An-Najah National University Faculty of Graduate Studies

# The Adsorption of Lead using Olive Cake Ash

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# Dedication

I dedicate this work to my family, to my teachers, to my friends, and for all who participated and supported me to end this work.

# Acknowledgments

I am deeply grateful to Allah who guided me and gave me strength to finish this work.

I want to express my gratitude to my supervisors, Dr. Maather Sawalha and Dr. Ibrahim Abu Shqair for their cooperation, feedback and who helped me to develop my skills and to write this thesis and get best results.

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أنا الموقع أدناه، مقدم الرسالة التي تحمل العنوان:

# The Adsorption of Lead using Olive Cake Ash

أقر بأن ما اشتملت عليه هذه الرسالة انما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة اليه حيثما ورد، وأن هذه الرسالة كاملة، أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

#### **Declaration**

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

Student's name:	اسم الطالب:
Signature:	التوقيع:
Date:	التاريخ:

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#### Abstract

The adsorption of Pb(II) ions from aqueous solution using olive cake ash was carried out. The effect of various parameters on the adsorption process such as pH, contact time and temperature were studied. Performed experiments included; binding capacity, stripping, hard cations interferences and adsorption isotherms on adsorption process. Results showed that the maximum adsorption of Pb(II) ions occurred at pH 5, equilibrium was achieved at 40 minutes. The removal of Pb(II) ions increased from 91.3% to 94.5% as the temperature increased from 0°C to 70°C. The binding capacity was determined to be 0.29 mg/g at 28°C. The highest total stripping for Pb(II) ions reached 100 % by 0.5 M HCl. The presence of combined Ca(II) and Mg(II) with Pb(II) ions causes a significant increase in binding. This increase in binding reached maximum (higher by 22%) when the following concentrations of Ca(II) and Mg(II) were present at 2 mM, 4 mM, 20 mM and 400 mM higher than when no Ca(II) and Mg(II) present. The isotherms results showed that the experimental data best obeys Fruindlich and Dubbinin models. Values of  $\Delta G^{\circ}$  at different temperatures (13°C, 23°C and 35°C) were 19.87 KJ/mol, 10.29 KJ/mol and 20.45 KJ/mol, respectively. This indicates that the adsorption process is non spontaneous. In addition, the negative value of  $\Delta H^{\circ}$  means that the adsorption of Pb(II) ions onto treated ash was exothermic, also the value of  $\Delta S^{\circ}$  was negative indicating a decrease in entropy. The values of mean free energy E per molecule sorbate at different temperatures are in the range (8 – 16) KJ/mol. This indicates a chemical adsorption.

### **Chapter One**

### Introduction

The pollution with heavy metal ions is one of the most important environmental problems due to their high toxicity, non-biodegradability, solubility in water and tendency to accumulate in the environment (Uc, ar et al., 2014; Akar & Tunali, 2005). The discharging of the industrial effluents loaded with heavy metals into the surface and ground water represents a threat to human health and environment (Unlu & Ersoz, 2006).

Although several methods have been used to remove heavy metals from the contaminated waters, biosorption has come up as an effective tool in which biomass of different organisms have been tested. It is characterized by its low cost, high efficiency in the removal of heavy metals, as well as being considered as an eco-friendly technique (Volesky & Holan, 1995). Many researchers have proved that the use of biomass derived from agricultural products has the potential to purify polluted water from heavy metals (Abu shqair et al., 2001; Igwe et al., 2005; Sawalha et al., 2006; Abu Sharbeh, 2015; Khan et al., 2016; Kumari, 2017; Shahzad et al., 2017).

This study investigates the effectiveness of olive cake ash as an adsorbent for Pb(II) ions from aqueous solution. It also investigates the optimal conditions such as; pH, temperature, contact time, amount adsorbed, and initial ion concentration for the uptake of lead ions.

#### 1.1. Heavy metals

Heavy metals are metallic elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava & Majumder, 2008). They can be classified as either essential or non-essential heavy metals. Essential heavy metals are necessary for the normal growth and development of living organisms in small concentrations. But they can be toxic when their concentration exceeds the acceptable limit for the organisms. Non-essential heavy metals could be toxic to living organisms even at low concentrations (Abu-shqair et al., 2001; Izah et al., 2017). The toxicity of heavy metals depends on many factors including the dose, route of exposure, and chemical species (Tchounwou et al., 2012).

#### 1.1.1. Lead

Lead is a naturally occurring element and is a member of Group 4 (IVA) of the periodic table, it exists in three oxidation states: Pb(0), Pb(II), and Pb(IV). It is a mixture of four stable isotopes, <sup>208</sup>Pb (51-53%), <sup>206</sup>Pb (23.5-27%), <sup>207</sup>Pb (20.5-23%), and <sup>204</sup>Pb (1.35-1.5%). In the environment lead metal is found in Pb(II) form (Abadin et al., 2007).

Lead is a chemical element that is toxic even at low concentrations. It affects the central nervous system, kidney, liver, and gastrointestinal system, and it may directly or indirectly cause diseases such as anaemia, encephalopathy, hepatitis, and the nephritic syndrome. Lead is used in acid battery, ceramic and glass manufacturing, metal planting and finishing, printing, tanning, and production of lead additives for gasoline (Momcilovic et al., 2011). The exposure to this metal causes World Health Organization (WHO) to recommend the maximum permissible limit to be 0.01 ppm (10  $\mu$ g/L) in drinking water (WHO, 2016).

#### 1.2. Olive cake

The olive itself consists of pulp, seed and nut. The chemical composition of the olive is water, oil, sugar, cellulose, minerals, polyphenols and others (Improlive, 2000). The process of olive fruit ends up as oil and olive cake. This process includes washing the fruit, crushing, pressing and centrifugation. Olive cake is a raw material obtained after extracting oil from olive fruit (Konstantinou et al., 2009; Abd El-Ghani, 2000).

In Palestine, the amount of raw olive cake ranges between (40,000 - 80,000) tons yearly (Ministry of agriculture, 1999).



(a)

(b)

Figure (1): Olive cake; a) olive cake raw, b) olive cake ash.

Olive cake has a limited use as a source of heat, fertilizer and feeding material, although it is considered of poor quality because of its low protein and energy content. The disposal of olive cake as waste is considered as a threat to the environment (Doyurum & Celik, 2006), because the untreated

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cake doesn't decay for a long time and accumulates over the years (Pagnanelli et al., 2003; Şensöz et al., 2006). The main chemical constituents of olive cake are cellulose, lignin, protein, oil, polyphenols and water (Alburquerque et al., 2004).

After processing the olives, the resulted olive cake is disposed as a waste. So converting these wastes into beneficial adsorbents contributes to treatment of contaminated water from heavy metals and reduces solid waste.

#### Physicochemical characterizations of olive cake ash:

Olive cake ash resulted from combustion at 600°C has chemical composition that mainly includes silicon oxide, aluminum oxide, calcite and other oxides are present in smaller quantities as shown in table 1.

Constituent	wt.%
SiO <sub>2</sub>	24.43
$Al_2O_3$	9.04
CaO	22.84
$Fe_2O_3$	2.51
$SO_3$	4.55
$P_2O_5$	16.17
K <sub>2</sub> O	3.40
MgO	2.62
N <sub>2</sub> O	2.67

Table 1: Chemical composition of olive cake ash (Elouear et al., 2008).

However, other components in the ash includes aluminosilicates, calcite and the oxides of aluminum, iron, magnesium, sodium and potassium (Elouear et al., 2008).

#### **1.3.** Traditional methods for removing heavy metals

The removal of heavy metals can be carried out by a number of conventional treatments, such as; chemical precipitation which is characterized by low cost and simple operation, but it forms excessive sludge (Aziz et al., 2008). Ion exchange is capable to exchange either cations or anions from the surrounding materials, but is highly sensitive to the pH of the solution and nonselective (Kurniawan et al., 2006). Membrane filtration is characterized by high efficiency, but this method is expensive and forms sludge (Ahmaruzzaman, 2011). Electrochemical treatment is effective but it is expensive, it involves high both energy and pressure, so it hasn't been widely applied (Wang et al., 2007b). Coagulation and flocculation is not costly, but it produces sludge, and consumes time (Ahmaruzzaman, 2011). Flotation has been used extensively, it is used to remove heavy metals by using surfactants forming product removed by bubbling gas to form foam (Lundh et al., 2000). These technologies have advantages but are limited in application. In recent years, it has been shown that adsorption is an alternative technology for removing dissolved metal ions from waste water (Kumar et al., 2010; Akpomie et al., 2015; Farhan et al., 2015; Kaushal & Singh, 2016; Benzaoui et al., 2018).

#### **1.4.** Adsorption methods for removing heavy metals

Sorption is used to describe transfer of ions from solution phase to the solid phase. Sorption comprises two processes: adsorption and absorption (Kurniawan & Babel, 2003).

Absorption refers to bonding within the solid structure of the sorbent (Bolis, 2013), while adsorption refers to bonding of desired substances (adsorbate) to solid surface (adsorbent) by physical and/or chemical interactions (Gottipati et al., 2012). The major advantages of adsorption technologies are that they are inexpensive, fast, and effective to reduce the concentration of heavy metals.

Various low-cost adsorbents derived from natural materials, industrial byproducts, agricultural wastes, and modified biopolymers have been used to remove heavy metals from wastewater (Barakat, 2011). Natural materials (such as zeolite, clay, ash dead biomass...etc), have great removal efficiency, low cost, and are available in large quantities (Mohana et al., 2007).

Adsorption on industrial by-products as; fly ash, waste iron, iron slags, can remove heavy metals significantly besides being inexpensive (Barakat, 2011). Adsorption on agriculture and biological wastes (biosorption) utilizes non-living biomass such as hazelnut shell, rice husk, jackfruit...etc. It accumulates heavy metals more than living biomass and eliminates the problems of waste toxicity. They are less expensive, biodegradable, abundant and efficient (Igwe et al., 2005; Ajmal et al., 2000). Activated carbon is the most effective method of adsorption for heavy metal removal at low concentrations from waste water, but it is expensive and must be renewed after each adsorption process (Villanueva, 2000). Biopolymers are widely available, and environmentally safe, they include hydroxyls and amines, which increase the efficiency of metal ion uptake (Crini, 2005). Hydrogels consist of polymer backbone, water and cross-linking agent. They respond to changes in external conditions, such as pH, ionic strength temperature and electric current. The removal is governed by the water diffusion into the hydrogel, carrying the heavy metals inside it. Hydrogels are capable of expanding their volumes due to their high swelling in water (Kesenci et al., 2002).

#### **1.4.1.** Types of adsorption:

- 1. Physical Adsorption: the attraction between adsorbent and adsorbate molecule is due to Vander Waals forces, and they are weak which make the bond easy to separate, and does not strongly affect the reactivity of the molecule adsorbed. That means no transmission of electrons occurs between adsorbent and adsorbate (Holmberg, 2006).
- 2. Chemical Adsorption: results from the chemical bonds between adsorbent and adsorbate molecule, these bonds are strong and need force to separate. The amount of chemical adsorption is based on the reactivity of the adsorbent and adsorbate (Tripathi & Ranjan, 2015).

#### 1.5. Research questions and identified problems

The proposal project is expected to answer the following questions:

- Can olive cake ash remove lead ions from aqueous solution efficiently?
- How to improve adsorption conditions (pH, temperature, contact time, binding capacity, concentration of metal ions, and effect of other competing ions)?
- How the binding capacity, metal interference and appropriate stripping agents can affect the adsorption process?

#### 1.6. Objectives

#### 1.6.1. General Objectives

The main objective of this study is to explore the efficiency of olive cake ash as a biosorbent for the removal of the toxic heavy metal (lead) from water.

#### 1.6.2. Specific Objectives

- Investigate the potential of olive cake ash to remove Pb(II) ions from aqueous solution.
- Determine the optimal conditions for the selected parameters (pH, temperature, contact time, binding capacity, concentration of Pb(II) ions, and effect of other competing ions) that give the highest removal of lead ions. Thermodynamics of the adsorption process will also be studied.
- Determine the binding capacity, effect of the presence of other metal ions and appropriate stripping agents on the adsorption process.

#### 1.7. Novelty

Numerous studies were performed on the removal of Pb(II) ions by biosorption. Few studies have used olive cake ash as an adsorbent for a limited number of heavy metal ions. To our knowledge, no previous studies used olive cake ash as an adsorbent for Pb(II) ions.

#### 1.8. Hypothesis

The hypothesis of this research is that the olive cake ash has the ability to adsorb Pb(II) ions from the aqueous solutions.

#### **1.9.** Previous studies

A study investigated that the removal of Zn(II) and Pb(II) from aqueous solutions was optimum at pH 6.0 using exhausted olive pomace ash as an adsorbent (Elouear et al., 2009). At the same pH, the efficiency of olive cake to remove cadmium from aqueous solution, was found to be 66% with temperature 28°C (Al-Anber & Marouq, 2008). Another study showed that the maximum removal efficiency of Fe(III) ions by using olive cake occurs at a temperature of 28°C and pH of 4.5. The removal efficiency of Fe(III) ions increases as the dosage of the adsorbent increases. The equilibrium removal of Fe(III) ions decreases as the temperature of solution increases. The removal of Fe(III) ions by this olive cake is an exothermic process (Al-Anber. Z & Al-Anber. M, 2008). A study found that the maximum monolayer adsorption capacities of the activated carbon which prepared from oil cake for the removal of lead (II) and nickel (II) ions were determined as 129.87 mg/L and 133.33 mg/L, respectively at pH 5.0 and pH 6.0, respectively (Ucar et al., 2014). Similarly, in another study, the adsorption capacities of Ni(II) and Cd(II) was 8.34 mg/g and 7.32 mg/g at pH 6 by olive cake ash. The optimum removal occurred up to 2 h contact time for Ni(II) and Cd(II) onto exhausted olive cake ash (EOCA) at pH 6. Langmuir isotherm correlated well than Freundlich isotherm (Elouear et al., 2008). Also, a study investigated a better sorption capacities for cadmium and

safranine by olive limestone were determined as (128.2 mg/g and 526.3 mg/g) respectively. The sorption process occurs fast enough so that the equilibrium is reached in less than 15 min of contact time. The kinetic and sorption data fitted well the second-order kinetic model and the Langmuir model, respectively (Aziz et al., 2009). Another study showed that the maximum adsorption capacities of Co (II) on olive cake were 45 mg/g, 49 mg/g and 153 mg/g at 303 K, 313 K and 323 K, respectively (Ackacha & Farjallah, 2015). A study showed that the maximum adsorption for zinc lies within pH 5-7 using olive cake (Fernando et al., 2009). While in another study, the optimal adsorption occurred at around pH 7. The removal of Pb and Cd ions by olive oil waste reached by acceptable levels of around 80 % and 75 %, respectively (Garcia et al., 2006). A study found that the maximum metal sorption for Pb(II), Ni(II), Cu(II) and Cd(II) by olive stone waste occur at initial pH around 5.5-6.0. The highest value of Langmuir maximum uptake was found for cadmium ( $6.88 \times 10^{-5}$  mol/g) followed by lead ( $4.47 \times 10^{-5}$ mol/g), nickel  $(3.63 \times 10^{-5} \text{ mol/g})$  and copper  $(3.19 \times 10^{-5} \text{ mol/g})$  (Fiol et al., 2006). A study used olive stones as an adsorbent for removing Cd(II) and Cr(VI) from aqueous solutions. The kinetic study has indicated that the adsorption process is of second order and the rate constants were determined for both cations (Rouibah et al., 2009). Another study found that the metal removal favored pseudo-second-order model when olive cake was used as an adsorbent for nickel removal from aqueous medium (Khan et al., 2012).

## **Chapter Two**

### Methodology

#### 2.1. Biomass Collection

Olive cake was collected from Tallouza village, which is located 10 km north to Nablus. The olive cake was burned in a furnace at 600°C for two hours to form ash (Elouaer et al., 2008). The ash was sieved to pass through a 150 mesh to get fine particles.

#### 2.2. Ash Treatment

The desired amount of ash was placed in a 5-mL test tube, washed once with 0.01M HCl then once with distilled water. The ash was centrifuged for 5 minutes at 6000 rpm after each washing. The washings were then evaporated in an oven at 200°C to calculate the loss in ash. The volume of distilled water that must be added to the ash test tube in order to obtain a solution that is 5 mg/mL was calculated and added to each test tube. The pH of the ash suspension was adjusted to the optimum pH 5.0 using NaOH and HCl solutions.

A 2.0-mL aliquot of the adjusted suspensions was transferred into each of 3 test tubes (5-mL each) for each factor studied and then centrifuged for 5 minutes at 6000 rpm. The supernatants were then discarded. A fourth empty (no ash) tube was used as a control for each experiment.

#### 2.3. Preparation of Metal Solutions

Solutions of Pb (II) ions were prepared by dissolving the required amount of Pb(NO<sub>3</sub>)<sub>2</sub> in certain volume to get the desired concentration. Some experiment were not buffered as pH-dependent and temperature dependence. The pH of Pb(II) solutions of each concentration was adjusted to the desired pH using NaOH and HCl solutions.

#### 2.4. Metal Quantification

The supernatants were analyzed using atomic absorption spectrophotometer

(AAS). The amount of metal adsorbed per unit mass is calculated as:  $q = \frac{C_o - C_f}{m} \cdot V$ (1)

The percentage of Pb(II) ions removal can be calculated by: Removal % =  $\frac{C_o - C_f}{C_o}$ . 100% (2)

q: the bio sorption capacity of the biomass at any given time (mg/g)

C<sub>o</sub>: the initial metal concentration (mg/L)

Cf: the final metal concentration in the solution (mg/L)

V: volume of the solution (L)

m: the mass of adsorbent (g)

#### Thermodynamic of the adsorption process:

The thermodynamic parameters ( $\Delta H^{\circ}$ ,  $\Delta G^{\circ}$ ,  $\Delta S^{\circ}$ ) and the rate of adsorption constant (K<sub>c</sub>) were measured according to (Fawl & Davis, 1985).

$$\Delta G^{\circ} = -RT \ln Kc \tag{3}$$

 $\Delta G^{\circ}$  is standard free energy change, b is Langmuir constant, R is universal gas constant and T is the absolute temperature in K.

$$\ln K_{\rm c} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(4)

 $\Delta H^{\circ}$  is the change in standard enthalpy,  $\Delta S^{\circ}$  is the standard entropy.

#### 2.5. Instrumentation

- Furnace.
- (ICE 3000 SERIES, Thermo Scientific) Flame atomic absorption spectrometer with acetylene-air flame (AAS).
- Mechanical shaker.
- JENWAY (3510) pH Meter.
- (Centurion, Scientific Ltd) Centrifuge.

#### 2.6. Effect of Various Parameters on Adsorption Process

#### 2.6.1. Effect of pH

The pH experiment was conducted to find the optimal pH value at which maximum quantity of Pb(II) ions can be loaded on the treated ash. The studied pH values were 2, 3, 4, 5 and 6.

For each pH value studied, four tubes were used; three of them were prepared to contain 10 mg of the treated ash. A fourth empty tube was used to serve as a control. Then, 2-mL of 0.1 mM Pb(NO<sub>3</sub>)<sub>2</sub> solution were added to each tube. The tubes were shaken for one hour and then centrifuged. The clear

solutions were then analyzed by AAS to measure the absorbance and the concentration of the metal ion.

#### 2.6.2. Time dependence studies

The time dependence experiment was performed to seek the shortest time to achieve the highest removal of Pb(II) ions by olive cake ash. Binding was performed at several periods of time 10, 20, 30, 40 and 80 minutes.

For each time period, three tubes were used to contain 10 mg treated ash. And a fourth empty tube to serve as a control. Then, 2-mL of 0.1 mM Pb(NO<sub>3</sub>)<sub>2</sub> prepared in 0.01 M sodium acetate adjusted to pH 5.0 were added to each tube. After that, the test tubes were placed in a shaker according to the time mentioned, and then centrifuged. The clear solutions were kept to measure the absorbance and the concentration of the metal ion using AAS.

#### **2.6.3.** Temperature Dependence

The adsorption of Pb(II) metal ion by olive cake ash was carried out at different temperatures ( $0^{\circ}C$ ,  $20^{\circ}C$  and  $70^{\circ}C$ ).

For each temperature, four tubes were used as previously mentioned. 2-mL of 0.1 mM Pb(NO<sub>3</sub>)<sub>2</sub> solution (pH 5) were added to each tube at each temperature. The tubes were shaken at the optimal time 40 minutes for each selected temperature and then centrifuged. The clear solutions were analyzed by AAS to measure the absorbance and the concentration of the metal ion.

#### 2.6.4. Capacity Studies

The adsorption capacity for Pb(II) ions onto the olive cake ash was studied at optimal parameters pH 5.0 and 40 minutes to find the capacity (mg/g) of the treated ash to adsorb the maximum amount of Pb(II) ions.

In order to explore when the treated ash becomes saturated with Pb(II) ions, the experiment was performed in ten cycles. For each cycle, three tubes were used to contain 10 mg treated ash (pH 5.0) and a fourth control tube. Then, 2-mL of 3 mM Pb(NO<sub>3</sub>)<sub>2</sub> prepared in 0.01 M sodium acetate that was adjusted to pH 5.0 were added to each tube. The tubes were shaken for 40 minutes and then centrifuged. The clear solutions were decanted for quantification. The remaining ash was mixed with a new 2-mL of lead metal solution, shaken, centrifuged and the clear solutions were decanted and quantified. This cycle was repeated for ten times. The clear solutions were analyzed by AAS, the mass of lead ions loaded on ash treated samples for each cycle was determined.

#### 2.6.5. Regeneration of ash

This experiment was performed in order to test HCl and sodium citrate (NaCit) as an extractant for the metal ions bounded on the treated ash samples (Gardea-Torresdey et al. 1996b). The studied concentrations of extractants were 0.1 M, 0.5 M or 1 M of HCl and sodium citrate (NaCit). For each extractant concentration, four tubes were used as previously mentioned. Then, 2-mL of 100 ppm of lead solution prepared in 0.01 M sodium acetate were added to each tube. The test tubes were shaken for 40

minutes, and then centrifuged. The clear solutions were then analyzed by AAS. After that, the residual ash samples were washed with 2-mL of 0.01M sodium acetate at pH 5.0 to remove any unbound metal ions. The supernatants were then discarded. Then, 2-mL of each extractant concentration (at pH 5 for HCl and pH 7 for NaCit) were added to the washed ash samples. The mixtures were shaken for 10 minutes and then centrifuged. The clear solutions were then decanted and analyzed by AAS. The residual (regenerated) ash was mixed again with another 2-mL of the same extractant and shaken for 10 minutes, and then centrifuged to analyze the clear solutions by AAS.

#### **2.6.6. Hard Cation Interferences**

The effect of  $Ca^{2+}$  and  $Mg^{2+}$  as competing ions with Pb(II) ions was studied as described by (Munoz et al. 2002).

A solution of 0.1 mM of Pb(NO3)2 was prepared to contain different concentrations of combined Ca<sup>2+</sup> and Mg<sup>2+</sup> (0.0 mM, 0.1 mM, 0.2 mM, 1 mM, 2 mM, 10 mM, 20 mM, 0.1 M, 0.2 M and 1 M). For each Ca<sup>2+</sup> and Mg<sup>2+</sup> concentration, four tubes were used as before. At pH 5.0, 2-mL aliquot of the metal ion solution combined with Ca<sup>2+</sup> and Mg<sup>2+</sup> was added to each tube. The tubes were shaken for 40 minutes, and then centrifuged for 5 minutes at 6000 rpm. The clear solutions were then analyzed by AAS to measure the absorbance and the concentration of Pb(II) ions.

#### 2.6.7. Thermodynamic of adsorption process

To find the appropriate model that fits the experimental adsorption data, the following experiments were performed.

Different concentrations of Pb(II) ions (0.0, 9.6, 19, 29, 38, 48, 58, 67 and  $77 \times 10^{-5}$  mol/L) were prepared. For each concentration, four tubes were used as usual. A 2-mL aliquot of the metal ion solution of the desired concentration (pH 5.0) was added to each tube. The tubes were shaken for 40 minutes and then centrifuged at 6000 rpm for 5 minutes. The clear solutions were then diluted to fit into the calibration range and analyzed by AAS.

#### 2.7. FT-IR Experiment

Infrared spectroscopy is an analytical method used to identify the physical and chemical properties of functional groups from the compounds (Segneanu & Gozescu, 2012). Three samples of olive cake were analyzed by IR to investigate the characteristics of the studied adsorbent.

The samples that were analyzed were; olive cake before combustion, olive cake after combustion at 600 °C, and olive cake ash loaded with Pb(II) metal ions.

The last one was prepared using 1g of ash mixed with 10-mL of 20 ppm of Pb(NO<sub>3</sub>)<sub>2</sub> solution shaken for 40 minutes. The mixture was then centrifuged for 5 minutes at 6000 rpm to separate the biomass from solution. Then, the ash sample was washed three times with distilled water and centrifuged again, the washed biomass was dried and then analyze by IR.

# **Chapter Three**

### **Results and Discussion**

#### 3.1. FT-IR Experiment

Infrared technique was used to determine the functional groups on the surface of olive cake ash responsible for the adsorption. The FTIR for olive cake ash (not loaded) is shown in Figure (2), while Figure (3) shows the IR spectrum of the loaded biomass. The main peaks of the IR spectra of both olive cake ash and metal loaded olive cake ash is presented in table (2).

Table 2: Main peak of the FTIR spectra of the olive cake ash and lead

metal	loaded	olive	cake	ash.
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Peak value	Standard	Functional groups	Functional groups
(cm <sup>-1</sup> ) from	peak value	using (Segneanu et	using (Shriner et al.
Figure (2) and	(cm <sup>-1</sup> )	al., 2012)	1935)
(3)			
2360	2100-2360	Si-H (Silane)	
	2250-2700		N-H stretching
	2280-2440	P-H (Phosphine)	
1622	1620-1680		alkene C≡C stretching
	1550-1650	NH <sub>2</sub> (Amines)	U
1399 and 1417	1350-1450	S=O (Sulfate)	
	1395-1440		O-H bending,
	1380-1415		S=O stretching
	1300-1600		Ring stretching C-H
			out-of-plane bending
1058 and 1060	1050-1200	C-O (Alcohol)	
	1050-1085		C-O stretching
	1000-1300	C-O (Ester)	
	1040-1100	O-C (Anhydrides)	
	1050-1200	C=S	
		(Thiocarbonyl)	
	1030-1060	S=O (Sulfoxide)	
	1000-1110	Si-OR (Silane)	
871 and 872	800-1000	C-C (Alkane)	
	610-700		C-H bending
	650-1000		C-H out of plane
			bending
	660-900	NH2& N-H	
		(Amines)	
	700-900	S-OR (Esters)	

As shown in Figure (3), the peak at 1622 cm<sup>-1</sup> has disappeared in the metal loaded biomass. This peak could be due to C=C stretching (Shriner et al. 1935) or NH<sub>2</sub> (amines) group (Segneanu et al., 2012). But most probably it

is due to NH<sub>2</sub> that is capable of metal binding. The peak at1399 cm<sup>-1</sup> in biomass spectra was shifted to 1417 cm<sup>-1</sup> and became smaller in the metal loaded biomass. This peak refers to S=O (Sulfate) group (Segneanu et al., 2012; Shriner et al. 1935) or O-H bending or C-H stretching (Shriner et al. 1935) and it became smaller and shifted due to participation in binding. The peak at 1058 cm<sup>-1</sup> became less sharp in the metal loaded biomass and shifted to 1060 cm<sup>-1</sup>. This peak represents the C-O stretching (Shriner et al. 1935) of alcohols, esters or anhydrides groups or C=S of thiocarbonyl or S=O of sulfoxide or Si-OR of silane (Segneanu et al., 2012).

The above IR analysis shows that the biomass could be binding using  $NH_2$  of amines, S=O of sulfate, C-O (alcohol & ester) and (anhydrides), C=S of thiocarbonyl or S=O of sulfoxide groups. However, further studies are required to confirm this conclusion.



Figure (2): FTIR for olive cake ash.

21



Figure (3): FTIR for olive cake ash loaded with lead metal. metal.

22

#### **3.2.** Effect of pH

The pH profile of olive cake ash indicates that the ability of olive cake ash to adsorb Pb(II) ions was pH dependent as shown in Figure (4).



**Figure (4):** pH profile for the reaction of a slurry (5mg/mL) of olive cake ash with 0.1 mM of Pb(II). The reaction time was 1 h. Error bars represent 95% confidence interval. Several studies showed that the adsorption of heavy metals on many types of ashes increases with pH (Sposito, 1989; Ricou-Hoeffer et al., 2002; Benzaoui et al., 2017).

In this study, the increases in binding of Pb(II) ions by increasing pH value could be explained by the high CaO content in the ash due to the formation of C and Si complexes such as calcium silicates(2CaO\*SiO<sub>2</sub>), in the alkali conditions, Pb(II) ions binds to the negative charges on surface of Ca-Si complexes (NGOH, 2006).

The adsorption of Pb(II) ions increases with increasing pH, higher pH causes rising of negative charges on surface which attributed to a high silica content of ash, while at low pH, the positive charges of silica dominates, and causes less binding of Pb(II) ions on ash (NGOH, 2006; Eluear et al., 2008).
From figure (4), as pH increased from 2 - 5, the percent removal of Pb(II) ions by the ash was increased. At the beginning of the adsorption process, the percentage removal of lead at pH 2.0 was 43%. At low pH values, the negative charges on the functional groups of the biomass are protonated causing less binding, and H<sup>+</sup> in solution competes with Pb(II) ions, which leads to repulsion of lead ions (Sukpreabprom et al., 2014).

The removal of Pb(II) by the ash reached maximum (93%) at pH 5.0. At higher pH, the negative charges on the biomass surface become more available (Mousavi et al. 2010). As a result, more attraction with the positive lead ions occurs. At pH greater than 5.0, the removal of Pb(II) ions was not significantly different from that at pH 5.0.

Similar studies showed that the maximum removal of Cd(II) and Ni(II) ions from aqueous solution on olive cake ash occurred at pH 6.0 (Elouear et al., 2008). The maximum removal for Pb(II) and Zn(II) ions from aqueous solution using olive pomace ash achieved at pH 6.0 (Elouear et al., 2009). A study showed that the maximum removal of Pb(II) ions from aqueous solution using activated carbon prepared from rapeseed oil cake occurred at pH 5.0 (Uc ar et al., 2014).

#### **3.3.** Time Dependence Experiment

The removal of Pb(II) ions by olive cake ash reached maximum at 40 minutes as shown in Figure (5).





with 0.1 mM of Pb(II) at pH 5.0. Error bars represent 95% confidence interval.

After 10 minutes, the removal of Pb(II) ions by olive cake ash was 89%. This is a reasonable removal which indicates that the binding with the functional groups on the surface of ash was fast. After 40 minutes, there was less than 3% increase in removal of Pb(II) ions compared to that at 20 minutes. However 40 minutes was chosen as the optimal time for the removal. At longer times, no further increase was noticed.

Several studies showed that the sorption of Cd(II) and Ni(II) ions on olive cake ash needed 2h to achieve the equilibrium (Elouear et al., 2008). The removal of Pb(II) and Zn(II) ions from aqueous solution using olive pomace ash required 2h to achieve the equilibrium (Elouear et al., 2009).

#### **3.4.** Temperature Dependence Studies

Different temperatures were selected to investigate the effect of temperature on the removal of Pb(II) ions onto olive cake ash as shown in Figure (6).





at pH 5.0 and 40 minutes. Error bars represent 95% confidence interval. It is noted from the above figure that the removal of Pb(II) ions increased slightly from 91.3% to 94.5% as the temperature increased from 0°C to 70°C. The slight increase in the percent removal by temperature can be explained by dissociation of protons from surface functional groups on the olive cake ash which produces more adsorption sites. In addition, the Pb(II) ions gain more kinetic energy to diffuse from the bulk to the solid phase (Akpomie et al, 2015; NGOH, 2006).

## **3.5.** Capacity Studies

The effect of binding capacity of the ash to adsorb Pb(II) ions was performed by exposing the same biomass to Pb(II) ions for 10 cycles at optimal parameters (pH 5.0, 40 minutes and 28°C). The results are presented in Figure (7).





saturation cycles at pH 5.0). Error bars represent 95% confidence interval. The results indicate that the percentage of lead removal decreased as the number of cycles increased. Binding capacity was 0.29 mg/g. The percent removal of adsorbent for Pb(II) ions in the first cycle was the highest because there are large number of vacant sites on the adsorbent surface to be occupied by metal ions. The removal of adsorbent decrease gradually until cycle five because the number of available sites decreases by increasing the cycle number (Sawalha et al., 2009). After cycle five, the removal capacity is almost negligible, because there are no other active sites to be filled with new ions.

A study showed that the binding capacity by the alfalfa shoot biomass (Medicago Sativa) were 42.1 mg/g for lead(II), 11.4 mg/g for chromium(III), 6.5 mg/g for copper(II), 4.4 mg/g for cadmium(II), 4.3 mg/g for zinc(II), and 0.5 mg/g for nickel(II) (Tiemann et al., 1998).

# **3.6. Regeneration of Ash**

The regeneration of Pb(II) ions from aqueous solution was performed using different concentrations (1M, 0.5M and 0.1M) of each HCl and sodium sitrate as stripping agents, the stripping was done in two cycle.

Figure (8) shows the effect of concentration of the stripping agent (HCl and sodium citrate) on the recovery of the Pb(II) ions from ash solution in each stripping cycle and in total of two cycles.



**Figure (8):** Metal percentage recovery from batch experiments for the loaded metals by stirring the metal loaded olive cake ash biomass with HCl or sodium citrate solution for 10 minutes. Olive cake biomass was loaded with metals by stirring the biomass for 10 minutes at pH 5.0 with 100 ppm (cycle 1, cycle 2, Total cycle). Error bars represent 95% confidence interval.

The regeneration of Pb(II) ions from aqueous solution was performed using different concentrations (1 M, 0.5 M and 0.1 M) for each of HCl and sodium citrate as stripping agents.

In the first regeneration cycle, the amount of Pb(II) ions that was regenerated by HCl from the biomass was higher than the amount of Pb(II) ions that was regenerated by sodium citrate. The largest amount of Pb(II) ions regenerated was by 0.5 M HCl and reached (92.43%). In the second cycle, the maximum regeneration of Pb(II) ions by HCl and sodium citrate ranged from 9.86% by 0.5 M sodium citrate to 13.11% by 0.1 M sodium citrate.

The total regeneration for HCl ranged from 96.3% by 1 M HCl to 100 % by 0.5 M HCl, and for NaCit ranged from 72.2% by 1 M sodium citrate to 78.3% by 0.5 M sodium citrate.

The decrease in the amount of metal regenerated may be due to a decrease in the mass of adsorbent and destructive effect of the regenerated agent during the process (Nessim et al. 2011).

Stripping studies showed that 85-100% of the bound Cu, Cr, and Pb ions and about 37% of the bound Cd and Zn ions by alfalfa could be recovered using 0.1 M HCl (Sawalha et al., 2009). The maximum desorption of Pb(II) and Cd(II) ions by olive cake were found to be 95.92 and 53.97% by 0.5 M HNO<sub>3</sub> and 0.2 M HCl respectively (Doyurum & Celik, 2006).

## 3.7. Hard Cation Interferences

Different concentrations of Ca(II) and Mg(II) ions were mixed with Pb(II) ions to explore the effect of these cations on the binding of Pb(II) ions with

ash at the optimal parameters ( pH 0.5 and 40 minutes) as shown in Figure



**Figure (9):** Interference of combined calcium and magnesium ions on the binding of 0.1 mM lead solution with olive cake ash at pH 5.0 for 40 minutes.

As noted, there are a significant increase in the binding of Pb(II) ions at 2 mM, 4 mM, 20 mM and 400 mM combined each of Ca(II) and Mg(II). This increase was up to 22% higher than that when no Ca and Mg ions were present. This may be due to the fact that, the lead ions have higher stability constants than the stability constants for Ca and Mg cations to bind with biomass. Which means that the Pb(II) ions have a higher binding force with the functional groups of the biomass (Arthur et al., 1974). While a small decrease in the binding of Pb(II) ions occurred at 40 mM and 2000 mM that reached 3% and 4% decreases, respectively, compared to results when no Ca(II) and Mg(II) ions were present.

A study observed that Pb(II) uptake by marine algae decreased over the four operational biosorption cycles from 93.8 mg/g to 6.8 mg/g for raw biomass, whereas for modified biomass it declined from 163.9 mg/g to 13.6 mg/g. The cadmium uptake decreased from 32.0 mg/g to 4.7 mg/g for raw biomass over the four biosorption cycles, whereas the modified biomass recorded a

decrease in cadmium uptake from 49.9 mg/g to 6.5 mg/g (Nessim et al., 2011). When the concentration of Ca and Mg ions reached 200 mM and 2000 mM, the binding of Cr(III) and Pb(II) with biomass alfalfa decreased about 40% and 70%, respectively. While when the combined concentrations of Ca and Mg ions lower than 4 and 40 mM, the binding of Cr(III) and Pb(II) was not affected (Sawalha et al., 2009).

### 3.8. Isotherm of the Adsorption Process

Adsorption isotherms are different models used to describe the interaction between the metal ions and the biomass surface at equilibrium. Several models such as Langmuir, Freunlich, Khan and Singh and Dubinin-Radshkevich were used in this study to determine which of these models best fits the experimental data.

#### ✤ Langmuir Model

The Langmuir adsorption isotherm is a nonlinear model which describes a monolayer sorption of metal ion adsorbed on homogeneous adsorbent sites. The adsorbent sites have uniform energy without interactions between adsorbed particles; this model is based on a first order kinetics (Langmuir, 1916). The Langmuir isotherm is given by:

$$Ce/qe = Ce/QL + l/b QL$$
(1)

Where C<sub>e</sub> is equilibrium concentration of metal ions (mol/L), q<sub>e</sub> is the amount of metal adsorbed at equilibrium (mol/g), QL is the maximum adsorption capacity (mol/g), b is Langmuir constant (mol/g). These

parameters were determined from a plot of Ce/qe versus Ce, as in Figures (10-12), where Langmuir isotherm has performed at three temperatures ( $13^{\circ}$ C,  $23^{\circ}$ C and  $35^{\circ}$ C).

The slope (1/QL) and the intercept (l/b QL) were determined from the plots. The dimensionless adsorption intensity (RL) was calculated by:

$$R_{L}=1/(1+bC_{o})$$
 (2)

Where  $C_o$  is the initial concentration of the metal ion in the solution (mol/L) (Weber & Chakrabarti, 1974). The value of RL indicates the type of isotherm; linear if (RL=1), unfavourable if (RL >1), favourable if (0 < RL<1), or irreversible if (RL=0) (Lin & Juang, 2002).



Figure (10): Langmuir isotherms for the biosorption of Pb(II) by olive cake ash at 13°C, pH 5.0 and 40 minutes.



Figure (11): Langmuir isotherms for the biosorption of Pb(II) by olive cake ash at 23°C, pH 5.0 and 40 minutes.



Figure (12): Langmuir isotherms for the biosorption of Pb(II) by olive cake ash at 35°C, pH 5.0 and 40 minutes.

The Langmuir parameters b and QL were determined from Figures (10-12) as summarize in Table (2).

Table 2: Langmuir parameters for the biosorption of Pb(II) ions on olivity	<i>i</i> e
cake ash at different temperatures (13°C, 23°C and 35°C) and pH 5.0.	,

ine asin at an	ter ente temp		0, <b>2</b> 0 0 unu	<b>ee</b> e) an	
Temp.(°C)	b	QL (mol/g)	QL (mg/g)	R <sup>2</sup>	Rl
13°C	6.3×10-6	5.8×10-6	1.201	0.8529	0.99
23°C	4.3×10-7	5.6×10-6	1.160	0.4118	1
35°C	$1.7 \times 10^{-6}$	7.1×10-6	1.471	0.9228	1

As noted in Table 2, when temperature values ranged from  $13^{\circ}$ C to  $35^{\circ}$ C, the Langmuir constant b values ranged from  $4.3 \times 10^{-7}$  to  $6.3 \times 10^{-6}$ , the QL ranged from  $5.6 \times 10^{-6}$  mol/g to  $7.1 \times 10^{-6}$  mol/g, and RL values range from 0 to 1, that means the adsorption process of lead is almost linear.

In previous studies, QL of Langmuir isotherm for Ni(II) and Cd(II) on olive cake ash was 8.38 and 7.37 mg/g respectively, and b equal to 0.05 and 0.02 with R<sup>2</sup> equal to 0.99 for each metal respectively (Elouear et al., 2008). A study showed that the QL of Langmuir isotherm for Pb(II) and Zn(II) on olive pomace ash was 8.76 and 7.75 mg/g respectively, and b equal to 0.05 and 0.04 with R<sup>2</sup> equal to 0.99 for each metal respectively (Elouear et al., 2009). In other studies, the QL for Cu(II), Pb(II) and Zn(II) was  $0.93 \times 10^{-2}$  mol/g, -  $0.04 \times 10^{-2}$  mol/g and  $-0.39 \times 10^{-2}$  mol/g, and has b equal to 9.09, -3491.2 and -24.84 with R<sup>2</sup> of 0.0001, 0.1380 and 0.0088, respectively when adsorbed on saltbush leaves biomass (Sawalha et al., 2007).

#### Freundlich Model

The Freundlich isotherm is a nonlinear model that describes a monolayer sorption of the adsorbed molecules on heterogonous adsorbent. The energy spreads irregularly on the surface of the adsorbent. The Freundlich isotherm can be written as:

$$q_e = K_F C e^{i \nu_n} \tag{3}$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{4}$$

Where  $K_F$  is the maximum adsorption capacity (mol/g), and n is the adsorption intensity, where n depends on the nature and strength of the sorption forces, and the distribution of active sites on the surface of the sorbent. The plots of ln qe versus ln Ce gives  $K_F$  and n resulting from the slope 1/n and the intercept ln  $K_F$ . The adsorption process is favourable when 1 < n < 10 (Davis et al., 2003).

The Figures (13-15) shows the results obtained by plotting ln qe versus ln Ce at different temperatures (13°C, 2°C and 35°C). The Freundlich parameters n and  $K_F$  are summarized in Table 3.



**Figure (13):** Freundlich isotherms for the biosorption of Pb(II) by olive cake ash at 13°C, pH 5.0 and 40 minutes.



Figure (14): Freundlich isotherms for the biosorption of Pb(II) by olive cake ash at 23°C,

pH 5.0 and 40 minutes.



**Figure (15):** Freundlich isotherms for the biosorption of Pb(II) by olive cake ash at 35°C, pH 5.0 and 40 minutes.

Table 3: Freundlich isotherm parameters for the biosorption of Pb(II) on olive cake ash at different temperatures (13°C, 23°C and 35°C) and

pН	5.0.				
	Temp.(°C)	n	$K_F (mol/g)$	$K_F (mg/g)$	R <sup>2</sup>
	13°C	2.1	0.0003	62.16	0.9481
	23°C	1.7	0.0005	103.6	0.8182
	35°C	2.5	0.0002	41.44	0.9682

As noted in Table 3, when the temperature values ranged from  $13^{\circ}$ C to  $35^{\circ}$ C, the adsorption intensity (n) values of Pb(II) ions adsorbed on treated ash ranged from 1.7 to 2.5. This indicates that the adsorption is favourable. The adsorption capacity K<sub>F</sub> was 0.0003 mol/g, 0.0005 mol/g and 0.0002 mol/g at  $13^{\circ}$ C,  $23^{\circ}$ C and  $25^{\circ}$ C, respectively. The adsorption intensity of Pb(II) ions was highest at  $35^{\circ}$ C.

The results suggest that the Freundlich model fits the data better than the Langmuir model. This could be because the biomass have more than one functional group on the surface to bind the metal ion (Sawalha et al., 2007). Adsorption capacity using Langmuir and Fruindlich models ranged from (1.160 mg/g to 1.471 mg/g) and from (41.44 mg/g to 103.6 mg/g), respectively. The resulted capacity from capacity experiment (0.29 mg/g) was more close to the Langmuir capacity.

A study showed that the adsorption of Pb(II) and Zn(II) ions by olive pomace ash have  $K_f$  equals to 1.25 mg/g and 0.8 mg/g with R<sup>2</sup> of 0.97 and 0.95 respectively, 1/n for each metal was 0.4 (Elouear et al., 2009). A study used olive cake to adsorb cadmium ions from aqueous solution and showed when the temperature increasing from 28°C to 45°C, the Freundlich constant  $K_f$ decreased from 19.9 to 15.7 (Al-Anber & Matouq, 2008). In another study, the adsorption of Zn(II) onto olive cake have n equal to 2.31, and  $K_F$  was found to be 3.23 mg/g with R<sup>2</sup> of 0.950 using Freundlich model (Thajeel, 2013).

## **3.9.** Thermodynamic of Adsorption Process

The equilibrium constant Kc for the adsorption of lead ions on ash can be found from the slope of the plot of  $q_e$  versus C<sub>e</sub> at different temperatures using Khan and singh equation Figures (14-16):

Kc = qe/Ce (5)

Where Kc is the standard equilibrium constant, qe is the amount of metal ion (mol/g) adsorbed on the biomass, Ce is the concentration of metal ion at equilibrium (mg.dm<sup>-3</sup>).

The following equation was used to calculate Gibbs free energy,  $\Delta G^{\circ}$  (kJ/mol) for the sorption of lead ions on ash:

$$\Delta G^{\circ} = -RT \ln Kc \tag{6}$$

Where T is the absolute temperature in Kelvin and R is the gas constant  $(8.314 \text{ J/mol}^{-1}\text{K}^{-1})$  (Fawl & Davis, 1985).

Figures (16-18) shows Khan and Singh plots of ln (qe/Ce) versus (qe) for Pb(II) ion adsorption on ash at different temperatures.







cake ash at pH 5.0, at 13°C and 40 minutes.

Figure (17): Khan and Singh plots of ln (qe/Ce) versus (qe) for Pb(II) adsorption on olive



**Figure (18):** Khan and Singh plots of ln (qe/Ce) versus (qe) for Pb(II) adsorption on olive cake ash at pH 5.0, 35°C and 40 minutes.

Figures (19-21) shows the results obtained by plotting (qe) versus (Ce) at different temperatures (13°C, 23°C and 35°C). The values of  $\Delta G^{\circ}$  and Kc were determined as summarize in Table 4.



Figure (19): Adsorption of Pb(II) on olive cake ash at pH 5.0, 13°C and 40 minutes.



Figure (20): Adsorption of Pb(II) on olive cake ash at pH 5.0, 23°C and 40 minutes.



Figure (21): Adsorption of Pb(II) on olive cake ash at pH 5.0, 35°C and 40 minutes.

Table (4): Thermodynamic parameters for the sorption of Pb(II) ions on olive cake ash at different temperatures (13°C, 23°C and 35°C) and pH 5.0.

		-
Temp.(°C)	∆G °(kJ/mol)	Kc from equation (5)
13°C	19.87	0.0002
23°C	10.29	0.015
35°C	20.45	0.0003

In the above Table, the positive values of  $\Delta G^{\circ}$  at different temperatures indicates that the adsorption process is non spontaneous. Also, the equilibrium constant Kc ranged from 0.0002 to 0.015 which is highest at 23°C.

A study found that the adsorption of Cu(II), Pb(II) and Zn(II) ions by leaves of saltbush has  $\Delta G^{\circ}$  values equal to 2.0587, -3.4062 and 1.7938 with Kc of 0.435, 3.97 and 0.484, respectively (Sawalha et al., 2007). Another study found that the adsorption of and by olive cake ash has  $\Delta G^{\circ}$  has values ranged from -19.13 to -21.13 kJ/mol for Ni(II) and -20.93 to -23.14 kJ/mol Cd(II) when the temperatures increases from 10°C to 40°C (Elouear et al., 2008). The adsorption of Pb(II) and Zn(II) by olive pomace ash have  $\Delta G^{\circ}$  ranged from -22.2 to -24.55 kJ/mol for Pb(II) and from -19.33 to -21.38 kJ/ mol for Zn(II) (Elouear et al., 2009).

# **3.9.1.** The Van't Hoff Equation

Values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are obtained by substituting equation (6) in equation (7) which describes the relation between  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  as follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{7}$$

 $-RT \ln Kc = \Delta H^{o} - T\Delta S^{o}$ (8)

Rearranging we get,

$$\ln \mathrm{Kc} = (-\Delta \mathrm{H}^{\mathrm{o}}/\mathrm{R}\,\mathrm{T}\,) + (\Delta \mathrm{S}^{\mathrm{o}}/\mathrm{R}) \tag{9}$$

Where  $\Delta H^{\circ}$  is the enthalpy change,  $\Delta S^{\circ}$  is the entropy change, T is the temperature in Kelvin, and R is the gas constant (8.314 kJ/mol).

The parameters  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were found from the slope (- $\Delta H^{\circ}/R$ ) and the intercept ( $\Delta S^{\circ}/R$ ) by the plot of ln Kc versus 1/T. The negative values of  $\Delta H^{\circ}$  suggest that the process is exothermic in nature. The negative  $\Delta S^{\circ}$  means decreasing randomness between metal molecules and the biomass, while the positive  $\Delta H^{\circ}$  suggests that the process is endothermic and positive  $\Delta S^{\circ}$  means increasing randomness (Epping & Gammon, 2009; Fawl & Davis, 1985). Figure (22) shows the results obtained by plotting ln Kc versus 1/T at





Figure (22): Van't Hoff plot of adsorption equilibrium constant Kc.

The values of  $\Delta$ H° and  $\Delta$ S° were found to be -14.08 and -0.09, respectively. The negative value of  $\Delta$ H° means that the adsorption of Pb(II) ions onto ash was an exothermic process. Also the negative value of  $\Delta$ S° means decreasing randomness at solid/liquid interface as mentioned previously (Epping & Gammon, 2009; Fawl & Davis, 1985).

The Dubinin-Radushkevich (D–R) isotherm is applied for both homogenous and heterogeneous surfaces to estimate sorption mean free energy, E in order to determine if the process is physical or chemical in nature. When the value of E is in the range of 8-16 (kJ/mol) the process is classified as chemical adsorption (Helfferich, 1962).

The mean free energy (E) per molecule of the sorbate was calculated using the following equation:

$$E = 1/(2K_E)^{1/2}$$
(10)

Where  $K_E$  is a constant related to the biosorption energy of adsorption  $(mol^2 \cdot kJ^2)$ . The parameters  $K_E$  and  $q_m$  can be found from the slope and the intercept of the plot of ln qe versus  $(\mathcal{E}^o)^2$  using equation (11):

$$\ln q_e = \ln q_m - K_E (\mathcal{E}^o)^2 \tag{11}$$

Where  $q_m$  is the monolayer adsorption capacity (mol/g). The parameter  $\mathcal{E}^{\circ}$  can be found from equation (12):

$$\mathcal{E}^{o} = \operatorname{RT} \ln \left( 1 + 1/\operatorname{Ce} \right) \tag{12}$$

Where E° is the Polanyi potential, Ce is the concentration of the metal in the solution at equilibrium (mol/dm<sup>3</sup>) (Dubinin-Radushkevich, 1947).

Figures (23-25) represents the plots of  $\ln q_e$  versus  $(\mathcal{E}^o)^2$  for the adsorption of Pb(II) ions onto olive cake ash.



**Figure (23):** Dubinin-Radushkevick plots for the biosorption of Pb(II) on olive cake ash at pH 5.0, 13°C and 40 minutes.



Figure (24): Dubinin-Radushkevick plots for the biosorption of Pb(II) on olive cake ash

11.8	E°2×10 <sup>-2</sup>
-12 (	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
9-12.2 9-12.4	y = -0.2892x - 10.532 $R^2 = 0.9655$
브 -12.6 -12.8	
-13	
-13.2	

at pH 5.0, 23°C and 40 minutes.

**Figure (25):** Dubinin-Radushkevick plots for the biosorption of Pb(II) on olive cake ash at pH 5.0, 35°C and 40 minutes.

Dubinin-Radushkevick parameters for the adsorption of Pb(II) ions by olive cake ash at different temperatures are given in Table 4.

(L)	if) on onve cake ash at 15°C, 25°C and 55°C and pit 5.0.					
		Е	qm	qm	Ke	
	Temp.(°C)	(kJ/mol)	(mol/kg)	(mg/g)	$(mol/kJ)^2$	R²
	13°C	12.90	2.8×10-5	0.0059	0.003	0.9553
	23°C	10.80	2.9×10-5	0.0060	0.004	0.826
	35°C	13.14	2.6×10-5	0.0055	0.002	0.9655

Table (5): Dubinin-Radushkevick parameters for the biosorption of Pb(II) on olive cake ash at 13°C, 23°C and 35°C and pH 5.0.

As noted in Table 5, the values of E at different temperatures (13°C, 23°C and 35°C) are in the range 8 -16 (kJ/mol), which indicates a chemical adsorption. The monolayer capacity, qm ranged from  $2.6 \times 10^{-5}$  to  $2.9 \times 10^{-5}$  (mol/kg) when the temperature ranged from 13°C to 35°C. Generally, Dubinin model is a good fit with R<sup>2</sup> > 0.826 for the biosorption of lead ions onto ash.

In previous studies, the adsorption of Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) had E values ranging from -11.05 to 11.18 kJ/mol onto raw ash, and E values ranging from -20.86 to 44.79 kJ/mol onto activated ash (Xiyili et al., 2017). The biosorption of Pb(II) on MX-80 bentonite had  $q_m$  of  $2.38 \times 10^{-3}$  and E was found to be 8.80 kJ/mol with R<sup>2</sup> of 0.994 respectively (Xu et al., 2008). The adsorption capacities for the different models used were gathered in Table (6).

Table (6): Comparison between Langmuir adsorption capacity  $Q_L$  (mg/g), Fruendlich adsorption capacity  $K_F$  (mg/g) and monolayer

			Dubinin-
Temp.	Langmuir model	Fruindlich model	Radushkevick model
(°C)	QL(mg/g)	$K_{\rm F}$ (mg/g)	$q_m (mg/g)$
13 °C	1.201	62.16	0.0059
23 °C	1.160	103.6	0.0060
35 °C	1.471	41.44	0.0055

adsorption capacity qm (mg/g) at 13°C, 23°C and 35°C and pH 5.0.

## Conclusions

- The results of experimental data show that the olive cake ash is a good adsorbent for the removal of lead ions from aqueous solutions.
- The maximum adsorption of metal occurred at pH 5.
- The adsorption of lead metal by olive cake ash needed 40 minutes to achieve the equilibrium state between the biomass and the aqueous solution.
- The room temperature was a good choice for binding, since the binding was more than 91% when the temperature is zero or more.
- The uptake of lead ions by olive cake ash has a capacity of 0.29 mg/g.
- The highest total stripping for Pb(II) ions reached 100 % by 0.5 M HCl.
- The presence of hard cations such as Ca(II) and Mg(II) with lead ions in the same aqueous solution causes a significant increase 22% in the binding of lead ions with the biomass.
- Freundlich isotherm better fitted the experimental data than the Langmuir isotherm, since the correlation coefficients for Freundlich isotherm was higher than the Langmuir isotherm.
- The values of thermodynamic parameters at different temperatures indicate that the adsorption process is nonspontaneous and exothermic. Also, the adsorption process was accompanied with a decrease in entropy. In addition to that the adsorption is considered as a chemical process.

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جامعة النجاح الوطنية

كلية الدراسات العليا

# ازالة معدن الرصاص من المياه الملوثة باستخدام رماد جفت الزيتون

إعداد

ميساء ابراهيم يونس سودي

إشراف د. مآثر صوالحة د. إبراهيم أبو شقير

قدمت هذه الاطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في العلوم البيئية بكلية الدراسات العليا، في جامعة النجاح الوطنية، في نابلس – فلسطين.
## ازالة معدن الرصاص من المياه الملوثة باستخدام رماد جفت الزيتون اعداد ميساء ابراهيم يونس سودي اشراف د. مآثر صوالحة د. إبراهيم أبو شقير

الملخص

تم اجراء هذه الدراسة بهدف امتزاز ايونات الرصاص من المحاليل المائية باستخدام رماد جفت الزيتون. حيث تم دراسة تأثير بعض العوامل المختلفة على عملية الامتزاز مثل درجة الحموضة، الوقت ودرجة الحرارة، السعة الأمتزازية، وتأثير وجود الأيونات التنافسية مع الرصاص في نفس المحلول، وتأثير حمض الهيدروكلوريك وسيتريت الصوديوم في نزع ايونات الرصاص من الكتلة الحيوية، وفعالية امتزاز رماد جفت الزيتون.

لقد بينت الدراسة ان فعالية رماد جفت الزيتون لامتزاز ايونات الرصاص تكون اعلى ما يمكن عند pH=5، وان الزمن اللازم لحصول التوازن هو 40 دقيقة. كما أظهرت النتائج أن زيادة درجة الحرارة من 0°0 الى 0°07 أدى الى زيادة عملية الامتزاز تتراوح من %8.19 الى %94.5 كما اظهرت الدراسة ايضا ان لرماد جفت الزيتون مقدرة على استيعاب 0.29 ملغرام /غرام من ايونات الرصاص عند 0°28. وتراوحت اعلى نسبة امتزاز لايونات الرصاص من %6.90 باستخدام 1 الرصاص عند 0°38. وتراوحت اعلى نسبة امتزاز لايونات الرصاص من %1.90 باستخدام 1 الرصاص عند 10% من 10% من 40% مندرة على استيعاب 0.29 ملغرام /غرام من ايونات الرصاص عند 0°38. وتراوحت اعلى نسبة امتزاز لايونات الرصاص من %1.90 باستخدام 1 الرصاص عند 10% مندرة من 10% مندرة من 10% من 10% من ايونات الرصاص مند 10% من 10% م

كما تم استخدام نماذج (isotherm adsorption) لتقييم مدى فعالية امتزاز رماد جفت الزيتون لمعدن الرصاص، وأظهرت النتائج أن افضل البيانات التجريبية تناسب نموذجي Fruindlich و Dubbinin وان قيم ΔG° عند درجات حرارة مختلفة (C، 23°C and 35°C) هي 19.87، 20.45 وان قيم 20.45 يلوجول /مول بالترتيب ، وهذه القيم الموجبة تدل على ان عملية الامتزاز هي عملية غير تلقائية، كما ان قيمة ΔH° السالبة يعني ان عملية الامتزاز هي عملية طاردة للحرارة ،

كذالك قيمة ∆S0 السالبة يعني تناقص درجة الفوضى. وقيم E تتراوح من ( 8 – 16) كيلوجول/ مول وهذا يعني ان عملية الامتزاز هي عملية كيميائية.