Deanship of Graduate Studies

Al-Quds University

Treatment of Olive Mill Wastewater (OMWW) Using Variable Coagulants with super Flocculants

Jamila Zhran Ibrahim Zhran

M.Sc. Thesis

Jerusalem-Palestine

2018/1439

Treatment of Olive Mill Wastewater (OMWW) Using Variable Coagulants with super Flocculants

By

Jamila Zhran Ibrahim Zhran

B.Sc. of chemistry-Al-Quds University-Palestine

Supervised by: Dr. Jawad Hasan Shoqeir

A Thesis Submitted in Partial Fulfillment of Requirements for the Degree of Master in Environmental Studies, Faculty of Graduated Studies, Al-Quds University.

Jerusalem-Palestine

2018/1439

Al-Quds University
Deanship of Graduate Studies
Environmental Studies

Thesis Approval

Treatment of Olive Mill Wastewater (OMWW) Using Variable Coagulants with super Flocculants

Prepared by: Jamila Zhran Ibrahim Zhran

Student NO: 21212962

Supervisor: Dr. Jawad Hasan Shoqeir

Master thesis submitted and accepted date: 6.5.2018

The names and signatures of examiners committee members:

Head of committee: Dr. Jawad Hasan Shoqeir Signature: …………

External Examiner: Dr. Saleh Sulaiman Signature:

Internal Examiner: Dr. Samer Khalaf Signature:

Jerusalem-Palestine

2018/1439

Dedication

TO my mother”Somaya” and the spirit of my father Zhran

To my uncle Mousa Zhran

To my lovely husband Mohammad and his family

To my brothers Ibrahem, Majd, Mohammad, Zhran and Hmam

To my babies Adnan and Fatima

To all those people whose support and helped me in this study

Jamila Zhran

Declaration

I Certify that this thesis submitted for the degree of Master, is the result of my own research, except where otherwise acknowledged, and that this study (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed: jamila ……………

Name: Jamila Zhran Ibrahim Zhran

Date: 6/5/2018

Acknowledgment

Many thanks and gratitude to GOD, who give me the power to finish this work. I'd like to thank my supervisor, Dr. Jawad Hasan, for his continuous support, patience, and tough love for all of his students. Without his guidance and relentless efforts my thesis wouldn't have been successful.
My sincere gratitude goes to the stuff of soil and hydrology lab Research Team work: Diya'Radeideh, Doha Awad and Derar, for further help and working together, cheerful and positive energy.

A lot of thank also for all the professors in the Department of Earth and Environmental Science in Al-Quds University. Special thanks for Dr. Amer Marei and his staff in Research lab.

I also would like to thank my mother, for her unconditional love and support. I wouldn't have made it without her.

Thanks also extended to my uncle Mousa Zhran for their support and for believing in me.

I would like to thank my husband and his family for being very supportive and help me achieve all my goals with ease. Last but not least, thanks to all these love and support me.

Abstract:

Olive mill wastewater (OMWW) management has been a major issue of environmental concern for olive oil producing countries. In Palestine, the problem of untreated OMWW discharge is urgent. Several hundred thousand cubic meters of untreated WW is discharged into open areas (wadies) and cesspools whereas the solid waste (olive husk) is dumped into lands nearby the olive mills without treatment. This increases the risk of contaminating soil, surface water resources, and groundwater aquifers. The negative environmental impact of OMWW is attributed to poor biodegradation and toxicity of polyphenols present in OMWW.

In this study, sample of OMWW were collected in October 2016 from Al-Qubayba village in the middle part of west bank (north western of Jerusalem), the level of pollution and their impact on the environment has been determined by measuring physical and chemical properties of OMWW such as: COD, pH, EC, TDS, TSS, TPs. The results revealed that the OMWW have a high risk on environment due to the high phenols concentration that exceeds the maximum allowable limits for discharge to environment or to the sanitary sewer system according to Palestinian standards.

The treatment of olive mill wastewater (OMWW) by means of coagulation–flocculation coupling various inorganic materials in different dose and organic polyacrylamide (PAM) was investigated. With respect to their efficiency in terms of total phenols removal and the effect of OMWW application on soil water drop penetration time test (WDPT).

This study aims to evaluate coagulation as a pre-treatment followed by flocculation using PAM to examine their efficiency on reducing total phenols concentration in olive mill wastewater.

Different dose of Fe(II), lime and PAM were tested by. Results showed that Fe(II) and Fe(II) with lime don’t make removal however, lime alone remove the phenols concentration up to (18.4, 34.1, 38, 40.8, 42.2, 44.8 %) for (1,2,3,4,5 and 6 g) Respectively. Increasing in lime mass means increasing in sludge mass, adding super flocculants polyacrylamide on OMWW with lime improves the percentage of phenols with removal lower sludge mass, the efficient dose of the highest value of phenols removal with lowest sludge’s is (1g lime with 0.1g PAM) for each 100 ml of OMWW, Where efficiency is (51.5%).

Irrigating soil with treated OMWW for 8 days comparison with fresh water and raw OMWW, showed that treated OMWW with (1g lime and 0.1 PAM) behaves as fresh water when water drop penetration time test have been applied, the drop of water takes 3 seconds to infiltrate into soil sample that irrigated with fresh water and treated OMWW. The drops of water take (27-30 minutes) to infiltrate into soil sample that irrigated with raw OMWW, which means that treated OMWW lead to improve the water penetration in soil.

معالجة المياه العادمة لمعاصر الزيتون (الزيبار) باستخدام مواد كيماوية مخثره و مبلمرات عضوية

إعداد : جميلة زهران إبراهيم زهران
إشراف: د.جواد شقير

الملخص

تعد إدارة ومعالجة المياه العادمة الناتجة من استخراج زيت الزيتون (الزيبار) قضية رئيسية ذات أهمية بيئية بالنسبة للبلدان المنتجة للزيت. يعتبر تصريف الزيبار في فلسطين دون معالجة مشكلة ملحة تحتاج معالجة عاجلة حيث يتم تفريغ مئات آلاف الأمتار المكعبة من المياه العادمة غير المعالجة إلى مناطق مفتوحه " الأودية " مما يزيد خطر تلوث التربة وموارد المياه السطحية و الجوفية, ويعود سبب الأثر السلبي لهذه المياه العادمة إلى سوء تحللها البيولوجي وسمية مادة الفينول الموجودة فيها بتراكيز عالية . في هذه الدراسة تم جمع عينة من المياه العادمة المستخرجة من عملية عصر الزيتون في شهر أكتوبر من عام 2016 من معصرة قرية القبيبة في الجزء الأوسط من الضفة الغربية شمال غربي القدس. تم تحديد مستوى تلوث هذه المياه من خلال قياس الخصائص الفيزيائية والكيميائية مثل درجة الحموضة والموصلية الكهربائية وإجمالي المواد الصلبة الذائبة والطلب الكيميائي على الأوكسجين وإجمالي المواد الصلبة والفينولات. أظهرت النتائج أن الزيبار يحوي تراكيز عالية من الملوثات البيئية ويتجاوز الحدود القصوى المسموح بها للتخلص من المياه في نظام الصرف الصحي وفقا للمعايير الفلسطينية.

للحد والتخفيف من تركيز الفينول في الزيبار والذي يعتبر الملوث الرئيس تم معالجة العينات بإستخدام مواد كيميائية عضوية مبلمرة تسمى(بولي أكريلامايد) باستخدام تراكيز مختلفة ومواد كيميائية غير عضوية تسمى (coagulants) مثل الحديد والجير.

كان التركيز الفعال والذي يعطي أعلى نتائج في تخفيف تركيز الفينول مع أقل كمية من المواد الجانبية الناتجة هو(1غم من الجير مع 0.1غم من البولي أكريلامايد) لكل 100 مل من الزيبار حيث وصلت نسبة الإزالة إلى (51.5%). ولدراسة تأثير الزيبار المعالج على التربة تم إجراء تجربة وقت اختراق قطرة الماء للتربة، النتائج أظهرت أن قطرة الماء تستغرق من 27-30 دقيقة لاختراق التربة التي سُقيت بالزيبار غير المعالج, بينما تستغرق قطرة الماء 3 ثوان لإختراق التربة التي سُقيت بالزيبار المعالج وهو الوقت ذاته الذي تستغرقه قطرة المياه بإختراق التربة التي سُقيت بمياه نقية, هذا يعني أن معالجة الزيبار باستخدام التركيز الفعال وتصريفها إلى التربة يحسن تغلغل المياه في التربة .

Table of Contents

List of Abbreviations

Abbreviation	**Full Name**
OMWW	Olive Mill Wastewater
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
TPs	Total Phenols
rpm	repetition per minute
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
EC	Electrical Conductivity
OM	Organic Matter
TDS	Total Dissolved Solids
EC	Electrical Conductivity
OM	Organic Matter
F.W	Fresh Water
UTOMWW	Un Treated Olive Mill Wastewater
TOMWW	Treated Olive Mill Wastewater
PAM	Polyacrylamide
PCBS	Palestinian Central Bureau of Statistics
UN	United Nations
IOC	International Olive Council
WW	Waste Water
FCR	Folin Ciocalteu reagent
WDPT	Water Drop Penetration Time

List of Tables

List of Figure

Chapter One:

Introduction

1.1 Background:

Scarcity and limited access to water resources in Palestine have been a major issue, which requires preservation of existed resources from possible contamination with pollutants. Different types of point and non-point pollution sources contribute to this problem, including industrial and agricultural activities. One of the major water pollution sources is Olive Mill Wastewater (OMWW), generated seasonally from olive oil extraction processes (Aladham, 2012). The annual production of OMWW in the Mediterranean countries exceeds $30x10^6m^3$ (Aly et al., 2014), and around 200 thousand m^3/year of OMWW are generated in the West Bank particularly (Shaheen and Abdelkarim, 2007).

Wastewater from the different olive-mills located in and around the different villages in Palestine are being disposed of into the wadies. Therefore, it is mixed with the untreated flowing municipal wastewater or with rainwater and may contaminate groundwater resources, mainly due to its high phenolic content. The resulting high organic polluted wastewater affects the soil and water receiving bodies. This occurs mainly during the olive season from early October to late December (Shaheen and AbdelKarim, 2007).

1.2 The olive tree

The olive tree grows almost exclusively around the Mediterranean Sea. This tree has been praised by every civilization around the Mediterranean. The olive tree is a small evergreen tree that averages 3 to 5 m in height. In general, cultivating olive trees takes time, as the first sizeable crop is expected after 8 to 10 years the olive fruit starts maturing in October, when it may be harvested for table olive as pickled green olive. It then slowly turns black until December and is consumed as salted or pickled black olives or is sent to oil production (Azbar et al., 2004). The composition of olives is given in Table (1.1).

Table (1.1): A representative chemical composition of olive fruit (Niaounakis and Halvadakis 2006).

Constituents	Pulp (%)	Stone (%)	Seed (%)
Water	50–60	9.3	30
Oil	15–30	0.7	27.3
Nitrogen containing compounds	2–5	3.4	10.2
Sugar	3–7.5	41	26.6
Cellulose	3–6	38	1.9
Minerals	1–2	4.1	1.5
Polyphenols (aromatic compounds)	2–2.25	0.1	0.5–1
Others	0-6	3.4	0-24

1.3 Olive oil production Worldwide

According to the official country data and the estimates of the International Olive Council (IOC)**.** Executive Secretariat, world olive oil production in 2017/18 is estimated at around 2,854,000 ton, with approximately 12% increase compared to the previous year. Spain was expected to produce

1,090,500 tons, or 15% less than the last crop year, Italy 320,000 tons (+76%), Greece 300,000 (+54%), Turkey 287,000 (+62%), Tunisia 220,000 (+120%), Morocco 140,000 (+27%), and the rest less than 100,000 metric tons olive trees cultivation and olive production depend on many factors including soil fertility, irrigation availability and climatic conditions (Tamimi, 2016).

In Palestine

Olive and olive oil production is an important source of income for a considerable sector of farmers. According to UN data (UN reports 2017) around 48% of the agricultural land in the West Bank and Gaza is planted with olive trees. From agricultural prospective, olives and their oil have major contributions in the Palestinian economy (Al-Khatib et al., 2005). The Palestinian Nation Information published that the olive farms covers almost half of the cultivated area in The West Bank, and oil production contributes by around 28.7% of the agricultural domestic income. Data indicate that there are more than 270 olive mills in Palestine, 75% of which are full automatic and continuous plants, while the remaining are half automatic or traditional mills.

Olive production is cyclical, in which good years following bad years, in Palestine, 63% of agricultural land areas are ‘under full Israeli control’ and only 18% are under full Palestinian control. Which that movement is severely restricted.

1.4 Manufacturing process of olive oil

Different oil extraction technologies have been advanced significantly during the past decades (Figure 1.1), they can be categorized into the traditional and continuous press process as described below.

The traditional or discontinuous press: the cold press process **figure (1.1)** shows the oldest and the most wide spread method for processing olive oil. The invention of the hydraulic press was a revolution for old mills, and these presses are still used in improved traditional mills. After grinding, the olive paste is spread onto fiber disks that are stacked on top of each other and then placed in the press. These disks were traditionally made of hemp or coconut fibers but are now made of synthetic fibers for easier cleaning and maintenance. Pressure is applied on the disks to compact the solid phase of the olive paste and to percolate the liquid phases (oil and vegetation water). Small quantity of water is added to easily separate the oil from the other phases. The press extraction sub process yields a solid fraction called olive pomace (olive cake) containing olive pulp, skin, stone and water. This byproduct mix, with an emulsion containing the olive oil, is separated by decantation from the remaining OMWW. This method offers advantages such as cheap equipment and technical simplicity (Dermeche et al., 2013).

The continuous press: figure (1.1) shows the modern method of olive oil extraction which uses an industrial decanter to separate oil from olive components by centrifugation (Tamimi, 2016). The press can be operated either by three-phase or two-phase decanter. In three-phase process, the olive fruits are crushed to form a paste. The paste is then stirred at 27 °C to improve the oil droplets aggregation. This step is called malaxation. The paste is then pumped to a large horizontal centrifuge called decanter, where water is added to facilitate the flow of the paste to the decanter and the separation of oil from the solid particles. The decanter has three outlets one for the olive oil, another for the olive mill wastewater, and a third outlet for the solids (pomace). (Abdellaoui, 2015)

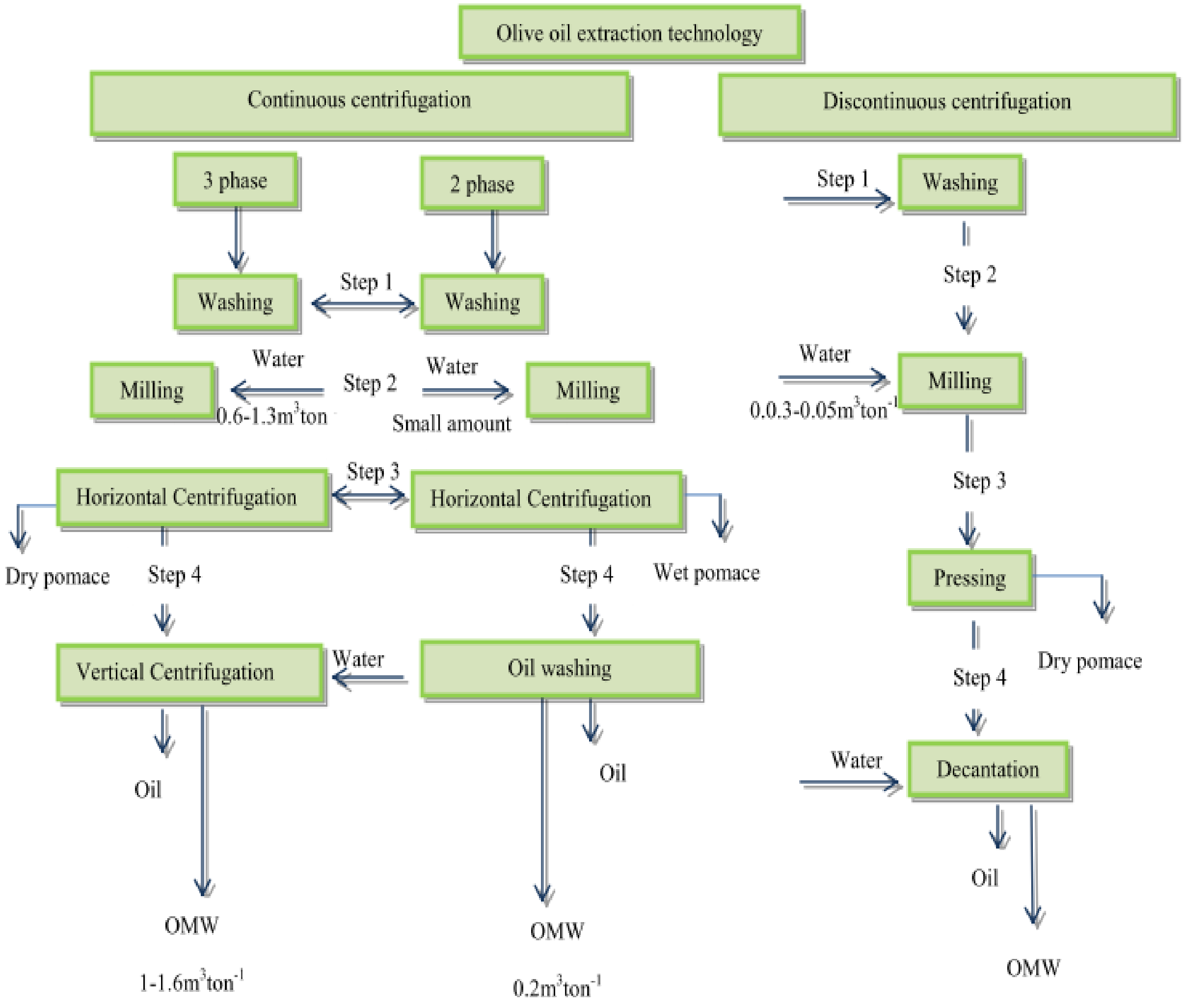


Figure (1.1): Olive oil extraction technologies (Dermeche et al., 2013).

1.5 Olive mill wastewater (OMWW)

1.5.1 Characterizations of olive mill wastewater:

The manufacturing process of the olive oil usually yields next to olive oil (20%), a semi-solid waste (30%), and aqueous liquor (50%) (Sawallha et al., 2014). The aqueous liquor comes from the vegetation water and the soft tissues of the olive fruits. The mixture of this water-based by-product with the water used in the different stages of oil production makes up the so-called ‘‘olive-mill waste water’’ (OMWW) (Sawallha et al., 2014). It is a mildly acidic, red-to-black colored and liquid of high conductivity. Its composition varies both qualitatively and quantitatively according to the olive variety, climate conditions, cultivation practices, the olive storage time and the olive oil extraction process. Apart from water (83–92%), the main components of OMWW are phenolic compounds, sugars, and organic acids (Dermeche et al., 2013)

OMWW characteristics depend on many factors such as the extraction technology employed, the variety and maturity of the olives, the climatic conditions, the cultivation management and the storage time (Tayoub et al., 2015). The typical characteristics of OMWW are: low pH ranges of 3-6 (Azbar et al., 2004), high biological and chemical oxygen demand (Hanafi et al., 2013), high concentration of oils and greases of ranges 1-23 g L^{-1} (Azbar et al., 2004), high salinity (Roig et al., 2006) and high content of phenolic compounds (Hanifi and El Hadrami, 2008), responsible for the typical black color of OMWW.

1.5.2 Phenolic compounds

Phenolics, are a class of chemical compounds consisting of a hydroxyl group (--OH) bonded directly to an aromatic hydrocarbon group.

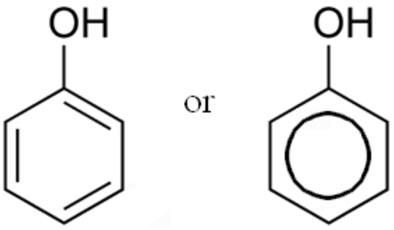


Figure (1.2): Simplest molecular structure of phenol

Both the stone and pulp of olives are rich in phenolic compounds. These compounds, once released or formed during processing of olives, they are distributed between the water and oil phases. Another part of the phenols is trapped in the olive cake. The distribution of the released amount of the phenols between water and oil is dependent on their solubilities in these two phases. The olive phenols are amphiphilic in nature and are more soluble in the water than in the oil phase. Phenolic compounds are present in OMWW at concentrations in the range from (0.5 to 24) g/l, and are strictly dependent on the processing system used for olive oil production (Niaounakis and Halvadakis, 2006). Phenols are strong antioxidant and complicating any detoxification process for the OMWW (Hatzinikolaou, 2007).

A range of phenols in olive oil provides some of its health benefits (Waterman et al., 2007). The concentration of phenols depends on a number of factors, including environmental growth conditions, method of oil production, and storage conditions (Visioli et al., 2002). More than 30 phenolic compounds have been identified in OMWW (Niaounakis and Halvadakis, 2006). The phenolic compounds contained in OMWW were classified by Hamdi roughly in two groups (Hamdi, 1993). The phenolic compounds of the first group contain simple phenolic compounds, oxidated tannins (of low molecular weight), and flavonoids. The polyphenols of the second group, which contain darkly colored polymers, result from the polymerization and auto oxidation of phenolic compounds of the first group. It was observed that OMWW becomes blacker when it has been stored for some time. This change in color might be as a result of the oxidation and subsequent polymerization of tannins giving darkly colored polyphenols (Hamdi, 1993).

1.5.3 OMWW Treatment and Disposal Options

The organic content in the OMWW is classified as one of the highest concentrated effluents, which is 100-150 times higher than the organic load of domestic wastewater (Khatib et al., 2009). Furthermore, it was estimated that the load of phenolic compounds in OMWW is 1000 times higher than in domestic wastewater (Niaounakis and Halvadakis, 2004). The seasonal large discharge of OMWW with high organic loads and high chemical oxygen demand (COD) and biological oxygen demand (BOD) (Azbar et al., 2004) and its associated effects on sewerage corrosion and sediments build up (Tsagaraki et al., 2007) are the main reasons for the prohibition of OMWW discharging into municipal sewerage system (Tamimi, 2016).

Many scientists work on efficient and cost-effective treatment alternatives. Several alternatives and their combinations were tested including the chemical, mechanical, physical, biological, and thermal methods (Azbar et al., 2004). Use of large lagoons (artificial evaporation ponds or storage lakes), with the sun’s energy to speed-up the evaporation process and drying of OMWW remain is the most common practice for the OMWW disposal. Moreover, OMWW is partially degraded by a natural biological route, over very long time periods. This technique for OMWW disposal imposes treatment times of the order 7–8 months (Niaounakis and Halvadakis, 2006).

In addition to other OMWW treatment technologies physicochemical, chemical, biological (aerobic or anaerobic), evaporation (natural or forced), and land application are considered(Azbar et al., 2004).

Such OMWW treatments are rare to non-existing due to the following factors: the high regional scattering of olive mills and their large variation in size and capacity, type of oil extraction press, the volume of OMWW produced and the land availability. These factors limit the possibility of economic design with reasonable operational cost of such treatment options for OMWW in these countries (Brunetti et al., 2007). Beneficial use of olive mill wastewater and its end products is anticipated, such as by recycling the treated water, and using the residues as fertilizer either directly or after composting or as raw material for antioxidant production (Azbar et al., 2004).

Palestine is an example of such countries that generates a large amount of OMWW annually. The quantity of olive oil produced in 2014 was 24,758.5 tons with an increase of 40.3 % compared to 2013 (PCBS, 2014). This waste (OMWW) is generated from 265 olive presses, of which 241 utilize “three-phase technology” and only 24 are traditional presses. Due to the absence of legislation and treatment facilities for OMWW in Palestine, the only disposal method available is the uncontrolled discharge to open fields and valleys which need to be regulated and standardized to limit potential pollution expected to soil and crop (Tamimi, 2016).

1.5.4 Effect of OMWW

1.5.4.1 Effect on soil

The Mediterranean region is characterized by arid and semi-arid climatic conditions. In addition to water deficiency in this region, the soil has a very low microbial activity and low nutrient availability (Di Bene et al., 2013), many studies considered OMWW disposal on soil as a fertilizer and organic amendment (Celano et al., 2010). In this perspective, the presence of organic matter (OM) and plant nutrients such as K, P, and Mg identifies the positive effect of OMWW on soil fertility and productivity as an organic amendment**.** OMWW has a beneficial effect on soil aggregation, soil structure stability, and the hydrodynamic properties of sandy soils (Niaounakis and Halvadakis, 2006).

Conversely, the uncontrolled disposal of OMWW can disturb the ecological balance of the soil (Paredes et al., 1986). OMWW cause increase in the organic carbon content of the soils and a reduction in soil porosity and limit air and water exchange between soil and atmosphere. These changes in porosity are attributed to the combined effect of the suspended and soluble organic matter and salts in OMWW and the Solubilization – Insolubilization of the soil carbonate minerals promoted by OMWW, these exchanges are indispensable for the development of the fauna and the micro flora of the soil as well for the respiration of the roots. (Niaounakis and Halvadakis, 2006).

OMWW also contains many acids, minerals, and organics that could destroy the cation exchange capacity of the soil, add to this increase in salinity and in soluble phenolic compound contents was detected. The enrichment diminished in deeper layers, due to OMWW soil retention, the discharge of OMWW in soils causes the release of heavy metals retained by them because of its acidic pH (Niaounakis and Halvadakis, 2006). Further studies reported a decrease in soil pH, an increase in soil salinity and toxicity in response to OMW application (Di Bene et al., 2013). The phytotoxic effect was conclusively attributed to phenolic substances in OMWW (Buchmann et al., 2015). In this sense, the OMWW disposal caused shift in soil microbial communities associated with abundant phenolic compounds as well as high salinity which negatively inhibited the bacterial growth (Barbera et al., 2013) and increased population ratio of fungi: bacteria (Di Bene et al., 2013).

1.5.4.2 Effect on water

OMWW was usually discharged into nearby rivers and streams with a considerable impact on the receiving waters, OMWW is presenting too much undeniable harm to the environment, such as the serious effect of ground and surface water pollution which cause the toxicity on aquatic fauna life (Danellakis et al., 2011). The main effects of OMWW on natural water bodies are related to their concentration, composition, and to their seasonal production. The most visible effect of OMWW pollution is the discoloring of natural waters. (Niaounakis and Halvadakis, 2006). This change in color is attributed to the oxidation and subsequent polymerization of tannins giving darkly colored polyphenols, which are difficult to remove from the effluent (Hamdi, 1993). OMWW also has a considerable content of reduced sugar which would be used as a substrate for microorganism. This leads to low dissolved oxygen in water and imbalance in the whole ecosystem (Niaounakis and Halvadakis, 2004).

1.5.4.3 Effect on sewerage system

Due to its high acidity and suspended solids content, OMWW could be highly corrosive to sewer pipes (Rozzi and Malpei, 1996). Suspended solids settle in the sewer system would cause clogging close to the mills discharge pipes the sediments also undergo anaerobic fermentation and increase the acidity content of wastewater (Niaounakis and Halvadakis, 2004). Relatively small spills of olive-mill effluents into the sewers have appreciable effects on the wastewater treatment plants, as pollution due to 1m^3 of OMWW corresponds to 100–200m^3 of domestic sewage (Niaounakis and Halvadakis, 2006).

1.6 Problem description

In Palestine, olive production is considered the backbone of Palestinian agriculture. In 2016, about 84 thousand tons of olives were pressed with an extraction rate of 23.8% producing about 200 thousand cubic meters OMWW (Zibar). The majority of Zibar (42.7%) is disposed in Tight Cesspit (PCBS, 2017), (Figure1.3). In addition to that, OMWW discharges into surface waters and spread to land which affects the soil's physical and chemical properties (Salman et al., 2014).

There is no appropriate method applied for treating OMWW in Palestine; it is usually disposed of in sewage systems and/or cesspools in addition to being discharged into water streams and valleys in the region (Khatib et al., 2009). Due to the presence of toxic compounds and because of their high organic loads, the improper discharge of OMWW causes the disruption of biological activities in domestic wastewater ponds, creates a strong and unpleasant odor due to aerobic digestion in open air systems, and poses a threat to surface and groundwater (Hamdi, 1993). The disposal of OMWW causes serious environmental problems during the olive harvest season. In addition to wastewater generation, a large amount of solid waste is generated (Khatib et al., 2009). (PCBS, 2017) indicated that 84.3% of the farmers retrieve the olive cake resulting from pressing their olive for their own use.

The high concentration of darkly colored polyphenols in OMWW can discolor streams and rivers. OMWW can also have a deleterious effect on soil porosity and pH (Anastasiou et al., 2011). The phenolic compounds in OMWW are mostly responsible for its phytotoxicity and properties (Ben Sassi et al., 2006). Due to high levels of phytotoxic and antimicrobial compounds such as monomeric-polymeric phenols, volatile acids and polyalcohol's, OMWW is toxic to plants and soil micro flora and can affect the soil quality (Afify et al., 2009).

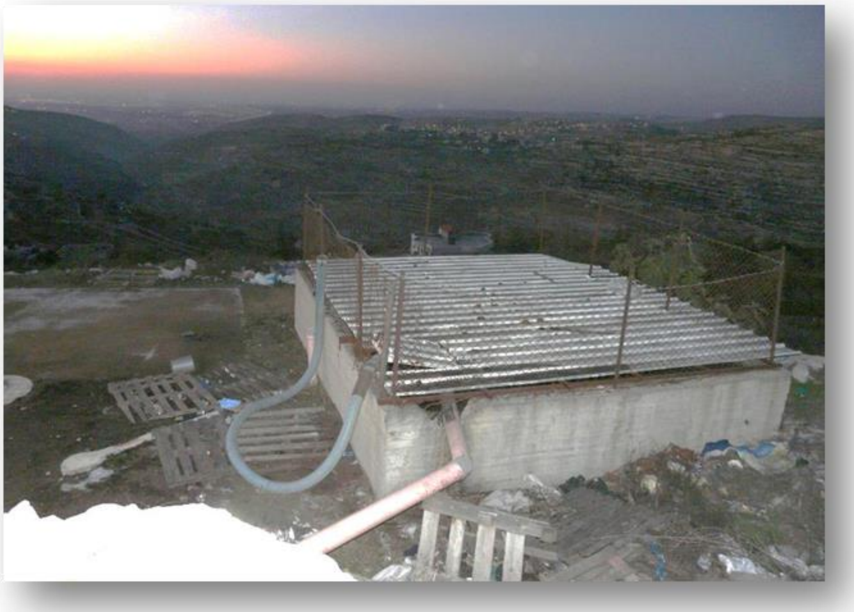


Figure (1.3): Final dumping sites of OMWW in Al-Qubayba village Northwest of Jerusalem

1.7 Literature review

The problem of disposal and treatment of OMWW has risen to several studies; some of these related studies are summarized by focusing on the treatment method that used in each study and main results of it as following:

1. **Kapellakis et al., 2012**: The objective of this study was to investigate the application of constructed wetlands as a mean to manage olive mill wastewater (OMWW). Two free water surface (FWS) constructed wetlands, one without (CW1) and one with effluent recirculation (CW2), were operated for a two-year period with diluted OMWW (1:10) and evaluated in terms of the removal of COD, TSS, TKN, NH_4 +-N, NO_3 −-N, TP and total phenols. Application of OMWW in CWs resulted in a significant reduction in the concentration of all parameters investigated. In CW1 the average removal efficiency was estimated at 80%, 83%, 78%, 80%, and 74% for COD, TSS, TKN, TP, and total phenols, respectively. The recirculation of OMWW in CW2 further improved effluent quality with removal efficiency approaching 90%, 98%, 87%, 85%, and 87% for COD, TSS, TKN, TP, and total phenols, respectively. With regard to the removal of NH_4^+-N and NO_3^--N, it was considerably lower compared to the other parameters monitored. The removal efficiency of NO_3^--N approached 40% and 52% in the CW1 and CW2, respectively. The removal of NH_4^+-N was not affected by the recirculation and averaged to 54% in both wetland basins.

2. **Salman et al., 2014**: The aim of this work was to investigate the ability in reduction of phenolic compounds in OMWW using the white rot fungus Ph. Chrysosporium. This fungus can significantly reduce the color of this effluent and degrade the high and low molecular-mass

aromatic. The results showed that fungus was able to grow on undiluted OMWW. Spectrophotometric studies revealed that after two weeks of treatment, total phenols were reduced by 60.1% compared to untreated OMWW. Interestingly, the toxicity of OMWW was significantly reduced. Barley seeds irrigated with olive mill wastewater treated with the fungus showed 81.6% seed germination.

3. **Hodaifa et al., 2015**: Were treated OMWW by UV-Light and UV/H_2O_2 System. The influence of ultraviolet light (UV) and the combined system of UV/H_2O_2, in the degradation of organic matter of OMWW, were studied. UV-light application at a short time (<30 min) implies a removal values in COD = 15-22%, total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) in the range 34% to 43%. The turbidity elimination was registered in the range 68% to 70%. In the case of combined UV/H_2O_2 system the removal percentages were 40-48% for COD, 39.4-51.9% for TC, 33.0-48.0% for TOC, 37.0-53.1% for TN, and 66.8-93.4% for turbidity.

4. **(Ziati et al., 2017)**: The objective of this study was the removal of phenolic compounds from olive mill wastewater by adsorption on activated carbon, prepared from a lino-cellulosic waste "peach stones" thermally treated. This processing technique is chosen because of its efficiency and ease of implementation. Adsorption tests on the obtained material results in about 83% removal rate of polyphenols (at 20 °C, 2 g of activated carbon and 1 hour of contact time). The study of the influence of pH and temperature shows that at acidic pH and ambient temperature (T = 20°C), the optimal adsorption of polyphenols was reached (91%).

1.7 Research hypothesis

The research is based on the hypothesis that OMWW can be detoxification. Dramatically phenol using "Physico-Chemical processes coagulation-precipitation-flocculation using inorganic coagulants following by super flocculants organic polymer polyacrylamide (PAM)."

1.8 Objectives

Our major aim was to treat OMWW in Palestine; West Bank in order to reduce environmental impact, to achieve this aim, specific objective will be adopted for this process:

1. Investigate the efficiency of Calcium hydroxide (lime) and Ferrous Sulfate $FeSO_4.7H_2O$. Fe(II) followed with Anionic polyacrylamide (PAM) in OMWW treatment and assess the effect of its in total phenols removal.
2. Investigate the efficiency of removal of phenols using different concentrations of coagulants and PAM to get optimal values of removals.
3. Assess the effect of treated OMWW on the soil properties.

Chapter Two:

Methodology

2.1 Methodology

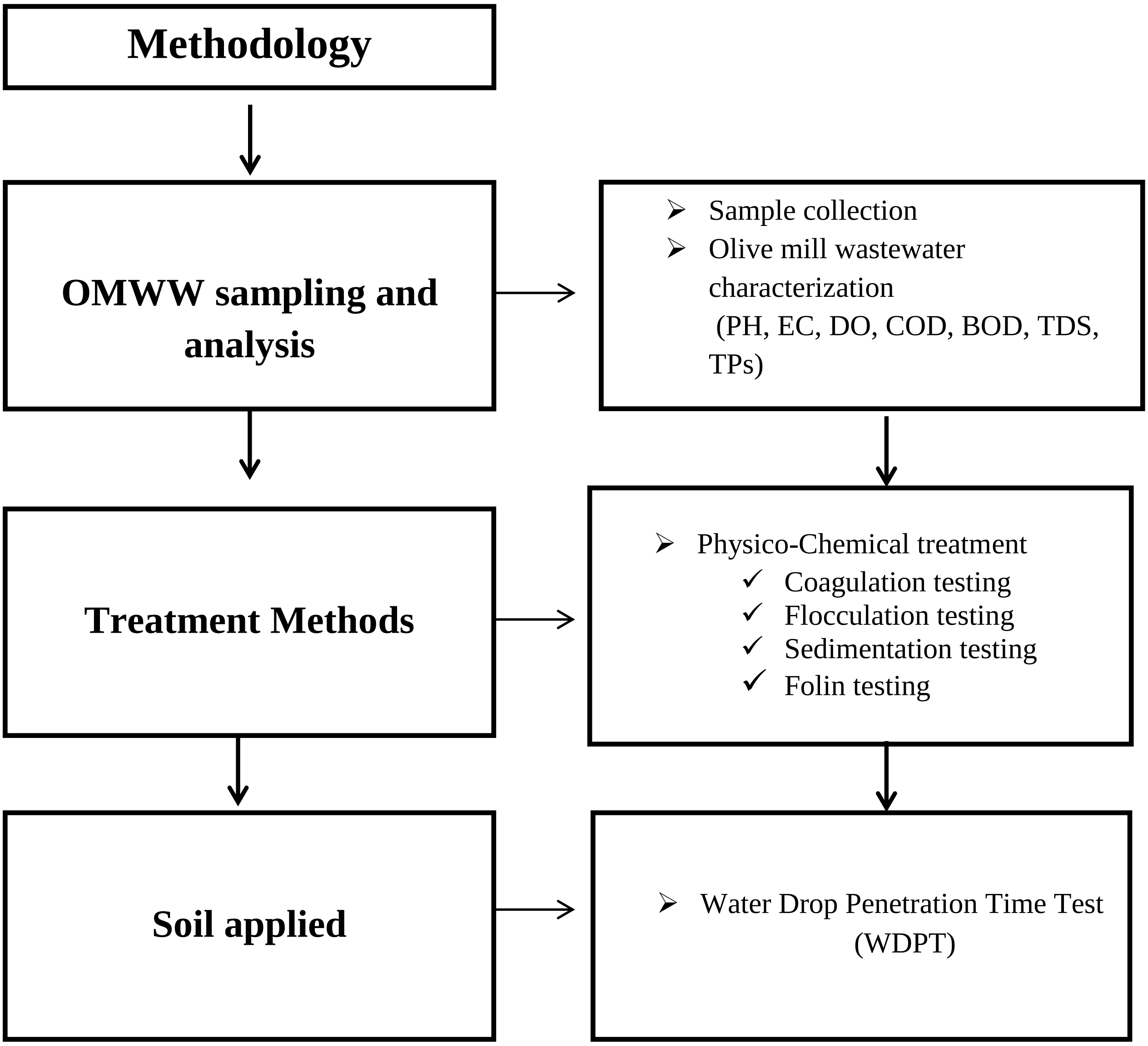


Figure (2.1): Research methodology

2.2 Sample collection

OMWW sample was collected without any pre-treatment during the olive oil production season (from September to November of 2016) in the region of Al-Qubayba village, Northwest of Jerusalem (full automatic olive mills). OMWW was collected directly from press and stored in 18L plastic containers in the dark at the laboratory, the analysis was done directly in soil and hydrology research lab in Alquds University.

2.3 Sample procedure

18L of olive mill wastewater was divided to 100ml. Samples were shaken using shaker for 20 min at 4000 rpm, The samples were filtered by filter paper then diluted by distilled water (taking into consideration the dilution factor difference 1:500), 12.5ml of diluted sample was poured in test tube, and then 0.25ml Folin-Coicalteus reagent and 2.5ml Carbonate-Tartrate reagent were added. The solution was turned to blue color. After half an hour the blue solution was examined spectrophotometrically at 700nm wavelength.

2.4 Standard solution procedure

- Stock solution: in 250ml volumetric flask dissolve 0.25g tannic acid which is equivalent to 1000ppm and dilute to volume with water.
- Carbonate reagent: dissolve 0.3g sodium tartrate and 5g sodium carbonate in 100ml volumetric flask mixed using stirrer plate 10min for a completely dissolving.
- Standard solution: prepare 1ppm standard solution , added 0.1ml stock solution to 100ml volumetric flask, depended on:

$$M_1*V_1=M_2*V_2$$

For prepare 2ppm standard solution we were added 0.2ml stock solution to 100ml volumetric flask and so on for 3,4,5,6 and 7ppm, 12.5ml of each standards sample was poured in test tube. Then both Folin-Coicalteus reagent and Carbonate-Tartrate reagent were added. The solution was turned to blue color. After half an hour the blue solution was examined spectrophotometrically at 700nm wavelength.

- For Blank preparation 0.25ml Folin-Coicalteus reagent and 2.5ml Carbonate-Tartrate reagent were added to 12.5ml distilled water, then the solution was examined spectrophotometrically in 700nm wavelength.

2.5 Olive mill wastewater characterization

The physicochemical characteristics of OMWW were determined according to standard analytical methods. All measurements were conducted in triplicate. pH, Electrical Conductivity (EC) and Dissolved Oxygen (DO) were measured by using a WTW multi meter 3430. Chemical Oxygen Demand COD, Biological oxygen demand (BOD) Total Phenols (TPs) and Total Dissolved Solid TDS were measured also.

- **pH**

Was measured in a suspension of 50ml of olive mill wastewaters at ambient temperature by pH-meter instruments previously calibrated with buffer solutions pH 4, 7 and 10 immediately after sampling, pH measurement is done directly in the raw effluent olive oil mills at room temperature according to CCBA-SOP-005 multi meter**.**

- **Electrical Conductivity (EC)**

Multi meter (CCBA-SOP-006) was used to measure the conductivity of the olive mill wastewaters samples. The conductivity measurement is a good assessment of the degree of mineralization of olive oil mill wastewaters, where each ion is characterized by its concentration and specific conductivity, the electrical conductivity is strongly related to the concentration of dissolved substances and to their nature; values ranging between (12 and 50 $mS.cm^{-1}$) (Bouknana et al., 2014).

- **Dissolved Oxygen (DO)**

Multi meter (CCBA-SOP-016) also used to measure (DO), study of dissolved oxygen parameter is very important because it provides information about the quality of the effluents studied (Bouknanaet al., 2014). This is one of the most sensitive test to pollution parameters; its value provides information on the degree of pollution and consequently the degree of self-purification in storage basin olive mill wastewater.

- **Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)**

The olive oil mill wastewaters are rich in organic matter expressed in terms of BOD_5 (biological oxygen demand) and COD (chemical oxygen demand). Carbon oxidation of organic matter of olive oil mill wastewaters can schematically be written using the following equation: organic matter + oxygen + microorganism nutrient will give biodegradation byproducts (CO_2, H_2O, NH_3 ...) + bacterial biomass. Certain reducing bodies as sulfides, sulfites, ferrous iron, that may be encountered in industrial effluents react also on the oxygen consumption.

Biological oxygen demand (BOD_5) signifies the biodegradable fraction of organic matter in olive oil mill wastewaters, involving bacteria and fungi, in a thermostat at 20°C for 5 days enclosure of olive mill wastewaters samples were previously diluted with water, pH of the sample must be between 6 and 8.

2.5 Treatment Methods

2.5.1 Physicochemical Treatment:

Coagulation-Flocculation is used widely during water or wastewater treatment. It is an integral treatment step in the surface or underground waters treatment, intended for human consumption. Typical applications are the removal/separation of colloids and suspended particles, of natural organic matter, or of metal ions. In wastewater treatment, additional applications include the removal of toxic metals, anions (i.e. phosphates), color, odor etc. (Tzoupanos and Zouboulis, 2008).

These processes involve the use of additional chemicals in order to destabilize the suspended and colloidal matter of OMWW and form an insoluble solid that can be removed easily from the waste (Tsagaraki et al., 2007). After coagulation /flocculation, gravity sedimentation, and sometimes filtration, is employed to remove the flocculated colloids.

Solids can be dispersed in liquids under several forms. The nature of such dispersions depends on the size of the solid particles. In general, one the following states are considered:

- Solutions
- Colloidal dispersions
- Suspensions

2.5.1.1 Coagulation:

the process through which colloidal particles and very fine solid suspensions are destabilized by addition of chemicals that neutralize the negative charges so that they can begin to agglomerate if the conditions are appropriate. Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the wastewater to promote destabilization of the colloid dispersion and agglomeration of the resulting individual colloidal particles.

Destabilization Mechanisms

Different destabilization mechanisms can be employed such as:

1. Repression of the double layer.
2. Neutralization of colloid charge by adsorption of counter ions on the surface of the colloid.
3. Bridging of colloidal particles via polymer addition.
4. Entrapment of colloidal particles by sweeping floc.

In a typical coagulation run two types of inorganic coagulants were used to reduce the pollutant concentration of OMWW, mainly phenolic compounds**.**

1. Ferrous Sulfate

$FeSO_4.7H_2O$ (Fe (II)) ferrous sulfate material, was an iron salt commonly used as a coagulant (Niaounakis and Halvadakis, 2006). The skeletal formula of Ferrous Sulfate was shown in figure (2.2) also.

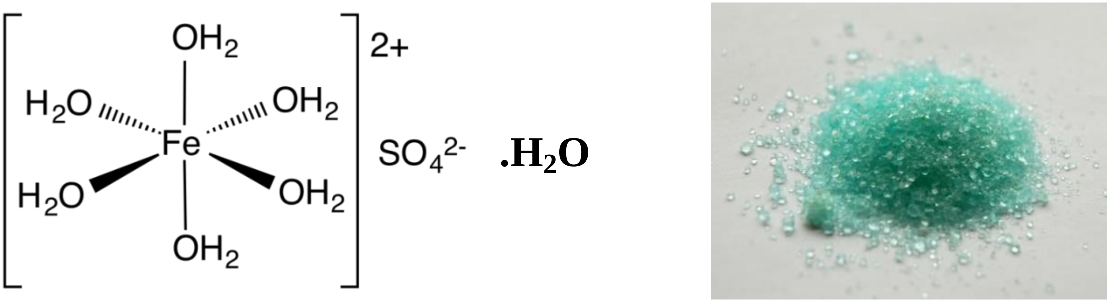


Figure (2.2): 1: Skeletal formula of Ferrous Sulfate, 2: Sample (white salt) of Ferrous Sulfate

- **Fe (II) preparation**

  All experiments on OMWW treatment were conducted using Jar-Test apparatus, at room temperature, the effect of Fe (II) on OMWW was investigated in terms of total phenols removal, and the Jar Test was done in wastewater by adding $FeSO_4.7H_2O$ (1000mg Fe^{2+}/100ml) to evaluate optimum coagulant dosage, the oxidant H_2O_2 (100,500 Mic) was added immediately after the addition of Fe (II) as shown in the equations bellow:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH + H^{+}$$

Fenton mixture was left to react for several minutes while stirring at 90rpm, the mixture was mixed in stirrer plat for 5 min. After resting period, the mixture was filtrate. The sample diluted with distilled water (1:500) then examine spectrophotometrically.

2. Calcium Hydroxide

Calcium Hydroxide which called Lime, figure (2.3) was used to reduce the pollutants concentration of OMWW mainly phenolic compounds. It is used primarily for pH control or chemical precipitation in wastewater treatment (Niaounakis and Halvadakis, 2006).

Figure (2.3) Lime (calcium hydroxide), chemical formula $Ca(OH)_2$.

Calcium hydroxide procedure

Lime (Calcium hydroxide) with the Chemical formula $Ca(OH)_2$ is a white powder. To determine efficiency of lime the following procedure was applied:

1. 100 ml of OMWW samples were treated with different mass of lime (1, 2,3,4,5 and 6 g).
2. The mixture was mixed by stirrer plate for 5 min.
3. The sample was then left to rest for 60 min and as soon as separation was achieved.
4. After resting period, the mixture was filtrated.
5. The sample diluted (1:500) with distilled water then examine spectrophotometrically at 700nm wavelength.

2.5.1.2 Flocculation

Flocculation refers to the process by which destabilized particles actually conglomerate into larger aggregates figure (2.4), by addition of organic polymer so that they can be separated from the wastewater.

Flocculation Principle

Once colloidal destabilization has occurred, random particle motion causes particle collision, resulting in formation of a larger particle or floc. These neutralized particles stick together forming floc masses. As this massing continues, particle size and weight increase to a point where the larger floc can be removed by filtration (Figure 2.4 and Figure 2.5).

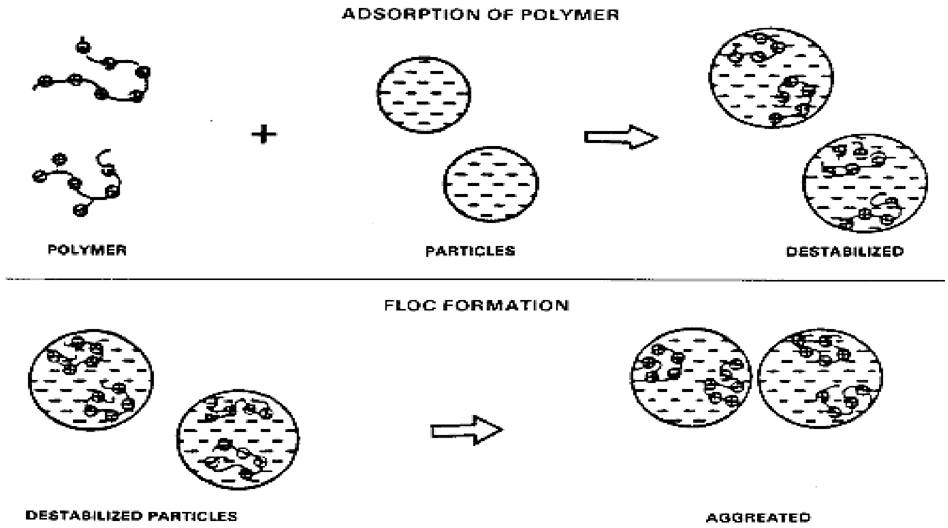


Figure (2.4): Flocculation formation process

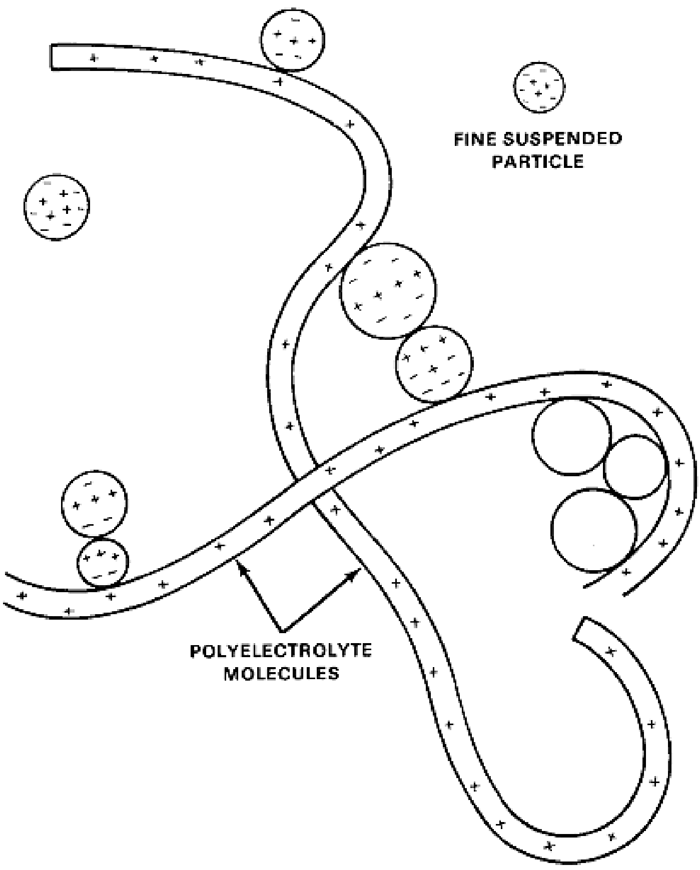
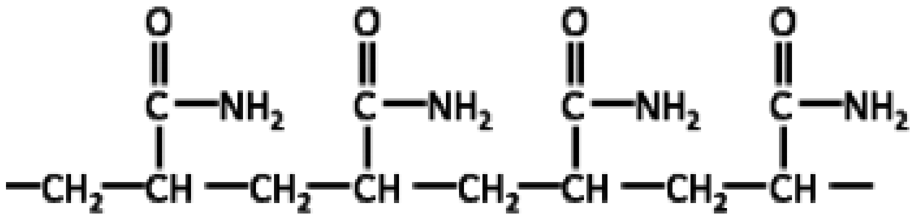


Figure (2.5): Forming flocculation particle

Polyacrylamide (PAM) is a water-soluble polymer formed from acrylamide (a compound with the molecular formula C_3H_5NO) and Chemical formula showed in figure (2.6). PAM is most often used to increase the viscosity of water (creating a thicker solution) or to encourage flocculation of particles present in water. PAM is a synthetic chemical that can tailor to fit a broad range of applications.



$$-CH_2-\overset{\overset{\overset{O}{\|}}{C-NH_2}}{\overset{|}{CH}}-CH_2-\overset{\overset{\overset{O}{\|}}{C-NH_2}}{\overset{|}{CH}}-CH_2-\overset{\overset{\overset{O}{\|}}{C-NH_2}}{\overset{|}{CH}}-CH_2-\overset{\overset{\overset{O}{\|}}{C-NH_2}}{\overset{|}{CH}}-$$

Figure (2.6): Chemical formula for PAM

PAM Mechanisms

1. Adsorption of polymers on surface of colloids.
2. Formation of bridges between particles.

PAM procedure

To determine the efficiency, the following procedure was applied:

1. 100 ml of OMWW samples were treated with different concentrations of lime (0.3, 0.6, 0.9, 1, 1.5, 2, 3, 4 and 6) g.
2. The mixture was mixed in stirrer plate for 5 min.
3. Super flocculants polyacrylamide as a solid white material was added (0.1, 0.2, 0.3)g while stirring for 15 min to facilitate flocs agglomeration.
4. The sample was then left to rest for 60 min and as soon as separation was achieved
5. After resting period, the mixture was filtrated.
6. The sample diluted with distilled water then examine spectrophotometrically in 700nm wavelength.

Folin test for total phenols

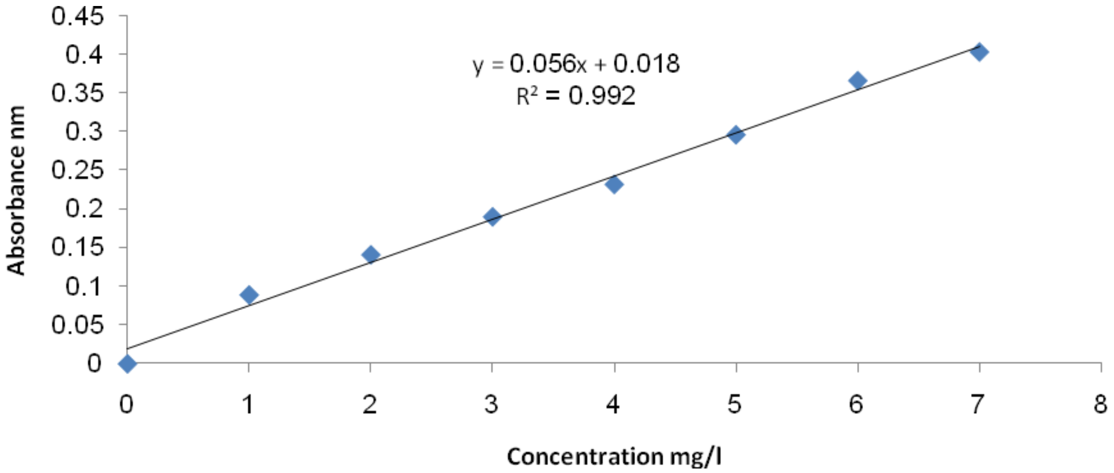
The total phenol content of Olive Oil Mill Wastewaters was determined calorimetrically on a UV spectrophotometer using the Folin–Ciocalteu reagent. In the presence of polyphenols, the mixture of phosphotungstic acid ($H_2PW_{12}O_{40}$) and Folin ($H_3PW_{12}O_{40}$) is reduced to tungsten blue oxide (W_8O_{23}), color has a maximum absorption at 700 nm (Bouknana et al 2014). The selective reagent for poly phenols (FCR) was used at 1:500 dilutions in distilled water.

Phenols Calculations

2.5.2 Tannic Acid Calibration Curve

A range of Tannic acid concentrations was used to prepare the calibration curves; the Tannic acid was used as standard to quantify the concentration of phenols in OMWW. Total phenol concentration was determined spectrophotometrically at 700 nm wavelength using Folin-Ciocaltue reagent. The results were expressed as tannic acid equivalent (Figure 2.7). The standard curve was prepared using 1, 2, 3, 4, 5, 6 and 7 mg/l. We've been working on them many times until we get almost ideal value of $\mathbf{R^2 = 0.99}$

To calculate the concentration of phenol in the sample by using the equation from standard curve:



(Figure 2.7): Standard curve for total phenols analysis

$y = 0.0561x + 0.018$

from the equation:

$X=(y-b)/a$

$a=0.056$, $b=0.0183$

X: the concentration of phenol.

Y: the absorbance value.

2.6 Water Drop Penetration Time (WDPT) Test:

Soil hydrophobicity is an environmental problem of soil repellency to water that hampers soil wetting. This is a global phenomenon, which affects infiltration as well as soil water retention and plant growth. (Vogelmann et al., 2013). Hydrophobicity can be responsible for enhanced surface runoff, erosion and preferential flow (Vogelmann et al., 2013). The method of water drop penetration time (WDPT), proposed by LETEY (1969), has been used to measure the persistence of water repellency in disaggregated soil samples (Mataix-solera et al., 2011).

The procedure was as following:

1. Three samples (60g) of soil were put on horizontal surface in Petri dishes
2. The first sample irrigated with (20ml) fresh water, the second irrigated (with 20ml) untreated OMWW, the third sample irrigated with (20 ml) treated OMWW for one week.
3. pH value was measured for each sample.
4. Five drops of fresh water were added to each sample, one drop every five second.
5. The time for the drop to infiltrate was recorded.

This test broadly determines the presence of soil water repellency and how long it persists in the contact area of a water droplet. WDPT test is used by scientists and practitioners more than any other because it is inexpensive (only a water dropper and stop are required) and easy to perform in the field and in the laboratory (Dekker et al, 2009).

Material and Tools:

1. Petri dishes
2. Soil samples
3. Pasteur pipette
4. Fresh water
5. Watch for time record

Chapter Three:

Results and Discussion:

3.1 Olive mill wastewater characterization

All physicochemical analysis were repeated three times, the reported results are averaged, and the results of OMWW characteristic of full automatic olive mills that located in Al-Qubayba village are shown in table (3.1).

Table (3.1): Characteristics of OMWW from Al-Qubayba village comparing with values in Palestine (khatib 2009)*.

parameter	**Units**	**Untreated OMWW**	**OMWW Palestine***
pH	**----**	5.17	4 - 6.7
EC	**$mS\cdot cm^{-1}$**	13.39	8 - 16
COD	**$g\cdot L^{-1}$**	74.95	45 - 220
TP	**$g\cdot L^{-1}$**	3.57	0.5 - 24
TDS	**ppm**	63.7	16.9 – 80.3
DO	**$mg\cdot L^{-1}$**	0.15	0.2 - 3.4
BOD_5	**$g.L^{-1}$**	37	35 - 110

According to Table (3.1) the pH value of OMWW in Al-Qubayba mill was (5.17). The acidic pH is a fundamental characteristic effluent mill with values between (4.5 and 5.32) (Eroglu et al., 2008). Presence of organic acids in OMWW makes it acidic.

The value of Electrical conductivity (EC) was (13.39 $mS\cdot cm^{-1}$). The results obtained in our study are comparable to those found in the literature such as (Bouknana et al., 2014), with values ranging between (13 and 50 $mS.cm^{-1}$.

The highest concentrations of the salt present in these effluents due to salting practices for the conservation of olives before crushing in addition to the natural wealth of olive oil mill wastewaters dissolved minerals (Bouknana et al., 2014).

Dissolved oxygen (DO) levels observed in the sample was ($0.15 mg·L^{-1}$). The low level of dissolved oxygen observed in the sample of olive mill wastewaters are caused by their consumption by bacteria to decompose biodegradable organic matter (Bouknana et al., 2014).

The value of COD ($74.95\ g·L^{-1}$) was high, this means high organic content of OMWW. The organic load of OMWW is considered one of the highest of all concentrated effluents, being 100- 150 time higher than organic load of domestic wastewater (Al Jabari, 2013). And the BOD_5 value also high.

Total phenol content of each OMWW samples was analyzed according to Folin-Ciocalteaucolorimetry method (Aladham, 2012). The value of total phenol ($3.57\ g·L^{-1}$) was high .The characteristics of OMWW in the study area indicate the necessity of physical treatment for the removal of solids and total phenol.

3.2 Olive Mill Wastewater Treatments

The treatment of OMWW is extremely difficult due to its large volume and the high concentration of organic matter. The major factor of the environmental problems imposed by the OMWW is the high concentration of polyphenols (Deeb et al., 2012). Physicochemical treatment was applied in this study by Coagulation-Flocculation-Sedimentation processes using Fe (II), $Ca(OH)_2$ and PAM in different dosage.

3.2.1 Fe (II) Treatment

Fe (II) at 1g\100mL failed to cause separation and the concentration of phenol got higher than the concentration of phenol in raw as shown in table (3.2), it appears that adding iron to OMWW gave a negative results of treatments.

Table (3.2): Concentration of total phenol in OMWW sample after adding 1g Fe(II) with H_2O_2/100ml OMWW.

	a The slope	**B Intersection point**	**Absorbance 1**	**Absorbance 2**	**Absorbance 3**	**Average Of absorbanc**	**Conc. of TPs g\l**	**Conc. Of TPs mg\l**
Raw OMW	0.0561	0.0183	0.429	0.411	0.419	0.419	7.15	3.57
Fe(II) with H_2O_2(100Mic)	0.0561	0.0183	0.5	0.497	0.499	0.498	8.56	4.28
Fe(II) with H_2O_2(500Mic)	0.0561	0.0183	0.42	0.491	0.418	0.419	7.14	3.57

The Results showed that the percent of treatment when we added 1g/100ml of Fe (II) with 100Mic H_2O_2 to OMWW is (-19.88 **%**), increased the oxidation dose to 500Mic showed that no removal occurs. Table (3.3) shows that Fe (II) with H_2O_2 worked in reverse to remove phenol from OMWW.

Table (3.3): Total Phenol removal percent by using Fe(II) with oxidation dose on OMWW.

	Conc. of TP mg\l	Percent of treatment %
Raw OMW	3.57	---------
Fe(II) + H_2O_2 (100Mic)	4.28	-19.88 %
Fe(II) + H_2O_2 (500Mic)	3.57	0.0 %

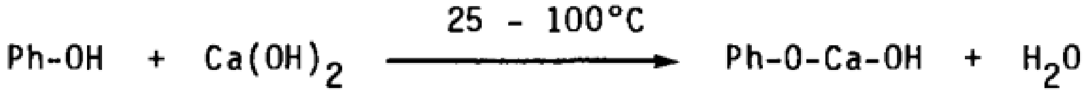
However mixing 1g Fe (II) with lime (Calcium hydroxide) in Different proportions to improve the removal of phenols gave us close results to table(3.3), table (3.4) shows the results of treatment of olive mill wastewater by adding Fe (II) with lime, 1g Fe (II) with 1 and 1.5g lime removal very slightly value = 5.3%

Table (3.4): Total phenol removal percent using Fe(II) and 1, 1.5g lime in 100ml OMWW.

	Conc. of TP (mg/l)	Percent of treatment %
Raw OMW	3.57	----------
Fe with 1g lime	4.09	-14.5 %
Fe with 1.5g lime	3.38	5.3%

3.2.2 Lime ($Ca(OH)_2$) treatment

Lime stabilization is a recognized means of treating municipal OMWW prior to land application. Lime is used primarily for pH control or chemical precipitation in wastewater treatment (Niaounakis and Halvadakis, 2006).The mechanism of lime and phenol interaction depends on the different of pH of phenol and lime in which phenol is weak acid and lime is base, so lime interact with phenol as following equation:



$$\text{Ph-OH} + \text{Ca(OH)}_2 \xrightarrow{25 - 100^{\circ}\text{C}} \text{Ph-O-Ca-OH} + \text{H}_2\text{O}$$

Figure (3.1): Neutralization process (Richard et al., 2003)

This process is called neutralization. The above results can be explained by the fact that the pectin substances present in OMWW in the form of negatively charged colloids can be destabilized, either by increasing [H+] concentration, or by adding Ca^{+2} ions. (Niaounakia and Halvadakis, 2006).

After lime treatment, the rising of pH and EC value was noticed; this increase due to the increase of Ca^{+2} ions concentration after lime adding (Al-Jabari, 2013).

Table (3.5) presents the changes of pH, EC after addition of (1, 2,3,4,5 and 6) g of lime /100ml raw OMWW. The pH of OMWW increased from (4.5) to (12.1, 12.7, 12.8, 12.8, 12.9 and 12.9) respectively, the EC value was increased from ($11mS \cdot cm^{-1}$) for raw OMWW to (13, 13, 14, 14, 15 and 16 $mS \cdot cm^{-1}$) respectively.

Table (3.5): EC and pH changes due to addition of (1, 2, 3, 4, 5 and 6 g lime/100 ml) on OMWW

	pH	**EC ($mS \cdot cm^{-1}$)**
Raw OMW	4.5	11
1g lime	12.1	13
2g lime	12.7	13
3g lime	12.8	14
4g lime	12.8	14
5g lime	12.9	15
6g lime	12.9	16

Figure (3.2): shows the pH changes values due to addition of different lime concentration. The values of pH going to stability after 2g/100ml dose of lime. The process of lime treatment is neutralization that restoration of the hydrogen H^+ or hydroxyl OH^-ion balance in solution so that the ionic charge of each are equal. Treatment of phenols by lime depends on raising the pH of OMWW to remove the phenolic compounds from it (Al-Jabari, 2013).

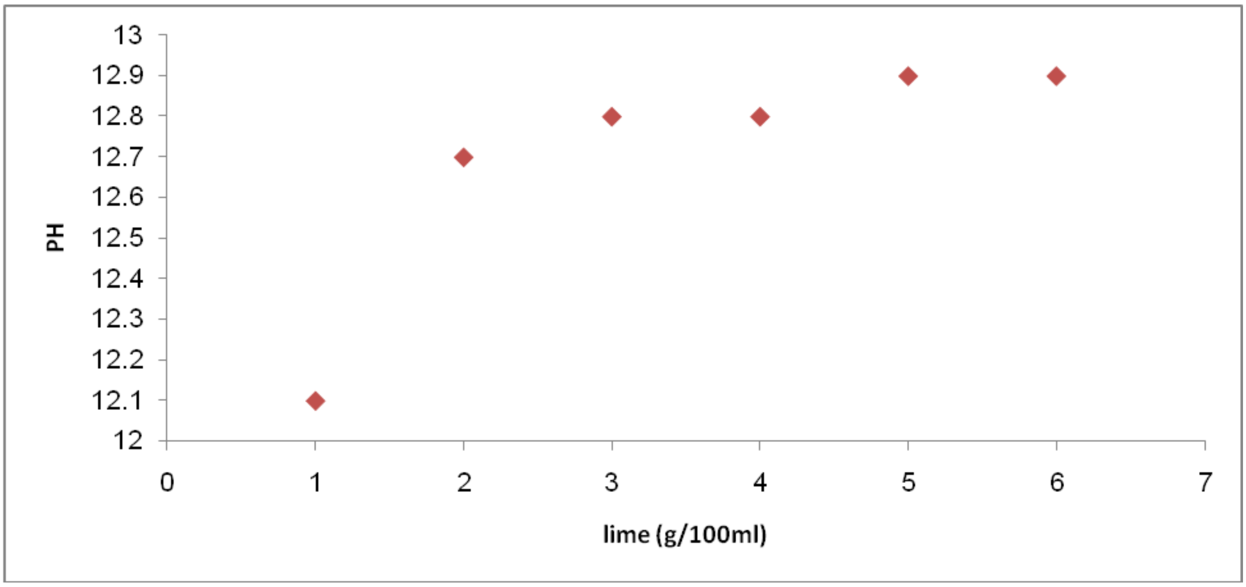


Figure (3.2): pH changes value after addition of (1, 2,3,4,5 and 6 g lime/100ml) on raw OMWW.

Figure(3.3) shows the increase of EC value from 11 to 16 after adding 1,2,3,4,5,6 g/100ml of lime in olive mill wastewater, increasing of lime dose means increasing in EC value due to increasing of Ca^{+2} ions from lime $Ca(OH)_2$. Upon the mechanism of lime treatment part of Ca^{+2} ions will bind with phenol and other well released in the OMWW(Al-Jabari, 2013).

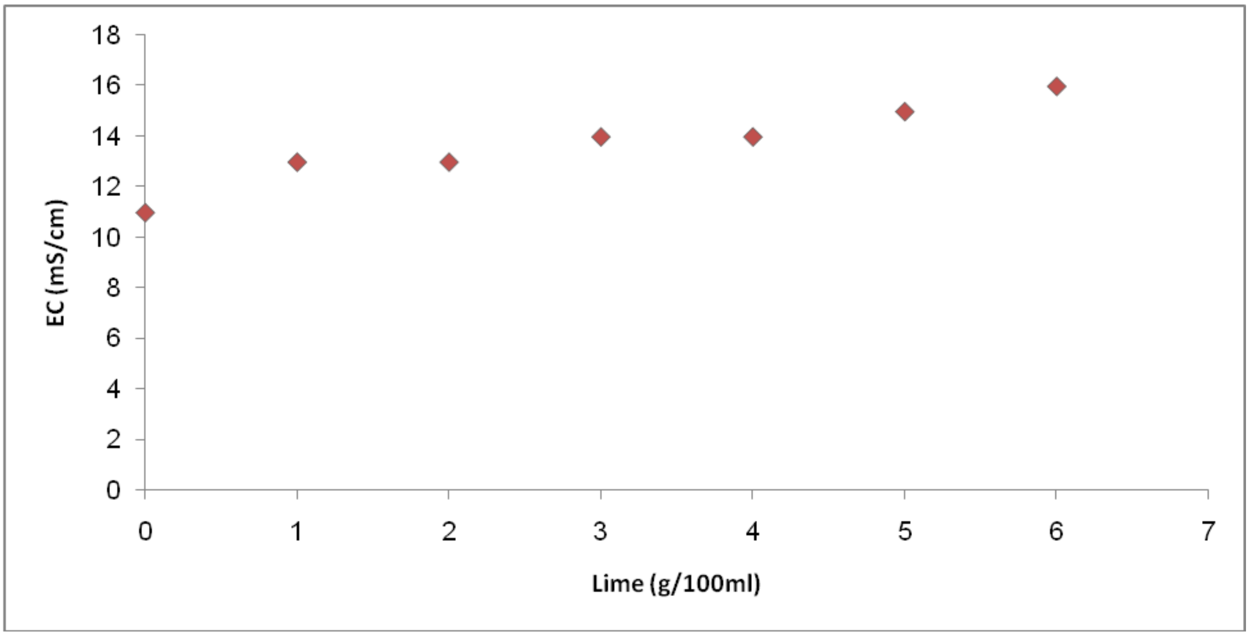


Figure (3.3): EC values after addition of (1,2,3,4,5 and 6 g lime/100ml) on raw OMWW.

Table (3.6): indicates the decreasing of total phenols concentrations after lime treatment with doses (1,2,3,4,5 and 6 g/100ml) to (2.91, 2.35, 2.21, 2.11, 2.06, 1.97mg/100ml) respectively. The concentration of total phenols was decreased with increased dose of lime, increasing in lime dose means increasing volume of sludge.

Table (3.6): Concentration of total phenol using different lime dose on OMWW.

	Conc. of TPs (mg/l)
Raw OMWW	3.57
1g lime	2.91
2g lime	2.35
3g lime	2.21
4g lime	2.11
5g lime	2.06
6g lime	1.97

(Figure 3.4) shows the percentage removal after lime treatment with doses (1, 2,3,4,5 and 6 g lime/100ml). The percentage of removal was increasing with increasing the dose of lime. (1, 2,3,4,5 and 6g/100ml) (18.4, 34.1, 38.0, 40.8, 42.2, 44.8 %) respectively. This increase of total phenols removal percent is related to the increase of pH value that increases with increase of lime dose.

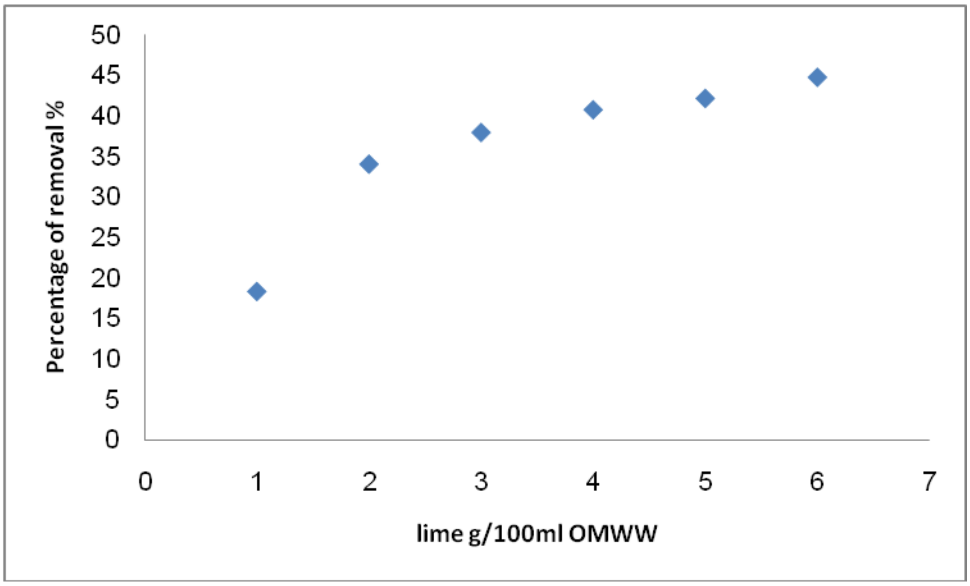


Figure (3.4): Percentage removal of phenols values after addition of (1, 2, 3, 4, 5 and 6 g lime/100ml) on raw OMWW.

Although the lime can remove a good percentage of total phenols concentration, major disadvantage of using inorganic chemicals, especially lime for OMWW conditioning is that large quantities of sludge with high pollution load are produced leading to serious disposal problems.

3.2.3 Lime and PAM treatment:

Polyacrylamide (PAM) is a polemar, (polymers are substances made up of recurring structural units, each of which can be regarded as derived from a specific compound called a monomer) makes the fine solids in treated water adhere to one another until they become big enough to settle out or be captured by filters to make sewage sludge. In either case, the floc. can be filtered or removed more easily. The main raw material used to produce PAM is acrylamide, which is a water-soluble monomer. Availability of acrylamide is widespread globally, with manufacturers locating world-scale production facilities closer to the sites of consumption and exploiting lower-cost production locations. Most of the world's acrylamide capacity is in the United States, Western Europe, Japan and China.

Table (3.7) presents that adding of lime (1,2,3,4,5 and 6g) with (0.1g) PAM to 100mL OMWW decreased the concentration of total phenols to (1.73, 1.53, 1.42, 1.37, 1.42, 1.5mg/L) respectively.

Table (3.7): Concentration of total phenols using (1, 2,3,4,5 and 6g) lime with o.1g of PAM

	Conc. of TPs(mg/L)
Raw OMWW	3.57
1g lime with 0.1g PAM	1.73
2g lime with 0.1g PAM	1.53
3g lime with 0.1g PAM	1.42
4g lime with 0.1g PAM	1.37
5g lime with 0.1g PAM	1.42
6g lime with 0.1g PAM	1.5

Figure (3.5) shows the percentage removal after lime treatment with dose (1, 2,3,4,5, and 6 g lime/100ml) with 0.1 g of PAM, the percentage of removal was (51.5, 57.1, 60.2, 61.6, 60.2, 57.9 %) respectively.

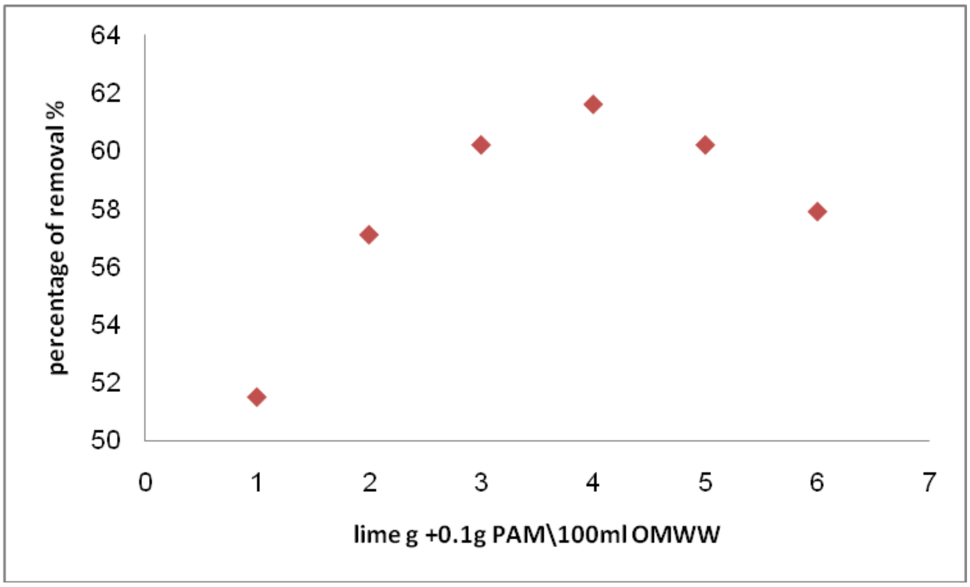


Figure (3.5): Percentage removal of phenols values after addition of (1,2,3,4,5 and 6 g lime/100ml) with 0.1g PAM on raw OMWW.

Figure (3.5) shown that the treatment ratio decrease above 4g lime that mean the increased of lime doesn't mean increased in removal of phenols, highest ratio of treatment appeared at (4g lime +0.1g PAM) with percentage removal (61.6%), 4g lime for 100ml OMWW produced large quantities of sludge, adding 0.1 of PAM to lime makes a big difference in percentage of removal of phenols Comparison with lime alone, (Figure 3.6) showed the comparison between it.

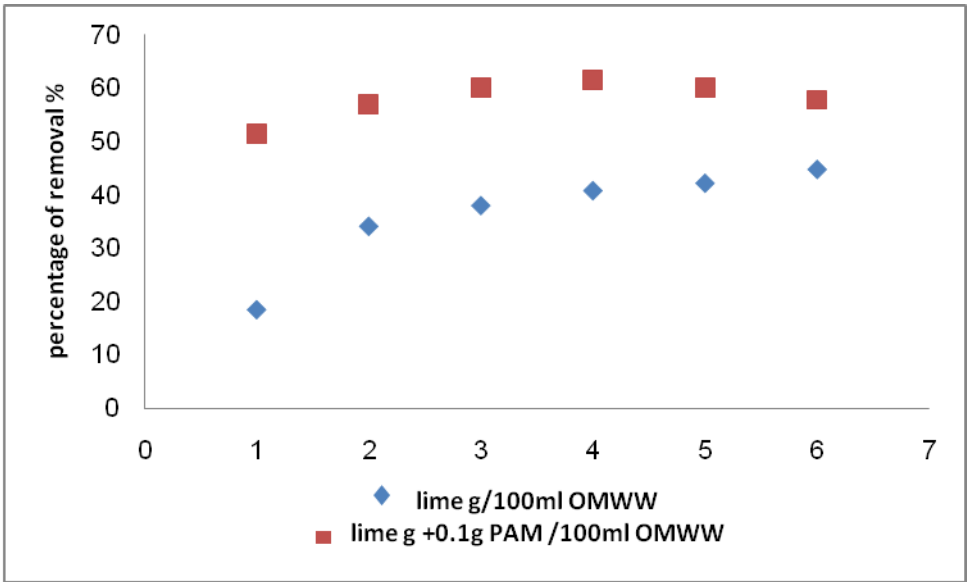


Figure (3.6): Comparing between Figure (3.4) and Figure (3.5).

At the same procedure, Table (3.8) shows that lime with dose (1, 2 g) with increasing concentration of PAM to 0.2 g to 100ml OMWW reduced the total phenols value from (3.57 to 2.12 and 1.91mg/L) respectively. Lime with dose (1, 2 g) with 0.1g PAM showed better results in removal percentage, which mean the increase in PAM dose from 0.1 to 0.2 don't make removal.

Table (3.8): Concentration of total phenols using (1,2g) lime with 0.2g of PAM.

	Conc. of TP mg\L	**Removal %**
Raw OMW (100ml)	3.57	------------
1g lime + 0.2g PAM	2.12	40.6%
2g lime + 0.2gPAM	1.91	46 %

by the way, if we compare between the effect of treatment with and without PAM adding in different dose 0.1, 0.2g to 1g lime we observe the results (table 3.9) showed that slightly amount of PAM(0.1g) that added to 1g lime gave high percentage removal compared with 1g lime alone from (18.4 % to 51.5%), 1g of lime with (0.2g) PAM reduce 40.6 % total phenols while 2g of lime with 0.2g of PAM reduce 46% of total phenols.

Table (3.9): The differences in treatment with and without PAM.

	Conc. of TP(mg/l)	**Removal %**
lime 1g	2.91	18.4%
lime 2g	2.35	34.1%
Lime 1g + 0.1 PAM	1.73	51.5%
Lime 2g + 0.1 PAM	1.83	57.1%
Lime 1g + 0.2 PAM	2.12	40.6%
Lime 2g + 0.2 PAM	1.91	46%

Table (3.10) presents that lime with dose (0.3 g) and PAM dose (0.4g) in 100ml OMWW reduced total phenol from (3.57 to 3.40 mg/l), removal percent of TP was 4.7%. If we increased the dose of lime doubled to (0.6 g)

With Fixed the dose of PAM (0.4 g) the percentage removal is 11.7 %. The percentage of removal reached to 32.7 % if the dose of lime reached (0.9g) and PAM is (0.4g).

Table (3.10): Total phenols concentration after addition of different lime (0.3, 0.6, 0.9 g with 0.4g PAM 100ml OMWW.

	Conc. g\L	**Conc. mg\L**	**Percentage of Treatment %**
Raw OMWW (100ml)	7.15	3.57	----------
lime 0.3g + 0.4g PAM	6.81	3.40	4.7%
lime 0.6g + 0.4g PAM	6.31	3.15	11.7%
lime 0.9g + 0.4g PAM	4.80	2.40	32.7%

As a result, the lime and PAM dose of (1g, 0.1g) respectively was determined to be the optimum with lowest sludge's, where the percentage of removal is (51.5%).

3.3.4 Water Drop Penetration Time (WDPT) test

The ideal dose of treated OMWW from phenols which we obtained (1g lime with 0.1 PAM), was reused to irrigate sample of 60g for eight days, the samples were put in Plastic dishes and irrigate with 20 ml of fresh water, 20ml of untreated olive mill wastewater and 20ml treated olive mill wastewater. (Table 3.11) shows the details of the first day of irrigation and pH value that measured.

Table (3.11): The parameters of the first day of irrigation

Type of water	**Weight of empty dish (g)**	**Weight of dish with soil (g)**	**Weight of dish after irrigation(g)**	**pH value**
F.W	7.86	67.86	87.23	7.21
UTOMWW	7.61	67.61	87.07	4.46
TOMWW	7.84	67.84	86.92	11.27

After 8 days of irrigations we applied water penetration drop time test using distilled water, dropper, and timer by drop five drops of distilled water one drop every five seconds then weight for the drop to penetrate into the soil and record the amount of time it take. (Table 3.12) indicates that the time of fresh water needed to penetrate the soil was 3 second, the time of the drop in the soil which irrigated with treated OMWW is also 3 seconds, for the soil that irrigated with untreated olive mill wastewater the time that the drop takes to penetrate the soil was (27-30) min

Table (3.12): Results of water drop penetration time test.

Types of water for irrigation	Time
F.W	3sec
TOMWW	3sec
UNOMWW	27-30 min

The drops in the soil sample that irrigated with untreated olive mill wastewater were very clear, Figure (3.7) shows the stopper of drops of water in the surface of soil and takes a long time to penetration the soil in the opposite, the penetration of the drop in treated olive mill waste water sample similar with fresh water sample that mean the un treated OMWW prevent soil water repellency, on the other hand irrigation the soil that irrigated by treated olive mill wastewater improves the penetration of water then improve the soil water repellency

The continuous discharge of untreated olive mill wastewater to soil will lead to wetland formation since the results indicated that untreated OMWW has a poor permeability on soil.

Figure (3.7): Sample of soil which irrigated with untreated olive mill wastewater, the drops was stooped in the surface for 30min.

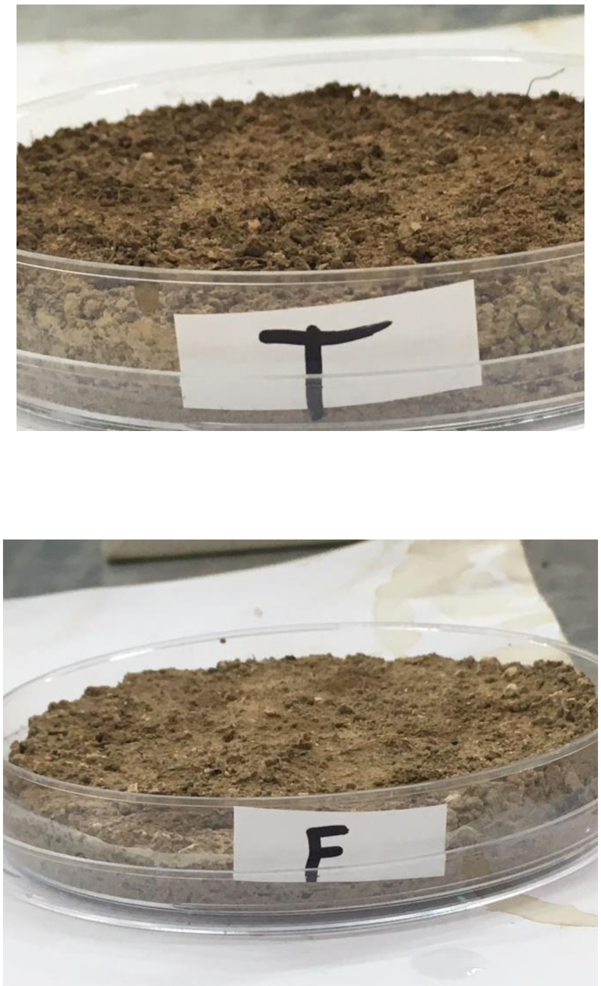


Figure (3.8): Samples of soil which irrigated with fresh water and treated water, the drop takes 3 seconds to penetration the soil for each sample.

Chapter four:

Conclusion and recommendations:

4.1 Conclusion

OMWW treatment and disposal is a problem with great complexity due to the strong nature of the waste and several economical, technical, and organizational constraints involved in the olive oil sector. Practically, all treatment processes developed for domestic and industrial wastewaters have been tested on OMWW but none of them appeared suitable to be generally adopted. From the results obtained OMWW, OMWW characteristics and from treatment method and soil applied during this research, the following conclusion obtained:

Physicochemical characteristics which worked (pH, EC, DO, COD, TDS, and TPs) were closed to the mean value of the reported literature for various researches.

This work has given good results for removal of phenols as following:

1. The polymer PAM was effective for phenols removal.
2. The higher percentage of removal = 51.5% occurs when the amount of dosage is (1g lime with 0.1g PAM).
3. Treated OMWW improve the water infiltration in soil and acting like fresh water.

The coagulation-flocculation- Sedimentation of OMWW coupling relatively inexpensive inorganic materials with moderate concentrations of anionic polyacrylamide was investigated regarding the effect of operating conditions on total phenols. This pre-treatment reduced concentration of total phenols. These results are encouraging in the context of developing a low-budget technology for the effective management of OMWW.

4.2 Recommendations

OMWW was a serious problem on Palestine; it is recommended for government to work hard to solve this problem and developed suitable actions.

- It is recommended for Awareness that must be raised among olive oil industry stakeholders concerning the environmental impact encountered with the uncontrolled and improper disposal of OMWW.

- It is recommended for further research to optimize the performance of coagulants and flocculants with different concentrations for OMWW pre-treatment and for complete OMWW treatment in order to meet the Palestinian treated wastewater reuse standards.

- It is recommended for further research in treatment by lime with polyacrylamide in different ratios to improve the removal efficiency.
- It is recommended researchers to implementation way to reuse the huge of sludge that output from lime treatment.
- It is recommended for further research for applied treated olive mill wastewater in irrigation soil to reuse it for reduces of effect in environment.
- Encouraging others researchers to make further research on polyacrylamide after lime treatment.

References

Abdellaoui. H, 2015. Catalytic Pyrolysis of Olive Mill Wastewater Sludge. Utah State University. Master thesis

Afify. A. S, Mahmoud. M. A, Emara. H. A, Abdelkreem. K. I, 2009. Phenolic Compounds and COD Removal from Olive Mill Wastewater by Chemical and Biological Procedures. Australian Journal of Basic and Applied Sciences. Vol. 3, No. 2, P. 1087-1095.

Aladham. R, 2012. Removal of Polyphenols from Olive Mill Wastewater using Activated Olive Stones. An-Najah National University. Master thesis.

Al-Jabari. T, 2013. Occurrence and Fate of Olive Mill Wastewater in the Environment: Feasible Treatment Alternative. Al-Quds University. Master thesis.

Al-Khatib. A , Al-Jabari. M , Sawalha. H, Yaghi. N, Sobih.Y, 2005. Olive Oil Production Palestine, Environmental Concern. Hebron University.

Aly. A. A, Hasan. Y. N. Y, Al-Farraj. A. S, 2014. Olive mill wastewater treatment using a simple zeolite-based low-cost method. Journal of Environmental Management.Vol. 145, P 341–348.

Anastasiou. C. C, Christou. P, Michael. A, 2011. Approaches to Olive Mill Wastewater Treatment and Disposal in Cyprus. Environmental Research Journal, Vol. 5, No. 2, P. 49- 58.

Azbar. N, Bayram. A, Filibeli. A, Muezzinoglu. A, Sengul. F, Ozer. A, 2004. A review of waste management options in olive oil production. Critical Reviews in Environmental Science and Technology journal. Vol. 34, No. 3, P 209–247.

Barbera. A. C, Maucieri. C, Cavallaro. V, Spagna. G, 2013. Effects of spreading olive mill wastewater on soil properties and crops: a review. Agricultural Water Management.No. 109, P. 43-53.

Ben Sassi. A, Boularbah. A, Jaouad.·A, Walker. ·G, Boussaid. A, 2006, comparison of Olive oil Mill Wastewaters (OMW) from three different processes in Morocco. Process Biochemistry. Vol. 41, No. 1, P. 74-78.

Bouknana. D, Hammouti. B, Salghi. R, Jodeh. S, Zarrouk. A, Warad. I, Aouniti. A, Sbaa. M, 2014. Physicochemical Characterization of Olive Oil Mill Wastewaters in the eastern region of Morocco. J. Master Environmental Science P. 1039-1058.

Buchmann. C, Felten. A, Peikert. B, Muñoz. K, Bandow. N, Dag. A, Schaumann. G.E, 2015. Development of phytotoxicity and composition of a soil treated with olive mill wastewater (OMW). Plant and Soil. No. 386, P. 99-112.

Brunetti. G, Senesi. N, Plaza. C, 2007. Effects of amendment with treated and untreated olive oil mill wastewaters on soil properties, soil humic substances and wheat yield. Geoderma, Vol. 138, No. 1-2, P. 144-152.

Celano. G, Palese. A. M, Parente. M, Rizzuti. L, Silvestri. N, 2010. Environmental impact evaluation of olive mill wastewater shedding on cultivated fields. Terrestrial and Aquatic Environmental Toxicology. Vol. 4, P. 39-44.

Eroğlu. E, Eroğlu. I, Gündüz. U, Yücel. M, 2008. Effect of clay pretreatment on photofermentative hydrogen production from olive mill wastewater. Bioresource Technology. Vol. 99, No. 15, P. 6799-6808.

Danellakis. D, Ntaikou. L, Kornaros. M, Stefanos Dailianis. S, 2011. Olive oil mill wastewater toxicity in the marine environment: alterations of stress indices in tissues of mussel Mytilus galloprovincialis. Aquatic Toxicology. No. 101, P. 358-366.

Deeb. A. A, Fayyad. M. K, Alawi. M. A, 2012. Separation of Polyphenols from Jordanian Olive Oil Mill Wastewater. Chromatography Research International. Vol. 2012, P. 8.

Dermeche. S, Nadour. M, Larroche. C, Moulti-Mati. F, Michaud. P, 2013. Olive mill wastes: Biochemical characterizations and valorization strategies. Process Biochemistry journal. Vol. 48, No. 10, P. 1532–1552.

Dekker. L, Ritsima. C. J, Oostindie. K, Moore. D, Wesseling. J. G, 2009. Methods for determining soil water repellency on field- moist samples. Water Resources Research. Vol. 45.

Di Bene. C, Pellegrino. E, Debolini. M, Silvestri. N, Bonari. E, 2013. Short- and long-term effects of olive mill wastewater land spreading on soil chemical and biological properties. Soil Biology and Biochemistry. Vol. 56, P. 21-30.

Hamdi. M, 1993. Future prospects and constraints of olive mill wastewaters use and treatment: A review. Bioprocess Engineering. Vol. 8, No. 5, P. 209-214.

Hanafi. F, Mountadar. M, Etahiri. S, Fekhaoui. M, Assobhei. O, 2013. Biodegradation of Toxic Compounds in Olive Mill Wastewater by a Newly Isolated Potent Strain: Aspergillus Niger van Tieghem. Journal of Water Resource and Protection. Vol. 5, P. 768-774.

Hanifi. S, El Hadrami. I, 2008. Phytotoxicity and Fertilizing potential of olive mill wastewaters for maize cultivation. Springer Verlag/EDP Sciences/INRA, Vol. 28, No. 2, P. 313-319.

Hatzinikolaou. D, 2007. Management and exploitation of mill wastes in the area of national marine park of zakynthos. Report, University of Athens.

Hodaifa. G, Páez. J. A, Agabo. C, Ramos, E, Gutiérrez, J. C Rosal A, 2015 Flocculation on the Treatment of Olive Oil Mill Wastewater: Pretreatment. International Journal of Chemical and Molecular Engineering. Vol. 9, No. 5.

IOC. 2017, International Olive Council, Market news Letter, No. 119 – September 2017.

Kapellakis. I. E, Paranychianakis. N. V, Tsagarakis. K. P, Angelakis. A. N, 2012. Treatment of Olive Mill Wastewater with Constructed Wetlands. Water journal. No. 4, P. 260-271.

Khatib. A, Aqra.F, Yaghi. N, Subuh. Y, Hayeek. B, Musa. M, Basheer. S, Sabbah. I, 2009. Reducing the Environmental Impact of Olive Mill Wastewater. American Journal of Environmental Sciences. Vol.5, No. 1, P. 1-6.

Letey, J, 1969. Measurement of Contact Angle, Water Drop Penetration Time, and Critical Surface Tension. Proceedings of a Symposium on Water Repellant Soils, Riverside, P. 43-47

Mataix-Solera. J, García-Irles. L, Morugán. A, Doerr. S. H, Garcia-Orenes. F, Arcenegui. V, Atanassova. I, 2011. Longevity of soil water repellency in a former wastewater disposal tree stand and potential amelioration. Geoderma, V. 165, No. 165, P. 78-83.

Niaounakis. M and Halvadakis. P, 2004. Olive-mill waste management: literature review and patent survey. Typothito-George Dardanos.

Niaounakis.M and Halvadakis. P, 2006. Olive processing waste management, literature review and patent survey. Second Edition. Waste management series 5.

PCBS, 2014. Olive presses Survey 2013-Main result. Palestinian Central Bureau of Statistics, Ramallah-Palestine.

PCBS, 2017. Olive Presses Survey 2016- Main result. Palestinian Central Bureau of Statistics, Ramallah-Palestine.

Pascuzzi. S, Santoro. F, 2017. Analysis of Possible Noise Reduction Arrangements inside Olive Oil Mills: A Case Study. University of Bari Aldo Moro.

Paredes. M. J, Monteoliva-Sanchez. M, Moreno. E, Perez. J, Ramos-Cormenzana. A, Martinez. J, 1986. Chemosphere. Vol. 15, No. 5, P. 659-664.

Richard. D, Delgado-Nunes. M , de Lourdes, 2003. Kinetics of degradation by catalytic hydrogenation of tyrosol, a model molecule present in olive oil waste waters. Journal of Chemical Technology and Biotechnology. Vol. 9, No. 78, P. 927-934

Rozzi. A and Malpei. F, 1996. Treatment and Disposal of Olive Mill Effluents. International Biodeteriorution and Biodegradation, P135-144.

Salman. M, Abu-Khalaf. N, Abu Rumaileh. B, Jawabreh. M, Abuamsha. R, 2014. Detoxification of Olive Mill Wastewater Using the White Rot Fungus Phanerochaete chrysosporium. International Journal of Environment and Sustainability, Vol. 3, No. 1, p. 1-6.

Sawalha. H, Houshia.O, Hussein.A, Mahariq.Q, Khader.A, 2014. Scope of Using Treated Olive Mill Wastewater in Tomato Production

Shaheen. H, Abdel Karim. R, 2007. Management of Olive-Mills Wastewater in Palestine. An - Najah University. Journal for Research (N. Sc.). Vol. 21.

Tamimi. N, 2016. Effects of Seasonal Olive Mill Wastewater Application on soil: Field Experiment in Bait Reema village, Palestine. University Koblenz-Landau. Master thesis.

Tayoub. G, Sulaiman. H, Alorfi. M, 2015. Oleuropein concentration in some Syrian olive oil mill wastewater. Journal of Natural Products. Vol. 8, P. 33-38.

Tsagaraki. E, Lazarides. H.N, Petrotos. K. B, 2007. Olive mill wastewater treatment, Utilization of by-products and treatment of waste in the food industry. Springer. P. 133-157.

Tzoupanos. N, Zouboulis. A, 2008. Coagulation–flocculation processes in water/wastewater treatment: the application of new generation of che. Aristotle University of Thessaloniki.

Visioli. F, Poli. A, Gall. C, 2002. Antioxidant and other biological activities of phenols from olives and olive oil. Vol. 22, P. 65-75.

VogelmannI. E. S, Reichert. J. M, Prevedello. J, Awe. G. A, Reinert. D. J, 2012. Soil hydrophobicity: comparative study of usual determination methods. Cienc. Rural, vol.45, NO. 2, P.260-266.

Vogelmann. E. S, Reichert. J. M, Prevedello. J, Awe. G. O, Mataix-Solera J, 2013. Can occurrence of soil hydrophobicity promote the increase of aggregates stability?, catena. Vol. 110, P. 24-31.

UN reports 2017

Waterman. E, Lockwood. B, 2007. Active Components and Clinical Applications of Olive Oil. Alternative Medicine Review. Vol. 12, No. 4, P. 331-342

Ziati. M, Khemmari. F, Cherifidi. O, Didouche. F. Y, 2017. Removal of polyphenols from olive mill waste water by adsorption on activated carbon prepared from peach stones. Revue Roumaine de Chimie. No. 11, P. 865-874.