removal of both pesticides based on the isothermal models used. However, based on the pore size formation on the surface of the activated date pits, it was found that carbofuran was adsorbed higher than bentazon due to the molecular size of the carbofuran smaller.

2.5.4 Nanomaterial as adsorbent in water treatment

Nanomaterials have shown a development in treating the water contaminated by pesticides (Sadegh et al. 2017). In recent different studies have been developed to observe the ability of nanomaterial as adsorbent. The chemical activity and adsorption capacity is improved due to the physical characterization of the nanoparticles, that is their high surface area and small size particle that helps is high efficiency to adsorb metals on the surface of the nanoparticles (Zhao et al. 2019 ; Bargougui et al. 2018).

However, the nano-adsorbents have shown a higher efficiency and faster adsorption rates in water treatment (Sadegh et al. 2017). Certain characters such as surface chemistry, chemical composition, crystal structure and solubility control properties of nano-adsorbents (Anjum et al., 2016).

Hence, nanotechnology methods have attracted today's research for their efficiency in detecting, degrading and also removing pesticides that harm the environment (Rawtani et al., 2018). The most widely used nanomaterials for wastewater treatment are:

i. Oxide-based nanoparticles (Iron oxide nanoparticles, zinc oxide nanoparticles).
ii. Graphene based nano-adsorbents.

iii. Carbon nanotubes (CNT's).

Nanotechnology-based recent approaches for sensing and remediation of pesticides. In recent years, nanotechnology have been used in detecting, degrading and removing pesticide contaminants in the environment either accumulation of pesticides in the soil or in water flow affecting lakes and rivers (Rawtani et al., 2018). The most common types used for removal of pesticides are nanotubes, nanoparticles and nanocomposite. In addition, for detecting low concentration of pesticides nanotechnology-based biosensors have been used. One of the examples of using nanotechnology in detecting pesticides is silver nanoparticle (AgNPs). The AgNPs has a unique size and shape that provides different magnetic, electrical and optical properties, thus helping in the detection of different types of pesticides.

2.5.4.1 Oxide based nanoparticle (iron oxide nanoparticle)

Oxide based nanoparticles are inorganic particles prepared by metals and non-metals. One of the types of oxide-based nanoparticles is iron oxide nanoparticles (Fe_3O_4). Iron oxide as nano adsorbent is believed to be effective and economical to adsorb and remove metal ions from wastewater (Xie et al., 2012). Fe_2O_3 is ecofriendly because it is safe and can be used directly to the contaminated source by having a low chance in producing a secondary contaminant, hence regarded as green chemistry (Ahmad & Mirza, 2018). Some of the factors affecting the adsorption of heavy metals on Fe_2O_3 nanoparticle are temperature, time and adsorbent quantity. It was reported by certain researchers that the modification of the surface of Fe_2O_3 adsorbent with 3-aminopropyltrimethoxysilane shows a high efficiency in the removal of different pollutants from wastewater (Anjum et al., 2016).

2.5.4.2 Graphene based Nano-adsorbents

Graphene is carbon allotropy having a unique characteristic features that makes it highly used in several environmental application (Nasir et al., 2018). One of the applications using graphene is in the removal of pollutants from water. Graphene oxide (GO) is a single layer that contains number of oxygen and other functional groups such as carboxyl and hydroxyl groups (Luo & Zhang, 2018). In today's studies many researchers our focusing on synthesis of different graphene based nano-materials, therefore, GO have shown a high sorption capacity in the removal of organic and inorganic pollutants from wastewater (Nupearachchi et al., 2017).

Moreover, nanomaterials are produced by the oxidation graphite layer either by chemical or physical methods (De Marchi et al., 2018). Moreover, due to the presences of hydroxyl and carboxyl as functional groups have increased the adsorption of GO in removing heavy metals. Hence, most of the researchers working on the removal of heavy metals focus on GO as nano-adsorbant due to its mechanical strength, flexibility, chemical stability and high surface area (Anjum et al., 2016).

2.5.4.3 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) is nano-adsorbent material to remove heavy metals from wastewater through adsorption. However, one of the negative effects of facing CNTs nanoparticles is that it shows difficulty in separation and poor dispersion ability. Therefore, researchers have modified CNTs to multi-wall carbon nanotubes (MWCNT) (Sadegh et al., 2017). MWCNT have a high surface area than CNT therefore, has a high ability in removal of heavy metals (Gangu et al., 2019).

2.5.4.4 Nano-Catalysts (Nanoparticle photocatalytic)

In recent years, nano-catalysts has become an emerging field in research due to its high selectivity, activity and productivity. Various elements like iron, aluminum, titanium dioxide, clays, and silica in nanoscale is used as catalysts for many years. Different kinds of nano-catalysts such as nano-photo catalysts and electro catalysts are used in wastewater treatment (Singh & Tandon, 2014). Nanoparticle photocatalytic is a nano-catalyst where the reaction is based on the interaction metallic nano-particles with light energy. This kind of nano-particle can degrade organic pollutants such as pesticides that are persistent in wastewater (Samanta et al. 2016).

2.5.4.5 Nano-membranes

Membrane filtration technology designed by nanomaterials is one of the most effective techniques in water purification and is considered to be a simple in designing and highly efficient compared to other treatments (Anjum et al., 2016). Many studies on nanotechnology particularly on nano-membrane have focused by creating multifunction membrane by adding metal oxide nanoparticle such as titanium oxide to polymeric ultrafiltration membrane. Therefore, the efficiency of the nanoparticles on the membrane depends on the dimension and quantity of the nanoparticles added (Samanta et al. 2016).

2.6 Different techniques used to analyze the adsorbent

The presences of pesticide in water is considered the most dangerous organic contaminate in water. The pesticide has a wide range of chemical attractions in the contaminates that makes the analysis of the pesticide a challenging task in the laboratory and the operator. There are several analytical methods to analysis pesticides residues in food products like-chicken and eggs (Hildmann et al. 2015 ; Tao et al. 2009) dairy products (Salem etl., 2009; Manav et al., 2018), fruits and vegetables (Loughlin et al., 2018) and water (Casado et al.,2018).

These analyses include Gas Chromatography (GC) by using different detectors such as GC-mass spectroscopy (GC-MS), GC-flame photometric detector (GC-FPD), GC-Flame ionization detector (FID), GC- Nitrogen Phosphorous Detector (NPD) and GC- electron capture detector (GC-ECD). Other analysis include High Performance Liquid Chromatography (HPLC). Table 2 summarizes the common techniques that are used to detect pesticides residues in water.

Hence, the most suitable technique used to separate mixtures and help in quantification and qualification is the chromatography techniques. The two most widely used are GC and HPLC. The different between GC and HPLC is that the mobile phase is unreactive carrier gas such as helium or nitrogen, and the stationary phase could be solid, liquid or combination of both.

Moreover, the samples injected into GC must be volatile liquid or gaseous and using small amount of sample (less than 10 μL) and the sample must not be prepared by water, it must be prepared by other solvents such acetonitrile (Roeraade, 2002). However, in some methodologies the extraction procedure is used such as, solid phase extraction and liquid-liquid extraction. In some experimental procedures, the samples are prepared by water that is direct injection; therefore, in this case the injection unit must include head space or purge and flow to avoid the damage to the GC column (Kiso et al., 1996).

HPLC can be used for direct analysis for samples prepared with water. HPLC is the theory of liquid chromatography, which is separation of chemical compounds in a sample. Different types of liquid chromatography include thin layer chromatography

(TLC) and ultra-performance liquid chromatography (UPLC). HPLC consists of a column packed with material made of silica or polymers that acts as the stationary phase. The most commonly used is the silica packing. The HPLC also consists of mobile phase it is important to choose the appropriate stationary phase since it has an effect on retention time. The importance of the pump in HPLC is pump mobile phase into the column. Therefore based on the phase used there are different HPLC used they include: reverse phase HPLC, normal phase HPLC (Poole & Lenca, 2017).

Different detectors used in HPLC technique are used to analyze water samples contaminated with pesticide. These detectors include UV absorbance, mass spectroscopy (LC-MS), refractive index, fluorescence, etc. The LC-MS has high sensitivity and selectivity that makes it extensively to be used in substances such as pesticide in complex matrices (Zaidon et al., 2018). The most commonly used detector is UV and UV Diode Array Detector (DAD) for it’s easy use and low cost (Christie and Christie 1992; Sodipo OA 2014). The other detectors such as fluorescence are used when the sample cannot be detcted in UV-visible range. Mass spectroscopy detector (MS) is commonly used for its ability to detect low concentrations and easily separates the analytic components compared to other detectors (Ramni et al. 2011).

Table 2. Techniques for determining pesticides in water.

Types of pesticides contaminating water	Technique	Reference
Aldicarb, Atrazine, Carbofuran, Carbendazim, Methoxychlor, Parathion methyl, Spiromesifen	Reverse phase high performance liquid chromatography (RP-HPLC)	(Rajput et al., 2018)
Parathion-methyl, Malathion Chlorpyrifos, Fenthion, Parathion-ethyl, Bromophos-methyl , Chlorfenvinphos , Methidathion, Bromophos-ethyl, Prothiophos, Profenofo	GC and LC-MS	(Guilherme et al., 2018)
Pyrazole, pyrrole pesticides	HPLC-DAD	(Ma et al., 2016)
Chlorpropham	HPLC UV/VIS)	(Douglas et al., 2018)
Azoxystrobin, Buprofezin, Chlorantraniliprole, Difenoconazole,Fipronil, Imidacloprid Isoprothiolane, Pretilachlor, Propiconazole , Pymetrozine , Tebuconazole , Tricyclazole , Trifloxystrobin	UHPLC-MS/MS*	(Zaidon et al., 2018)

Types of pesticides contaminating water	Technique	Reference
Organochlorine pesticide- Lindane, α-Chlordane, Mirex, DDT**	GC-MS	(Wang et al., 2017)

*Ultra-high performance liquid chromatography coupled with tandem mass spectrometry

** Dichlorodiphenyltrichloroethane.

Beside analysis technique, other characterizations are used to study the bonding and interaction between the adsorbent and adsorbate. The most common techniques used are Fourier Transform Infrared (FTIR) (Chahkandi et al., 2018), X-ray diffraction pattern (XRD) and elemental dispersive X-ray (EDX) analysis (Yallappa et al., 2017), Scanning Electron Microscopy (Ilomuanya et al., 2017), Transmission Electron Microscopy (Ahmad et al., 2019).

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Material

3.1.1 Chemicals and reagents

The date pits samples were collected from different sources cultivated in Qatar. The profenofos standard solutions were prepared from stock solution (100 ppm). Distilled water was used for the preparation of standards. Acetonitrile: Water 90:1 v/v used as mobile phase in HPLC analysis. Potassium bromide (KBr) was used in the chemical characterization in FTIR analysis and Nitrogen gas was used for BET analysis.

3.1.2 Glassware and instruments

A scanning electron microscopy (SEM) Nova nanoSEM 450 taken at a voltage 5 kV and 5-100 microns particle size was used to characterize the prepared adsorbents. Horizontal tubular furnace MTI, OTF-1200 X. CryoMill grinder using agate ball. Kern 770 analytical balance. An Eppendorf centrifuge 5418FT-IR Spectroscopy BX Perkin Elmer model was used to get the supernatant. For sieving the samples, test sieves (model RETCH) were used. To determine the surface area of the adsorbents Brunauer–Emmett–Teller (BET) model Aim Sizer-AM301 was used. To adjust the pH, Vernier pH probe sensor was used connected to LabQuest 2. Additionally, a mortar, pestle, collection vials (5 ml), pipettes (1000 and 5000 µl). Moreover volumetric flasks (25 and 250 ml) beakers (10, 50,100 ml), and for quantification analysis HPLC-UV was used.

3.2 Preparation of Standard solutions

The profenofos standard solutions were prepared from a stock (100 ppm). For calibration purposes, standard solutions were prepared from the 28 ppm (highest solubility) stock solution with a range between 2 to 28 ppm (appendix B). The chromatogram and calibration curve of the prepared standard solution for profenofos is shown in appendix C.

3.3 Sample collection and Preparation

The date pits were washed thoroughly with distilled water to remove impurities, and later the date pits were roasted under a temperature of 130^{o}C for 24h. Next, the date pits were crushed and sieved to form a granular material, which were stored in glass bottles. This was the preparation for the first adsorbent and it was labeled as roasted date pits (RODP) (appendix A). Then, the prepared sample was sieved into different particle sizes (1-0.5, 0.5-0.25, 0.25-0.125, and 0.125-0.0625) mm (appendix A). In this project the experiments were carried out using particle size (0.5-0.25) mm.

3.3.1 Activated Date Pits (ACDP)

The roasted date pits were converted to activate dated pits by physical activation under continuous flow of argon gas in a horizontal tubular furnace MTI, OTF-1200 X (Appendix A). The furnace was first maintained at room temperature for 50 min to make sure that air is completely purged and replaced with the inert argon gas. Then, the furnace was heated up to a temperature of (500°C) with a heating rate of 10°C/min. The roasted date pit was maintained at 500 °C for 3 h, after that the sample was allowed to cool down spontaneously to room temperature while still passing argon gas.

3.3.2 Nano Activated Date pits (NACDP)

Mechanical preparation of nano sized activated date pits was prepared using a CryoMill grinder with agate balls. The activated date pits were distributed into two jars each with seven balls with 10mm size. The instrument was set at a speed rate of 800 (rounds per minute) rpm for 48 hours (appendix A).

3.4 Sample Analysis

3.4.1 Optimization and validation

The sample analysis was conducted using HPLC-UV detector, Agilent 1260 infinity (Appendix B).The instrument was equipped with auto sampler injection. The column used was Hibar C18 (250 mm X 4.6 mm, 5 µ) as stationary phase. The mobile phase was Acetonitrile: Water (90:1, v/v). The samples were analyzed as follows: the initial temperature was set at 25°C. The flow rate of the mobile phase was set at 1 ml/min. The injection volume was 10 µl. The total run time for each sample was 6 minutes. The UV detector was fixed at wavelength 230 nm. The data were acquired and processed with Agilent Chemstation Libraries (appendix B).

3.4.2 Sample characterization

SEM is a multipurpose instrument used for the characterization of 2D and 3D materials. It is used to measure the particle size and describe the aspect ratio and morphology of the material. In this study, a Nova nanoSEM 450 was used to take images at a voltage 5 kV and 5-100 microns particle size in order to characterize the three adsorbent samples, RODP, ACDP and NACDP. In this study, we aim to have small particle size adsorbents with high surface area having a high porosity to have maximum efficiency in pesticide removal from aqueous solution. To determine surface area of adsorbents a Brunauer–Emmett–Teller (BET) model Aim Sizer-AM301 was used. The instrument uses nitrogen (77K) as adsorbate. The samples were first dried in an oven at 100°C for 1 hour to make sure the sample is dry. The instrument gives the pore surface area distribution of the particle along with the particle size. Therefore, depending on the pore radius and particle size, the capacity for adsorption can be determined. The BET equation was applied to P/Po ranges of the N_2 isotherms.

$$\frac{\mathrm{P}}{\mathrm{V(Po-P)}} = \frac{1}{\mathrm{CVm}} + \frac{\mathrm{C-1}}{\mathrm{CVm}} * \frac{\mathrm{P}}{\mathrm{Po}}$$

Where Vm is monolayer adsorption amount and V is the adsorption amount at equilibrium pressure FTIR analysis was performed to study functional groups of the three adsorbents before and after adsorption. A spectrum BX Perkin Elmer model FTIR Spectroscopy was used and the spectra were recorded at a range (4000-400) cm^{-1}. Potassium bromide (KBr) discs were prepared first as background for the instrument and then the samples were analyzed. Then the samples were mixed with the KBr (approximately 0.05 mg) in the agate motor followed by pressing manually with hydraulic press to form wafer discs. The pH meter Lab quest was used to read the pH values. First, the Lab quest meter was calibrated using buffer solutions borate (pH 9.2) and phthalate (pH 4).

After calibration, the experiment carried as follows, in each 5 ml tube a mass of 0.001 g from RODP, ACDP and NACDP were added separately in each tube followed by adding 1 ml of 10 ppm profenofos in each tube. Next, the pH was fixed in each vial according to the pH to be studied (2, 4, 6, 8, and 10). Hence, to ensure quality control, two trials and blanking of each batch experiment were conducted. Then all samples were placed on a mechanical shaker at 150 (rounds per minute) rpm for 24 h under room temperature of 25 °C.

3.5 Methodology

3.5.1 Determining the effect of solution pH

Batch remediation experiments were performed under different pH values, temperatures, initial concentrations and particle sizes. The batch remediation experiments were conducted in 5 mL tubes, each with 1 mL profenofos pesticide and 0.001 g of the adsorbent. In order to ensure quality control, two trials and blanking of each batch experiment were conducted. The samples of each batch experiment were shaken using a mechanical shaker under a constant speed of 150 (rpm) for 24 h. After each batch experiment, the sample were micro centrifuged for 10 minutes at a speed 5000 rpm to separate the supernatant to be analyzed in HPLC-UV. The remaining precipitate (adsorbent) was collected and dried in the oven at temperature of 100^{o}C for an hour, for further analysis using SEM and FTIR analysis.

Studying the effect of pH is an important parameter that affects the adsorption process. Moreover studying this effect explains how different pH of the aqueous solution affects both adsorbate and adsorbent, hence explaining the electrostatic interactions occurring on the surface of the adsorbent and the adsorbed molecule (Njoku & Hameed, 2011). In this experiment, the pH of the solution was adjusted to be optimized in all experiments to ensure good adsorption capacity. The experiment was performed by fixing the concentration of the profenofos at different pH values 2, 4, 6, 8, 10. The concentration was fixed at 10 ppm and the pH was set by adding minute amounts of sodium hydroxide (NaOH) and hydrochloric acid (HCl) to the profenofos solution as needed (Appendix D and E).

3.5.2 Determining the effect of initial concentration

In order to understand the role of profenofos concentration on the adsorption capacity of the adsorbents (RODP, ACDP and NACDP) batch experiments of variable profenofos concentrations (2 – 28 ppm) were conducted. The batch experiment was conducted in 5 ml vials, each of 11 vials had different concentrations of profenofos (2, 5, 7, 10, 12, 15, 18, 22, 25, 28) ppm. The pH was adjusted to the optimum pH from the results of the previous experiment on the effect of pH. Next, a mass of 0.001 g of the three adsorbents was added to each vial having different concentrations. All samples was then placed on a mechanical shaker at 150 rpm for 24 hours under room temperature of 25℃.

3.5.3 Determining the effect of temperature

Adsorption processes are greatly affected by the temperature at which the process is taking place. The adsorption capacity of the adsorbent was tested and analyzed under 35℃ and 45℃. For each adsorbent type and temperature, batch adsorption experiments was conducted in 5 mL vial with 1 mL profenofos solution. Similar to the previous experiment, the concentrations of profenofos tested will be 2 –28 ppm. A mass of 0.001 g of the adsorbent was added to the profenofos solutions. The pH was adjusted to the optimum pH found in the effect of pH experiment. All samples were then placed in a mechanical shaker at 150 rpm for 24 h under temperatures of 35 ℃ and 45℃.

3.6 Adsorption Isothermal Model

In the study, isothermal model and statistical analysis tests were used. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were applied in order to understand the interactions between the adsorbate and adsorbent were analysed to study as shown in Table 3.

Table 3. Various Adsorption Models used in the Current Study.

Model	Equation	Parameters
Langmuir adsorption isotherm	$\frac{C_e}{q_e} = \frac{1}{b.Q_o} + \frac{C_e}{Q_0}$	q_e is the mount of adsorbate on the adsorbent at equilibrium (mg/g). Q_0 is the maximum monolayer coverage capacities (mg/g). B is the Langmuir isotherm constant (L/mg). C_e is the equilibrium concentration (mg/L). From the Langmuir isotherm, favorability of mercury adsorption on the adsorbents was tested as shown in equation, $R_L = \frac{1}{1+b(Ce)}$ R_L describes the feasibility of adsorption process. If $R_L > 1$, the adsorption process would be unfavorable; $R_L=0$ the adsorption process will be irreversible, while $0<R_L<1$ indicates the adsorption process is energetically favorable.

Model	Equation	Parameters
Freundlich adsorption isotherm	$\mathrm{Log}q_e = \mathrm{Log}K_f + \frac{1}{n}\mathrm{Log}C_e$	q_e is the amount of adsorbate on the adsorbent at equilibrium (mg/g). K_f is the Freundlich adsorption constant (mg/g)(L/g)^n. C_e is the equilibrium constant. The value of n indicates the type of isotherm. When $\frac{1}{n}$ is greater than zero ($0 < \frac{1}{n} < 1$), the adsorption is favorable, when $\frac{1}{n} = 1$, the adsorption is irreversible, and when $\frac{1}{n} > 1$ the adsorption is unfavorable.
Dubinin–Radushkevich adsorption isotherm	$\ln q_e = \ln q_s - k_{ad}\varepsilon^2$	q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g). q_s is the theoretical isotherm saturation capacity (mg/g). $k_{ad}\varepsilon^2$ is the Dubinin–Radushkevich isotherm constant (mol^2/kj^2).

Model	Equation	Parameters
Temkin Adsorption Isotherm	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e$	q_e is the mount of adsorbate in the adsorbent at equilibrium (mg/g), R is the universal gas constant (8.314 J/mol K), T is the temperature (K), b_T is the Temkin isotherm constant, A_T is the Temkin isotherm equilibrium binding constant (L/g), and C_e is the equilibrium concentration (mg/L).

Finally, in all experiments the removal percentage of profenofos from the aqueous medium was calculated using,

$$\text{Removal Percentage} = \frac{Ci - Ce}{Ci} X\ 100\%$$

Where Ci is the initial concentration and C_e is the Equilibrium constant.

To gain further information an investigation of the adsorption thermodynamics has performed. Thermodynamics give an indication about the nature of adsorption, if it is spontaneous or non-spontaneous and if it is endothermic or exothermic nature of adsorption (Chowdhury et al., 2011). Hence, a thermodynamic study was performed to determine the adsorption process of profenofos on RODP, ACDP and NACDP to estimate the adsorption mechanism. The study was performed by determining the effect of temperature on the profenofos adsorption on the three adsorbents (RODP, ACDP and

NACDP). The thermodynamic parameters ΔG, ΔH and ΔS are; Gibbs free energy, change in enthalpy of a reaction and entropy measuring the disorder respectively (Al-Saidi, 2016). Hence, the thermodynamic parameters were calculated using the following equations,

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

$$\Delta G = -RT.\ln KL$$

Where, K_L is Langmuir constant. First, ΔG is been calculated for the three adsorbents, and then graph is plot between ΔG and Temperature in Kelvin. In each parameter the value and sign indicates the nature of adsorption. If ΔH is positive, the adsorption process is considered as an endothermic in nature, and if negative, the adsorption process is exothermic in nature and energy in the form of heat is released during binding of the adsorbate and adsorbent. Moreover, when ΔS is positive, the adsorption process indicates spontaneous process and if negative a non-spontaneous adsorption process (Al-Anber, 2011).

Finally, statistic data analysis t-test was conducted using Microsoft excel for the results of the batch experiments (appendix F).

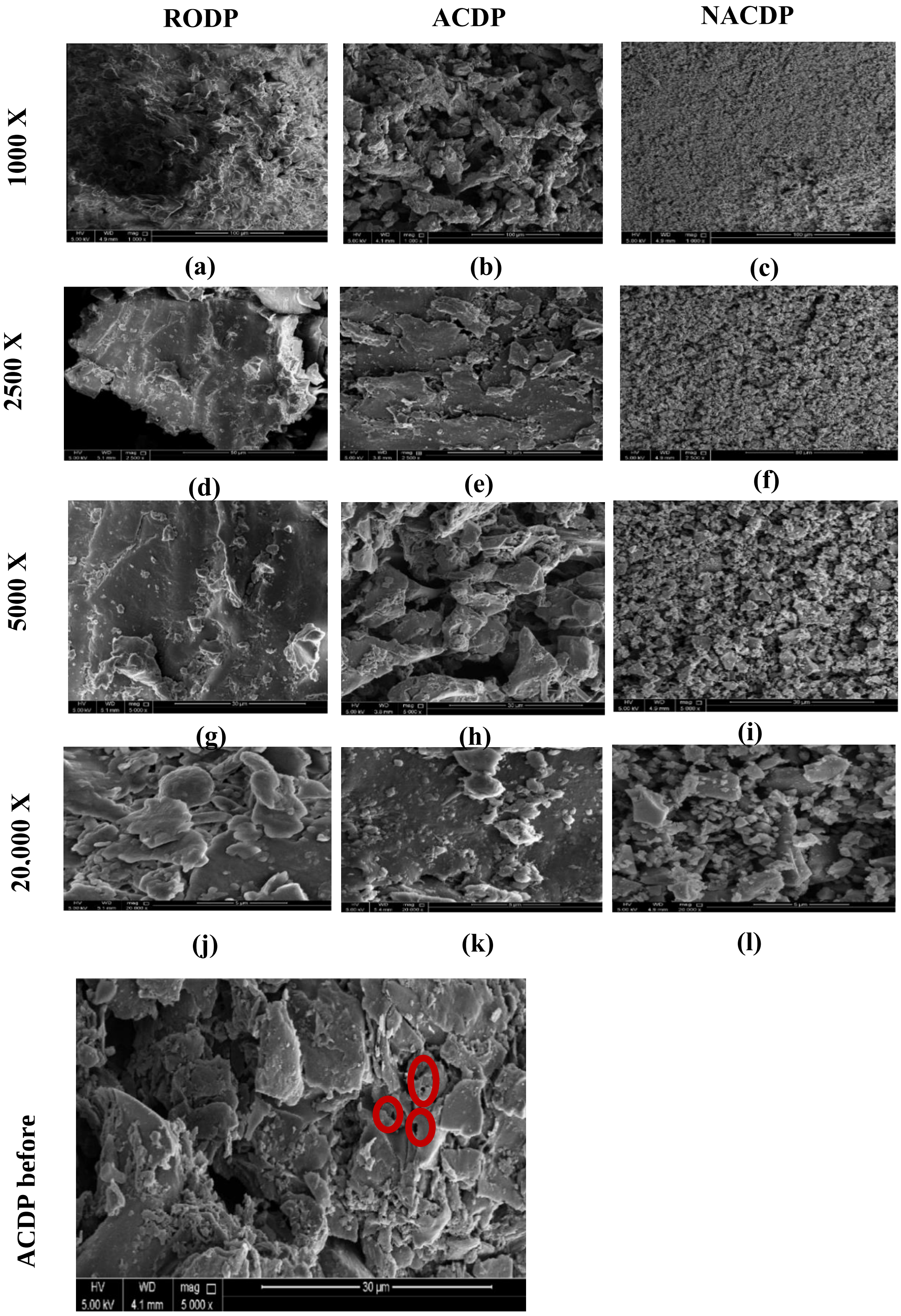
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization

4.1.1 Morphology

Figure 3 shows the SEM morphology of the three adsorbents before treatment. Figures 3a, 3b, 3c show the SEM morphology at magnification 1000, Figures 3d, 3e, 3f show at magnification at magnification 2500, while Figures 3g, 3h, 3i show the SEM morphology at magnification 5000. Lastly, Figures 3j, 3k, 3l show the SEM morphology at magnification at magnification 20,000.

SEM images of RODP before adsorption show the surface morphology has no porosity and contains irregular clusters; this is due to the presence of cellulose. Moreover, the absence of porosity is because the RODP has not undergone thermal activation treatment. The morphology of the ACDP showed sharp a particle size; indicating the effects of physical activated treatment. However, the process of activation influences the formation of pores as can be seen in figure 3m at 5000x magnification. Some pores are formed at the smaller particle sizes compared to the bigger particles.



(m)

Figure 3. SEM characterization before treatment.

After profenofos adsorption onto the adsorbents, changes can be seen in the adsorbents morphology as shown in Figure 4. In Figure 4b, the surface of RODP formed a paste surface when treated with the profenofos when comparing with figure 4a of RODP before adsorption. NACDP after treatment in figure 4f smooth layer with formation of pores is formed when compared with before adsorption (figure 4e). On the other hand, the ACDP shown in figure 4d, the particles show coagulation when compared with before treatment (figure 4c).

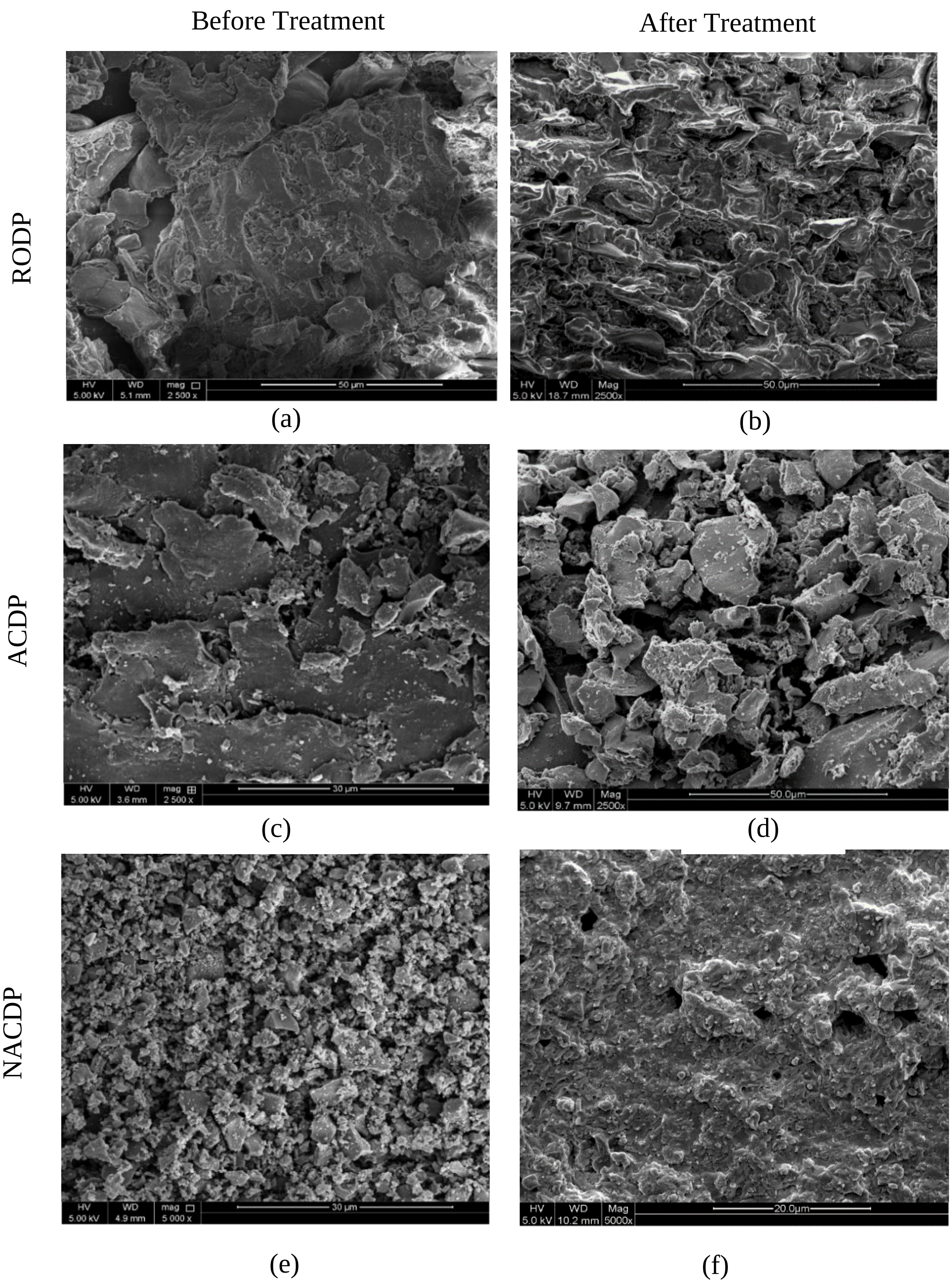


Figure 4. SEM image before and after treatment with profenofos.

4.1.2 Thermal Desorption Technique

Table 4 shows the BET isothermal analysis for the prepared adsorbents. The surface area of the RODP is 3.184 m^2/g and Langmuir surface area has given a surface area of 4.039 m^2/g. However, the surface areas of the ACDP and NACDP were increased, and this is due to the small particle size. As shown in the table, the surface area by Langmuir of ACDP and NACDP are 39.658 and 485.441 m^2/g, respectively. Moreover, the pore diameter of the ACDP is 2.68 nm, which indicates mesoporous material.

Table 4. BET Isothermal Analysis.

Adsorbents	BET Surface Area (m^2/g)	Langmuir Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Radius (Å)
RODP	3.184	4.039	0.009	55.0
ACDP	30.397	39.658	0.041	26.8
NACDP	380.626	485.441	0.338	17.8

4.1.3 Chemical characterization of Adsorbent Surface (FTIR and CHN analysis)

4.1.3.1 Fourier transform infrared (FTIR)

Fourier Transform Infra-Red Spectroscopy is an analytical technique used widely to identify the surface functional groups of any state in samples namely; liquid, gas, or solid. Figure 5 shows the FTIR spectra of the three adsorbents before treatment with profenofos. Broad bands at 3366.93, 3436.38, and 3448.31 cm^{-1} were noticed for RODP (figure 5A), ACDP (figure 5B), and NACDP (figure 5C), respectively; corresponding to hydroxyl group (O-H) stretching. The 2926 cm^{-1} and 2854 cm^{-1} band which fall in the $=CH_2$ functional group range and corresponding to C-H symmetric and asymmetric stretching vibrations (Adewole and Sultan, 2014; Al-Saidi 2016; Abbas and Ahmed, 2016; Salman and Abid, 2013).

The carbonyl groups (C=O) and hydrogen bonded carbonyl groups available in cellulose and hemicellulose showed in the region 1746 cm^{-1} and 1625 cm^{-1} respectively. These bonds also represent ester, ketone and aldehyde groups (Al-Ghouti et al., 2017). The C=C aromatic symmetric stretch was shown at the region 1508 cm^{-1}. Other peaks falling at the range of (1600-1400) cm^{-1} recognized to deformation C-H bonds of methylene present in cellulose, hemicellulose and lignin (Fan et al., 2012 ; Al-Saidi, 2016). Finally, the peak at 871.5 cm^{-1} is assigned to the C-H deformation in cellulose. Hence, it can be concluded that the main oxygen groups shown in the spectrum are from the group’s carbonyl, alcohols, hydroxyl and ether components that are available in the cellulose (Abbas & Ahmed, 2016).

Moreover, for the ACDP and the NACDP spectra; Figures 5B and 5C, respectively, some of the peaks are not available due to the physical activation. Other peaks are also shown in the ACDP spectrum; namely at (3438, 2360, 1628, 1393 and 1225) cm^{-1} (Seyedzadeh et al., 2017). In some literature reviews, the FTIR spectrum of the ACDP prepared by chemical activation differs from that of physical preparation. In the chemical treatment, peaks such 1769 cm^{-1}, 1287 cm^{-1}, 1059 cm^{-1} and 908 cm^{-1} represent carboxyl, carbonyl, alkyl halide and aromatics, respectively (Krishnamoorthy et al., 2018).

Moreover, Islam et al. (2015), noted the disappearance of some peaks when prepared by chemical activation. When sodium hydroxide (NaOH) was used as the chemical agent in the ACDP, formation and disappearance of some peaks occurred. This is due to the presence of the free electron pair in the hydroxide, which makes NaOH as reducing agent. Therefore, it decomposes hemicellulose, cellulose and lignin. However, the physical treatment may eliminate some peaks due to the decrease in moisture content and reduction in aliphatic compounds (Ogungbenro et al., 2018). From the Figure 5B, the most predominate peaks in the ACDP spectrum appeared are 3428 cm^{-1} and 1596 cm^{-1}; corresponding to the OH and C=C aromatic stretch, respectively. Similar peaks are formed in NACDP (figure 5C) but with broader and higher intensities.

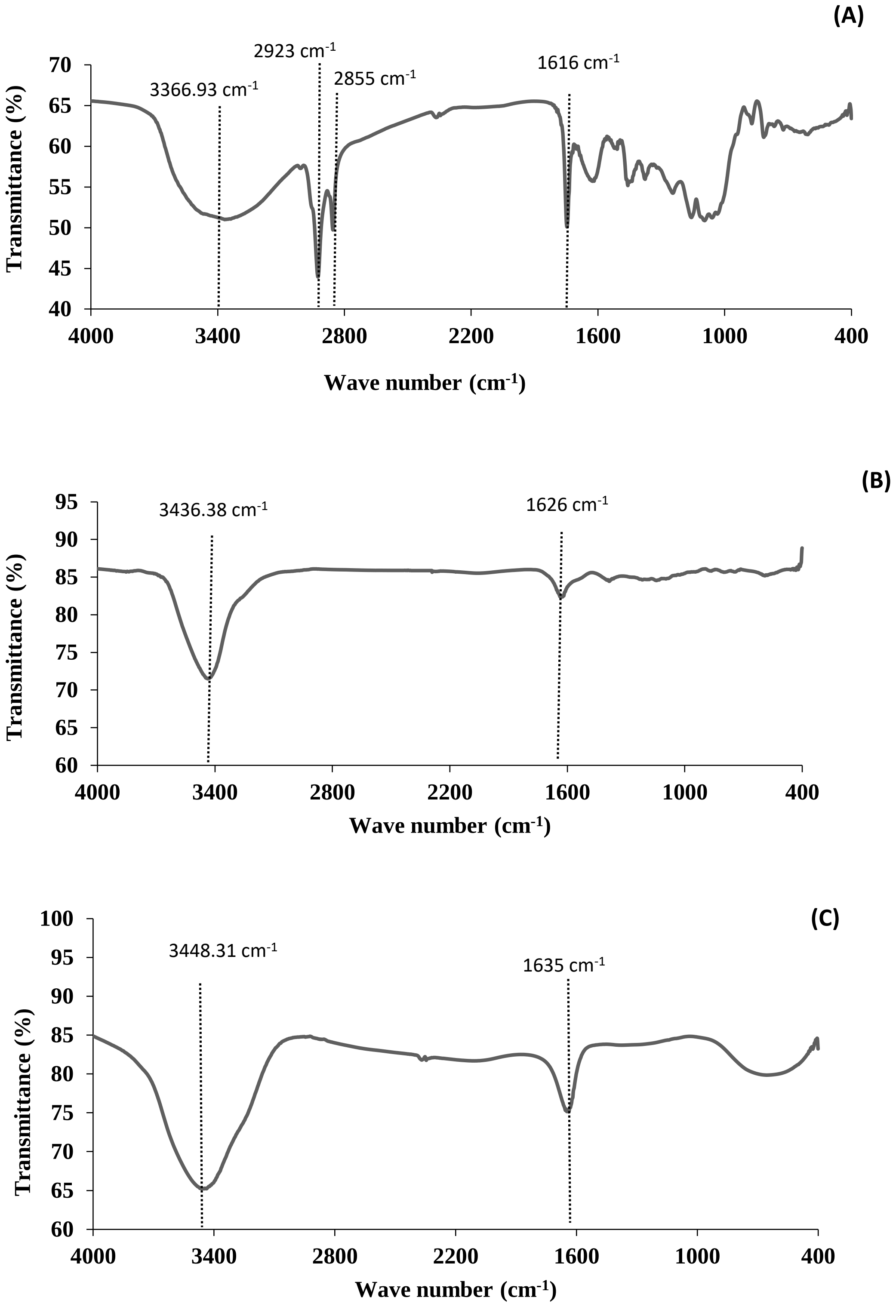


Figure 5. FTIR Spectra of: (A). RODP, (B). ACDP and (C). NACDP.

4.1.3.2 Elemental analysis (CHN)

Elemental analysis was performed using CHN analysis and EDX spectroscopy to determine the percentage of carbon, hydrogen and nitrogen. Tables 5 and 6 shows the elemental analysis for the three adsorbents. The CHN analysis in Table 5 shows the percentage of the carbon was predominant in all three adsorbents and the percentage increased in ACDP (%) and NACDP (%) due to the thermal treatment. Moreover, it is reported that the increase in carbon percentage after thermal treatment is due to the decomposition of cellulose, hemicellulose, and lignin (Bouchelta et al. 2012). Additionally, as the temperature of the pyrolysis increases the percentage of carbon increases. However, the EDX spectroscopy in Table 6 shows the presence of different elements such as calcium, magnesium, potassium, silicon and phosphorus mostly available in ACDP and NACDP in low percentages; indicating the presence of some contamination (Sekirifa et al., 2013).

Table 5. CHN Elemental Analysis of prepared adsorbents.

Adsorbent	C %	H%	N%
RODP	46.61C%	6.76H%	1.3N%
ACDP	75.78C%	3.29H%	2.7N%
NACDP	79.63C%	3.23H%	2.4N%

Table 6. EDX Spectroscopy Elemental Analysis.

Adsorbent	Mg%	Cl %	K %	Si%	Ca%	P%
RODP	ND	ND	ND	ND	ND	ND
ACDP	0.08	ND	0.31	0.19	0.13	0.10
NACDP	0.13	0.09	0.23	0.09	ND	0.13

ND: Not Detected

4.2 Remediation Isotherm by adsorbents (RODP, ACDP, NACDP)

4.2.1 Effect of solution pH

Figure 6 shows the removal percentages of profenofos adsorption by the RODP, ACDP and NACDP at different pH values. As shown from the figure 6, the removal percentage of profenofos using RODP increased with increasing pH. However, for the ACDP, it was noticed that the adsorption removal increased with increase in pH and then decreased at higher pH. The NACDP have showed the maximum removal percentage of profenofos in all the pH range (2, 4, 6, 8, and 10). Whereas, the ACDP has shown high adsorption removals in acidic medium at pH 2, 4 and 6, while at basic medium (pH 8 and 10), the removal percentage was low. However, the highest adsorption for all three adsorbents was at pH 6. Hence, the optimized pH for all isotherm experiments was at pH 6.

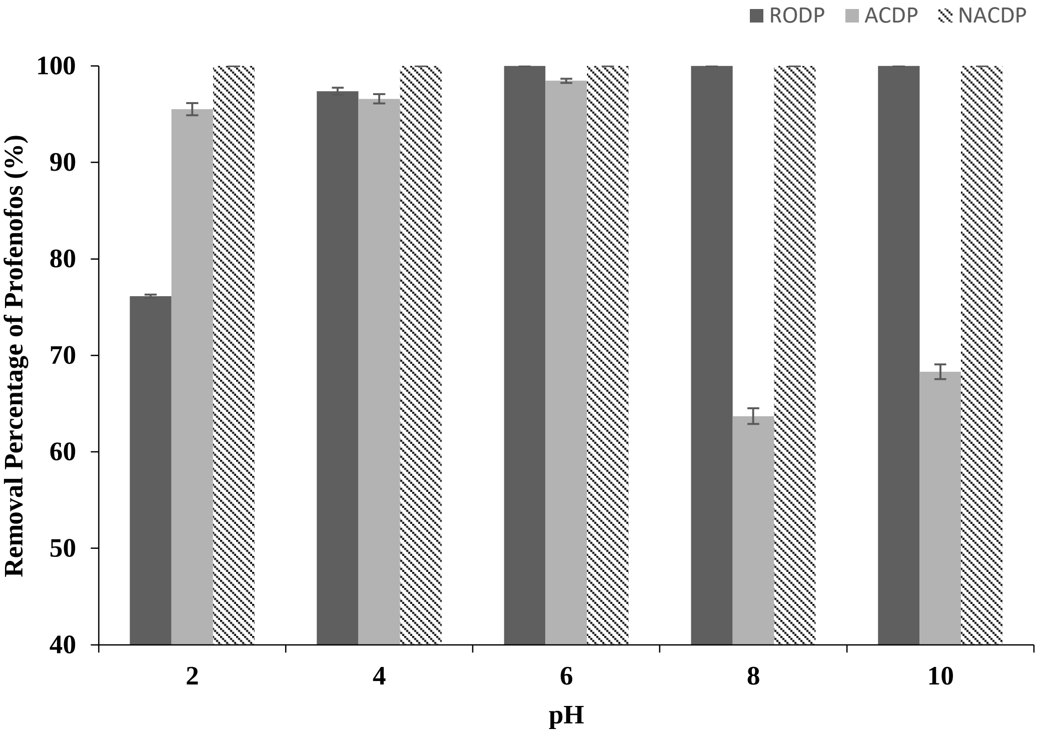


Figure 6. Effect of pH on the adsorption of profenofos onto RODP, ACDP and NACDP.

4.2.2 Effect of Initial Concentration

The FTIR spectra in Figure 8 shows how the adsorption mechanisms of profenofos is complex due to the presence of the benzene ring and the functional groups such as O, P, S, Br and Cl. These functional groups have the ability to interact with the adsorbent forming certain hydrogen bonds as shown in Figure 7.

From the Figure 8A, it is seen that the OH peak is shifted to a higher wavenumber after profenofos adsorption onto the RODP in addition the intensity of the peak has increased. Moreover, after adsorption, the disappearance of some peaks is observed, and the difference in peak to peak ratio were also observed between 2926 and 820 cm^{-1}. The peak at 2926 cm^{-1} representing =CH_2 has disappeared after adsorption. The C=O peak at 1746 cm^{-1} has also disappeared and this is due to various vibration modes of C-O, C-H and C=O. The peaks between 1600-1400 cm^{-1} that represented cellulose, hemicellulose and lignin have disappeared after adsorption; except for one peak at 1643 cm^{-1}; resulting in shifting to the lower wavenumber and having a higher intensity after the adsorption of profenofos.

It is also shown very low intensity peaks at 863 and 714 cm^{-1} (figure 8A) after profenofos adsorption onto RODP. This could be explained due to a new bonding formation as a result of the interaction of Br in profenofos and carbon from cellulose (C-Br bond) (Li et al. 2011). Similarly, the same interaction can be seen in ACDP (Figure 8B) where a peak has appeared at 670 cm^{-1} (Al-Ghouti et al., 2017).

In the case of NACDP (Figure 8C), the bands appeared at similar wavenumbers, however the intensities were higher. Additionally, the OH peak became broader after adsorption. For the ACDP (Figure 8B), there was shift in the OH peak to the lower wavenumber (3422 cm^{-1}) and the intensity of the peak band at 1643 cm^{-1}; representing the CH in lignin, has increased.

Understanding the structure of profenofos, certain interactions can be proposed with the surfaces of the RODP, ACDP and NACDP adsorbents. Figure 7 proposes an interaction mechanism between profenofos and the cellulose structures. Hydrogen bonding can be formed between the surfaces of RODP and profenofos. As mentioned earlier that the surface of RODP is rich in OH and carboxylic groups, that could facilitate the formation of hydrogen bonding. It is inferred from the Figure 7 that the OH could interact with Br, Cl and S. H-S is a weak bond since sulfur is less electronegative than oxygen, while H-Br forms a covalent bond and H-Cl forms a polar covalent bond. Therefore, it was found that the functional groups containing oxygen, phosphorous, sulfur and the pi-bonding network of benzene promote adsorption (Suo et al., 2018). Al-Ghouti et al. (2010) illustrated that the reaction occurring on the surface of RODP are due to the nuclei present in the aromatic rings that are associated with the RODP functional group such as –OH and –COOH.

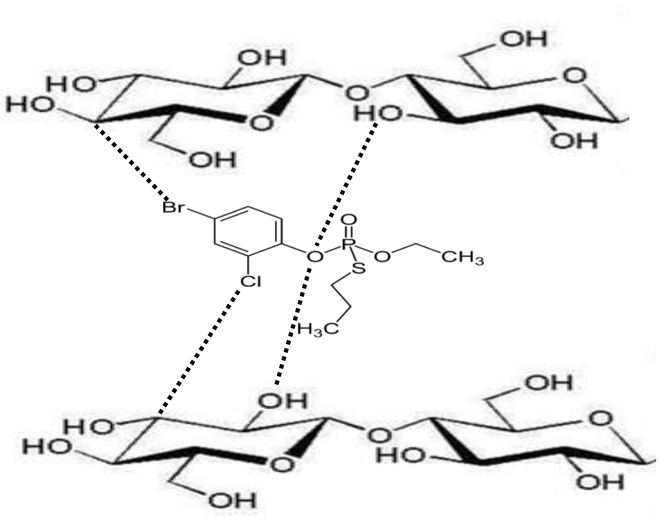
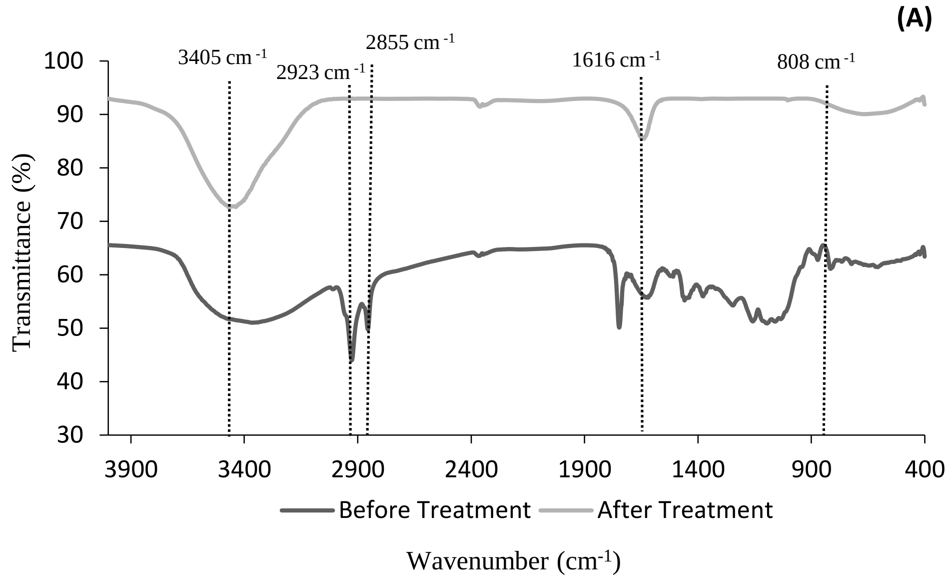
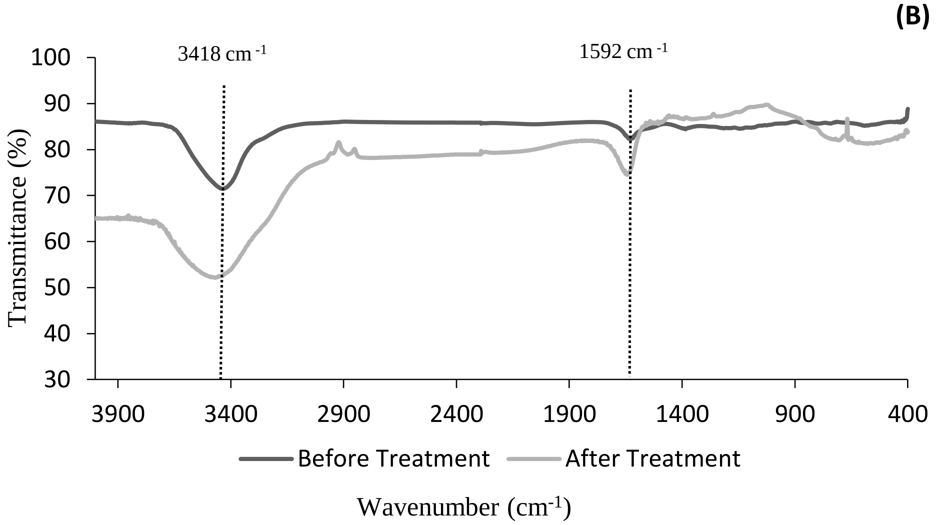


Figure 7. Proposed adsorption mechanisms between profenofos and the cellulose structures.


(A)
3405 cm -1
2923 cm -1
2855 cm -1
1616 cm -1
808 cm -1
100
90
80
70
60
50
40
30
Transmittance (%)
3900
3400
2900
2400
1900
1400
900
400
Before Treatment
After Treatment
Wavenumber (cm-1)


(B)
3418 cm -1
1592 cm -1
100
90
80
70
60
50
40
30
Transmittance (%)
3900
3400
2900
2400
1900
1400
900
400
Before Treatment
After Treatment
Wavenumber (cm-1)

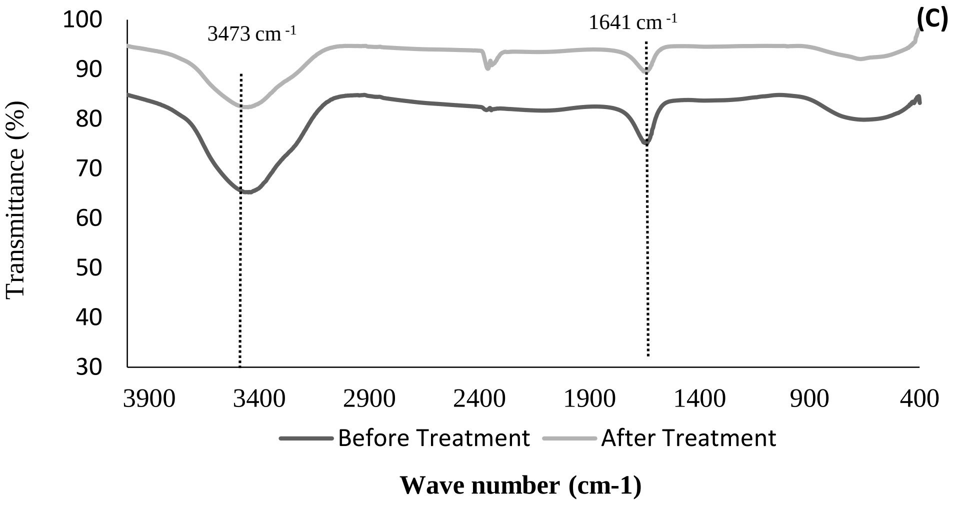
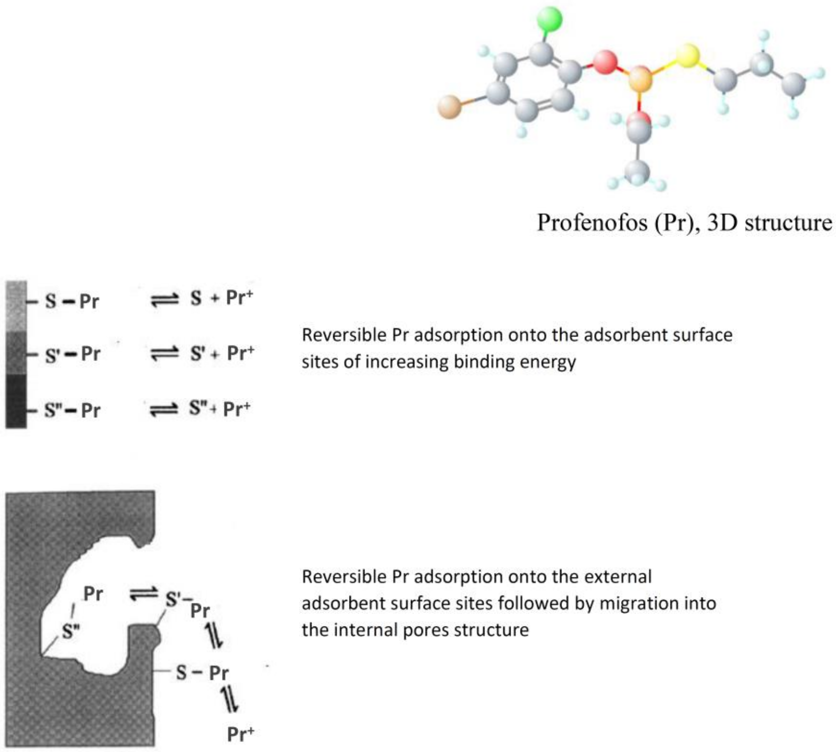


Figure 8. FTIR spectra after profenofos adsorption onto (A).RODP, (B).ACDP, (C). NACDP.

Figure 11 shows effect of initial concentration on profenofos adsorption onto RODP, ACDP, and NACDP. It was shown that the removal percentage of profenofos decreased with increasing the concentration. The highest removal (100%) was attained at low concentrations namely 2, 5, 7 and 10 ppm for the three adsorbents. However, at 28 ppm, the highest removal percentage of profenofos was achieved at NACDP (55%), whereas, in the other adsorbents the removal were ACDP (10.5%) and RODP (11.2%). It was also noted that the removal percentage for the three adsorbents at concertation 10 ppm of profenofos was 100% which was also observed in the experimental effect of pH while the optimizing the pH value.

The variation in the removal percentage among the three adsorbent is due largely to the surface area and total pore volume that were much higher for RODP and NACDP. Therefore, the adsorption mechanisms of profenofos onto the RODP and NACDP could be enhanced by the surface adsorption as the surface areas and pore radius. The intraparticle mechanism onto RODP would be higher than ACDP and NACDP as the average pore radius is high, as shown in Figure 9.

Figure 10 show also the possible mechanisms of profenofos at different pH values.



Reversible Pr adsorption onto the adsorbent surface sites of increasing binding energy

Reversible Pr adsorption onto the external adsorbent surface sites followed by migration into the internal pores structure

Figure 9. Possible profenofos (Pr) interaction onto the adsorbent in addition to the intraparticle mechanism.

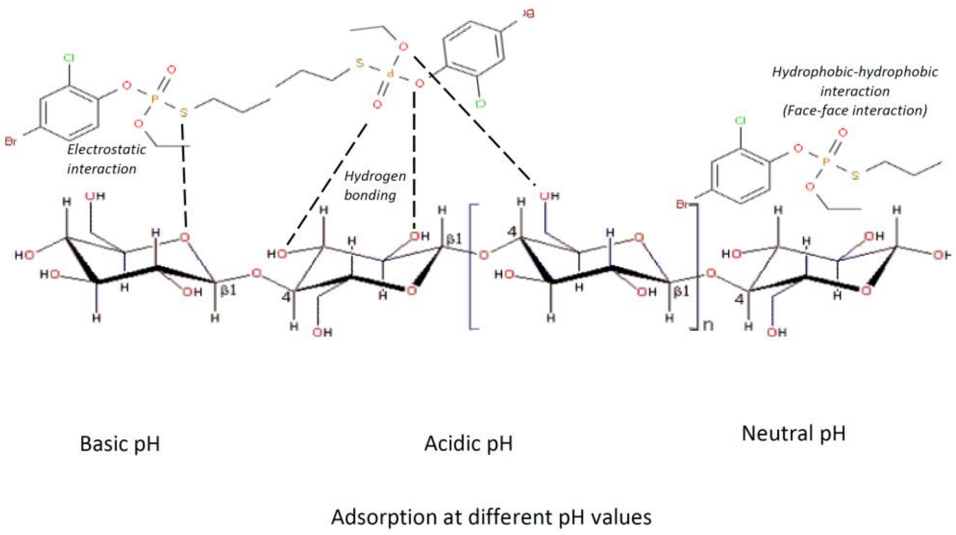


Figure 10. Possible mechanisms of profenofos at different pH values.

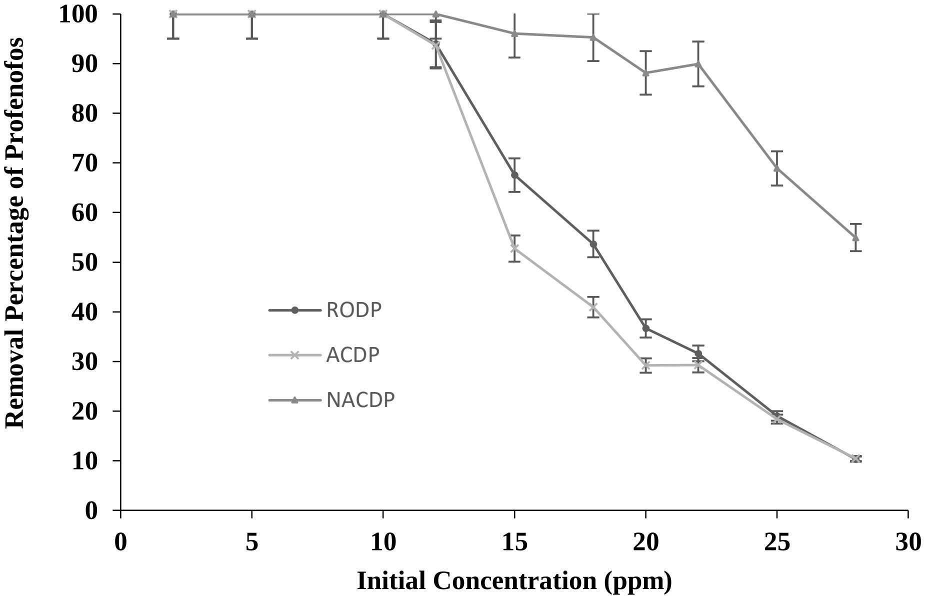


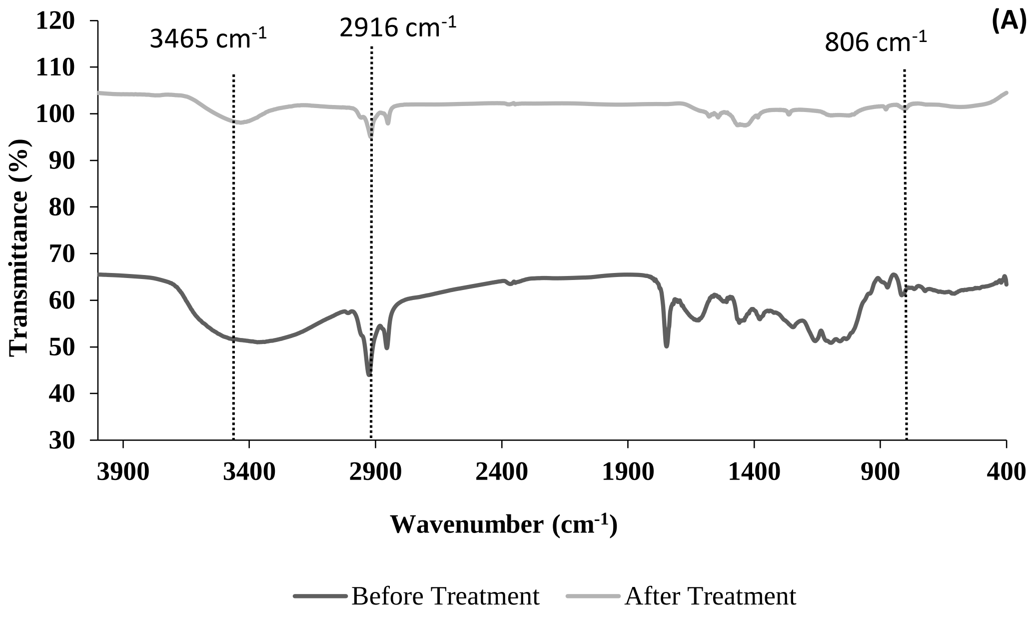
Figure 11. Removal percentage of profenofos onto RODP, ACDP, and NACDP at different initial concentration.

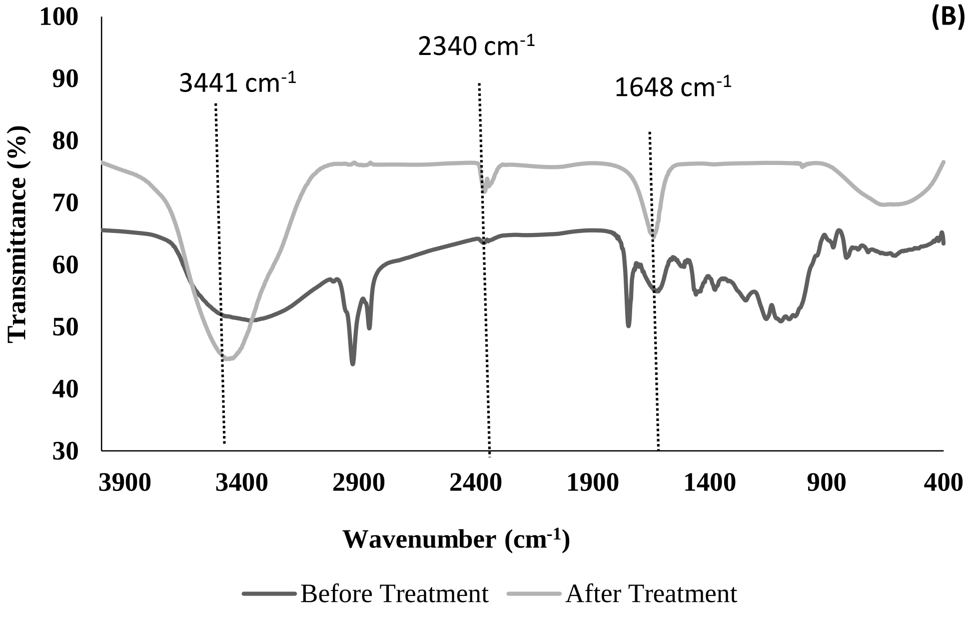
4.2.3 Effect of Temperature

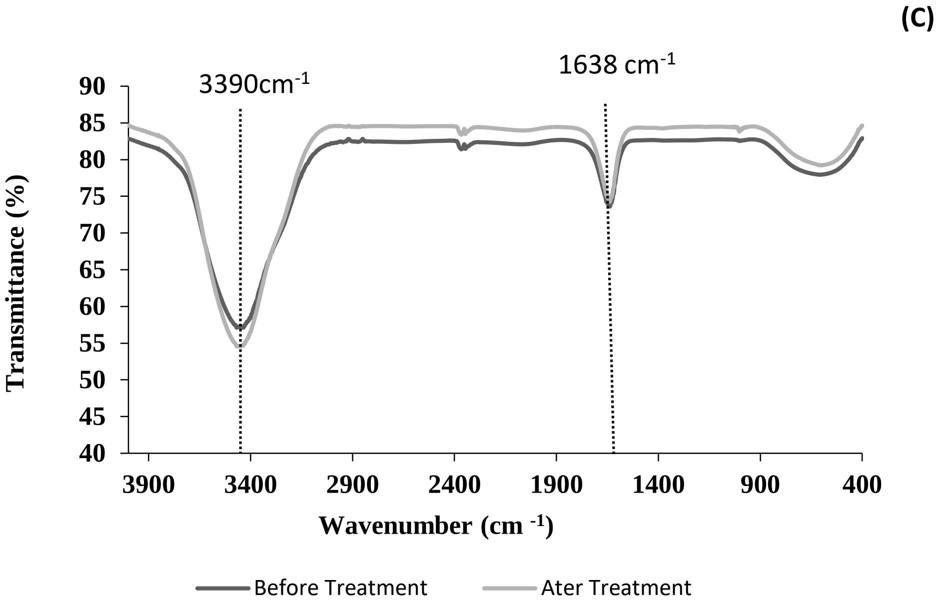
The FTIR spectra of profenofos adsorption onto RODP, ACDP, and NACDP at different temperature are shown in Figures 12 and 13. Figure 12A for RODP, shows the -OH peak has shifted to a lower wavenumber and the intensity became lower at 35^{o}C. However, compared with temperature 45^{o}C (Figure 12B), the –OH peak has become broader; indicating dihydrogen bonding, which means more hydrogen bonding occurred between profenofos and RODP.

Figure 14 shows the removal percentage of profenofos at different temperatures. It is shown a decrease in removal percentage at higher initial concentrations for three adsorbents. From the Figures 14A and 14B, it is found that the removal percentages were higher at 45^{o}C than temperature 35^{o}C for RODP and ACDP, whereas, in the NACDP (figure 14C) the removal percentage was almost similar at both temperatures. However, at concentration 25 and 28 ppm there were variations in removal of profenofos at both temperatures. Similarly to the other two adsorbents (RODP and ACDP), the removal percentage was higher at temperature 45^{o}C. Further clarification of the three adsorbents at temperatures 35 ^{o}C and 45^{o}C is shown in figure 15.

The adsorption behavior of profenofos due the effect of temperature can be explained based on the solubility (water solubility of profenofos is 28 mg/l). The solubility of profenofos increases as the temperature increases; therefore causing low adsorption on the surface of the adsorbents. Additionally if there is, any decrease in the uptake at high temperature, this is due to adsorptive forces between the active site of the adsorbent and adsorbate becoming weak. The current result are in agreement with result obtained by El-Kady et al. (2013).


(A)
3465 cm^{-1}
2916 cm^{-1}
806 cm^{-1}
Transmittance (%)
120
110
100
90
80
70
60
50
40
30
3900
3400
2900
2400
1900
1400
900
400
Wavenumber (cm^{-1})
Before Treatment
After Treatment


(B)
2340 cm^{-1}
3441 cm^{-1}
1648 cm^{-1}
Transmittance (%)
100
90
80
70
60
50
40
30
3900
3400
2900
2400
1900
1400
900
400
Wavenumber (cm^{-1})
Before Treatment
After Treatment



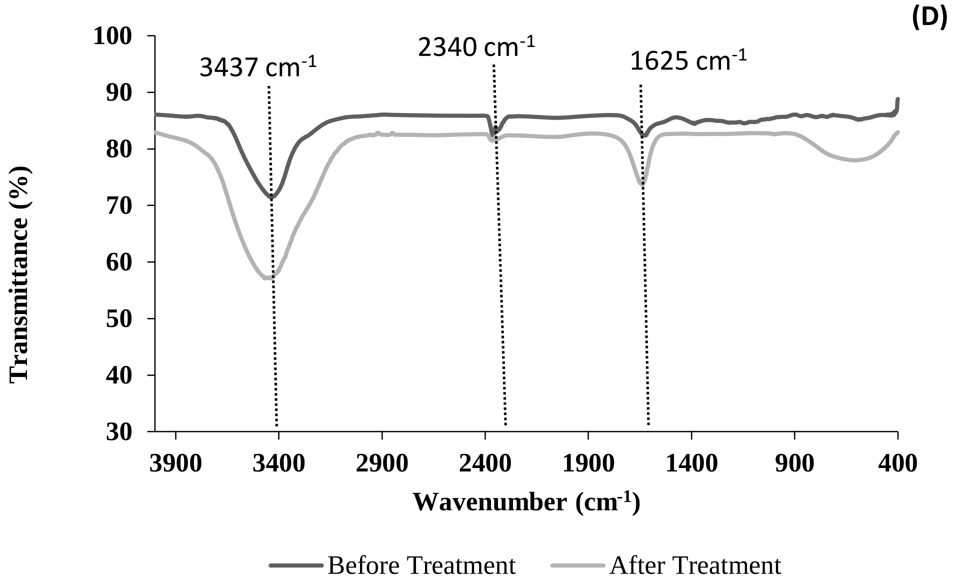


Figure 12. Effect of Temperatures 35 °C and 45°C of profenofos adsorption onto: (A). RODP Temperature 35°C, (B). RODP Temperature 45°C, (C). ACDP Temperature 35°C, and (D). ACDP Temperature 45°C.

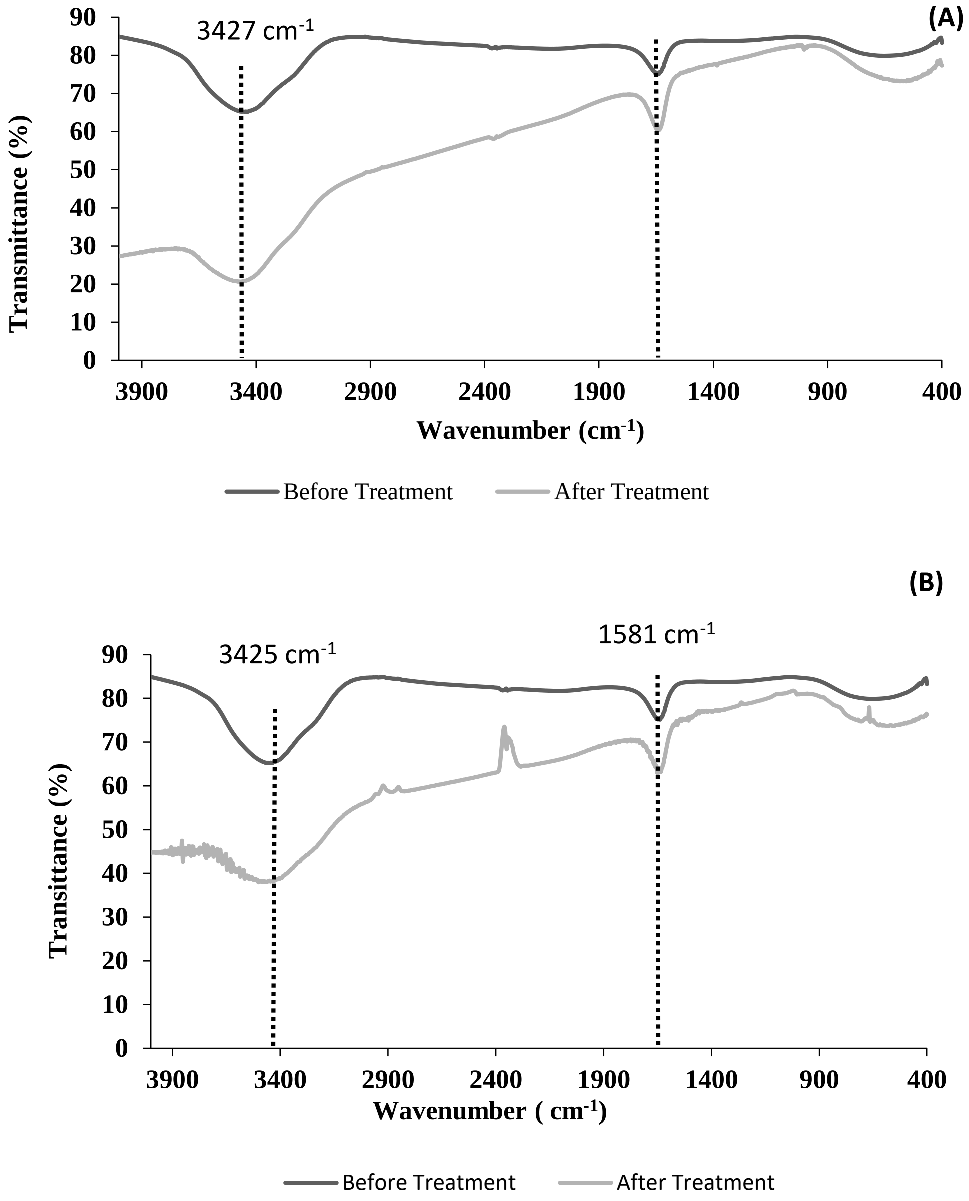
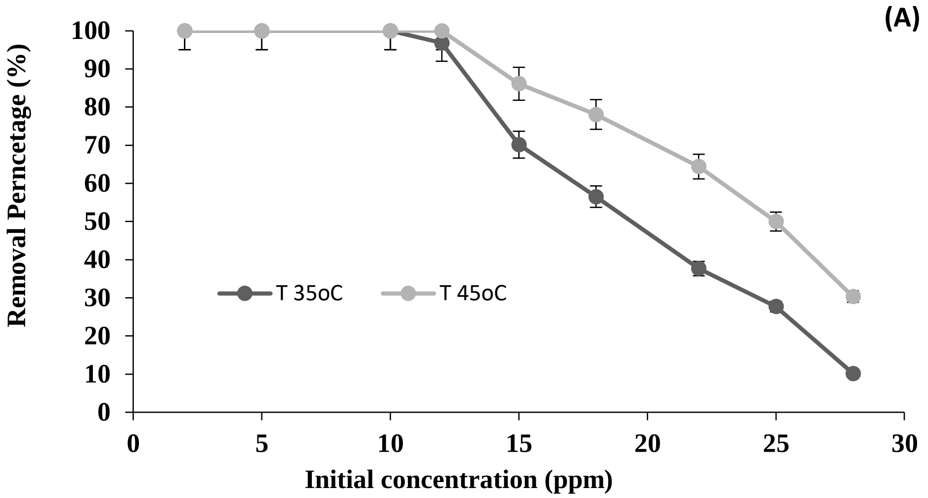
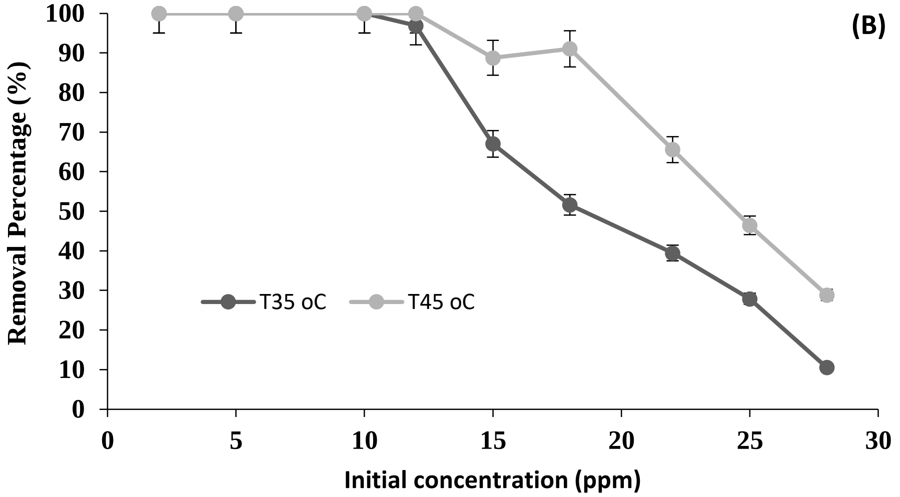


Figure 13. Effect of Temperatures 35 °C and 45°C of profenofos adsorption onto: (A). NACDP Temperature 35°C and (B). NACDP Temperature 45°C.


(A)
Removal Perncetage (%)
100
90
80
70
60
50
40
30
20
10
0
T 35oC
T 45oC
0
5
10
15
20
25
30
Initial concentration (ppm)


(B)
Removal Percentage (%)
100
90
80
70
60
50
40
30
20
10
0
T35 oC
T45 oC
0
5
10
15
20
25
30
Initial concentration (ppm)

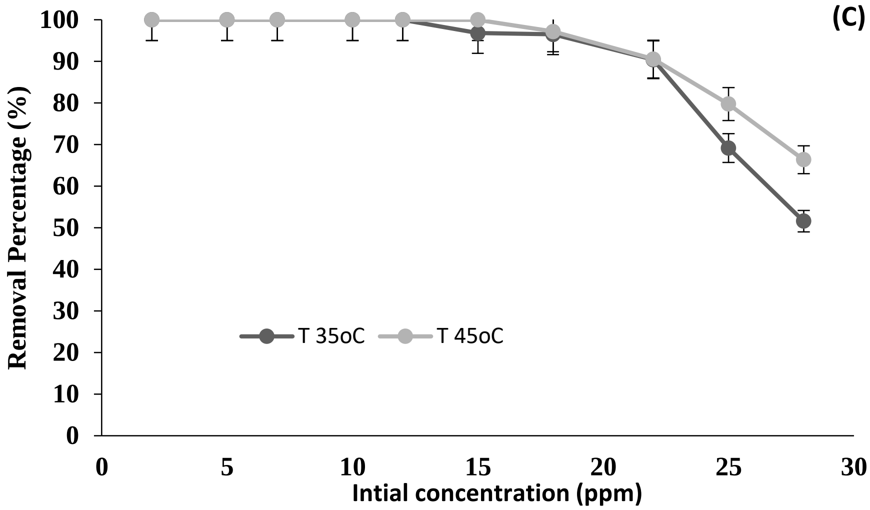


Figure 14. Effect of Temperatures 35 °C and 45°C of profenofos adsorption onto: (A). RODP, (B). ACDP, and (C). NACDP.

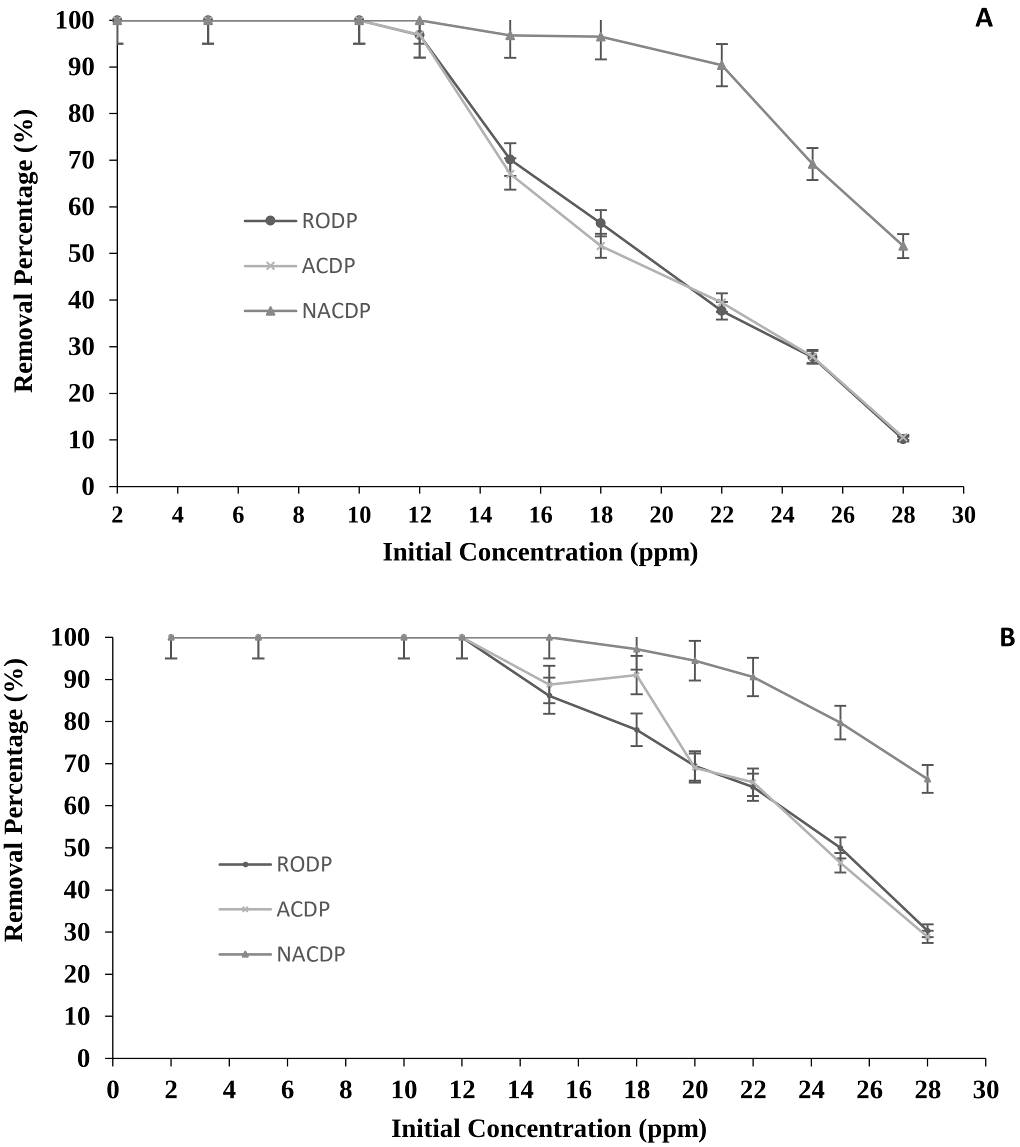


Figure 15. Effect of Temperatures at (A). 35 °C and (B). 45°C of profenofos adsorption onto RODP, ACDP, and NACDP.

4.3 Adsorption Isothermal Model

4.3.1 Effect of Initial Concentration

The adsorption isotherm models Langmuir, Freundlich, Temkin and Dubinin-Radushkevich have been used to study the adsorption performance of profenofos onto RODP, ACDP and NACDP as shown in Table 7 and Figures 16, 17and 18 respectively. It was interpreted from the figures that the experimental results showed that the effects for initial concentration performed at 25^{o}C using RODP the data fitted to the Freundlich model better than the other models. As seen from the Table 7, the R^2 (0.918) is highest for the Freundlich model. However, another study showed that the adsorption equilibrium data for the date pits were best described by the Langmuir model by having a high adsorption monolayer capacity (Al-Ghouti et al. 2010). This difference might be explained due to the type of date pits, type of adsorbent material and the adsorption mechanisms. Moreover, the type of adsorbent and how it attaches on the surface of the adsorbate are of importance. It could be concluded here that the adsorption is a heterogeneous adsorption process.

Comparing the Langmuir constant (qm) for the three adsorbents, the experimental results showed NACDP has the highest qm value (370.4 mg/l); suggesting the high surface area and average pore size from BET analysis.

Moreover, from the Freundlich model, the constants n and K_F reflect the adsorption intensity and capacity, respectively and the 1/n value explains the adsorption process how it occurs on the surface of the adsorbent, that is, the relative distribution of energy site (Al-Ghouti et al., 2017). The 1/n value for NACDP is 1.003 which indicates 100% adsorption takes place on the active site that have equal energy. Furthermore, when the n value is closer to 1 it means that the surface is homogenous. Therefore, from the Table 7, it is seen that the value of n in NACDP indicates a more homogenous surface compared to other two adsorbents.

Modification of the activation based on chemical or physical activation can also effect the adsorption isotherm model. Such as a study done by using activated carbon from date stone using microwave potassium carbonate (K_2CO_3) to remediate methylene blue from aqueous medium, the results have shown high adsorption by the activated carbon fitted the Langmuir model. The activated carbon by microwave K_2CO_3 and date stones have resulted in high Langmuir adsorption capacities (qm) with values (256.15 and 485.44) mg/g respectively (Abbas & Ahmed, 2016).

In comparison with the studied performed by (Abbas & Ahmed, 2016) with (Foo & Hameed, 2011), the activated date stone with potassium hydroxide (KOH) had less adsorption capacity 316.11 mg/g. Hence, different activation technique can influence on the adsorption capacity, due to modification techniques that enhance the surface area and formation of porosity and pore diameter.

Hameed et al., (2009) in his study the activated date pit prepared by physical and chemical activation using potassium hydroxide have used the three models (Langmuir, Freundlich and Temkin), the R^2 was high in all three models however, the equilibrium data fitted well with the Langmuir model having maximum adsorption capacity of 238.10 mg/g.

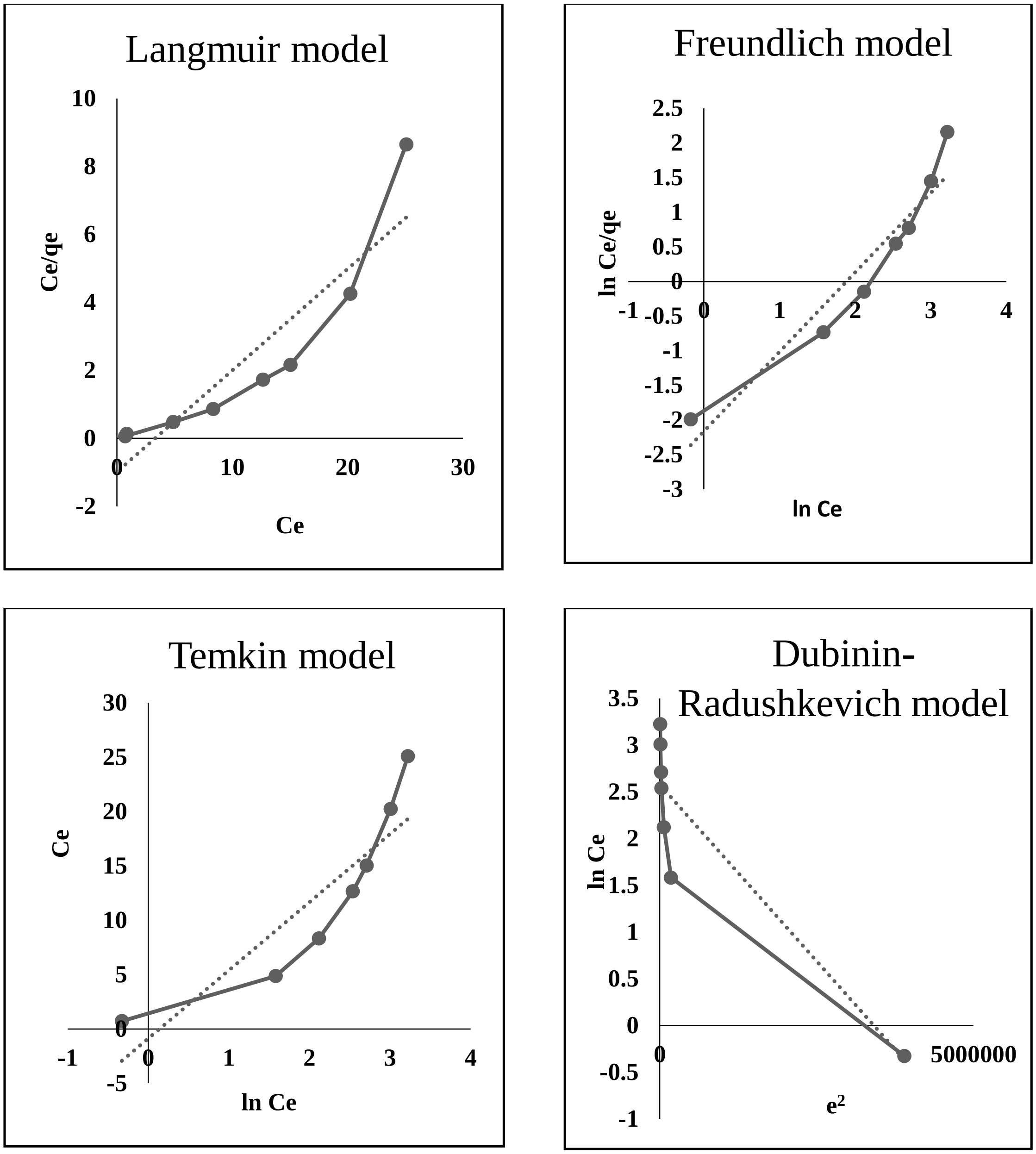


Figure 16. RODP adsorption isotherm models at different initial concentrations.

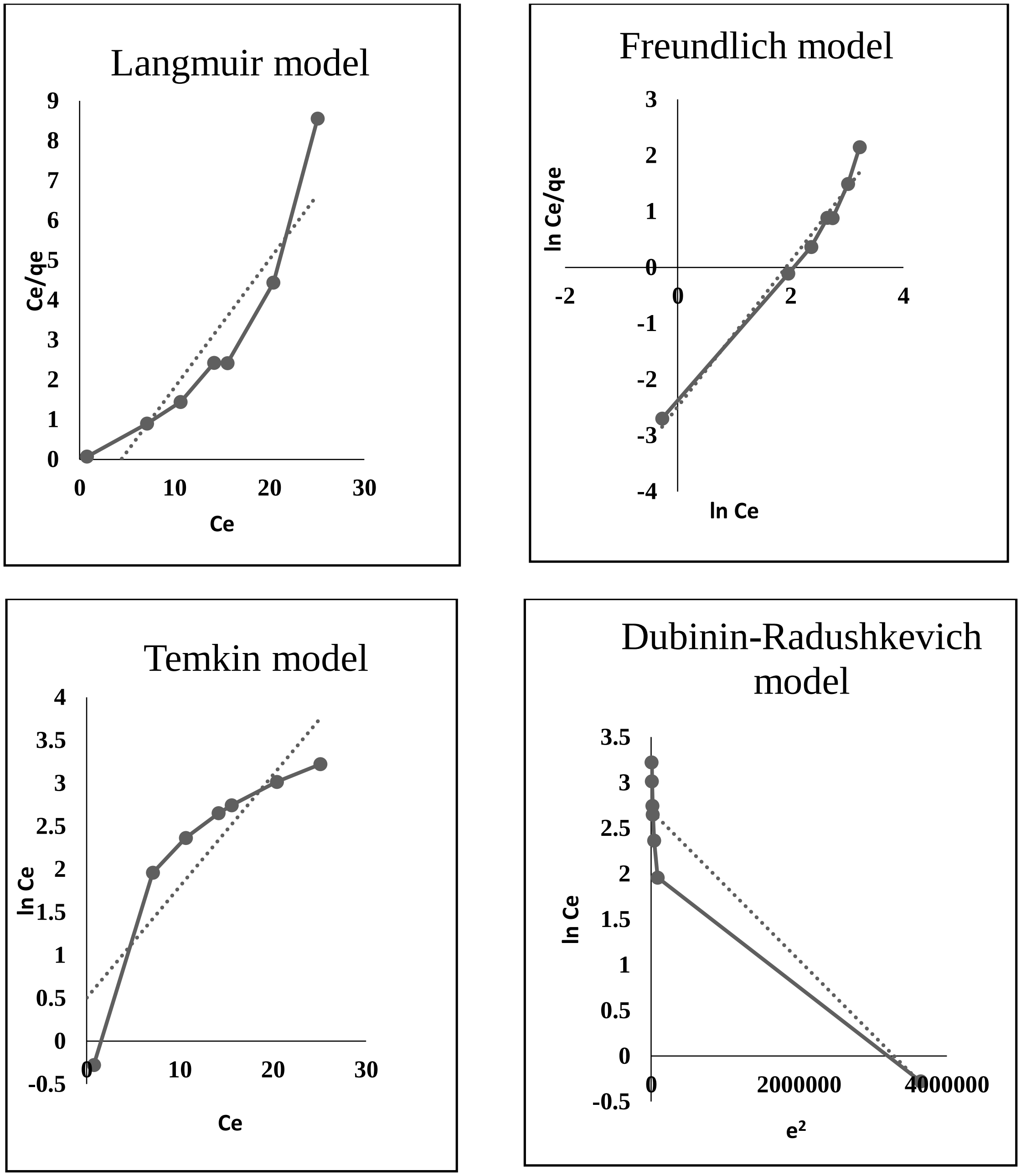


Figure 17. ACDP Adsorption Isotherm Models at different initial concentrations.

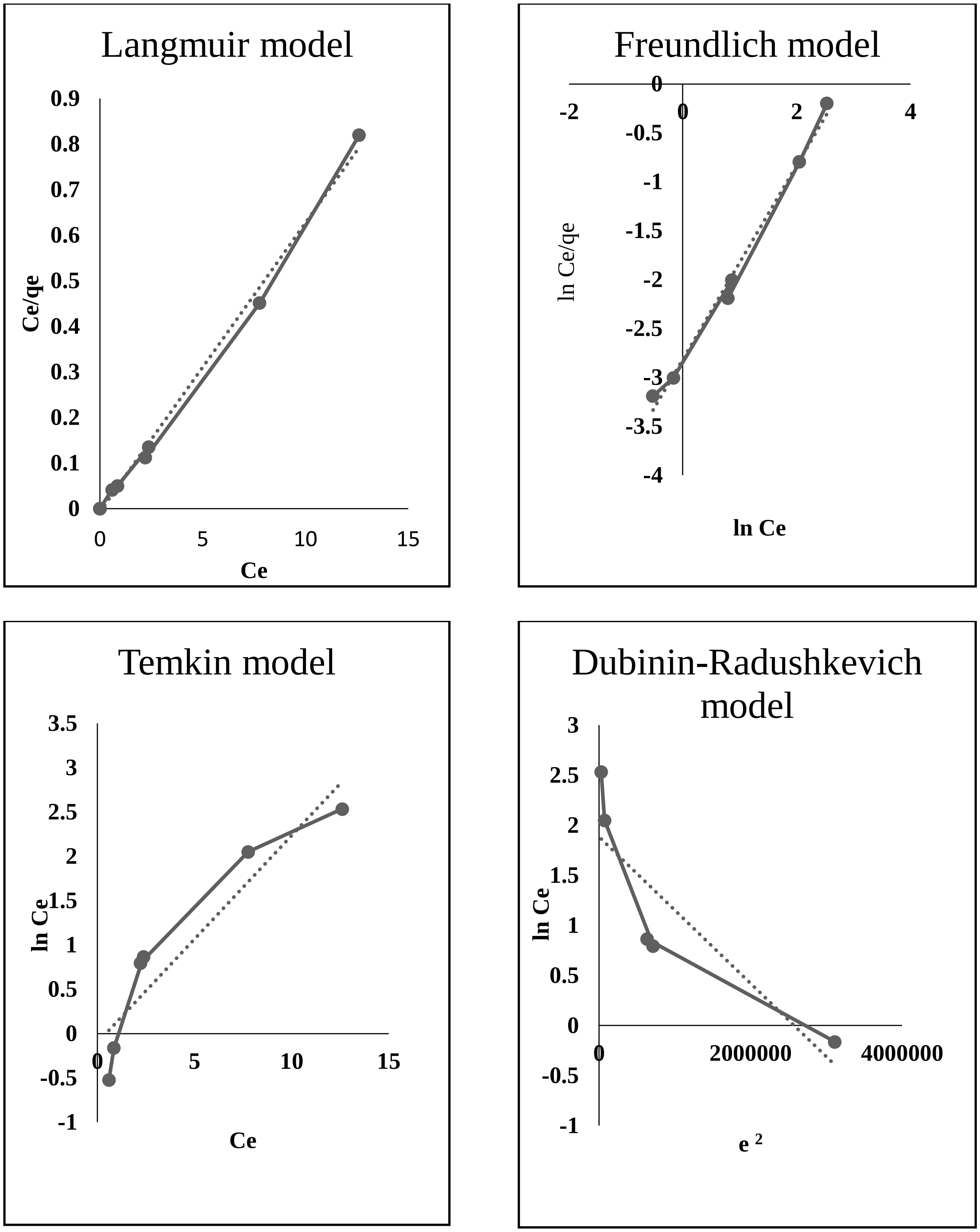


Figure 18. NACDP adsorption isotherm models at different initial concentrations.

4.3.2 Effect of Temperature at 35^{o}C

The isotherm model for the three adsorbents was carried to study the effect of temperature at 35^{o}C. The similar models used for the initial concentration were used for the effect of temperature for both at 35 and 45^{o}C. The adsorption models of effect of temperature at 35^{o}C for the three adsorbents RODP, ACDP and NACDP are shown in Figures 19, 20 and 21, respectively. From Table 7, it is seen that the R^2 was the least for Temkin model for RODP and ACDP, whereas for NACDP the R^2 was the least for Dubinin-Radushkevich in all experimental effects studied. The R^2 values in RODP and ACDP were highest in Freundlich model, whereas for the NACDP, was relatively high in all the three models (Langmuir, Freundlich and Temkin), but it was the highest in Langmuir model.

Moreover, the adsorption capacity (qm) value was different in the three adsorbents for the uptake of profenofos performed under the same experimental conditions. This difference could be explained due to the bonding attraction available on the surface of the adsorbents (Mahdi et al., 2018). Furthermore, due to the pore radius that makes the profenofos can easily penetrate through the pores of the NACDP (Salman et al., 2011).

Therefore, from the Figure 21 and Table 7 NACDP, it is shown that the isotherm data obey the Langmuir model and to further prove this interpretation, the separation factor RL was used which is expressed as the characteristics of the Langmuir isotherm. The RL value is dimensionless constant that explains the shape and favorability of the model. Therefore, if the value is RL=1 it is a linear shape, unfavorable if RL > 1, and adsorption is considered to be favorable if RL is between 0 and 1. Hence, the value calculated for

NACDP is RL=0 which means the adsorption of profenofos on NACDP is favorable (Hameed et al., 2009).

For the Freundlich model, the 1/n value for the NACD at 35 ^{o}C was 1.007, which indicates 100 % adsorption takes place on the active sites that have equal energy. Moreover, since the n value is mentioned in previous literature when the value is between 1 to 10, adsorption surface is heterogeneous and adsorption is favorable (Radwan et al. , 2018). Therefore from the Table 7, the value of n for the NACDP is 0.9928 which is almost equal to 1, therefore favors adsorption condition (Al-Ghouti et al., 2017), more than RODP and ACDP where the n values are 0.8197 and 0.8308 respectively.

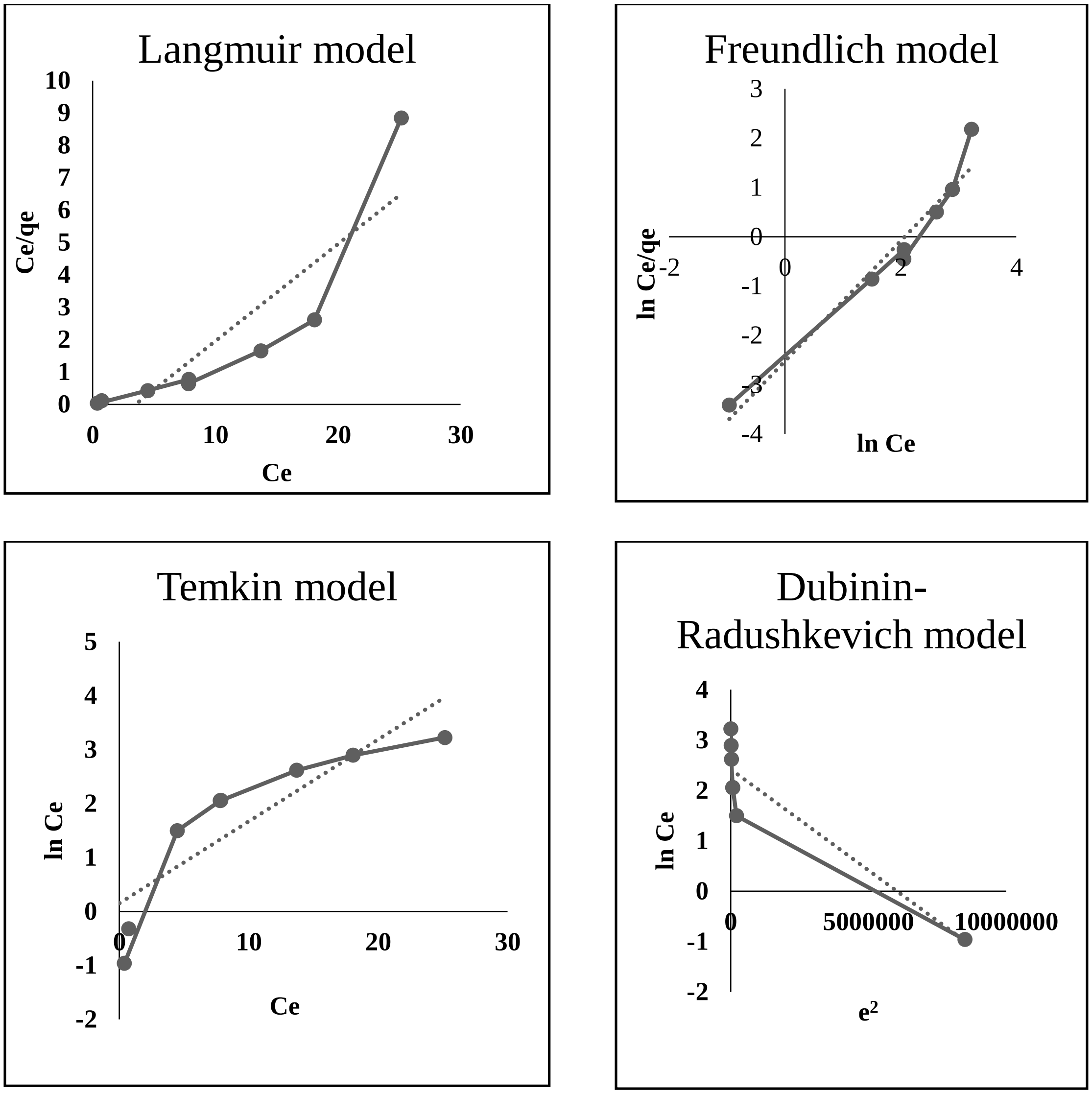


Figure 19. RODP Adsorption Isotherm Model at 35ºC.

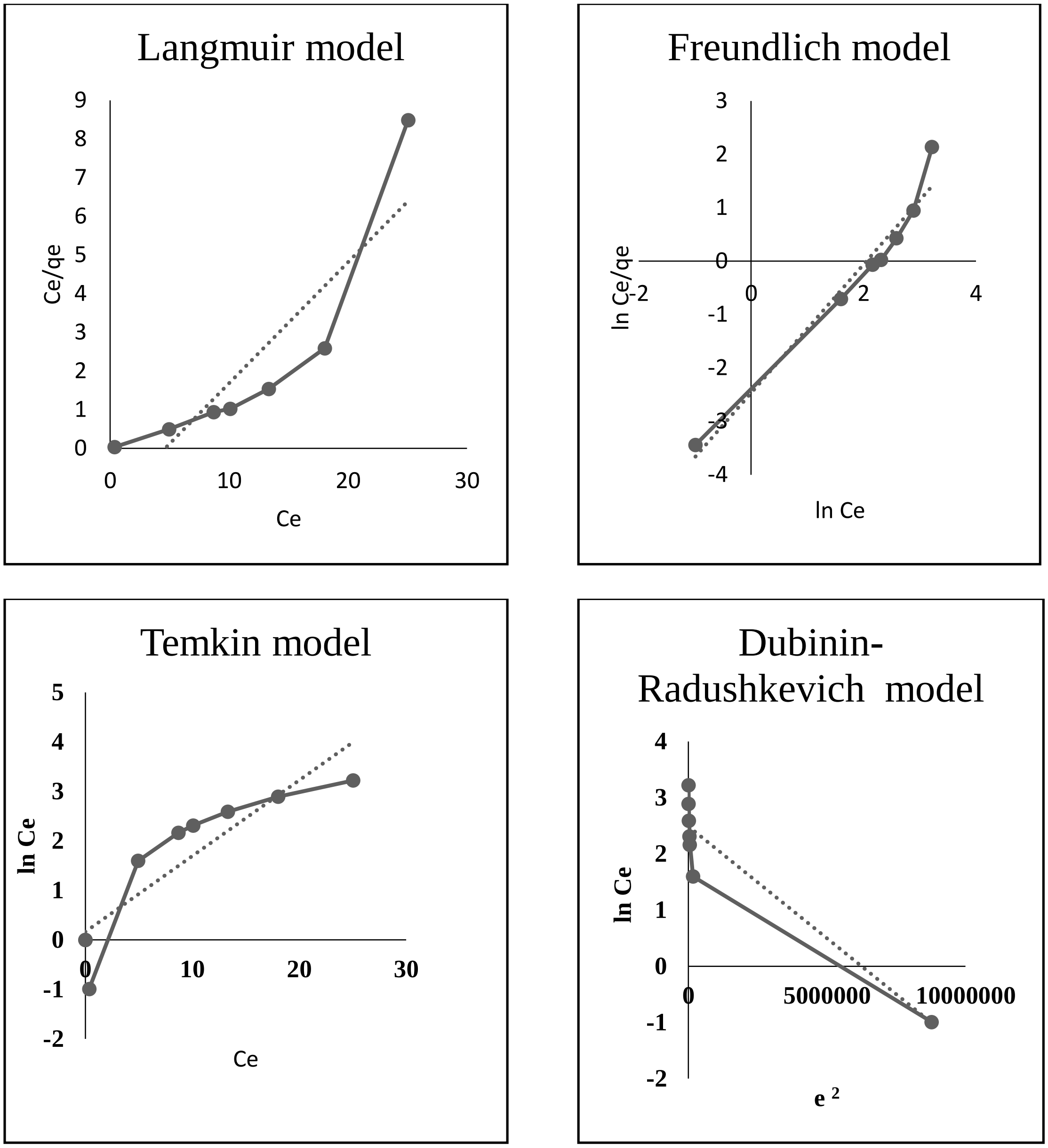


Figure 20. ACDP Adsorption Isotherm Model at 35^{o}C.

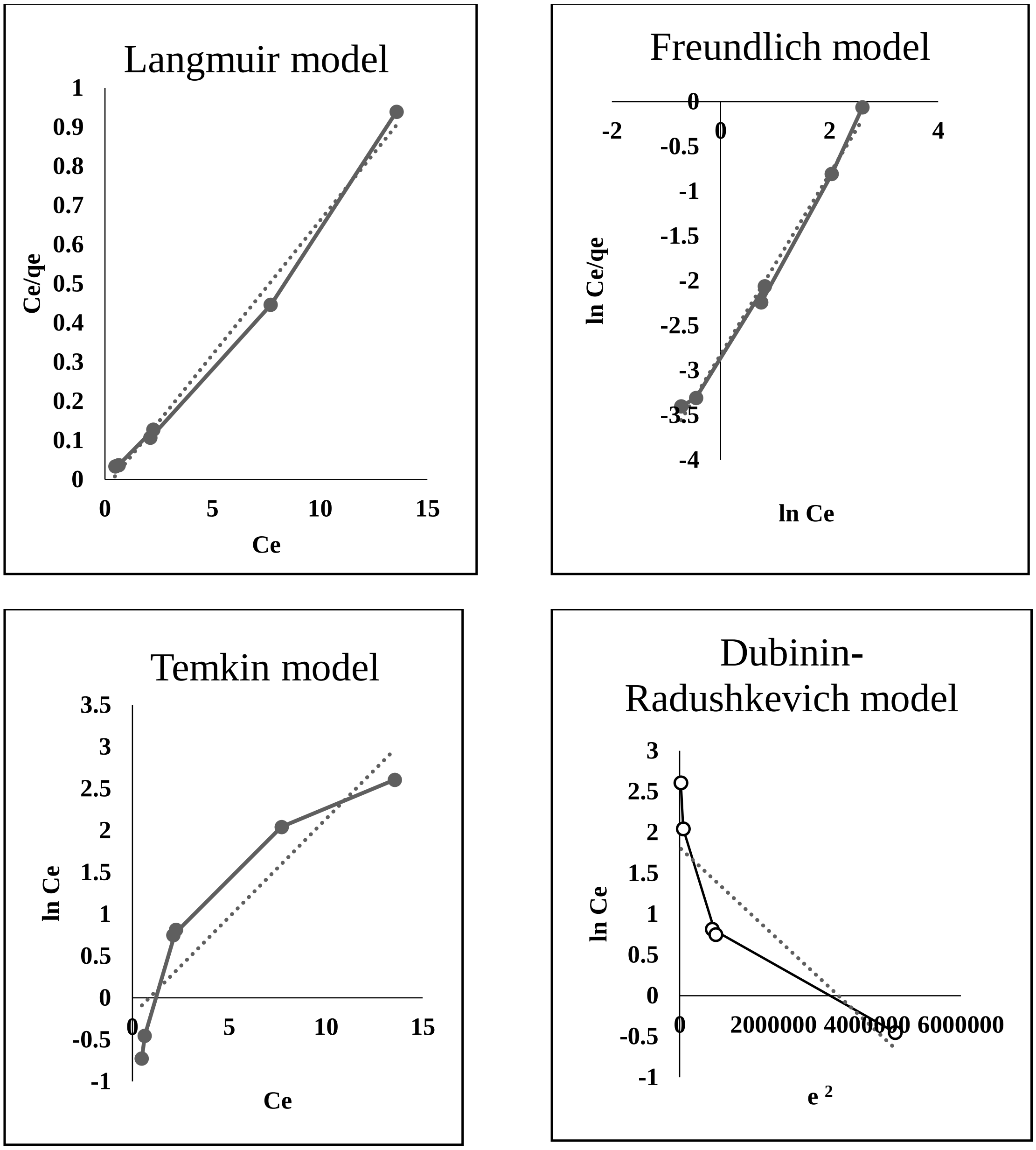


Figure 21. NACDP Adsorption Isotherm Model at 35^oC.

4.3.3 Effect of Temperature at 45°C

The isotherm model for the three adsorbents was carried out to study the effect of temperature at 45°C. The results are shown in Table 7, further illustrated in Figures 23, 24 and 25, for RODP, ACDP and NACDP respectively. From Table 7, it is shown that the adsorption capacity (qm) for the RODP increased when the experiment was carried out at 45°C. This could be explained by increasing the mobility of profenofos with temperature. Additionally, it can be further explained that the effect of temperature on adsorption has three main effects. One of the effects that supports to our results is that, by increasing temperature of the adsorbate solution the diffusion rate of the molecules increases, and overall increasing the pore of the adsorbent (El-Kady et al., 2013).

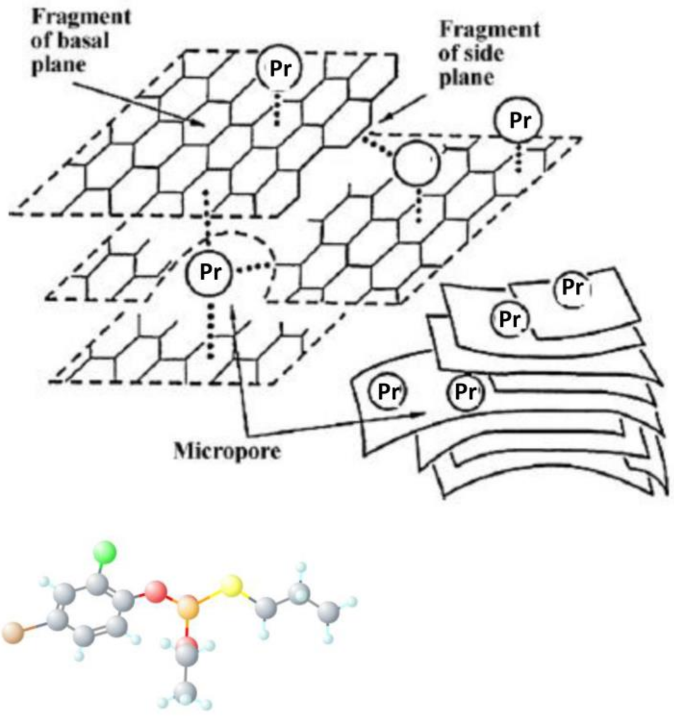
Additionally, the solubility of the profenofos increases with increasing the temperature (Al-Qodah et al., 2007). Moreover, the K_L value for RODP has increased at high temperature. The K_L value at temperature 35°C was 3.203 L/mg and increased to 136.724 L/mg at 45°C. Furthermore, the R^2 value also increased. Nevertheless, the R^2 value for RODP at 45°C is a maximum for the Freundlich model with a value is 0.975, and the n value is 0.864, hence, the adsorption fits into Freundlich model.

Similarly, there was an increase in all parameters with the increase in temperature in ACDP and NACDP. The R^2 of both ACDP and NACDP increased in all models. The R^2 of ACDP was maximum for the Freundlich model (0.9835) compared to the Langmuir model (0.949). The R^2 of NACDP was relatively higher in Langmuir than the Freundlich model. However, when comparing the Langmuir constant (K_L) for the three adsorbents, it was shown that NACDP has the highest K_L value with 6948. L/mg followed by RODP (136.7) and ACDP (35.67). Similarly, the adsorption capacity (qm) was a maximum for

NACDP followed by RODP and ACDP having values (370.4, 14.49 and 4.380) mg/g respectively. Moreover, from table 7 it is shown that the n value for NACDP is 1.024 showing a homogenous surface. However, in the study performed by El-Kady et al. (2013) on using ACDP for the removal of profenofos from aqueous medium, have shown a decrease in the adsorption capacity with increase in temperature.

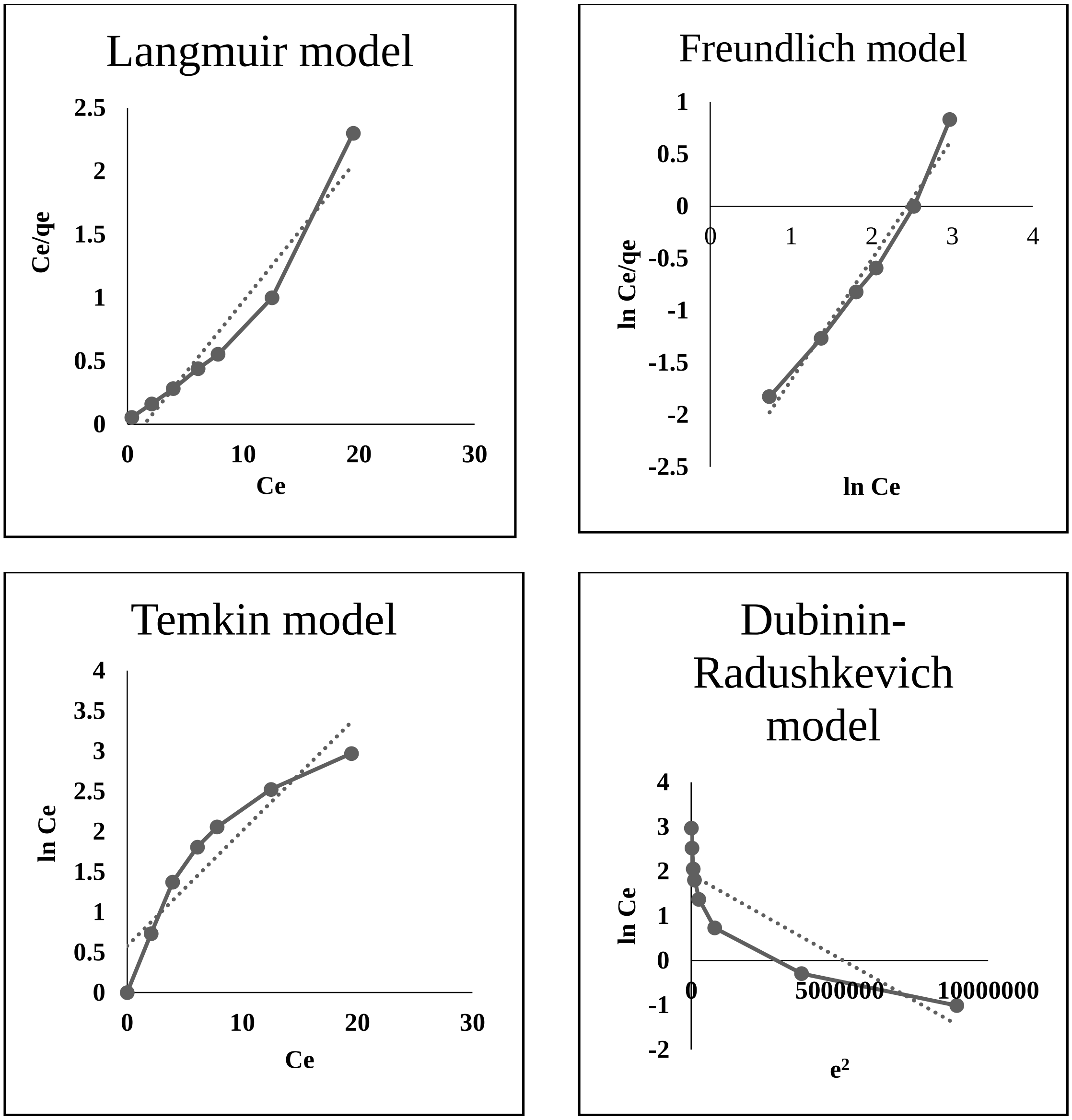
Figure 22 proposes adsorption mechanisms of profenofos onto ACDP and NACDP. A clear change in the FTIR spectral range, 900–690 cm^{-1}, for the treated ACDP and NACDP was observed. This spectral range would be attributed to the n-π interactions between the profenofos and aromatic sheets of the ACDP and NACDP. The n-π complexation bond is typically a weak bond that can be formed between the adsorbent and the adsorbate. The extent of n-π complexation between the adsorbate and the adsorbent depends, for a given adsorbent, on the density of the n-π electrons in the adsorbate with more than two double bonds (e.g., dienes), triple bonds, and polynuclear aromatics. The results revealed that the aromatics present in the ACDP and NACDP compete with profenofos for the available adsorption active sites. Thus, in the adsorption process, a likely tough and mandatory competition between aromatics and the Br, Cl containing compounds for the active sites will detriment the adsorbent capacity and selectivity as well.

The first adsorption process may take place near the exterior surface of the ACDP and NACDP particles and the external functional groups will participate in the adsorption. The second process may take place on the entire surface of the adsorbent and results in a uniform distribution of adsorbed profenofos. The profenofos adsorbed on the ACDP and NACDP surfaces resulting in the formation of n-π complexes with the C=C fragments of the ACDP and NACDP network. On the ACDP and NACDP surface at least three types of adsorption sites might occur on: basal plane, edge plane and micropores, as shown in Figure 22.



Profenofos (Pr), 3D structure

Figure 22. Probable positions of the profenofos (Pr) adsorption onto the surface of ACDP and NACDP.



Langmuir model

Freundlich model

Temkin model

Dubinin-Radushkevich model

Figure 23. RODP Adsorption Isotherm Model at 45^{o}C.

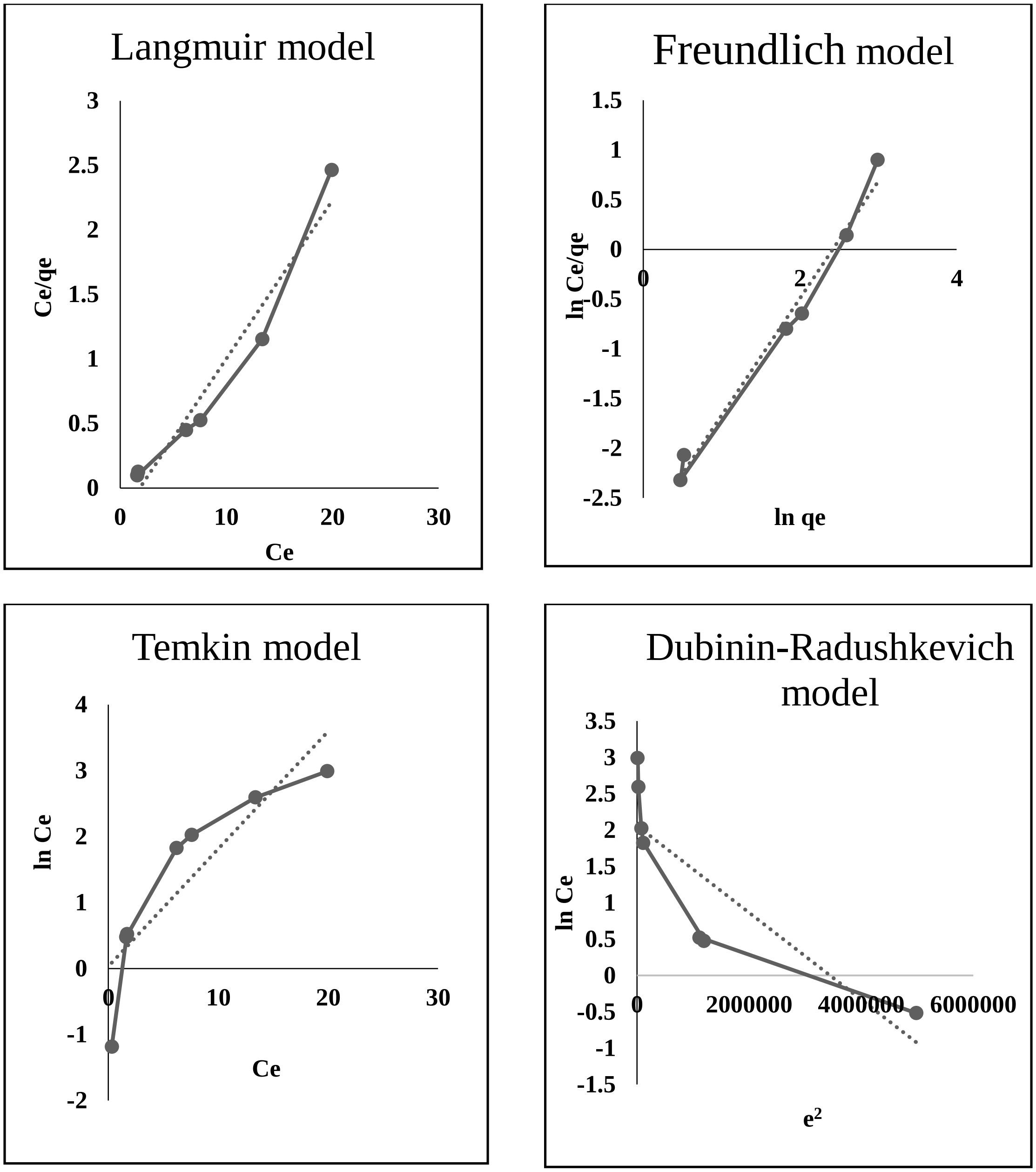


Figure 24. ACDP Adsorption Isotherm Model at 45^{o}C.

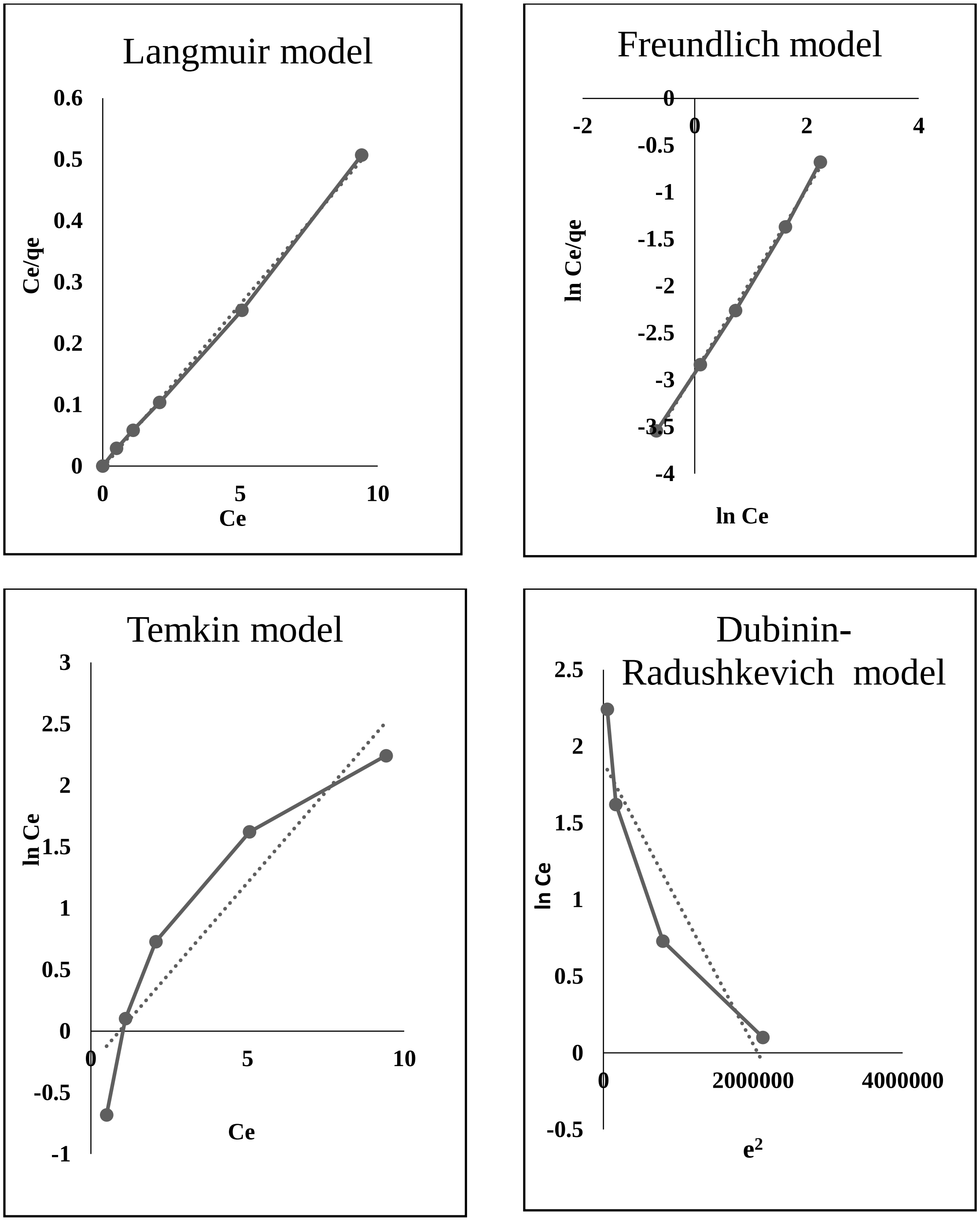


Figure 25. NACDP Adsorption Isotherm Model at 45^{o}C.

Table 7. Parameter of the Adsorption Isotherm Models for the profenofos adsorption onto RODP, ACDP, NACDP at 25 ^{o}C, 35 ^{o}C and 45^{o}C.

Model	Parameter	Temperature 25^{o}C			Temperature 35^{o}C			Temperature 45^{o}C		
		RODP	ACDP	NACDP	RODP	ACDP	NACDP	RODP	ACDP	NACDP
Langmuir	qm (mg g^{-1})	1.019	0.709	169.5	3.337	0.694	41.32	14.493	4.380	370.4
	K_L (L mg^{-1})	3.419	2.209	2678.	3.203	2.218	603.2	136.7	35.67	6948.
	R^2	0.831	0.8390	0.9960	0.7820	0.7830	0.9910	0.9470	0.9490	0.9990
Freundlich	K_F (L mg^{-1})	8.728	12.01	16.708	12.48	11.80	16.87	16.86	17.26	18.58
	1/n	1.147	1.299	0.991	1.22	1.204	1.007	1.157	1.179	0.976
	n	0.872	0.769	1.009	0.819	0.831	0.993	0.864	0.848	1.025
	R^2	0.9180	0.9760	0.9910	0.9470	0.9560	0.9910	0.9750	0.9840	0.9980

Model	Parameter	Temperature 25^{o}C			Temperature 35^{o}C			Temperature 45^{o}C		
		RODP	ACDP	NACDP	RODP	ACDP	NACDP	RODP	ACDP	NACDP
Temkin	B (J mol^{-1})	6.276	0.1452	0.233	0.151	0.1531	0.234	0.143	0.173	0.296
	B_T	361.64	15630.	9723.4	14960	14823	9686.1	15893	13118.	7664.5
	A_T (L mg^{-1})	1.153	4.915	1.542	2.706	2.883	2.412	57.542	1.194	2.516
	R^2	0.7890	0.7930	0.8740	0.7570	0.8020	0.8460	0.8660	0.7700	0.8720
Dubinin-Radushkevich	ln qs	13.17	14.71	6.592	11.27	12.04	6.117	6.874	7.848	6.667
	R^2	0.8250	0.8900	0.7450	0.8410	0.8730	0.7250	0.7470	0.7070	0.8570

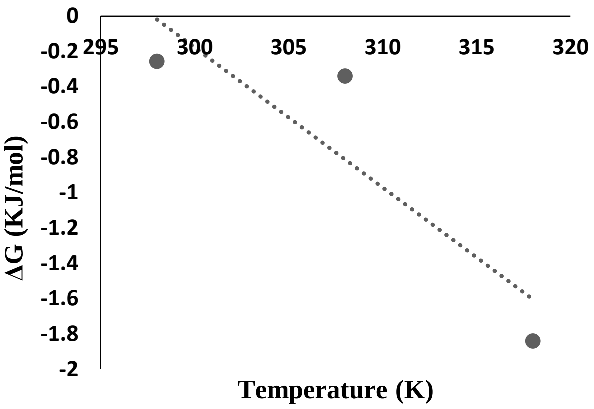
4.4 Adsorption Thermodynamic

Figure 26 shows the adsorption thermodynamics of profenofos adsorption onto RODP, ACDP, NACDP. The graph was plotted between ΔG (kJ mol^{-1}) and Temperature (K). The values of ΔH (kJ mol^{-1}) and ΔS (kJ mol^{-1}) were calculated from the slope and intercept respectively. Table 8 show the adsorption thermodynamic for RODP, ACDP and NACP, respectively. Hence from the table and graphs, it is obserevd that the value of ΔG in all three adsorbents is negative, therefore a negative values of ΔG indicates the feasibility and spontaneous nature of profenofos adsorption onto RODP, ACDP and NACDP (Tan et al., 2008). The value of ΔG increases with temperature in all three adsorbents; indicating the degree of spontaneity increased with temperature (Mansouriieh et al. 2016).

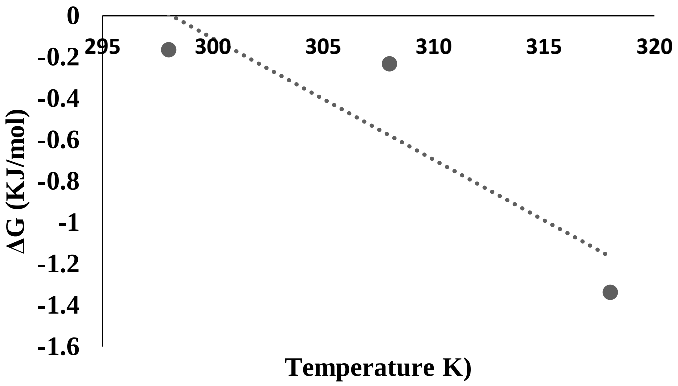
Moreover, the values of ΔH for the three adsorbents were positive and the highest for RODP (23.590 $KJmol^{-1}$). In the reaction between the adsorbent and profenofos, energy in the form of heat was adsorbed; resulting in an endothermic reaction (Mohammad, 2013). Whereas, the value of ΔS values were negative in the three adsorbents and were the highest for NACDP (-0.084 $KJmol^{-1}$). Hence, the ΔH positive and ΔS negative indicates a non-spontaneous reaction and the three adsorbents are endothermic in nature (Bouhamed et al., 2012).

Furthermore the above results gives support to the results obtained in the adsorption isothermal analysis. Since the value of ΔH is positive that indicates an endothermic reaction. This explains the reason of increase in the adsorption capacity (qm) at higher temperature. Moreover, the value of ΔG increased with temperature for the three adsorbents, this is an indication of the high adsorption capacity at temperature 45^{o}C as seen in Table 7 (Tan et al., 2008).

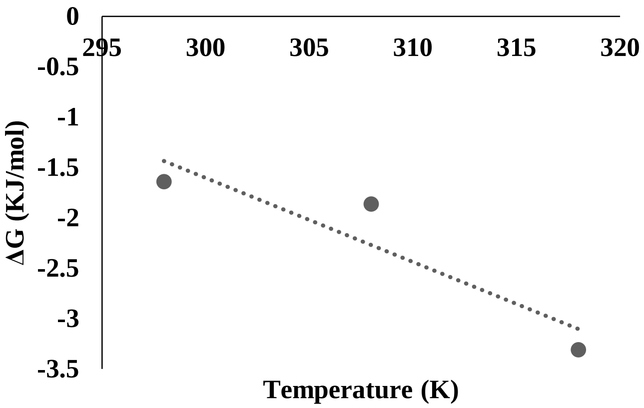
The preparation of RODP also plays role in the adsorption capacity and the values of thermodynamic adsorption. The value of ΔH for ACDP at temperature 308 K (ΔH=-0.232 KJ/mol) and 318 K (ΔH=-1.337 KJ/mol) obtained in this study was relatively high compared to the study done by Salman & Al-saad, (2012). The values obtained in their study at temperature 303 K and 313 K were 8.374 KJ/mol and 8.357 KJ/mol, respectively. The temperature was not very high and was only a variation of 5 K, but the values were small. This can be explained due to the chemical preparation of activated date pit. Moreover, this variation can also be explained due to the high surface area obtained in their study which was 806 m^2/g compared to the current study which was 30.397 m^2/g. Additionally, the values of ΔG increased with increase in temperature as shown in table 8 for the three adsorbents. Therefore, this shows how the adsorption process favors a high temperature (Al-Saidi, 2016). Finally, ΔH is positive and is lower than 40 KJ/mol, the adsorption process shows endothermic and physisorption characteristics (Wakkel et al., 2019).



(a)



(b)



(c)

Figure 26. Adsorption Thermodynamic of profenofos adsorption onto (a). RODP, (b). ACDP, (c). NACDP.

Table 8. Adsorption Thermodynamic parameters of profenofos adsorption onto RODP, ACDP, NACDP.

Temperature (K)	ΔG (kJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS (KJ mol^{-1} K^{-1})
		RODP	
298	-0.256	23.582	-0.079
308	-0.339		
318	-1.840		
		ACDP	
298	-0.165	17.410	-0.059
308	-0.232		
318	-1.337		
		NACDP	
298	-1.641	23.416	-0.083
308	-1.863		
318	-3.309		

For three adsorbents, the maximum adsorption capacity was the highest at temperature 45^{o}C. Therefore, the below Table 9 shows a comparison between the values obtained in this study with previous literature studies. When comparing RODP and ACDP, of the qm values shown in Table 7 it is noticed that the RODP had the higher value. Moreover from the removal percentage of profenofos at temperature 45^{o}C the RODP value had a higher value than ACDP, this can be explained due to more functional groups available on RODP that was seen from the FTIR spectrum (figure 5).

It is also seen from the spectrum Figure (12) that how the temperature has affected the adsorption of profenofos by RODP, the -OH peak has become broader and narrower in figure 12B, whereas in figure 12A the -OH peak was less intense. Therefore, this explains the high removal percentage occurs more at a temperature of 45 ^{o}C rather than 35 ^{o}C, whereas in the case of ACDP the peaks were only slightly shifted.

Table 9. Comparison of Adsorption Capacity and Freundlich Constant with Previous Studies.

Adsorbents	Maximum adsorption capacity (qm) mg/g at 45^{o}C	Freundlich Constant KF (L/mg)	Temperature studied ^{o}C	Adsorbate	Activation Preparation	Reference
RODP	14.493	136.724	45	Profenofos	Physical	Current study
ACDP	4.380	35.669				
NACP	370.370	6948.787				
*AC	196.1	20.16	40	**2,4-D	Chemical	(Jasim M Salman & Al-saad, 2012)
AC	464.3	28.6	40	Methylene Blue	Chemical	(Islam et al., 2015)
AC	206	59.6	40	Phenol	Physical	(El-Naas et al.,2010)
AC	238.10	2.529	40	2,4-D	Physical and Chemical	(Hameed et al., 2009)
Adsorbents	Maximum	Freundlich	Temperature	Adsorbate	Activation	Reference

	adsorption capacity (qm) mg/g at 45^{o}C	Constant KF (L/mg)	studied ^{o}C		Preparation	
AC	344.8	232.2	30	MB	chemical	(Suresh et al., 2012)
AC	55.27	64.87	30	Lead ion	chemical	(Krishnamoorthy et al., 2018)
Raw Date pit	185.2	22.4	30	Bromide	-	(Al-Ghouti et al., 2017)
AC	142.9	26.6	30	Bromide	commercial	(Al-Ghouti et al., 2017)
AC	86.26 137.04	6.47 13.03	30	Bentazon Carbofuran	chemical	(Salman et al., 2011)
Raw Date pit	281	93.5	25	MB	-	(Al-Ghouti et al., 2010)
Adsorbents	Maximum	Freundlich	Temperature	Adsorbate	Activation	Reference

	adsorption capacity (qm) mg/g at 45°C	Constant KF (L/mg)	studied °C		Preparation	
AC	30.140	6.302	45	Phenol	Physical	(Banat et al., 2004)

*AC: Activated Carbon

**2, 4-D: 2, 4-Dichlorophenoxyacetic Acid

*** MB: Methylene Blue

CHAPTER 5: CONCLUSIONS

This study is the first of its kind done in Qatar to investigate the adsorption of profenofos in wastewater and adsorbed by agricultural biomass date pits. Three adsorbents (RODP, ACDP, and NACDP) were prepared to adsorb profenofos from aqueous solution. According to the results, the surface area of the three adsorbents was the highest for the nano-activated date pits. The surface area was 485.4 m^2/g. Moreover, the pore volume and pore radius were also highest for NACDP with values 0.338 cm^3/g and 17.8 Å. Hence, the NACDP have resulted in high removal percentage and removal capacity of profenofos from aqueous solution, therefore this adsorption behavior is favored high surface area, pore volume and pore radius.

Moreover, four types of adsorption isotherm models namely, Langmuir isotherm, Freundlich isotherm, Dubinin-Radushkevich isotherm and Temkin isotherm models investigated the adsorption isotherm data in order to understand the interactions between the adsorbate (profenofos pesticide) and the adsorbents. The values have showed the R^2 was highest for NACDP in all experimental effects studied. However, the maximum values occurred at higher temperature 45°C, where it is observed that the adsorption was enhanced by temperature. Moreover, the adsorption maximum capacity (qm) increased with temperature and was maximum for NACDP based on Langmuir adsorption isotherm model.

In the case of RODP, K_L values have highly increased at high temperature. The K_L value at temperature 35°C was 3.203 L/mg and increased to 136.7 L/mg. Furthermore, the R^2 value increased. Nevertheless, the R^2 value for RODP at 45°C is maximum in the Freundlich model; however, the n value is 0.864. Therefore, the adsorption fits best into the Freundlich model. Similarly, there was an increase in parameters with increase in temperature for ACDP. The R^2 of ACDP was a maximum in the

Freundlich model (0.9835) compared to the Langmuir model (0.949). Hence, from the above assumptions, RODP and ACDP fits into best into the Freundlich model and NACDP fits best into Langmuir model.

Finally, based on thermodynamic parameters, the ΔG values were negative in all three adsorbents and the value increased with temperature. The ΔH values were positive in the three adsorbents and highest in RODP (23.59 $KJmol^{-1}$), therefore, in the reaction between the adsorbent and profenofos, energy in the form of heat was adsorbed, hence resulting in an endothermic reaction. Whereas, the value of ΔS is negative in the three adsorbents and highest in NACDP (-0.084 $KJmol^{-1}$). Hence, ΔH positive and ΔS negative indicates a non-spontaneous reaction and the three adsorbents are endothermic in nature.

Therefore, in conclusion the results show date pits are effective as an adsorbents in removing organic compounds such as organophosphate pesticide profenofos) from aqueous media, and hence can be used in treating wastewater.

REFERENCES

Abbas, A. F., & Ahmed, M. J. (2016). Mesoporous activated carbon from date stones (Phoenix dactylifera L.) by one-step microwave assisted K $_2$ CO $_3$ pyrolysis. *Journal of Water Process Engineering*, *9*, 201–207. https://doi.org/10.1016/j.jwpe.2016.01.004

Adewole, J. K., & Sultan, A. (2014). A Study on Processing and Chemical Composition of Date Pit Powder for A Study on Processing and Chemical Composition of Date Pit Powder for Application in Enhanced Oil Recovery, (March 2018). https://doi.org/10.4028/www.scientific.net/DDF.353.79

Adib Yahya, M., Al-Qodah, Z., & Zanariah Ngah, C. W. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable and Sustainable Energy Reviews*, *46*, 218–235. https://doi.org/10.1016/j.rser.2015.02.051

Ahmad, R., & Mirza, A. (2018). Facile one pot green synthesis of Chitosan-Iron oxide (CS-Fe2O3) nanocomposite: Removal of Pb(II) and Cd(II) from synthetic and industrial wastewater. *Journal of Cleaner Production, 186,* 342–352. https://doi.org/10.1016/j.jclepro.2018.03.075

Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., & Ibrahim, M. N. M. (2012). The use of date palm as a potential adsorbent for wastewater treatment: A review. *Environmental Science and Pollution Research, 19*(5), 1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Ahmad, Z. U., Yao, L., Wang, J., Gang, D. D., Islam, F., Lian, Q., & Zappi, M. E. (2019). Neodymium embedded ordered mesoporous carbon (OMC) for enhanced adsorption of sunset yellow: Characterizations, adsorption study and adsorption mechanism. *Chemical Engineering Journal*, *359*(November 2018), 814–826.

https://doi.org/10.1016/j.cej.2018.11.174

Ahmed, M. J. (2011). *Preparation of activated carbons from date stones by chemical activation method using $FeCl_3$ and $ZnCl_2$ as activating agents*. *Journal of Engineering* (Vol. 17). Retrieved from https://www.iasj.net/iasj?func=fulltext&aId=24513

Ahmed, M. J. (2016). Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments: Review. *Process Safety and Environmental Protection*, *102*, 168–182. https://doi.org/10.1016/j.psep.2016.03.010

Aktar, W., Sengupta, D., & Chowdhury, A. (2009). Impact of pesticides use in agriculture: their benefits and hazards. *Interdisciplinary Toxicology*, *2*(1), 1–12. https://doi.org/10.2478/v10102-009-0001-7

Al-Anber, M. (2011). Thermodynamics Approach in the Adsorption of Heavy Metals. In *Thermodynamics - Interaction Studies - Solids, Liquids and Gases*. InTech. https://doi.org/10.5772/21326

Al-Ghouti, M. A., Al Disi, Z. A., Al-Kaabi, N., & Khraisheh, M. (2017). Mechanistic insights into the remediation of bromide ions from desalinated water using roasted date pits. *Chemical Engineering Journal*, *308*, 463–475. https://doi.org/10.1016/j.cej.2016.09.091

Al-Ghouti, M. A., Li, J., Salamh, Y., Al-Laqtah, N., Walker, G., & Ahmad, M. N. M. (2010a). Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. *Journal of Hazardous Materials*. https://doi.org/10.1016/j.jhazmat.2009.11.059

Al-Ghouti, M. A., Li, J., Salamh, Y., Al-Laqtah, N., Walker, G., & Ahmad, M. N. M. (2010b). Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. *Journal of Hazardous Materials*, *176*(1–3), 510–520. https://doi.org/10.1016/j.jhazmat.2009.11.059

Al-nahari, H. (2015). Effects of Profenofos and Chlorpyrifos Pesticides on Oxidative Stress Biomarker , Biochemical Toxicity , DNA and RNA Content of Male Albino Mice. *Jounal o*f *British Biomedical Bulletin.*

Al-Qodah, Z., Shawaqfeh, A. T., & Lafi, W. K. (2007). Adsorption of pesticides from aqueous solutions using oil shale ash. Journal of Desalination. Desalination 208 (2007) 294–305 https://doi.org/10.1016/j.desal.2006.06.019

Al-Saidi, H. M. (2016). The fast recovery of gold(III) ions from aqueous solutions using raw date pits: Kinetic, thermodynamic and equilibrium studies. *Journal of Saudi Chemical Society*, *20*, 615–624. https://doi.org/10.1016/j.jscs.2013.06.002

Amer, H., El-Gendy, A., & El-Haggar, S. (2017). Removal of lead (II) from aqueous solutions using rice straw. *Water Science and Technology*, *76*(5), 1011–1021. https://doi.org/10.2166/wst.2017.249

Angelakis, A., & Salgot, M. (2016). Water Recycling and Reuse in EUREAU Countries : Trends and Challenges, (March 2016).

Anjum, M., Miandad, R., Waqas, M., Gehany, F., & Barakat, M. A. (2016). Remediation of wastewater using various nano-materials. *Arabian Journal of Chemistry*. https://doi.org/10.1016/j.arabjc.2016.10.004

Awwad, N. S., El-Zahhar, A. A., Fouda, A. M., & Ibrahium, H. A. (2013). Removal of heavy metal ions from ground and surface water samples using carbons derived from date pits. *Journal of Environmental Chemical Engineering*, *1*(3), 416–423. https://doi.org/10.1016/j.jece.2013.06.006

Banat, F., Al-Asheh, S., & Al-Rousan, D. (2012). *A Comparative Study of Copper and Zinc Ion Adsorption on to Activated and Non-activated Date-pits*. Retrieved from https://journals.sagepub.com/doi/pdf/10.1260/02636170260295515

Bargougui, R., Bouazizi, N., Brun, N., Fotsing, P. N., Thoumire, O., Ladam, G., Vieillard, J. (2018). Improvement in CO2 adsorption capacity of cocoa shell through functionalization with amino groups and immobilization of cobalt nanoparticles. *Journal of Environmental Chemical Engineering*, *6*(1), 325–331. https://doi.org/10.1016/j.jece.2017.11.079

Belhachemi, M., Rios, R. V. R. A., Addoun, F., Silvestre-Albero, J., Sepúlveda-Escribano, A., & Rodríguez-Reinoso, F. (2009). Preparation of activated carbon from date pits: Effect of the activation agent and liquid phase oxidation. *Journal of Analytical and Applied Pyrolysis*, *86*(1), 168–172. https://doi.org/10.1016/j.jaap.2009.05.004

Bennett, A. (2015). *Developments in desalination and water reuse*. *Filtration & Separation* (Vol. 52). https://doi.org/10.1016/S0015-1882(15)30181-6

Bernardes, M. F. F., Pazin, M., Pereira, L. C., & Dorta, D. J. (2015). Impact of Pesticides on Environmental and Human Health. *Toxicology Studies - Cells, Drugs and Environment*, (July). https://doi.org/10.5772/59710

Borgesen, C. D., Fomsgaard, I. S., Plauborg, F., Schelde, K., & Spliid, N. H. (2015). *Fate of Pesticides - In Agricultural Soils*.

Bouchelta, C., Medjram, M. S., Bertrand, O., & Bellat, J.-P. (2008). Preparation and characterization of activated carbon from date stones by physical activation with steam. *Journal of Analytical and Applied Pyrolysis* https://doi.org/10.1016/j.jaap.2007.12.009

Bouhamed, F., Elouear, Z., & Bouzid, J. (2012). Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics. *Journal of the Taiwan Institute of*

Chemical Engineers, *43*, 741–749. https://doi.org/10.1016/j.jtice.2012.02.011

Bushra, R., & Shahadat, M. (2017). Mechanism of Adsorption on Nano materials *Advanced Environmental Analysis: Applications of Nanomaterials, Volume1.*

Cara, I. G., & Jităreanu, G. (2015). Application of Low-Cost Adsorbents for Pesticide Removal. *Bulletin USAMV Series Agriculture, 72*(1), 1843–5386. https://doi.org/10.15835/buasvmcn-agr

Casado, J., Santillo, D., & Johnston, P. (2018). Multi-residue analysis of pesticides in surface water by liquid chromatography quadrupole-Orbitrap high resolution tandem mass spectrometry. Analytica Chimica Acta https://doi.org/10.1016/j.aca.2018.04.026

Chahkandi, M., Amiri, A., Roghayyeh, S., & Arami, S. (2018). Extraction and preconcentration of organophosphorus pesticides from water samples and fruit juices utilizing hydroxyapatite/Fe_3O_4 nanocomposite. https://doi.org/10.1016/j.microc.2018.09.018

Chakra Reddy, N., & Rao, J. V. (2008). Biological response of earthworm, Eisenia foetida (Savigny) to an organophosphorous pesticide, profenofos. *Ecotoxicology and Environmental Safety*, *71*, 574–582. https://doi.org/10.1016/j.ecoenv.2008.01.003

Chang, J. H., Dong, C. Di, & Shen, S. Y. (2018). The lead contaminated land treated by the circulation-enhanced electrokinetics and phytoremediation in field scale. *Journal of Hazardous Materials*, *368*(October 2017), 894–898. https://doi.org/10.1016/j.jhazmat.2018.08.085

Chao, Chih-Kai, S. Kaleem Ahmed, John M. Gerdes, and C. M. T. (2016). Novel Organophosphate Ligand O-(2-Fluoroethyl)-O-(p Nitrophenyl)Methylphosphonate: Synthesis, Hydrolytic Stability and Analysis of the Inhibition and Reactivation of Cholinesterases, *35*(14), 1252–1260. https://doi.org/10.1177/0333102415576222.Is

Chiou, C. T. (2003). Fundamentals of the Adsorption Theory. *Partition and Adsorption of Organic Contaminants in Environmental Systems*, 39–52. https://doi.org/10.1002/0471264326.ch4

Chowdhury, S., Mishra, R., Saha, P., & Kushwaha, P. (2011). Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination*, *265*(1–3), 159–168. https://doi.org/10.1016/j.desal.2010.07.047

Christie, W. W., & Christie, W. W. (1992). Detectors for HPLC of lipids with special reference to evaporative light-scattering detection detectors for high-performance liquid chromatography of lipids with special reference to evaporative light-scattering detection. Oily Press. Retrieved from https://pdfs.semanticscholar.org/b798/34624b4b107678cf8829f0dfd52613c2c32d.pdf

Correa Torres, S. N., Kopytko, M., & Avila, S. (2016). Efficiency of modified chemical remediation techniques for soil contaminated by organochlorine pesticides. *IOP Conference Series: Materials Science and Engineering*, *138*(1). https://doi.org/10.1088/1757-899X/138/1/012020

Darko, G., & Akoto, O. (2008). Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana. *Food and Chemical Toxicology*, *46*(12), 3703–3706. https://doi.org/10.1016/j.fct.2008.09.049

De Marchi, L., Pretti, C., Gabriel, B., Marques, P. A. A. P., Freitas, R., & Neto, V. (2018). An overview of graphene materials: Properties, applications and toxicity on aquatic environments. *Science of the Total Environment*, *631–632*, 1440–

1456. https://doi.org/10.1016/j.scitotenv.2018.03.132

Demiral, H., Demiral, İ., Karabacakoğlu, B., & Tümsek, F. (2010). Production of activated carbon from olive bagasse by physical activation. *Chemical Engineering Research and Design*, *89*, 206–213. https://doi.org/10.1016/j.cherd.2010.05.005

Douglas, L., Mackinnon, G., Cook, G., Duncan, H., Briddon, A., & Seamark, S. (2018). Determination of chlorpropham (CIPC) residues, in the concrete flooring of potato stores, using quantitative (HPLC UV/VIS) and qualitative (GCMS) methods. https://doi.org/10.1016/j.chemosphere.2017.12.010

El-Hendawy, A. N. A. (2009). The role of surface chemistry and solution pH on the removal of Pb^{2+} and Cd^{2+} ions via effective adsorbents from low-cost biomass. *Journal of Hazardous Materials*, *167*(1–3), 260–267. https://doi.org/10.1016/j.jhazmat.2008.12.118

El-Kady, A. A., Abdel Ghafar, H. H., Ibrahim, M. B. M., & Abdel-Wahhab, M. A. (2013). Utilization of activated carbon prepared from agricultural waste for the removal of organophosphorous pesticide from aqueous media. *Desalination and Water Treatment*, *51*(37–39), 7276–7285. https://doi.org/10.1080/19443994.2013.792137

El Atrache, L. L., Sghaier, R. Ben, Kefi, B. B., Haldys, V., & Mohamed Dachraoui, J. T. (2013). Factorial design optimization of experimental variables in preconcentration of carbamates pesticides in water samples using solid phase extraction and liquid chromatography–electrospray-mass spectrometry determination. *Talanta*, *117*(2013), 392–398. https://doi.org/10.1016/j.talanta.2013.09.032

Fan, M., Dai, D., & Huang, B. (2012). Fourier Transform Infrared Spectroscopy for

Natural Fibres. Intech. Retrieved from www.intechopen.com

Fatiha Mahammedi, B. B. (2016). Adsorption of Methylene Blue from Aqueous Solutions using Fe $_3$ O $_4$. *Open Access Scientific Reports.* https://doi.org/10.4172/2157-7587.1000143

Fishel, F. M. (2014). Pesticide Toxicity Profile: Organophosphate Pesticides. Retrieved from https://edis.ifas.ufl.edu/

Fonseca-Correa, R. A., Murillo-Acevedo, Y. S., Giraldo-Gutiérrez, L., & Moreno-Piraján, J. C. (2016). Microporous and Mesoporous Materials in Decontamination of Water Process. *Journal of Microporous and Mesoporous Materials*. InTech. https://doi.org/10.5772/64393

Foo, K. Y., & Hameed, B. H. (2011). Preparation of activated carbon from date stones by microwave induced chemical activation: Application for methylene blue adsorption. *Chemical Engineering Journal*, *170*, 338–341. https://doi.org/10.1016/j.cej.2011.02.068

Gangu, K. K., Maddila, S., & Jonnalagadda, S. B. (2019). A review on novel composites of MWCNTs mediated semiconducting materials as photocatalysts in water treatment. *Science of the Total Environment*, *646*, 1398–1412. https://doi.org/10.1016/j.scitotenv.2018.07.375

Gao, Y., Li, J., Xu, J., Lu, L., Zhang, X., Liu, M., … Chen, Y. (2018). Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. *Chemosphere*, *211*, 235–253. https://doi.org/10.1016/j.chemosphere.2018.06.179

Girgis, B. S., & El-Hendawy, A.-N. A. (2002). Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid. *Journal of Microporous and Mesoporous Materials*.Retrieved from www.elsevier.com/locate/micromeso

Goodarzi, M., dos Santos Coelho, L., Honarparvar, B., Ortiz, E. V., & Duchowicz, P. R. (2016). Application of quantitative structure-property relationship analysis to estimate the vapor pressure of pesticides. *Ecotoxicology and Environmental Safety*, *128*, 52–60. https://doi.org/10.1016/j.ecoenv.2016.01.020

Greish, S., Ismail, S. M., Mosleh, Y., Loutfy, N., Dessouki, A. A., & Ahmed, M. T. (2011). Human risk assessment of profenofos: A case study in Ismailia, Egypt. *Polycyclic Aromatic Compounds*, *31*(1), 28–47. https://doi.org/10.1080/10406638.2011.545727

Guilherme Schwanz, T., Carpilovsky, C. K., Castagna, G., Weis, C., & Hilda Costabeber, I. (2018). Article in press Model Validation of a multi-residue method and estimation of measurement uncertainty of pesticides in drinking water using gas chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*. https://doi.org/10.1016/j.chroma.2018.11.058

Gupta, S. Sen, & Pradeep, T. (2013). Affordable and Clean Drinking Water Using Nanomaterials, 87–95. Retrieved from http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.731.4371&rep=rep1&type=pdf

Hameed, B. H., Salman, J. M., & Ahmad, A. L. (2009). Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones. *Journal of Hazardous Materials*, *163*, 121–126. https://doi.org/10.1016/j.jhazmat.2008.06.069

Hegazi, H. A. (2013). Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*, *9*(3), 276–282. https://doi.org/10.1016/j.hbrcj.2013.08.004

Hildmann, F., Gottert, C., Frenzel, T., Kempe, G., & Speer, K. (2015). Pesticide residues in chicken eggs – A sample preparation methodology for analysis by gas and liquid chromatography/tandem mass spectrometry. *Journal of Chromatography A*, *1403*, 1–20. https://doi.org/10.1016/j.chroma.2015.05.024

Ilomuanya, M. O., Nashiru, B., Ifudu, N. D., & Igwilo, C. I. (2017). Effect of pore size and morphology of activated charcoal prepared from midribs of Elaeis guineensis on adsorption of poisons using metronidazole and Escherichia coli O157:H7 as a case study. *Journal of Microscopy and Ultrastructure*, *5*, 32–38. https://doi.org/10.1016/j.jmau.2016.05.001

Ioannidou, O. A., Zabaniotou, A. A., Stavropoulos, G. G., Islam, M. A., & Albanis, T. A. (2010). Preparation of activated carbons from agricultural residues for pesticide adsorption. *Chemosphere*, *80*(11), 1328–1336. https://doi.org/10.1016/j.chemosphere.2010.06.044

Islam, M. A., Tan, I. A. W., Benhouria, A., Asif, M., & Hameed, B. H. (2015). Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. https://doi.org/10.1016/j.cej.2015.01.058

Jasim, S. Y., Saththasivam, J., Loganathan, K., Ogunbiyi, O. O., & Sarp, S. (2016). Reuse of Treated Sewage Effluent (TSE) in Qatar. *Journal of Water Process Engineering*, *11*, 174–182. https://doi.org/10.1016/j.jwpe.2016.05.003

Jayaraj, R., Megha, P., & Sreedev, P. (2016). Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, *9*(3–4), 90–100. https://doi.org/10.1515/intox-2016-0012

Kaur, H., & Garg, H. (2014). Pesticides: Environmental Impacts and Management

Strategies. *Pesticides - Toxic Aspects*. https://doi.org/10.5772/57399

Kaushal Ramni, Kaur Navneet, Upadhyay Ashutosh, Suri O. P, T. A. (2011). High performance liquid chromatography detectors – a review. *International research journal of pharmacy. ISSN 2230 – 8407*

Kerle, E. A., Jenkins, J. J., & Vogue, P. A. (2007). Understanding pesticide persistence and mobility for groundwater and surface water protection. Em8561-E (Pesticide Persistence).

Kiso, Y., Li, H., Shigetoh, K., Kitao, T., & Jinno, K. (1996). Pesticide analysis by high-performance liquid chromatography using the direct injection method. *Journal of Chromatography A*, *733*(1–2), 259–265. https://doi.org/10.1016/0021-9673(95)01058-0

Krishnamoorthy, R., Govindan, B., Banat, F., Sagadevan, V., Purushothaman, M., & Show, P. L. (2018). Date pits activated carbon for divalent lead ions removal. *Journal of Bioscience and Bioengineering*. https://doi.org/10.1016/j.jbiosc.2018.12.011

Kulshreshtha, A., & Shinde, C. P. (2012). A Review: General Base Catalysis Hydrolysis of Organophosphorus Insectisides by Different Amines. *International Journal of Science and Research (IJSR) ISSN (Online Impact Factor, 3*(10), 2319–7064. Retrieved from https://pdfs.semanticscholar.org/212c/0cc7ddaf0cf9d15c772fed2ed31423167917.pdf

Kumar, A., & Mohan Jena, H. (2016). Removal of methylene blue and phenol onto prepared activated carbon from Fox nutshell by chemical activation in batch and fixed-bed column. https://doi.org/10.1016/j.jclepro.2016.07.177

Kumar, A., & Mohan Jena, H. (2017). Adsorption of Cr(VI) from aqueous solution by prepared high surface area activated carbon from Fox nutshell by chemical activation with H 3 PO 4. *Biochemical Pharmacology*, *5*, 2032–2041. https://doi.org/10.1016/j.jece.2017.03.035

Lambert, L. A., & Lee, J. (2018). Nudging greywater acceptability in a Muslim

country: Comparisons of different greywater reuse framings in Qatar. *Journal of Environmental Science and Policy*. https://doi.org/10.1016/j.envsci.2018.07.015

Lambropoulou, D. A., & Albanis, T. A. (2007). Liquid-phase micro-extraction techniques in pesticide residue analysis. *Journal of Biochemical and Biophysical Methods*, *70*(2), 195–228. https://doi.org/10.1016/j.jbbm.2006.10.004

Dan-Wei Zhang and Zhan-Ting Li (2011). Intramolecular N−H···X (X = F, Cl, Br, I, and S) Hydrogen Bonding in Aromatic Amide Derivatives - The X-Ray Crystallographic Investigation. *Intech.* Retrieved from www.springer.com/series/8431

Li, X., Yang, T., Song, Y., Zhu, J., Wang, D., & Li, W. (2019). Surface-enhanced Raman spectroscopy (SERS)-based immunochromatographic assay (ICA) for the simultaneous detection of two pyrethroid pesticides. *Journal of Sensors and Actuators, B: Chemical*, *283* 230–238. https://doi.org/10.1016/j.snb.2018.11.112

Loughlin, T. M. Mac, Peluso, M. L., Etchegoyen, M. A., Alonso, L. L., Cecilia De Castro, M., Percudani, M. C., & Marino, D. J. G. (2018). Pesticide residues in fruits and vegetables of the argentine domestic market: Occurrence and quality. *Journal of Food Control*. https://doi.org/10.1016/j.foodcont.2018.05.041

Luo, D., & Zhang, X. (2018). The effect of oxygen–containing functional groups on the H2 adsorption of graphene–based nanomaterials: experiment and theory. *International Journal of Hydrogen Energy*, *43*(11), 5668–5679. https://doi.org/10.1016/j.ijhydene.2018.01.164

Ma, J., Yao, Z., Hou, L., Lu, W., Yang, Q., Li, J., & Chen, L. (2016). Metal organic frameworks (MOFs) for magnetic solid-phase extraction of pyrazole/pyrrole pesticides in environmental water samples followed by HPLC-DAD determination. *Jounral of Talanta*. https://doi.org/10.1016/j.talanta.2016.09.035

MacLachlan, D. J., & Hamilton, D. (2010). Estimation methods for Maximum Residue Limits for pesticides. *Journal of Regulatory Toxicology and Pharmacology*, *58*(2), 208–218. https://doi.org/10.1016/j.yrtph.2010.05.012

Mahdi, Z., Jimmy Yu, Q., & El Hanandeh, A. (2018). Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar. *Journal of Environmental Chemical Engineering.* https://doi.org/10.1016/j.jece.2018.01.021

Mahmood, I., Imadi, S. R., Shazadi, K., & Gul, A. (2016). Plant, Soil and Microbes. *Journal of Implications in Crop Science, Volume 1.* https://doi.org/10.1007/978-3-319-27455-3

Maliva, R. G., & Missimer, T. M. (2010). Reverse Osmosis Desalination Facilities. *Veolia Water Technologies*

Manav, Ö. G., Dinç-Zor, Ş., & Alpdoğan, G. (2018). Optimization of a modified QuEChERS method by means of experimental design for multiresidue determination of pesticides in milk and dairy products by GC-MS. *Microchemical Journal.* https://doi.org/10.1016/j.microc.2018.08.056

Mannan, M., Alhaj, M., Mabrouk, A. N., & Al-Ghamdi, S. G. (2018). Examining the life-cycle environmental impacts of desalination: A case study in the State of Qatar. Journal of Desalination https://doi.org/10.1016/j.desal.2018.11.017

Mansouriieh, N., Sohrabi, M. R., & Khosravi, M. (2016). Adsorption kinetics and thermodynamics of organophosphorus profenofos pesticide onto Fe/Ni bimetallic nanoparticles. *International Journal of Environmental Science and Technology*, *13*(5), 1393–1404. https://doi.org/10.1007/s13762-016-0960-0

Mariana Furio Franco Bernardes, M. P., & Lilian Cristina Pereira and Daniel Junqueira Dorta. (2015). IntechOpen. https://doi.org/10.5772/32009

McDaniel, K. L., & Moser, V. C. (2004). Differential profiles of cholinesterase inhibition and neurobehavioral effects in rats exposed to fenamiphos or profenofos. *Neurotoxicology and Teratology*, *26*(3), 407–415. https://doi.org/10.1016/j.ntt.2004.01.001

Memon, G. Z., Bhanger, M. I., Akhtar, M., Talpur, F. N., & Memon, J. R. (2008). Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent. *Chemical Engineering Journal*, *138*(1–3), 616–621. https://doi.org/10.1016/j.cej.2007.09.027

Mohammad, S. G. (2013). Biosorption of Pesticide onto a low cost carbon produced from Apricot Stone (Prunus armeniaca): Equilibrium, Kinetic and Thermodynamic Studies. *Journal of Applied Sciences Research* Retrieved from http://www.aensiweb.com/jasr.html.

Mohd Din, A. T., Hameed, B. H., & Ahmad, A. L. (2009). Batch adsorption of phenol onto physiochemical-activated coconut shell. *Journal of Hazardous Materials*, *161*(2–3), 1522–1529. https://doi.org/10.1016/j.jhazmat.2008.05.009

Morillo, E., & Villaverde, J. (2017). Advanced technologies for the remediation of pesticide-contaminated soils. *Science of the Total Environment*, *586*, 576–597. https://doi.org/10.1016/j.scitotenv.2017.02.020

Nasir, S., Hussein, M. Z., Zainal, Z., & Yusof, N. A. (2018). Carbon-based nanomaterials/allotropes: A glimpse of their synthesis, properties and some applications. *Materials*, *11*(2), 1–24. https://doi.org/10.3390/ma11020295

Navarro, T. (2018). Uncorrected Proof Uncorrected Proof, 1–16. https://doi.org/10.2166/wrd.2018.043

Njoku, V. O., & Hameed, B. H. (2011). Preparation and characterization of activated carbon from corncob by chemical activation with H_3PO_4 for 2,4-dichlorophenoxyacetic acid adsorption. *Chemical Engineering Journal*, *173*, 391–399. https://doi.org/10.1016/j.cej.2011.07.075

Njoku, V. O., Islam, M. A., Asif, M., & Hameed, B. H. (2014). Utilization of sky fruit husk agricultural waste to produce high quality activated carbon for the herbicide bentazon adsorption. *Chemical Engineering Journal*, *251*, 183–191. https://doi.org/10.1016/j.cej.2014.04.015

Nupearachchi, C. N., Mahatantila, K., & Vithanage, M. (2017). Application of graphene for decontamination of water; Implications for sorptive removal. *Journal Groundwater for Sustainable Development.* 206–215. https://doi.org/10.1016/j.gsd.2017.06.006

Nyangaresi, P. O., Qin, Y., Chen, G., Zhang, B., Lu, Y., & Shen, L. (2018). Effects of single and combined UV-LEDs on inactivation and subsequent reactivation of E. coli in water disinfection. *Water Research*, *147*, 331–341. https://doi.org/10.1016/j.watres.2018.10.014

Ogungbenro, A. E., Quang, D. V, Al-ali, K. A., & Vega, L. F. (2018). Physical synthesis and characterization of activated carbon from date seeds for CO 2 capture. *Journal of Environmental Chemical Engineering*, *6*(4), 4245–4252. https://doi.org/10.1016/j.jece.2018.06.030

Omo-Okoro, P. N., Daso, A. P., & Okonkwo, J. O. (2018). A review of the application of agricultural wastes as precursor materials for the adsorption of per- and polyfluoroalkyl substances: A focus on current approaches and methodologies. *Environmental Technology and Innovation*, *9*, 100–114. https://doi.org/10.1016/j.eti.2017.11.005

Pallarés, J., González-Cencerrado, A., & Arauzo, I. (2018). Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam. *Journal of Biomass and Bioenergy.* https://doi.org/10.1016/j.biombioe.2018.04.015

Patel, J. (2016). Ion exchange resins. Journal of *Metal Finishing*, *97*(12), 69–70. https://doi.org/10.1016/S0026-0576(00)81191-5

Phondani, P. C., Bhatt, A., Elsarrag, E., Alhorr, Y. M., & El-Keblawy, A. (2016). Criteria and indicator approach of global sustainability assessment system for sustainable landscaping using native plants in Qatar. *Ecological Indicators*, *69*, 381–389. https://doi.org/10.1016/j.ecolind.2016.05.003

Poole, C. F., & Lenca, N. (2017). Reversed-phase liquid chromatography. *Journal of Liquid Chromatography (second edition).* https://doi.org/10.1016/B978-0-12-805393-5.00004-X

Popp, J., Peto, K., & Nagy, J. (2013). Pesticide productivity and food security. A review. *Agronomy for Sustainable Development*, *33*(1), 243–255. https://doi.org/10.1007/s13593-012-0105-x

Pradhan, S., Al-Ghamdi, S. G., & Mackey, H. R. (2018). Greywater recycling in buildings using living walls and green roofs: A review of the applicability and challenges. *Journal of Science of total environment* https://doi.org/10.1016/j.scitotenv.2018.10.226

Pradnya p. kanekar, Bharati J. Bhadbhade, Neelima M. Deshpande, S. S. S. (2004). Biodegradation of organophosphosphorous pesticide.

Prequalification document for consultant professional services for Integrated Industrial Wastewater Treatment .(2014) Retrieved from http://www.ashghal.gov.qa/en/Tenders/Lists/PrequalificationLibrary/CONSULT

Radwan, A. M. Y., Magram, S. F., & Ahmed, Z. (2018). Adsorption of Acenaphthene Using Date Seed Activated Carbon. *Journal of Environmental Science and Technology*, *11*(1), 10–15. https://doi.org/10.3923/jest.2018.10.15

Rajput, S., Kumari, A., Arora, S., & Kaur, R. (2018). Multi-residue pesticides analysis in water samples using reverse phase high performance liquid chromatography (RP-HPLC). *Journal of Method X*. https://doi.org/10.1016/j.mex.2018.07.005

Rashed, M. N. (2018). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. *Intech Open*. https://doi.org/10.5772/32009

Rawtani, D., Khatri, N., Tyagi, S., & Pandey, G. (2018). Nanotechnology-based recent approaches for sensing and remediation of pesticides. *Journal of Environmental Management, 206,* 749–762. https://doi.org/10.1016/j.jenvman.2017.11.037

Roeraade, J. (2002). Sample introduction in capillary gas chromatography, Vol. 1. *TrAC Trends in Analytical Chemistry*, *5*(6), https://doi.org/10.1016/0165-9936(86)87014-5

Rojas, R., Vanderlinden, E., Morillo, J., Usero, J., & El Bakouri, H. (2014). Characterization of sorption processes for the development of low-cost pesticide decontamination techniques. *Science of the Total Environment*, *488–489*(1), 124–135. https://doi.org/10.1016/j.scitotenv.2014.04.079

Sadegh, H., Ali, G. A. M., & Gupta, V. K. (2017). The role of nanomaterials as effective adsorbents and their applications in wastewater treatment, 1–14. https://doi.org/10.1007/s40097-017-0219-4

Salem, N. ' M., Ahmad, R., & Estaitieh, H. (2009). Organochlorine pesticide residues in dairy products in Jordan. *Journal of Chemosphere, 77,* 673–678. https://doi.org/10.1016/j.chemosphere.2009.07.045

Salman, J. M., & Abid, F. M. (2013). Preparation of mesoporous activated carbon from palm-date pits: Optimization study on removal of bentazon, carbofuran, and 2,4-D using response surface methodology. *Water Science and Technology*, *68*(7), 1503–1511. https://doi.org/10.2166/wst.2013.370

Salman, J. M., Njoku, V. O., & Hameed, B. H. (2011a). Bentazon and carbofuran adsorption onto date seed activated carbon: Kinetics and equilibrium. *Chemical Engineering Journal*, *173*, 361–368. https://doi.org/10.1016/j.cej.2011.07.066

Salman, J. M., Njoku, V. O., & Hameed, B. H. (2011b). Bentazon and carbofuran adsorption onto date seed activated carbon: Kinetics and equilibrium. *Chemical Engineering Journal*, *173*, 361–368. https://doi.org/10.1016/j.cej.2011.07.066

Samanta, H. ., Das, R., & Bhattachajee, C. (2016). Influence of Nanoparticles for Wastewater Treatment- A Short Review. *Austin Chem Eng*, *3*(3), 1–6.

Sekirifa, M. L., Hadj-Mahammed, M., Pallier, S., Baameur, L., Richard, D., & Al-Dujaili, A. H. (2013). Preparation and characterization of an activated carbon from a date stones variety by physical activation with carbon dioxide. *Journal of Analytical and Applied Pyrolysis*, *99*, 155–160. https://doi.org/10.1016/j.jaap.2012.10.007

Seyedzadeh, A., Mwafy, A., Ahmed, W. K., Pandurangan, K., & Hilal-Alnaqbi, A. (2017). Activating Carbon Fibers and Date Pits for Use in Liver Toxin Adsorption. In *Poisoning - From Specific Toxic Agents to Novel Rapid and Simplified Techniques for Analysis*. InTech. https://doi.org/10.5772/intechopen.71891

Shomar, B., Al-Saad, K., & Nriagu, J. (2014). Mishandling and exposure of farm workers in Qatar to organophosphate pesticides. *Environmental Research*, *133*, 312–320. https://doi.org/10.1016/j.envres.2014.06.010

Shuttle, F. (2006). *Hand book for the operation of Water Treatment Works.The water Reseaech Commission,The water Institure of south Africa.*

Singh, N. B., Nagpal, G., Agrawal, S., & Rachna. (2018). Water purification by using Adsorbents: A Review. *Environmental Technology and Innovation*. https://doi.org/10.1016/j.eti.2018.05.006

Singh, S., & Tandon, P. (2014). Catalysis: A brief review on Nano-Catalyst. *Journal of Energy and Chemical Engineering(JECE)*, *2*(November), 106–115.

Singh, Z. (2017). Toxic Effects of Organochlorine Pesticides: A Review. *American Journal of BioScience*, *4*(3), 11. https://doi.org/10.11648/j.ajbio.s.2016040301.13

Sirry, S. M., Aldakhil, F., Alharbi, O. M. L., & Ali, I. (2018). Chemically treated date stones for uranium (VI) uptake and extraction in aqueous solutions. *Journal of Molecular Liquids*, *273*, 192–202. https://doi.org/10.1016/j.molliq.2018.10.018

Sodipo OA, A. J. (2014). Determination of Organochlorine, Organophosphorus and Pyrethroid Pesticide Residues in Water and Sediment Samples by High Performance Liquid Chromatography (HPLC) with UV/visible Detector. *Journal of Analytical & Bioanalytical Techniques*, *5*(6). https://doi.org/10.1021/cm00040a025

Songa, E. A., & Okonkwo, J. O. (2016). Recent approaches to improving selectivity and sensitivity of enzyme-based biosensors for organophosphorus pesticides: A review. *Talanta*, *155*, 289–304. https://doi.org/10.1016/j.talanta.2016.04.046

Srivastava, P., Singh, A., & Pandey, A. K. (2016). Pesticides toxicity in fishes: Biochemical, physiological and genotoxic aspects. *Biochemical and Cellular*

Archives, *16*(2), 199–218.

Struger, J., Grabuski, J., Cagampan, S., Sverko, E., & Marvin, C. (2016). Occurrence and Distribution of Carbamate Pesticides and Metalaxyl in Southern Ontario Surface Waters 2007-2010. *Bulletin of Environmental Contamination and Toxicology*, *96*(4), 423–431. https://doi.org/10.1007/s00128-015-1719-x

Suo, F., Liu, X., Li, C., Yuan, M., Zhang, B., Wang, J., … Ji, M. (2018). Mesoporous activated carbon from starch for superior rapid pesticides removal. https://doi.org/10.1016/j.ijbiomac.2018.10.132

Suresh, K., Reddy, K., Al Shoaibi, A., & Srinivasakannan, C. (2012). A comparison of microstructure and adsorption charac-teristics of activated carbons by CO 2 and H 3 PO 4 activation from date palm pits. *New Carbon Materials*, *27*, 344–351. https://doi.org/10.1016/S1872-5805(12)60020-1

Tan, I. A. W., Ahmad, A. L., & Hameed, B. H. (2008). Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials*, *154*, 337–346. https://doi.org/10.1016/j.jhazmat.2007.10.031

Tang, W., Wang, D., Wang, J., Wu, Z., Li, L., Huang, M., … Yan, D. (2018). Pyrethroid pesticide residues in the global environment: An overview. *Chemosphere*, *191*(308), 990–1007. https://doi.org/10.1016/j.chemosphere.2017.10.115

Tano, Z. J. (2011). Identity , Physical and Chemical Properties of Pesticides, Pesticides in the Modern World - Trends in Pesticides Analysis, *1873*, 1–18. Retrieved from http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides- analysis/identity-physical-and-chemical-properties-of-pesticides%0AInTech

Tao, S., Liu, W. X., Li, X. Q., Zhou, D. X., Li, X., Yang, Y. F., … Coveney, R. M. (n.d.). Organochlorine pesticide residuals in chickens and eggs at a poultry farm in Beijing, China. *Environmental Pollution*, *157*, 497–502. https://doi.org/10.1016/j.envpol.2008.09.005

Tiwari, D., & Sen, P. (2015). Application of Nanoparticles in Waste Water Treatment Application of Nanoparticles in Waste Water Treatment, (January 2008).

Tolerance, I. (2006). US Environmental Protection Agency Office of Pesticide Programs Reregistration Eligibility Decision for Profenofos, 1–121.

Trong Dieu Hien Lea, Scharmüllera, A., Kattwinkela, M., Kühnec, R., Gerrit Schüürmannc, D., & Schäfera, R. B. (2017). Contribution of waste water treatment plants to pesticide toxicity in agriculture catchments. *Ecotoxicology and Environmental Safety*, *145*(July), 135–141. https://doi.org/10.1016/j.ecoenv.2017.07.027

Wakkel, M., Khiari, B., & Zagrouba, F. (2019). Textile wastewater treatment by agro-industrial waste: Equilibrium modelling, thermodynamics and mass transfer mechanisms of cationic dyes adsorption onto low-cost lignocellulosic adsorbent. *Journal of the Taiwan Institute of Chemical Engineers*, (xxxx). https://doi.org/10.1016/j.jtice.2018.12.014

Wang, H., Qu, B., Liu, H., Ding, J., & Ren, N. (2017). Analysis of organochlorine pesticides in surface water of the Songhua River using magnetoliposomes as adsorbents coupled with GC-MS/ MS detection. https://doi.org/10.1016/j.scitotenv.2017.11.046

Wong, K. K., Lee, C. K., Low, K. S., & Haron, M. J. (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, *50*(1), 23–28. https://doi.org/10.1016/S0045-6535(02)00598-2

Wu, F.-C., Wu, P.-H., Tseng, R.-L., & Juang, R.-S. (2010). Preparation of activated carbons from unburnt coal in bottom ash with KOH activation for liquid-phase adsorption. https://doi.org/10.1016/j.jenvman.2009.12.011

Wu, Z., Li, Y., Meng, H., Yang, W., & Yang, B. (2018). On-line analysis on fast pyrolysis of lignocellulosic biomass: Thermal behavior and kinetic analysis of hemicellulose. *Energy Procedia*, *152*, 1290–1295. https://doi.org/10.1016/j.egypro.2018.09.184

Xie, G. X., Wei, Z., Lai, C., Liu, Z. F., Huang, C., Zhao, M. H., … Xu, P. (2012). Use of iron oxide nanomaterials in wastewater treatment: A review. *Science of The Total Environment*, *424*, 1–10. https://doi.org/10.1016/j.scitotenv.2012.02.023

Yadav, I., & Devi, N. (2017). Pesticides Classification and Its Impact on Human and Environment. *Environmental Science and Engineering*, *6*(February), 140–158.

Yadav, I. H., & Devi, N. L. (2017). Pesticides Classification and Its Impact on Human and Environment. *Environmental Science and Engineering*, *6*(February), 140–158.

Yakout, S. M., & Sharaf El-Deen, G. (2016). Characterization of activated carbon prepared by phosphoric acid activation of olive stones. https://doi.org/10.1016/j.arabjc.2011.12.002

Yalçın, N., & Sevinç, V. (2000). *Studies of the surface area and porosity of activated carbons prepared from rice husks*. *Carbon* (Vol. 38). Retrieved from https://ac.els-cdn.com/S0008622300000294/1-s2.0-S0008622300000294-main.pdf?_tid=ccabac5e-ef63-4f7b-8f51-a7f3b9dd793c&acdnat=1546457302_1816eb0ab3ae5a04a86535ab310d8929

Yallappa, S., Deepthi, D. R., Yashaswini, S., Hamsanandini, R., Chandraprasad, M., Kumar, S. A., & Hegde, G. (2017). Natural biowaste of Groundnut shell derived nano carbons: Synthesis, characterization and itsin vitro antibacterial activity. *Nano-Structures & Nano-Objects*, *12*, 84–90. https://doi.org/10.1016/j.nanoso.2017.09.009

Yan, X., Liu, G., Xu, J., & Wang, S. (2018). Plasmon heating of one-dimensional gold nanoparticle chains. *Solar Energy*, *173*(May), 665–674. https://doi.org/10.1016/j.solener.2018.08.003

Zaidon, S. Z., Ho, Y. Bin, Hamsan, H., Hashim, Z., Saari, N., & Mangala Praveena, S. (2018). Improved QuEChERS and solid phase extraction for multi-residue analysis of pesticides in paddy soil and water using ultra-high performance liquid chromatography tandem mass spectrometry. *Microchemical Journal*. https://doi.org/10.1016/j.microc.2018.11.025

Zenilda L. Cardeal, A. G. S. and L. C. A. A. (2012). Analytical Methods for Performing Pesticide Degradation Studies in Environmental Samples. *Pesticides* - Formulations, Effects, Fate. Intech. https://doi.org/10.5772/14148

Zhao, M., Zhou, W., Lu, M., Guo, Z., Li, C., & Wang, W. (2019). Novel AgCl nanotubes/BiOCl nanosheets composite with improved adsorption capacity and photocatalytic performance. *Journal of Alloys and Compounds*, *773*, 1146–1153. https://doi.org/10.1016/j.jallcom.2018.09.257

APPENDIX

appendix (A): Adsorbent Preparation

(a). Raw date pits collected and Roasted

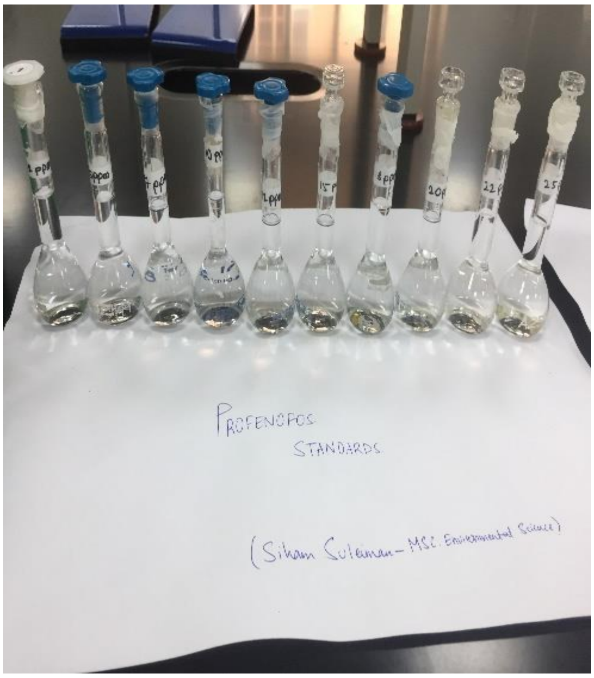
(b). Sieving RODP

(c). Physical Activation Preparation ACDP

(d). Physical nano-size Preparation

Figure A. 1 Adsorbent Preparation.

appendix (B): Preparation of Standards



(a). Standard Preparation

(b). Agilent 1260 infinity

(c). Agilent chemstation Libraries

Figure B. 1 Preparation of standards of profenofos, followed by calibration.

appendix (C): Calibration Curve

Table C. 1 Calibration Curve

Concentration	**Height**
2	6.18372
5	16.20795
7	23.05708
10	33.22946
12	39.35755
15	50.28919
18	58.96318
20	66.23273
22	73.0323
25	82.78023
28	92.03778

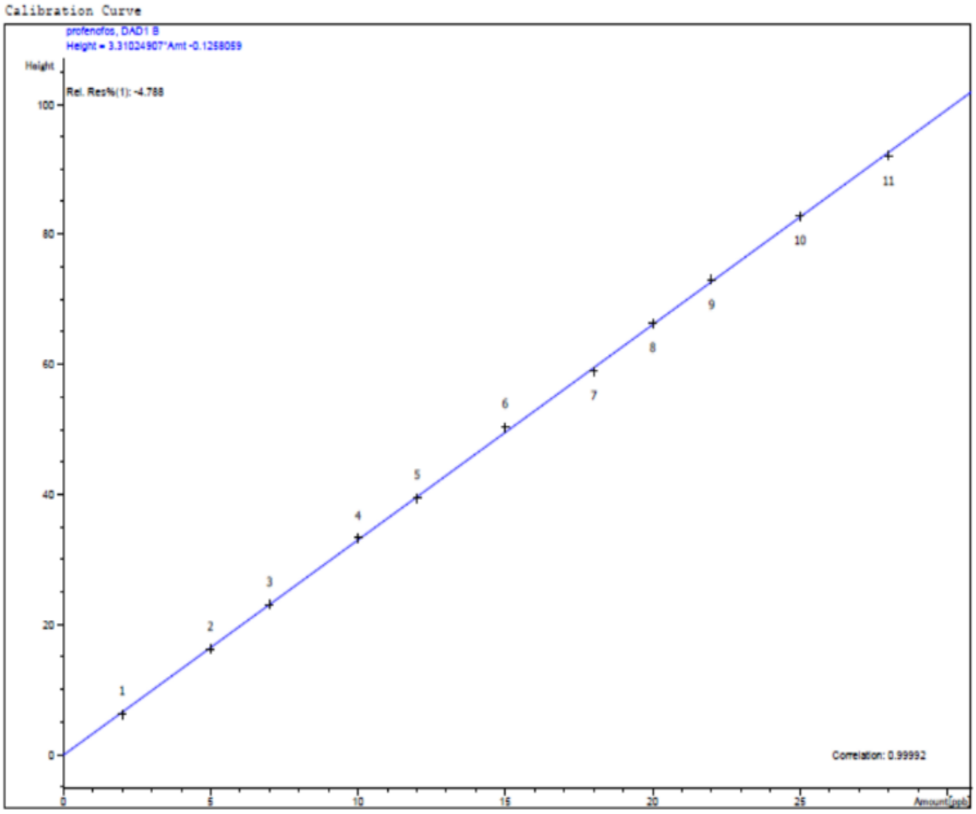
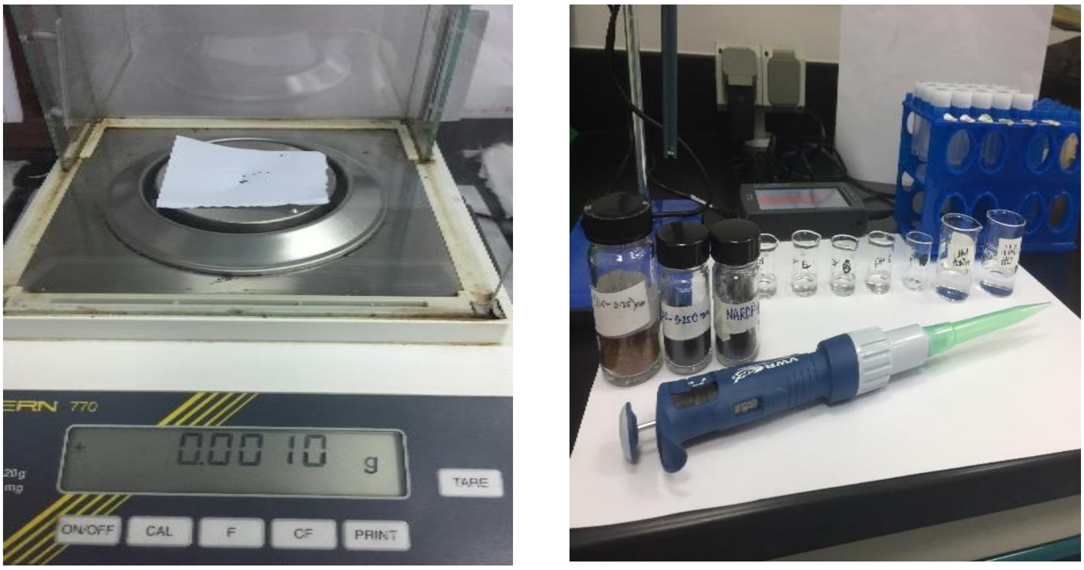


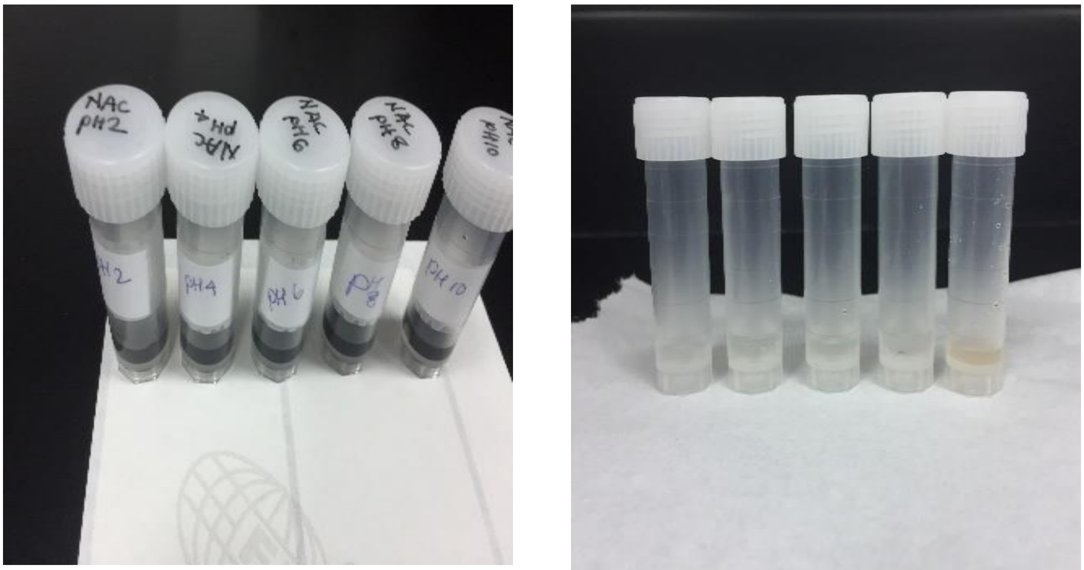
Figure C. 1 Calibration curve of Standard concentrations of profenofos

appendix (D): pH Optimization of Adsorbents RODP and NACDP



(a). Mass of adsorbent

(b). pH optimization

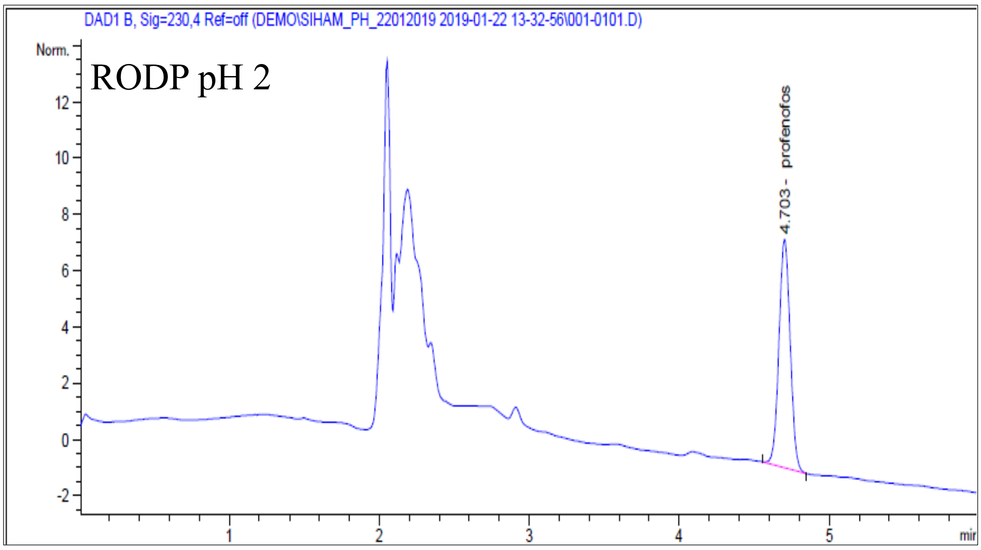


(c). Effect of pH studied for NACDP

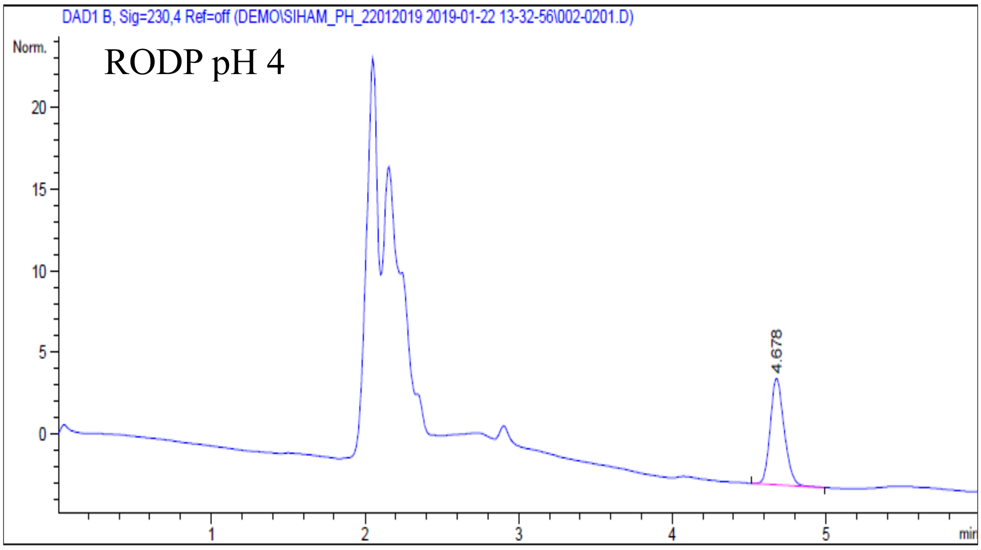
(d). Effect of pH studied for RODP

Figure D. 1 pH optimization for the three adsorbents RODP and NACDP.

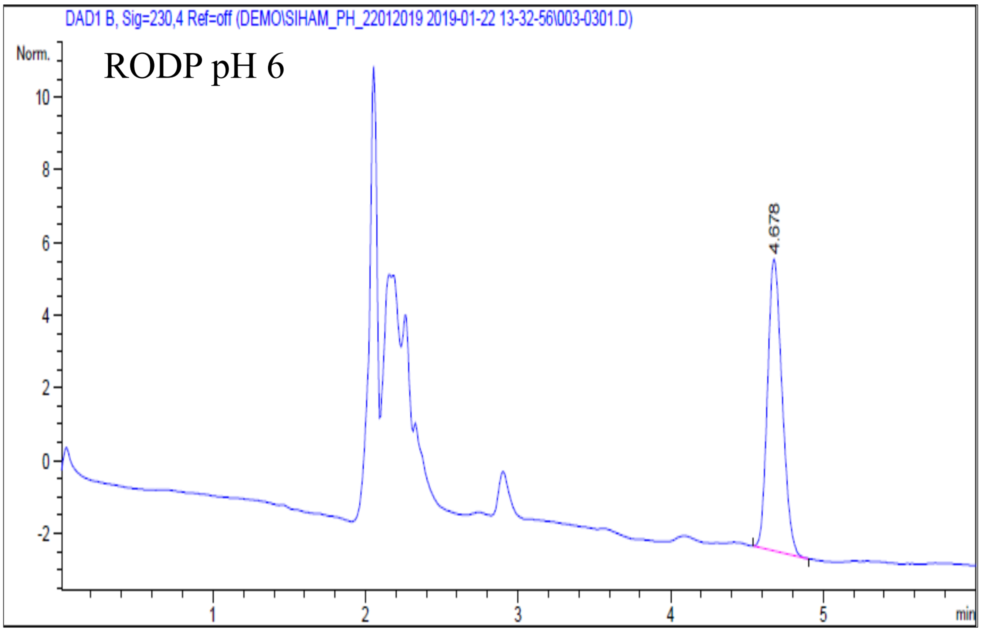
appendix (E): Effect of pH chromatogram of adsorbents RODP and ACDP



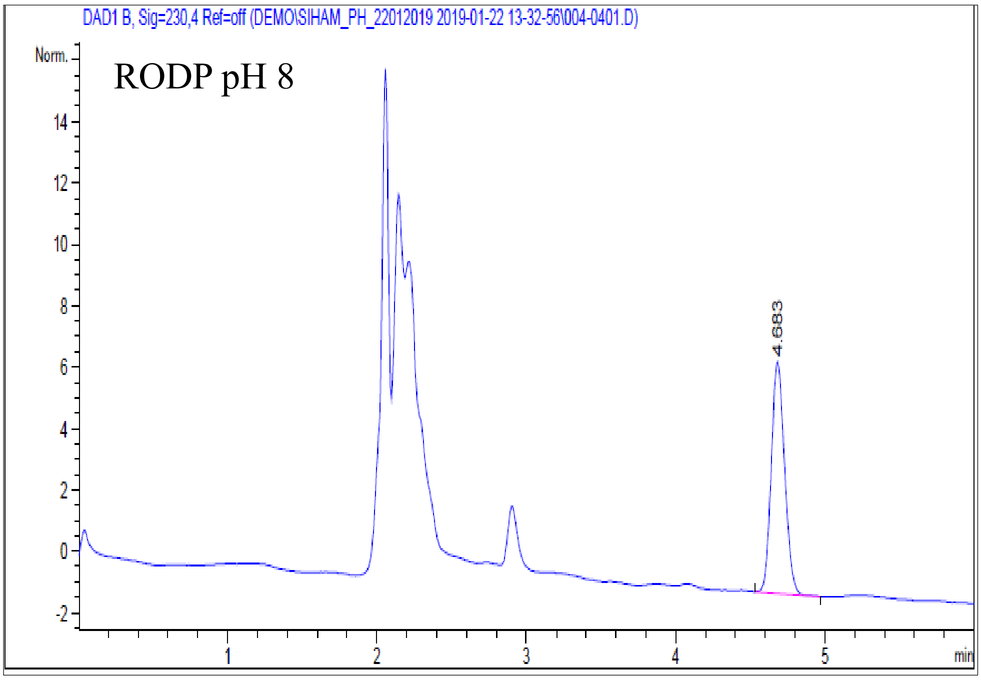
(a). RODP chromatogram at pH 2



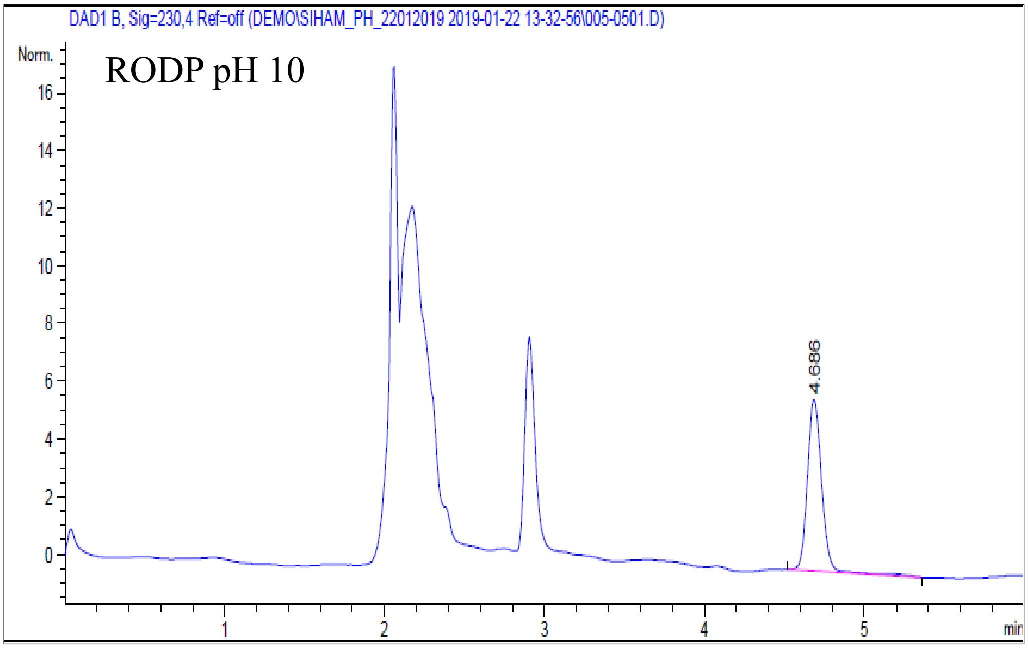
(b). RODP chromatogram at pH 4



(c). RODP chromatogram at pH 6

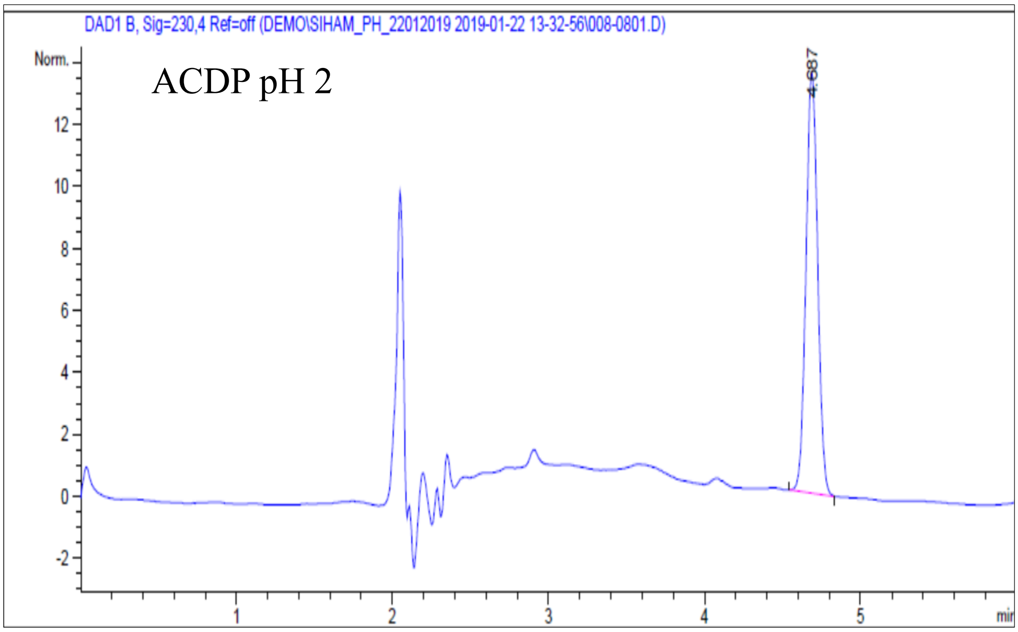


(d). RODP chromatogram at pH 8

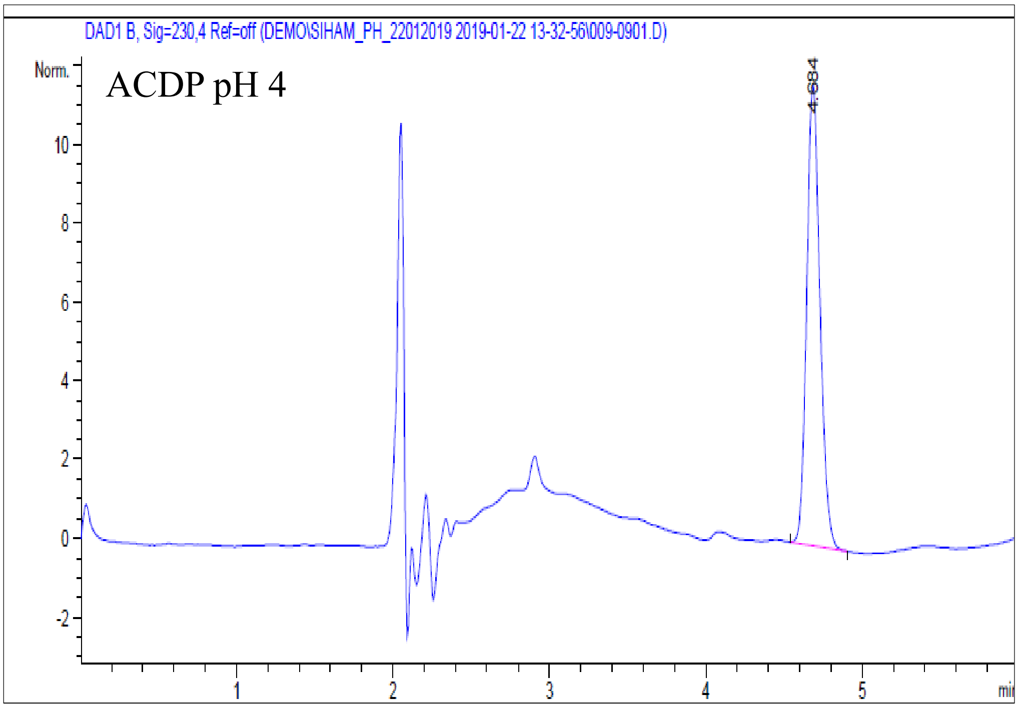


(e). RODP chromatogram at pH 10

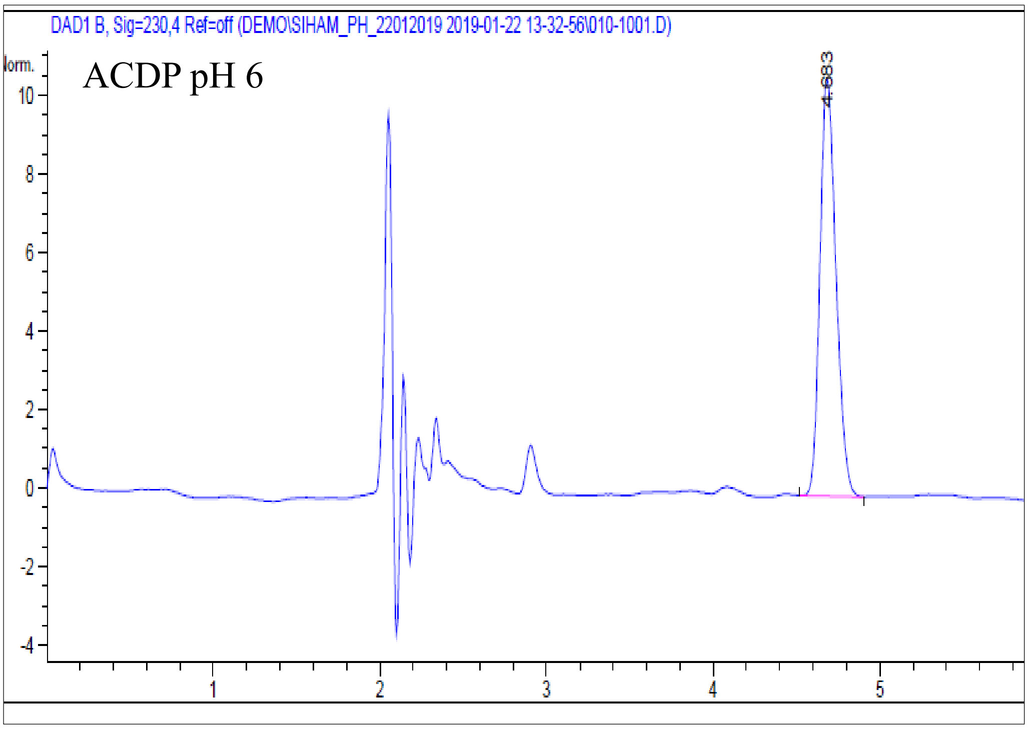
Figure E. 1 Effect of pH chromatogram of adsorbents RODP



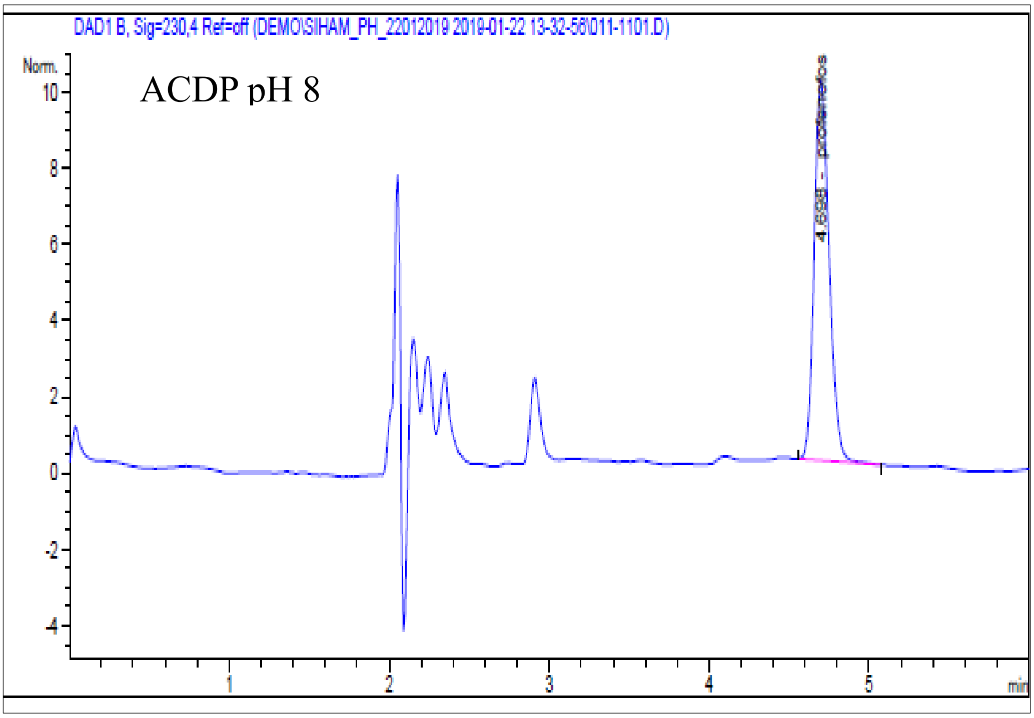
(a). ACDP chromatogram at pH 2



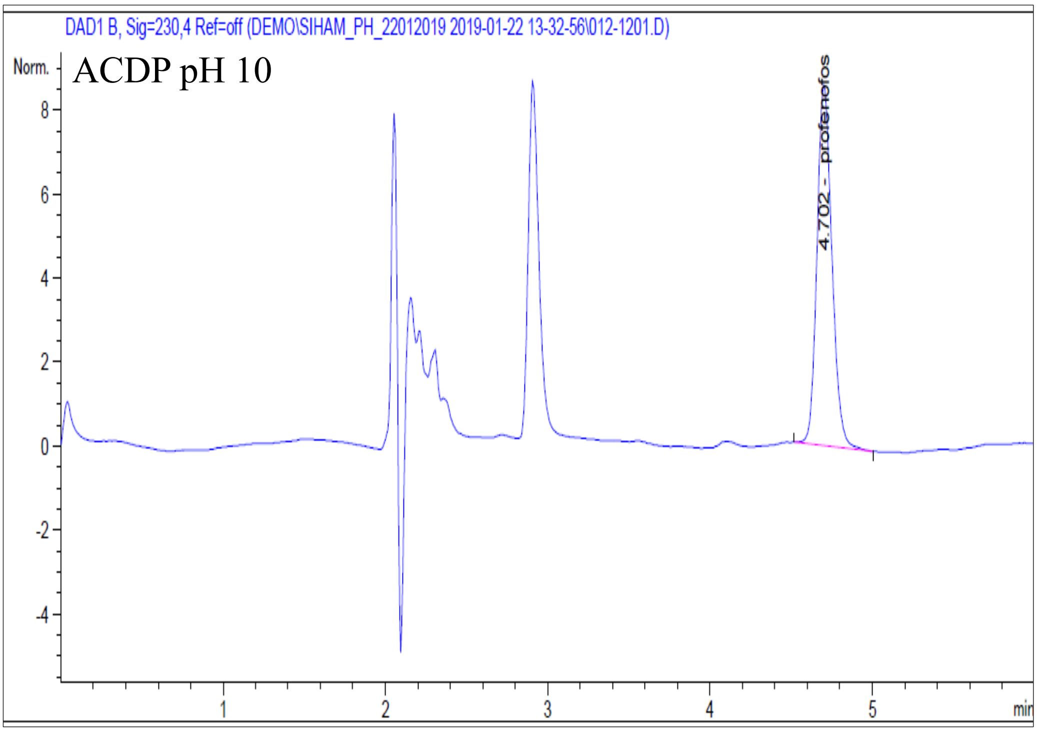
(b). ACDP chromatogram at pH 4



(c). ACDP chromatogram at pH 6



(d). ACDP chromatogram at pH 8



(e). ACDP chromatogram at pH 2

Figure E. 2: Effect of pH chromatogram of adsorbents ACDP

appendix (F): T-test Analysis Results

F-I: Effect of initial concentration

Table F. 1 Effect of initial concentration - RODP

Effect of initial concetration- RODP	
Before Treatment	After Treatment
2	0
5	0
7	0.839786
10	0
12	0.7209815
15	4.866165
18	8.33965
20	12.664395
22	15.04335
25	20.24074
28	25.099125

Table F. 2 t-test Effect of initial concentration – RODP

	Variable 1	*Variable 2*
Mean	14.90909091	7.983108409
Variance	71.89090909	81.97670716
Observations	11	11
Pearson Correlation	0.939765214	
Hypothesized Mean Difference	0	
df	10	
t Stat	7.421881132	
P(T<=t) one-tail	0.0000113	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	0.000023	
t Critical two-tail	2.228138852	

Table F. 3 Effect of initial concentration – ACDP

Effect of initial concetration- ACDP	
Before Treatment	After Treatment
2	0.000
5	0.000
7	1.195
10	0.000
12	0.758
15	7.087

18	10.630
20	14.162
22	15.560
25	20.401
28	25.069

Table F. 4 t-test Effect of initial concentration – ACDP

	Variable 1	*Variable 2*
Mean	14.90909091	8.623708545
Variance	71.89090909	83.44794464
Observations	11	11
Pearson Correlation	0.953225568	
Hypothesized Mean Difference	0	
df	10	
t Stat	7.524075881	
P(T<=t) one-tail	0.000010	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	**0.000020**	
t Critical two-tail	2.228138852	

Table F. 5 Effect of initial concentration – NACDP

Effect of initial concentration- NACDP	
Before Treatment	After Treatment
2	0.000
5	0.000
7	0.000
10	0.000
12	0.000
15	0.593
18	0.850
20	2.374
22	2.213
25	7.771
28	12.611

Table F. 6 t-test Effect of initial concentration – NACDP

	Variable 1	*Variable 2*
Mean	14.90909091	2.401176409
Variance	71.89090909	16.76254888
Observations	11	11
Pearson Correlation	0.7892291	

Hypothesized Mean Difference	0
df	10
t Stat	7.129301606
P(T<=t) one-tail	0.000016
t Critical one-tail	1.812461123
P(T<=t) two-tail	**0.000032**
t Critical two-tail	2.228138852

F-II: Effect of Temperature at 35 °C

Table F. 7 Effect of Temperature 35 °C- RODP

Before Treatment	After Treatment
2	0
5	0
7	0.724566
10	0
12	0.382742
15	4.47686
18	7.829925
20	7.79502
22	13.705335
25	18.071925
28	25.15482

Table F. 8 t-test Effect of Temperature 35 °C- RODP

	Variable 1	*Variable 2*
Mean	14.90909091	7.103744818
Variance	71.89090909	73.48843801
Observations	11	11
Pearson Correlation	0.916682274	
Hypothesized Mean Difference	0	
df	10	

t Stat	7.435740845
P(T<=t) one-tail	0.000011
t Critical one-tail	1.812461123
P(T<=t) two-tail	**0.000022**
t Critical two-tail	2.228138852

Table F. 9 Effect of Temperature 35 ^{o}C- ACDP

Before Treatment	After Treatment
2	0.000
5	0.000
7	0.925
10	0.000
12	0.372
15	4.946
18	8.708
20	10.103
22	13.322
25	18.030
28	25.048

Table F. 10 t-test Effect of Temperature 35 ^{o}C- ACDP

	Variable 1	*Variable 2*
Mean	14.90909091	7.4048985
Variance	71.89090909	73.01739289
Observations	11	11
Pearson Correlation	0.931253481	
Hypothesized Mean Difference	0	
df	10	
t Stat	7.883869931	
P(T<=t) one-tail	0.0000067	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	**0.000013**	
t Critical two-tail	2.228138852	

Table F. 11 Effect of initial Temperature 35 ^{o}C- NACDP

Before Treatment	After Treatment
2	0.000
5	0.000
7	0.000
10	0.000
12	0.000
15	0.483

18	0.636
20	2.258
22	2.114
25	7.708
28	13.560

Table F. 12 t-Test Effect of initial Temperature 35 ^{o}C- NACDP

	Variable 1	*Variable 2*
Mean	14.90909091	2.432572136
Variance	71.89090909	18.83892181
Observations	11	11
Pearson Correlation	0.77111294	
Hypothesized Mean Difference	0	
df	10	
t Stat	7.099348935	
P(T<=t) one-tail	0.000016	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	**0.000033**	
t Critical two-tail	2.228138852	

F-III Effect of Temperature at 45°C

Table F. 13 Effect of Temperature 45 ºC- RODP

Before Treatment	After Treatment
2	0
5	0
7	0.365467
10	0
12	0
15	2.08157
18	3.955495
20	6.10714
22	7.82863
25	12.502605
28	19.513275

Table F. 14 t-test Effect of Temperature 45 ºC- RODP

	Variable 1	*Variable 2*
Mean	14.90909091	4.759471091
Variance	71.89090909	40.66018644
Observations	11	11
Pearson Correlation	0.883623315	
Hypothesized Mean Difference	0	
df	10	

t Stat	8.163461385
P(T<=t) one-tail	0.0000049
t Critical one-tail	1.812461123
P(T<=t) two-tail	**0.0000099**
t Critical two-tail	2.228138852

Table F. 15 Effect of Temperature 45 ^{o}C- ACDP

Effect of Temperature 45 ^{o}C- ACDP	
Before Treatment	After Treatment
2	0.000
5	0.000
7	0.000
10	0.000
12	0.000
15	1.685
18	1.612
20	6.206
22	7.573
25	13.389
28	19.920

Table F. 16 t-test Effect of Temperature 45 ^{o}C- ACDP

	Variable 1	*Variable 2*
Mean	14.90909091	4.580375455
Variance	71.89090909	44.65764924
Observations	11	11
Pearson Correlation	0.858261021	
Hypothesized Mean Difference	0	
df	10	
t Stat	7.799968746	
P(T<=t) one-tail	0.0000073	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	**0.0000147**	
t Critical two-tail	2.228138852	

Table F. 17 Effect of initial Temperature 45 ^{o}C- NACDP

Before Treatment	After Treatment
2	0.000
5	0.000
7	0.000
10	0.000
12	0.000
15	0.000
18	0.506

20	1.108
22	2.075
25	5.065
28	9.422

Table F. 18 t-Test Effect of initial Temperature 45 ^{o}C- NACDP

t-Test: Paired Two Sample for Means		
	Variable 1	*Variable 2*
Mean	14.90909091	1.6523565
Variance	71.89090909	9.018590295
Observations	11	11
Pearson Correlation	0.771209724	
Hypothesized Mean Difference	0	
df	10	
t Stat	6.814009609	
P(T<=t) one-tail	0.000023	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	**0.000047**	
t Critical two-tail	2.228138852	