

An-Najah National University

Faculty of Graduate Studies

**Nitrate and Nitrite Ion Removal from Aqueous Solutions by
Activated Carbon Prepared from Olive Stones**

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the Degree of Master of Science in Chemistry, Faculty of Graduate
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Dedication

To everyone who cares about the environment and works to save it.....

To everyone who inspires me by his/her science.....

To my dear family.....

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الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان :

Nitrate and Nitrite Ion Removal from Aqueous Solutions by Activated Carbon Prepared from Olive Stones

أزالة أيونات النترات والنتريت من المحاليل المائية بوساطة الكربون المنشط المحضر
من نوى الزيتون

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Declaration

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

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Table of Contents

No.	Content	Page
	Dedication	iii
	Acknowledgments	iv
	Table of Contents	Vi
	List of Tables	ix
	List of Figures	X
	List of Abbreviation	xiii
	Abstract	xv
	Chapter One: Introduction	1
1.1	Overview	1
1.2	Nitrate and Nitrite in Drinking Water	1
1.2.1	Nitrate and Nitrite Sources and Chemistry	1
1.2.2	Nitrate and Nitrite Health and Environmental Concerns and Drinking Water Regulations	3
1.2.3	Nitrate and Nitrite Treatment Options	4
1.3	Adsorption	4
1.3.1	Adsorption Definition and Operation	4
1.3.2	Adsorption Features	5
1.3.3	Adsorbents Used to Remove Nitrate and Nitrite from Water	5
1.4	Activated Carbon (AC)	5
1.4.1	AC Properties	5
1.4.2	Historical Use of AC	6
1.4.3	AC Application	6
1.4.4	AC Efficiency	6
1.4.5	Precursors of AC	7
1.5	Olive Stones	8
1.5.1	Olive Stone Components	9
1.5.2	Advantages of Olive Stones as Precursor for AC	9
1.5.3	Olive Stone Uses	9
1.6	Carbon Activation	11
1.6.1	Physical Activation	11
1.6.2	Chemical Activation	12
1.6.2.1	Operation of Chemical Activation	12
1.6.2.2	Activating Agents	13
1.6.2.2.1	Phosphoric Acid (H ₃ PO ₄)	14
1.6.2.2.2	Zinc Chloride (ZnCl ₂)	14
1.7	What is New in this Work?	15

1.8	Objectives of This Work	15
1.8.1	Strategic Objectives	15
1.8.2	Technical Objectives	16
	Chapter Two: Experimental Work	17
2.1	Chemicals and Reagents	17
2.2	Preparation and Characterization of AC	17
2.2.1	Preparation of Olive Stones	17
2.2.2	Oil Recovery	18
2.3	Experimental Set-Up for Carbonization Experiment	19
2.4	Carbon Activation	19
2.4.1	Carbonization with no Chemical Activation	20
2.4.2	Chemical Activation	21
2.4.2.1	Carbon Activation by Phosphoric Acid	21
2.4.2.2	Carbon Activation by Zinc Chloride	21
2.4.2.3	Carbon Activation by Sodium Bicarbonate	23
2.5	Characterization of the Products	23
2.5.1	Surface Area Measurement	24
2.5.2	Scanning Electron Microscopy (SEM)	25
2.6	Adsorption Experiments	25
2.6.1	Nitrite Adsorption Experiments	26
2.6.1.1	Effect of Adsorbent Type	26
2.6.1.2	Effect of Adsorbent Dosage	27
2.6.1.3	Effect of Initial pH	27
2.6.1.4	Effect of Temperature	27
2.6.1.5	Effect of Particle Size	28
2.6.1.6	Effect of Contact Time (Kinetic Study)	28
2.6.1.7	Effect of NO_2^- Concentration	28
2.6.2	Nitrate Adsorption Experiments	30
2.6.2.1	Effect of Adsorbent Type	31
2.6.2.2	Effect of Initial pH	31
2.6.2.3	Effect of Temperature	31
2.6.2.4	Effect of Contact Time (Kinetic Study)	32
2.6.2.5	Effect of Nitrate Ion Concentration	32
2.7	Nitrate Desorption Experiments	32
2.8	Determination Methods of Nitrite and Nitrate Ion Concentration	33
2.8.1	Determination Method of Nitrite Ion Concentration	33
2.8.1.1	Nitrite Standard Solutions Preparation	34
2.8.1.2	Sample Preparation	34
2.8.2	Determination Method of Nitrate Ion Concentration	34

2.8.2.1	Nitrate Standard solutions preparation	35
2.8.2.2	Sample Preparation	35
	Chapter Three: Results and Discussion	36
3.1	Carbon Characterization	36
3.1.1	SEM Analysis of the AC	36
3.1.2	Surface Area	38
3.2	Nitrite and Nitrate Determination Methods	39
3.2.1	Nitrite Determination by Differential Pulse Polarography	39
3.2.2	Nitrate determination by UV-VIS Spectrometry	39
3.3	Nitrite and Nitrate Adsorption Experiments	41
3.3.1	Nitrite Adsorption Experiments	41
3.3.1.1	Effect of Adsorbent Type	41
3.3.1.2	Effect of Adsorbent Dosage	42
3.3.1.3	Effect of pH	43
3.3.1.4	Effect of Temperature on Adsorption	44
3.3.1.5	Effect of Particle Size	45
3.3.1.6	Effect of Contact Time	45
3.3.1.7	Kinetics of Nitrite Adsorption	46
3.3.1.8	Adsorption Isotherms	52
3.3.2	Nitrate Adsorption Experiments	55
3.3.2.1	Effect of Adsorbent Type	55
3.3.2.2	Effect of pH on Adsorption	56
3.3.2.3	Effect of Adsorption Temperature	57
3.3.2.4	Effect of Contact Time	58
3.3.2.5	Kinetics of Nitrate Adsorption	59
3.3.2.6	Adsorption Isotherms	62
3.3.2.7	Adsorption Thermodynamics	66
3.4	Nitrate Desorption Experiments	68
	Conclusion	70
	Suggestions for Future Work	71
	References	72
	Appendix	84
	الملخص	ب

List of Tables

No.	Table	Page
Table 2.1	AC samples identification, description of activation methods and yield.	20
Table 3.1	Surface area of different AC according to acetic acid method.	39
Table 3.2	Pseudo-first-order and pseudo-second-order kinetic model parameters for nitrite adsorption onto AC No.7 and CAC at 30°C.	50
Table 3.3	Intra-particle diffusion kinetic model parameters for nitrite adsorption onto AC No.7 and CAC at 30°C.	51
Table 3.4	Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrite adsorption on to AC No7.	54
Table 3.5	Comparison of specific nitrite adsorption capacity by different materials.	55
Table 3.6	Pseudo-first-order and pseudo-second-order kinetic model parameters for nitrate adsorption onto AC No.7 and CAC at 20°C.	62
Table 3.7	Intra-particle diffusion kinetic model parameters for nitrate adsorption onto AC and CAC at 20°C.	62
Table 3.8	Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrate adsorption onto AC No7.	64
Table 3.9	Comparison of specific nitrate adsorption capacity by different materials.	65
Table 3.10	The values of the thermodynamic of adsorption at various temperatures and various adsorbents.	68

List of Figures

No.	Figure	Page
Figure 2.1	Flow diagram for the activation process.	23
Figure 3.1	SEM micrographs of (a) OS, (b) OSC/H ₃ PO ₄ /450, (c) OSC/ZnCl ₂ B/450, (d) OSC/ZnCl ₂ C/450, (e) OSC/ZnCl ₂ B/600 and (f) OSC/ZnCl ₂ A/600.	37
Figure 3.2	Langmuir plots for acetic acid adsorption onto different AC. All experiments were conducted at room temperature using 1.00 gm AC.	38
Figure 3.3	A typical calibration curve for nitrite analysis by a differential pulse polarographic method.	40
Figure 3.4	A typical calibration curve for nitrate analysis by UV-VIS spectrometric method.	40
Figure 3.5	Percentage of nitrite removal by activated carbon prepared by different techniques at (initial conc: 20 mg/L, initial pH: 4, temperature: 25°C, contact time: 60 min and solid/liquid ratio: 0.30 g/50 mL).	41
Figure 3.6	Effect of adsorbent dosage on nitrite removal by OSC/ZnCl ₂ C/450 (AC No.7) at (initial conc: 30 mg/L, initial pH: 4, temperature: 25°C and contact time: 60 min).	42
Figure 3.7	Effect of pH on to the removal of nitrite by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 30 mg/L, temperature: 25°C, contact time: 60 min and solid/liquid ratio 0.3 g/50 mL).	43
Figure 3.8	Effect of temperature on nitrite removal by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 30 mg/L, initial pH: 4, contact time: 60 min and solid/liquid ratio 0.30 g/50 mL).	45
Figure 3.9	Effect of contact time on the removal of nitrite by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).	46
Figure 3.10	Kinetics of nitrite removal according to the pseudo-first-order model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).	49

Figure 3.11	Kinetics of nitrite removal according to the pseudo-second-order model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).	50
Figure 3.12	Kinetics of nitrite removal according to the intra-particle diffusion model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).	51
Figure 3.13	Equilibrium adsorption isotherm of nitrite onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).	52
Figure 3.14	Langmuir plot for nitrite adsorption onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).	53
Figure 3.15	Freundlich plot for nitrite adsorption onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).	53
Figure 3.16	Percentage of nitrate removal by the activated carbon prepared by different techniques at (initial conc: 100 mg/L, initial pH: 4, temperature: 25°C, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).	55
Figure 3.17	Effect of pH on nitrate removal by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 150 mg/L, temperature: 25°C, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).	57
Figure 3.18	Effect of temperature on nitrate removal by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 150 mg/L, initial pH: 4, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).	58
Figure 3.19	Effect of contact time on nitrate removal by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).	58
Figure 3.20	Kinetics of nitrate removal according to the pseudo-first-order model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).	60

Figure 3.21	Kinetics of nitrate removal according to the pseudo-second-order model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).	61
Figure 3.22	Kinetics of nitrate removal according to the intra-particle diffusion model by OSC/ZnCl ₂ C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).	61
Figure 3.23	Equilibrium adsorption isotherm of nitrate onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 20°C, initial pH: 4 and solid/liquid ratio 1.00 g/50 mL).	63
Figure 3.24	Langmuir plot for nitrate adsorption onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 20°C, initial pH: 4 and solid/liquid ratio 1.00 g/50 mL).	64
Figure 3.25	Freundlich plot for nitrate adsorption onto OSC/ZnCl ₂ C/450 (AC No.7) at (temperature: 20°C, initial pH: 4 and solid/liquid ratio: 1.00 g/50 mL).	65
Figure 3.26	Plot of $\ln K_d$ versus $1/T$ for 150 mg/L NO ₃ ⁻ concentration adsorption on (A) AC No.7 and (B) adsorption on CAC.	67
Figure 3.27	Percentage of nitrate desorption at different pH values.	69

List of Abbreviation

Symbol	Abbreviation
A	Intra-particle diffusion constant gives an idea about the thickness of the boundary layer.
Abs	Absorbance.
AC	Activated carbon.
b	Langmuir constant related to the rate of adsorption.
C	Concentration of acetic acid at equilibrium.
C₀	Initial liquid-phase concentration of adsorbate.
C_{Ae}	The amount adsorbed on solid at equilibrium.
C_e	Equilibrium liquid-phase concentration of the adsorbate.
CAC	Commercial activated carbon.
GAC	Granular activated carbon.
k₁	Equilibrium rate constant of pseudo-first-order kinetic model.
k₂	Equilibrium rate constant of pseudo-second-order kinetic model.
K_a	Ionization constant of weak acid.
K_d	The distribution coefficient.
K_F	Freundlich constant represents the quantity of adsorbate onto activated carbon per a unit equilibrium concentration
KHP	Potassium hydrogen phthalate.
k_p	Equilibrium rate constant of intra-particle diffusion kinetic model.
N	Number of moles of acetic acid adsorbed per 1.00g AC.
n	Freundlich constant gives an indication of how favorable the adsorption process is.
N_m	Number of moles of acetic acid per gram required to form monolayer.
OS	Olive stones.
PAC	Powder activated carbon.
Q_o	Langmuir constant related to the adsorption capacity.
q_e	Amount of adsorbate per unit mass of adsorbent at equilibrium.
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min).
R	The universal gas constant (8.314 J/mol K).

R²	Correlation coefficient.
SEM	Scanning Electron Microscopy.
V	Volume of the solution.
W	Mass of dry adsorbent.
WHO	World Health Organization.
T	The absolute solution temperature.
ΔH^o	Standard enthalpy.
ΔS^o	Standard entropy.
ΔG^o	Standard free energy.

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Abstract

Many different parts of the world have been facing the problem of nitrate and nitrite contamination of surface and ground water. Excessive use of nitrate-based chemical fertilizers is considered to be the main reason for this contamination.

Therefore a simple, practical and economic process to reduce nitrate and nitrite concentrations in aqueous solutions was the major objective of this research. To achieve this goal, bench-scale nitrate and nitrite adsorption experiments were conducted using activated carbon as adsorbent. Two research methods were used to minimize the cost of activated carbon production. The first one is by choosing a cheap available starting material (*Jift*), the other one is by a good choice of the production method. Moreover, by choosing *Jift* as starting material, we may reduce solid waste pollution, while reducing the cost of raw material for the production of activated carbon.

In this study, activated carbon was produced from olive stones by chemical activation technique using different activating agents such as ZnCl_2 , H_3PO_4 and NaHCO_3 . The precursor/activating agent weight ratio

was 1:1. Different impregnation methods and different carbonization temperatures 450 -750°C were used.

Scanning electron microscopy (SEM) images revealed that the carbon prepared by ZnCl_2 activation involved higher cavities than other counterparts. The highest surface area calculated by acetic acid adsorption method for carbon activated by ZnCl_2 activation (AC No.7) was $1482.57 \text{ m}^2 \text{ g}^{-1}$.

Activated carbon prepared by the chemical activation of olive stone was examined for the adsorption of nitrite and nitrate ions from aqueous solutions. Carbon activated by ZnCl_2 was found to be the most effective adsorbent for nitrate and nitrite removal. Commercial activated carbon (CAC) was used for comparison purposes.

The adsorptive properties of CAC and activated carbon prepared from olive stone were investigated in terms of adsorbent dose, pH, temperature, contact time and contaminant concentration in a batch system. Results indicate that the adsorption effectiveness for OSC/ ZnCl_2 C/450 (AC No. 7) was higher than for CAC. The total sorption capacities were found to be 7.00 and 5.53 mg/g for nitrite and nitrate, respectively. Lowering pH led to a significant increase in nitrite and nitrate adsorption. The effect of temperature on adsorption by AC No.7 and CAC has also been investigated in the range of 10-40°C. The results indicate that the temperature slightly affected effectiveness of AC No. 7 adsorption. This fact indicates that AC

No. 7 can be used for in situ treatment of nitrite and nitrate in underground and surface water.

The equilibrium adsorption data were interpreted using Langmuir and Freundlich models. The adsorption of nitrite on AC No.7 at 30°C was better represented by the Freundlich equation. On the other hand, nitrate adsorption on AC No.7 at 20°C was better represented by the Langmuir equation.

In order to investigate the adsorption mechanisms, three simplified kinetic models, i.e., pseudo-first-order, pseudo-second-order and intra-particle diffusion were applied to fit the kinetic data obtained by using both adsorbents. The rate constants for the three models were determined and the correlation coefficients were calculated. The kinetic data for both adsorbents supports pseudo-second order model for nitrite adsorption. Adsorption followed pseudo-second-order rate kinetics for nitrate onto AC No.7 and pseudo-first-order rate kinetics onto CAC. Thermodynamic parameters such as standard free energy ΔG° , standard enthalpy ΔH° and standard entropy change ΔS° of the nitrate adsorption process were calculated for both adsorbents.

Chapter One

Introduction

1.1 Overview

Pollution is one of the most serious problems that affect our environment, and its effects on all life aspects are clear to everyone. Because of this, pollution is one of the most serious issues that all the world countries are concerned about.

As time goes, the pollution problem increases and also the population growth increase. The increase in demand for water and food supplies place an increasing stress on the ground and surface water quality and quantity. One of the environmental problems that has become an increasingly important problem in developed and developing countries is nitrite and nitrate contamination of surface and ground water [1-4].

1.2 Nitrate and Nitrite in Drinking Water

1.2.1 Nitrate and Nitrite Sources and Chemistry

Nitrate is found in moderate concentrations in most of the natural waters. It occurs naturally due to the degradation of nitrogen-containing compounds from natural sources as soil, bedrock and organic materials [5]. Nitrate is also present as natural constituent of plants. Together with sulfates, nitrates are main components of acid rains [6]. However, the largest loading of nitrate and nitrite originates from anthropogenic sources,

which mostly result from excessive application of nitrate-based chemical fertilizers in agricultural activities [1-2, 7-13] and from many industrial processes [9-10, 12, 14]. The other most common sources of nitrate and nitrite are overflowing septic tanks [7, 12, 14], livestock, domestic wastes effluents, pesticides and herbicides that are used in industrial agriculture [12], the wastes of the production of explosives [11], decomposition of decaying organic matters buried in the ground [14] and the plantation of leguminosae crops which fix atmospheric nitrogen in the form of nitrate [7].

All these products can be converted to nitrate by biochemical oxidation. The nitrite ion occurs as intermediate during the biodegradation which happens through a series of bacterial reactions collectively known as nitrification. In the nitrification process bacteria degrade nitrogen-containing compounds and release ammonia. Then, some bacteria such as *Nitrosomonas* oxidize the released ammonia to nitrite which is converted to nitrate by other bacteria such as *Nitrobacter* [5, 15-16].

Nitrates are extremely soluble in water and can move easily through soil into the drinking water supply [14] and when their concentrations become excessive in water sources they cause several health and environmental problems.

1.2.2 Nitrate and Nitrite Health and Environmental Concerns and Drinking Water Regulations

Nitrate in water has low toxicity, but may be converted via microbacteria or in vivo reduction to nitrites [1, 6]. Nitrites transform hemoglobin to methaemoglobin by oxidation of ferrous iron (Fe^{2+}) in hemoglobin to ferric form (Fe^{3+}) preventing or reducing the ability of blood to transport oxygen. Such a condition is described as methaemoglobinaemia which is dangerous especially in infants (so-called “blue-baby syndrom”) [1, 8-9, 12-15, 17]. In addition, the reaction between nitrite and secondary or tertiary amines may result in the formation of carcinogenic, mutagenic and teratogenic *N*-nitroso compounds (*N*-nitrosoamines) [1-2, 9, 14, 17] which may cause cancer of the alimentary canal [3-4, 10]. In adults, high amounts of nitrate may cause abdominal pain, blood in stool and urine, weakness, mental depression [7], dyspepsia, headache [12], diarrhea, vomiting, diabetes, hypertension, respiratory tract infections and changes in the immune system [18]. The high concentrations of nitrate in water causes a phenomenon known as “Eutrophication”, which means an excessive growth of the algae in water which consumes the oxygen gas dissolved in water causing fish death [1, 10, 17].

For these reasons, removal of nitrate and nitrite from water is a necessity. To limit the risk to human health from nitrate and nitrite in drinking water, the World Health Organization (WHO) set a maximum acceptable concentration to be 50 mg NO_3^-/L and 3 mg NO_2^-/L [19].

1.2.3 Nitrate and Nitrite Treatment Options

At high nitrate and nitrite concentrations, water must be treated to meet regulated concentrations. The following treatment processes have been studied or applied to remove nitrate from drinking water: biological denitrification [7-8, 13, 20], ion exchange [7, 13, 20], reverse osmosis [7, 10, 13, 20], electrodialysis [7, 10-11, 13, 20], chemical denitrification [3, 20], chemical reduction [7, 11, 13, 20] and adsorption [2-3, 10, 13].

1.3 Adsorption

1.3.1 Adsorption Definition and Operation

Adsorption is the process which involves the transfer of a substance from a solution onto the surface of solid adsorbents by either chemical, physical attraction [21] or more frequently both [22]. Physical adsorption involves the attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent surface and the adsorbate [22].

Adsorption involves transport of the soluble substances to the surface of the solid adsorbent, where the adsorbate then moves into the adsorbent pores. The adsorbate then adsorbs onto the interior porous network of the adsorbent [23].

1.3.2 Adsorption Features

Adsorption has been found to be better than other techniques for water purification in terms of: ease of application, cost, simplicity of design and feasibility for in situ treatment of underground and surface water. Moreover adsorption does not need skilled maintenance and equipment-intensive processes and can thus be applied in rural areas [7, 9, 24].

1.3.3 Adsorbents Used to Remove Nitrate and Nitrite from Water

Different adsorbents were used for water purification from nitrate such as: agar, bentonite, mustard [7], slag [8], impregnated almond shell activated carbon by zinc and zinc sulfate [4], charcoal prepared from bamboo [9], zinc chloride activated carbon from coconut coir pith [25], wheat and mustard straw [14]. Nitrate and nitrite ions were also removed from water using carbon cloth [3, 11], sepiolite [8, 10] and activated carbon [7-8, 10, 14].

1.4 Activated Carbon (AC)

1.4.1 AC Properties

AC has been the most efficient and commonly used adsorbent in water purification all over the world [26-28]. The reason that AC is such an effective adsorbent material is due to its high surface area, porous structure, and high degree of surface activity [26, 29]. AC is also highly inert, thermally stable and can be used over a broad pH range [26].

1.4.2 Historical Use of AC

The use of carbon for water purification extends far back into history. The Egyptians used carbonized wood as a medical adsorbent and purifying agent as early as 1500 B.C [30]. Ancient Hindus filtered their drinking water with charcoal [22]. By 1901, scientists developed ways to synthesize AC from coal [31]. AC was first introduced industrially in the first part of the 20th century, when activated carbon from vegetable material was produced for use in sugar refining. Since then, AC has been used in many industries [30].

1.4.3 AC Application

There are many applications for activated carbon in many fields, including separation and purification processes of gases and liquids [32-34], food and pharmaceutical industries [33], AC is also used as catalyst and catalyst support [32].

1.4.4 AC Efficiency

AC efficiency for removing a given pollutant depends on both its surface chemistry and its adsorption capacity [35]. The AC adsorption capacity is usually attributed to its internal pore volume that may be distributed throughout the solid as pores ranging in width from micropores to macropores [4, 35]. When the pore sizes of the activated carbon are in the size range of the pollutants, adsorption process will be enhanced and is

expected to be efficient [30]. Adsorption capacity of the finished activated carbons also depends essentially on the type of the activation methods and on the structural properties of the original precursor material [36].

1.4.5 Precursors of the AC

Activated carbon is a relatively costly adsorbent [10]. Therefore, researchers are looking for new low-cost sources of AC. In addition to cost, there are many considerations that should be taken into account while choosing the precursors of activated carbon, such as abundance, purity, manufacturing process and further application of the product [29, 37].

Precursors of activated carbons are organic materials with high carbon content [38]. The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood and coconut shell [34, 39].

In the recent years, many agricultural by-products have been used as sources for activated carbons production [27-28, 33, 40]. They have attracted considerable attention because they are widely available [40], they are renewable sources and their products give an economic gain [33]. Also by choosing these precursors some polluting wastes were removed from environment [40].

Many agricultural by-products were used for activated carbon preparation such as; peach stones [41], apricot stones [42], cherry stones [43], date stones [36] and pits [44], waste apple pulp [45], nut shells [29],

pecan shell [46], walnut shells [47], almond shells [48], oil palm waste [49], bagasse [50], rice husks [51], tea waste [52], coffee bean and grounds [38], corncob [53], cotton stalks [54] and olive waste [33-34, 55-56]. Olive wastes are available in large amounts in many countries at very low cost [56].

1.5 Olive Stones

One of the important agricultural activities in Mediterranean countries is the commercial production of olive [57]. Even in small countries, like Palestine, more than 6×10^4 ha of land is planted with olive trees [58].

Unfortunately, the by-products that are produced during the manufacturing process of olive oil in mills constitute a serious environmental problem. The wastes produced contain olive-mill waste water [59] and olive solid waste [60]. The aqueous fraction is composed of vegetation water and suspended solids and is hazardous to the environment due to high phenolic content [61]. The solid by-product of olive oil extraction, which is equivalent to approximately 35% by weight of the olive fruit [56], consists of stones, skin and pulp of the olive fruit and has significant remaining oil content depending on the extraction technology [61]. Most of olive wastes are dumped in the environment without any management, where they may be contaminated by fungi or release toxic compounds [62].

1.5.1 Olive Stone Components

As a lignocellulosic material, the hemicellulose, cellulose and lignin are the main components of olive stone [57, 63]. The olive stone also has considerable proportion of fats, proteins, water-soluble carbohydrates and a small (but active) fraction of hydrosoluble phenolic substances [57, 63].

1.5.2 Advantages of Olive Stones as Precursor for AC

Olive stones can be considered as one of the best agricultural by-products for AC preparation [27, 29]. That is because it is an inexpensive material that is available in large quantities [27, 37]. In addition to removal of polluting waste materials, the preparation of activated carbon from this material would also include economic gains for products manufactured from the abundant waste sources. Moreover, olive stone-based carbon seems to have special features such as mechanical stability [59], robustness, lack of swelling in aqueous media and low sulfur and ash content [28].

1.5.3 Olive Stone Uses

Olive solid pre-dried residue is more frequently used for bioenergy production by direct combustion [56, 64] to produce electric energy or heat [65]. Olive stones have been recently employed to produce bio-oils [60]. It is also utilized in many sectors including fertilizers, additives in animal nutrition [65-66], herbicides, road construction materials, bricks and worm

breeding material [56]. Other uses are known such as furfural production, plastic filling, abrasives, cosmetics, resin formation and different chemical compound productions [63].

In preliminary studies, olive stone was used as adsorbent material for different heavy metals such as lead, nickel, copper, cadmium [65], mercury and zinc [67]. Chemically modified olive stone was used for heavy metal removal such as copper and cadmium [68]. Removal of basic dye from aqueous solutions such as safranin was also studied [69].

Most of the recent studies have been devoted to the preparation of activated carbon from different olive oil production residues [70]. For example olive husk was used for the preparation of activated carbon by chemical activation with potassium hydroxide and was used for adsorption of polyphenol mixtures [71]. Olive pulps were also used to prepare activated carbon by chemical activation with phosphoric acid [72]. Olive stones have been used as raw material to produce activated carbon by both chemical and physical activation methods [59]. Activated carbon was prepared from olive stones using different activating agent such as potassium carbonate [73], potassium hydroxide [70], zinc chloride [72], phosphoric acid [34], carbon dioxide and steam [55]. Activated carbon prepared from olive stones was used to remove different materials from aqueous solution such as methylene blue [70], textile dyeing effluent [72], copper ions [34], chromate ions [28], uranium and thorium [35]. In this

work, activated carbon prepared from olive stones is used in water purification from nitrate and nitrite ions.

1.6 Carbon Activation

In addition to the nature of the precursor, the activation process affects activated carbon characteristics [29, 34]. Different methods are used to prepare carbon with good affinity for adsorption by developing excellent surface properties and specific functionalities [30]. The main methods for the preparation of activated carbons can be divided into physical and chemical activations [29, 74-76].

1.6.1 Physical Activation

The physical activation process involves two steps: the first one is the carbonization (so-called pyrolysis) of the carbonaceous precursor [74] at elevated temperatures (500-1000°C) under inert atmosphere in order to eliminate oxygen and hydrogen elements as far as possible [36]. Many of the non-carbon elements, mainly volatiles, are removed during this process [36-37, 55, 76] yielding a solid residue (char) whose carbon content is considerably higher than that of the precursor [55]. High-porosity carbons can be obtained only at high extents of char burn-off [76].

The second stage involves thermal activation of this char. This can be done at the same temperature as for pyrolysis or at a higher temperature (800-1000°C) [27, 55], in the presence of oxidizing gas such as steam [36,

55, 77], carbon dioxide [55] or air [74]. Activation may also be achieved by changing temperature heating rate [78].

High temperatures are used in the physical activation process. That is because it is widely accepted that primary decomposition occurs between 200 and 400°C, and secondary decomposition which involves the amortization process, continues to occur in the solid matrix above 400°C [33].

1.6.2 Chemical Activation

In comparison with physical activation, chemical activation has two important advantages when a lignocellulosic material is especially used as a raw material. One is the lower temperature at which the process is accomplished making the process more economical compared to physical activation. The other is that the yield of chemical activation is relatively higher, since carbon burn-off char is not required [29, 76, 79]. The formation of tar and other by-products is inhibited by the chemical agent [78-79].

1.6.2.1 Operation of Chemical Activation

In chemical activation, the carbonaceous precursor is impregnated with an activating agent, carbonization and activation are carried out simultaneously. The impregnated material is carbonized in an inert atmosphere [27, 76, 79]. In chemical activation, there will be a reaction

between the precursor and the activating agent used in activation, leading to developments in porosity [29].

The chemical activating agents act by dehydration of the sample during the chemical treatment stage and inhibit the formation of tar and volatiles and thereby increase the product yield [80].

1.6.2.2 Activating Agents

The chemical groups found on an activated carbon surface are directly attributed to the method of activation [14], the type and concentration of the activating agents [29, 34, 80], pyrolysis temperature [34, 80], activation time [29, 68] and any additional treatment conditions [68, 78].

Chemical activation involves impregnation of the raw material with chemicals that generally act as dehydrating materials and promote the pyrolytic decomposition and the formation of crosslinks and inhibit formation of tar [29, 81]. Examples are potassium hydroxide [82-83], sodium hydroxide [84], sulphuric acid [82], hydrochloric acid [30], phosphoric acid [38, 72, 85-87], calcium chloride [29-30], aluminium chloride [29], potassium chloride [36], zinc chloride [24, 75-76, 88-89], ammonium chloride [74], potassium carbonate [73, 90] and sodium carbonate [90].

Among the numerous activating agents the most widely used chemicals are zinc chloride [79-80] and phosphoric acid [38]. These compounds are considered more effective and less expensive activating agents [89].

1.6.2.2.1 Phosphoric Acid (H_3PO_4)

Phosphoric acid is known to be the most environmentally sound chemical for the activation processes [79]. The use of phosphoric acid is also preferred due to economical concerns [29, 85] and its assumed ease of elimination by leaching with water after carbonization [91].

Phosphoric acid has catalytic effect on the bond cleavage reactions that promote the pyrolytic decomposition of the initial material like the hydrolysis of the glycosidic linkages in hemicellulose and cellulose and it cleaves aryl ether bonds in lignin [72]. This catalytic effect promotes the formation of cross-linked structure by the interaction between the acid and the organic precursor leading to formation of phosphate linkages between the fragments in the biopolymer [85]. These reactions promote the release of water, carbon monoxide, carbon dioxide and methane at low temperatures [72]. Phosphoric acid reaction within the internal cellulose structure is assumed to lead to an enhancement in pore volume [38].

1.6.2.2.2 Zinc Chloride (ZnCl_2)

Impregnation with ZnCl_2 causes degradation of the cellulosic material. On carbonization, it produces dehydration [75]. These processes result in charring and aromatization of the carbon skeleton and creation of the pore structure [79, 88-89]. These processes improve the pore development in the carbon structure [80].

1.7 What is New in this Work?

Nitrate and nitrite contamination of ground and surface water is a serious problem in all over the world. In this work, removal of nitrate and nitrite ions from water will be conducted by adsorption onto activated carbon produced from olive stones, for the first time. Adsorption is a simple method that can be applied in rural areas. In this research we hope to make this method more efficient and more economic by choosing olive stones as precursor of the activated carbon. We will activate olive stones with H_3PO_4 and ZnCl_2 using the condition that gave the highest surface area in earlier work with some modification on the impregnation methods and carbonization temperatures. NaHCO_3 will be used for the first time to activate olive stones.

1.8 Objectives of this Work

1.8.1 Strategic Objectives

In Palestine, nitrate contamination of ground water sources is becoming a major problem. According to a study done in (2005) 90 % of the water supply wells exceeded 50 mg NO_3^-/L in the Gaza Costal Aquifer [92]. Therefore the overall goal of this research was to find practical and economical way to reduce nitrate and nitrite concentrations in ground and surface water that can be used in Palestine and other Mediterranean countries.

1.8.2 Technical Objectives

The objective of this project is focused on preparing low cost carbon adsorbent from solid olive stones and using it for water purification from nitrate and nitrite ions. While achieving this objective, the following technical objectives will be achieved:

- 1- Oil remaining in solid olive waste (*Jift*) will be recovered.
- 2- Carbon will then be prepared from the resulting solid using zinc chloride, phosphoric acid, and sodium bicarbonate as activating agent.
- 3- Characterization of the prepared activated carbon will be done.
- 4- The efficiency of the prepared activated carbon in nitrate removal and nitrite ions from pre-contaminated aqueous solutions will be studied.
- 5- Effects of pH, temperature, contaminant concentration, activated carbon dosage and time of contact will be studied.
- 6- The used activated carbon in nitrate adsorption will be regenerated and reused.

Chapter Two

Experimental Work

2.1 Chemicals and Reagents

All chemicals used were of analytical grade and were used without further treatment. Phosphoric acid (85%), potassium nitrate, methanol, acetic acid, diphenyl amine and sodium hydroxide were purchased from Frutarom. Zinc chloride and KHP were purchased from Alfa Aesar. Sodium nitrite was purchased from Avokado.

2.2 Preparation and Characterization of AC

The activating agent and the general conditions of carbonization and activation in this work were chosen considering previous works [24, 80], with some modification.

2.2.1 Preparation of Olive Stones

In this study olive waste (*Jift*) obtained from oil mills located in Nablus area, Palestine, was used as raw material for the production of activated carbon via different procedures. The *Jift* samples were collected during the olive cultivation season (October-December), and stored with no treatment until they were used.

Jift is the wet solid by-product that results after milling olives to produce oil. It is composed of crushed hard stones, soft pulp in addition to

moisture and oil remains. The soft pulp was mainly removed away by immersing the raw material in tap water. The soft pulp particulates floated onto the water surface allowing easy separation by decantation. The desired olive stones were separated and dried in an oven at 110°C.

The resulting particles were then sieved. The particles in the range (1.18-2.36 mm) were used throughout this work. Any additional oil remaining in the olive stones were removed by toluene extraction with a Soxhlet apparatus, as described below.

2.2.2 Oil Recovery

Toluene (300 mL) was refluxed over 100.00 g olive stone sample in a 1.0 L Soxhlet apparatus for 20 min. The same toluene system (with oil inside) was used 5 times, by replacing the solid stone batch with fresh one every time.

The oil was recovered from the isolated toluene mixture by distillation. In each distillation, the evaporated toluene was recovered in a cooled container, with percentage loss no more than 25%. The measured oil ratio inside the dried olive stones was only 1%. It should be noted however that the raw wet Jift contains up to 7% of its mass as oil, which can also be recovered by extraction.

2.3 Experimental Set-Up for Carbonization Experiment

The samples were carbonized separately in a heavy duty tubular regulated furnace (Lindberg 9001). Each sample was inserted in the middle of the furnace in a 0.25 cm thick cylindrical stainless steel tube (4 cm inner diameter and 74 cm length). The furnace was heated from room temperature to the final desired carbonization temperature at a heating rate increase (30°C/min). The sample was kept at the desired temperature for 2 h, under inert atmosphere (N₂ gas 99.9%) at a flow rate of (0.5 L min⁻¹). The activated carbon was then cooled at room temperature under the same nitrogen flow. A final product yield was recorded.

2.4 Carbon Activation

Different methods for carbon activation were used to prepare the desired activated carbon, prior to carbonization. Batches, 50.00 g, of the prepared olive stones were used in activation and carbonization experiments, unless otherwise noted. AC samples identification, description of activation methods and yield are given in Table 2.1. The yield of the activated carbon was estimated from the following equation:

$$\text{Yield of activated carbon (wt \%)} = \frac{\text{weight of activated carbon}}{\text{weight of waste olive stones}} \times 100 \quad (2.1)$$

2.4.1 Carbonization with no Chemical Activation

For comparison purposes, one olive stone sample was carbonized at 450°C for 2h without prior chemical activation by any compound. After cooling, the sample was washed with deionized water to remove dust then dried in an oven at 110°C and finally stored in a desiccator for further use. This sample was named as (OSC).

Table 2.1: AC samples identification, description of activation methods and yield.

Sample Code	Sample No.	Activation condition	Carbonization Temperature (°C)	Yield (%)
OSC	1	–	450	34.90
OSC/H ₃ PO ₄ /450	2	H ₃ PO ₄ 50% wt.ratio1:1	450	54.00
OSC/ZnCl ₂ A/450	3	ZnCl ₂ 20% wt.ratio1:1	450	40.00
OSC/ZnCl ₂ A/600	4	ZnCl ₂ 20% wt.ratio1:1	600	31.40
OSC/ZnCl ₂ B/450	5	ZnCl ₂ 20% wt.ratio1:1	450	49.20
OSC/ZnCl ₂ B/600	6	ZnCl ₂ 20% wt.ratio1:1	600	33.20
OSC/ZnCl ₂ C/450	7	ZnCl ₂ 20% wt.ratio1:1	450	47.40
OSC/ZnCl ₂ C/600	8	ZnCl ₂ 20% wt.ratio1:1	600	42.90
OSC/ZnCl ₂ C/750	9	ZnCl ₂ 20% wt.ratio1:1	750	42.60
OSC/NaHCO ₃ 5%/450	10	NaHCO ₃ 5% wt.ratio1:1	450	40.00
OSC/NaHCO ₃ 10%/450	11	NaHCO ₃ 10% wt.ratio1:1	450	36.50

2.4.2 Chemical Activation

To prepare activated carbon from olive stones different chemical reagents were used, as explained below. The impregnated samples were then carbonized.

2.4.2.1 Carbon Activation by Phosphoric Acid

Phosphoric acid solution (100 mL, 50% w/w) was used in chemical activation of solid olive stones. This concentration was reported in literature to give the best surface area for carbon activated by H_3PO_4 [29]. The solution was added to the olive stone sample and the mixture was thoroughly stirred at 85°C for 4 h.

After this impregnation procedure, the solution was filtered to separate the residual acid. The olive stones were then washed with deionized water, dried in an oven at 110°C , before carbonization at 450°C . After carbonization, the product was washed with hot deionized water and then with cooled deionized water until pH of the filtrate became 4.5-5. The product was then dried in an oven at 110°C and stored in a desiccator for further use. This sample was named as (OSC/ H_3PO_4 /450).

2.4.2.2 Carbon Activation by Zinc Chloride

Olive stone samples were mixed by stirring with zinc chloride solution (250 mL, 20 % w/w). This concentration was reported in literature to give the best surface area for carbon activated by ZnCl_2 [80].

In this work, impregnation with zinc chloride followed different methods. This was to find activated carbon with highest quality. Three methods were followed, namely:

A) Firstly, impregnation was carried out at 70°C in a water bath until excess water evaporated. Then the samples were filtered and dried after washing with distilled water at 110°C in an oven.

B) Secondly, impregnation was carried out at 70°C in a water bath until excess water evaporated. Then the samples were dried at 110°C in an oven **without** washing.

C) Thirdly, olive stone samples were impregnated with zinc chloride solution for 24 h at room temperature. The impregnation was then carried out at 70°C in a water bath until excess water evaporated. Then the samples were dried at 110°C in an oven **without** washing.

The resulting chemical-loaded samples were then carbonized at varying temperatures ranging from 450°C to 750°C. The carbonized products were washed with 0.50 M hydrochloric acid solution, hot deionized water and cooled deionized water sequentially, to remove residual organic and mineral matters and to get the pH in the range 4.5-5. The final product was dried in an oven at 110°C and stored in a desiccator for further use. Those carbon series was named OSC/ZnCl₂A, OSC/ZnCl₂B and OSC/ZnCl₂C respectively followed by the carbonization temperature.

2.4.2.3 Carbon Activation by Sodium Bicarbonate

Two samples of olive stones (10.00 g each) were mixed by stirring with sodium bicarbonate solution (200 mL, 5% (w/w), 100 mL, 10% (w/w)) respectively. The impregnation was carried out at 40°C for 5 h. The samples were then filtered and dried at room temperature. Sample carbonization was performed at 450°C. Finally, the products were treated as the ones obtained by ZnCl₂ activation. This AC was named as OSC/NaHCO₃ followed by sodium bicarbonate concentration and carbonization temperature respectively. The general procedure followed in experiments is schematically outlined in Figure 2.1.

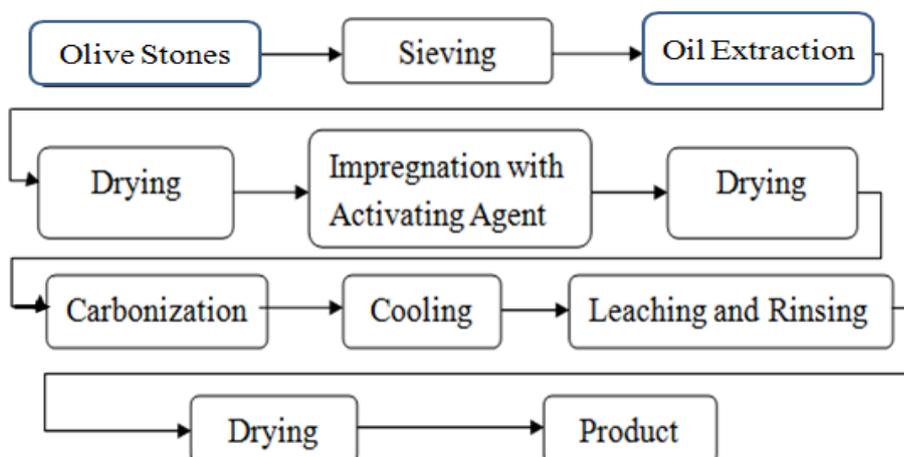


Figure 2.1: Flow diagram for the activation process.

2.5 Characterization of the Products

Activated carbon adsorption capacity is affected by different parameters, mainly: porous structure and surface area [35]. Therefore, it is necessary to characterize activated carbon solids in terms of these parameters.

2.5.1 Surface Area Measurement

The surface area of the final activated carbon was measured using the method of acetic acid adsorption [93], assuming mono-layer coverage, according to Langmuir isotherm. Seven dry clean flasks were used, the flasks were pretreated with acetic acid 0.50 M for 1 h to eliminate possible loss of acetic acid on container surfaces. To each flask (1.00 g) of activated carbon was added. Then, solutions (100 mL) with different molarities of acetic acid ranging from 0.015 to 0.15 M were added to each flask. The flasks were covered with stoppers and shaken in a thermostat at 25°C for one hour to reach equilibrium. The samples were filtered and titrated with standardized (0.10 M) sodium hydroxide solution using phenolphthalein indicator. KHP was used for pre-standardization of sodium hydroxide solutions.

The total number of moles of acetic acid adsorbed onto one gram of adsorbent (N) was calculated for different acetic acid concentrations at equilibrium (C). Plots of C/N versus C were then constructed, using Langmuir adsorption isotherms according to the equation:

$$\frac{C}{N} = \frac{1}{N_m b} + \frac{1}{N_m} C \quad (2.2)$$

The number of acetic acid moles per gram activated carbon required to form mono layer (N_m) was calculated from the slope ($1/N_m$). Acetic acid molecules per one gram adsorbent were then calculated assuming mono layer coverage. The surface area of adsorbent was then calculated by

multiplying the cross sectional area of one acetic acid molecule ($2.1 \times 10^{-19} \text{ m}^2 \text{ molecule}^{-1}$) by the number of molecules per gram adsorbent [94].

2.5.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy analysis was conducted for a number of adsorbent surfaces (olive stone and activated carbon) using a field emission-scanning electron microscopy (FE-SEM. JEOL JSM-6700F) with an energy dispersive x-ray spectrometer (EDS). This was to study the morphologies (surface textures) of different solids.

2.6 Adsorption Experiments

Nitrite and nitrate adsorption onto activated carbon surfaces was studied by batch experiments. Experiments were conducted in a set of 100 mL capped conical flasks. All used apparatus were thoroughly pre-cleaned with distilled water. After the addition of nitrite or nitrate solution to the activated carbon and the adjustment of the pH of the solutions, experiments flasks were shaken at 120 rpm using a temperature controlled water bath (Tuttnauer) with shaker (Burrell 75). The flasks were left under continued constant-speed shaking for the desired time.

Initial pH of nitrite and nitrate solutions, used in adsorption experiments, was adjusted by adding few drops of dilute solutions of sodium hydroxide or sulphuric acid as desired. Measurement of pH was performed on a Jenway pH-meter 3510.

For comparison purposes, adsorption behaviors of activated carbons prepared here and commercial activated carbon (CAC; Donau carbon, Hydriffin, cc8x30) were studied. Such comparison experiments were made using granular CAC with same particle sizes of the prepared one.

2.6.1 Nitrite Adsorption Experiments

A fresh nitrite stock solution (1000 mg/L NO_2^-) was prepared daily by dissolving a mass of 1.499 g sodium nitrite in 100 ml distilled water and diluted to 1000.00 ml scale in a volumetric flask. From this solution, different solutions (10-80 mg/L) were prepared by dilution. In each nitrite adsorption experiment, an aliquot (50 mL) of these solutions was used. Nitrite concentration was analyzed at the end of each experiment. Each experiment was performed in duplicate using identical conditions.

2.6.1.1 Effect of Adsorbent Type

Nitrite adsorption on different types of adsorbents was investigated. Olive stone and activated carbon were experimented. In each case, a fixed amount of the adsorbent (0.300 g) was placed in a conical flask. A nitrite solution (50 mL, 20 mg/L) was then added to each adsorbent, followed with pH adjustment (4) as explained earlier. The flasks were then capped and shaken for 1 h at 25°C. This procedure was followed for all carbon solid types described in this work. Carbon solids activated using ZnCl_2 by the third method (OSC/ ZnCl_2 C/450) showed high adsorption efficiency

towards nitrite. Therefore, these solids were used for further study throughout this work unless otherwise stated.

2.6.1.2 Effect of Adsorbent Dosage

Different amounts (0.10-0.70 g) of OSC/ZnCl₂C/450 (AC No.7) were placed into conical flasks, then solutions (50 mL, 30 mg/L NO₂⁻) were added to each flask and the pH was adjusted to 4. The mixtures were then shaken for 1 h at 25°C.

2.6.1.3 Effect of Initial pH

Effect of initial pH on adsorption was investigated in the pH range 2-8. The pH was varied as desired, by adding sodium hydroxide or sulphuric acid solutions, as explained earlier. Nitrite solutions (50 mL, 30 mg/L each) were added to adsorbent samples (0.30 g). The mixtures were then shaken for 1 h at 25°C.

2.6.1.4 Effect of Temperature

The effect of temperature on adsorption was studied. Nitrite solutions (50 mL, 30 mg/L each) were added to adsorbent samples (0.30 g) at pH 4. The mixtures were shaken for 1 h at different temperatures in the range 10-40°C.

2.6.1.5 Effect of Particle Size

Nitrite solution (50 mL, 40 mg/L) was added to two AC No.7 samples with different particle sizes, powder AC and granular AC (0.25 g) at pH 4. The mixture was shaken at 30°C for 4 h. After that time nitrite concentration was determined.

2.6.1.6 Effect of Contact Time (Kinetic Study)

The effect of time on adsorption was studied. Nitrite solution (50 mL, 40 mg/L) was added to adsorbent sample (0.25 g) at pH 4. The mixture was shaken at 30°C. Aliquots (0.5 mL each) of the clear solution were pipetted out at different time intervals until equilibrium was reached after 24 h.

2.6.1.7 Effect of NO₂⁻ Concentration

In each adsorption experiment, nitrite-contaminated water of a given concentration ranging from 20 to 80 mg/L NO₂⁻ was added to 0.25g adsorbent, with initial pH 4. The flasks were shaken at 30°C for 24 h to reach equilibrium. The initial and final concentrations of NO₂⁻ were measured.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2.3)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of nitrite initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g). The data were fitted to Langmuir and Freundlich isotherms to evaluate the adsorption parameters.

Langmuir equation:

It assumes a mono layer adsorption onto a uniform adsorbent surface with energetically identical sorption sites [95]. The linear form of Langmuir isotherm equation is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (2.4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

Freundlich equation:

It describes equilibrium on heterogeneous surfaces and hence does not assume mono layer capacity [95]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (2.5)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), K_F and n are Freundlich constants with n giving an indication of how favorable the adsorption process is. K_F ((mg/g) (L/mg)^{1/n}) is related with adsorption capacity of the adsorbent. The slope ($1/n$) ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [96]. A value for (n) below one indicates a normal Langmuir isotherm, while (n) above one is indicative of efficient adsorption [97].

2.6.2 Nitrate Adsorption Experiments

Nitrate stock solution of 1000 mg/L concentration was prepared by dissolving 1.63 g potassium nitrate which was pre-dried at 105° C for 24 h in 100 mL distilled water. The solution was then diluted to 1000.00 mL scale in a volumetric flask. From this solution different standard solutions of (50-300 mg/L) were prepared by dilution, 50 mL of each of these solutions was used in every experiment.

At the end of each experiment, 20 mL of the solution of adsorption was taken from each sample and was preserved with 0.04 mL of concentrated sulfuric acid 98% (w/w). Those solutions were stored at 4°C in polyethylene containers until nitrate concentration was analyzed in the Palestinian Central Public Health Laboratory in Ramallah.

2.6.2.1 Effect of Adsorbent Type

Different adsorbents were experimented in nitrate adsorption. In each case a known amount of adsorbent (1.00 g) was placed in a (100 mL) capped conical flask. The nitrate solution (50 mL, 100 mg/L) was then added and the pH was adjusted to be 4. Each conical flask was shaken and kept at 25°C for 1h. In the next experimental work the produced activated carbon prepared by the third method of ZnCl₂ impregnation OSC/ZnCl₂C/450 (AC No.7) was used.

2.6.2.2 Effect of Initial pH

Adsorption of nitrate was investigated in the pH range 2-8. The pH was varied as desired, by adding sodium hydroxide or sulfuric acid solutions, as explained earlier. Nitrate solution (50 mL, 100 mg/L) was added to (1.00 g) adsorbent. The mixture was then shaken at 25°C for 1h.

2.6.2.3 Effect of Temperature

The effect of temperature on nitrate adsorption was evaluated in the range 10-40°C. Adsorbent (1.00 g) was added to nitrate solution (50 mL, 100 mg/L) and the pH was adjusted to be 4. The mixture was then shaken at the desired temperature for 1h.

2.6.2.4 Effect of Contact Time (Kinetic Study)

To study the kinetics of nitrate ion adsorption process, nitrate solutions (50 mL, 200 mg/L) were added to 1.00 g adsorbent at 20°C and pH 4. The experiment was repeated for different time intervals.

2.6.2.5 Effect of Nitrate Ion Concentration

In each adsorption experiment, nitrate solutions with different concentrations (100-300 mg/L NO_3^-) were added to adsorbent samples (1.00 g each). The initial pH was adjusted to be 4. The flasks were then shaken at 20°C for 24 h to reach equilibrium. Initial and final nitrate concentrations were recorded. The amounts of adsorption at equilibrium q_e (mg/g) were calculated according to equation number (2.3). The equilibrium data were then fitted to Langmuir and to Freundlich isotherms to evaluate the adsorption parameters.

2.7 Nitrate Desorption Experiments

Reversible adsorption experiments were conducted by studying the ability of nitrate pre-treated AC to desorb the ions at different pH values (7, 9 and 11) controlled by dilute solution of sodium hydroxide and sulfuric acid. AC samples (1.00 g) were first treated with (50 mL, 200 mg/L NO_3^-) solutions at pH 4 until reaching equilibrium at 20°C. Percentage nitrate removal was (52%). The nitrate pre-treated AC samples (1.00 g) were then isolated, rinsed several times with distilled water and placed in controlled

pH nitrate-free solutions (20 mL) to examine desorption. The bottles were shaken at room temperature using a mechanical shaker for 24 h. The nitrate amount in the aqueous solution was then determined.

2.8 Determination Methods of Nitrite and Nitrate Ion Concentration

2.8.1 Determination Method of Nitrite Ion Concentration

Nitrite concentration measurements were made by a differential pulse polarographic method described by Nordantec analytical procedure manual for polarographic technique [98], with some modifications. The measurements were conducted in situ during the study of the adsorption process.

Measurements were performed using a PC-controlled POL150 polarograph, equipped with a MDE150 polarographic stand using three electrodes. The reference electrode was an Ag/AgCl electrode, and the counter electrode was a platinum electrode. The working electrode was a hanging drop mercury electrode.

The polarogram was recorded for the sample using the following parameters:

E_{initial} -400 mV, E_{final} -1000 mV, Step duration 0.2 s, Step amplitude 5 mV, Purge time 30 s, Pulse duration 20 ms and Pulse amplitude 25 mV.

2.8.1.1 Nitrite Standard Solutions Preparation

Nitrite ion intermediate solution (100 mg/L NO_2^-) was prepared by diluting 100.00 mL of the stock solution to 1.00 L with distilled water, and then this intermediate solution was used to prepare different calibration standard solutions with concentrations in the range (0.0-50 mg/L NO_2^-).

Calibration curves for NO_2^- were constructed using the standard NO_2^- solutions at different pH values in the range 2-8. It was found that polarographic results were independent of used pH values.

2.8.1.2 Sample Preparation

To 5.00 ml of distilled water placed in the polarographic vessel, 1.00 mL of reagent (0.10 M diphenylamine) and 0.40 mL sample were added. The diphenyl amine reagent was prepared as follows: diphenyl amine (0.169 g) was dissolved in 100.00 mL of (methanol 99% and concentrated acetic acid 99%) with volume ratio (1:1).

2.8.2 Determination Method of Nitrate Ion Concentration

Nitrate concentration was determined by a standard method called “Ultraviolet Spectrophotometric Screening Method”. This method followed exactly the procedure described in the *Standard Methods for the Examination of Water and Wastewater* [99].

Nitrate ion concentration was spectrophotometrically measured on a Perkin-Elmer Lambda 25 UV-VIS spectrometer. Quartz cells with 1 cm

path length were used. For nitrate ion, maximum absorbance at 220 nm was measured against redistilled water background. The absorbance at 275 nm was measured to determine interference with dissolved organic matter.

Net absorbance due to NO_3^- ions was calculated by the following equation:

$$\text{Absorbance due to } \text{NO}_3^- = \text{Abs}_{220} - [2 \times \text{Abs}_{275}] \quad (2.6)$$

when the absorbance was more than one, proper dilution was made and the conversion factor was used in calculation.

2.8.2.1 Nitrate Standard solutions preparation

Nitrate ion intermediate solution (100 mg/L NO_3^-) was prepared by diluting 100.00 mL of the stock solution to 1.00 L with distilled water, and then this intermediate solution was used to prepare different calibration standard solutions with concentrations in the range 0.0-12.0 mg/L NO_3^- . Calibration curve were constructed by plotting value of net absorbance vs. concentration of standard NO_3^- solution.

2.8.2.2 Sample Preparation

To prevent the interference of hydroxide and carbonate ion with nitrate ion, HCl solution (1.00 mL, 1.00 M) was added to 50 mL clear nitrate solution sample, filtered if necessary using a Millipore Synig Filter; 0.45 μm , nozsterile, MA01730. The solution was then mixed thoroughly. Standards were treated in the same manner as samples.

Chapter Three

Results and Discussion

3.1 Carbon Characterization

3.1.1 SEM Analysis of the AC

Scanning Electron Microscopy (SEM) technique was employed to observe the surface physical morphology of the olive stones-derived activated carbon. Figure 3.1 shows the SEM micrographs of the raw material (olive stones) and the prepared activated carbon under different conditions.

According to the SEM micrographs the raw material Figure 3.1 (a) does not have porous surface. The external surface of the chemically activated carbon by ZnCl_2 Figure 3.1 (c, d, e and f) is rich with cavities, whereas the surface of the carbon activated by H_3PO_4 Figure 3.1 (b) has no porous structure except for some occasional cracks or curves; see appendix A.

The clearly porous structure of the ZnCl_2 -activated carbon resulted from the evaporation of ZnCl_2 during carbonization, leaving the empty space previously occupied by the ZnCl_2 . From Figure 3.1 (d) it can be seen that some salt particles are scattered on the surface of the activated carbon, presumably due to the presence of remaining zinc chloride on the activated carbon. Some particles were even trapped inside the pores which may decrease the adsorption capacity of the activated carbon. Clearly, Figure 3.1 (c and d) demonstrates that the adsorption capacity of the products

could be further increased by an improved washing procedure especially when impregnation time is long; see appendix A.

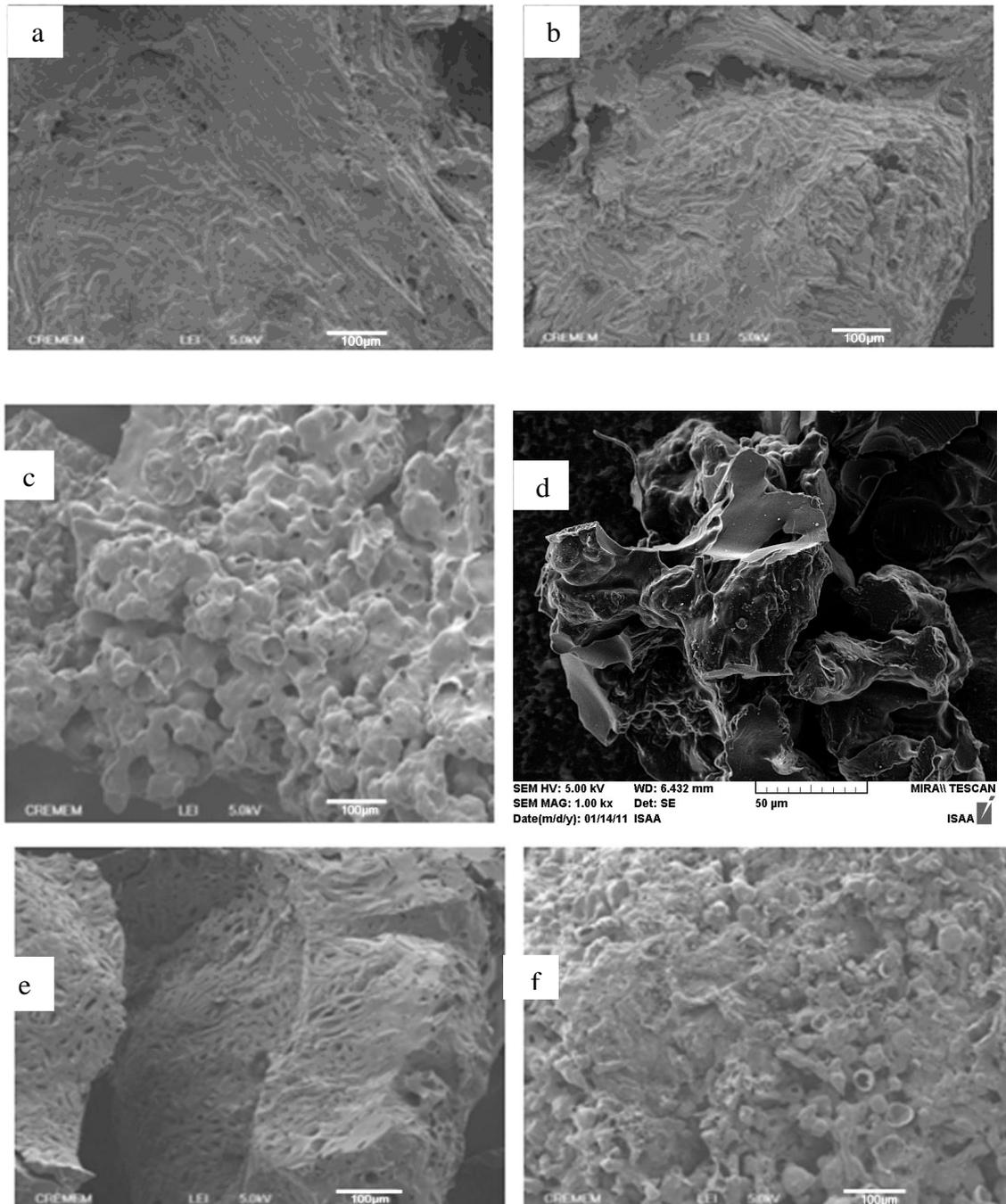


Figure 3.1: SEM micrographs of (a) OS, (b) OSC/H₃PO₄/450, (c) OSC/ZnCl₂B/450, (d) OSC/ZnCl₂C/450, (e) OSC/ZnCl₂B/600 and (f) OSC/ZnCl₂A/600.

3.1.2 Surface Area

Surface areas were measured using the adsorbed acetic acid method. This method has low accuracy, also it has low efficiency to measure the internal surface area of AC. Therefore, the measured values of the surface areas should be considered as approximate ones. Plots of C/N versus C were constructed according to equation (2.2) as shown in Figure 3.2. The surface area of adsorbent was then calculated as explained earlier in page. 24.

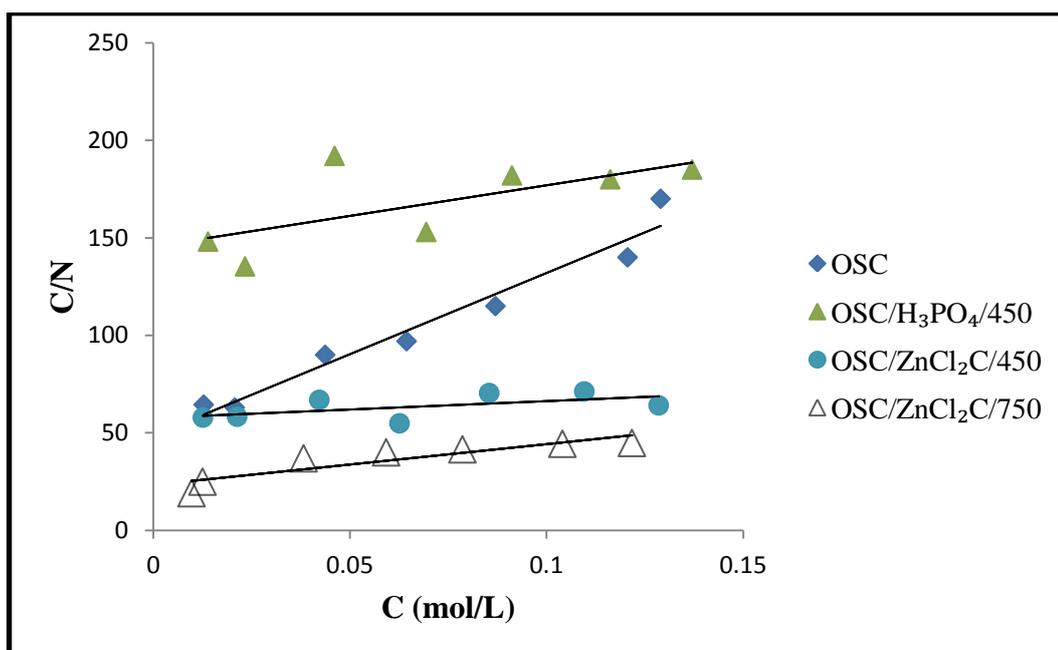


Figure 3.2: Langmuir plots for acetic acid adsorption onto different AC. All experiments were conducted at room temperature using 1.00 gm AC.

The calculated surface areas for different ACs are shown in Table 3.1. The largest surface area ($1482.576 \text{ m}^2/\text{g}$) was observed for OSC/ZnCl₂C/450. The decrease in surface area of OSC/ZnCl₂C when it

was carbonized at 750°C might be due to the shrinkage in carbon structure, which leads to a reduction in porosity [100-101].

Table 3.1: Surface area of different AC according to acetic acid method.

Sample Code	Surface area (m ² /g)
OSC	151.716
OSC/H ₃ PO ₄ /450	402.987
OSC/ZnCl ₂ C/450	1482.576
OSC/ZnCl ₂ C/750	606.040

3.2 Nitrite and Nitrate Determination Methods

3.2.1 Nitrite Determination by Differential Pulse Polarography

This was a fast and convenient technique. It could be used to study the kinetics of the nitrite concentration change. It can also be applied simultaneously at the end of each experiment. A typical calibration curve at pH ranges 2-8 for nitrite analysis by this method is shown in Figure 3.3.

3.2.2 Nitrate Determination by UV-VIS Spectrophotometry

UV-VIS spectrophotometry was chosen and preferred to many other methods. That is due to its low pollution effects, simplicity, speed and suitability to indicate the kinetic change of the nitrate concentration. A typical calibration curve for nitrate analysis is shown in Figure 3.4.

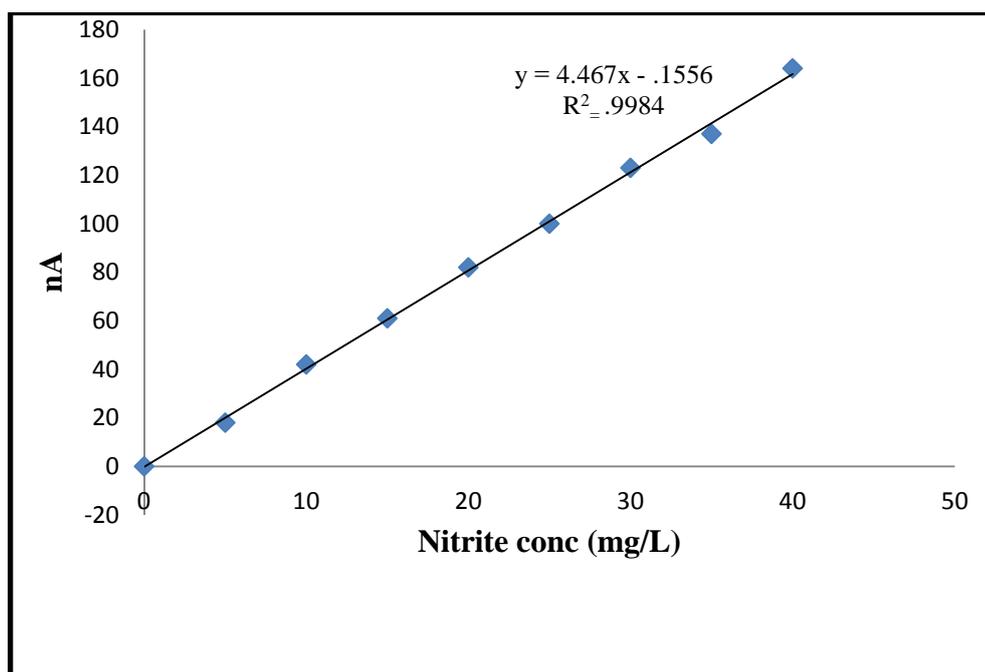


Figure 3.3: A typical calibration curve for nitrite analysis by a differential pulse polarographic method at pH (2-8).

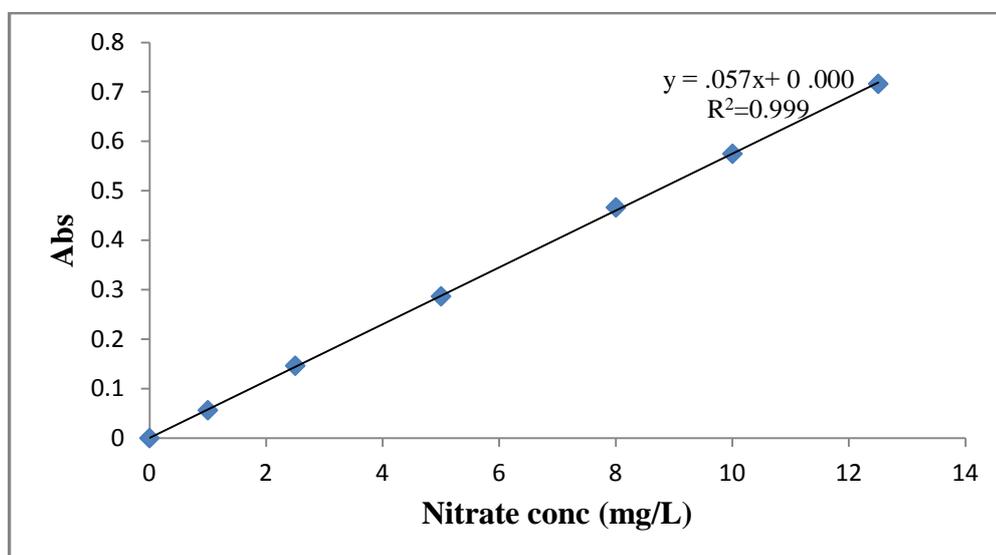


Figure 3.4: A typical calibration curve for nitrate analysis by UV-VIS spectrometric method.

3.3 Nitrite and Nitrate Adsorption Experiments

3.3.1 Nitrite Adsorption Experiments

3.3.1.1 Effect of Adsorbent Type

The percentage of nitrite removal on adsorbents prepared by different techniques is shown in Figure 3.5. The Figure shows that ZnCl_2 -activated carbon has greater adsorption capacities than H_3PO_4 -activated carbon and NaHCO_3 -activated carbon. This can be attributed to the difference in their surface area.

As the produced activated carbon (OSC/ ZnCl_2 C/450) is one of the best prepared activated carbon in this study, that has high surface area ($1482.576 \text{ m}^2/\text{g}$), good efficiency on nitrite removal and its carbonization temperature is (450°C), it was used in the next adsorption experiment because it's an efficient and economic adsorbent.

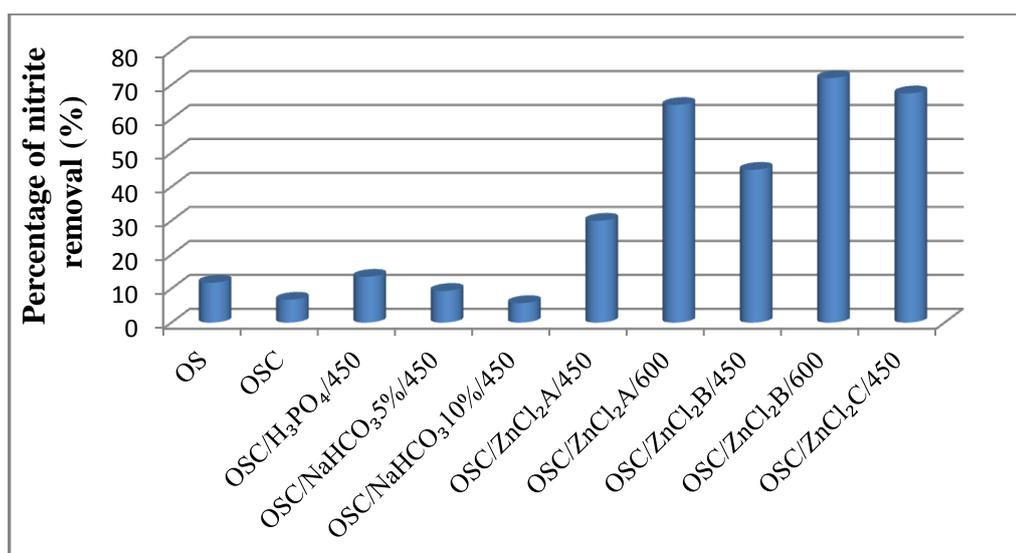


Figure 3.5: Percentage of nitrite removal by activated carbon prepared by different techniques at (initial conc: 20 mg/L, initial pH: 4, temperature: 25°C , contact time: 60 min and solid/liquid ratio: 0.30 g/50 mL).

3.3.1.2. Effect of Adsorbent Dosage

The effect of AC No.7 dosage on nitrite removal was studied, using 0.100 to 0.700 g AC at an adsorption time of 60 min. Contact time was ended before reaching equilibrium. The results are summarized in Figure 3.6.

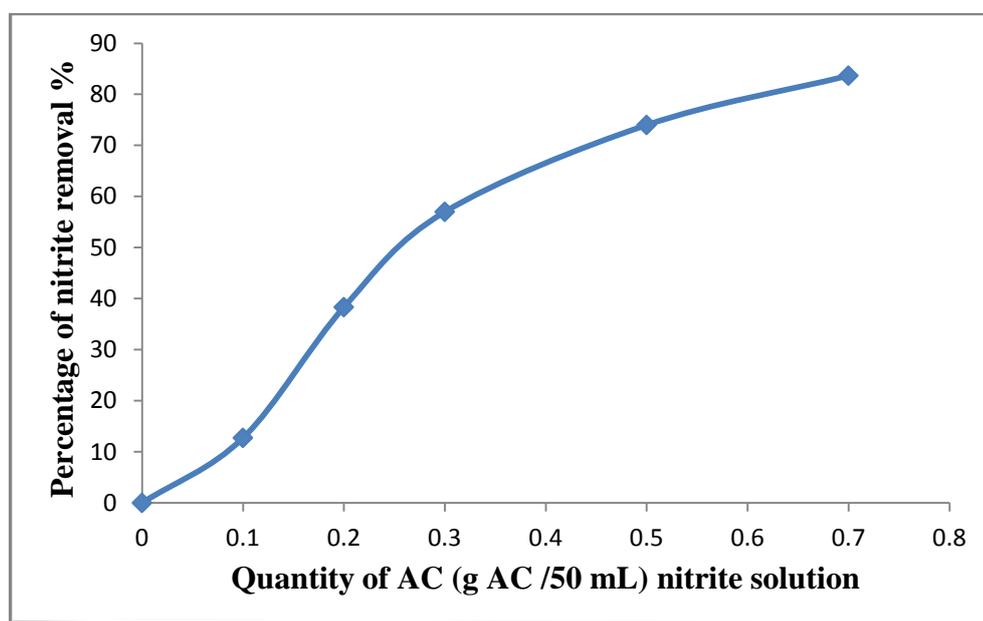


Figure 3.6: Effect of adsorbent dosage on nitrite removal by OSC/ZnCl₂C/450 (AC No.7) at (initial conc: 30 mg/L, initial pH: 4, temperature: 25°C and contact time: 60 min).

The percent of nitrite removal increased by increasing adsorbent dosage. Adsorption increases up to 84% with adsorbent dosage of (0.700 g/ 50 mL), because increasing adsorbent dosage at fixed nitrite concentration provided more available adsorption sites and thus increased the extent of nitrite removal.

3.3.1.3 Effect of pH

The variation of nitrite adsorption onto AC No.7 and CAC was investigated in the pH range 2-8. Contact time was ended before reaching equilibrium. Figure 3.7 summarizes the results. The Figure shows that the amount of adsorbed nitrite increases at lower pH. This behavior is due to the excess of protons in solution at lower pH. This increases the number of positively charged sites on adsorbent surfaces, which favor the adsorption of the nitrite anions due to electrostatic attraction. The acid-base interaction between base nitrite and acid on the adsorbent surface also favors adsorption.

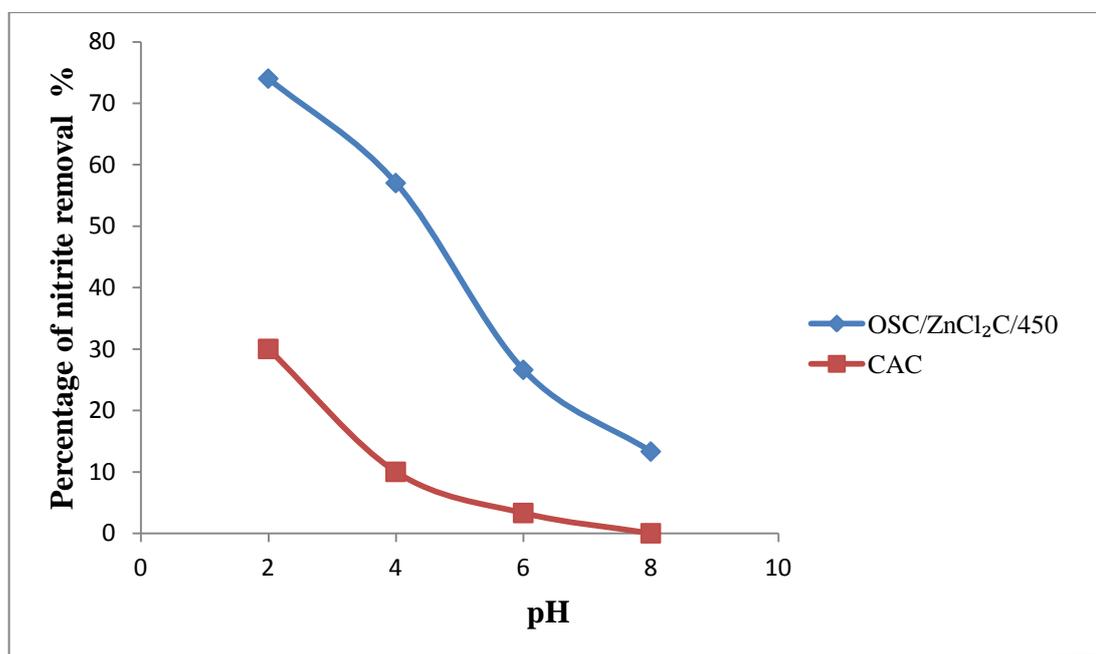
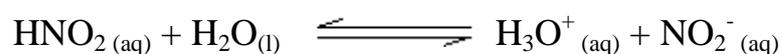


Figure 3.7: Effect of pH on to the removal of nitrite by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 30 mg/L, temperature: 25°C, contact time: 60 min and solid/liquid ratio 0.3 g/50 mL).

The adsorption capacity for AC is higher than that of the CAC at all used pH values. At the initial pH 2, the percentage of nitrite removal by AC No.7 was ~44% higher than that for CAC.

It should be noticed that at lower pH values, nitrite ion may exist in the solution in the HNO_2 form, since HNO_2 is a weak acid with K_a value 5.1×10^{-4} [102].



This should not cause any difficulty, since polarographic measurements did not vary with pH value for same nominal NO_2^- concentrations, as explained earlier.

3.3.1.4 Effect of Temperature on Adsorption

The effect of temperature on nitrite adsorption onto AC No.7 and CAC was investigated in the range 10-40°C. The results are shown in Figure 3.8. The Figure shows that nitrite adsorption increased with higher temperature. AC No.7 shows more adsorption performance than CAC at different temperatures. Percentage of nitrite removal at 40°C onto AC No.7 is ~50% higher than CAC at 60 min adsorption time.

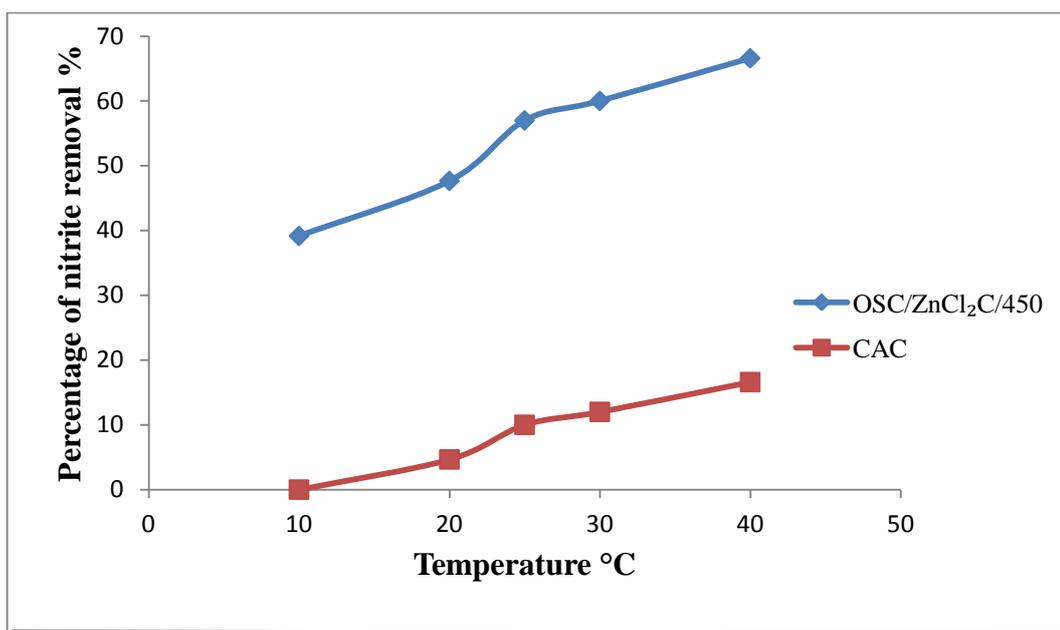


Figure 3.8: Effect of temperature on nitrite removal by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 30 mg/L, initial pH: 4, contact time: 60 min and solid/liquid ratio 0.30 g/50 mL).

3.3.1.5 Effect of Particle Size

The effect of AC No.7 particle size on nitrite uptake was studied. The percentage of nitrite removal for PAC and GAC were 100% and 85% respectively. Such a tendency is not unexpected, as smaller particle sizes have higher relative external surface areas and consequently higher uptakes.

3.3.1.6 Effect of Contact Time

Effect of contact time on removal of nitrite by AC No.7 and CAC are shown in Figure 3.9.

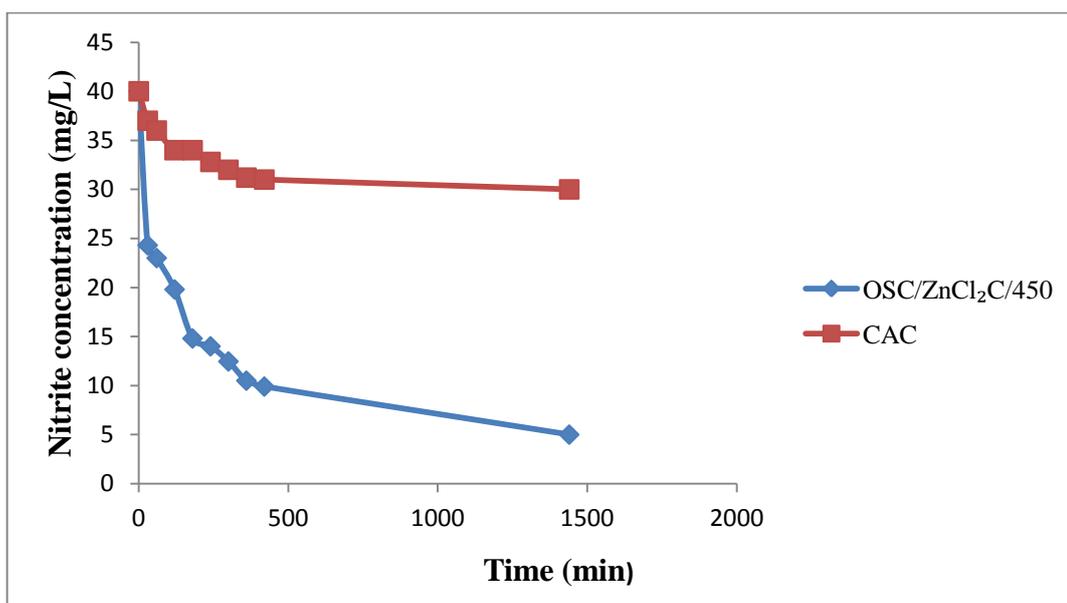


Figure 3.9: Effect of contact time on the removal of nitrite by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).

Maximum nitrite removal for AC and CAC were 87.5% and 25% respectively, for adsorbent dosage 0.250 g/ 50 mL, initial pH 4, 25°C, and initial conc 40 mg/L in 24 h. Nitrite removal is fast for the first 3.5-4 h and then it was slowed down with time until saturation.

3.3.1.7 Kinetics of Nitrite Adsorption

The mechanism of adsorption depends on the physical and/or chemical properties of the adsorbent and on the mass transfer process as well [24]. In order to find out the controlling mechanism of this adsorption process, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model were used to test the experimental data. These mechanisms are briefly described as follows:

Pseudo-first-order model: Lagergren proposed a pseudo-first-order kinetic model [8, 24, 80, 103]. The integral form of this model is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3.1)$$

Pseudo-second-order model: The adsorption kinetics may also be described by a pseudo-second-order mechanism [8, 24, 80]. The linearised-integral form of the model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.2)$$

Intra-particle diffusion model: According to the theory proposed by Weber and Morris [80, 104]. The Weber and Morris equation is:

$$q_t = k_p t^{1/2} + A \quad (3.3)$$

where q_e and q_t (mg/g) are the amounts of adsorbate per unit mass of adsorbent at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. In addition, k_2 (g/mg min) and k_p ($\text{mg/g min}^{1/2}$) are the pseudo-second-order rate constant of adsorption and the rate constant of intra-particle diffusion respectively, and (A) gives an idea about the thickness of the boundary layer [105].

In order to quantify the applicability of pseudo-first-order model and pseudo-second-order model, linear plots of $\log(q_e - q_t)$ versus t and (t/q_t) versus t were used to check the fit of the above models respectively. If any

of these models is applicable, it should give a linear relationship, from which the parameters and their correlation coefficients (R^2) can be determined. The intra-particle diffusion model has been applied in literature in three different forms:

A) The amount of adsorption at any time (q_t) is plotted against $t^{1/2}$ to get a straight line that is forced to pass through the origin. This means that the rate is not limited by mass transfer across the boundary layer [106].

B) Multi-linearity (two or three steps are involved) in q_t versus $t^{1/2}$ plot is considered. In this form, the first step is attributed to the diffusion of adsorbate to the external surface of adsorbent. The second step describes the gradual adsorption step, where intra-particle diffusion rate is rate-limiting. The third step is the finale equilibrium step, where the solute moves slowly from larger pores to micropores causing a slow adsorption rate [80, 104].

C) The amount of adsorption at any time (q_t) is plotted against $t^{1/2}$ to obtain a straight line, but does not necessarily pass through the origin. This means that the rate is limited by mass transfer across the boundary layer [107].

In order to investigate the mechanism of nitrite adsorption process on AC No.7 and CAC, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model were all used to test the experimental data. The results are shown in Figures 3.10-3.12 respectively.

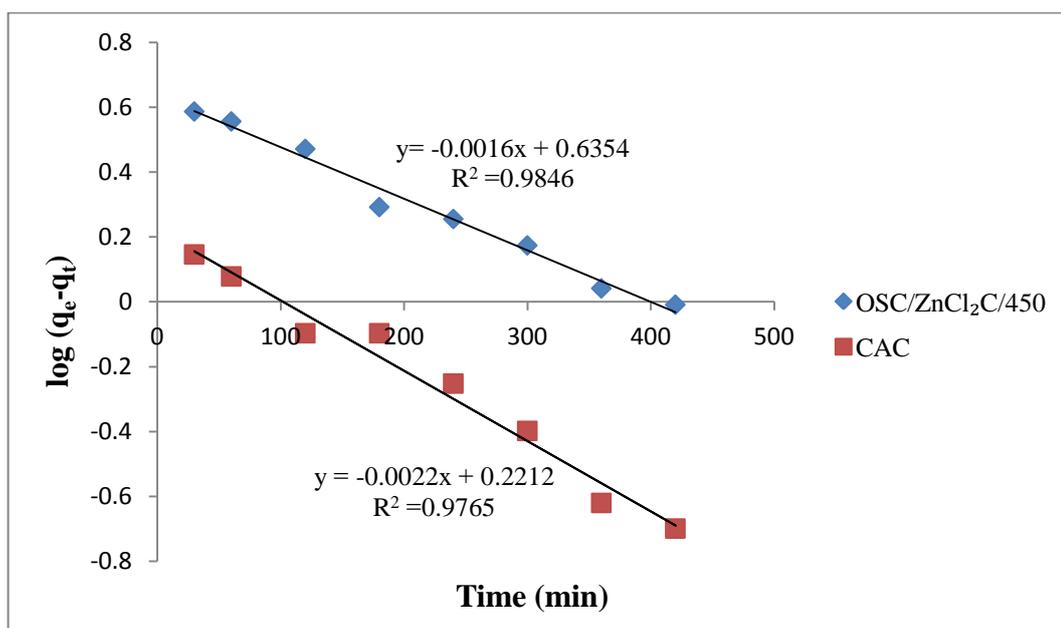


Figure 3.10: Kinetics of nitrite removal according to the pseudo-first-order model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).

The correlation coefficients and other parameters calculated for the pseudo-first-order model and pseudo-second-order model are listed in Table 3.2. From Table 3.2, it is clear that the correlation coefficient values (R^2) of the pseudo-second-order model for both adsorbents are slightly greater than those obtained for the pseudo-first-order model. On the other hand, $q_{e (exp)}$ values for the first-order-rate expression do not agree with the calculated ones obtained from the linear plots. In contrast, $q_{e (calc)}$ values for the second-order-model are close to $q_{e (exp)}$ for both adsorbents. Thus, higher correlation coefficients of pseudo-second-order equation and the $q_{e (calc)}$ values close to the experimental ones indicates that the pseudo-second-order kinetic model might be more suitable to describe the kinetic of adsorption processes of nitrite onto both adsorbents. This suggests that

during the adsorption of nitrite, there was chemisorption between the adsorbent surface and adsorbate [104, 108-109].

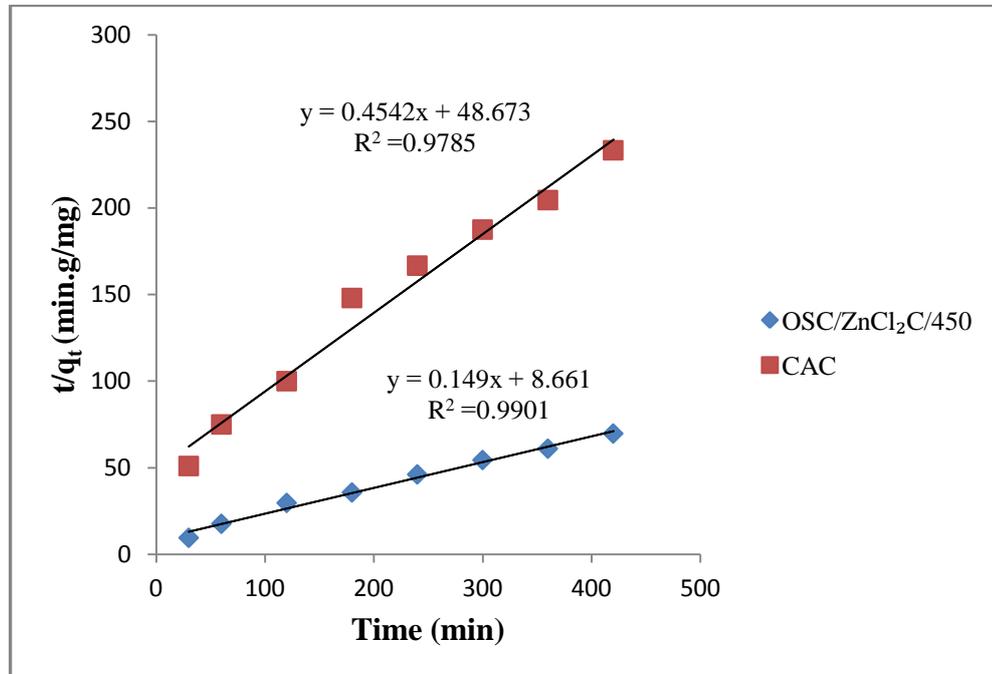


Figure 3.11: Kinetics of nitrite removal according to the pseudo-second-order model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).

Table 3.2: Pseudo-first-order and pseudo-second-order kinetic model parameters for nitrite adsorption onto AC No.7 and CAC at 30°C.

Adsorbent	q _e (exp) (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k ₁ (min ⁻¹) 10 ⁻³	q _e (calc) (mg/g)	R ²	k ₂ (g/mg min) 10 ⁻³	q _e (calc) (mg/g)	R ²
AC No.7	7.000	3.684	4.319	0.984	2.563	6.711	0.990
CAC	2.000	5.066	1.664	0.976	4.232	2.202	0.978

Table 3.3 summarizes correlation coefficients and other parameters for nitrite adsorption according to intra-particle diffusion model. The straight line in Figure 3.12 does not pass through the origin, this implies that the rate is limited by mass transfer across the boundary layer.

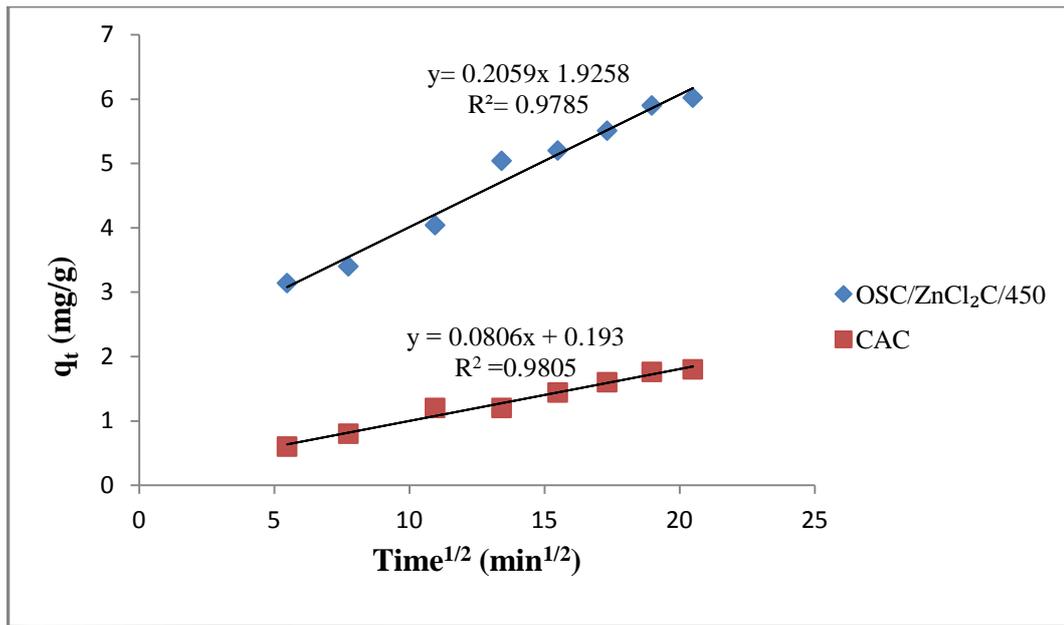


Figure 3.12: Kinetics of nitrite removal according to the intra-particle diffusion model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 40 mg/L, initial pH: 4, temperature: 30°C and solid/liquid ratio 0.250 g/50 mL).

Table 3.3: Intra-particle diffusion kinetic model parameters for nitrite adsorption onto AC No.7 and CAC at 30°C.

Adsorbent	k_p (mg/g min ^{1/2})	R^2	A
AC No. 7	0.205	0.979	1.952
CAC	0.080	0.981	0.193

3.3.1.8 Adsorption Isotherms

In order to design an adsorption system, it is important to study the adsorption isotherms. This is because they give an idea about the adsorption capacity [24, 110]. Adsorption isotherm for nitrite onto AC at 30°C is given in Figure 3.13.

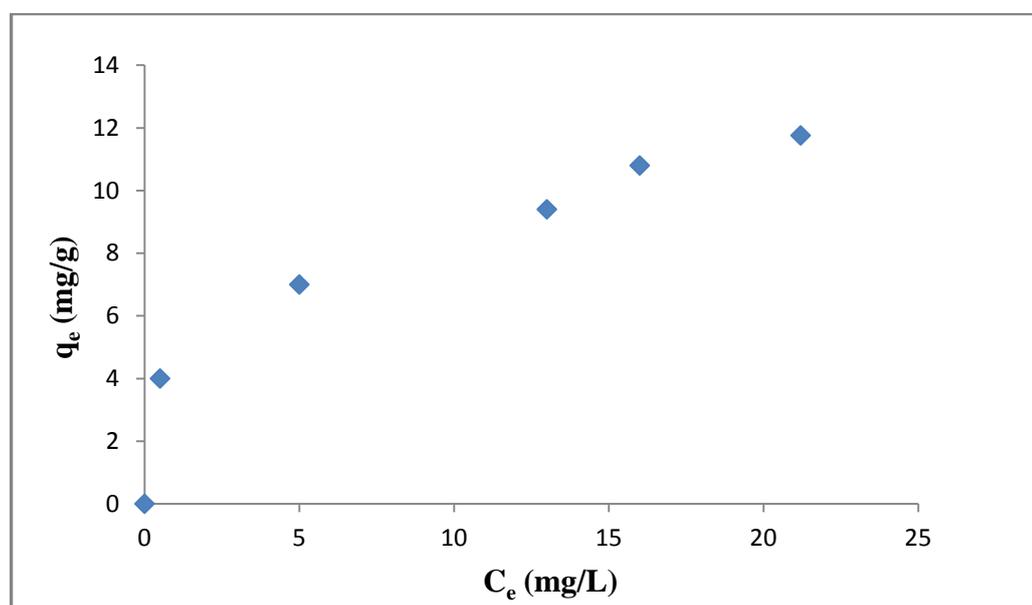


Figure 3.13: Equilibrium adsorption isotherm of nitrite onto OSC/ZnCl₂C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).

In this study, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of nitrite adsorbed and its equilibrium concentration in solution at 30°C. The fitting of adsorption data to Langmuir and Freundlich isotherm equations was investigated by plotting C_e/q_e versus C_e Figure 3.14 and $\log q_e$ versus $\log C_e$ Figure 3.15 respectively.

The adsorption isotherm parameters which were calculated from the slope and intercept of the linear plots using the linearized form of the Langmuir (equation 2.4) and Freundlich (equation 2.5) together with the R^2 values are given in Table 3.4.

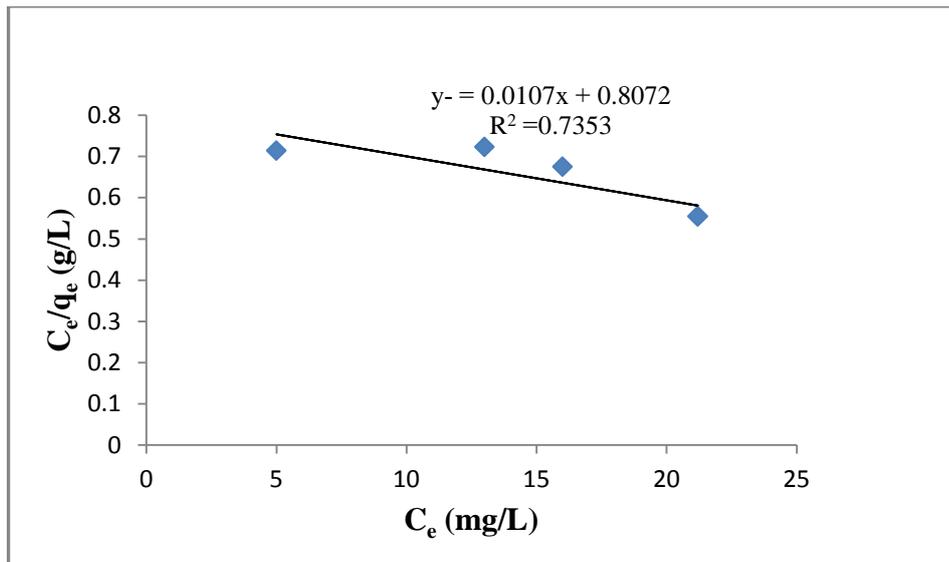


Figure 3.14: Langmuir plot for nitrite adsorption onto OSC/ZnCl₂C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).

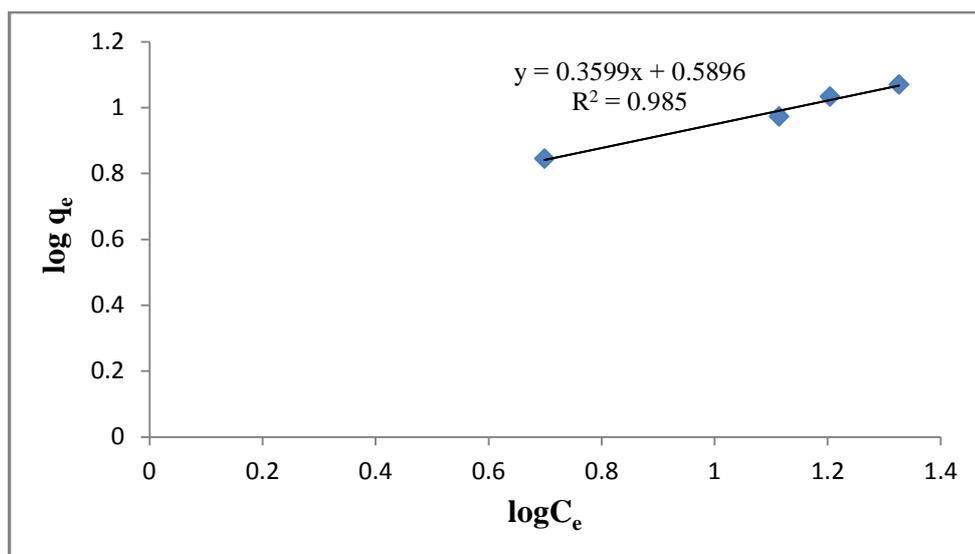


Figure 3.15: Freundlich plot for nitrite adsorption onto OSC/ZnCl₂C/450 (AC No.7) at (temperature: 30°C, initial pH: 4 and solid/liquid ratio 0.250 g/50 mL).

Table 3.4: Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrite adsorption onto AC No7.

Isotherm	Langmuir			Freundlich		
Adsorbate	Parameters			Parameters		
	Q_o (mg/g)	b (L/mg)	R²	K_F ((mg/g) (L/mg) ^{1/n})	n	R²
NO₂⁻	-93.457	-0.013	0.735	3.887	2.779	0.985

Negative values for the Langmuir isotherm constants indicate the inadequacy of the isotherm model to explain this adsorption process [111]. Data in Table 3.4 indicate the fitting of the Freundlich model to this adsorption process.

Adsorption capacity and intensity is affected by the Freundlich adsorption isotherm constants. In general, the adsorption capacity of the adsorbent increases as the K_F value increases. Adsorption process is considered as beneficial when n value is between 1 and 10 [8]. So nitrite adsorption on the activated carbon (OSC/ZnCl₂C/450) prepared in this study is a beneficial adsorption. Comparison of nitrite adsorption capacity on this adsorbent with different materials used for nitrite adsorption is given in Table 3.5. The results indicate that adsorption efficiency of AC prepared here is higher than earlier reported values.

Table 3.5: Comparison of specific nitrite adsorption capacity by different materials.

Material	Adsorption capacity (mg/g)	Nominal NO_2^- conc. (mg/L)	Reference
Sepiolite	0.65	25	10
Powder Activated carbon	1.17	25	10
AC No.7	7.00	40	This work
CAC	2.00	40	This work

3.3.2 Nitrate Adsorption Experiments

3.3.2.1 Effect of Adsorbent Type

The percentage of nitrate removal on different adsorbents is shown in Figure 3.16.

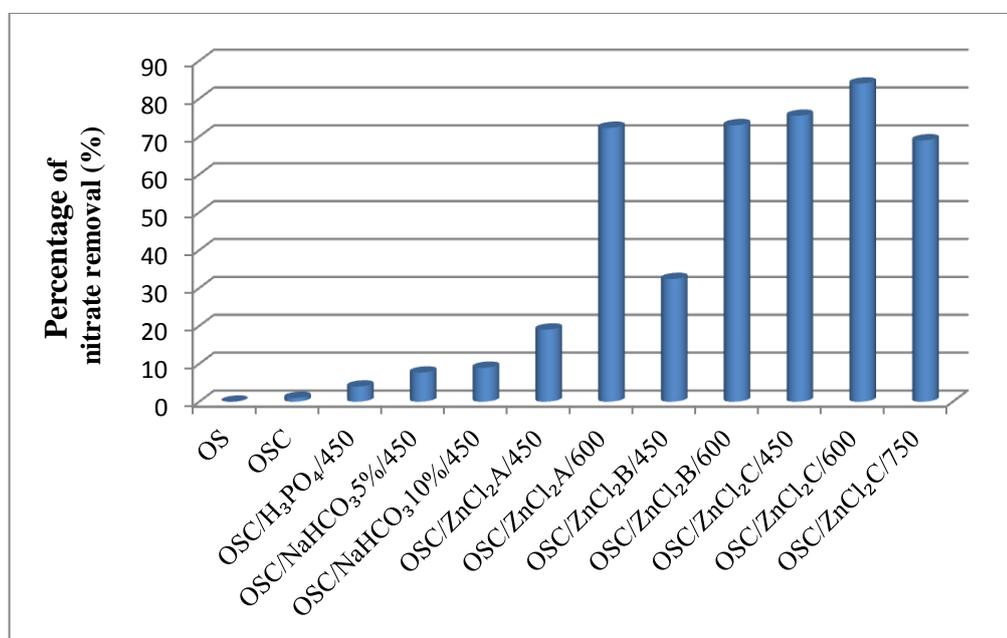


Figure 3.16: Percentage of nitrate removal by activated carbon prepared by different techniques at (initial conc: 100 mg/L, initial pH: 4, temperature: 25°C, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).

The Figure shows that ZnCl_2 -activated carbon has greater adsorption capacity than H_3PO_4 -activated carbon and NaHCO_3 - activated carbon. This observation can be explained by the fact that there was high surface area available for nitrate adsorption on the surfaces of ZnCl_2 -activated carbon. As the produced activated carbon (OSC/ $\text{ZnCl}_2\text{C}/450$) is an efficient and economic adsorbent it was used in the next adsorption experiments.

3.3.2.2 Effect of pH on Adsorption

The effect of initial pH on the removal of nitrate by AC No.7 and CAC is shown in Figure 3.17. Contact time was 60 min, where the equilibrium was reached.

The adsorption of nitrate from aqueous solution onto the surface of activated carbon is highly dependent on solution pH. However, the effect in AC No.7 is more pronounced than that of the CAC. The reason for good removal of nitrate at lower pH is the electrostatic attraction between nitrate ions and the positively charged surface site on the adsorbent. The adsorption capacity for AC No.7 is higher than that of the CAC at all pH values. At the initial pH 2 the percentage of nitrate removal by AC No.7 was ~34.6% higher than that for CAC.

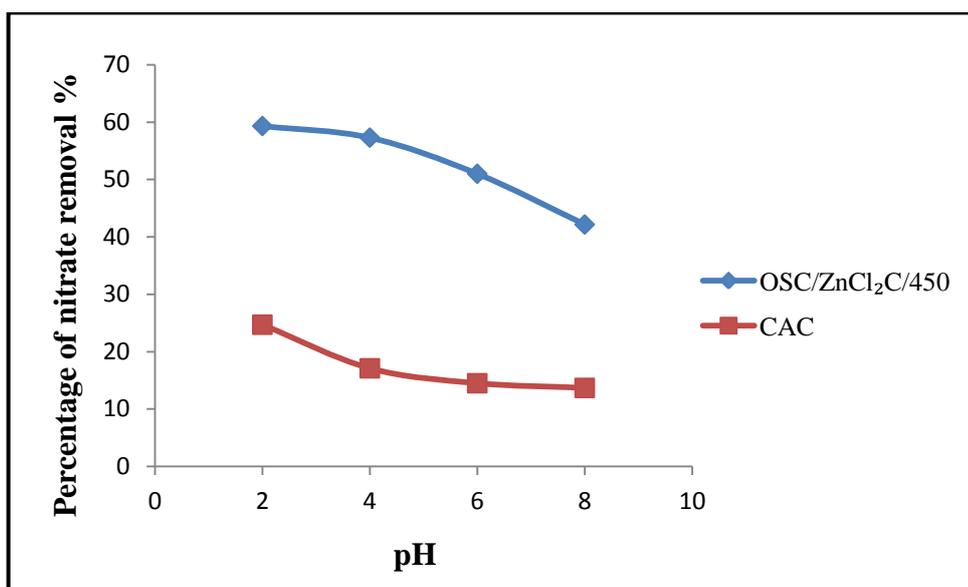


Figure 3.17: Effect of pH on nitrate removal by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 150 mg/L, temperature: 25°C, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).

3.3.2.3 Effect of Adsorption Temperature

The effect of temperature on nitrate adsorption onto AC No.7 and CAC was investigated in the temperature range 10-40°C. The results are presented in Figure 3.18.

The Figure shows that the nitrate adsorption slightly increased at lower temperature. Changing in adsorption performance is not significantly affected by temperature. This behavior adds to the adsorbent advantages. Thus the adsorbent can be used in surface water purification under various temperatures without affecting the adsorbent efficiency. The prepared AC No.7 showed higher adsorption performance than CAC at different temperatures. Percentage of nitrate removal at 10°C by AC No.7 is ~35.70% higher than by CAC after 60 min.

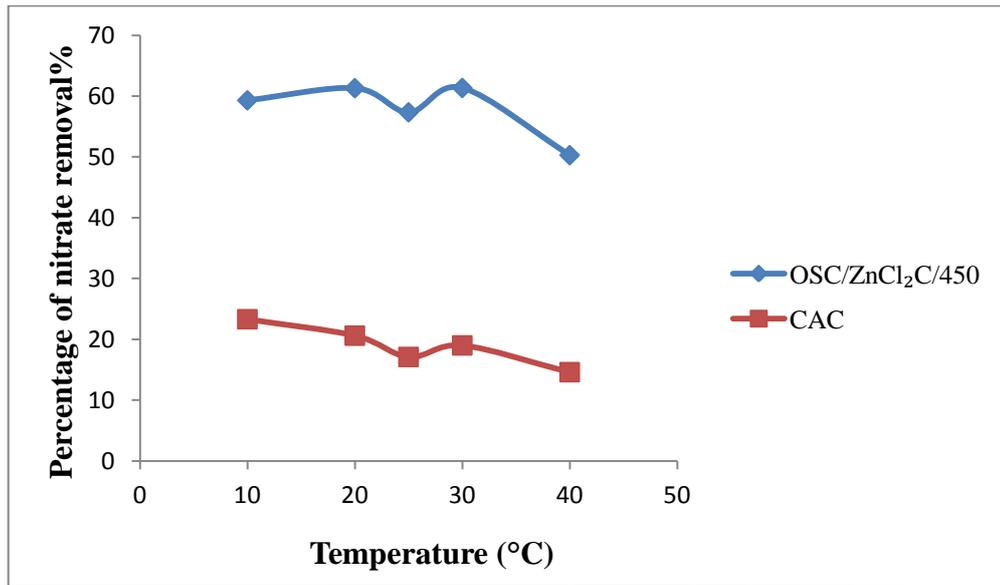


Figure 3.18: Effect of temperature on nitrate removal by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 150 mg/L, initial pH: 4, contact time: 60 min and solid /liquid ratio 1.00 g/50 mL).

3.3.2.4 Effect of Contact Time

Effects of contact time on removal of nitrate by AC No.7 and CAC are shown in Figure 3.19.

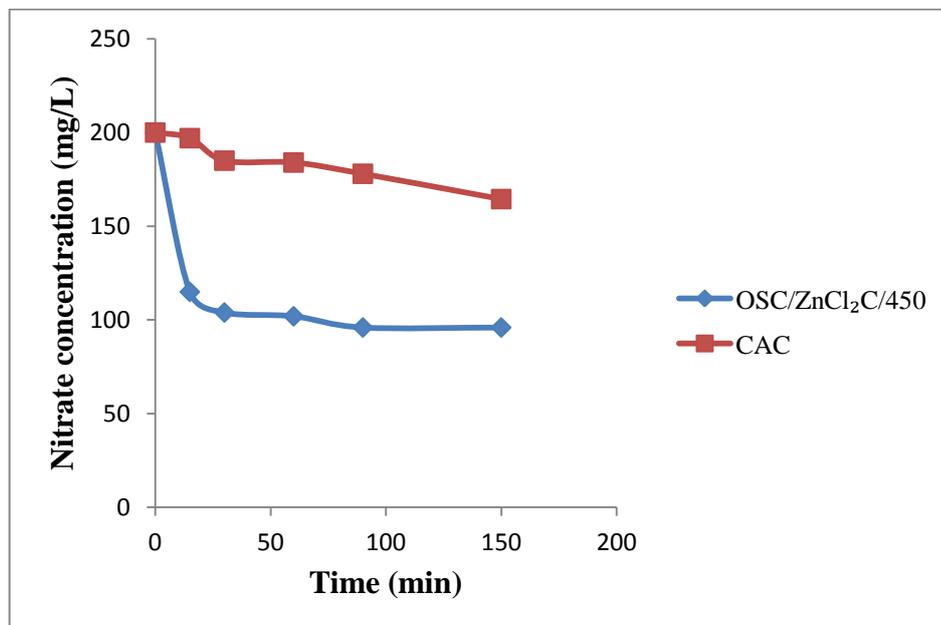


Figure 3.19: Effect of contact time on nitrate removal by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).

The Figure indicates that nitrate adsorption onto AC No.7 and CAC increases when increasing treatment time starting from “0 to 30” min and then becomes constant after about 40 min. The percentage of nitrate removal by AC No.7 was higher ~68.5% than by CAC.

3.3.2.5 Kinetics of Nitrate Adsorption

In order to investigate the mechanism of this adsorption process, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model were all used to test the experimental data. The results are shown in Figures 3.19-3.21 respectively.

From the linear plots of $\log (q_e - q_t)$ versus t and t/q_t versus t , Figure 3.20 and Figure 3.21 respectively, the correlation coefficients and kinetics parameters have been calculated. Table 3.6 summarizes these data. The data show good agreement between experimental and calculated values of q_e for AC No.7 based on the pseudo-second-order model. On the other hand, good agreement between experimental and calculated values of q_e for the CAC based on the pseudo first-order model is noticed. The correlation coefficient of the first-order-model for AC No.7 (0.793) was also smaller than for CAC (0.938), but the correlation coefficient of the second-order-model was smaller for CAC (0.637) than for AC No.7 (0.999). These results indicate the applicability of the first-order-model to describe the nitrate adsorption process on the CAC. The data also indicate applicability of the second-order-model for nitrate adsorption process on the activated

carbon prepared from this study, suggesting that chemisorption process took place [104, 108-109].

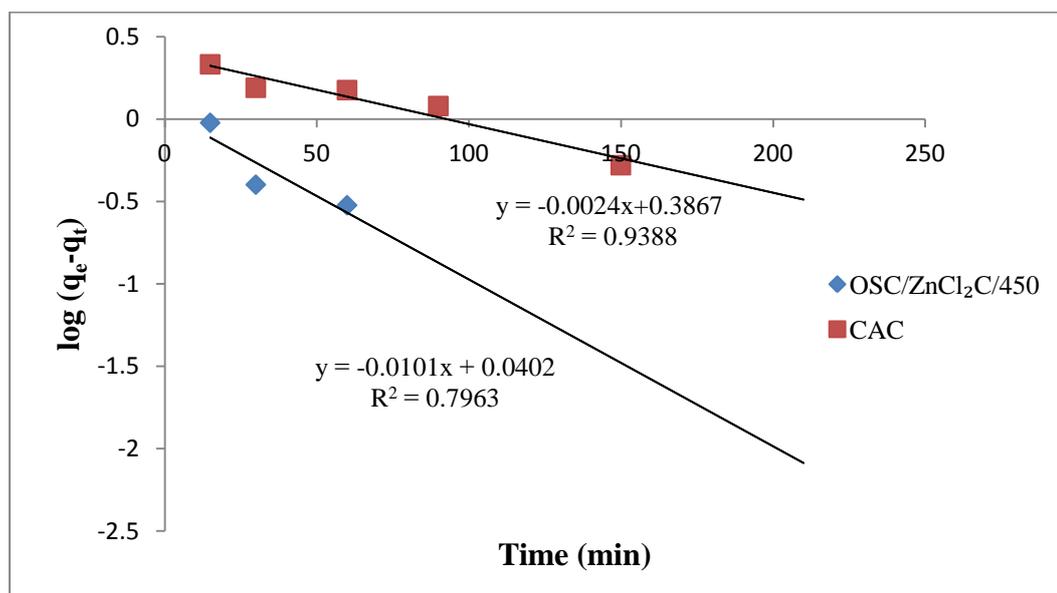


Figure 3.20: Kinetics of nitrate removal according to the pseudo-first-order model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).

The values of the intra-particle diffusion constants and the correlation coefficients obtained from the linear plots of q_t versus $t^{1/2}$, given in Figure 3.22, are summarized in Table 3.7. Figure 3.22 implies that the rate of nitrate adsorption onto AC No.7 is limited by mass transfer across the boundary layer, while nitrate adsorption onto CAC is not limited by mass transfer across the boundary layer.

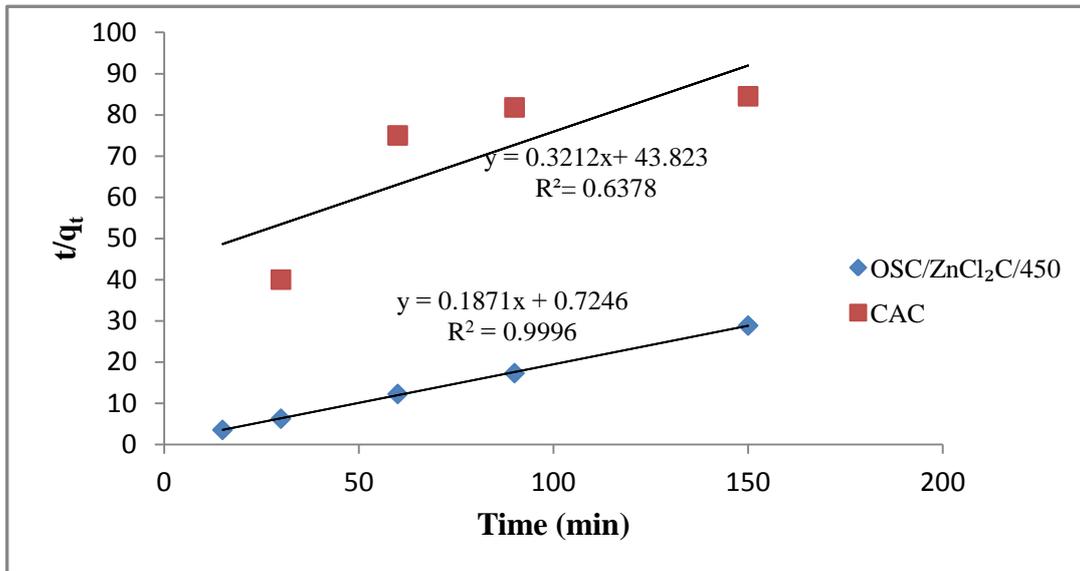


Figure 3.21: Kinetics of nitrate removal according to the pseudo-second-order model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).

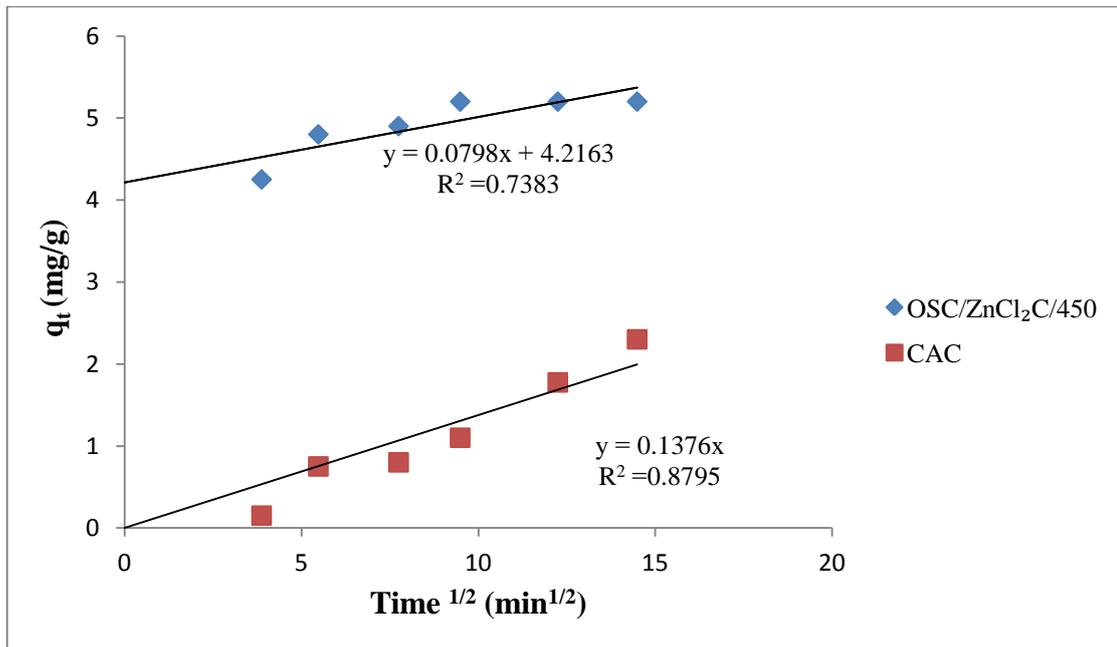


Figure 3.22: Kinetics of nitrate removal according to the intra-particle diffusion model by OSC/ZnCl₂C/450 (AC No.7) and CAC at (initial conc: 200 mg/L, initial pH: 4, temperature: 20°C and solid/liquid ratio 1.00 g/50 mL).

Table 3.6: Pseudo-first-order and pseudo-second-order kinetic model parameters for nitrate adsorption onto AC No.7 and CAC at 20°C.

Adsorbent	q_e (exp) (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (min ⁻¹) 10 ⁻³	q_e (calc) (mg/g)	R^2	k_2 (g/mg min) 10 ⁻³	q_e (calc) (mg/g)	R^2
		AC No.7	5.200	23.260	1.097	0.793	48.306
CAC	2.300	9.673	2.436	0.938	2.355	3.113	0.637

Table 3.7: Intra-particle diffusion kinetic model parameters for nitrate adsorption onto AC and CAC at 20°C.

Adsorbent	k_p (mg/g min ^{1/2})	R^2	A
AC No. 7	0.079	0.738	4.216
CAC	0.138	0.879	–

3.3.2.6 Adsorption Isotherms

In this study, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of nitrate adsorbed and its equilibrium concentration in solution at 20°C. Adsorption isotherm for nitrate onto AC No.7 at 30°C is given in Figure 3.23.

The fitting of adsorption data, to Langmuir and Freundlich isotherm equations was investigated by plotting C_e/q_e versus C_e and $\log q_e$ versus

$\log C_e$ which are presented in Figure 3.24 and Figure 3.25 respectively. The adsorption isotherm parameters which were calculated from the slope and intercept of the linear plots using the linearized form of the Langmuir and Freundlich equations given in equation 2.4 and 2.5 respectively, together with the R^2 values are given in Table 3.8.

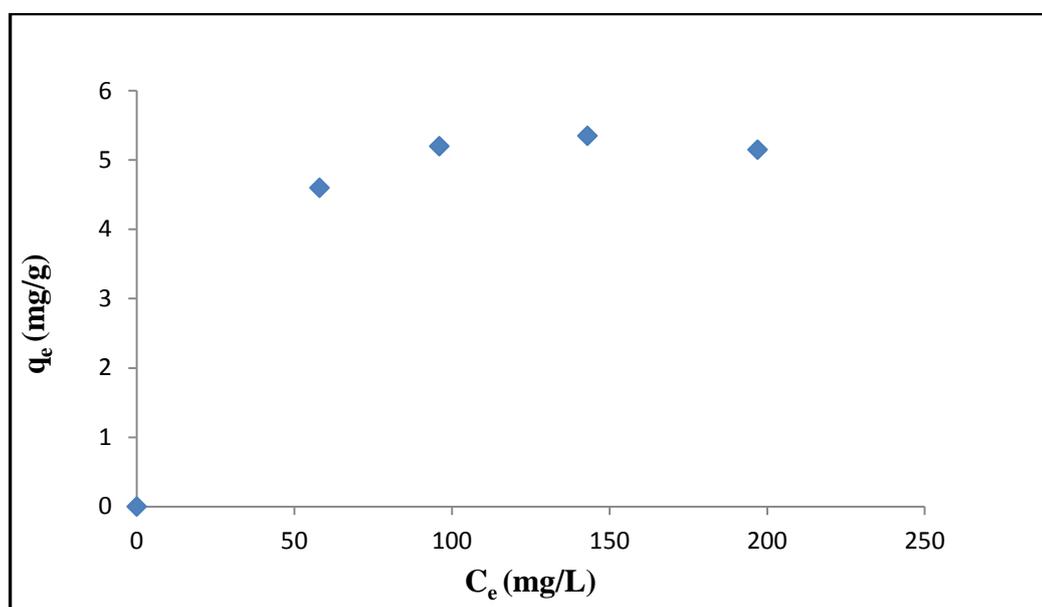


Figure 3.23: Equilibrium adsorption isotherm of nitrate onto OSC/ZnCl₂C/450 (AC No.7) at (temperature: 20°C, initial pH: 4 and solid/liquid ratio 1.00 g/50 mL).

It is clear from the R^2 values that the Langmuir isotherm is fitted to the experimental data better than Freundlich isotherm model. The Langmuir isotherm shows that adsorption will increase with increasing anion concentration up to a saturation point, in which all of the sites are occupied. Any further increase in concentrations of anions will not increase the amount of adsorbed anions on adsorbents. On average, a favourable

adsorption tends to have Freundlich constant (n) between 1 and 10. Larger value of n (smaller value of $1/n$) implies stronger interaction between the adsorbent and the adsorbate [8]. From Table 3.8 it can be seen that (n) value was between 1 and 10 showing favourable adsorption of nitrate onto the activated carbon prepared here. Comparison of nitrate adsorption capacity on this adsorbent with other reported materials used for nitrate adsorption is given in Table 3.9.

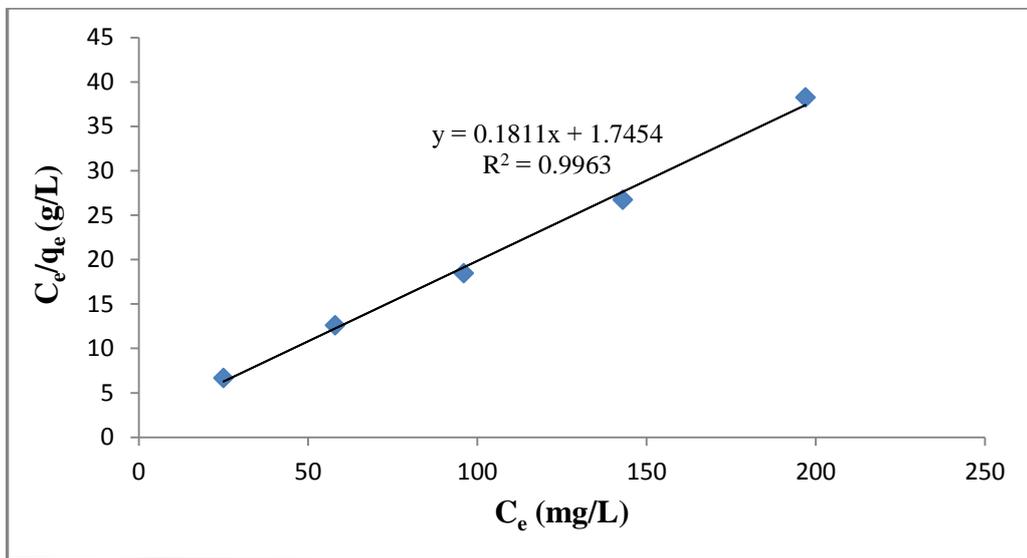


Figure 3.24: Langmuir plot for nitrate adsorption onto OSC/ZnCl₂C/450 (AC No.7) at (temperature; 20°C, initial pH: 4 and solid/liquid ratio 1.00 g/50 mL).

Table 3.8: Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrate adsorption onto AC No7.

Isotherm	Langmuir			Freundlich		
	Parameters			Parameters		
Adsorbate	Q_0 (mg/g)	b (L/mg)	R^2	K_F ((mg/g) (L/mg) ^{1/n})	n	R^2
NO_3^-	5.525	0.104	0.996	2.269	5.949	0.869

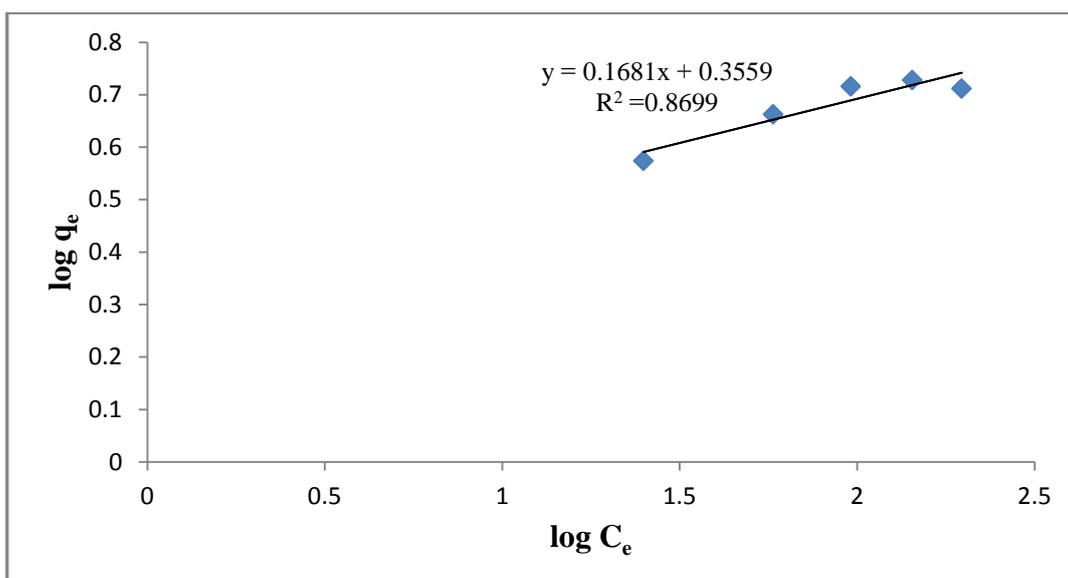


Figure 3.25: Freundlich plot for nitrate adsorption onto OSC/ZnCl₂C/450 (AC No.7) at (temperature: 20°C, initial pH: 4 and solid/liquid ratio: 1.00 g/50 mL).

Table 3.9: Comparison of specific nitrate adsorption capacity by different materials.

Material	Mono layer capacity of the adsorbent (Q_0) (mg/g)	Nominal NO_3^- conc. (mg/L)	Reference
Wheat straw charcoal	1.10	110.75	14
Mustard straw charcoal	1.30	110.75	14
CAC; retail outlet of Eureka Frobes Limited Aquaquad	1.22	110.75	14
Bamboo powder charcoal	1.25	0-44.30	9
CAC; Nacalai tesque Model 079-39, Japan	1.09	0-44.30	9
Coconut activated by ZnCl_2	10.30	20	25
AC No.7	5.53	100-300	This work

3.3.2.7 Adsorption Thermodynamics

The thermodynamic parameters including changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) of adsorption can be calculated by means of the following equations [104].

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3.4)$$

Where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_d is the distribution coefficient which can be calculated as:

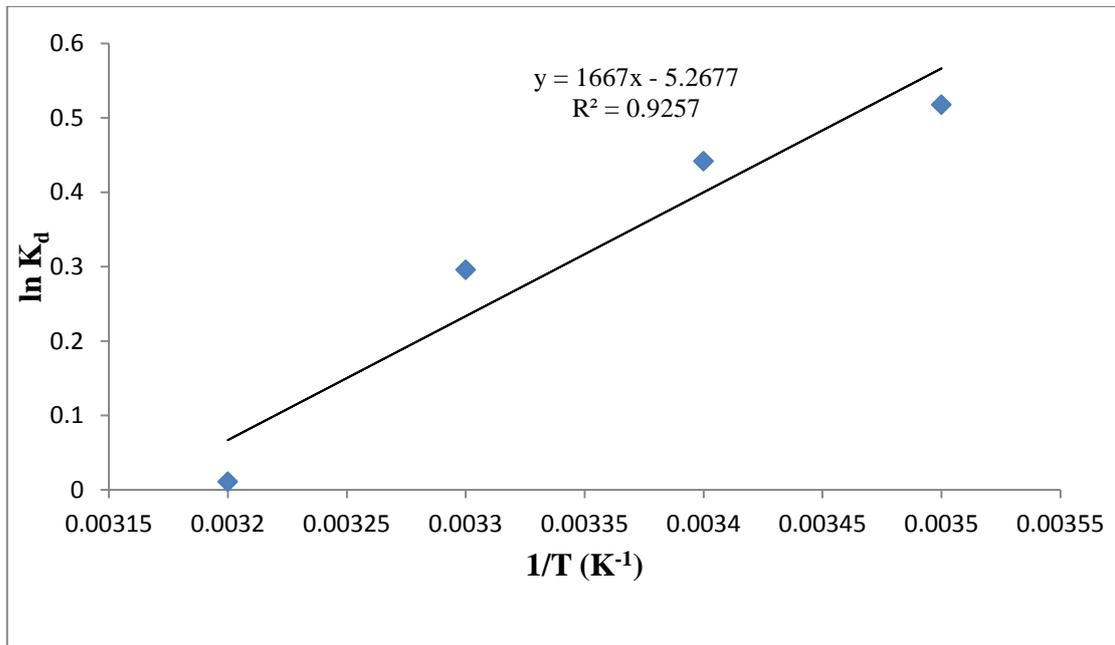
$$K_d = \frac{C_{Ae}}{C_e} \quad (3.5)$$

where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration. ΔG° can be calculated using the relation below:

$$\Delta G^\circ = -RT \ln K_d \quad (3.6)$$

The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear variation of $\ln K_d$ with reciprocal temperature (1/T) Figure 3.26. The obtained thermodynamic values are given in Table 3.9.

A:



B:

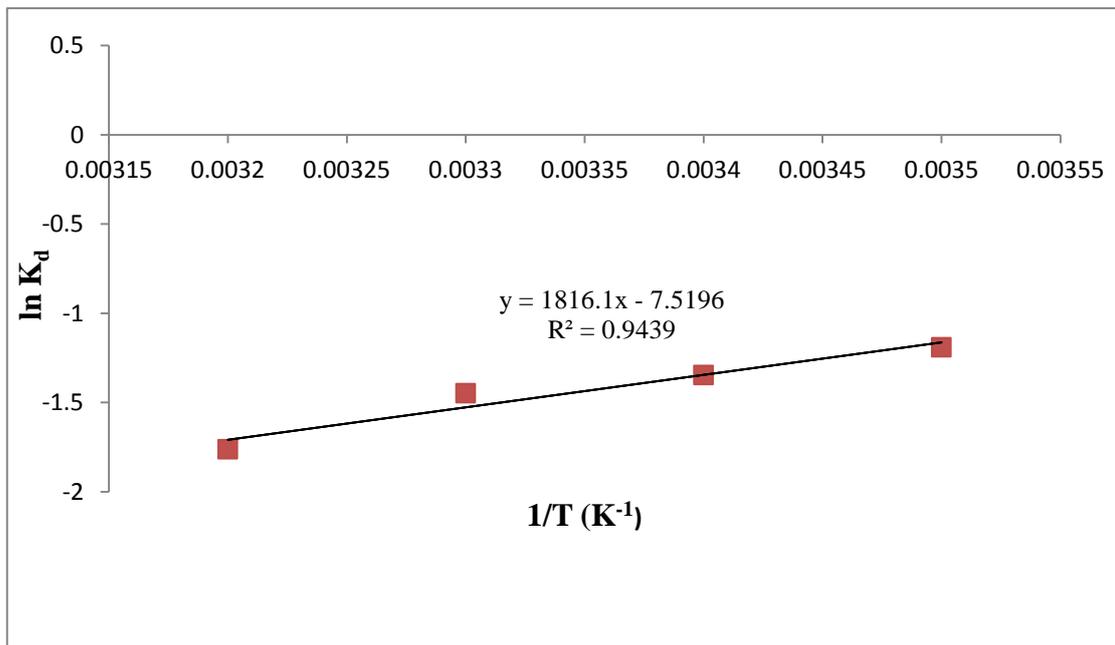


Figure 3.26: Plot of $\ln K_d$ versus $1/T$ for 150 mg/L NO_3^- concentration, (A) adsorption on AC No.7 and (B) adsorption on CAC.

Table 3.10: The values of the thermodynamic of adsorption at various temperatures and various adsorbents.

Adsorbent	ΔH° (KJ/mol)	ΔS° (J/mol K)	ΔG° (KJ/mol)			
			283K	293K	303K	313K
AC No.7	-13.859	-43.795	-1.217	-1.075	-0.745	-0.028
CAC	-15.099	-62.518	2.798	3.276	3.645	4.582

The negative values of ΔG° at various temperatures indicated that the adsorption process on AC No.7 is spontaneous and the negative values of ΔH° show that the adsorption is exothermic. Furthermore, the negative value of entropy indicates the affinity of adsorbent material for nitrate ion. Increase in the value of ΔG° with rise in temperature show that the adsorption is more favorable at lower temperature.

3.4 Nitrate Desorption Experiments

Nitrate desorption experiments were studied for the purpose of recovering and reusing the adsorbing carbon. Nitrate desorption experiments were conducted under different pH values, the percentage of desorbed nitrate was affected by the pH value, as shown in Figure 3.27.

The Figure shows that desorption increased with increasing pH. At pH 11, up to 20% of pre-adsorbed ions were desorbed. This low percentage gives an idea about the occurrence of relatively strong interactions between

the AC surface and the pre-adsorbed nitrate ions. The results indicate efficient binding of nitrate by the adsorbent.

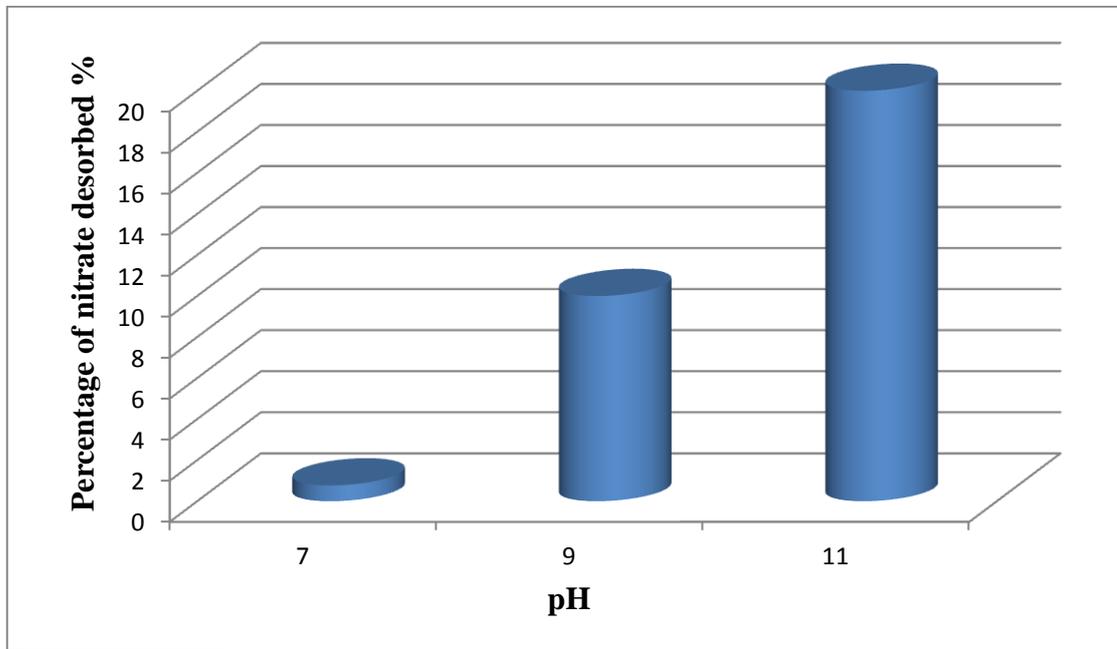


Figure 3.27: Percentage of nitrate desorption at different pH values.

Conclusion:

- 1- Carbon activated by ZnCl_2 was effective for nitrite and nitrate removal more than the other adsorbents.
- 2- Experimental data showed that nitrite and nitrate adsorption increase by decreasing pH value of the solution.
- 3- The results showed that equilibrium time for nitrite adsorption is 24h and for nitrate adsorption is 60 min.
- 4- The results showed that the change in NO_2^- and NO_3^- adsorption uptakes onto OSC/ $\text{ZnCl}_2\text{C}/450$ with temperature is small.
- 5- Nitrite adsorption uptake slightly increases when temperature is increased, whereas nitrate adsorption slightly increases at lower temperature.
- 6- The results showed that nitrate and nitrite adsorptions onto OSC/ $\text{ZnCl}_2\text{C}/450$ can be described by pseudo-second-order model.
- 7- Rates of adsorption of nitrate on both prepared and CAC are greater than those for nitrite.
- 8- Equilibrium adsorption data on OSC/ $\text{ZnCl}_2\text{C}/450$ for nitrate followed Langmuir isotherm, where nitrite adsorption followed Freundlich for nitrite. The adsorption capacity of OSC/ $\text{ZnCl}_2\text{C}/450$ for nitrite is larger than that for nitrate. This shows the value of AC produced in this work.
- 9- The results show that the adsorption uptakes, onto OSC/ $\text{ZnCl}_2\text{C}/450$, for nitrite and nitrate were higher than that of CAC.

10-Since olive stone is a waste material from agriculture activity, the treatment method seems to be economic.

Suggestions for Future Work:

Although the strategy used in this work has given very promising results, there are number of areas that need further investigation. These include:

- 1- Studying the adsorption efficiency of the prepared activated carbon on combined nitrate and nitrite solutions at the same time.
- 2- Studying the effect of other ions in the aqueous medium on both nitrate and nitrite adsorption.
- 3- More study on the effect of AC particle size on nitrate and nitrite adsorption.
- 4- Studying chemical composition of the raw material and the prepared ACs.
- 5- More study of NO_2^- ion desorption from adsorbents.
- 6- More analysis on the water quality after treatment with AC.
- 7- Checking the possibility for using the by-product of the adsorption processes as fertilizers.
- 8- More study on the economic feasibility of the activated carbon prepared from olive stones.
- 9- More investigation on mode of action of ZnCl_2 in carbon activation.

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Appendix

SEM micrographs for the raw material (olive stones) and for some of the prepared activated carbon under different conditions.

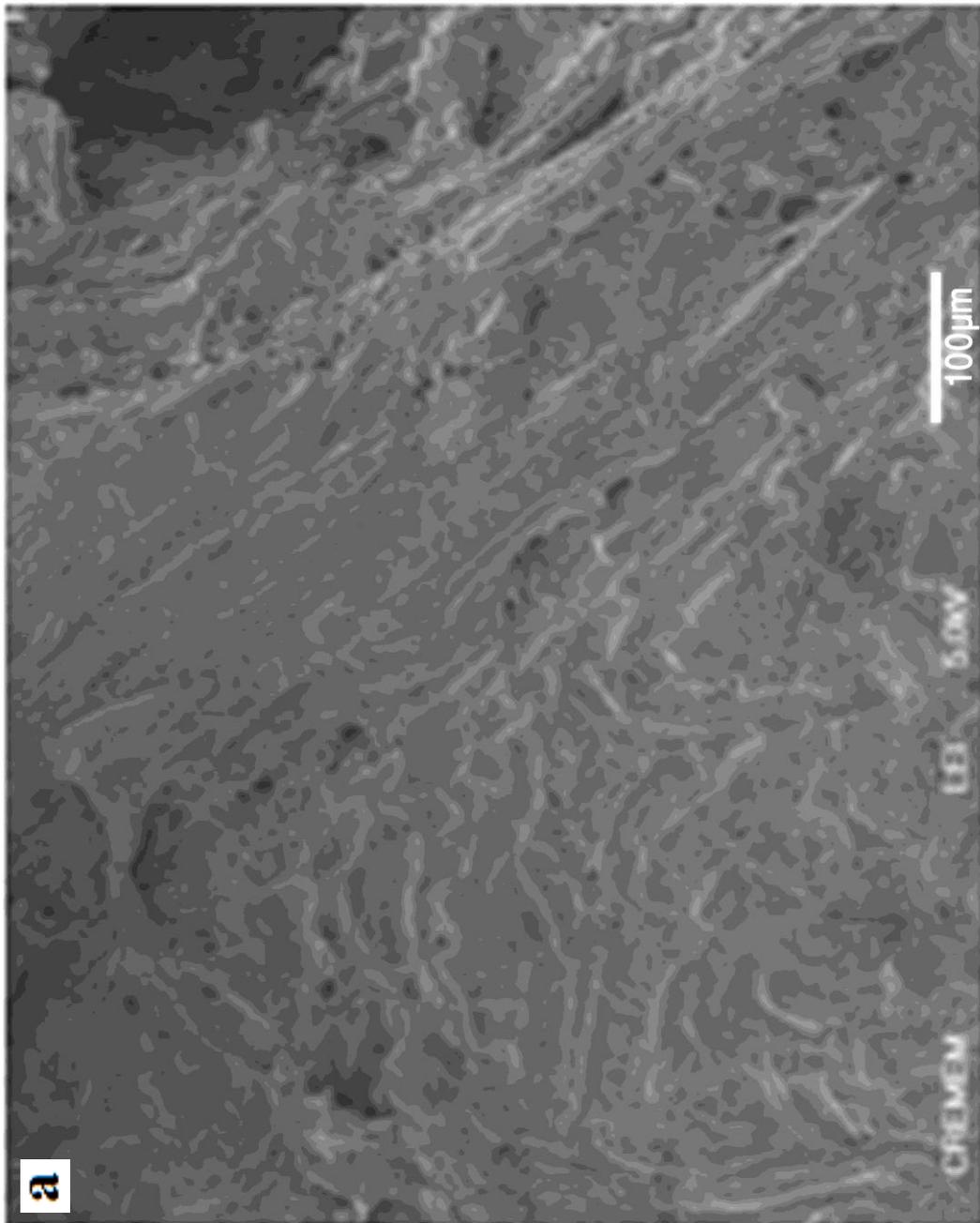


Figure 1: SEM micrograph of OS.

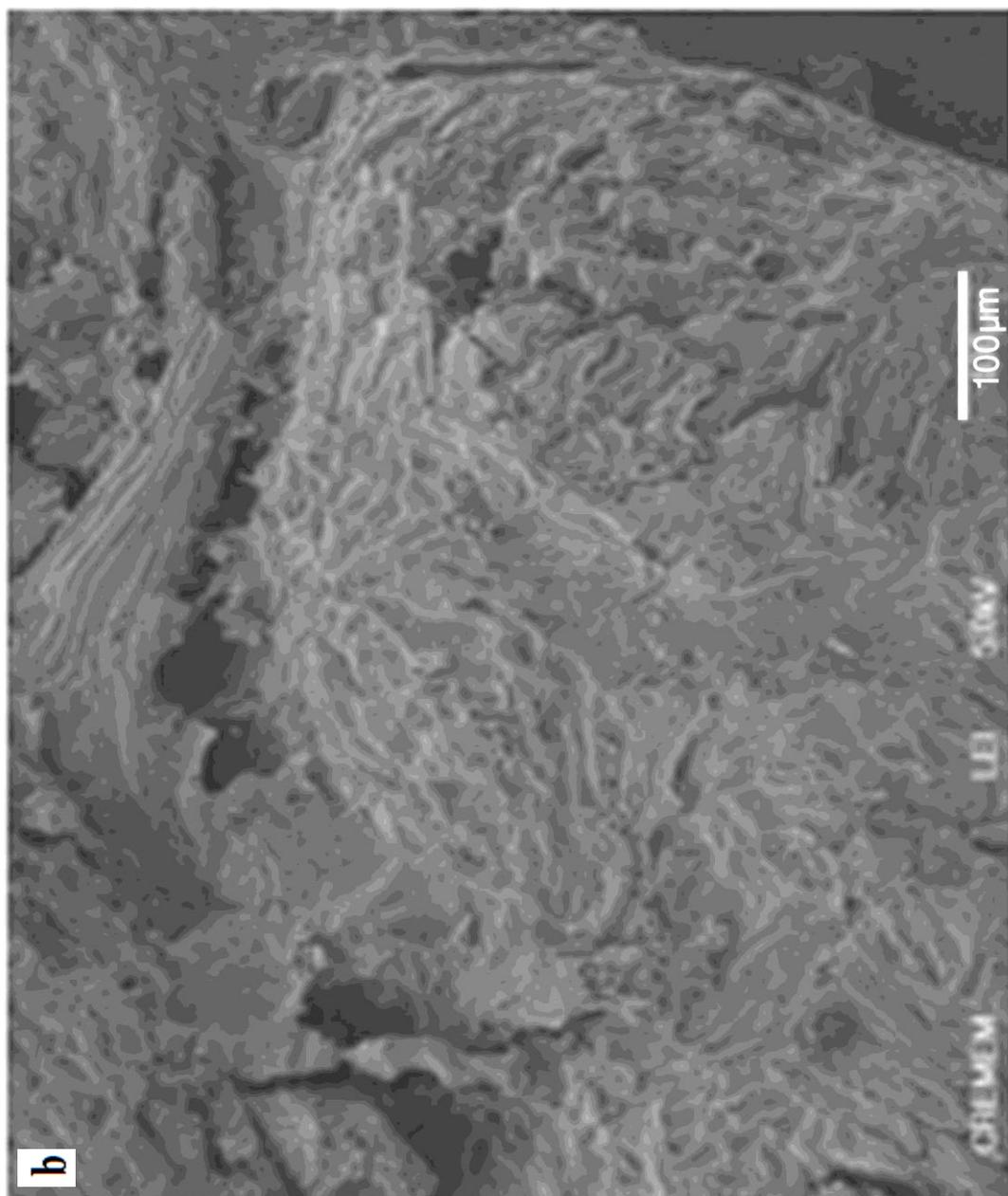


Figure 2: SEM micrograph of OSC/H₃PO₄/450.

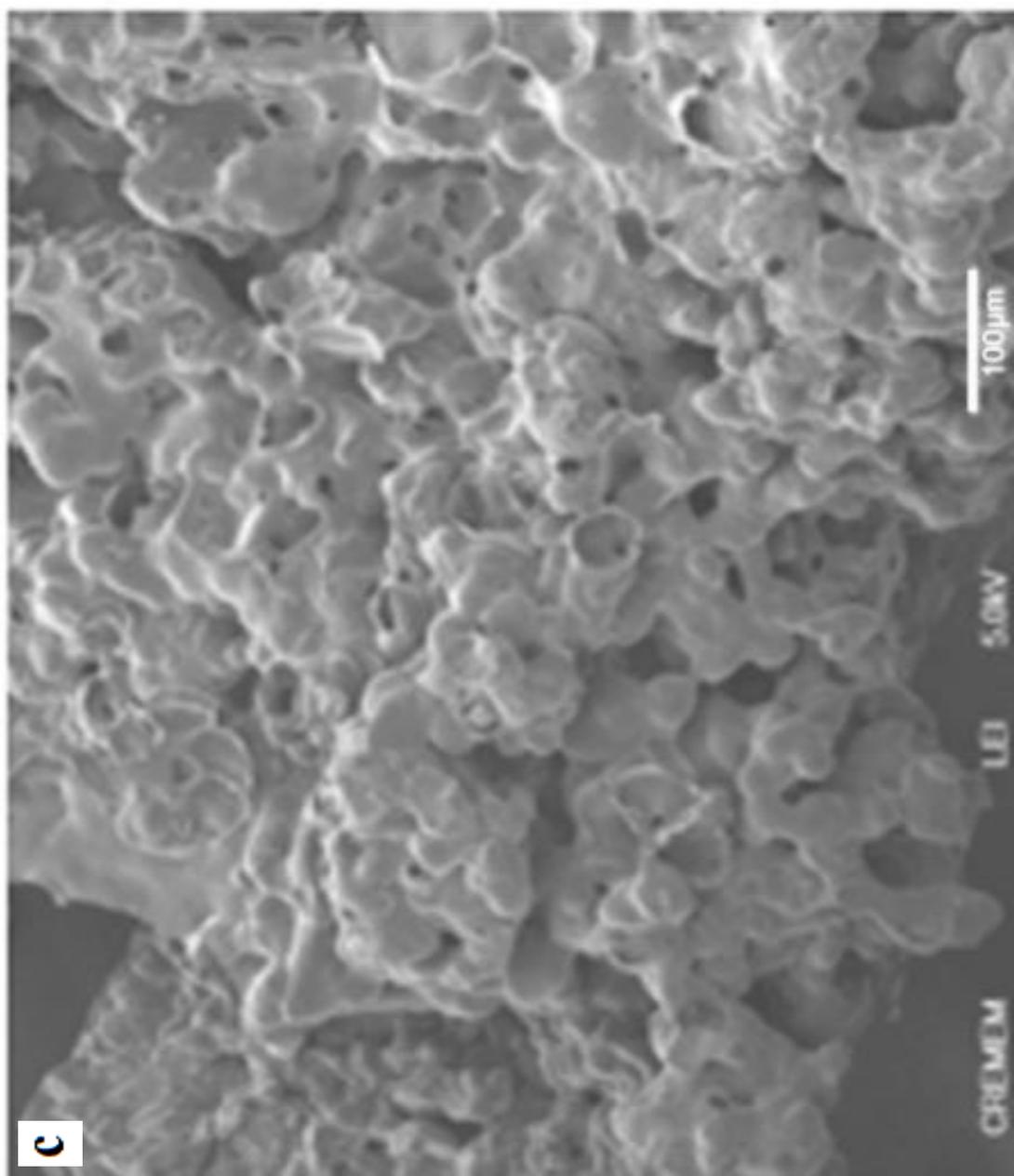


Figure 3: SEM micrograph of OSC/ZnCl₂B/450.

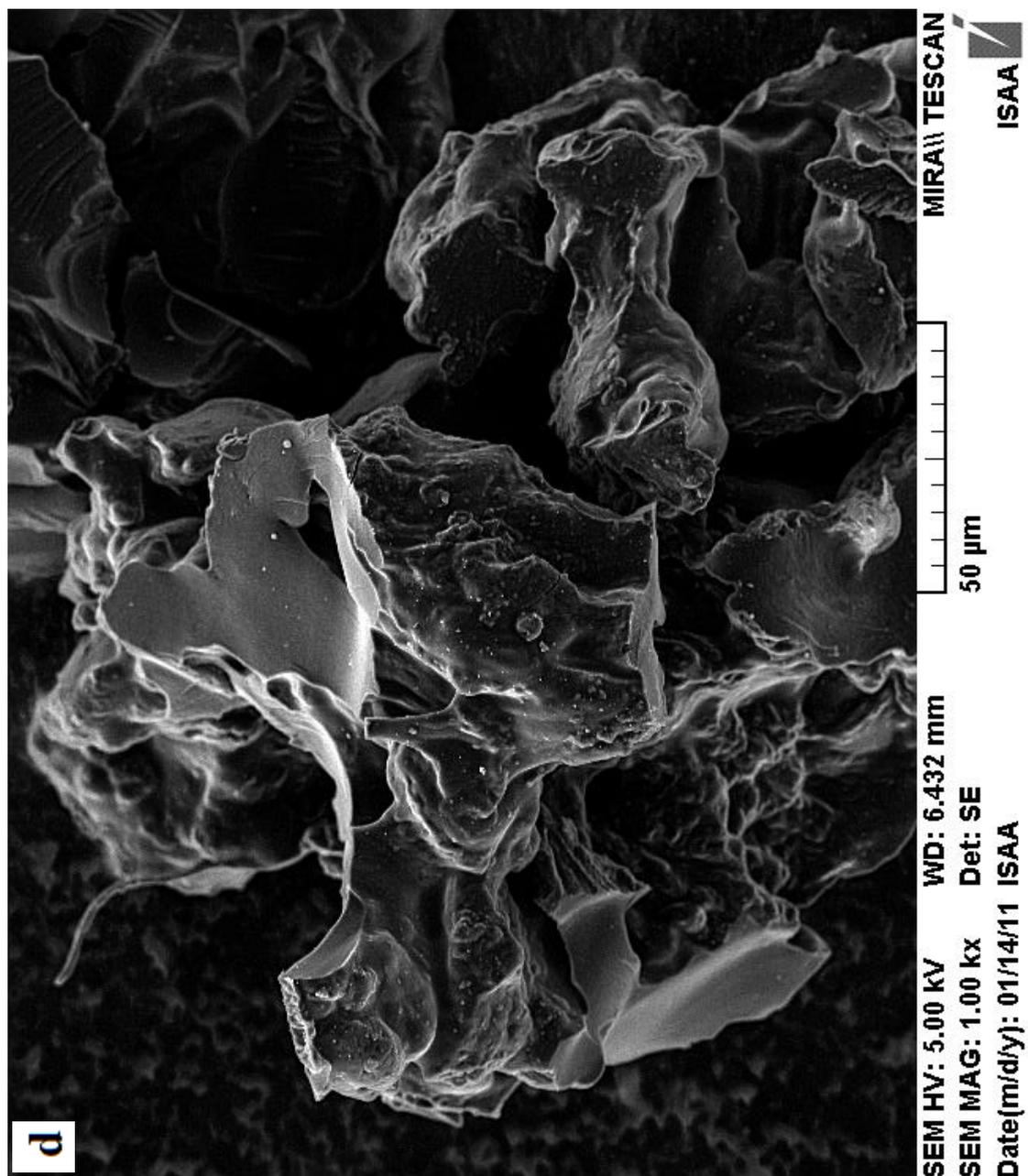


Figure 4: SEM micrograph of OSC/ZnCl₂C/450.

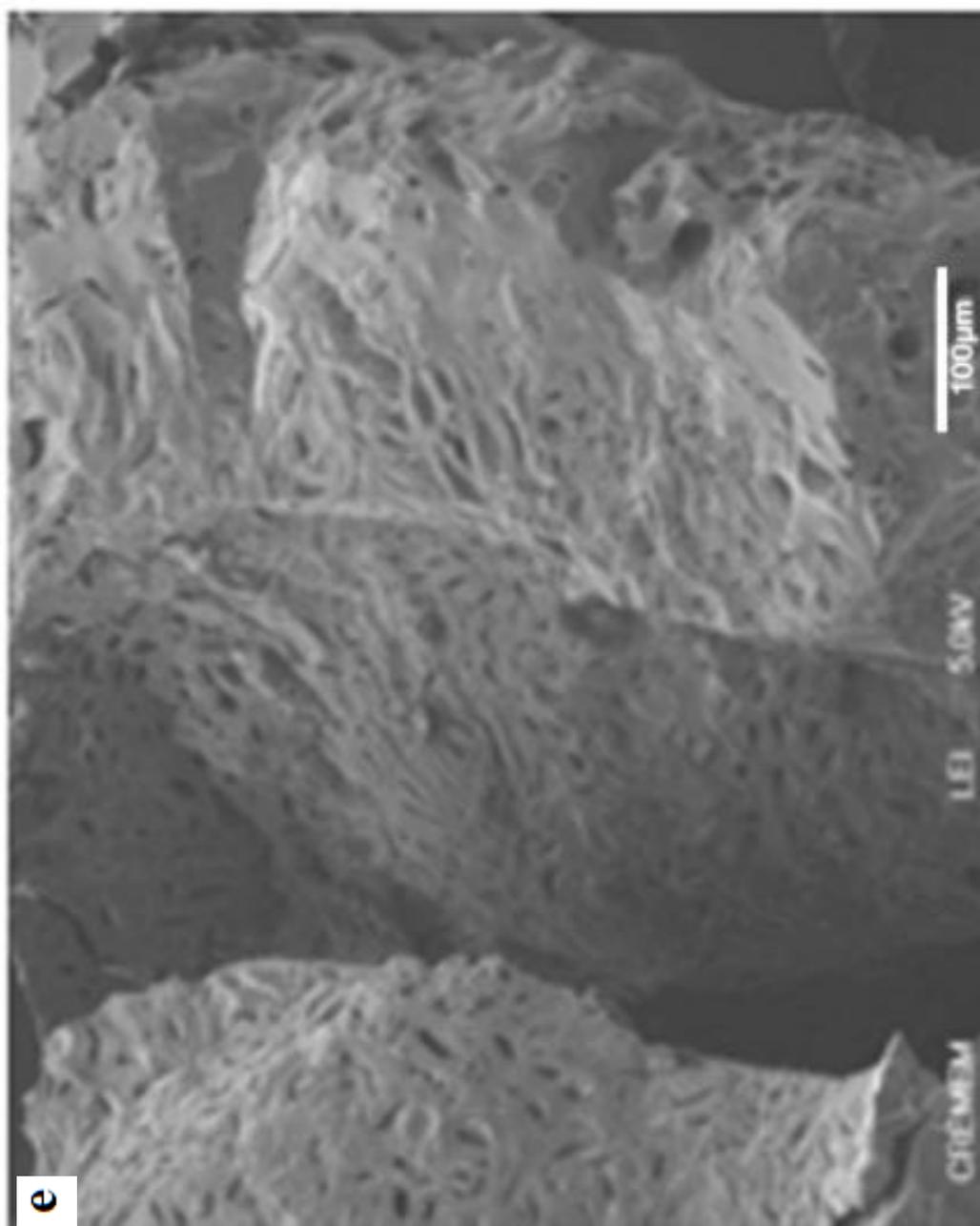


Figure 5: SEM micrograph of OSC/ZnCl₂B/600.

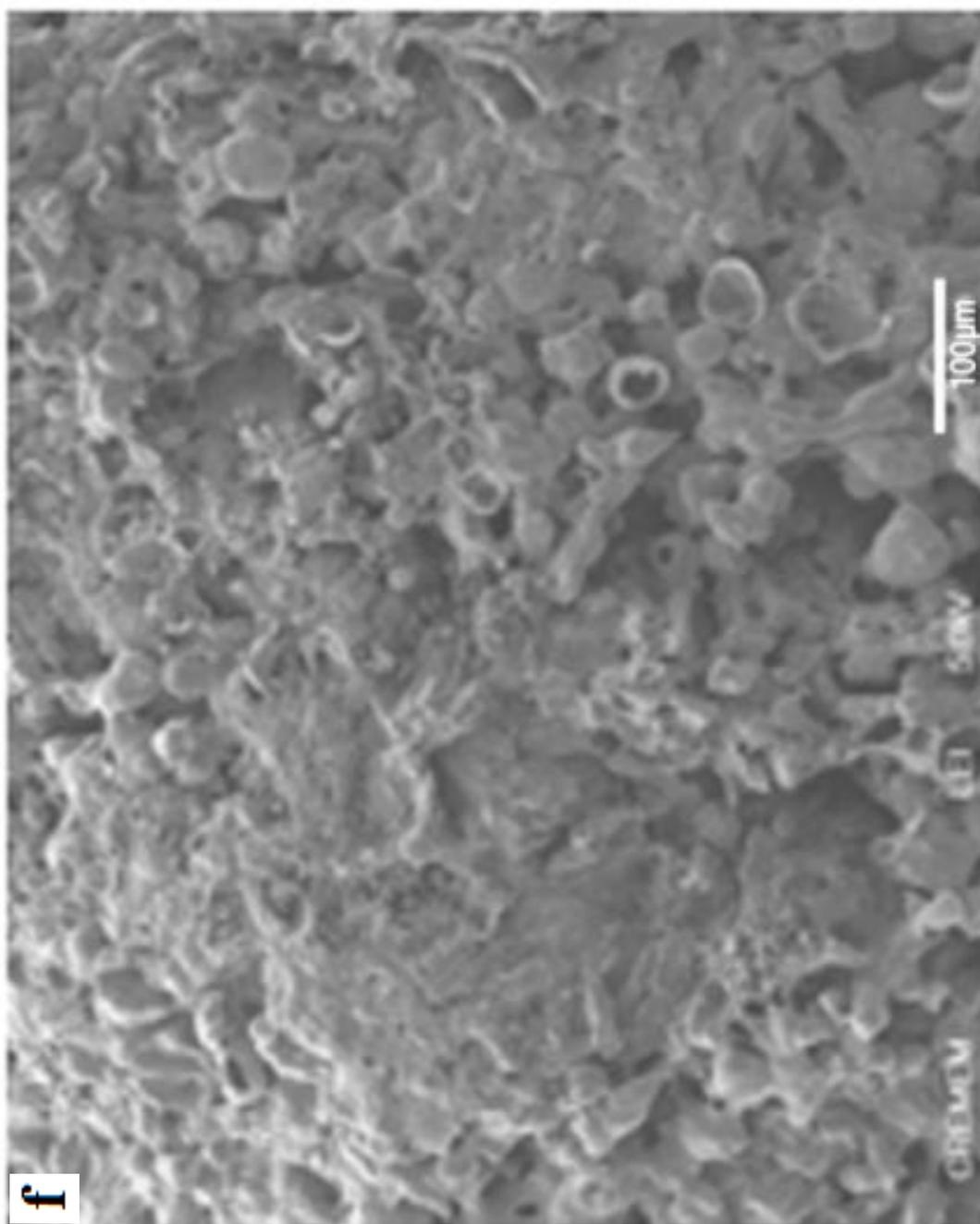


Figure 6: SEM micrograph of OSC/ZnCl₂A/600.

جامعة النجاح الوطنية
كلية الدراسات العليا

ازالة أيونات النتترات والنتريت من المحاليل المائية بوساطة الكربون المنشط المحضر
من نوى الزيتون

إعداد
هبة نصّار عزت نصّار

إشراف
أ. د. حكمت هلال
أ. د. عامر الهموز

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

2012م

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الملخص

يواجه العديد من مناطق العالم مشكلة تلوث المياه السطحية والجوفية بأيونات النترا والنتريت. ويعتبر الاستخدام المفرط للأسمدة الكيميائية مصدراً أساسياً لهذا التلوث. يهدف هذا البحث الى المساهمة في ازالة أيونات النترا والنتريت من مياه الشرب باستخدام طريقة اقتصادية وعملية يمكن تطبيقها في المناطق النائية. ولتحقيق هذا الهدف تم القيام بالعديد من التجارب المخبرية على امتزاز أيونات النترا والنتريت بوساطة الكربون المنشط .

في بحثنا هذا حاولنا تقليل سعر الكربون المنشط عن طريق تحضيره بالاعتماد على مادة أولية متوفرة ورخيصة وهي الجفت، كما تم اختيار طرق تحضير قليلة الكلفة. بالإضافة لكون الجفت مادة رخيصة ومتوفرة في البيئة فان اختيارها كمادة أولية لتحضير الكربون يقلل من النفقات الصلبة ومن اثار الجفت السلبية على البيئة.

تم في هذه الدراسة تحضير عدة أنواع من الكربون المنشط من أجل الحصول على نوع ذي كفاءة عالية في امتزاز أيونات النترا و النتريت. ولتحقيق ذلك تم دراسة استخدام أكثر من مادة لتنشيط الكربون المحضر من نوى الزيتون، مثل كلوريد الخارصين وحمض الفوسفوريك وبايكربونات الصوديوم، بحيث كانت النسبة بين كتلة نوى الزيتون وكتلة العامل المنشط (1:1). وتمت عملية التنشيط باكثر من طريقة تطعيم، كما وتمت عملية التفحيم على درجات حرارة مختلفة تتراوح بين 450-750°س.

وجد أن الكربون المحضر باستخدام كلوريد الخارصين كعامل منشط هو الأفضل في امتزاز النترات والنترت، كما أنه أعطى نتائج أفضل من الكربون المنشط التجاري عندما تمت المقارنة بينهما. كشفت صور مسح المجهر الإلكتروني (SEM) أن الكربون الذي تنشيطه باستخدام كلوريد الخارصين يحتوي على كمية أعلى من التجايف مقارنة بالأنواع المحضرة باستخدام عوامل منشطة أخرى. وكانت أعلى مساحة سطح تم حسابها باستخدام طريقة امتزاز حمض الخليك، للكربون المنشط باستخدام كلوريد الخارصين (AC No.7) هي $1482.57 \text{ م}^2/\text{غم}$.

تم التحقق من خصائص الإمتزاز بواسطة الكربون المنشط والكربون المحضر من نوى الزيتون المنشط باستخدام كلوريد الخارصين من خلال دراسة أثر كمية الكربون و درجة الحموضة ودرجة الحرارة و زمن التعريض وتركيز الملوثات. وتشير النتائج إلى أن فعالية الامتزاز للكربون المنشط OSC/ZnCl₂C/450 (AC No. 7) كانت أعلى من تلك الخاصة بالكربون التجاري. حيث كانت كفاءة الامتزاز للكربون (AC No. 7)، 7.00 و 5.53 ملغ/غم لأيونات النترت والنترات على التوالي. وحين خفض الرقم الهيدروجيني لوحظت زيادة كبيرة في امتزاز النترت والنترات. وتم أيضا دراسة تأثير درجة الحرارة على الامتزاز بواسطة الكربون التجاري و (AC No.7) على درجات حرارة تتراوح بين 10-40 درجة مئوية. وتشير النتائج إلى أن درجة الحرارة تؤثر قليلا على فعالية (AC No. 7) في الامتزاز. هذه الحقيقة تشير إلى أنه يمكن استخدام هذا الكربون في ازالة أيونات النترت والنترات من المياه السطحية والجوفية دون أن تتأثر كفاءته.

تم تفسير نتائج عملية الامتزاز التي تم الحصول عليها عند الاتزان باستخدام معادلة لانجموير وفرندليش. حيث كان نموذج فرندليش أنسب لتفسير امتزاز النترت على

(AC No. 7) عند 30 درجة مئوية. من ناحية أخرى كان نموذج لانجموير هو الأنسب لتفسير

امتزاز النترات على (AC No. 7) عند 20 درجة مئوية.

من أجل التحقق من آليات الامتزاز، تم تطبيق النتائج على ثلاثة نماذج مبسطة للحركة

هي: نموذج الاعتماد من الدرجة الأولى ظاهريا ونموذج الاعتماد من الدرجة الثانية ظاهريا

ونموذج تدفق الدقائق الى داخل الجسيمات. هذا وقد اتفقت البيانات التي تم الحصول عليها لامتنزاز النترت من قبل الكربون التجاري و (AC No. 7) مع نموذج الاعتماد من الدرجة الثانية ظاهريا. أما امتزاز النترات من قبل الكربون التجاري فانفق مع نموذج الاعتماد من الدرجة الأولى ظاهريا بينما كان امتزاز النترات من قبل (AC No. 7) اكثر اتفاقا مع الاعتماد من الدرجة الثانية ظاهريا. تم أيضا حساب بعض ثوابت التيرموديناميك لامتنزاز النترات على الكربون التجاري و (AC No. 7) مثل المحتوى الحراري ΔH° وطاقة غيبس ΔG° والتغير في الاعتلاج ΔS° .

