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Al-Quds University

Occurrence and Fate of Olive Mill Wastewater in the Environment: Feasible Treatment Alternative

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M.Sc. Thesis

Jerusalem-Palestine

2013/1434

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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

2013/1434

Al-Quds University
Deanship of Graduate Studies
Department of Earth& Environmental Sciences
Environmental Studies

Thesis Approval

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Jerusalem-Palestine

2013/1434

Dedication

To my parents (Joudi and En’am) symbol of life

To my lovely husband Amjad and his family

To my sisters (Areej and Rabab)

To my brothers and their families

To my small coming little man

To my friends

To all those who love and support me

Declaration

I declare that, this thesis submitted for the degree of environmental sciences master the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not be submitted for a higher degree to any other university or institution.

Signature: …………….

Tasneem Al-Jabari

Date: 14/ 5/ 2013

Acknowledgment

I would like to thank GOD, who gave me the power and patience to finish this work. I would like to express my great appreciation and thanks to my supervisor Dr. Jawad Hasan for his fruitful work and invaluable guidance during this work.

My sincere gratitude goes to the Palestinian Water Authority (PWA) along with Austrian Development Agency (ADA) for their funding of this study as a part of "Building capacity and institutional reform for an integrated management of water and sanitation services in rural communities project".

My thanks go also to PWA staff: Dr. Subhi Samhan, Eng. Adel Yasen, Eng. Hazem Kittana and Miss Suhad Al-Malki for their help.

I would like to thank the staff of the Center for Chemical and Biological Analysis specially Dr. Jihad Abbadi, Mr. Mohanad Qrai, Mr. Samah Nusaiba and Mr. Ibrahem Ayad for their great help.

Thanks are also extended to my husband Amjad Darabi, Sabreen Al-bargothi, Mahmoud Abu-garfha and my brothers Muhanad and Muntaser Al-jabari for their help through this work. Thanks are also to the olive mills owners and director of agriculture in Dura for their cooperation and giving the information needed.

Great regards and thanks go to all faculty members in the department of Earth and Environmental Sciences.

My most sincere thanks to my family and to everyone who contributed to the progress this work, and provided help and encouragement.

Abstract

Olive mill wastewater (OMW) is considered as one of the serious environmental pollution problems in Palestine due to their unique composition and toxicity with the abundant of antibacterial and phytotoxic phenolic compounds, furthermore, the seasonal production, the difficulties in disposing and the lack of appropriate treatment of OMW. OMW is one of the most potential threats to the surface and groundwater sources along with other negative impacts on the environment.

In this study, a survey was conducted on the olive mills located in the southern part of the West Bank mainly in Hebron and Bethlehem governorates, by covering the number of olive mills and its location, the automation level, the quantity of produced oil, the quantity of produced and the final dumping sites of OMW. The results revealed that the total amount of pressed olives in the study area during the period of study 2010/2011 was 5810 ton, 35% and 65% of the quantity was in Bethlehem and Hebron governorates respectively. The total amount of produced OMW in the study area was 10386 m^3, 37% and 63% of the quantity was in Bethlehem and Hebron governorates respectively. In addition OMW was disposed without any previous treatment to nearby wadis/ or lands and to sewage network with 67%, and 33% respectively.

The physical and chemical properties of OMW were determined in the study area. The 19 samples (16 and 3 samples collected from full and half automatic olive mills in the study area respectively) were collected to determine the level of their pollution and their impact on the environment by measuring parameters like: Total phenols, Chemical Oxygen Demands (COD), pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Oil and Grease (O& G) and Total Solids (TS). The results revealed that the OMW have high risk for environment pollution mainly for, Total phenols, COD, TDS, TSS, O& G that exceed the maximum allowable limits to discharge in the environment or to the sanitary sewer system according to the Jordanian and Palestinian standards.

This study proposes treatment to reduce the concentration of total phenols in OMW by using lime $Ca(OH)_2$ as a pre-treatment stage followed by biological treatment using *Aspergillus niger* fungi, to examine their efficiency on reducing total phenol concentration. The treatment experiments divided into two types of experiments, batch system experiment (by using conical flasks) and according to the results of batch system, pilot treatment experiments was applied under lab condition (by using tanks with storage capacity 3 litter).

Different doses of lime were tested and the result showed that the most efficient dose in total phenol removal was 10 g/L with efficiency of 56%. In addition, this also reduces the COD and TS concentrations to 17% and 5.7% respectively. The biological treatment depends on *Aspergillus niger* species was tried on pre-treated OMW with lime. The results indicated that *A.niger* can reduce the total phenols on pre-treated OMW to 23.5%.

After lime and biological treatment, the final concentration of total phenol was 920 mg/L treatment in batch system and 2002 mg/L in pilot system that still exceed the allowable concentration of total phenol to be discharged in the sanitary sewer system or to open wadies. This research is recommending using lime adsorbent as a primary treatment of OMW mainly for OMW with low concentrations of total phenol.

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List of Abbreviations

A .niger	*Aspergillus niger*
Avg.	Average
B.ash	Bottom ash
BOD	Biological Oxygen Demand
cfu/ml	colony forming unit per milliliter
CM	Cubic Meter
COD	Chemical Oxygen Demand
EC	Electrical Conductivity
EEC	European Economic Community
US EPA	United State Environmental Protection Agency
HCl	Hydrochloric acid
Km^2	Kilometer square
m	Meter
m^3	Cubic meter
Max.	Maximum
MEnA	Ministry of Environmental Affair
mg/L	milligram per Litter
Min.	Minimum
MoA	Ministry of Agriculture
O& G	Oil and Grease
OMW	Olive Mill Wastewater
PCBS	Palestinian Central Bureau of Statistics
PDA	Potato Dextrose Agar
PWA	Palestinian Water Authority
rpm	repletion per minute
Std	Standard deviation
TDS	Total Dissolved Solids
Temp.	Temperature
TKN	Total Kejndal Nitrogen
TS	Total Solids
TSS	Total Suspended Solids

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1 Chapter One: Introduction

1.1 Olive oil industry and the resulting wastes

Olive oil industry is one of the most traditional food industires and it is in constant growth worldwide, concentrated essentially in the countries of Mediterranean basin, like Italy, Spain, Tunisia, Morocco and Palestine (Khateeb et al., 2009, Hanifi and Elhadrami, 2009). Globally, more than 2.5 million metric tons of olive oil is produced per year (Christos et al., 2011). In Palestine Olive production is a major contribution to the gross national income, it is used for oil extraction, which is considered as a food source and used in many manufacturing activities (Shaheen and Abdelkarim, 2007, PCBS, 2010). According to agricultural ministry report for the year 2010, the total cultivated area with olive trees were 984463 donums in the Palestine and the donums production rate of olives was 122 kg (MoA, 2010). Annually, around 120 and 24 thousand tons of olive fruit and olive oil respectively are produced in the West Bank from 246 functioning olive mills (Shaheen and Abdelkarim, 2007, Khateeb et al., 2009).

The main by-products of olive oil industry are: Olive Mill Wastewater (OMW) and olive husks (or olive cake) both cause serious environmental problems in the olive oil producing countries (Sobhi et al., 2004, Khateeb et al., 2009). The OMW defined as "The mixture of aqueous liquor comes from the vegetation water and the soft tissues of the olive fruits with the water used in the different stages of oil production makes up. Furthermore, olive washing water, waters from filtering disks and from washing of equipment and rooms are to be included into this wastewater" (Niaounakis and Halvadakis, 2006). The olive cake (jeft) defined as the solid residue that remains after the pressing of the olives and is composed of a mixture of olive pulp and olive stones (Niaounakis and Halvadakis, 2006, PCBS, 2010). The OMW cause environmental problems due to its composition and the difficulties in disposing and treatment, in which the olive cake can be used as a source of fuel because of its high heating energy or as animal feed supplement. It also can be used as natural fertilizers, preparation of activated carbon and other uses (Tsagaraki et al., 2007, Khatib et al., 2010). In the West Bank, the olive cake is dumped on neighboring lands, dumped at the dumpsite or used as a fuel to produce heat energy during winter season or to be used as animal feed (ARIJ, 1994).

Annually, around 10-30 million m^3 of OMW are generated from olive oil industry worldwide (Christos et al., 2011), and around 200,000 m^3 of OMW are generated in the West Bank particularly (Shaheen and Abdelkarim, 2007). With this large volume of wastewater during November to December, the disposal of OMW is considered as one of the most environmental problems in the olive oil producing countries (Rozzi and Malpei, 1997, Fiorentino et al., 2003,). In addition to the large volume of OMW and its seasonal production, their composition makes its treatment also difficult; with lack of appropriate alternative technologies to treat OMW. Much of it is discharged directly into the soil, rivers or open wadies. At best, it is stored in evaporation ponds, where anaerobic conditions are quickly established leading to unpleasant odors, breading of insects and has risks for surface and groundwater (Jatboui et al., 2009).

1.2 Olive mill wastewater (OMW) composition

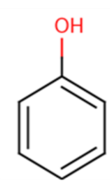
The difficulties with OMW disposing and treatment are due to its unique composition which has a high pollution effect. The OMW composition may vary according to cultivar, harvesting time, olive variety, health of the olives, climatic conditions, the use of pesticides and fertilizers and technology used in the extraction process (Piperidou et al, 2000, Borja et al, 2006). In general, OMW is liquid effluent, brown to reddish brown color due to the presence of phenols. It is a turbid liquid that has a strong foul smell characterized by highly acidic pH and high electrical conductivity. It contains high concentration of solid materials and high organic and inorganic load (high COD and BOD load) (Yesilada et al., 1999, Kavvadiasa et al., 2010).

OMW resists biological degradation due to high concentration of phytotoxic and antibacterial phenolic substances (Aktas et al., 2001, Paraskeva and Diamadopoulos, 2006, Tsagaraki et al., 2007). In addition, OMW contains number of monocyclic and polymeric aromatic molecules that inhibits anaerobic micro organism population (Sobhiet al., 2004, Khateb et al., 2009). The maximum and minimum values of basic OMW characteristics are shown in Table (1.1).

Table (1.1): Basic characteristics of OMW (Hatzinikolaou, 2007, * Khateb et al., 2009).

Parameter	**Value**	**Value In Palestine***
pH	4.0- 6.7	4.9
Conductance (mS/cm)	8.0-16.0	6.7
COD (g/L)	45.0- 220.0	99.0
BOD (g/L)	35.0- 110.0	46.0
Suspended solid (g/L)	1.0- 9.0	17.0
Phenols (g/L)	0.5- 24.0	3.2

1.2.1 Description of phenols



Phenols are class of organic compound that contains the hydroxyl functional group bonded to aromatic ring.

Phenols are present in the stone and pulp of olives, the concentration of it in the olive oil ranges from 50 to 100 μg/g of oil depending on the olive variety, this concentration represent 1-2% of total phenolic content in the olive fruits. During oil extraction about 53% of phenols are lost in OMW and 45% of it lost in olive cake; this due to the solubility of phenols in water and oil. The olive phenols are more soluble in the water than in the oil phase (Niaounakis and Halvadakis, 2006). The concentration of phenols that found in OMW ranges from 0.5 -24 g/L. Phenols are strong antioxidant, antimicrobial and phytotoxic compounds that resist biological degradation and complicating any detoxification process for the OMW (Hatzinikolaou, 2007).

More than 30 different phenolic compounds have been identified in OMW, the major phenol types that have been found in OMW are phenyl acids, phenyl alcohols and flavonoids (Hatzinikolaou, 2007), in addition to the presence of other phenols like caffeic acid, catechol, cresol and others (Niaounakis and Halvadakis, 2006, Christos et al., 2011).

There are two phenol groups in the OMW and the color of OMW determined according to the ratio between them, which they are:

1. The simple and small molecular weight phenols: the non-auto-oxidating tannins and the flavonoids.
2. The darker polymers, which occur from the polymerization and the auto-oxidation of the compounds of the first group (Hamdi et al., 1992, Niaounakis and Halvadakis, 2006).

1.3 Olive mill wastewater effect on the environment

1.3.1 Effect on soil

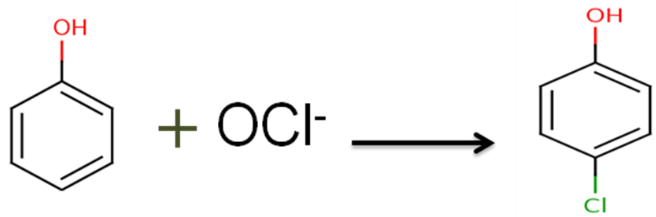
The chemical composition of OMW is quite variable. It contains significant level of organic compounds, considerable quantities of nutrients such as carbohydrates and nitrogenous compounds and possibly a water source. The organic compounds in OMW plays a role in increasing the stability of soil aggregates and reduce soil erosion rates due to the binding action of certain organic components, in particular polysaccharides. These characters enhance recycling of OMW and reuse it as an organic fertilizer to restore the quality of Mediterranean agro- ecosystem (Hanifi and Elhadrami, 2009, Jatbouiet al., 2009). Also OMW has a high concentration of potassium, nitrogen, phosphorus, calcium, magnesium and iron which are important parameters in soil fertility (Paredes et al., 2001).

On the other hand, random disposal of OMW on lands have negative impacts. It effects the physical properties of soil; it causes both reduction of soil porosity and limit air and water exchange between soil and atmosphere (the physical prosperities of soil). These exchanges are needed for the development of the fauna and the micro-flora of the soil, in addition to the respiration of the roots, these changes in porosity are attributed to the combined effect of the suspended and soluble organic matter and salts in OMW and the solubilization–insolubilization of the soil carbonate minerals promoted by OMW (Niaounakis and Halvadakis, 2006).

OMW component also can destroy the cation exchange capacity of the soil due to the presence of acids, minerals, and organic materials. OMW causes significant shifts in the structure and the function of the microbial community. For example, OMW shows toxicity towards nitrifying bacteria which plays critical role in nitrogen cycle, which in turn may influence the viability of the soil for agriculture (Jatbouiet al., 2009). OMW can also cause both release and mobilization of heavy metals from soil and sediments because of its acidic pH. Add to this the presence of lipids which can form an impermeable film on both the soil surface and plant leaves. This film reduces the permeability to sunlight, oxygen and water. The growth of plants is therefore reduced (Niaounakis and Halvadakis, 2006). Other impact of OMW is the high and unbalanced ratio of C/N which can alter the soil microbial community lead to competition between microorganisms and plants on nitrogen. Additionally, the presence of phytotoxic and antibacterial phenolic compounds in OMW can lead to inhibition of plant seed germination and early plant growth and it also causes leaf and fruit abscission (Niaounakis and Halvadakis, 2006, Christoset al., 2011). This heterogeneity of OMW composition is considered as one of the main limiting factors that allow OMW reuse.

1.3.2 Effect on water

OMW is considered as one of the potential threats to surface and groundwater sources (Khateeb et al., 2009). The effects of OMW on natural water bodies are related to its composition, mainly the abundant of phenolic compounds on it, in which small amount of phenolic compounds in water makes it undrinkable (Spandre and Dellomonaco, 1996), because it gives the water an unpleasant taste and smell (Roche and Benanou, 2007). In addition, OMW pollution will be visible because of the ability of phenolic compound to discolor (change the color) the natural water. This change in color is attributed to the oxidation and subsequent polymerization of tannins that give dark colored due to polyphenols, which are difficult to remove from the effluent. According to European Economic Community regulations (EEC), the maximum concentration of total phenol in drinking water is 0.5 µg/L (Spandre and Dellomonaco, 1996). The problem is more serious when chlorine residue (OCl^-) is used to disinfect drinking water in which the chlorine will react with phenols (class of compound that contain the hydroxyl functional group bonded to aromatic ring) to form chlorophenols as shown in the following formula which is more dangerous on human health than phenols (Spandre and Dellomonaco, 1996, Roche and Benanou, 2007).



Chlorophenols are widely described as a potential source of taste in water. In France, the maximum concentration allowed in surface water is (100 µg/L) (Roche and Benanou, 2007). The United State Environmental Protection Agency (US EPA) has compiled a list of several phenol derivatives as severe pollutants of natural aqueous sources. Among them, chlorophenols are with especial toxic and potentially carcinogenic (Nogueraet al., 2002).

The dumping of OMW into surface water cause depletion of dissolved oxygen concentration in water because of the presence of reduced sugar in it. Because of the increase of the microorganism number that uses reducing sugar as a substrate so affect on the whole ecosystem balance by reducing the available dissolved oxygen for other living organisms. In addition to the presence of high phosphorus concentration that can cause eutrophication (Niaounakis and Halvadakis, 2006, Christoset al., 2011).

1.3.3 Effect on sewer network and treatment plants

The disposal of OMW in urban sewage treatment plants is not practicable because of its high concentration of organic and inorganic load that make 1 m^3 of OMW is equal to 100-200 m^3 of domestic wastewater (Fiorentino, 2003, Hatzinikolaou, 2007, Tsagaraki et al., 2007). A comparison between OMW and domestic wastewater properties are shown in Table (1.2).

Table (1.2): Comparison between domestic wastewater and OMW characteristics.
([1]: Kling, 2007, [2]: Hatzinikolaou, 2007, [3]: Saleh, 2011, [4]: Kateb et al., 2009).

Parameter	Domestic wastewater[1]	OMW[2]	Domestic wastewater in Palestine[3]	OMW in Palestine[4]
pH	6.7 - 7.5	4.0 – 6.7	7.2	4.9
COD (mg/L)	250.0 – 800.0	45000.0 – 220000.0	150.0	99000.0
BOD (mg/L)	110.0 – 350.0	35000.0 – 110000.0	40.0	46000.0
TSS (mg/L)	120.0 – 400.0	1000.0 – 9000.0	50.0	17000.0

Due to the OMW acidity and its suspended solids contents, in addition to the high concentration of organic acids (mainly volatile fatty acids). OMW effluents are very corrosive to the sewer pipes .The suspended solids present in OMW will settle in the sewers close to the mills discharge pipes and sediments build up. These sediments will undergo anaerobic fermentation that cause bad odor and increase the acidity content of wastewater and this will increase the corrosion (Rozzi and Malpei, 1997). The tangible effects of OMW on the wastewater treatment plants is due to the presence of some classes of non biodegradable toxic and antibacterial compounds which is polyphenols that appear toxicity to microorganisms and complicate the biological treatment of OMW (Rozzi and Malpei, 1997, Tsagarakiet al., 2007).

1.4 Olive oil extraction method

The quality and quantity of OMW are highly dependent on the extraction process (Shaheen and Abdelkarim, 2007). There are two main olive oil extraction processes; traditional (classical pressing) and continuous (centrifuging) method, starting from the pulp of olive fruits obtained by grinding them in stone mills. According to the traditional method, the ground olives are pressed in cloth bags then the liquid mixture is settled in a series of tanks to separate the oil (Aktas et al., 2001). The quantity of OMW produced by traditional way is smaller than the quantity produced by continuous method, but more concentrated with pollutants (Tsagaraki et al., 2007).

In the continuous method two processes are applied; the two -phase decanters system and the three-phase decanters system depend on aqueous phase centrifugal separation. Both include the following stages in olive oil extraction with difference in the last stage:

1. Leaves removing: The olive fruit is placed in the hopper to remove the leaves that may affect the oil taste if it is not removed.
2. Olive washing: The olives should be washed to remove any waste or dust that may present on the olives surface.
3. Olive Crushing: The washed olives transferred to the next stage of producing olive oil in which the olives are crushed to facilitate the oil production.
4. Malaxation: when the crushed olives transferred to the malaxtor to produce the oil by facilitating the separation between water and oil on 35°C for 45 min.
5. Oil extraction: the final products are: the olive cake contains water, olive oil and OMW; and the central centrifuge used to separate the oil from the other remaining. See Figure (1.1) that showed the previous steps in olive mill in Hebron area.

The main difference between two-phase and three-phase systems is the addition of additional water in the three-phase system which increases the amount of produced OMW. So, there is a global trend to use the two-phase system to reduce the amount of OMW (Hatzinikolaou, 2007).

Figure (1.1): Olive oil production process from the olive washing stage to oil production, and up to waste disposal. Full automatic olive mill, Hebron, Palestine.

The main differences between the oil extraction processes technology in the study area, presented in Figure (1.2).

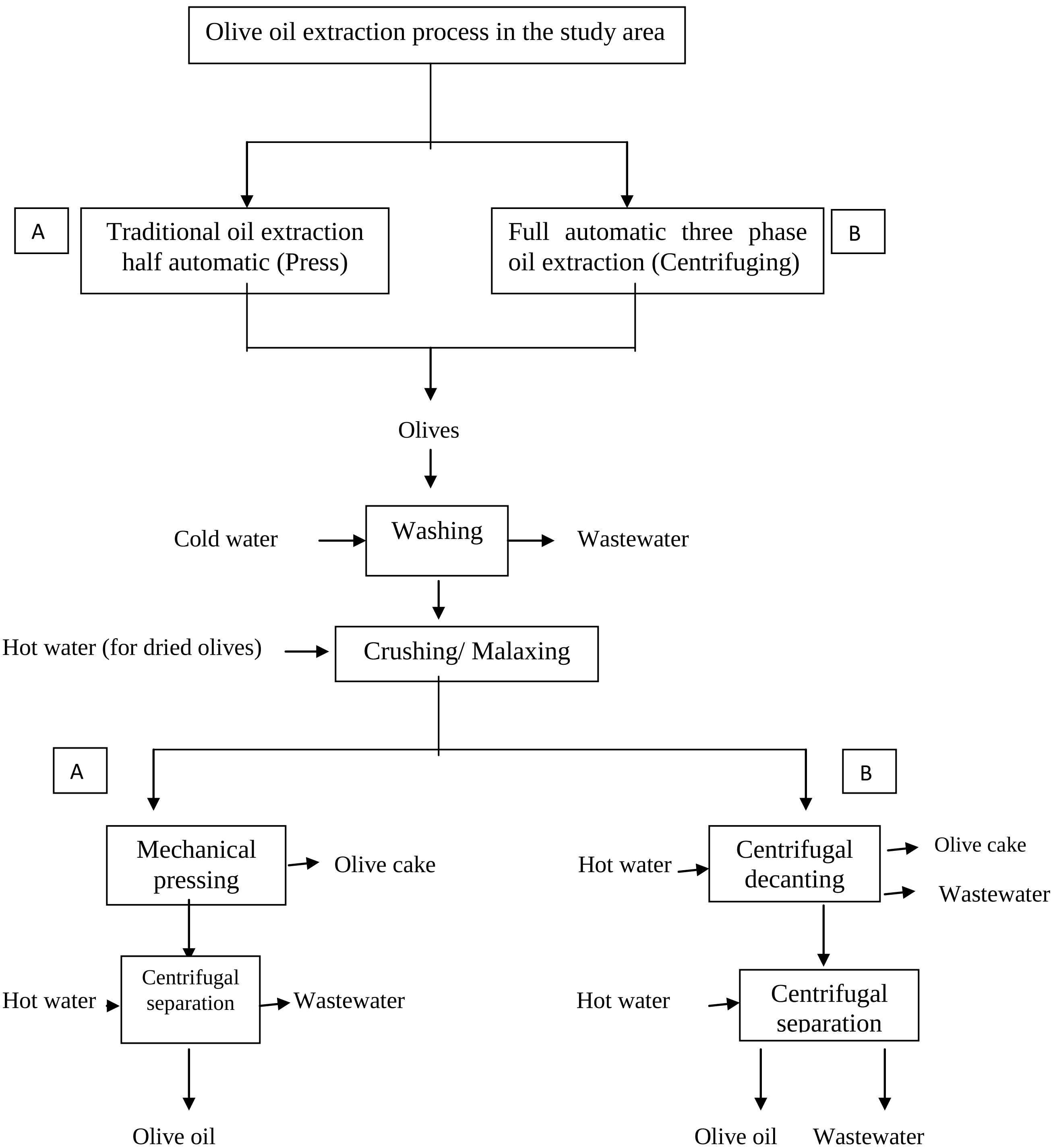


Figure (1.2): Main stages of oil extraction processes in the study area (Niaounakis and Halvadakis, 2006).

1.5 Olive mill wastewater treatment technologies

There are several treatment processes and technologies proposed for the treatment of OMW. This varies from physical, physico-chemical, to biological processes.

1.5.1 Physical processes

It depends on separation of different phases (from solid–liquid or liquid–liquid) by mechanical methods. It includes dilution, sedimentation, filtration, centrifugation and membrane technology (Niaounakis and Halvadakis, 2006). These processes alone are not able to reduce the organic load and OMW toxicity to acceptable limits. Dilution is used before biological treatment to reduce OMW toxicity on microorganisms. Sedimentation is the simplest and most widely used physical method, removal of the sediment contribute of large reduction in BOD of OMW. But it also considered as a slow method and produces a sludge that needs further treatment (Paraskeva and Diamadopoulos, 2006, Niaounakis and Halvadakis, 2006). Membrane processes they are effective for separation of oil-water mixtures without adding solvents and could recover some valuable components to compensate for the high capital and operating costs of waste detoxification. The uses of membrane processes for OMW treatment are limited; the basic problem is that severe fouling of the membrane occurs very easily, strongly reducing the membrane efficiency due to gelling substances contained in OMW and lifetime of membranes are limited to one working cycle (Tsagaraki et al., 2007, Otles and Selek, 2012).

1.5.2 Physico-thermal processes

It includes evaporation/ distillation of OMW. These processes concentrate the organic and inorganic content of OMW by evaporation of water (Rozzi and Malpei, 1997). The evaporation of OMW reduces its volume by 70 to 75% and brings down the polluting load to more than 90% in terms of COD. The residue produced can be used as animal feed, fertilizer, or put back in the distillation process. The condensed vapor can then be used in the olive washing step in the olive-mill (Niaounakis and Halvadakis, 2006). This method need large area and produces several problems such as bad odor, infiltration and insect proliferation (Hatzinikolaou, 2007).

1.5.3 Physico-chemical processes

It depends on addition of certain chemicals that make: neutralization, flocculation, precipitation, adsorption, chemical oxidation, and ion exchange of OMW.

Neutralization depends on pH increasing to be around 11 by adding caustics like NaOH, $Ca(CO_3)$ or $Ca(OH)_2$ or pH decreasing to be ranges from (2-4) by adding acids like HCl or H_2SO_4. By increasing the hydrogen ion (H) concentration or by adding specifically absorbed ions (Ca_2) the negative surface charge of the suspended hydrophilic colloids is reduced and this leads to their neutralization and destabilization (Niaounakis and Halvadakis, 2006). Precipitation/ flocculation depend on adding a precipitate-inducing agent to convert dissolved chemicals into an insoluble solid to precipitate it out. It also depends on adding aggregation inducing agent to convert suspended particles in OMW into larger one used as pretreatment procedures for the removal of organic matter from OMW. The main disadvantage is the need of disposed the precipitated material (Niaounakis and Halvadakis, 2006).

1.5.4 Biological processes

Biological treatment is able to remove organic matter and inorganic nutrients. The microorganism that used in biological treatment must have the ability to adapt and survive in the presence of antioxidant phenolic compounds. It includes: anaerobic and aerobic processes.

- **Anaerobic processes**

Anaerobic biodegradation most widely investigated technique for the decontamination of OMW. It depends on use anaerobic microorganism mainly bacteria that live in the absence of oxygen that can convert the organic matter to methane gas which can be used as energy source (Otles and Selek, 2012). Other advantage of it that it can treat OMW with high organic-load, low nutrient requirements are necessary, low energy consumption and produce small quantities of excess sludge (Paraskeva and Diamadopoulos, 2006). On the other hand, anaerobic biodegradation is affected by temperature, retention time, pH, chemical composition of wastewater, and the presence of substances inhibitory to the anaerobic process such as lipids and polyphenols, so pretreatment and/or post-treatment steps may also be necessary (Niaounakis and Halvadakis, 2006, Otles and Selek, 2012).

- **Aerobic processes**

It depends on use aerobic microorganisms that live in the presence of oxygen. The aerobic bacteria have a minimal effect on complex polyphenolics compound in OMW and they appear to be very effective against some low molecular phenolic compounds (Otles and Selek, 2012).

OMW treatment is a complex problem. None of the previous treatment technologies can alone solve the problem of it. So the combination between different technologies can effectively treat OMW to the desired standards (Paraskeva and Diamadopoulos, 2006).

1.6 Study importance

Management of OMW is one of the key problems associated with the agriculture industry in olive oil producing countries including Palestine. In the West Bank, there are more than 246 functioning olive mills scattered in both rural areas and cities generating more than 200, 000 m^3 of OMW (Shaheen and Abdelkarim, 2007). These effluents are confronted to a serious ecological problem in the West Bank due to their toxicity and their seasonal production. Add to this the lack of appropriate alternative technologies to treat OMW. The disposal of OMW in the West Bank occurs randomly by dumping the olive mill effluents into the environment, open wadies, sewage networks or water receiving bodies that will mix with the municipal wastewater or rain water and will pollute the surface and ground waters. An example, Wadi Zeimar in Nablus-Tulkarem region, where OMW is discharged and flow to the west contributing to the flow of Alexander River behind the green line (towards the Mediterranean, causing severe environmental problems. This also causes death to the aquatic life in the river (Odi, 2007).

There was a follow up on olive mills periodically from a group of governmental ministries like, Ministry of Agriculture, Ministry of Health, Ministry of Labor, Ministry of the Palestinian environment, Palestinian Water Authority, Municipalities and the Palestinian Central Bureau of Statistics. They focused on; the availability of hygiene conditions in the olive mills before the beginning of the olive oil production season, the quantity of pressed olives, the extraction rate, the quality and the quantity of produced oil during the season, the number of employers, the automation levels of the Olive mills, the economical values of this production and other things; without focusing on the risk of the polluting effects of OMW on the Palestinian environment (mainly on surface and ground water resources) and without taking any action to solve this environmental problems. With the presence of this governmental follow up on olive mills activities still there are no any alternatives or solutions of the problem of OMW disposal and its negative impacts on the Palestinian environment, and there is no applied of Palestinian regulations that prevent disposing of OMW into wadies or sewage network (Khateeb et al., 2009) .

So in the absence of application of Palestinian regulation that prevent the disposing of OMW effluents to the environment, this effluent is considered as one of the main environmental problems in the West Bank as there is lack of dependent technologies to treat it so far. According to the previous description of OMW will have impacts on Palestinian environment, this study will summarizes the current status of olive mills in the south part of the West Bank (Hebron and Bethlehem governorates) and follows the final dumping site of OMW. Then it will out a possible pre-treatment technology that can reduce the toxicity of OMW applied in the West Bank. The proposed treatment in this study is the use of lime material to reduce the polluting effect of OMW mainly to reduce the toxic phenol compounds concentration as a pre-treatment step, followed by biological treatment using *Aspergillus niger* fungi.

1.7 Literature review

The problem of disposal and treatment of OMW 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:

1.7.1 Previous researches in Palestine:

Subuh, 2000: Olive oil production is a major contributor to the national economy of the West Bank. There was 220 functioning olive mills in the West Bank producing about 0.2 million CM of OMW that contains high levels of organic pollutants. These OMW is discharged to the environment without any treatment. The aim of this research was to find out a workable method for treating OMW based on anaerobic treatment by using Up-Flow Anaerobic Sludge Blanket (UASB) reactor. The results showed that anaerobic treatment of OMW is feasible, and 82- 90 % of COD and 64% of total phenol were removed after treatment process (during the steady state).
The disadvantage of this research was the need of dilution of OMW because of high COD content and toxicity of phenols.

Shaheen and Abdelkarim, 2007: In the Palestinian Territories, water is the most precious resource and its relative scarcity and quality is a major constraint on economic development. The random dumping of untreated wastewater into the wadies and watercourses is threatening the groundwater aquifers as the main source of water; this problem should be solved in the Palestinian Territories to protect the water resources and environment. The aim of this study was to evaluate and investigate the management options and possible treatment alternatives for olive mill wastes in the Palestinian territories. The results of this study recommended three management options to be applied in the Palestinian territories. They are: using anaerobic treatment or forced evaporation, modifying the technology of olive oil extraction by using 2 phase decanter and reusing OMW option.

This research makes theoretical comparatives between different OMW treatment options without any applying of his recommended options on Palestinian OMW.

Awni et al. 1, 2009: The olive mill wastewater is the main by product of olive oil industry. It considered as a significant source of environmental pollution because it is negatively impacts the regional environment due to its toxicity to micro organisms in domestic wastewater treatment plants, its strong and unpleasant odor after anaerobic digestion, and its potential threat to surface and groundwater sources. The aim of this study was to reduce the COD concentration as a major pollutant on OMW based on biological treatment process by using Up-flow Anaerobic Sludge Blanket reactor (UASB) with different sludge types to examine the most appropriate one. The results showed that the effluent pH was in the range: 7.5-7.75 and the COD removal percent using UASB was 84%.
The disadvantages of this research were: the long-term start-up period of UASB system, instability of biological activity because of washing out part of the biomass from the reactor and the need of pH modification. Add to this, the toxicity of phenols which is very important to be removed from OMW.

Awni et al. 2, 2009: Olive oil extraction is one of the most traditional food industries in Palestine. This industry produces olive oil and other by products (olive mill wastewater and olive husks) that represent serious environmental problems in Palestine. the aim of this study was to evaluate the level of environmental impact of Olive oil industry in the West Bank by carry out a survey including 92 olive mills in Hebron (south), Nablus (center), and Jenin (north). It also aimed to analyze the physical and chemical parameters (pH, BOD, COD, TDS, TSS and TKN) of OMW of 61 samples. The results showed that olive oil yield was 23.7%, the solid waste product was 40%, and the olive fruit water content was 37.7%. In addition the value of the analyzed physical and chemical parameters of OMW was high to discharge in the environment or to the sewer system.

Our research concentrated on removal of total phenol from OMW by using different feasible treatment options to protect Palestinian environment and water resources. So this will add value to the previous researches.

1.7.2 Previous researches worldwide:

Aktas et al., 2001: Olive mill wastewater generated by the olive oil extracted industry is a great pollutant because of its high organic load and also phytotoxic and antibacterial phenolic substances present which resist biological degradation. OMW cause serious environmental problems in producing countries. The aim of this study was to reduce the polluting effect of OMW based on the use of lime material for treatment process. The results showed that 62.5% of total phenols and 46.3% of COD was reduced by using lime.
Our research used the treatment technology of Aktas et al., to try it on Palestinian OMW as a pretreatment step to be followed with biological treatment using *Aspergillus niger*.

Kotsou et al., 2004: Olive processing wastewater causes an important environmental problem, it is unsuitable for disposal at municipal or industrial wastewater treatment plants due to its high organic and phenol content. The aim of this study was to treat OMW through aerobic biological treatment using Aspergillus niger strain in a bubble column in combination with chemical oxidation using Fenton's reagent to reach quality to allow its discharge into the wastewater treatment plants. The results showed that 70% of COD and 41% of total phenol were reduced after biological treatment. Additional removal of phenoilc compounds was obtained after chemical oxidation.
Our research using *Aspergillus niger* strain with different procedure that use in Kotsou et al. research with combination with lime adsorbent.

Petalas et al., 2007: Olive mill wastewater is a characteristic of by-product of olive oil production and a major environmental problem in the Mediterranean area because of its high organic load and the existence of phytotoxic phenolic compounds. The aim of this study was to determine the ability and the efficiency of olive pomace to reduce phenol concentration in OMW as a pre-treatment step. The results showed that 40% of phenolic compound was reduced by using olive pomace adsorbent.

Mebirouk et al., 2007: Pollution by olive mill wastewaters is becoming a crucial problem in the Mediterranean area which produces more than $3*10^7$ m^3 of OMW per year. The aim of this study was to develop an integrated process to treat OMW. The integrated process comprizes different steps of treatment, the first one were aimed to reduce COD and BOD by coagulation–decantation treatment process. The second step was aimed to remove polyphenols from OMW through absorption via sawdust to improve OMW biodegradation by using P.Chrysosporium species. The results showed the total polyphenols, color, and COD reduction efficiencies were 95%, 75% and 90% respectively.

Boukhoubza et al., 2009: Olive mill wastewater is discharged into the nature without any prior treatment what causes acute deterioration of the quality of the receiving environments including rivers, groundwater and agricultural soils. For these reasons, OMW are currently a major concern leading many environmentalists and researchers to develop techniques for treatment and valorization of these effluents. The aim of this study was to make dephenolisation and discolouration of OMW by using a combination between lime and calcium hypochlorite. The results showed that the OMW color was highly reduced with calcium hypochlorite, in addition to reduction in other studied parameters like phenolic compounds and COD.

Hanifi and El Hadrami, 2009: Discharge of olive mill wastewater is known to have adverse effects on the environment. Several treatment technologies were proposed for these effluents, they limited by economical and technical constraints. The aim of this study was to discuss the ability of OMW re-use as agronomical amendment of poor soils through making a review of the worldwide studies in the last two decades. It was focused on the OMW bio-transformation in soil and their expected environmental impact. The results of this study showed that there was a cumulative effect of salt and toxic phenolic compounds that would lead to soil degradation in the long term application of OMW on soil. In addition, there was a need to both technical and scientific interventions for a safe OMW re-use.

Christos et al., 2011: Globally, olive production exceed 15 million metric tons of olive per year and generating about 10-30 million m^3 of olive mill wastewater that disposed directly to the environment and cause serious environmental problems. The aim of this study was to describe the impact of OMW disposal in Cyprus and to find out an economically and environmentally acceptable treatment of OMW. A review of three biological treatments were compared in this study; aerobic treatment, anaerobic treatment and compositing. The results of the study recommend making more research to develop a cost effective and efficient process for OMW remediation.

Cerrone et al., 2011: Treatment and disposal of olive oil mill wastewater is presently one of the most serious environmental problems in the Mediterranean countries due to its high organic load and the abundant of phenolic compounds. The aim of this study was to remove OMW pollutants by using bubble-column bioreactor by Trametes versicolor. The results showed that the Trametes versicolor was a good pollutant degrader reducing color, COD and phenols by 65%, 73% and 89% respectively.

1.8 Study objectives

The main objective of this study is to reduce OMW toxicity (mainly total phenols) on the Palestinian environment by:

1. Summarize the current situation of operating olive mills in the southern part of the West Bank (Hebron and Bethlehem governorates) and determine the physical and chemical properties of resulting OMW from these mills.

2. Investigate the efficiency of different adsorbent like: lime, sawdust and bottom ash followed by biological treatment using *Aspergillus niger* strain in total phenol removal.

1.9 Study hypothesis

1. OMW generated from Hebron and Bethlehem olive mills have polluting effect on the environment and threat ground water resources.
2. The polluting effect of OMW in Palestine mainly total phenols can be reduced by using lime adsorbent as a pre-treatment followed with biological treatment using *Aspergillus niger*.

1.10 Study area

1.10.1 Location of study area

The study area is including Hebron and Bethlehem governorates, see Figure (1.3). Hebron governorate located at the southern part of the West Bank, it is bounded by Bethlehem governorate from the north and by the 1984 cease fire line from the other directions with an area of about (1036 Km^2), the elevation ranges are from (100 to 1021 m) above sea level and the population number is (552,164) (PCBS, 2009, ARIJ 1, 1994). Land use in Hebron governorate divided into built up areas, Israel colonies, nature reserve and cultivated areas (ARIJ 1, 1995).

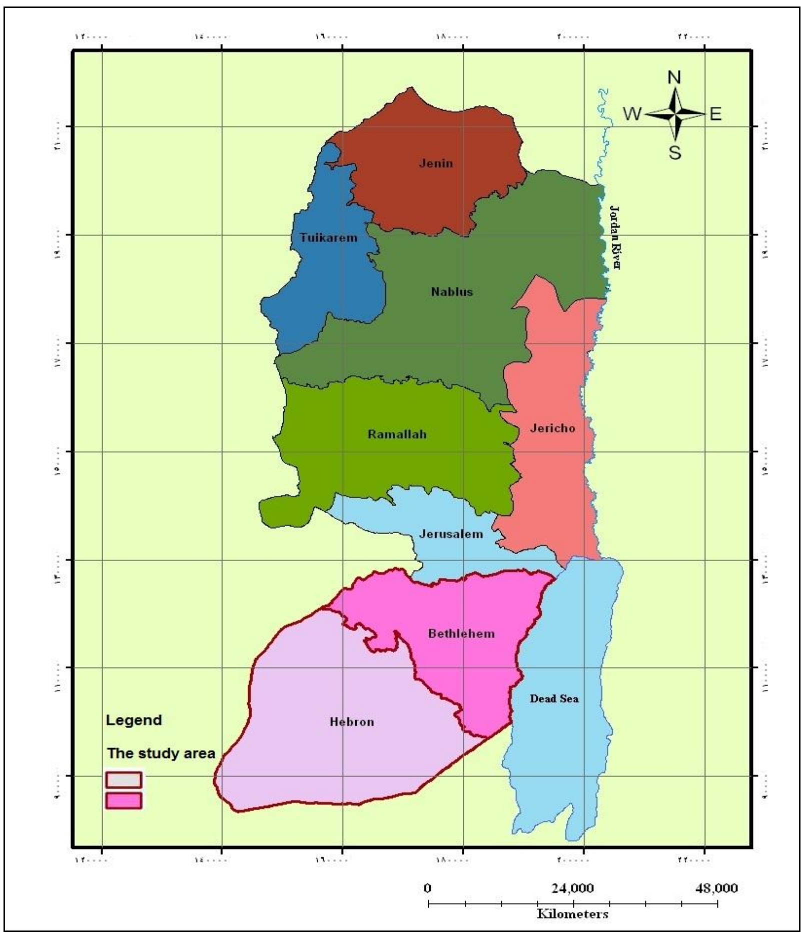


Figure (1.3): Location of the study area: Hebron and Bethlehem governorates (source of shape files from Al-Quds University database).

Bethlehem governorate is bounded by Jerusalem city from the north and by Hebron governorate from the south, with an area of about (659 km^2), it includes within its boundaries the three major municipalities of Bethlehem, Bet Jala, Bet Sahour and 71 Palestinian towns and villages. The elevation ranges from (400 to 900 m) above sea level and the population number are (169,966) (PCBS, 2009). Land use in Bethlehem governorate divided into built up areas, Israel colonies, nature reserves and cultivated areas (ARIJ 2, 1994).

1.10.2 Climate of study area

The climate in Hebron and Bethlehem governorates ranged from arid to semi arid climate, characterized by long, hot, dry summer and short, cool, rainy water. The average annual rainfall in Hebron and Bethlehem is (588 mm) and (517mm) respectively (ARIJ 1, 1994, ARIJ 2, 1995).

1. 10.3 Water resources of study area

Water shortage is a serious problem facing Hebron and Bethlehem governorates not only to the arid climatic condition and rainfall variability in the region but also due to the Israel strict control over the Palestinian water resources (ARIJ 1, 1994, ARIJ 2, 1995).
There are 4 licensed groundwater wells in Hebron governorates that are used for domestic purposes (Figure 1.4), that are originate from lower cenomanian aquifer and upper cenomanian aquifer systems, and there are also 64 traditional shallow groundwater wells which are unlicensed use for irrigation purposes. In addition to the presence of 57 springs (ARIJ 1, 1994).

There are 6 groundwater wells are functioning in Bethlehem governorate that are used for domestic purposes, these wells pumps from underground aquifers that originate from cenomanian touronian aquifer system. In addition to the presence of 15 major springs (ARIJ 2, 1995).

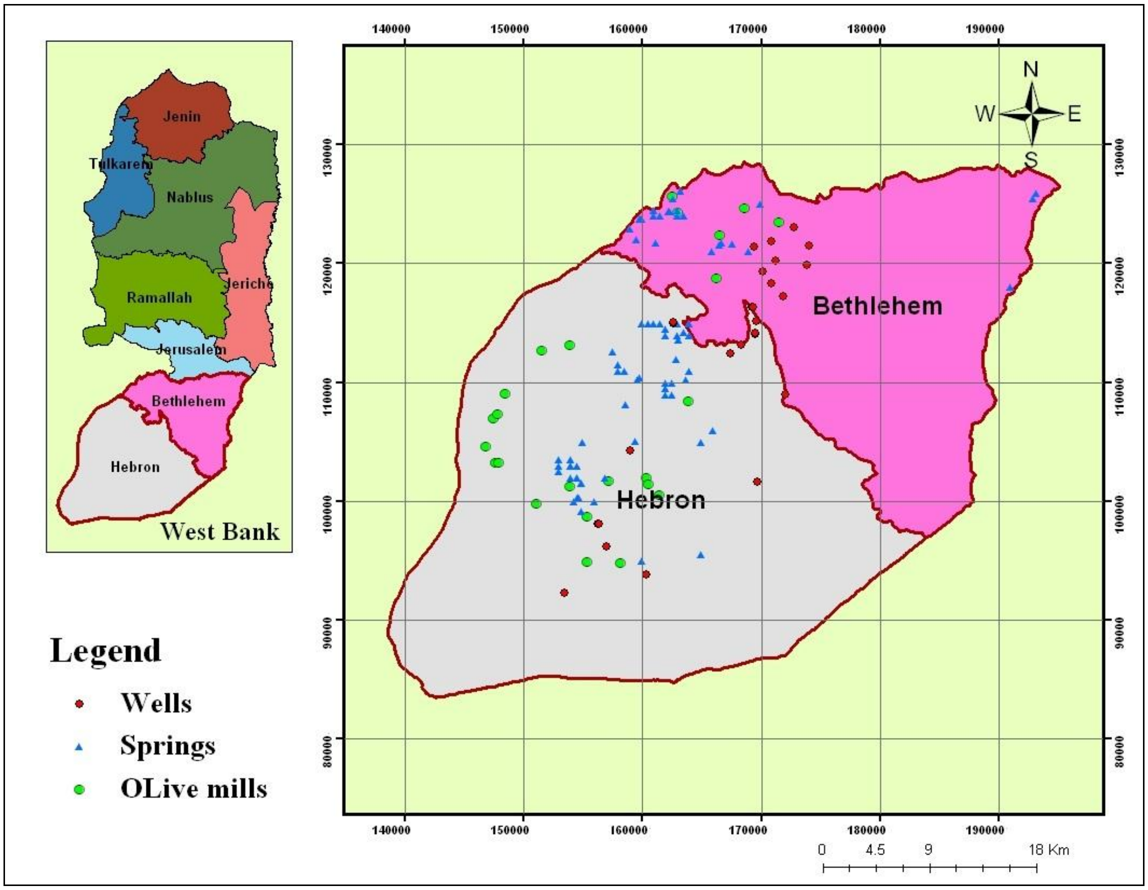


Figure (1.4): Distribution of wells, springs and olive mills in the study area (source of shape files from Al-Quds University database).

Figure (1.4) shows the risk on water recourses pollution from olive mills in the study area. So the relevant Palestinian ministers must attention to the OMW threat to water resources. The geological structure of the study area is presented in Figure (1.5).

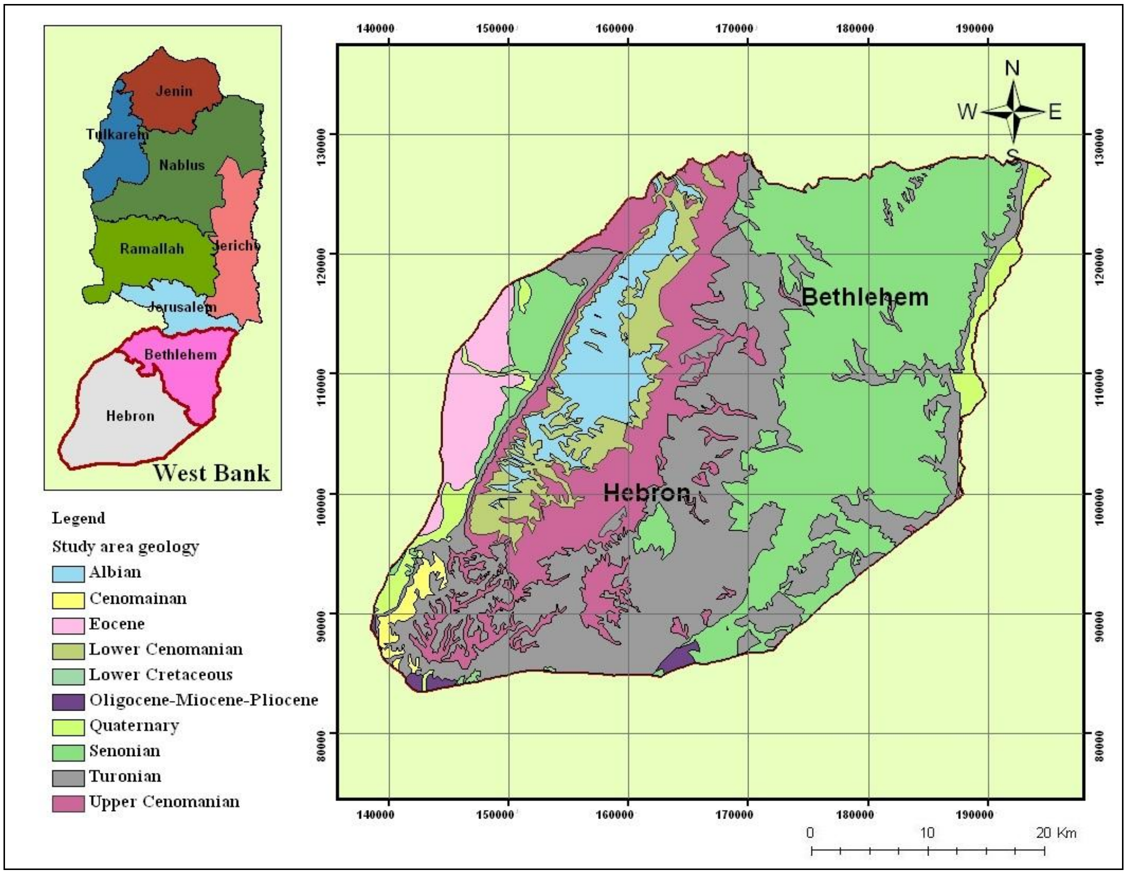


Figure (1.5): The geological structure of the study area (source of shape files from Al-Quds University database).

1. 10.4 Agriculture and soil of study area

In Hebron governorate 34% of total land area are under cultivation; field crops, fruit trees and rainfed vegetables. Field crops are including barley, wheat, lentils and sorghum. Fruit crops are including grape vines, apples and olives, that almost grown rainfed. Olive orchards cover more area than other fruit trees. The total cultivated area with olive trees was 100,502 dunums and very important the production rate of olives per dunum was 340 kg. The olive production is contributed to the economy of the governorate (ARIJ 1, 1994, Agriculture ministry, 2010). The major types of soils are classified as: dark brown soil, terra rossas, brown and pale rendzina, bare rocks and desert lithosols, brown litholsols and loessial arid brown soils and loessial serozems (ARIJ 1, 1994). See Figure (1.6).

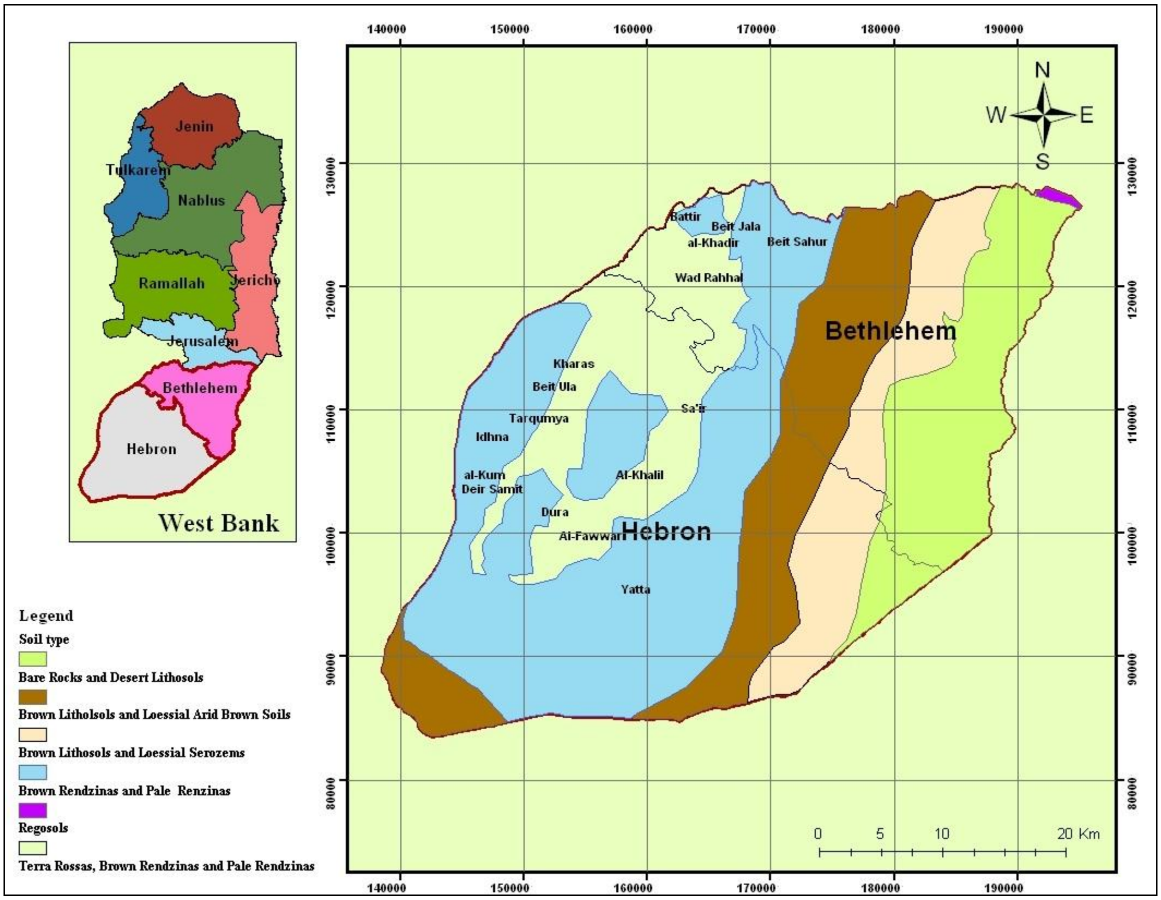


Figure (1.6): Soil types in the study area (source of shape files from Al-Quds University database).

In Bethlehem governorate the olive trees and grape vines are the most dominant fruit trees in the governorate, the total cultivated area with olive trees was 26550 dunums and the production rate of olives per dunum was 80 kg (Agriculture ministry, 2010). In addition to the presence of almonds, apples, apricots and plums fruit trees. The most cultivated field crops are wheat and barley in addition to bitter vetch, lentil, chickpeas and other legumes (ARIJ 2, 1995). The major types of soils are classified as: bare rocks and desert lithosols, brown litholsols and loessial arid brown soils, brown and pale rendzinas, and brown litholsols and loessial serozems (ARIJ 2, 1995).

2 Chapter Two: Materials and Methods

2.1 Field work

Filed visits of olive mills in the southern area of the West bank (Bethlehem and Hebron governorates) were done during the season of the olive oil production for 2010/ 2011: in order to carry out a survey, to determine olive mills location using GPS and to collect OMW samples. The survey covered all olive mills in the study area (Bethlehem and Hebron governorates). The survey questionnaire was prepared (Appendix 1) and both the obtain data was analyzed and organized according to the quantity of pressed olives, amount of consumed water during olive oil production process and amount of OMW by-product. Then, the data was categorized according to governorates and automation level of olive mills. The coordination of olive mills locations were taken by GPS. Then the data was inserted and analyzed by using (Reproject me software) and (GIS software) to draw a map (Figure 2.1).

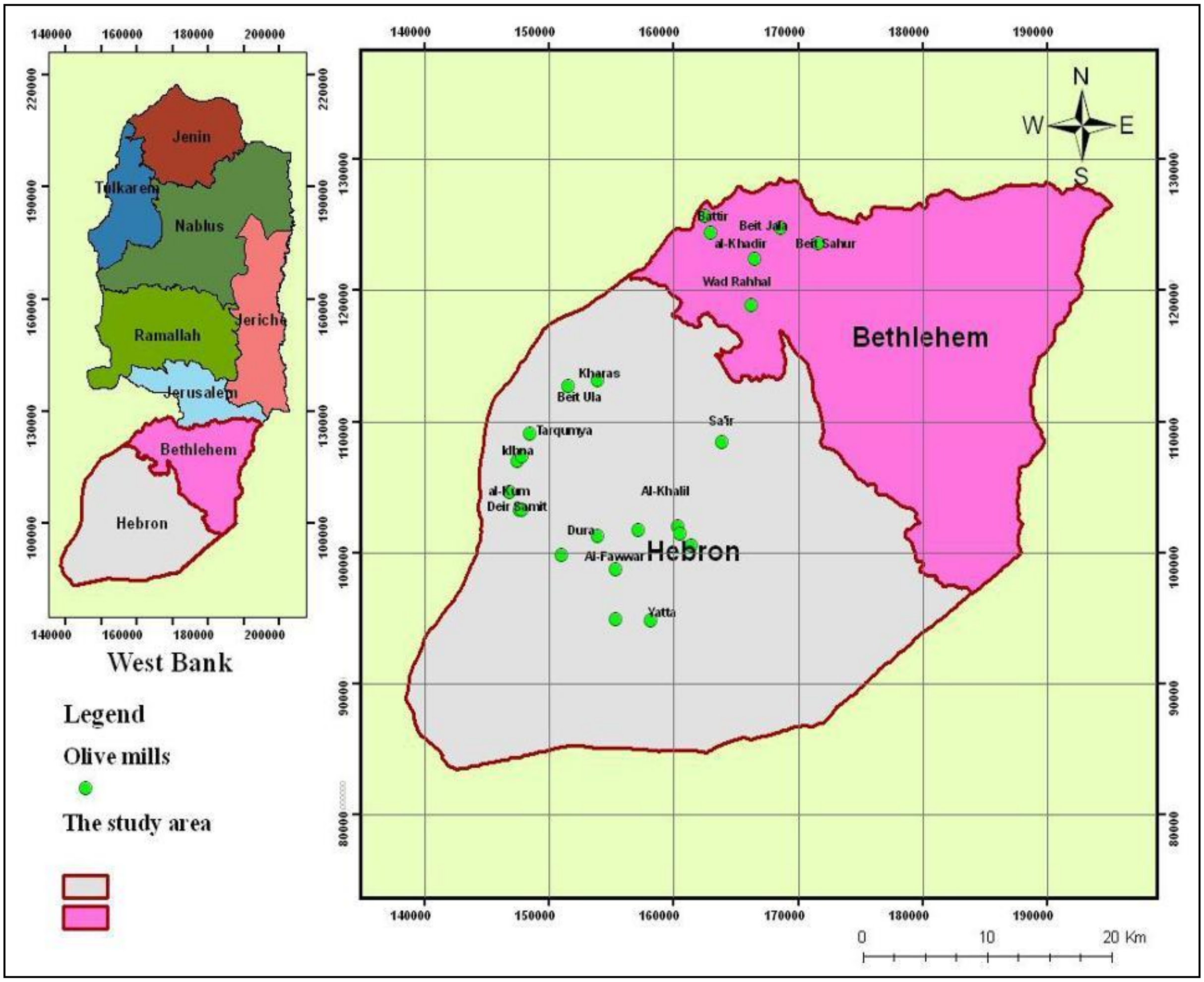


Figure (2.1): The distribution of olive mills in the study area, 2010/2011 (source of shape files from Al-Quds University database).

2.2 Samples

Samples of OMW were collected during the olive oil production season for 2010/ 2011 from Bethlehem (5 full automatic olive mills and 1 half automatic olive mill) and Hebron governorates (11 full automatic olive mills and 2 half automatic olive mills) Table (2.1). One sample was collected from each olive mill (19 samples in total). Samples were taken in 1 liter glass bottles, and stored at 4°C in ice boxes. Collected samples were taken immediately to the laboratory at Al-Quds University.

Table (2.1): Locations of olive mills for determining the physical and chemical properties of OMW.

No.	Sample code	Location	Automation level
1	B1*	Batter	Full automatic
2	B2	Batter	Full automatic
3	B3	Al-dheasha	Full automatic
4	B4	Bet jala	Full automatic
5	B5	Bet sahor	Full automatic
6	H1**	Deir samet	Full automatic
7	H2	Deir samet	Full automatic
8	H3	Wadi abu alqmra	Full automatic
9	H4	Al-Fawwar	Full automatic
10	H5	Yatta	Full automatic
11	H6	Yatta	Full automatic
12	H7	Kharas	Full automatic
13	H8	Bet ola	Full automatic
14	H9	Hebron	Full automatic
15	H11	Hebron	Full automatic
16	H12	Hebron	Full automatic
17	S1***	Wadi rahal	Half automatic
18	S2	Al kom	Half automatic
19	S3	Nuba/ Kharas	Half automatic

*: B means sample from full automatic olive mill in Bethlehem. **: H means sample from full automatic olive mill in means Hebron. ***: S means sample from half automatic olive mills.

2.3 Methods of analysis

Physical and chemical analysis was measured on the collected samples. The measured parameters were analyzed according to standard procedures that used for the examination of water and wastewater (APHA, 1995). The measured parameters including: Total phenol, Chemical Oxygen Demand (COD), Oil& Grease (O& G), pH, Electrical Conductivity

(EC), Total Dissolved Solids (TDS), Total Solids (TS), and major cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}). (To see full description of each test except total phenols see Appendix 2).

2.3.1 Total phenol analysis

Total phenol was measured according to Folin- ciocalteu method. The sample was firstly filtrated then diluted by distilled water (the dilution factor differs according to the sample). 12.5 ml of diluted sample was poured in clean test tube. Then, both 0.25 ml of Folin-coicalteus reagent and 2.5 ml of Carbonate -tartrate reagent were added. The solution was turned to blue color. After half an hour the blue solution was examined spectrophotometrically at wavelength equal to 700 nm. The same procedure was used to determine the calibration curve by using standard reference Tannic acid (APHA, 1995).

2.4 Treatment methods

2.4.1 Physico-chemical treatment

Three types of adsorbents were used to reduce the pollutant concentrations of OMW, mainly phenolic compounds. They are: Lime, Bottom ash and Sawdust.

Lime (calcium hydroxide) material, Figure (2.2) was used to reduce the pollutants concentration of OMW mainly phenolic compounds. To determine lime efficiency the following procedure was applied according to (Aktas et al., 2001):

- 100 ml of OMW samples were treated with different concentrations of lime (0.5, 1, 1.5, 2 and 4 g).
- The mixture was mixed rapidly at 200 rpm for 5 min and then allowed to flocculate at 60 rpm for 10 min.
- After resting period, the mixture was filtrated.

- pH, EC and total phenol were measured before and after lime treatment. The removal percentage of total phenol after lime treatment was measured, and according to it, the lime dose to treat 1 CM of OMW was determined.

Figure (2.2): Lime (calcium hydroxide) material is soft white powder with chemical formula $Ca(OH)_2$.

The saturation index of the recommended dose was calculated by treatment of OMW with this dose of lime as the same procedure above, then filtrate OMW and take lime from the filter to reuse it for several times depend on the same procedure and calculate the same parameter.

Wood sawdust material and bottom ash (Figure 2.3**)** were used the same procedure as that described for lime treatment with different time (2 hrs).

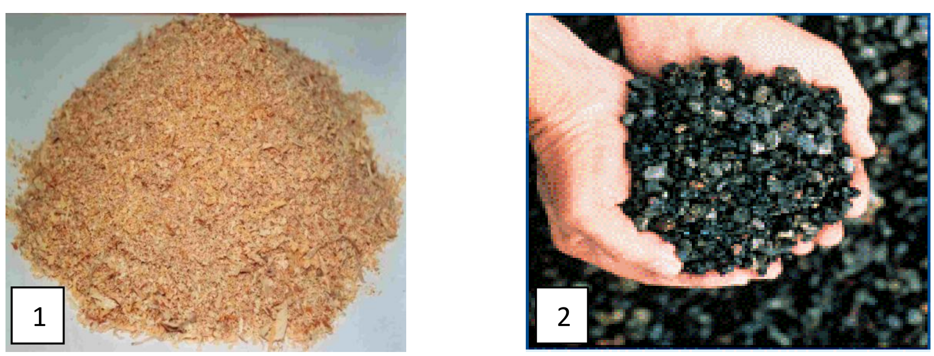


Figure (2.3): Different adsorbent**,** 1: Sawdust (its main component cellulose and lignin, 2: Bottom ash (is black in color and has a porous surface structure).

2.4.2 Biological treatment

The biological treatment depended on certain species of microorganism (*Aspergillus niger)* that have the ability to degrade phenolic compound (Kotsou et al., 2004, Afify et al., 2009).

Table (2.2): The suitable conditions for Aspergillus niger growth.

Test	Medium	Incubation Temp. (°C)	Time (Days)	Colonies color	
A.niger	PDA	25 – 30	5 – 7	Black	

To determine the inoculum size:

- *A.niger* was cultured on potato dextrose agar plates for 7 days at 28°C.
- 5-ml of sterile peptone water was poured on plate of heavy fungal growth.
- *A.niger* colonies were harvested by L-shape sterile glass rod and were collected in a sterile bottle.
- 9 ml of peptone water was poured in screw-caped culture tubes then were autoclaved to make serial dilutions of fungal suspension.
- 1 ml of the harvested fungi was transferred using a sterile pipette to the first test tube then 1ml of second tube was transferred to the third and consequently to obtain optical density between 0.3 -0.45 on spectrophotometer at wavelength 545 nm that corresponds to 10^5 cfu/ml (Saleh, 2011).

The experiment of biological treatment was done as following:

- 100 ml sample of treated OMW with lime and acidified with HCl to pH around 6 was transferred into a volumetric flask, and then 10 ml of *A.niger* suspension (10^5 cfu/ml) was added.

- The flasks were shaken at 150 rpm for one week at 28ºC on the orbital incubator (orbital shaker).

- pH, EC and total phenol were analyzed before and after biological treatment to determine the efficiency of the used strain in the treatment process.

2.4.3 Pilot treatment

The treatment pilot system was design to connect the lime treatment stage and the biological treatment stage. There were three tanks; storage tank, lime treatment tank and biological tank. The tanks were connected to each other by pipes. On each pipe there was a tap as shown in Figure (2.4). In addition there were 2 mixers, one in lime tank and the other in biological tank.

Figure (2.4): Treatment pilot system: storage tank, lime tank, biological tank and mixers.

The inlet of OMW was 3 liters transferred from the storage tank to the lime tank. It was mixed with 30g of lime then mixed on 250 rpm for 15 mins. After that, it remained still for

2 hrs. During this time, the *A.niger* inoculum was prepared. Then, the pre-treated OMW was transferred from lime tank to biological tank. The HCl was added to correct pH to be suitable for biological treatment. After that *A.niger* inoculum (10% of the sample volume) was added onto the pre-treated OMW and mixed with 250 rpm for one week. Samples from each stage were taken to measure pH, EC and total phenol.

3 Chapter Three: Results and Discussion

In order to answer the study objectives, the results were arranged into four parts (3.1: impacts of OMW on water and soil, 3.2: olive mills survey, 3.3: OMW characteristics and 3.4: OMW treatment).

3.1 Olive mill wastewater impacts on water and soil in the study area

To take a look about OMW impact on the environment in the study area, water samples were taken from wells in Wadi abu al qmra in Dura and from Al-Fawwar wells in Al-Fawwar camp, and soil samples from both Wadi abu al qmra in Dura and Wadi rahal in Bethlehem to measure the concentration of total phenol, pH and EC.

Wadi abu al qmra is an important source of water in Dura, there is about 45 shallow dug groundwater wells in it with an average depth of 6 meters. These wells mainly used for agricultural purposes, and few of them used for domestic purposes (Al-Sweity, 2009). There is an olive mill located in Wadi abu al qmra, which release the OMW to near lands that is an agricultural region. According to the lands and dug wells owners, when the mill started in work and dumped the OMW, a layer of oil appeared on the surface of water. 4 samples collected from 4 wells in Wadi abu al qmra and one sample from surface runoff in it. Wadi abu al qmra present with Al-Fawwar wells in the same catchment area, so the surface runoff from Wadi abu al qmra could reach Al-Fawwar wells.

Al Fawwar wells (Figure 3.1) are a major source of drinking water in Al-Fawwar camp and other near communities with an average depth of 100 m. Chlorine disinfectant used to sterilize drinking water of Al Fawwar wells (Awadallah and Owaiwi, 2005). These wells have pollution risk from near olive mills.

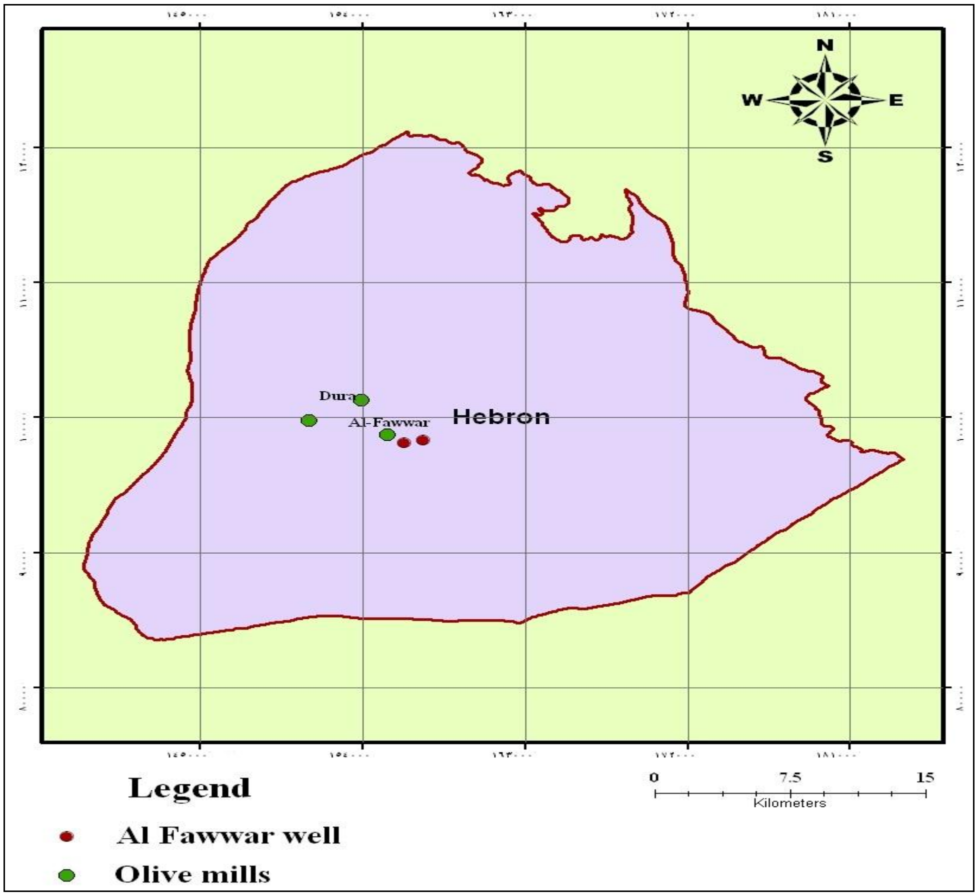


Figure (3.1): Al Fawwar wells and near olive mills from it, Hebron governorates.

The results of water samples from Dura and Al-Fawwar are shown in Table (3.1).

Table (3.1): Water samples analysis of pH, EC and total phenol.

No.	Well name	pH	EC (mS/cm)	Total phenol (μg/L)
1	Adel musallam well	7.1	1.9	4910.0
2	Al-Drawesh well	7.6	1.7	4860.0
3	Abd el aziz well	7.6	1.4	4560.0
4	Higia well	7.7	1.5	5670.0
5	Al-Fawwar well 1	7.7	0.9	2740.0
6	Al-Fawwar well 2	7.5	1.0	3430.0
7	Surface runoff	7.3	1.4	74490.0

According to the EEC regulations the maximum allowable concentration of phenol compounds permitted in drinking water is 0.5 µg/L and according to WHO standards the total phenol content of water to be chlorinated should be kept below 1 µg/L. Adding to this, the Jordanian standards determined the maximum allowable limits of phenols compound in any effluents that will discharged to rivers or wadies should be kept below 2 µg/L. This mean, the phenol concentration in Al-Fawwar wells and other wells exceeded the allowable limit. So, theses wells are polluted with phenol compounds. So there is a risk of chlorophenol compound formation in Al Fawwar wells (see section 1.3.2).

Wadi rahal in Bethlehem have an olive mill that dumped the OMW directly to the near wadi that cultivated with olive trees. To compare the effect of direct dumping of OMW on soil, 2 soil samples were collected from the wadi where OMW dumped; one sample was not in contact with OMW and another one contaminated with OMW (soaked with OMW). Also 2 samples from Wadi abu al qmra were collected; one sample was not in contact with OMW and another one contaminated with OMW (soaked with OMW), the sampling date was on August month of year 2011 before beginning on new olive oil season. The results of soil samples are shown in Table (3.2).

Table (3.2): Soil samples from Wadi rahal and Wadi abu al qmra analysis of pH and total phenol.

Soil sample	Site of sample	pH	Total phenol (mg/L)
Not in contact with OMW	Wadi rahal	7.9	0.7
Soaked with OMW	Wadi rahal	7.9	152.8
Not in contact with OMW	Wadi abu al qmra	8.1	3.7
Soaked with OMW	Wadi abu al qmra	8.2	104.4

pH it wasn’t change after soil contamination with OMW, but phenol concentration was increased. Most soils will contain very little phenol from natural processes, is formed during the natural decomposition of organic matter (NSW, 2004). But from the previous results, the phenol concentration increased after soil contamination with OMW, these organic compounds (phenols) can be toxic to essential soil organism. Phenol generally does not adsorb very strongly to soils and tends to leach rapidly through soil, since any phenol released to soils is likely to leach to groundwater so it is expected to attenuate its levels in soil (NSW, 2004). More extensive analysis and larger amount of data is needed to determine the behavior of phenols in soil to determine the needed time of it to leach to the groundwater and why it doesn’t adsorb strongly in the soil.

3.2 Olive mills survey

This survey was carried out during the period of the study that was carried on 2010/2011 olive season. Results of the survey achieved the objective of this study. Results of this survey were compared with the survey results of the Palestinian Central Bureau of Statistics (PCBS) in the same season.

3.2.1 Number of olive mills and automation level

The results showed that there were 31 olive mills in the study area during the time of the study; 25 in Hebron and 6 in Bethlehem. There were 19 full automatic (three -phase), 2 half automatic and 2 temporary closed olive mills located in Hebron governorate. There were 5 full automatic (three -phase) and 1 half automatic olive mills located in Bethlehem governorate Figure (3.2). The quality and quantity of OMW were highly dependent on the extraction process. There were 2 Olive mills owners who weren’t cooperative with the research, so the study covered 27 Olive mills.

The results of this study are compatible with PCBS Olive Presses Survey results for the year 2010/2011 that were: 33 olive mills in the study area, 26 of them were in Hebron (22 full automatic, 2 half automatic and 2 temporary closed olive mills), and 7 of them were in Bethlehem (5 full automatic and 2 half automatic olive mills).

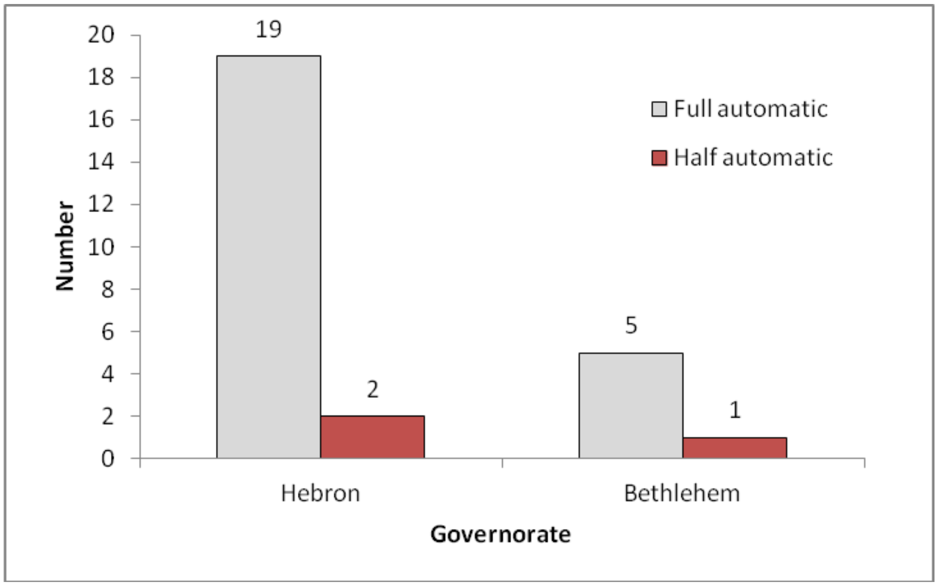


Figure (3.2): Number of Olive mills according to automation level and governorate, 2010/2011.

3.2.2 Quantity of the pressed olives

The total quantity of the pressed olives during the time of the study was 5810 ton, 35% of the quantity was in Bethlehem governorate and 65% of the quantity was in Hebron governorate. The quantity of extracted oil was 1162 ton. These results were compatible with PCBS Olive Presses Survey results (with slightly difference) for the year 2010/2011 (Table 3.3).

Table (3.3): Quantity of pressed olives and extracted oil (in ton) according to governorates in the study area, 2010/2011.

Governorate	Pressed olives* (ton)	Extracted oil* (ton)	Pressed olives** (ton)	Extracted oil** (ton)
Hebron	3755	751	4180	855
Bethlehem	2055	411	1735	394
Total	5810	1162	5915	1249

*: Results of this study. **: Results of PCBS, 2010.

3.2.3 Quantity of olive mills wastes

During olive oil extraction process, the water consumption divided into 2 types; water used for olives wash (wash water) and water used during oil extraction (oil extraction water). The produced OMW include the consumption water (extraction water and wash water) added to the vegetation water that result from olives. Table (3.4) shows the OMW generation rate from full automatic olive mills in the study area.

Table (3.4): OMW generation rate from full automatic (three phase decanter) extraction process.

Governorate	Water consumption* (m3/ton)	Vegetation water** (m3/ton)	OMW*** (m3/ton)
Hebron	1.24	0.49	1.73
Bethlehem	1.20	0.50	1.70
Avg.	1.22	0.50	1.72

*: Water consumption during oil extraction. **: Vegetation water from olives fruits. ***: OMW is the sum of water consumption and vegetation water.

The average value of the produced OMW per ton olives in the study area for full automatic (three phase) process was 1.72 m^3 OMW/ton olives (this result was compatible with Khateeb et al. result on 2009). Table (3.5) shows the OMW generation rate from half automatic olive mills in the study area.

Table (3.5): OMW generation rate from half automatic extraction process.

Governorate	Water consumption* (m^3/ton)	Vegetation water** (m^3/ton)	OMW*** (m^3/ton)
Hebron	1.15	0.50	1.65
Bethlehem	1.00	0.50	1.50
Avg.	1.01	0.50	1.60

*: Water consumption during oil extraction. **: Vegetation water from olives fruits. ***: OMW is the sum of water consumption and vegetation water.

For semi automatic olive mills the average value of the produced OMW per ton olives was 1.65 m^3 OMW/ton and 1.5 m^3 OMW/ton in both Hebron and Bethlehem respectively. According to literature the range of OMW produced per ton olive was 1.2-1.8 m^3/ton for continuous olive oil production process and 0.5 -0.8 m^3/ton for semi automatic olive oil production process (Hamdi et al., 1992, Khateeb et al., 2009). For full automatic process in the study area, the average value of OMW volume was fits within the range, but it also more close to the maximum limits. While the average value of OMW volume for semi automatic process exceed the range. This needs a review of the used technology of olive oil extraction process in olive mills to determine the causes of the use of these high amounts of water mainly because of the limited water sources in the study area so the water consumption must be minimized and to minimize the volume of produced OMW and minimize the demand on fresh water.

The total volume of OMW that generate in the study area can be calculated according to the OMW generating rate Table (3.6). The total quantity of water consumption in olive oil extraction process (include wash water and extraction water) during the time of study was 7581 m^3. The total quantity of OMW (include the water consumption and vegetation water) produced from olive oil extraction process in the time of this study was 10386 m^3 (Table 3.6). 37% of the quantity was for Bethlehem governorate and 63% of the quantity was for Hebron governorate. This compiles with quantity of the pressed olives in each governorate. On the other hand, the quantity of the olive cake (jeft) was 2334 ton.

Table (3.6): Number of olive mills and total volume of OMW according to automation level in the study area.

Governorate	**No. of full automatic mills**	**Volume of OMW (m^3)***	**No. of half automatic mills**	**Volume of OMW (m^3)****
Hebron	19	6730	2	198
Bethlehem	5	2933	1	525
Total	24	9663	3	723

*: Volume of OMW from full automatic olive mills. **: Volume of OMW from half automatic olive mills.

According to the previous results, the mass balance of full automatic (three phase) olive oil extraction process in the study area summarized in Figure (3.3).

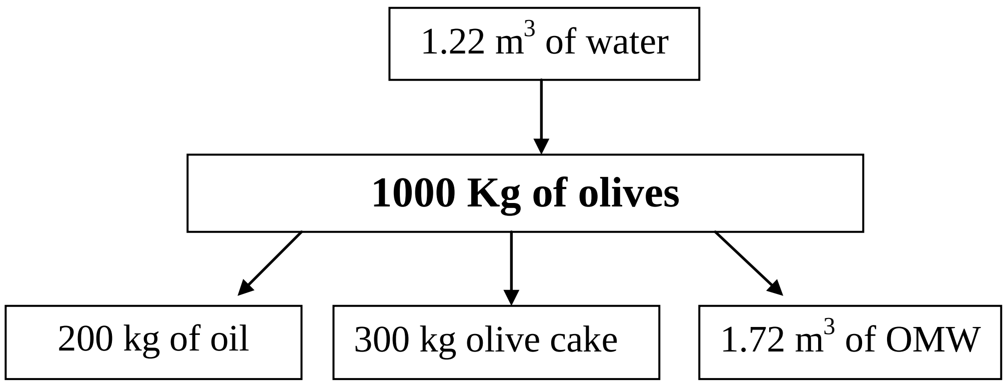


Figure (3.3): The mass balance of full automatic (three phase) olive oil extraction process in the study area, 2010/2011.

3.2.4 Olive mills waste disposal

The results showed that the final dumping sites of OMW was disposing to near (wadis/ or lands) at 67%, and to (sewage network) at 33%. The primary storage of OMW during working period of mills was using storage pond with 59% and using the sewage network with 30% and direct discharge to near lands or wadis were with 11%, see in Figure (3.4). Where, 96.3% of the olive cake *(jeft)* was returned to the olive farmers themselves to be used for heating during winter or to be used as animal feed. Figure (3.5) showed images from different dumping sites in the study area. The input data of olive mills survey in the study area for the season 2010/2011 presented in Appendix (3).

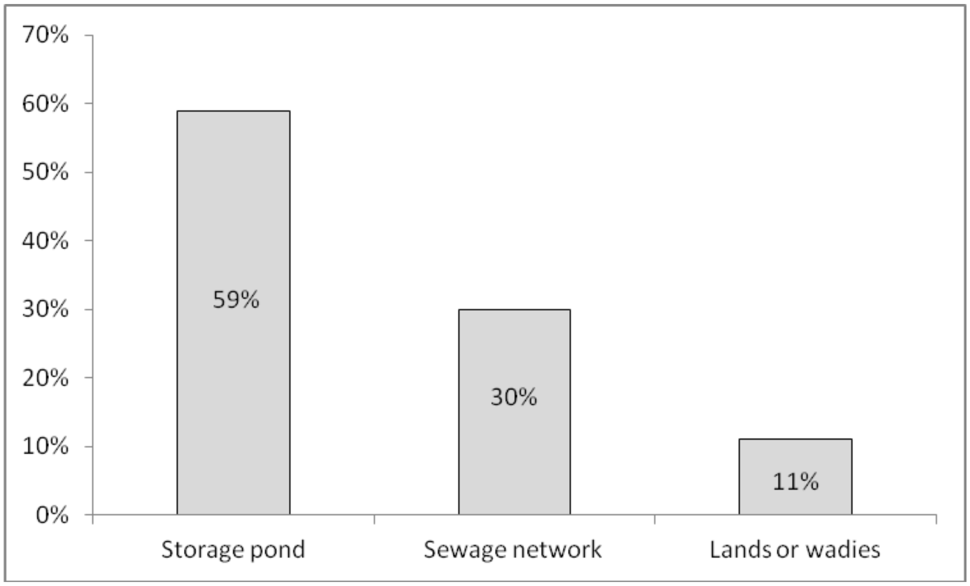


Figure (3.4): Olive mills waste disposal, 2010/2011.

1. Wadi rahal in Bethlehem: OMW disposed to the bottom of the wadi and there is a leakage of it along the wadi	2. Wadi abu al qammra in Dura/ Hebron: OMW disposed to the near land where it’s an agricultural area with many dug wells

3. Oyon abu saeif in Dura/ Hebron: OMW disposed to evaporation pond that has bad smell and breeding of insects	4. Al sael in Yatta/ Hebron: OMW and municipal wastewater from Hebron city and Yatta are disposed in Al sael.

Figure (3.5): The final dumping sites of OMW: 1: Wadi rahal 2: Wadi abu al qmra, 3: Oyon abu safe and 4: Yatta.

3.3 Olive mill wastewater characterization

The results of OMW characteristics were arranged and divided according to automation level, full automatic and half automatic olive mills. Then the results of OMW characteristics resulted from full automatic olive mills were divided according to governorates, Hebron and Bethlehem. Then, the results of OMW characteristics according to automation level (full vs half) were compared to both the Jordanian and Palestinian standards for industrial wastewater disposal.

The results of OMW characteristic of full automatic olive mills that located in both Hebron and Bethlehem governorates are shown in Tables (3.7 and 3.8).

Table (3.7): OMW characteristics of Bethlehem full automatic olive mills.

Parameter	Unit	Sample code					Avg.	Min.	Max.
		B1*	B2	B3	B4	B5			
pH	_____	4.9	5.1	5.3	5.2	5.1	5.1	4.9	5.2
EC	mS/cm	13.6	4.9	5.0	9.7	9.4	8.5	4.9	13.6
TDS	g/L	6.8	2.2	2.5	4.9	4.8	4.2	2.2	6.8
TS	g/L	123.0	56.0	36.0	91.0	93.0	80.0	36.0	123.0
TSS	g/L	116.0	54.0	33.0	87.0	88.0	76.0	33.0	116.0
COD	g/L	66.0	64.0	31.0	62.0	55.0	56.0	31.0	66.0
Total phenol	g/L	4.3	2.0	1.9	5.1	4.9	3.6	1.9	5.1
O& G	g/L	44.3	83.6	33.0	8.5	10.1	35.9	8.5	83.6
K^+	mg/L	2890.0	694.0	679.0	2255.0	2322.0	1768.0	679.0	2890.0
Na^+	mg/L	199.0	141.0	33.0	121.0	141.0	127.0	33.0	199.0
Ca^{+2}	mg/L	363.0	493.0	789.0	733.0	849.0	645.0	363.0	849.0
Mg^{+2}	mg/L	176.0	44.0	102.0	106.0	4.0	86.0	4.0	176.0

* B: OMW samples from full automatic olive mills in Bethlehem governorate, 5 samples from 5 olive mills.

The typical composition of OMW includes water (83%), organic compound (15%) and inorganic chemical (15%) (Khateeb et al., 2009). According to comparison between the average values in Tables (3.7 and 3.8), we notice the following:

The average pH of OMW in both Bethlehem and Hebron was slightly acidic (5.0). This acidity is due to the presence of organic acids in OMW. The average values of EC (7.7- 8.5 mS/cm) and TDS (3.8- 4.2 g/L) were high in both governorates; this due to the high mineral content of olive fruits.

The average values of COD (56- 61 g/L) and total phenol (3.6- 5.5 g/L) were high. This means high organic content of OMW. The organic load of OMW is considered one of the highest of all concentrated effluents, being 100- 150 times higher than the organic load of domestic wastewater.

The average values of oil& grease was very high in both governorates (30- 3g/L). This might be due to the reduction of the time needed in malaxation stage (45 min.) during olive oil extraction process (see section 1.3). If there was a pressure on the mill so they reduced malaxation time that increased the lost percent of oil so increased its concentration in OMW.

The OMW contained high total solids concentration in both governorates according to the average values of TS (83- 84 g/L) and TSS (78 -80 g/L). The high solids content must be taken in consideration before the disposing of OMW into sewer system because it can settle and close the mill pipes and build sedimentation (see section 1.3.3), and it also must be taken in consideration in the technology that will be used for OMW treatment (it need physical treatment).

There were different mineral salts present in OMW, potassium has the highest concentration, and these minerals are important factors in soil fertility.

There was variation between OMW characteristics from olive mill to another during olive oil season. This variation also reported by other Palestinian researcher like (Khateeb et al., 2009). This variation due to the fact that the composition of OMW is not stable and varies significantly according to different factors like: kind of olives, composition of vegetation water, storage time of olives after harvesting, maturity of the olives when it harvested, cultivation soil, the use of pesticides and fertilizers and type of extraction process (Hatzinikolaou, 2007).

So the management of OMW problem needs periodic follow up of the OMW characteristic each season and make several analyses to determine the causes of OMW characteristic variation. Any treatment technology will be applied in Palestine must take attention toward the variation of OMW characteristics from season to other or from region to other.

Table (3.8): OMW characteristics of Hebron full automatic olive mills.

Parameter	Unit	Sample code											Avg.	Min.	Max.
		H1 *	H2	H3	H4	H5	H6	H7	H8	H9	H11	H12			
pH	—	5.0	4.8	5.1	5.4	5.2	5.2	4.9	4.8	5.0	4.9	4.7	5.0	4.7	5.4
EC	mS/cm	7.1	8.6	7.3	3.1	8.9	8.8	8.8	6.1	7.6	11.3	6.8	7.7	3.1	11.3
TDS	g/L	3.7	4.3	3.6	1.5	4.5	4.4	4.5	3.0	3.8	5.6	3.4	3.8	1.5	5.6
TS	g/L	77.0	68.0	82.0	39.0	111.0	88.0	76.0	55.0	60.0	115.0	63.0	76.0	39.0	115.0
TSS	g/L	73.0	64.0	78.0	37.0	107.0	84.0	72.0	52.0	56.0	101.0	60.0	72.0	37.0	101.0
Ash	g/L	17.6	11.9	23.7	5.1	31.8	23.1	9.4	14.5	38.9	68.2	42.8	26.1	5.1	68.2
COD	g/L	61.9	60.4	66.6	38.4	82.8	72.3	69.0	46.8	69.7	72.7	33.7	61.3	33.7	82.8
Total phenol	g/L	5.4	3.8	6.5	2.1	7.8	9.9	5.7	3.6	4.4	6.4	4.9	5.5	2.1	9.9
O& G	g/L	ND	ND	21.1	24.7	45.9	19.4	22.0	ND	41.5	ND	32.7	29.6	19.4	45.9
K^+	mg/L	3534.0	3268.0	3290.0	1094.0	4761.0	4599.0	1714.0	958.0	1208.0	2890.0	1275.0	2599.0	958.0	4761.0
Na^+	mg/L	385.0	385.0	360.0	309.0	373.0	321.0	121.0	112.0	218.0	180.0	121.0	262.0	112.0	385.0
Ca^{+2}	mg/L	ND	ND	ND	ND	ND	ND	153.0	144.0	250.0	316.0	324.0	222.0	144.0	324.0
Mg^{+2}	mg/L	ND	ND	ND	ND	ND	ND	20.0	47.0	61.0	155.0	56.0	60.0	20.0	155.0

*: H: OMW samples from full automatic olive mills in Hebron governorate, 12 samples from 12 olive mills. ND: not determined.

To compare if there was any significant difference between the characteristics of OMW that resulted from full automatic olive mills in Hebron or in Bethlehem, Mann- Whitney test was applied. Mann- Whitney test is non parametric statistic that used when the number of samples small (below 30). The following hypothesis was tested:

H_0: There is no evidence of statically significant difference between Hebron OMW characteristic and Bethlehem OMW characteristics at level of significance 0.05.

$$H_0: OMW_{H} = OMW_B$$

$$H_A: OMW_{H} \neq OMW_B$$

$$\text{Accept } H_0 \text{ if p -value} > \alpha\ (0.05)$$

Where,

H_0 and H_A are the null and alternative hypothesis, respectively.

OMW_H: OMW characteristic in Hebron.

OMW_B: OMW characteristic in Bethlehem.

P –value (results from applying Mann-Whitney test).

α: Level of significance (0.05)

Mann-Whitney test (SPSS program) was applied on main parameters (pH, EC, TDS, TS, and COD, total phenol and oil and grease). The results are shown in Table (3.9).

Table (3.9): Mann-Whitney test results to compare the difference of OMW characteristics between both Hebron and Bethlehem governorates (full automatic olive mill).

Parameter	**pH**	**EC**	**TDS**	**TS**	**COD**	**Total phenol**	**O& G**
Calculated U	17.0	22.0	22.0	20.0	17.0	24.0	17.0
P-value	0.2	0.5	0.5	0.4	0.2	0.7	0.9

Based on the results of Mann-Whitney test, we found that the p-value of all parameters tested greater than 0.05. So accept the H_0 hypothesis (there is no evidence of statically significant differences between OMW characteristics from full automatic olive mills in Hebron or in Bethlehem) and reject H_A hypothesis. This may due to the similarity in some factors, like geographical location, climate, amount of water, type of olive fruits and others.

The results of OMW characteristic according to automation level (Half automatic olive mills) in both Bethlehem and Hebron governorates are shown in Table (3.10).

From the Table (3.10) we notice that the OMW from half automatic olive mills had acidic pH, high organic content, high salinity and high solids content.

Table (3.10): OMW characteristic of half automatic olive mills in both Hebron and Bethlehem governorates.

Parameter	**Unit**	**Sample code**			**Avg.**	**Min.**	**Max.**
		S1*	**S2****	**S3****			
pH	_____	5.2	5.1	4.9	5.1	4.9	5.2
EC	mS/cm	8.7	6.5	10.4	8.5	6.5	10.4
TDS	g/L	4.4	3.2	5.2	4.2	3.2	5.2
TS	g/L	96.0	107.0	146.0	117.0	96.0	146.0
TSS	g/L	91.0	103.0	141.0	112.0	91.0	141.0
COD	g/L	61.0	74.0	56.0	63.0	56.0	74.0
Total phenol	g/L	5.5	5.8	8.7	6.7	5.5	8.7
O & G	g/L	10.5	62.7	ND	36.6	10.5	62.7
K^+	mg/L	21540.0	2935.0	5604.0	3564.0	2154.0	5604.0
Na^+	mg/L	170.0	360.0	347.0	292.0	170.0	360.0
Ca^{+2}	mg/L	528.0	ND	ND	528.0	-	-
Mg^{+2}	mg/L	98.0	ND	ND	98.0	-	-

* S1: OMW sample from half automatic olive mill in Bethlehem governorate. **S2& S3: OMW samples from 2 half automatic olive mill in Hebron governorate. ND: not determined

According to literature reviews, the quality and quantity of OMW are highly dependent on the extraction process. The quantity of OMW produced by traditional way is smaller than the quantity produced by continuous method (because the amount of used water during oil extraction is smaller), but more concentrated with pollutants (Awni et al., 2009). To make sure if the OMW that resulted from half automatic olive mills more concentrated with pollutants than OMW that resulted from full automatic olive mills.

The following hypothesis was tested:

$H_{0:}$ There is no evidence of statically significant difference between full automatic OMW characteristic and half automatic OMW characteristics at level of significance 0.05.

$$H_0: OMW_F = OMW_H$$

$$H_A: OMW_F \neq OMW_H$$

$$\text{Accept } H_0 \text{ if p -value} > \alpha\ (0.05)$$

Where,

H_0 and H_A are the null and alternative hypothesis, respectively.

OMW_F: OMW characteristic from full automatic olive mill.

OMW_H: OMW characteristic from half automatic olive mill.

P –value (results from applying Mann-Whitney test).

α: Level of significance (0.05).

Mann-Whitney test (SPSS program) was applied on main parameters (pH, EC, TDS, TS, COD and total phenol). The results are shown in Table (3.11).

Table (3.11): Mann-Whitney test results to compare the difference of OMW characteristics between both full automatic and half automatic olive mills in the study area.

Parameter	**pH**	**EC**	**TDS**	**TS**	**COD**	**Total phenol**
Calculated U	22.0	21.0	21.0	4.0	22.0	13.0
P-value	0.8	0.7	0.7	0.03	0.8	0.2

Based on the results of Mann-Whitney test, we found that the p-value of all parameters tested greater than 0.05 (except for TS). So accept H_0 hypothesis (there is no significant differences between OMW characteristics from full automatic olive mills and half automatic olive mills) and reject H_A hypothesis

This can be explained by compared these results with the results of olive mills survey (section 3.1.4), for half automatic olive mills the average values of the produced OMW per ton olives was 1.65 m^3 OMW/ton and 1.5 m^3 OMW/ton in both Hebron and Bethlehem respectively. According to litteratur the range of OMW produced per ton (0.5 m^3/ton-0.8 m^3/ton) for half automatic olive oil production process (Shaheen and Abdelkarim, 2007, Khateb et al., 2009). So the quantity of produced OMW from half automatic olive mills is approximately equal to the OMW quantity produced from full automatic olive mill so the characteristics of OMW nearly the same.

The results of OMW characteristics according to automation level (full vs half) were compared to both the Jordanian and Palestinian standards for industrial wastewater disposal in Table (3.12).

Table (3.12): OMW characteristics according to automation level: full automatic vs. half automatic, compared to Jordanian and Palestinian standards for industrial wastewater discharge.

Parameter	**Unit**	**Full automatic Avg.**	**Half automatic Avg.**	**Maximum allowable limit (mg/L) (Jordanian standards)**		**Maximum allowable limit (mg/L) (Palestinian standards)***	
				Disposal to Wadies or river	**Discharge to Sanitary sewer system**	**Ground water Recharge****	**Discharge to Sanitary sewer system*****
pH	——	5.1	5.1	6.5-9.0	5.5-9.5	6.0-9.0	5.5-9.5
EC	mS/cm	8.1	8.5	-	-	-	-
TDS	mg/L	4030.0	4240.0	3000.0	-	1500.0	-
TS	mg/L	77880.0	116100.0	-	-	-	-
TSS	mg/L	73850.0	111800.0	50.0	1100.0	60.0	600.0
COD	mg/L	58400.0	63420.0	150.0	2100.0	150.0	1500.0
Total phenol	mg/L	4570.0	6660.0	0.002	10.0	0.002	10.0
O& G	mg/L	32750.0	36550.0	5.0	50.0	-	100.0

*: Palestinian standards still as draft. **: MEnA, 2000. ***: PWA, 2010 (present in Appendix 4).

According to the OMW characteristic results (including both full and half automatic OMW in the study area), OMW have high polluting effect. This polluting effluent was discharged directly to the environment in wadies and lands, or into the sewage network (according to survey results in section 3.2). The Palestinian law prevents the discharge of OMW to the sewage network before treatment, to reach the allowable limits for discharge (PWA, 2010). Table (3.12) show the Jordanian and the Palestinian standards for discharge of industrial wastewater to the environment or to sewage network in addition to OMW characteristic compared to the study area we found that the OMW pollutants concentration mainly, COD, TDS, TSS, Total phenols and oil and grease exceed the maximum allowable limits to discharge in the environment or to the sanitary sewer system. So, this leads to a serious ecological problem in Palestine by increasing the risk of ground water and surface water resources contamination. Adding to this other negative impacts like, reduction of plant growth, inhibition of seed germination, change soil properties and microbial communities, damage and corrosion of sewer pipes and others (see section 1.2).

For this, a treatment of OMW must be applied before direct discharge to the environment or to sewage network. This study will out a possible pre-treatment technology that can reduce the toxicity of OMW and can be applied in the West Bank.

3.4 Olive mill wastewater treatment

Testing of OMW treatment was divided into two stages, batch system and pilot system under lab condition. The pilot system application depended on the results of batch system.

3.4.1 Lime treatment mechanism

The mechanism of lime and phenol interaction depends on the difference of pH of phenol and lime in which phenol is weak acid and lime is base, so lime interact with phenol as the following equation:

$C_6H_5OH + Ca(OH)_2 \longrightarrow C_6H_5\text{-}O\text{-}Ca\text{-}OH + H_2O$ (Schlosberg and Scouten, 1983).

This process is called neutralization. It depends on rising pH by addition of caustics like lime (calcium hydroxide $Ca(OH)_2$) by adding specifically absorbed ions Ca^{+2} (Niaounakis and Halvadakis,2006).

After lime treatment, the raising of EC value was noticed; this increase of EC due to the increase of Ca^{+2} ion concentrations after lime treatment. Measurement of Ca^{+2} ion was done by using atomic absorption on OMW both before and after lime treatment. The results were: 474 ppm of Ca^{+2} ion on OMW before lime treatment, and 2381 ppm of Ca^{+2} ion on OMW after lime treatment (lime dose was 10 g/L).

3.4.2 Lime treatment

Lime adsorbent was used in this research to examine their efficiency in reduction of phenol concentration to reduce the polluting effect of OMW.

The effect of adding different lime doses on OMW was measured on the following parameters: pH, EC and total phenol that are shown in Figure (3.6, 3.7, and 3.8).

Figure (3.6) indicates that pH value increases by adding lime from 4.71 to 12. The increase of pH depends on the lime concentration. After 10 g/L dose of lime, the pH values show no change in pH values. The process of lime treatment called neutralization that depend on raising the pH of OMW to remove the phenolic compounds from it, this explain the change of pH value from 4.71 to 12, at the same time this mean that the lime treatment was going on the right way to reduce phenol concentration.

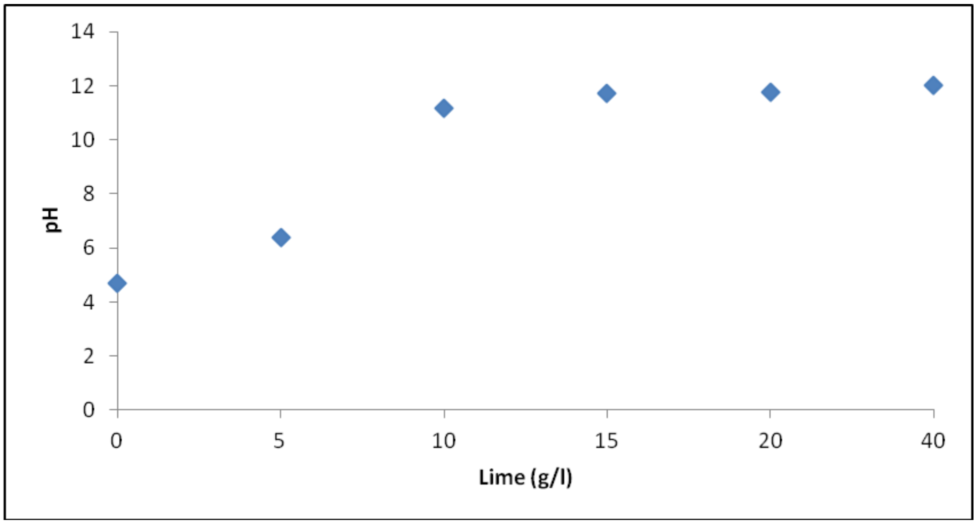


Figure (3.6): pH changes due to addition of different lime concentration on raw OMW.

Figure (3.7) indicates an increase of EC values from 8 up to 16 after lime addition. The maximum increase of EC value was at 40 g/L of lime dose. The increase of EC after lime ($Ca(OH)_2$) addition due to the increase of Ca^{+2} ion concentration as a result of lime mechanism in OMW treatment as shown in (section 3.3.1). Part of Ca^{+2} ions will bind with phenol and other well released in the OMW.

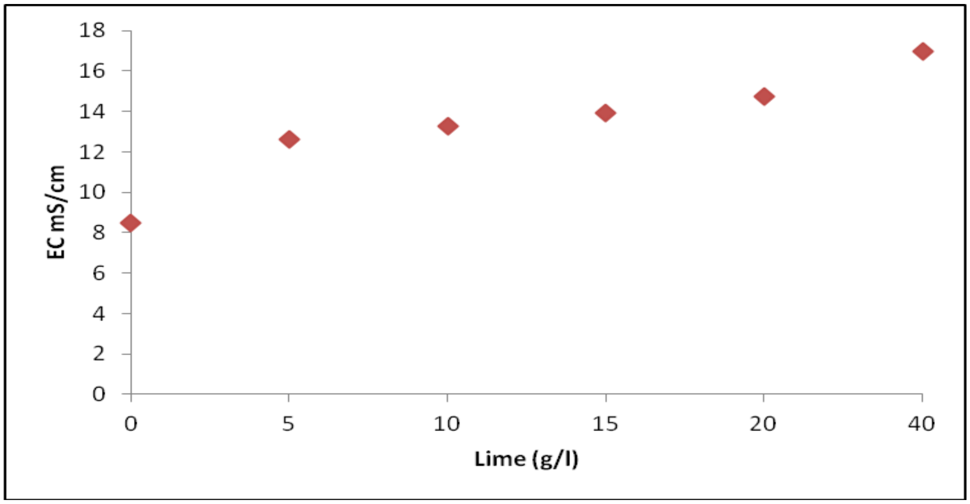


Figure (3.7): EC changes due to the addition of different lime concentrations on raw OMW.

Figure (3.8) indicates that the removal percent of total phenol after lime treatment increased with the increase of lime concentration. The removal percent of total phenol after adding of (10, 15, 20, 40) g/L dose of lime was (56, 57, 58, and 60%) respectively that is slightly different from each other (without significant difference between them). The increase of total phenol removal percent is related to the increase of pH value to around 12 even if there is an increase of lime dose.

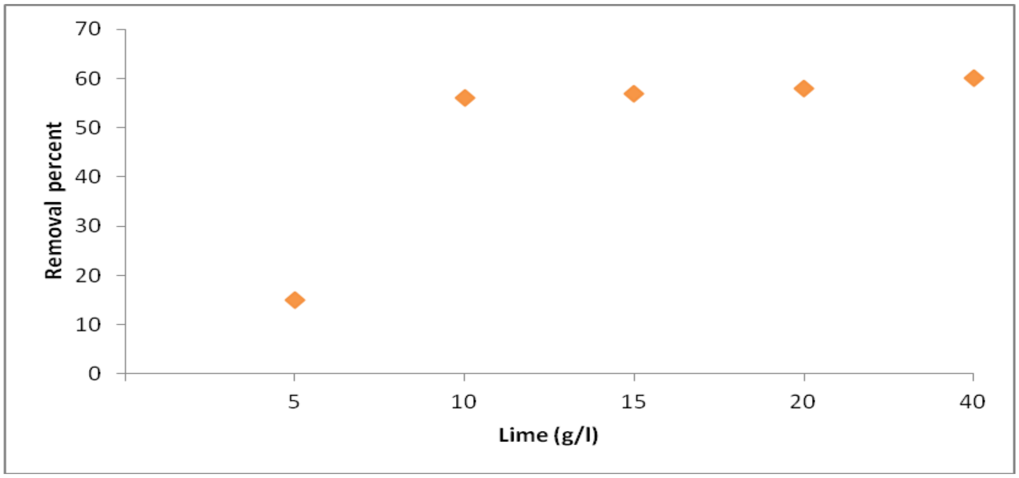


Figure (3.8): The removal percent of total phenol concentrations after addition of different lime concentrations on raw OMW.

According to these results the most efficient dose in total phenol removal was 10 g/L dose of lime at 56%. The slight difference in phenol removal efficiency enhances to consider the lime dose 10 g/L the most suitable dose in phenol removing and minimizing the amount of sludge that is resulted from lime treatment. After we identify the efficient lime dose (10 g/L) we tested the OMW treatment on other parameters (COD and TS) as presented in Figure (3.9).

Figure (3.9) indicates that lime treatment (dose 10 g/L) reduced COD from (44.9 g/L to 31.57 g/L) so removal percent of COD was 17.43%. It also reduced TS from (33.4 g/L to 29.81 g/L), so removal percent of TS was 5.74%. Aktas et al conducted a research on OMW treatment with lime, the results of their research incompatible with our research results. Aktas et al results showed that the removal percent of total phenol, COD and TS was: 63%, 46% and 53% respectively.

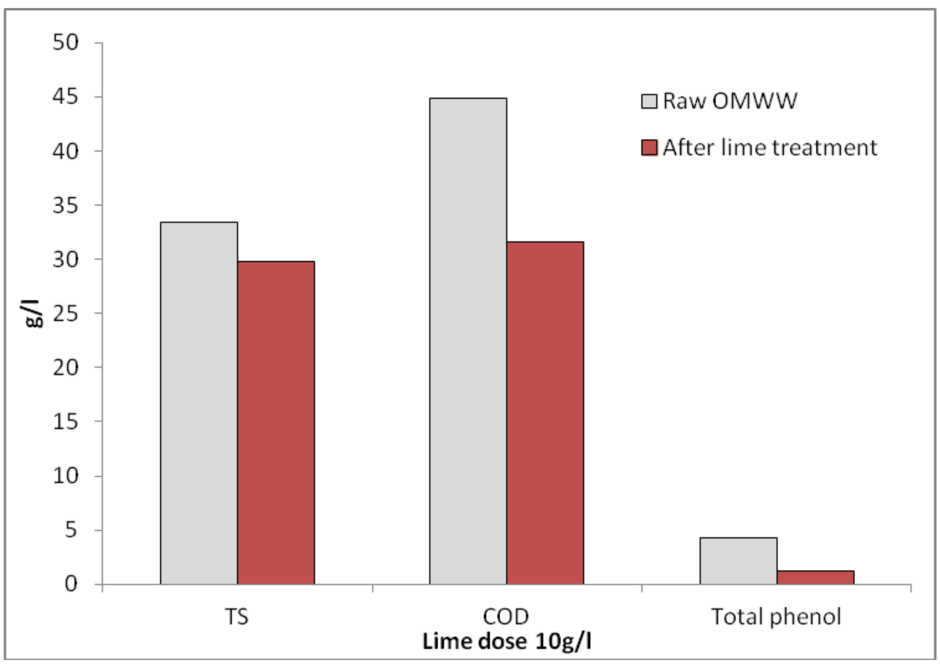


Figure (3.9): The percentage removal of total phenol, COD and TS after lime treatment of dose (10 g/L).

3.4.3 Lime saturation index

According to the previous results, a further experiment was done to calculate the saturation index of lime dose (10 g/L). The results are shown in (Table 3.13). The saturation index was calculated by treatment of OMW with lime, using batch system depend on flocculation of OMW with lime then filtrate OMW and take lime from the filter to reuse it for several times with raw OMW sample depends on the same procedure and calculate parameters like pH, EC and total phenol.

Table (3.13): Saturation index of lime dose (10g/L).

Sample	pH	EC (mS/cm)	Total phenol (g/L)
Raw OMW	4.79	9.26	4.3
After lime treatment	5.98	12.16	3.41
After reuse of previous lime dose	5.293	11.46	3.55
After 2nd reuse of previous lime dose	4.932	10.61	3.57
After 3rd reuse of previous lime dose	4.81	9.2	4.2

Table (3.13) presents the changes of pH, total phenol concentration and EC after addition of 10 g/L of lime on raw OMW sample and Figure (3.10) presents the changes of removal percent of total phenol after lime treatment. The pH of OMW was increased from 4.79 to 11.15 associated with the decrease of total phenol concentration from 4.3 g/L to 1.17 g/L (removal percent was 57%) and the EC was increased from 9.2 mS/cm to 14.23 mS/cm. Then the OMW filtered from the lime; the same lime was taken and used with new OMW sample. The pH of OMW was increased from 4.79 to 5.98 associated with decrease of the total phenol from 4.3 g/L to 3.41 g/L (the percent removal was 11.5%) and the EC was increased from 9.2 mS/cm to 12.16 mS/cm. The previous step was repeated several times until the removal efficiency of total phenol by lime treatment was reach to 1.2%, pH was 4.81 and EC was 9.26.

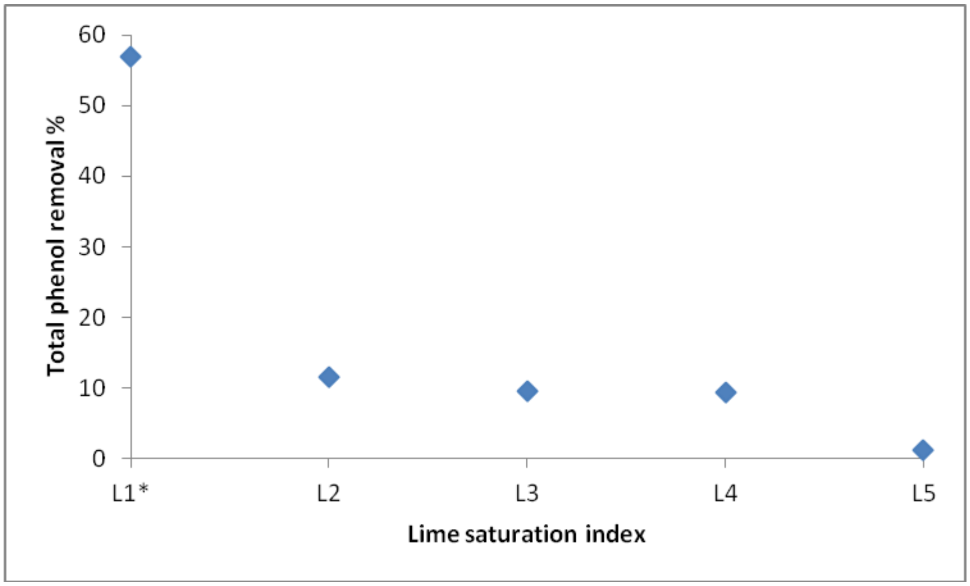


Figure (3.10): The percentage removal of total phenol after lime treatment and reuse of the same lime dose (10 g/L) for several times.

According to the lime mechanism in OMW treatment (neutralization), the maximum removal of total phenol by lime was when the pH of OMW increased between (11.5-12). From the Table (3.13) we found that the efficiency of re-used lime in removing total phenol was decreased because its efficiency to increase the pH decreased. For EC, it was increase from 9.2 to 14.23, but when the lime reused with new OMW sample the EC was increased from 9.2 to 12.16 and the final re use of lime the EC was increased from 9.2 to 9.26, re-used lime can't increase the EC as when it used in the first time. This depend on the free Ca^{+2} ions that result from lime so the several use of the same lime dose was decrease the free Ca^{+2} ions in OMW samples so the lime can't increase the EC like the first use of it.

3.4.4 Olive mill wastewater (OMW) treatment with other adsorbent

Other adsorbent like Bottom ash and sawdust were used in OMW treatment to examine their efficiency in total phenol removal in comparison to lime efficiency.

Different dose of sawdust adsorbent was used to achieve maximum total phenol removal. As presented in Table (3.14) the most efficient of sawdust dose was 25 g/L with total phenol efficiency removal 21.6% without affecting the pH and EC. The results of other sawdust doses weren't shown. These results were not compatible with Mebirouk et al., 2007 results. This is due to the unchanged of OMW pH after sawdust treatment. In Mebirouk et al. research the removal percent of total phenol after sawdust treatment was 39% and the pH was 8. The sawdust mechanism in phenol removal from OMW depends on neutralization of the acidic pH of OMW then phenols absorbed in the sawdust by dispersive interactions between the basic carbons and basics phenols aromatics in the sawdust.

Bottom ash has different granule diameters so it was divided according to diameter into 2 groups B.ash diameter < 4 mm and B.ash diameter > 4 mm then each group was tested for total phenol removal as presented in Table (3.14).

Table (3.14): Results of OMW treatment by using sawdust and bottom ash adsorbents.

Sample	**Dose (g/L)**	**pH**	**EC (mS/cm)**	**Total phenol (g/L)**	**Total phenol removal percent**
Raw	___	4.8	9.6	4.2	___
Sawdust	25.0	4.8	9.4	2.7	21.6
Bottom ash*	20.0	4.7	9.5	3.0	16.4
Bottom ash*	50.0	4.7	9.4	3.2	13.9
Bottom ash *	70.0	4.8	9.5	3.1	14.8
Bottom ash**	10.0	4.7	8.0	3.4	10.2
Bottom ash **	20.0	4.7	8.3	3.5	9.1

*: Bottom ash diameter < 4 mm. **: Bottom ash diameter > 4 mm.

The efficiency of bottom ash in total phenol removal is low without significant efficiency with the increase of dose. Bottom ash can be reduced OMW EC without any change on pH. No previous study showed the mechanism of bottom ash – phenol interaction.

3.4.5 Adsorbent series

An experiment was done by the use of series of adsorbents, Table (3.15) show the results of this series in which the OMW was treated firstly with lime, and then the extracted filter was divided and was treated with both bottom ash and sawdust.

Table (3.15): OMW treatment with series of adsorbent: lime, bottom ash and sawdust.

Sample	**Dose (g/L)**	**pH**	**EC (mS/cm)**	**Total phenol (g/L)**	**Total phenol removal percent**
Raw OMW	____	5.7	7.6	3.9	____
After lime	10.0	12.5	10.2	1.1	56.0
After B.ash	10.0	12.0	10.5	1.1	56.0
After sawdust	25.0	10.2	8.7	1.1	56.0

From the Table (3.15) that shown above, we notice that both the bottom ash and sawdust can’t increase the removal percent of phenol after treatment of OMW with lime. In which the sawdust can reduce treated OMW pH and EC. From all the previous results, lime is the most efficient adsorbent in total phenol removal from OMW.

Sawdust can’t increase the removal percent of phenols from OMW with previous treatment (with lime) because of the alkaline pH of the OMW. Sawdust treatment mechanism depends on the incremental of the pH in OMW. Sawdust release basic compounds (the surface of sawdust contains important oxygen sites mainly in basic functional form: phenolic hydroxyl groups). That contributes to OMW acidic pH neutralization. Phenols are absorbed in the sawdust by dispersive interactions between the basic carbons and basics phenols aromatics in the sawdust (Mebirouket al., 2007).

3.4.6 Biological treatment

Biological treatment using *Aspergillus niger* species (size of inoculum is 10^5 cfu/ml) was tested on pre-treated OMW by using lime according to the procedure determined in section (2.4.2). The results are shown in Table (3.16). *A.niger* has the ability to degrade phenolic compounds like tannins that is highly toxic compound and others. At the same time there are other phenolic compounds that are show less toxicity but not easily biodegradable.

Before biological treatment of pre-treated OMW with lime, HCl was added to correct the pH of OMW between (5- 6.5) to be suitable for *A.niger* activity. The addition of HCl reduced the pH of treated OMW with lime to 6.3 but at the same time, it increased its EC. The removal percent of total phenol after lime treatment was 55% but after pH correction by addition of HCl the removal percent of total phenol was 38% this means that the removal percent of total phenol was reversed about 17%. This decrease might occurred due to the leakage of some lime with OMW extraction after lime treatment so reverse the interaction process that depend on rising pH and the ability of lime to interact with HCl as the following formula:

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O$$

So instead of phenol Ca^{+2} ions binding the Ca^{+2} ions bind with HCl.

Table (3.16): Changes of pH, EC and total phenol concentrations after biological treatment by using *Aspergillus niger* of previous treated OMW with lime.

Sample	**pH**	**EC (mS/cm)**	**Total phenol (g/L)**	**Total phenol removal percent**
Raw OMW	4.7	9.0	3.2	________
Treated OMW with lime and HCl	6.3	15.3	1.5	38.0
Biological Treatment using *A. niger* after lime treatment				
After *A.niger* treatment	7.8	15.7	0.9	23.5
Final concentrations	7.8	15.7	0.9	55.0

After biological treatment of the pre-treated OMW sample (with lime and HCl), the total removal percent of phenolic compounds was 55% and the final concentration of total phenol was 920 mg/L that still exceeded the allowable concentration limits of total phenol to be discharged in the sanitary sewer system, or to open wadies. This was according to the Jordanian and Palestinian regulations of industrial wastewater discharge see Table (3.12).

3.4.7 Pilot treatment

The pilot was operated according to the procedure determined in section (2.4.3) according to the results of batch experiments. The results of OMW treatment stages presented in Table (3.17).

Table (3.17): Changes of pH, EC and total phenol concentrations after the operation of pilot treatment.

Treatment Stages	pH	EC (mS/cm)	Total phenol (g/L)
Inlet	5.5	8.8	3.8
Lime treatment	12.0	15.8	1.0
HCl treatment	5.5	20.9	3.1
Biological treatment	7.8	28.3	2.2
Outlet	7.8	28.3	2.2

Table (3.17) indicates the changes of pH, EC and total phenol concentration according to different stages of OMW pilot treatment. After lime treatment the pH was 12.03, the EC was 15.77 mS/cm and the total phenol concentration was 1.04 g/L. The results of lime treatment in the pilot treatment system were compatible with results of batch system experiments.

After HCl stage the pH was 5.5, the EC was 20.9 mS/cm and the total phenol concentration was 3.09 g/L. The results of HCl stage showed a problem in total phenol concentration that was 1.04 g/L before HCl treatment. HCl was used only for pH correction (to be suitable for biological treatment) without any role of it in OMW treatment. The explanation of the increase of total phenol after the HCl addition may due to the problem in OMW filtration after lime stage so in HCl stage lime still mixed with OMW this contrary with the lime mechanism in phenol removal and the HCl can bind with lime as the following formula:

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O$$

After biological treatment pH and EC was increased due to the activity of *A.niger* and phenolic compound was decreased.

Figure (3.11) indicates the changes of removal percent of total phenol during pilot operation. The removal percent was 57% after lime treatment, then it reversed to 10.56% after HCl stage, then it was increased to 16.8% after biological treatment. The outlet effluent characteristics after pilot operation: pH was 7.76, EC was 28.3 mS/cm, total phenol concentration was 2.2 g/L and the final removal percent of total phenol was 27%.

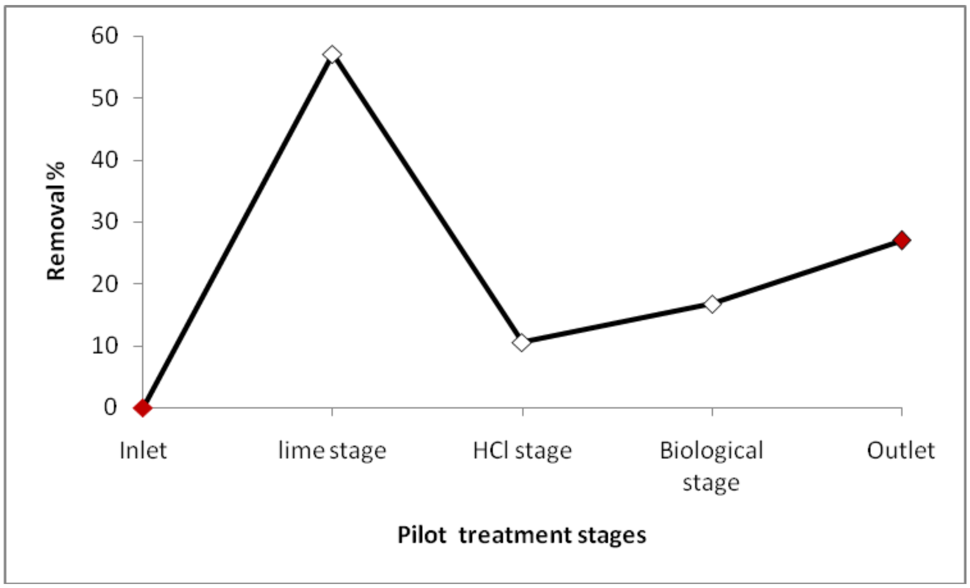


Figure (3.11): The percentage removal of total phenol after pilot treatment operation.

The problem in the pilot operation was the filtration of OMW from lime after lime treatment stage and the use of HCl.

4 Chapter Four: Conclusions and Recommendations

4.1 Conclusions

From the results obtained on olive mills survey, OMW characteristics and from the treatment method applied during this research the following conclusion can be typed:

Olive mills survey:

- 89% of the olive mills in the study area used full automatic (3 phase decanter) oil extraction process and the remaining used the semi automatic oil extraction process.

- The average value of the produced OMW per ton olive of full automatic olive mills in the study are**a** was: 1.86 m^3/ton (it is high compared to other places in the world). This requires the attention of Palestinian authorities to take their responsibilities and make a technical review of the technology and operation of olive mills in the study area to minimize the water consumption because of water scarcity in Palestine and so minimize the volume of OMW.

Olive mill wastewater characteristics:

- As compared to literature values, all measured physicochemical characteristics were close to the mean of the reported literature limits for OMW from various sites.

- Direct discharge of OMW into the open wadies or lands or into the sewer system cause high polluting effect on the environment, according to its characteristics that exceeded the maximum allowable limits to be disposed neither to the environment nor to the sanitary sewer system based on both Jordanian and Palestinian regulations so the uncontrolled dumping of OMW without any previous treatment is a threat to the groundwater aquifers and the environment.

Olive mill wastewater treatment:

- According to the batch experiments of OMW treatment, lime was the most efficient adsorbent of total phenol reduction mainly the dose (10g/L) at removal percent of total phenol, COD and TS 56%, 17.4%, and 5.7% respectively. The results of lime treatment in the pilot system were compatible with the results of batch system experiment.

- The main disadvantage of lime adsorbent was the rising of EC.

- Lime is proposed to be applied in Palestine as a pretreatment. It is easy to operate and can reducing the polluting effect of OMW mainly for total phenols in short time (especially for OMW with low concentration of total phenol).

- Post treatment after lime pre-treatment is essential mainly to reduce the COD.

- Sawdust and bottom ash adsorbents still need more studies to examine their efficiency in total phenol removal.

- After lime and biological treatment of OMW sample, the total removal percentage of total phenol was 55% and the final concentration of total phenol was 920 mg/L which still exceeded the allowable concentration of total phenol to be discharged in the sanitary sewer system, or to open wadies according to the Jordanian and Palestinian standards of industrial wastewater discharge.

- This study doesn’t encourage using *A.niger* after lime treatment because using lime treatment alone is better. The disadvantage of biological treatment was the need of pH correction.

4.2 Recommendations

- It is recommended for governmental agencies to take their responsibilities towards the problem of waste that results from olive oil extraction process and find the suitable actions to solve this serious problem on the Palestinian environment.

- It is recommended to hold awareness seminars to olive mill owners and workers to inform them of the dangers of OMW on the environment, and on the mechanism of olive oil extraction according to the type of technology used in the mill and the amount of water that should be used.

- It is recommended to carry out a study about the number of the existing olive mills and the market need; and if there is a need to create new olive mills or not.

- It is recommended to use (apply) lime as pre-treatment of OMW in the study area to reduce the polluting effect of OMW on the environment.

- Encouraging other researchers to study how we can recycle the used lime in OMW treatment and if we can benefit from it, or not.

- Encouraging others to make further research on *A.niger* and other microorganisms after lime treatment.

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Appendix 1: The questioner of olive mills survey

Questioner number:

Date:

1**. General information**:

- The name of OM owner: ______________________
- The location of the OM:______________________
- The purchasing date of OM: ______________________
- The working period in the OM seasonally: ____________
- The mill production capacity:__________ __________
- There is any follow up from any environmental protection society or any governmental ministry:

  Yes: No:

  If the answer yes,

  What's the name of this group?

  What is the interest aspect of this group?

  1. The quality of the product (olive oil)
  2. The waste resulting from this production

  Is this follow up periodically?

  Yes: No:
- If there is any chemicals that used in the washing of olives or the oil production process:
- Yes: No:

  If the answer yes;

  Type these chemicals:

  Is the sewer system of the mill connected to the municipal sewage system?

  Yes: No:

2**. About olive oil production process:**

- What is the type of olive oil production process that used in this mill:

1. The traditional oil extraction process ☐
2. The semi oil extraction process ☐
3. The full-automatic oil extraction process(three phase decanter) ☐

- What is the total amount of olives that was pressed in oil production during the working period: ________Ton.
- What is the amount of water that is needed during of all olive oil production stages: ________
- What is the amount of water that is needed to press 1 ton of olive:________ .
- What is the quantity of wastes that result from the used olive oil production process:
  1. Solid waste: ________________________
  2. Liquid waste:________________________
- What is the fate of the wastes that result from the oil production process:
  1. Storage ponds ☐
  2. Treatment of the waste ☐
  3. Drying ☐
  4. Dumping ☐
  5. Others (specify) ☐

Appendix 2: Methods of analysis

pH, EC and TDS: were determined by using pH-EC meter with suitable buffers for calibration for each test.

Total solids: the empty evaporating dish was weighted on analytical balance, and then a known volume of sample was transferred to the evaporating dish. Then, the evaporating dish was heated in an oven at 100°C until constant weight is reached. After cooling the evaporating dish, they were weighed. Then, the TS was calculated (in ppm) as: ((weight of evaporating dish+ residue in grams) – (weight of empty dish in grams)) * 1000/ sample volume (in Liters).

COD: the stock solution of potassium hydrogen phthalate KHP was prepared by dissolve 425 mg of dried KHP in 1000 ml of distilled water. Then, dilutions were made to prepare standards to prepare calibration curve. 2.5 ml of the sample, or the KHP standard or blank were transferred to culture tubes, then 1.5 ml of the digestion solution and 3.5 ml of sulfuric acid reagent were added. The culture tubes was capped then mixed well on vortex mixer. The culture tubes were placed in an oven at 150°C for 2 hours. After that, the samples were centrifuged at 2000 rpm for 4 minutes. The absorbance of the clear samples and standards were measured by using spectrophotometer at wavelength 600 nm. The calibration curve was drawn to calculate the concentration of samples.

Oil and grease: the sample was acidified by using 5 ml of HCl, the sample was transferred to a separatory funnel. 50 ml of extracting solvent (n-hexan) was added, shacked for 2 minutes to separate layers, the lower layer (aqueous layer) was removed. The solvent layer was dried through a funnel containing a filter paper and 10g of sodium sulfate into distilling flask. Then the solvent was distilled from the flask in water bath at 85°C. The flask was removed from water bath after stopping of visible solvent condensation. Then the flask was weighed. Finally Oil and grease (in mg) were calculated as: ((weight of flask + residue in grams) – (weight of empty flask in grams)) * 1000/ sample volume (in ml).

Major cations: the samples were filtrated using micro-pore filters (0.45Mm), then **K^+ and Na^+** were measured using the flame photometer. **Ca^{+2} and Mg^{+2}** were measured using the atomic absorption.

Appendix 3: Olive mills survey data in the study area**.**

#	Governorate	Location	Olive mill name	Season (days)	Opening date
1	Bethlehem	Batter	Batter Al Hadetha	40	2006
2	Bethlehem	Batter	Al Battere	50	2004
3	Bethlehem	Wadi rahal	Wadi rahal	30	2003
4	Bethlehem	Dhesha	Modern olive pressing company	30	1986
5	Bethlehem	Bet jala	Cooperative association for olive pressing	60	1963
6	Bethlehem	Bet sahour	Central company for plant oils	30	2008
7	Hebron	Al kom	Al kom	20	1993
8	Hebron	Deir samet	Deir samet	30	1995
9	Hebron	Deir samet	Al zaytona	20	2009
10	Hebron	Oyon abu saif	Al Okhowa for olive pressing	30	1994
11	Hebron	Wadi abu al qmra	Al janoub Al Hadetha	45	2006
12	Hebron	Al fawar	Cooperative association to press olive	60	1984
13	Hebron	Yatta	Al janoub modern automatic	30	2004
14	Hebron	Yatta	Yatta Al Hadetha	60	1991
15	Hebron	Kharas	Ahmed Qdamate	30	1992
16	Hebron	Nuba-KHa	Farmeres Union	35	1986
17	Hebron	Bet ola	Al dababsa	40	1992
18	Hebron	Ethna	Ethna Al automatic	20	1986
19	Hebron	Hebron	Al Haramen	30	1995
20	Hebron	Hebron	Modern automatic olive mill	___	1990
21	Hebron	Sheokh	Al zayton Al Hadetha	20	2002
22	Hebron	Al dahrea	Al sabar olive pressing company	20	2005
23	Hebron	Al dahrea	Al Janoub	10	1996
24	Hebron	Hebron	Al Amana	35	1972
25	Hebron	Hebron	Al Amal	60	2003
26	Hebron	Al majd	Al majd	20	1985
27	Hebron	Ethna	Musallm	17	1996

Continued

#	Olive mill name	Mill production capacity	Oil extraction process	Pressed olives (ton)*
1	Batter Al Hadetha	1 ton/hr	Full automatic	250
2	Al Battere	4 ton/hr	Full automatic	275
3	Wadi rahal	2 ton/hr	Half Automatic	350
4	Modern olive pressing company	2800 kg/hr	Full automatic	450
5	Cooperative association for olive pressing	2.5 ton/hr	Full Automatic	500
6	Central company for plant oils	1.5ton/hr	Full Automatic	230
7	Al kom	1 ton/hr	Half Automatic	60
8	Deir samet	2 ton/hr	Full Automatic	100
9	Al zaytona	1.5 ton/hr	Full Automatic	200
10	Al Okhowa for olive pressing	1.5 ton/hr	Full Automatic	200
11	Al janoub Al Hadetha	4 ton/hr	Full Automatic	700
12	Cooperative association to press olive	0.5 ton/hr	Full Automatic	75
13	Al janoub modern automatic	_____	Full Automatic	10
14	Yatta Al Hadetha	1.5 ton/hr	Full Automatic	130
15	Ahmed Qdamate	1 ton/hr	Full Automatic	250
16	Farmeres Union	700 kilo/hr	Half Automatic	60
17	Al dababsa	2 ton/hr	Full automatic	600
18	Ethna Al automatic	1.5 ton/hr	Full automatic	100
19	Al Haramen	2 ton/hr	Full automatic	55
20	Modern automatic olive mill	1 ton/hr	Full automatic	100
21	Al zayton Al Hadetha	1.5 ton/hr	Full automatic	35
22	Al sabar olive pressing company	2 ton/hr	Full automatic	200
23	Al Janoub	600 kg/hr	Full automatic	20
24	Al Amana	1500 kg/hr	Full automatic	180
25	Al Amal	1.5 ton/hr	Full automatic	200
26	Al majd	1 ton/hr	Full automatic	80
27	Musallm	3 ton/hr	Full automatic	400

*: In season 2010/2011

Continued

#	Olive mill name	Water consumption (m^3)*	OMW (m^3)*	OMW disposal
1	Batter Al Hadetha	250	375	Storage pond
2	Al Battere	300	438	Storage pond
3	Wadi rahal	350	525	Wadi
4	Modern olive pressing company	450	675	Sewer system
5	Cooperative association for olive pressing	1500	1700	Sewer system
6	Central company for plant oils	230	345	Sewer system
7	Al kom	100	130	Storage pond
8	Deir samet	150	200	Storage pond
9	Al zaytona	300	400	Storage pond
10	Al Okhowa for olive pressing	400	500	Storage pond
11	Al janoub Al Hadetha	1400	1750	Lands
12	Cooperative association to press olive	450	488	Sewer system
13	Al janoub modern automatic	10	15	Storage pond
14	Yatta Al Hadetha	260	325	Storage pond
15	Ahmed Qdamate	720	845	Storage pond
16	Farmeres Union	90	120	Storage pond
17	Al dababsa	550	850	Lands
18	Ethna Al automatic	150	200	Storage pond
19	Al Haramen	55	80	Sewer system
20	Modern automatic olive mill	50	100	Sewer system
21	Al zayton Al Hadetha	21	40	Storage pond
22	Al sabar olive pressing company	200	300	Storage pond
23	Al Janoub	20	30	Storage pond
24	Al Amana	180	270	Sewer system
25	Al Amal	300	400	Sewer system
26	Al majd	80	120	Storage pond
27	Musallm	400	500	Storage pond

*: In season 2010/2011.

Continued

#	Olive mill name	Olive cake disposal
1	Batter Al Hadetha	Traced back to olive owner
2	Al Battere	Traced back to olive owner
3	Wadi rahal	Traced back to olive owner
4	Modern olive pressing company	Traced back to olive owner
5	Cooperative association for olive pressing	Reuse it in factory
6	Central company for plant oils	Traced back to olive owner
7	Al kom	Traced back to olive owner
8	Deir samet	Traced back to olive owner
9	Al zaytona	Traced back to olive owner
10	Al Okhowa for olive pressing	Traced back to olive owner
11	Al janoub Al Hadetha	Traced back to olive owner
12	Cooperative association to press olive	Traced back to olive owner
13	Al janoub modern automatic	Traced back to olive owner
14	Yatta Al Hadetha	Traced back to olive owner
15	Ahmed Qdamate	Traced back to olive owner
16	Farmeres Union	Traced back to olive owner
17	Al dababsa	Traced back to olive owner
18	Ethna Al automatic	Traced back to olive owner
19	Al Haramen	Traced back to olive owner
20	Modern automatic olive mill	Traced back to olive owner
21	Al zayton Al Hadetha	Traced back to olive owner
22	Al sabar olive pressing company	Traced back to olive owner
23	Al Janoub	Traced back to olive owner
24	Al Amana	Traced back to olive owner
25	Al Amal	Traced back to olive owner
26	Al majd	Traced back to olive owner
27	Musallm	Traced back to olive owner

Appendix 4: نظام ربط المساكن والمنشآت بشبكة المجاري العامة لمقدمي خدمات المياه والصرف الصحي 2010

المادة (10)

صرف المياه العادمة التجارية والصناعية

1. يمنع صرف المياه العادمة التجارية والصناعية الملوثة وغير الملوثة إلى شبكة المجاري العامة إلا بعد معالجتها والحصول على موافقة خطية من مقدم خدمات المياه والصرف الصحي وفقاً للتعليمات المبينة في الملحق رقم (1).
2. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف أية مواد مشعة أو أية نظائر مشعة صناعية إلى شبكة المجاري العامة.
3. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف المياه العادمة والفضلات الناتجة عن مصانع الأدوية ومخلفات المستشفيات الملوثة وباقي عينات التحليل إلى شبكة المجاري العامة، إلا بعد معالجتها والحصول على تصريح خاص من الجهات الرسمية المختصة.
4. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف المياه العادمة والزيبار الناتجين من معاصر الزيتون إلى المجرى العام، ويجب على أصحاب المعاصر تعديل طريقة الإنتاج للالتزام بالتعليمات المبينة في الملحق رقم (1).
5. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف المياه العادمة من المطابخ التجارية والمطاعم والمصانع الغذائية والفنادق إلى المجرى العام، إلا بعد إنشاء وحدة مصيدة الدهون وبعد الحصول على موافقة خطية من مقدم خدمات المياه والصرف الصحي، مع الإلتزام بصيانة مصيدة الدهون.
6. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف المياه العادمة من محطات غسيل وتشحيم السيارات إلى المجرى العام، إلا بعد إنشاء وحدة مصيدة الزيوت وبعد الحصول على موافقة خطية من مقدم خدمات المياه والصرف الصحي، مع الإلتزام بصيانة مصيدة الزيوت.

7. يحظر على أي شخص أن يصرف أو يسبب أو يسمح بصرف المياه العادمة والرواسب الناتجة من مناشير الحجر ومصانع مواد البناء إلى شبكة المجاري العامة أو إلى أي مجرى طبيعي أو إلى الوديان أو أي مكان مكشوف. وعلى مقدم خدمات المياه والصرف الصحي توفير مواقع محددة لتجفيف أو للتخلص من رواسب مناشير الحجر.

8. يحظر تخفيف تركيز الملوثات في المياه العادمة الصناعية بخلطها بالمياه العذبة أو الصالحة للشرب للوصول إلى التراكيز المذكورة في التعليمات المرفقة في الملحق رقم (1).

الملحق رقم (1)

تعليمات صرف المياه العادمة التجارية والصناعية إلى شبكة المجاري العامة

المادة (1)

يمنع صرف المياه العادمة التجارية والصناعية الملوثة وغير الملوثة إلى شبكة المجاري العامة إلا بعد معالجتها والحصول على موافقة خطية من مقدم خدمات المياه والصرف الصحي وفقاً لهذه التعليمات.

المادة (2)

يحظر على أي شخص أن يصرف أو يسبب أو يسمح بتصريف المياه والفضلات التالية إلى شبكة المجاري العامة:

أ- أية مواد صلبة أو سائلة بكميات أو بأحجام أو بخصائص بيولوجية أو كيميائية أو فيزيائية يمكن أن تؤدي إلى إعاقة التدفق في خطوط شبكة المجاري العامة أو تسبب ضرراً بالصحة العامة أو تؤدي إلى انبعاث المكاره أو تلحق ضرراً بشبكة المجاري العامة أو بالموظفين أو تتعارض مع أعمال صيانة وتشغيل محطات المعالجة أو مع عملية المعالجة فيها أو يمكن أن ينتج عنها مياه معالجة تهدد الصحة والسلامة العامة، وعلى سبيل المثال لا الحصر، الرماد وبقايا الفحم المحترق والرمال والطين والقش والنشارة والمعادن والزجاج والخزف والريش والقار والبلاستيك والخشب والنفايات والدماء وأحشاء الحيوانات والسماد الحيواني والشعر والأطباق

الورقية والعبوات بمختلف أنواعها والدهون والشحوم والزيوت، والحوامض والكربون والأملاح المعدنية والبخار والغازات الحارة والأصباغ والمبيدات والمخلفات السائلة من معاصر الزيتون ومنتجات الألبان ودماء الحيوانات الناتجة من المسالخ.

ب- أية مواد صلبة أو سائلة أو غازية تحتوي على مواد سامة أو عناصر معدنية أو معادن ثقيلة يمكن حسب رأي مقدم خدمات المياه والصرف الصحي أن تضر أو تتعارض مع عملية المعالجة أو يمكن أن تشكل منفردة أو نتيجة تفاعلها مع الفضلات الأخرى خطراً على الإنسان أو الحيوان أو النبات.

ج- أية مواد يمكن أن تؤدي إلى:-

1- عدم إمكانية المعالجة خلال عملية المعالجة.

2- تكوين مواد يمكن أن تترسب أو تتجمد أو تصبح لزجة على درجات حرارة بين صفر – 40 درجة مئوية.

3- إعاقة الاستخدام النهائي للمياه المعالجة، كالتسبب في ارتفاع تركيز الأملاح المذابة مثل المخلفات السائلة الناتجة من معاصر الطحينة ومغاسل الجينز.

د- أية سوائل يقل رقم الأس الهيدروجيني pH فيها عن (5.5) ويزيد على (9.5).

هـ- المخلفات السائلة الناتجة عن مناشير الحجر ومصانع البلاط والرخام والطوب وخلاطات الاسمنت، وأية مخلفات سائلة يزيد تركيز المواد الصلبة العالقة فيها على (50) ملغم/لتر وبوزن نوعي يزيد على (1.5)غم/سم3.

و- أي سائل أو بخار تزيد درجة حرارته على (65) درجة مئوية، وإذا ثبت لمقدم خدمات المياه والصرف الصحي أن تلك السوائل أو الأبخرة بدرجات اقل يمكن أن تضر بمنظومة الصرف الصحي أو تسبب أضرار أخرى فلها الحق بمنع صرفها.

ز- السوائل التي تحتوي على الزيوت والشحوم والدهون النباتية والحيوانية او الشمع بشكل مستحلب (Emulsified) وبتركيز يزيد على (100ملغم/لتر).

ح- أية سوائل أو مواد تحتوي على السيانيد أو مركباته بتركيز يمكن أن ينتج عنه (2) ملغم /لتر مقدرة على شكل سيانيد.

ط- أية سوائل أو مواد تحتوي على مركبات الفينول بتركيز يزيد عن (10) ملغم/لتر مقدرة على شكل فينول أو بتركيز يزيد عن (100) ملغم/لتر مقدرة على شكل فينول خالي من الهالوجينات.

ي- أية سوائل أو مواد تحتوي على مركبات الكبريتيد بتركيز يزيد عن (2.0) ملغم/لتر مقدرة على شكل كبريتيد الهيدروجين.

ك- أية سوائل أو مواد تحتوي المذيبات العضوية المكلوره (CHLORINATED ORGANIC SOLVENTS) .

ل- أية سوائل أو مواد تحتوي على المنظفات الكيميائية مقاسه كـ MBAS بتركيز يزيد عن (40) ملغم/لتر.

م- السوائل التي تحتوي على الزيوت المعدنية من الات القطع والمقطرات بتركيز يزيد عن (20) ملغم/لتر.

ن- أية سوائل أو مواد تحتوي على مركبات السلفات (SO4) بتركيز يزيد عن عن (1000) ملغم/لتر.

س- أية سوائل أو مواد تحتوي على مركبات الكلوريدات (Cl) بتركيز يزيد عن (500) ملغم/لتر.

ع- أية سوائل أو مواد تحتوي على مركبات الفلورايد بتركيز يزيد عن (60) ملغم/لتر.

ف- أية سوائل تحتوي على المواد الصلبة العالقة الكلية (TSS) بتركيز يزيد عن (600) ملغم/لتر.

ص- أية سوائل يكون الأكسجين الممتص كيماويا (COD) فيها يزيد عن (1500) ملغم/لتر.

أية سوائل أو مواد تحتوي على مركبات الصوديوم بتركيز يزيد عن (500) ملغم/لتر.

الملخص بالعربية

واقع معاصر الزيتون في جنوب الضفة الغربية وآلية التخلص من مخلفاتها وإيجاد طريقة مجدية لمعالجة المياه العادمة لمعاصر الزيتون (الزيبار)

الاسم: تسنيم "محمد جودي" الجعبري

تعرف المياه العادمة الناتجة من عملية استخراج زيت الزيتون بالزيبار وهي تعد واحدة من أخطر المشاكل الملوثة للبيئة في فلسطين، ويعود ذلك لوجود نسبة عالية من المركبات العضوية و وجود مركبات الفينول السامة والمضادة للتحلل البيولوجي. إضافة إلى ذلك يتم إنتاج الزيبار بشكل سنوي مع صعوبة التخلص منه او معالجته في ظل غياب التقنية المناسبة لعلاجه مما يزيد من مخاطر تلوث مصادر المياه الجوفية والسطحية وتلوث التربة.

في هذه الدراسة تم عمل مسح لمعاصر الزيتون الواقعة ضمن منطقة الدراسة الواقعة في جنوب الضفة الغربية (محافظتي الخليل و بيت لحم)، حيث شمل المسح عدد المعاصر و مستوى الاتمتة وكمية الزيتون المدروس وكمية الزيت المستخرج وكمية الزيبار الناتج وكيفية التخلص من الزيبار. أظهرت النتائج أن إجمالي كمية الزيتون المدروس في منطقة الدراسة خلال فترة الدارسة 2010-2011 كانت 5810 طن، 35% منها كان بمحافظة بيت لحم و65% منها كان بمحافظة الخليل. إجمالي كمية الزيبار الناتج كانت 10386 متر مكعب. كما أنه يتم التخلص من الزيبار مباشرة في الوديان والاراضي القريبة او في شبكة المجاري بنسبة 67% و 33% على التوالي.

تم تحديد الخصائص الفزيائية والكيميائية للزيبار في منقطة الدارسة من خلال جمع 19 عينة لتحديد مستوى التلوث على البيئة الناتج من الزيبار من خلال قياس عوامل معينة مثل: درجة الحموضة (pH)

والموصلية (EC) واجمالي المواد الصلبة الذائبة (TDS) والفينولات والطلب الكيميائي على الاوكسجين (COD) وإجمالي المواد الصلبة (TS). أظهرت النتائج أن الزيبار يحتوي على تراكيز عالية من الملوثات والتي تتجاوز الحد الأقصى المسموح به ليتم التخلص منه في البيئة او شبكات المجاري حسب المعايير الأردنية والفلسطينية.

في هذا البحث كان المقترح لعلاج الزيبار والحد من تركيز الملوثات خاصة الفينولات هو استخدام مادة الجير (Lime) ثم عمل معالجة بيولوجية باستخدام فطر (*Aspergillus niger*) لدراسة كفاءته في التخلص من الفينولات.

بعد اجراء التجربة بتراكيز مختلفة من مادة الجير(Lime) تبين أن الجرعة الأكثر فاعلية في إزالة الفنيولات كانت الجرعة (10 g/L) حيث كانت نسبة ازالة الفينولات 56% وبالإضافة إلى ذلك فقد تم تخفيض تركيز COD بنسبة 17% وتخفيض تركيز TS بنسبة 5.7% . وقد تم اجراء المعالجة البيولوجية على الزيبار المعالج باستخدام مادة الجير (Lime) وبينت النتائج أن نسبة ازالة الفينولات كانت 23.5%.

بعد معالجة الزيبار بمادة الجير(Lime) والمعالجة البيولوجية كان التركيز النهائي للفينولات 920 ملغم/ لتر في نظام العينة المحصورة حيث ما يزال تركيز الفينول اعلى من التركيز المسموح به للتخلص من الزيبار في نظام الصرف الصحي أو في الوديان. في نهاية هذا البحث يوصى باستخدام مادة الجير (Lime) في معالجة الزيبار بشكل أولي.