



Treatment and Decolourization of Olive Mill Wastewater Using Magnetic Assisted Nanoparticle Adsorption Technology

by

Laith A. Arar

Mahmoud M. Abu Ghanim

Marwan S. Dwaikat

Supervisor

Dr. Nashaat N. Nassar

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ABSTRACT

Olive mill wastewater (OMW) is an environmental concern that have been highlighted as a serious environmental problem in the Mediterranean basin countries because of its high organic load and phytotoxic and antibacterial phenolic compounds which resist biological degradation. In addition, this type of wastewater represents a huge challenge for the conventional wastewater treatment techniques. Nonetheless, a number of physical, chemical and biological treatment methods for OMW have been reported in literature. These methods, however, are limited because they are too expensive to find a wide application, ineffective in meeting stringent effluent standards, and resulted in huge amount of sludge. Magnetic iron oxide nanoparticle technology has emerged as a fascinating area of interest for removal of various contaminants from wastewater effluents. Iron-oxide nanoparticles are attractive for wastewater treatment for two important reasons. First, nanoparticles can remove contaminants from wastewater rapidly. Second, this magnetic type of nanoparticles could be separated easily using a magnet after finishing treatment process. In this project we aimed at investigating the effectiveness of the magnetic iron oxide nanoparticles in the removal of large organic contaminants from OMW. Batch-mode was applied on OMW and model molecule to determine the effect of contact time, solution pH, coexisting contaminants and the adsorption isotherm.

Results showed that the adsorption was fast for both OMW and model molecule and the adsorption reach equilibrium within less than 30 and 10 min respectively. The adsorption equilibrium data fit very well to the Brunauer-Emmet-Teller Model (BET), indicating multi-layers adsorption. Functionalizing γ -Fe₂O₃ nanoparticles with methylene blue has a significant effect on enhancing adsorption process. The adsorption of major pollutant contaminants was associated to an efficient removal of coexisting contaminants such as heavy metals and free ions. The adsorption of OMW showed a huge dependence on pH of the solution, while the model molecule adsorption was independent on pH. Finally, continuous-mode process was tested successfully using a packed bed column that combines sand filtration with magnetic nanoparticles to decolorize OMW effluent. After seeing the successful achievement of integrating nanoparticles with packed bed filtration, a preliminary plant and design wastewater treatment facility process were considered in this study. Process capital cost and annual operating cost were estimated to be 12,226 and 476 USD/year, respectively.

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DISCLAIMER

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NUMENCLATURE

₪: New Israeli Shekel.
Ø: porosity or void fraction.
ρ: density of the liquid (Kg/m³).
μ: viscosity of fluid passing through the bed (kg/m.s).
A.A: atomic absorption test.
A: cross sectional area of the pipe (m²).
AOC: annual operating cost (₪/year).
A_{sh}: area of one sheet (m²) = 2 m².
ASTM: American Society of Testing and Materials.
A_T: surface area of the tank (m²).
BET: Brunauer-Emmet-Teller adsorption model.
BOD₅: biochemical oxygen demand (mg O₂/L).
C: final concentration of contaminants in the supernatant (mg/L).
CA: corrosion allowance of steel (m).
CC: capital cost (USD).
C_e: concentration of contaminants in the supernatant at equilibrium (mg/L).
C_E: the equilibrium concentration of contaminants in the aqueous phase (mg/L).
C_o: initial concentration of contaminants in the solution (mg/L).
COD: chemical oxygen demand (mg O₂/L).
D/ε: relative roughness (dimensionless).
D₀: external diameter of the pipe (m).
D₀: external diameter of the tank (m).
D_i: internal diameter of the pipe (m).
D_i: internal diameter of the tank (m)
D_i: internal diameter of the tank (m).
DN: nominal diameter (mm).
D_p: diameter of particle in the bed (m).
EC: electrical conductivity (mS/cm).
f: friction factor (dimensionless).
f_T: friction factor for fittings and valves (dimensionless).
g: standard acceleration of gravity (9.81 m/s²).
G: superficial mass velocity = ρu (kg/m².s).
g_c: conversion factor (1).
h: length down the packed bed bed of pipe (m).
h_A: head added to the pump (m).
H_B: height of the base (m).
HDPE: High Density Poly Ethylene.
H_L: height of liquid in the tank (m).
h_L: major loss inside the pipe (dimensionless).
H_T: height of the tank (m).
IUPAC: International Union of Pure and Applied Chemistry.

K : resistance coefficient (dimensionless).
 K_1 : equilibrium rate constants of first order adsorption (min).
 K_2 : equilibrium rate constants of second order adsorption (g/mg.min).
 K_L : equilibrium constants of adsorption for the upper layers (L/mg).
 K_L : Langmuir isotherm constant (L/mg).
 K_S : equilibrium constants of adsorption for the first layer (L/mg).
 L : length of the pipe (m).
 Le/D : length over diameter ratio (dimensionless)
 m : dry mass of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (g).
 MB : methylene blue dyes.
 MCM : million cubic meter.
 MOA : Palestinian Ministry of Agriculture.
 NIS : New Israeli Shekel.
 $OMSR$: olive mill solid residue.
 OMW : olive mill wastewater.
 P : output power of the pump (W).
 P : pressure (KPa).
 $PCBS$: Palestinian Central Bureau of Statistics.
 P_i : internal pressure of the liquid in the tank (Pa).
 P_{in} : input power of the pump (W).
 PP : poly phenols concentration (mg/L).
 $PPIC$: Palestine Plastic Industrial Company.
 PWA : Palestinian Water Authority.
 Q : amount of adsorbate adsorbed (mg adsorbate/ g adsorbent).
 q : amount of contaminants adsorbed at equilibrium (mg/g).
 Q : volumetric flow rate (m^3/s).
 $Q_{e,exp}$: experimental amount of adsorbate adsorbed at equilibrium (mg adsorbate/ g adsorbent).
 Q_e : amount of adsorbate adsorbed at equilibrium (mg adsorbate/ g adsorbent).
 Q_{model} : the adsorbed amount of contaminants obtained by model fitting (mg/g).
 Q_{in} : flow rate enters the tank (m^3/day).
 q_{max} : the maximum adsorption capacity (mg/g).
 Q_{out} : flow rate leaves the tank (m^3/day).
 Q_t : amount of adsorbate adsorbed at any time (mg adsorbate/ g adsorbent).
 Re : Reynolds number (dimensionless).
 t : thickness of the tank wall (m).
 TAC : total annual cost (USD/year).
 TDS : total dissolved solids (mg/L).
 TKN : total Kjeldahl nitrogen (mg N/L).
 TOC : total organic carbon (mg O_2/L).
 t_{sheet} : thickness of one steel sheet (m)
 TSS : total suspended solids (mg/L).
 t_T : thickness of the tank (m).
 t_{total} : total thickness of the tank wall (m)

u : superficial velocity (m/s).
UN: United Nations.
USEPA: United States Environment Protection Agency.
 V : solution volume (L).
 v : velocity inside the pipe (m/s).
 V_B : volume of the base (m³).
 V_L : volume of the liquid in the tank (m³).
WHO: World Health Organization.
WWO: World Water Organization.
 ρ : fluid density (kg/m³).
 μ : viscosity of the liquid (Pa.s).
 σ : maximum allowable stress of the steel (Pa).
 ϵ : roughness of the pipe (dimensionless).
 γ : specific weight (KN/m³).
 ϵ : efficiency of the pump (dimensionless).

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CHAPTER ONE

INTRODUCTION

Water shortage is a worldwide problem that has been highlighted by various environmentalist groups and societies (UN, 2008). This problem is attributed to many reasons such as desertification, population growth, extended droughts, more stringent health-based regulations, and industrial enlargement and others (UN, 2008).

In Palestine, however, there are many sources of water, surface and ground water, most of these sources currently are controlled by the Israeli occupation, therefore quantity of water does not support the needs and requirements of the Palestinians (PWA, 2012). For instance, 309 Million Cubic Meter (MCM) is the Palestinian consumption yearly that subdivided into: agricultural, industrial and human use. The generated wastewater produced is 62 MCM per year (PWA, 2011).

Industrial sector is one of the major consumers of fresh water as well as generator of wastewater. The main industrial sectors that contribute towards generating huge amount of wastewater include textile industry, tanneries, stone cutting, food industry and olive mill, to name only a few.

In the current content, most of the generated wastewater effluent is discharged into the environment without treatment. It should be noted here that several methods have been applied for OMW treatment such as aerobic treatment, anaerobic treatment, filtration, wet oxidation, precipitation, evaporation, electrolysis, decolourization and adsorption by classical adsorbents.

This project aims to treat the OMW by an effective, economical, easy to apply and environmental friendly method that called magnetic nanoparticle technology. Also, it focuses on the treatment of olive mill wastewater effluent. This because olive oil production is one of the backbone of the Palestinian economy. This solution for olive mill wastewater treatment will not just help in reducing the environmental impact of this effluent, but it will sustain the olive oil industry and help in water recyclability.

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CHAPTER TWO

LITERATURE REVIEW

This chapter focuses on the literature review that is related to the water scarcity worldwide and locally. This chapter introduces the OMW problem and treatment methods used nowadays.

2.1 Water Scarcity in the World

There is no doubt that water scarcity is becoming a global issues and the competition on the water resources become as the competition on the oil sources (UN, 2008), with the rapid in population, industrialization and droughts, The world will be facing a number of challenges in meeting water demand.

Therefore, many innovations will be needed to avoid future conflicts over water among nations and, within nations, among farmers, urbanites, energy producers, environmentalists, and industries (UN, 2008). Figure 2.1 and 2.2 show the global water scarcity in years of 2000 and 2050, respectively.

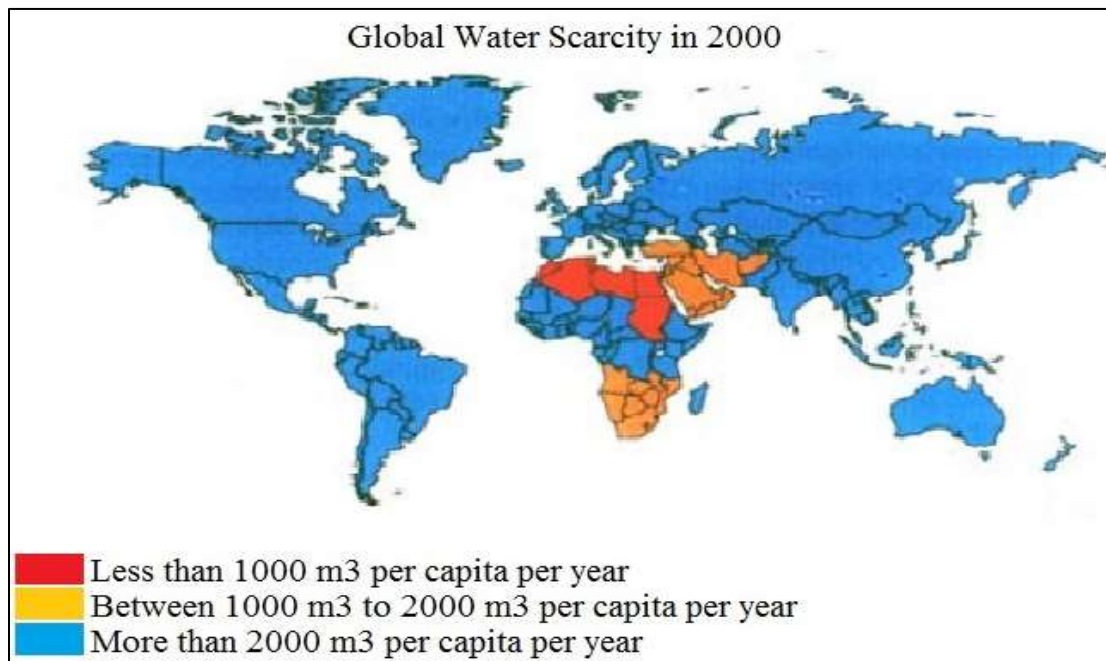


Figure 2.1: Global water scarcity in the year 2000 (Fischer & Heilig, 1997)

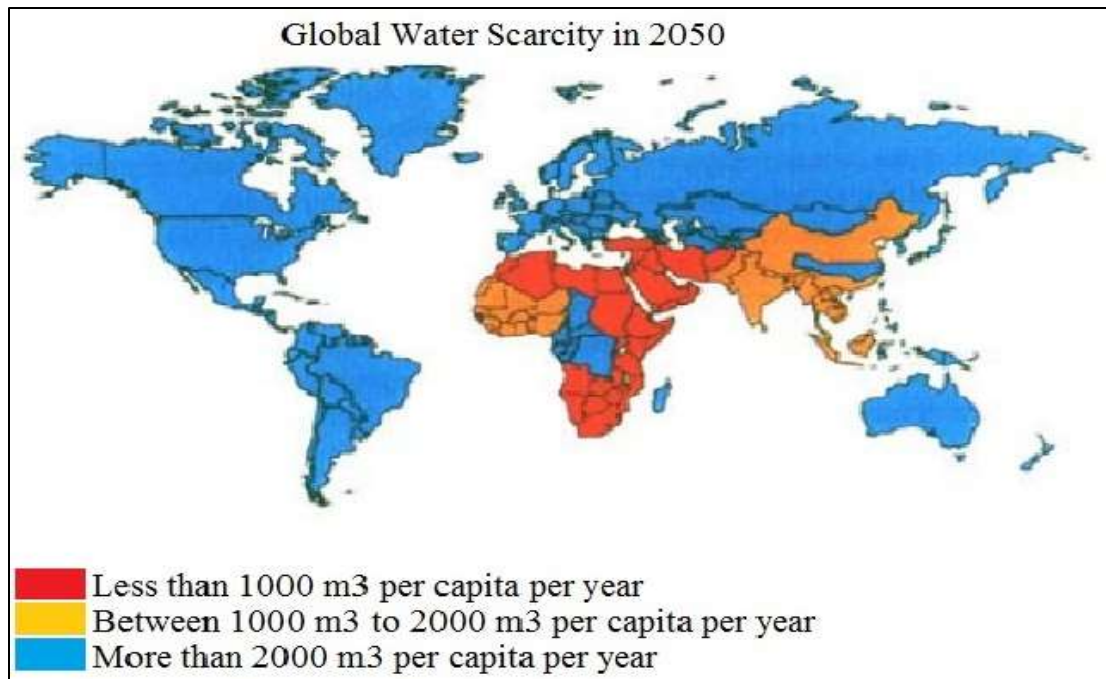


Figure 2.2: Global water scarcity objection for the year 2050 (Fischer & Heilig, 1997)

Clearly, the water stress in the world is aggravate year after year, in the year 2000 more than 1.4 billion capita in more than 30 countries have a water access less than 1000 m³ per capita per year and by the year of 2050 the number will raise to more than 4 billion capita in more than 50 countries, and as the global population is expected to increase from six billion to ten billion people as the water demand will increase (Fischer & Heilig, 1997).

2.2 Water Shortage in Palestine

Severe water shortages and acute water quality problems continue to negatively affect the lives and livelihoods of millions of Palestinians living in the West Bank and Gaza Strip. Rather than caused by environmental factors, both are attributable to the discriminatory water policies and practices Israel has instituted across the occupied Palestinian territory over the last forty five years (PWA, 2012).

Israel currently exploits over 90 per cent of these resources for exclusive Israeli use, including for use in Israeli settlements, and allocates less than 10 per cent for Palestinian use. As a result, Palestinian water consumption in the West Bank is limited to an average to just 70 liters per

capita per day, below the ‘absolute minimum’ of 100 liters per capita per day recommended by the World Health Organization, and far below the average of 300 liters per capita per day in Israel. Moreover, Israel sells to Palestinians part of the water supply – 56MCM in 2010 – allocated to them under the 1995 Interim Agreement (PWA, 2012).

The total consumption of fresh water in the West Bank and Gaza Strip according to the Palestinian Central Bureau of Statistics (PCBS) for the year 2008 is 309 MCM and the sewage wastewater according to the Palestinian Water Authority (PWA) is estimated to be 62 MCM from the Palestinian Territories and 35 MCM from the Israeli settlements (PWA, 2011). In addition to the domestic use, the major consumer of fresh water in Palestine is agriculture and industrial sectors. Figure 2.3 shows the percentage of water consumption in Palestine by the major consumers.

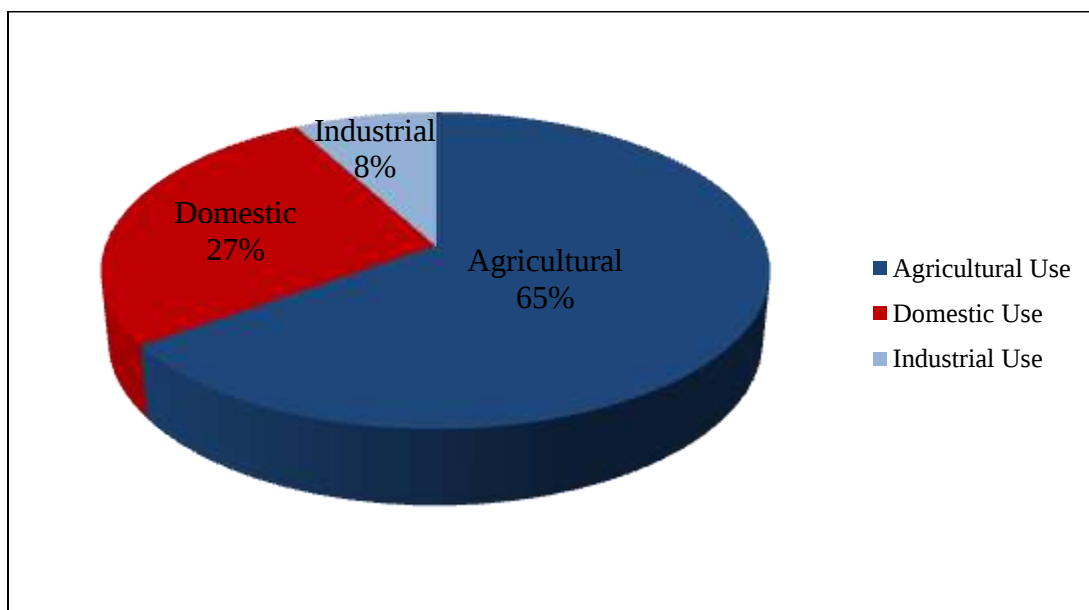


Figure 2.3: Percentages of water consumption in Palestine (PCBS, 2008)

As seen, the major water consumption in Palestine is in the agricultural sector (65%) followed by domestic sector (27%) and finally the lowest one is the industrial sector (6%); which -in numbers- equal to 18.5 MCM per year (PCBS, 2008).

Palestinians living in the Gaza Strip are forced to rely on the underlying portion of the coastal aquifer as their only water supply. With an estimated annual recharge of 55MCM, the aquifer falls far short of the basic water needs of Gaza's 1.6 million residents. Prevented from utilizing any water from "Wadi Gaza", and unable to import additional quantities of water, Gaza's population presently extracts almost three times the aquifer's sustainable yearly recharge (PWA, 2012).

Following lengthy discussions between Israel and the Palestinian National Authority (PNA), agreement was reached that Israel will provide an additional 5 MCM to the Gaza Strip through the "Nahal Oz" connection as per its obligations under the 1995 Interim Agreement, as well as an additional quantity of 2500 cubic meters per day to Hebron, and 2500 cubic meters per day to Bethlehem upon Palestinian request (PWA, 2012).

Furthermore, since 1996 Israel has unilaterally deducted over \$US42 million from Palestinian tax revenues for the construction and maintenance of wastewater treatment plants in Israel exclusive to treat Palestinian wastewater (PWA, 2012).

2.3 Wastewater Treatment History

From the sixteenth century onward, it became increasingly clear that some form of treatment of large quantities of water was essential to maintaining the water supply in large human settlements (Crittenden, 2012). Table 2.1 summarizes some of the major historical developments of water treatment that contributed to researchers understanding of the importance of water quality.

Table 2.1: Historical development of water treatment methods (Crittenden, 2012)

Year	Event
1500 B.C.	Egyptians reportedly use the chemical alum to cause suspended particles to settle out of water. Pictures of clarifying devices were depicted on the wall of the tomb of Amenophis II at Thebes and later in the tomb of Ramses II.
Fifth century B.C.	Hippocrates, the father of medicine, notes that rainwater should be boiled and strained. He invents the "Hippocrates sleeve," a cloth bag to strain rainwater.

1676	Anton van Leeuwenhoek first observes microorganisms under the microscope.
1703	French scientist La Hire presents a plan to French Academy of Science proposing that every household have a sand filter and rainwater cistern.
1746	French scientist Joseph Amy is granted the first patent for a filter design. By 1750 filters composed of sponge, charcoal, and wool could be purchased for home use.
1846	Ignaz Semmelweiss (in Vienna) recommends that chlorine be used to disinfect the hands of physicians between each visit to a patient. Patient mortality drops from 18 to 1 percent as a result of this action.
1856	Thomas Hawksley, civil engineer, advocates continuously pressurized water systems as a strategy to prevent external contamination.
1892	The New York State Board of Health uses the fermentation tube method developed by Theobald Smith for the detection of E. coli to demonstrate the connection between sewage contamination of the Mohawk River and the spread of typhoid fever.
1897	G. W. Fuller studies rapid sand filtration [5 cubic meters per square meter per day (2 gallons per square foot per day)] and finds that bacterial removals are much better when filtration is preceded by good coagulation and sedimentation.
1902	The first drinking water supply is chlorinated in Middelkerke, Belgium. Process is actually the “Ferrochlor” process wherein calcium hypochlorite and ferric chloride are mixed, resulting in both coagulation and disinfection.
1903	The iron and lime process of treating water (softening) is applied to the Mississippi River water supplied to St Louis, Missouri.
1906	First use of ozone as a disinfectant in Nice, France. First use of ozone in the United States occurs some four decades later.

Starting in 1970, public health concerns shifted from waterborne illnesses caused by disease-causing microorganisms, to anthropogenic water pollution such as pesticide residues and industrial sludge and organic chemicals. Regulation now focused on industrial waste and industrial water contamination, and water treatment plants were adapted. Techniques such as aeration, flocculation, and active carbon adsorption were applied. In the 1980s, membrane development for reverse osmosis was added to the list. Risk assessments were enabled after 1990 (Crittenden, 2012).

2.4 Olive Mill Wastewater

2.4.1 Olive Oil Extraction

Fresh water is necessary for oil extraction from olive fruits. Figure 2.4 shows a schematic representation of olive oil extraction in two and three phases full automatic presses that most commonly used in Palestine.



Figure 2.4: A schematic representation of olive oil extraction in two and three full automatic presses (2013).

The process begins by placing the olive fruits into the basin which is connected with a moving belt that takes the olive fruits up to a fan used to separate the leaves from the olive fruit; and then the purified fruits are washed by fresh water, the washing basin which also contains a screener to remove stones. The olive fruits are then crushed and milled with hot water and then the resulting paste is sent to the decanters which separate the mixture into solid and liquid. Finally, the liquid is centrifuged to separate the oil and the olive mill wastewater (OMW).

2.4.2 General Characteristics of OMW

OMW is considered a major pollutant because of its high organic load and its high content of phytotoxic and antibacterial phenolic substances, which resist biological degradation (Coskun, et al., 2010). OMW color varies between red and black depending on olive fruit source and its freshness. The solution pH varies from 4 to 5.5, and has an unpleasant smell. The density of OMW is slightly higher than water due to organic and inorganics contaminated with it (Nassar, 2007). Table 2.2 shows the major contents of OMW.

Table 2.2: Olive mill wastewater contents (Nassar, 2007)

Content	(wt/wt)%
Water	83.2
Sugars	2.8
Nitrogen Compounds	1.2-2.4
Organic Acids	0.5-1.5
Carboxylic Acids	1-1.5
Pectin	1-1.5
Oil	0.03-1
Other	1.8

As seen in Table 2.2, the nitrogen compounds are significant, as well as organics contaminants. The major organics contaminants of the OMW are phenols and poly phenols (Nassar, 2007). Further, high COD values are recorded and it varies from 50 to 200 g/L BOD values are high as well, and the ratio of COD/BOD₅ varies from 2 to 4 (Khatib et al., 2009). The treatment of production is still a major challenge facing this industry. The main problem is attributed to its dark color, high organic content and toxicity which are due to the presence of phenolic compounds.

2.4.3 Olive Mill Wastewater Problems

Olive mill wastewater generated by the process olive oil extraction is considered to be the main waste product of this industry (Khatib et al., 2009). Approximately 1.8×10^6 tons of olive oil are produced annually worldwide where the majority of it is about (98%) produced in the Mediterranean basin. The average amount of olive mill wastewater produced during the milling process is 1.2–1.8 m³/tons of olive. OMW resulting from the production processes in the

Mediterranean basin surpasses 30 MCM per year (El-Gohary, et al., 2009). The problems created in managing OMW have been extensively investigated during the last 50 years without finding a sustainable solution, which is technically feasible, economically viable and socially acceptable. Therefore, a new strategy for OMW management must be adapted (Shaheen & Karim, 2007).

In Palestine, more than 938 km² of lands covered by 11 million of olive trees (MOA, 2004). Annual production of olive fruit varies widely from a year to another. The total production of olive fruits for the year 2011 was 93,565 tons which is equivalent to 20,745 tons oil, while the average production of olive fruit for the years from 2003 to 2011 was 72,745 tons, and is equivalent to 16,643 tons oil (PCBS, 2012). Figure 2.5 shows a histogram of quantities of olive pressed between the years 2003 to 2011.

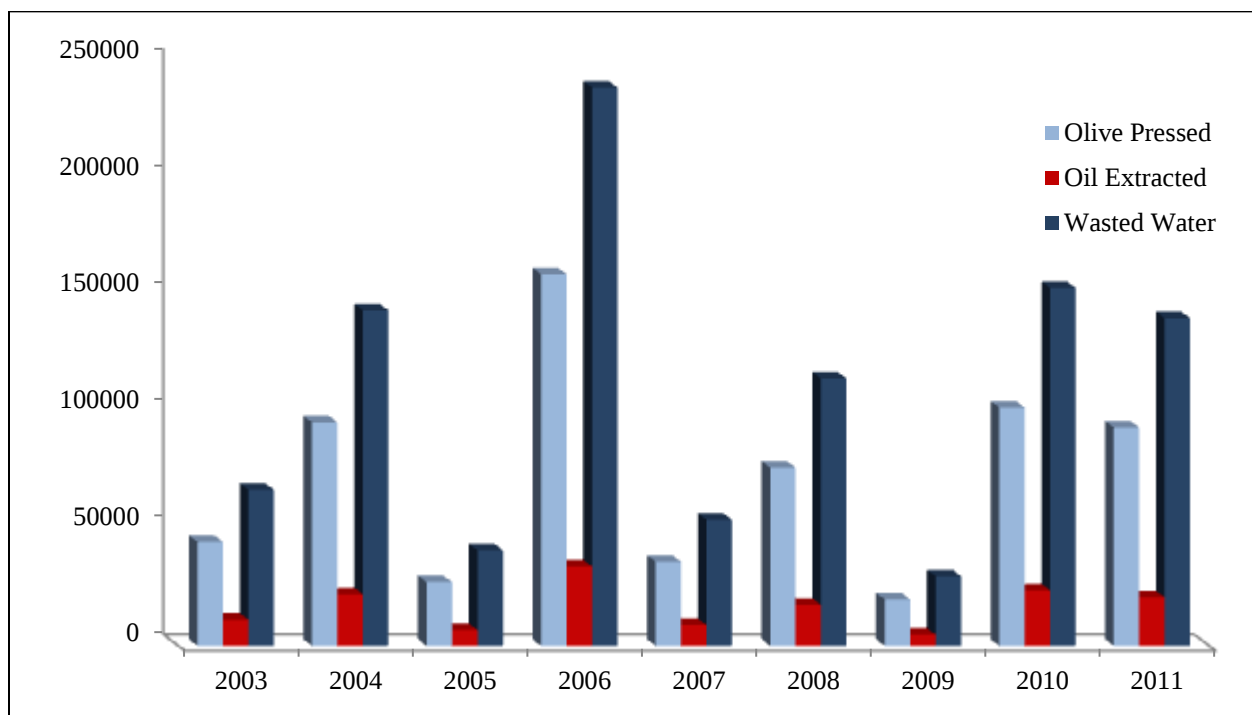


Figure 2.5: Quantities of olive pressed between the years 2003 to 2011 (PCBS, 2012)

As seen, the quantity of the olive pressed in the year 2009 was the lowest; while the quantity for the year 2006 was the highest during these nine years, these values are varied for many climate reasons. The average wastewater generated is approximately $1.1 \times 10^5 \text{ m}^3$ per year. The total

operating olive presses for the year 2011 was 272 presses which are subdivided to 240 full automatic presses and 32 old and semi-automatic presses. Therefore, the average annual production of OMW in Palestine may reach 200,000 m³ (PCBS, 2012). Figure 2.6 shows a histogram of the distribution of the olive presses over the Palestinian governorates.

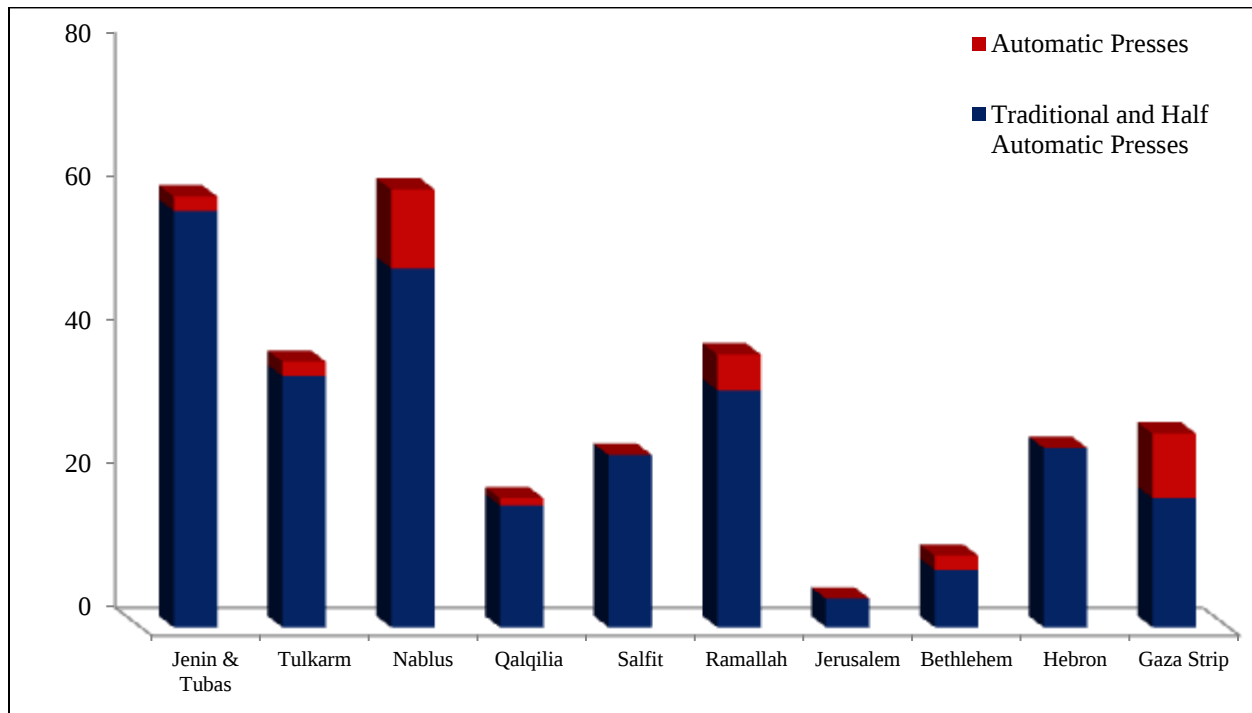


Figure 2.6: Distribution of olive presses over the Palestinian governorates (PCBS, 2012)

Clearly, the number of presses in Jenin and Tubas was the greatest due to wide agricultural areas and activities in opposite to Jerusalem, Bethlehem and Gaza Strip governorates which suffer the huge urbanization and high population density and many other reasons. Semi-automatic and old presses produce 40-55 L OMW/100 Kg olive, while full automatic presses produce 85-120 L OMW/100 Kg olive, and the average global OMW production per oil ratio (WOR) is 1:6 (Nassar, 2007). Figure 2.7 shows a schematic flow chart of the olive extraction process.

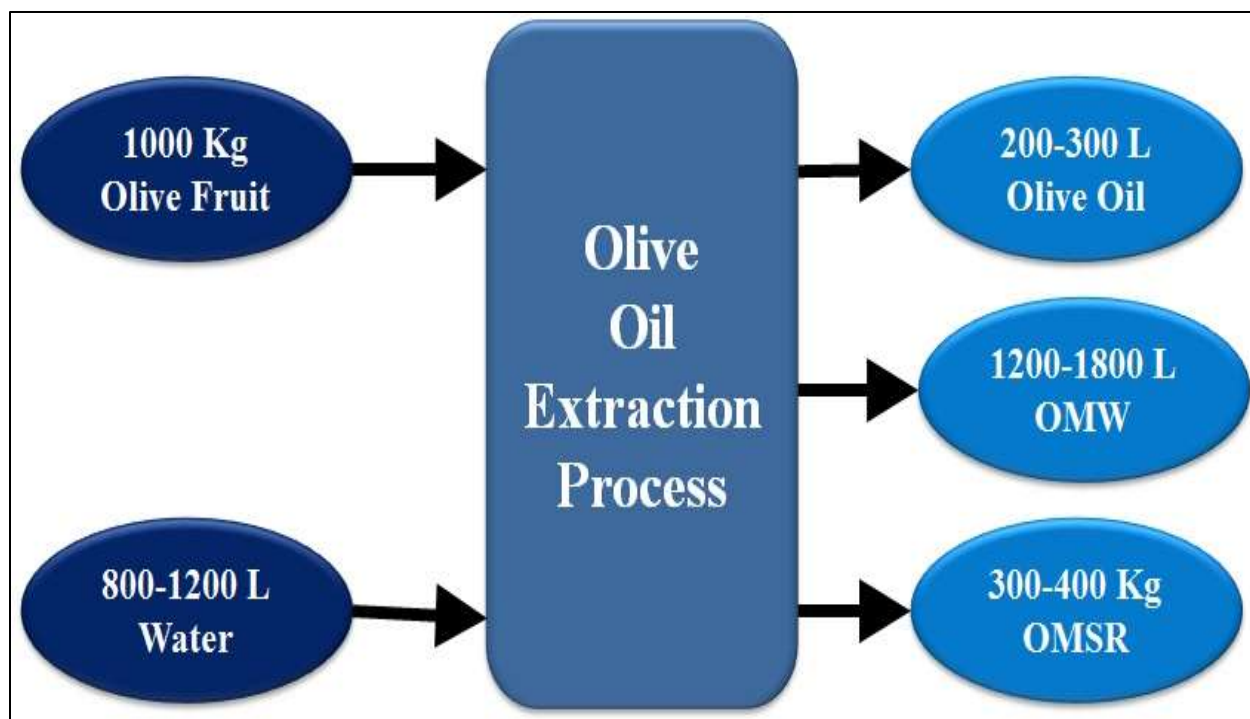


Figure 2.7: Schematic representation of olive extraction process

As illustrated in Figure 2.7, for every tons of olive fruit, correspondingly 1 m³ of fresh water is required for extraction. However, the generated OMW is about 1500 L as olive fruit contains approximately 42% water initially. It is worth noting here that olive remnants are subdivided into three main categories; namely olive solid waste residue (OSWR), leaves, and olive mill wastewater (OMW). Locally, 88% of OSWR is used for energy production; such as, source of fire for ovens and heating systems. The leaves are used as organic compost, while the OMW is discharged into the environment which represents a serious environmental challenge due to absence of serious treatment methods, where 45.2% of OMW is disposed into ponds or drilling holes, and the rest are discharged into the sewer systems and valleys (PCBS, 2012). Therefore, OMW is mixed with the untreated flowing municipal wastewater or with rainwater. Uncontrolled disposal of OMW into the environment is resulted in high organic polluted wastewater that affects the soil, ground water and water receiving bodies. This disposal is unsafe, uncontrolled and considered as an urgent ecological problem that deteriorates the environment in Palestine (Shaheen & Karim, 2007).

2.5 Olive Mill Wastewater Treatment

The discharge of these pollution loads into the sewage system and water receiving bodies leads to high pH values, high temperature (due to hot wastes) and high content of chemicals (Shaheen & Karim, 2007). Several treatment methods for OMW have been reported in literature including: anaerobic combined with aerobic, forced evaporation, filtration, ultrafiltration, membrane filtration, wet oxidation, precipitation/flocculation, adsorption, evaporation, electrolysis and decolonization, chemical and biological treatment methods (Shaheen & Karim, 2007). Other advanced methods for treatment of the secondary effluent of OMW have been recommended as well. Table 2.3 lists the commonly used advanced water treatment technology and their limitations. These methods have been reported to be costly and/or insufficient in meeting standard environmental regulations. This search for a new method or improving the currently available methods is of paramount importance to sustain the olive oil industry in Palestine and worldwide.

Table 2.3: Commonly used water treatment methods

Method	Description	Ability	Disadvantages
Reverse osmosis	Flow of water across semi-permeable membrane under pressure	Remove heavy metals and microorganisms	Pretreatment needed, High maintenance and Brine disposal
Activated carbon	Adsorption of contaminants on porous surface	Remove color, odor and VOCs	Doesn't remove microbial and hardness
UV	Free radical UV lamp on water.	High filtration capacity and microorganisms removal.	High cost
Electro-dialysis	Charge separation under electric field	High TDS removal.	Doesn't remove microorganisms and high cost
Distillation	Reduce pressure evaporation then condensation	Removes high range of contaminants, high initial efficiency	Regular maintenance and high cost

From Table 2.3, we note that the common factor between all the common methods is the high cost, thus, many companies and governmental institutes are reluctant to treat this type of wastewater by the advanced methods and hence use the traditional disposal methods.

2.6 Nanotechnology in Wastewater Treatment

Nanotechnology is a new technology that emerging for wastewater treatment (Savage & Diallo, 2005). It is manipulation of matter with at least one dimension sized from 1 to 100 nanometers. This definition reflects the fact that not just the size but also surface functionalities are important, as their nanoparticle possess a high surface area and aspect ratio. Therefore common to see the plural form "nanotechnologies" as well as "nano-scale technologies" to refer to the broad range of research and applications whose common trait is size (Drexler, 1992).

Research states that nanotechnology has the potential to increase the effectiveness of the existing water treatment solutions at a more affordable cost. Techniques such as purification by magnetic nanoparticles have the ability to effectively remove contaminants even at very low concentrations (Nassar, 2012). This can be accomplished by using nanoparticle as adsorbent for removing contaminants by adsorption or catalyst for removing contaminants by photo-catalytic oxidation or catalytic oxidation/gasification.

In this project, we aim to use magnetic nanoparticles as adsorbent for the removal of contaminants from OMW. A later project will consider the removal of these contaminants by nanoparticle catalyst or catalytic gasification of the adsorbed contaminants.

2.7 Adsorption

Because nanoparticles are used in this project for wastewater treatment by adsorption mechanisms, it become very important to understand the adsorption phenomina before using the nanoparticles.

Adsorption is a mass transfer process that is widely used in practice to remove substances from fluid phases (gases or liquids) onto a solid surface. It can also be observed as natural process in different environmental compartments. The most general definition describes adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid. Figure 2.8 shows a schematic represintation of the typical adsorption process in water treatment, adsorption has been proven as an efficient removal process for a multiplicity of solutes. Here, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces (Worch, 2012). Solid surfaces are characterized by active, energy-rich sites that are able to interact with solutes in the adjacent aqueous phase due to their specific electronic and spatial properties. Typically,

the active sites have different energies, (i.e., surface is energetically heterogeneous) (Worch, 2012).

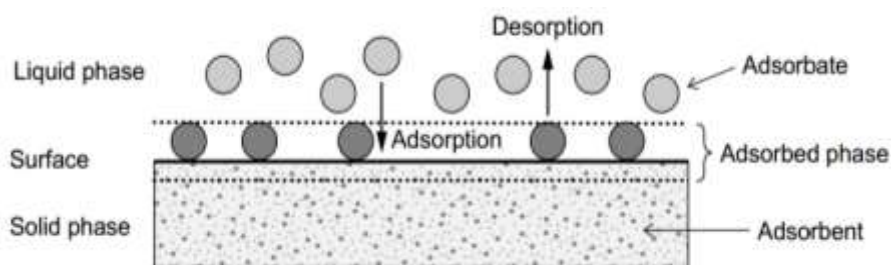


Figure 2.8: Schematic representation of adsorption process (Worch, 2012)

2.8 Magnetic Nanoadsorbents

Magnetic nanoparticles are very effective as a separation medium for water purification as they contain a number of key physio-chemical properties. They are known for their high surface area to mass ratio which occurs as a result of decreasing the size of the adsorbent particle from bulk to nano-scale dimensions (Savage & Diallo, 2005). This property of magnetic nanoparticles leads to the availability of a high number of atoms or molecules on the surface of contaminants thereby enhancing the adsorption capacities (Pradeep, 2009). Moreover, this large surface area coupled with their size, electronic and catalytic properties provide unparalleled opportunities to develop more efficient water purification adsorbents catalysts and redox active media. Nanoparticles can also be functionalized with various chemical groups to increase their affinity toward a given compound (Savage & Diallo, 2005). Lastly, since more adsorbent atoms/molecules are present per unit mass of the adsorbent, less waste will be generated post treatment as these atoms will be actively utilized for adsorption (Tiwari, et al., 2008).

The value of their application to wastewater treatment has grown. Because of their multifunctionalities and magnetic properties, iron-oxide nanoparticles are the most commonly used adsorbent and/or catalyst for wastewater remediation (Nassar, 2012). Furthermore, iron oxide is naturally occurring, inexpensive, and stable over a wide range of temperatures and acidity levels. In fact, nanoparticles of iron oxide are advantageous over other metal oxides. There have been numerous studies on the use of iron-oxide nanoparticles as catalysts for degradation of

contaminants, usually organic materials from wastewater, and as adsorbents for adsorptive removal of pollutants, mainly metal ions, from wastewater (Nassar, 2012).

Due to these unique properties, nanoparticles have potential applications for the treatment of wastewater and drinking water recently; our research group have successfully employed the nanoparticles for textile wastewater treatment as well (Marei & Nassar, 2014)

CHAPTER THREE

OBJECTIVES

3.1 General Objectives

Apply magnetic nanoparticle technology for treatment of OMW effluents for the first time.

3.2 Specific Objectives

The specific objectives of this work are:

1. Conduct a survey on the production of olive oil industry in Palestine.
2. Characterize the different kinds of the liquid waste samples from olive oil industries.
3. Employ nanoparticle technology in the treatment of OMW for the first time.
4. Establish a new method and employ it for the treatment of olive mill wastewater in Palestine using magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoadsorbents.
5. Study, evaluate and maximize the effect of the following variables on the treatment process efficiency:
 - a. Contact time (kinetics).
 - b. Initial concentration of OMW.
 - c. Dosage of nanoparticles.
 - d. Solution pH.
 - e. Coexisting contaminants.
6. Construct models that capture the effect of the above variables on the adsorption removal efficiency.
7. Incorporate nanoparticle technology with bed filtration for cleaning OMW for the first time.
8. Construct an integrated in-situ process for the treatment of OMW.

CHAPTER FOUR

EXPERIMENTAL WORK

This chapter describes the materials used, the characterization techniques employed, and the experimental methodology and procedure applied in this study.

4.1 Materials

The following materials were used during this research.

4.1.1 Nanoparticles Adsorbent

Magnetic iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) prepared by water-in-oil (W/O) microemulsion followed the technique reported by Nassar (Nassar, 2007) was used as an adsorbent. The particles size ranged between 20 and 50 nm.

4.1.2 Adsorbates

The following adsorbates were used during this research.

4.1.2.1 OMW Samples

Different real wastewater samples obtained from different local olive mill factories in the West Bank were used in this study. Before conducting any adsorption experiment, OMW samples were subjected to a stability test, and their components were analyzed.

Three olive mill wastewater samples was obtained from three different governorates in Palestine, the first one obtained from the city of Nablus (eastern region) and the second one was obtained from Kufur Thilth (Qalqilia governorate) and the third one from Burqeen (Jenin governorate). The three samples obtained in November, 1, 2013 and from a two phase full automatic presses. The samples stored in an incubator at 21°C in a sealed glass container and allowed to settle down. Table 4.1 shows the characteristics of the three OMW samples.

Table 4.1: Characteristics of different OMW samples

	Nablus	Qalqilia	Jenin
Avg. COD (mg O ₂ /L)	153×10 ³	136×10 ³	10×10 ³
pH	5.04	4.41	4.49

As seen in Table 4.1, the COD value for Nablus governorate was the highest one which is equal to 153×10^3 mg O₂/L, followed by Qalqilia governorate sample with a slight difference equal to 17×10^3 mg O₂/L, and finally Jenin governorate sample was the lowest COD value which is equal to 10×10^3 mg O₂/L. Also the pH value ranged from 4.41 to 5.04. In fact the variety of COD and pH values may refer to many reasons, such that the type of olive, type of farm land, availability of irrigation water, etc.

Nablus governorate sample was considered to be investigated as a worst case sample. Table 4.2 shows the main characteristics of Nablus fresh-sample before treatment.

Table 4.2: Main characteristics of Nablus OMW fresh-sample before treatment

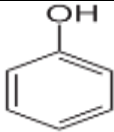
Parameter	Value
COD (mg O ₂ /L)	153×10^3
BOD₅ (mg O ₂ /L)	71.4×10^3
TOC (mg O ₂ /L)	57.5×10^3
TSS (mg/L)	51×10^3
TDS (mg/L)	57.2×10^3
EC (mS/cm)	8.29
Density (Kg/m ³)	974
pH	5.04

As seen in Table 4.2, COD was very high with 153×10^3 (mg O₂/L). Also BOD₅ value was high with 71.4×10^3 (mg O₂/L), and the value of TOC was calculated according to the relation $COD = 2.66 TOC$ (Kiely, 1997). It is obvious that the suspended and dissolved solids are very high with 51×10^3 and 57×10^3 , respectively. The electrical conductivity (EC) also was higher than that for water, and this indicates the degree of pollutants and free ions in the solution. The density of the solution was closer to the water and the pH was in the acid range.

4.1.2.2 Phenol and Methylene Blue Dyes

Methylene blue dyes purchased from Sigma Aldrich, Germany were used to functionalize γ -Fe₂O₃ nanoparticles. A 91% (w/w) phenol purchased from Riedel de Haen, Germany was used as a model molecule. Table 4.3 shows the main characteristics of phenol used in this study.

Table 4.3: The main characteristics of phenol used in this study

Formula	C ₆ H ₅ OH
Structure	
Density (g/cm³)	1.07
Molar mass (g/mol)	94.11
λ_{max} (nm)	264

4.2 Precursors

A 70 % (w/w) nitric acid (HNO₃) and 99% (w/w) sodium hydroxide (NaOH) purchased from Riedel de Haen were used at concentration of 0.5 M for pH adjustment. For heavy metals determination tests, a standard solution containing CrCl₂.6H₂O, Cu(NO₃)₂.5H₂O and FeCl₃ obtained from Riedel de Haen, Germany were used as sources for Cr⁺² and Cu⁺² and iron. A calibration curve was constructed between 0 and 20 ppm, by using prescribed standard solutions. A KHP purchased from Sigma Aldrich, Germany, used to prepare a COD calibration curve. A 97 % (w/w) ethyl acetate and methanol, and a 70 % (w/w) HCl purchased from Frutarom Ltd. “Israel”, a 99 % (w/w) sodium sulphate (Na₂SO₄) and 97 % 3,4 dihydroxy benzoic acid purchased from Sigma Aldrich, Germany used for poly phenols determination test. A 99 % KOH purchased from Sigma Aldrich, Germany used for BOD₅ test.

4.3 OMW Characterization and Adsorption Measurement

The following devices and instrument were used during this research to characterize and measure the contaminants concentration in OMW samples and adsorption parameters.

4.3.1 UV-VIS Spectrophotometer

UV-VIS Spectrophotometer for detecting phenol concentration and COD test (UV-2550) manufactured by Labomed. Inc. U.S.A. A range of wavelength between 200 and 1100 nm was covered. Distilled water was used as a blank during the UV measurements. All measurements were carried out using quartz cells 10-mm width at room temperature.

4.3.2 Digital Reactor Block (DRB) for Chemical Oxygen Demand (COD) Measurements

COD measurements were performed following the USEPA method (USEPA, 1990) using (Digital Reactor Block DRB 2000, HACH[®], U.S.A). COD sample was prepared by adding 2 ml of OMW sample to a 16 mm (HH/21259-51) mid. range (0-1500 mg O₂/L) vials from HACH containing 65% (w/w) of H₂SO₄, HgSO₄ and K₂CrO₇. Then the solution vial was transferred to the DRB instrument for 2 h at 150 °C for COD monitoring. Deionized water was used as a blank in this test.

4.3.3 pH, Electrical Conductivity and Density Meter

A pH meter (3310) and electrical conductivity meter (4310) manufactured by Jenway, UK, (Densito 30PX) manufactured by Mettler Toledo, Italy were used to measure the pH, electrical conductivity and density of solutions respectively.

4.3.4 Biochemical Oxygen Demand (BOD) Test Bottles

A BOD test bottles of 500 mL volume (DSB 620T manufactured by WTW[®], Germany) were used to determine the BOD of OMW sample.

4.3.5 Kjeldahl Distillation Unit

Kjeldahl distillation unit model (DNB-1500) were used to determine the total Kjeldahl nitrogen (TKN) manufactured by Raypa[®], Spain.

4.3.6 Atomic Absorption Spectrometer

AA measurements were performed using (iCE 3400, Thermo Fisher Scientific, U.S.A) atomic absorption unit for heavy metals detecting Fe⁺², Cr⁺² and Cu⁺² using standard solutions purchased from Riedel de Haen, Germany.

4.3.7 Flame Photometer

A PFP7 flame photometer manufactured by Jenway, UK, was used to determine the concentration of Na⁺, Ca⁺² and K⁺ ions in OMW.

4.3.8 Balance, Oven and Magnet

Electronic balance (ABS/ABJ-SH-e-0921) Version 2.1 manufactured by KERN, Germany used for weighing the iron nanoparticles. Heating oven manufactured by Ary J. Levy Company,

“Israel” were used to dry the samples for the TDS and TSS tests, and a simple kitchen magnet was used for separation of nanoparticles from the OMW samples after adsorption.

4.3.9 Rotary Evaporator

RE300 rotary evaporator manufactured by Stuart, United Kingdom was used in the determination of poly phenols.

4.3.10 Water Bath Shaker

A JSSB-50T water bath shaker manufactured by JSR Inc. North Korea was used to keep up a specified temperature with shaking.

4.4 Experimental Procedure

This section introduces the experimental procedure and methodology of this project, which is divided into two parts, the first one is OMW part and the second is OMW model molecule (phenol).

4.4.1 Application of Nanoparticles on OMW Model Molecule (Phenol)

Batch-mode adsorption method was employed in this study by exposing a specified dried mass of nanoparticles to an aqueous solution containing a certain concentration of phenol, unless otherwise specified. Then, the mixture was shaken for a certain time at 25 °C. In all experiments, the γ -Fe₂O₃ nanoparticles containing adsorbed phenol were separated from the mixture by a magnet and the supernatant was decanted. Figure 4.1 shows a photograph presenting the separation of nanoparticles after adsorption from wastewater by a simple magnet.



Figure 4.1: Separation of γ -Fe₂O₃ nanoparticles from OMW sample by a magnet. Photo taken by Laith Arar in March 2014

The residual concentration of phenol in the solution was measured by UV-vis spectrophotometry. Concentration of phenol was measured at the specified wavelength (λ_{max}). A calibration curve of UV-vis absorbance at same wavelengths against the phenol concentration was established (Appendix A), using prepared standard model solutions with known concentrations (i.e., 0, 5, 12.5, 25, 35 ppm). UV-vis spectra of phenol in solution were selected on the basis of the absorption linearity range. The adsorbed amount of phenol (mg of phenol/g of nanoparticles) was determined by the mass balance in Equation 4.1:

$$Q = \frac{C_0 - C}{m} V \quad (4.1)$$

where C_0 is the initial concentration of phenol in the solution (mg/L), C is the final concentration of phenol in the supernatant (mg/L), V is the solution volume (L), and m is the dry mass of γ -Fe₂O₃ nanoparticles (g). For equilibrium data, C_e replaces C , and Q_e replaces Q in Equation 4.1.

4.4.2 Application of Nanoparticles for OMW Treatment

4.4.2.1 Stability Test

The obtained OMW sample was placed in a sealed container in an incubator at 21°C and was monitored at different times for 24 hours. Different parameters were measured before and after sedimentation process which are: COD, TOC, BOD₅, TSS, EC, TDS and density.

4.4.2.2 Batch-Mode Application

Batch-mode adsorption method was employed in this study by exposing a specified dried mass of nanoparticles to an aqueous solution containing a certain concentration of OMW contaminants, unless otherwise specified. Then, the mixture was shaken for a certain time at 25 °C. In all experiments, the γ -Fe₂O₃ nanoparticles containing adsorbed OMW contaminants were separated from the mixture by a magnet and the supernatant was decanted.

The initial and residual concentration of contaminants in OMW was measured by COD test via UV-vis spectrophotometry. A COD calibration curve established (Appendix A) by Potassium hydrogen phthalate (KHP) standard (HOOC₆H₄COOK) which crushed slightly and then dried to a constant weight at 110 °C, then 425 mg of KHP dissolved into distilled water and diluted to 1000 ml. This solution has a theoretical COD (ASTM, 1995) of 500 mg O₂/L. Different solutions concentrations were prepared and the calibration curve was established on the basis of the absorption linearity range. The maximum wavelength for COD test is 620 nm (ASTM, 1995).

The adsorbed amount of OMW contaminants (mg of OMW contaminants/g of nanoparticles) was determined by the mass balance in Equation 4.2:

$$Q = \frac{COD_0 - COD}{m} V \quad (4.2)$$

where COD₀ is the initial chemical oxygen demand of OMW contaminants in the solution (mg O₂/L), COD is the final chemical oxygen demand of OMW contaminants in the supernatant (mg O₂/L), V is the solution volume (L), and m is the dry mass of γ -Fe₂O₃ nanoparticles (g). For equilibrium data, COD_e replaces COD, and Q_e replaces Q in Equation 4.2.

4.4.2.3 Packed Bed Column for Decolourization of OMW

A combination of 10 g of fine sand particles mixed with 1 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles placed into a 50 cm height glass column with diameter of 1 cm. The mixture supported with cotton and 2 cm height of pure sand as seen in Figure 4.2.



Figure 4.2: Packed bed column of sand/iron oxide nanoparticles used for decolourization of OMW effluent. Photo taken by Laith Arar in March 2014

The flow rate was adjusted to be 0.03 L/h by maintaining a constant level of OMW effluent in the bed. Different samples were taken during 4 hour time intervals and the color change was noted.

4.4.3 Effect of Contact Time

Typically, time-dependent adsorption process is conducted by exposing a certain amount of nanoadsorbents to a solution containing a specified concentration of pollutant for fixed preselected time intervals. In this study, for OMW model molecule (phenol), 0.05 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were added to 5 ml aqueous solution containing a 100 ppm concentration of phenol at 25 °C and a pH equal to 7.4. The mixture was shaken for 180 minutes, unless otherwise noted. To determine the adsorption equilibrium time required for saturation, samples were selected at different times during the 180 minutes and analyzed for phenol concentration.

In a similar manner, for OMW, 0.1 g of γ -Fe₂O₃ nanoparticles were added to a 5 ml aqueous solution 100 times diluted (i.e. specified COD) at 25 °C and a pH equal to 3. The mixture was shaken for 90 minutes, unless otherwise noted. To determine the adsorption equilibrium time required for saturation, samples were selected at different times during the 90 minutes and analyzed for phenol concentration.

4.4.4 Effect of Solution pH

For pH-dependent studies, OMW model (phenol) and OMW adsorption pH experiments were conducted at 25 °C for a mixing time of 24 h for a pH range of 2 to 12. To adjust the pH of the solution, HNO₃ or NaOH, were used.

4.4.5 Isotherm Study

4.4.5.1 OMW Model Molecule (Phenol) Isotherm

For isotherm experiment, 0.05 g of γ -Fe₂O₃ nanoparticles were added to a set of 5 ml test tubes containing different concentration ranged from 0 to 400 ppm at a pH equal to 7.4 and at temperature of 25 °C. The mixture was left shaking for 24 h. After that, nanoparticles with adsorbed phenol were separated by magnet and the supernatant was decanted. The adsorbed amount of phenol (mg phenol/g of nanoparticles) was determined by the mass balance in Equation 4.1.

4.4.5.2 OMW Isotherms

In a similar manner, for OMW, 0.1 g of γ -Fe₂O₃ nanoparticles were added to a set of 5 ml test tubes containing different concentration (i.e. dilution) ranged from 100 to 3200 times dilution at different pH values (i.e. 3, 7, 11) and at temperature of 25 °C. The mixture was left shaking for 24 h. After that, nanoparticles with adsorbed OMW contaminants were separated by magnet and the supernatant was decanted. The adsorbed amount of OMW contaminants (mg OMW contaminants/g of nanoparticles) was determined by the mass balance in Equation (4.1) and then three isotherms at different pH values were established.

Another isotherm experiment was conducted by adding 0.05 g of γ -Fe₂O₃ nanoparticles to a 10 ml solution containing different concentrations of methylene blue dye (MB) (i.e. 0, 2, 3, 8, 15, 36, 89, 143, 256, 633 ppm). The mixture was left shaking for 24 h at a pH value equal to 9 and at temperature of 25 °C. After that, nanoparticles with adsorbed methylene blue dye were separated

by magnet and the supernatant was decanted, and then the sample was transferred to the oven and dried. The adsorbed amount of methylene blue dyes (mg MB dyes/g of nanoparticles) was determined by the mass balance in Equation 4.1.

After that, 0.05 g of methylene blue coated γ -Fe₂O₃ nanoparticles were added to a set of 5 ml test tubes containing different concentration (i.e. dilution) ranged from 100 to 3200 times dilution at pH equal to 9 and at temperature of 25 °C. The mixture was left shaking for 24 h. After that, nanoparticles with adsorbed OMW contaminants and methylene blue were separated by magnet and the supernatant was decanted. The adsorbed amount of OMW contaminants (mg OMW contaminants/g of MB coated γ -Fe₂O₃ nanoparticles) was determined by the mass balance in Equation 4.2.

4.4.6 Coexistent Contaminants

As wastewater effluent contains more than one pollutant, the presence of other pollutants may interfere in the removal efficiency of an individual one. As a result, the effect of coexisting pollutants should be addressed when conducting an adsorption study. This test should give us good expression about the nature of the particles surface, and if it can effect on the adsorption itself.

OMW have been tested by several methods (i.e. A.A, flame photometer) and the removal of heavy metals and free ions such as: Cu⁺², Cr⁺², iron, Na⁺, Ca⁺², K⁺ was determined.

4.4.7 Removal of Poly Phenols

10 ml of diluted OMW was treated with 0.1 g of γ -Fe₂O₃ nanoparticles and the supernatant was decanted. 1 ml of decanted OMW was diluted to 100 ml distilled water. The sample was acidified up to pH=2 with HCl and then extraction with 20 ml ethyl acetate at 25°C three times was done. The sample was dried by contact with 2 g sodium sulphate crystals for 30 to 40 min. The ethyl acetate left in the extract was vaporized in a rotary evaporator and the residual solution was mixed with 50 ml of a mixture of water/methanol 40/60 volumetric ratio, respectively (Garcia, et al., 2000). The final solution was a liquid which contained all the phenolic compounds of the olive mill wastewater. For measuring total polyphenol, the sample extracted by ethyl acetate was measured by a spectrophotometer at 725 nm and by using a standard curve for 3,4 dihydroxy benzoic acid, total polyphenol could be determined (Box, 1983).

CHAPTER FIVE

MODELING

This chapter introduces the mathematical models employed in this study and the evaluation of their performance in describing the adsorption kinetics and isotherms studies of OMW and OMW model molecule (phenol).

5.1 Adsorption Kinetics

Adsorption kinetics is one of the important factors that represent the efficiency of the adsorption process. Modeling of the adsorption kinetics was achieved using Lagergren pseudo first-order model in equation (5.1) (Ho, 2004) and pseudo-second-order modeling equation (5.2) (Ho & McKay, 1998).

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (5.1)$$

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (5.2)$$

where Q_e and Q_t are the amount of pollutant adsorbed onto the nanoadsorbents (mg/g) at equilibrium and at any time, t (min), respectively, and K_1 and K_2 are the equilibrium rate constants of first order and second order adsorption, respectively.

Nonlinear Chi-square analyses were conducted for comparing the best-fit-model, using Equation 5.3 (Montgomery & Runger, 2006):

$$\chi^2 = \sum \frac{(Q_e - Q_{emodel})^2}{Q_{emodel}} \quad (5.3)$$

where Q_e and Q_{emodel} are the adsorbed amount of contaminants obtained experimentally and by model fitting, respectively. The lower value of χ^2 the better for fitting.

5.2 Adsorption Isotherms

Adsorption isotherms are common models that compare adsorbent surface properties and their adsorption capacity of pollutants. Several adsorption models are available for interpreting the adsorption equilibrium data (Langmuir, 1916; Freundlich, 1906). In this study, the shapes of

adsorption isotherms were fitted to Langmuir and Brunauer-Emmet-Teller (BET) and adsorption models.

5.2.1 Langmuir Adsorption Model

Langmuir adsorption isotherm is one of the most commonly used model (Langmuir, 1916). Equation 5.5 expresses the Langmuir adsorption isotherm linearly.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \quad (5.5)$$

where Q_e is the amount of pollutant adsorbed onto the nanoadsorbents (mg/g), C_e is the equilibrium concentration of pollutant in solution (mg/L), K_L (L/mg) and Q_{max} (mg/g) are Langmuir constants. K_L is the equilibrium adsorption constant related to the affinity of binding sites, and Q_{max} is the monolayer saturation capacity, representing the maximum amount of pollutant adsorbed per unit weight of nanoadsorbents for complete monolayer coverage (mg/g). Again, χ^2 analyses (Equation 5.3) were also employed for finding the goodness of fittings.

5.2.2 Brunauer-Emmet-Teller Adsorption Model (BET)

The BET model has been widely used to correlate adsorption isotherm experimental data (Teller, et al., 1938). This model describes the multilayer adsorption phenomena for gas-solid equilibrium systems and liquid-solid systems (Ebadi, et al., 2009; Wang, et al., 1998). The BET model can be expressed as follows:

$$q = q_{max} \frac{K_S C_E}{(1 - K_L C_E)(1 - K_L C_E + K_S C_E)} \quad (5.4)$$

where q is the amount of contaminants (mg/g) adsorbed at equilibrium; q_{max} the maximum adsorption capacity (mg/g); C_E the equilibrium concentration of contaminants in the aqueous phase (mg/L); and K_S (L/mg) and K_L (L/mg) are the equilibrium constants of adsorption for the first layer and the upper layers, respectively.

CHAPTER SIX

RESULTS AND DISCUSSION

This chapter presents the results of all experiments of OMW and model molecule. The obtained data were fit to the BET adsorption isotherm and the kinetic data were modeled using first pseudo order and second order models.

6.1 Model Molecule (Phenol)

In this section, the results pertaining to the effect of experimental and operation conditions on the adsorptive removal of model molecule by $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles are presented.

6.1.1 Effect of Contact Time (Phenol Adsorption Kinetics)

Adsorption kinetics is one of the important factors that represent the efficiency of the adsorption process. Figure 6.1 shows the change in the amount adsorbed of model molecule as a function of contact time.

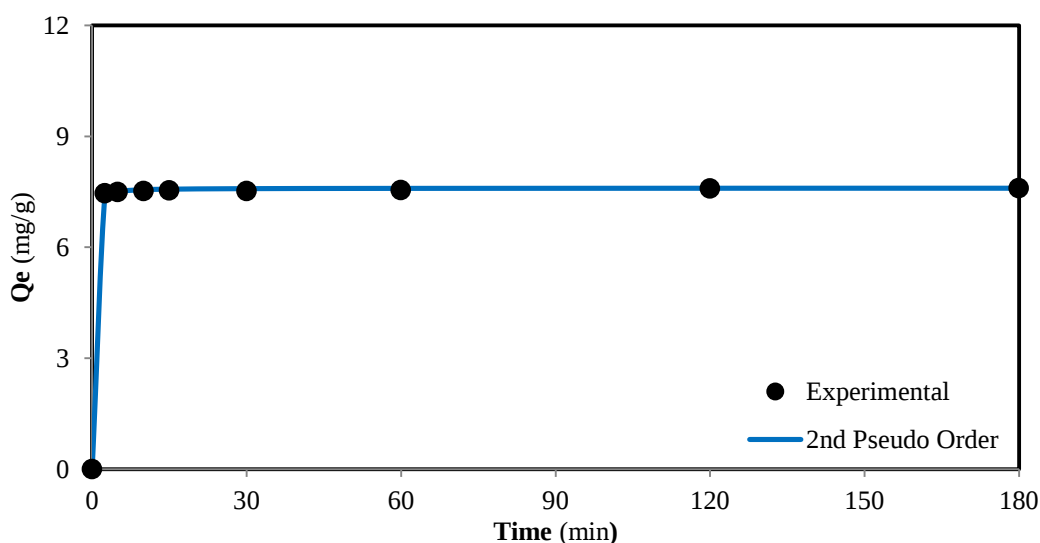


Figure 6.1: Effect of contact time on the adsorptive removal of phenol. Points are experiments, line is second-pseudo-order in Equation (5.2). Other experimental conditions are $T = 298\text{ K}$, $\text{pH} = 7.4$, shaking rate = 300 rpm and $C_0 = 100\text{ ppm}$

As seen, in all cases, adsorption of phenol was fast, as adsorption equilibrium was reached within 10 minutes or less. This is not surprising as the selected nanoparticles are nonporous. Therefore,

one would anticipate that external adsorption is dominant and no intraparticle diffusion is available to retard the adsorption rate (Nassar, 2010; Nassar & Ringsred, 2012). Unlike the classical adsorbents such as activated carbon and activated alumina, where adsorption equilibrium time could take days (Crittenden, 2005). This is illustrated schematically in Figure 6.2, which shows a schematic representation for adsorption mechanism of X molecules onto different surfaces of adsorbents. Clearly, there will be more mass transfer resistances for the case of porous adsorbent in comparison of non-porous nanoparticles.

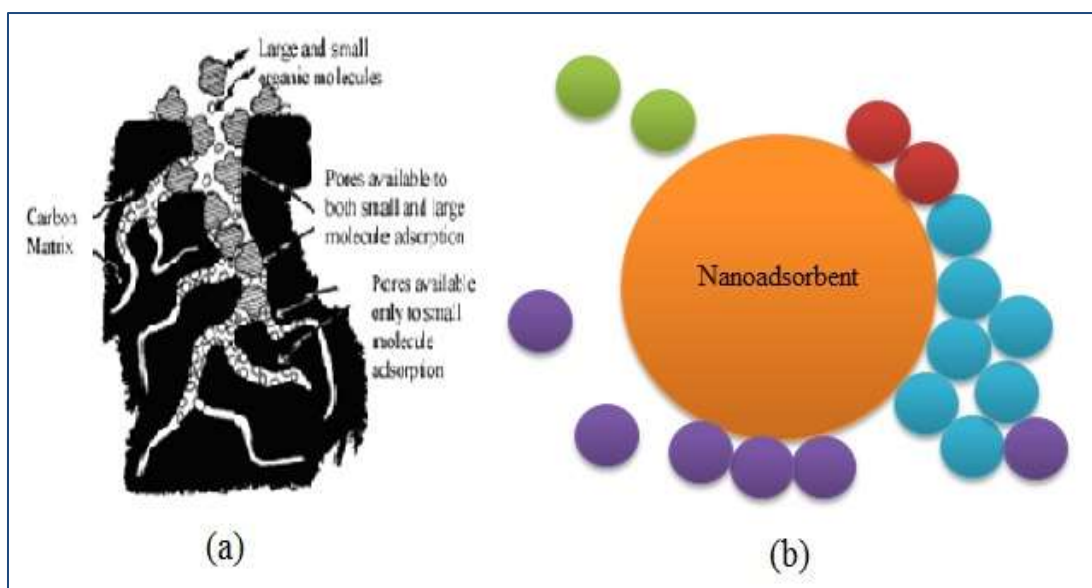


Figure 6.2: Schematic representation of adsorption mechanism of organic molecules onto different surfaces of adsorbents; (a) activated carbon and (b) nanoadsorbents

To further investigate the kinetic mechanism that controls the adsorption process, the experimental data were fitted to the Lagergren pseudo-first-order model (Ho, 2004) and pseudo-second-order model (Ho & McKay, 1998) presented previously in Equations 5.1 and 5.2; respectively. Table 6.1 shows the estimated kinetic parameters pertaining to the two models as obtained by the Excel solver.

Table 6.1: Estimated Effect of contact time on the adsorption removal of model molecule by γ -Fe₂O₃ nanoparticles. Pseudo-first- order model fit and pseudo-second-order model fit. Other experimental parameters are T= 298K, pH = 7.4, shaking rate = 300 rpm and Co = 100 ppm

	Pseudo-first-order			Pseudo-second-order		
$Q_{e,exp}$ (mg/g)	Q_e (mg/g)	K_1 (min)	χ^2	Q_e (mg/g)	K_2 (g/mg.min)	χ^2
7.6000	7.6038	1.6023	0.0043	7.5976	2.333	0.0013

As shown in Figure 6.1 , and on the basis of chi values presented in Table 6.1, both models fit well to the experimental data with the pseudo-second-order model being the best fit for the model molecule. This suggests that, owing to good degree of mixing and extent dispersion of nanoparticles, adsorption is only affected by two mechanisms; first, rapid adsorption due to electrostatic attraction followed by slow adsorption due to complication of the phenol model molecule with the adsorbed phenol on the nanoparticle surface (Nassar & Ringsred, 2012). It is worth noting here that the estimated theoretical values of Q_e (i.e., by the kinetic model) were in excellent agreement with the ones obtained experimentally, as seen in Table 6.1.

6.1.2 Effect of pH

The adsorption of polar or charged organic contaminants by iron oxide nanoadsorbent depends significantly on the electrostatic interactions between the nanoadsorbent surface and the contaminants (Nassar, 2012). These interactions are influenced mainly by the pH of the solution, provided that it directly affects the surface charge of the nanoparticles (Nassar, 2012; Shaw, 1992). Figure 6.3 shows the effect of pH on the adsorptive removal of phenol from water by γ -Fe₂O₃ nanoparticles.

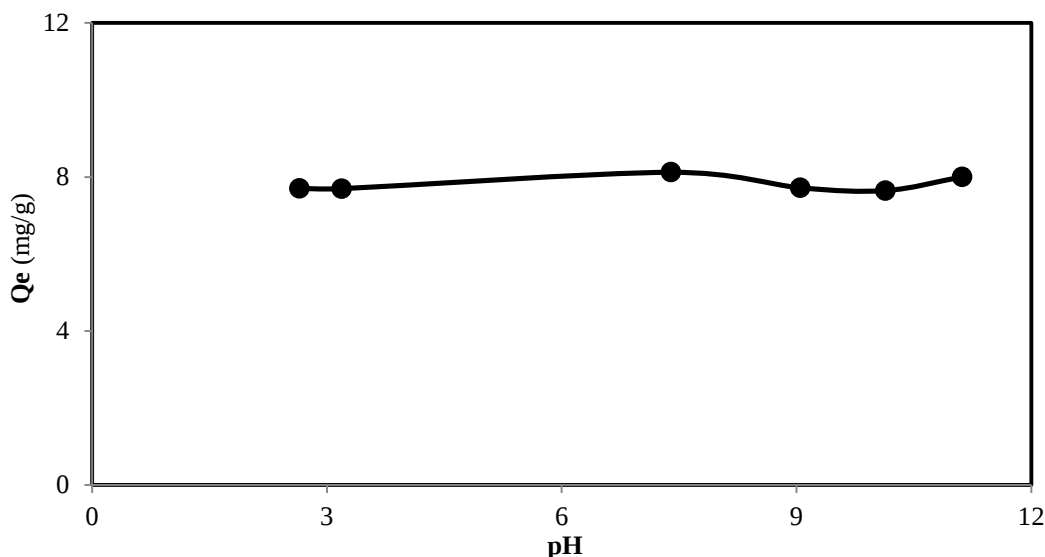


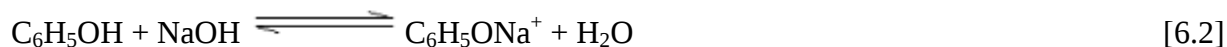
Figure 6.3: Effect of pH on the adsorptive removal of model molecule from water by γ -Fe₂O₃ nanoparticles at initial concentration of 100 ppm. Nanoparticle dose = 0.1 g per 10 mL, T = 298 K, mixing time 24 h

As shown in Figure 6.3, the maximum value of Q_e is 8.12 (mg/g) at pH equal to 8.12 and the minimum value is 7.65 (mg/g) at pH equal to 10.14. It can be clearly seen that the removal of phenol from water is independent of pH. In fact, this is not surprising as the point of zero charge (pH_{pzc}) of iron oxide particle is around 7.5 (Balistrieri & Murray, 1981) (Nassar & Ringsred, 2012). Therefore, at a pH higher than pH_{pzc} , the nanoadsorbent surface is negatively charged attracting cations, whereas at a lower pH, the surface is positively charged attracting anions.

Phenol is a weak acid, contain an -OH group, a hydrogen ion can break away from the -OH group and transfer to a base. In water, as shown in Reaction 6.1, hydrogen atom leaves the molecule to form H_3O^+ and a phenoxide ion which is negatively charged. When the media is acidic (i.e. high H^+ concentration) the phenoxide molecules would prefer to attach to the positive surface of nanoadsorbents (Clifford & Luis, 1979).



In the other hand, in a basic media containing strong base like NaOH, phenol react will according to Reaction 6.2 to form sodium phenoxide which is positively charged and it would prefer attaching a negatively charged surface (Clifford & Luis, 1979).



6.1.3 Adsorption Isotherm

Adsorption isotherms are common models that compare adsorbent surface properties and their adsorption capacity of pollutants. Figure 6.4 shows the adsorption isotherm of phenol by $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

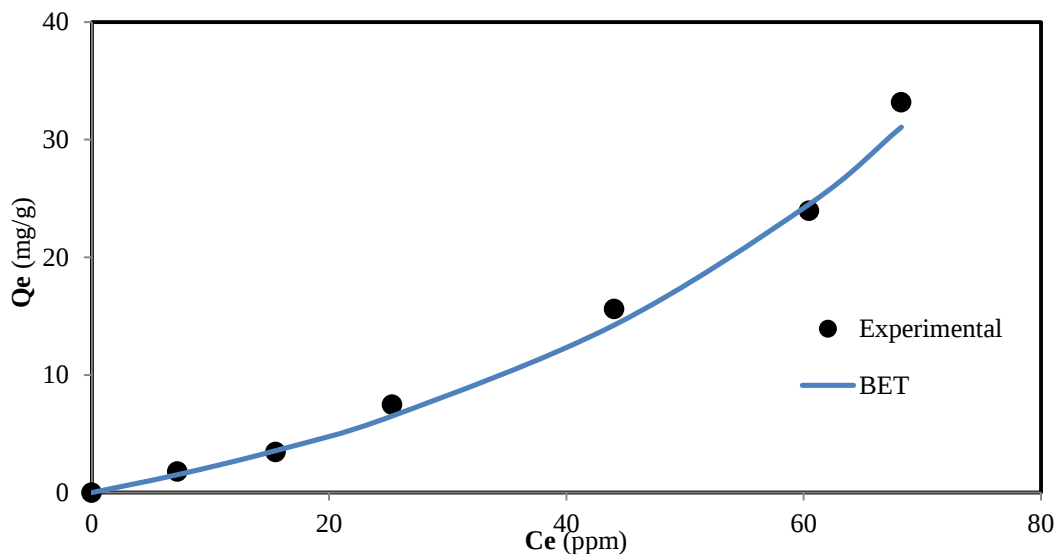


Figure 6.4: Adsorption isotherm of model molecule by $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Points are experiments and solid line is the fitting to BET model. Other experimental parameters are: $T=298\text{K}$, $\text{pH}=7.4$, mixing time is 24 h

As shown in Figure 6.4, it is clear that the value of Q_e increases exponentially with the equilibrium concentration. This type of adsorption corresponds to Type III adsorption isotherm behavior according to IUPAC. This type is characteristic of system with low affinity between the surface and the adsorbent. This will lead to the formation of multilayer of phenol on the nanoparticle surface, mainly at high concentrations.

Accordingly, the BET model was used to describe the experimental data of adsorption isotherms. The estimated model parameters are listed in Table 6.2. Based on chi value and as seen in Figure 6.4, the BET showed a good fit to the experimental data which confirms the multilayer adsorption mechanism. For deep understanding, Table 6.2 shows the obtained values of BET model parameters.

Table 6.2: BET isotherm parameters obtained from the fitting of experimental data in Figure 6.4

K_l (L/mg)	K_s (L/mg)	q_{max} (mg/g)	χ^2
0.00509	7.60×10^{-5}	2564	0.4264

6.2 Application of Nanoparticles to Real OMW Sample

In this section, the results pertaining to the effect of experimental and operation conditions on the adsorptive removal of OMW contaminants by γ -Fe₂O₃ nanoparticles are presented.

6.2.1 Stability Test (Effect of Sedimentation)

Before running any adsorption test, the OMW sample was stored at 21 °C in a sealed container in an incubator and allowed to settle down. The following photographs were taken at different times for a period of 36 hour to investigate the phase behavior.



Figure 6.5: Photographs taken at different time for a selected OMW sample for a period of 36 h. Photographs taken by Laith Arar in October 2013

As seen in Figure 6.5, the fresh OMW sample was initially completely turbid and homogeneous. After 12 hours it start to separate into two phases, the upper layer which is mainly the supernatant, and the lower layer which contain sludge, dirt and suspended solids. After 24 hours, the sample was completely stable and separated into two clear layers. Then, the two layers were remains unchanged after 36 hours. Hence, the sedimentation time needed is concluded to be 24 hours to obtain a very clear supernatant.

Several important parameters of concern had been measured and the sample was characterized before and after the sedimentation process. Table 6.3 lists the obtained parameters.

Table 6.3: Effect of sedimentation on the characteristics of OMW sample

	Mother Solution	Supernatant
pH	5.04	
COD (mgO ₂ /L)	153×10 ³	89×10 ³
TOC (mgO ₂ /L)	57.5×10 ³	33.5×10 ³
BOD₅ (mgO ₂ /L)	71.4×10 ³	52.8×10 ³
Density (kg/m ³)	974	961
TSS (mg/L)	57.2×10 ³	1.3×10 ³
TDS (mg/L)	51×10 ³	35×10 ³
EC mS/cm	8.29	9.22

As seen in Table 6.3, the pH of the sample is slightly acidic due to presence of high phenolic compounds and carboxylic acids concentration which is categorized as a weak acid. COD value was very high as seen. The reduction in the COD value by sedimentation is approximately 40%. Also, the reduction in the BOD₅ value was approximately 21 %. TOC was calculated according to the relation $COD = 2.66 TOC$ (Kiely, 1997).

Finally, as the amount of suspended solid decrease by approximately 98%, the density of the solution decreased a little bit as it become more concentrated and also the electro-conductivity increased due to the increase in free ions in the solution.

6.2.2 Effect of Contact Time (Adsorption Kinetics)

Figure 6.6 shows the change in the amount adsorbed of OMW contaminants as a function of contact time at different initial COD concentrations.

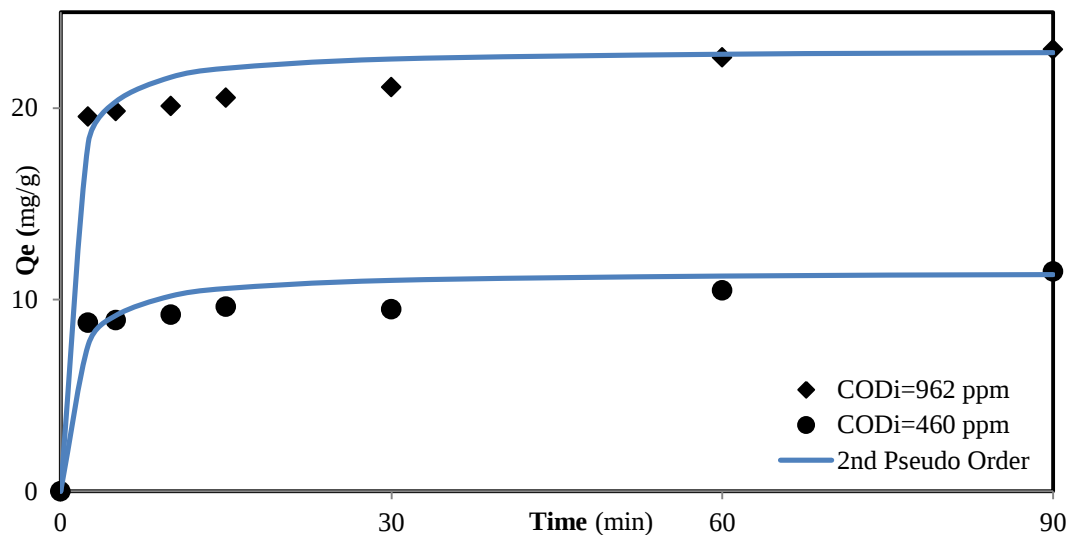


Figure 6.6: Effect of contact time on the adsorptive removal of OMW contaminants. Points are experiments at two different initial COD value; solid line is second-pseudo-order model in Equation (5.2). Other experimental conditions are $T = 298\text{ K}$, $\text{pH} = 3$, shaking rate = 300 rpm

As seen, in both cases, the adsorption was fast, as adsorption equilibrium was reached within 30 minutes or less. Again, this is not surprising as the selected nanoparticles are nonporous. Therefore, one would anticipate that external adsorption is dominant and no intraparticle diffusion is available to retard the adsorption rate (Nassar, 2010; Nassar & Ringsred, 2012) where adsorption equilibrium time could take days (Crittenden, 2005).

Again, the experimental data were fitted to the Lagergren pseudo-first-order model (Ho, 2004) and pseudo-second-order model (Ho & McKay, 1998) presented previously in Equations 5.1 and 5.2, respectively. Table 6.4 shows the estimated kinetic parameters at different initial concentration pertaining to the two models as obtained by the Excel solver.

Table 6.4: Estimated effect of contact time on the adsorption removal of OMW contaminants by γ -Fe₂O₃ nanoparticles at different initial concentrations. Pseudo-first- order model fit and pseudo-second-order model fit. Other experimental parameters are T= 298K, pH = 3, shaking rate = 300 rpm

	CODi (mg O₂/L)	962	460
	$Q_{e,exp}$ (mg/g)	23.1	11.5
Pseudo-first-order	Q_e (mg/g)	23.06	11.47
	K_1 (min)	12.5098	17.7959
	χ^2	0.7513	0.8286
	Q_e (mg/g)	23.1	11.5
Pseudo-second-order	K_2 (g/mg.min)	0.0646	0.0698
	χ^2	0.4408	0.6462

As shown in Figure 6.6 , and on the basis of chi values presented in Table 6.4, both models fit well to the experimental data with the pseudo-second-order model being the best fit for the OMW contaminants. Again, this suggests that OMW contaminants are transported due to electrostatic attraction to the external surface of the nanoparticle through film diffusion within a very short time followed by slow complication adsorption (Nassar & Ringsred, 2012). It is worth noting here that the estimated theoretical values of Q_e (i.e., by the kinetic model) were in excellent agreement with the ones obtained experimentally, as seen in Table 6.3.

6.2.3 Effect of pH

As prescribed in section 6.1.2, the adsorption of polar or charged organic contaminants by iron oxide nanoadsorbent depends significantly on the electrostatic interactions between the nanoadsorbent surface and the contaminants (Nassar, 2012). These interactions are influenced mainly by the pH of the solution. Figure 6.7 shows the effect of pH on the adsorption of OMW contaminants by γ -Fe₂O₃ nanoparticles.

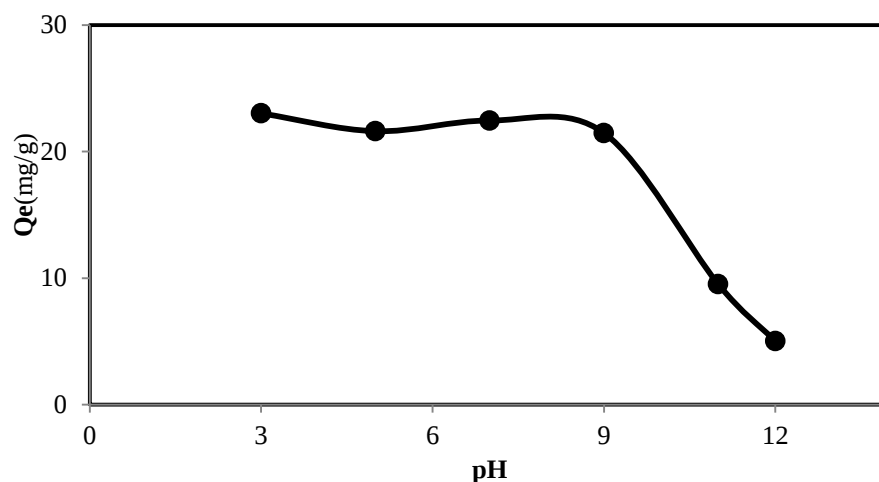


Figure 6.7: Effect of pH on the adsorptive removal of OMW contaminants by $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles at initial concentration $\text{COD}_i = 978 \text{ mg O}_2/\text{L}$. Nanoparticle dose = 0.2 g per 10 mL, $T = 298 \text{ K}$, mixing time 24 h

As seen in Figure 6.7, the maximum value of Q_e take place at a pH equal 3. Taking the experimental error in consideration, there is no significant effect of pH value on the adsorption starting from a pH of 3 up to a pH of 9. In fact, this result is expected and not far away from the simulation theory with phenol model molecule. This indicates that OMW, which contain a plenty contaminant, has a considerable extent of negatively charged molecules that is more favorable by the major adsorbate than the nanoadsorbents surface which would be negatively charged in a basic media (i.e. $\text{pH} \geq 7.5$), as mentioned before.

6.2.4 Adsorption Isotherms

Figure 6.8 shows the adsorption isotherms of OMW contaminants onto $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles at temperature of 25°C and different pH values of 3, 7 and 11 and with MB dyes.

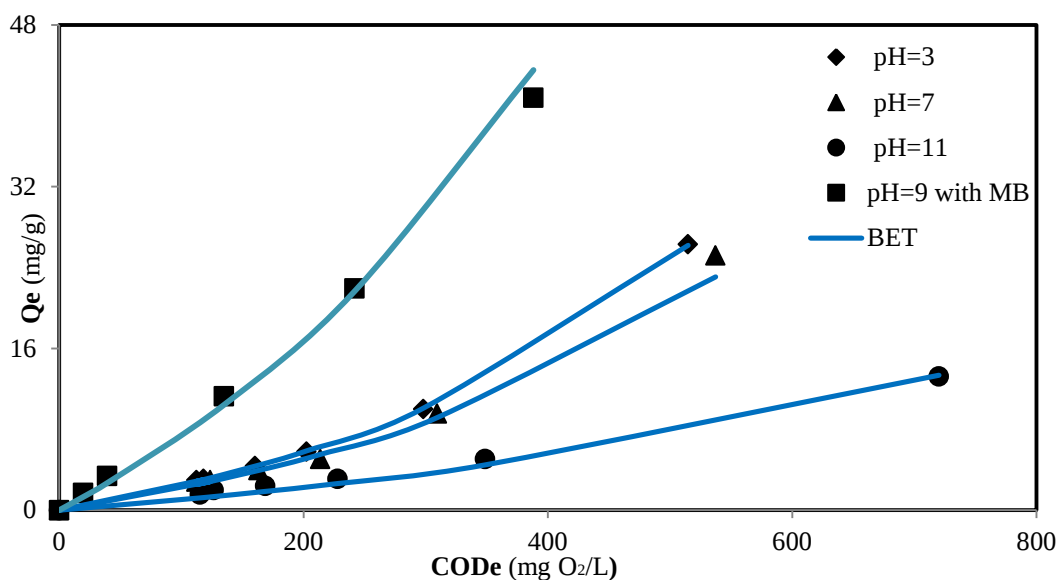


Figure 6.8: Adsorption isotherm of OMW contaminants by γ -Fe₂O₃ nanoparticles. Points are experiments at different values of pH, blue line is the fitting to BET model. Other experimental parameters are: T=298K, mixing time is 24 hr.

Again, the BET model fit well to the experimental data. The estimated fitted model parameters are listed in Table 6.5. As seen, adsorption isotherm is strongly dependent on pH and exhibited Type III behavior. This confirms the multilayer formation. As shown in the figure, the isotherm shifts to the left as the pH decreased, suggesting that the amount adsorbed increases in the acidic medium.

Table 6.5: BET isotherm parameters obtained from the fitting of experimental data in Figure 6.8 at different pH values

pH	K_l (L/mg)	K_s (L/mg)	q_{max} (mg/g)	χ^2
3	0.0008	0.0002	100	0.0094
7	0.0007	0.0002	98	0.2649
11	0.0004	0.0001	96	0.5274
9 with MB	0.0008	0.0004	165	0.4689

To further enhance the adsorption process, the nanoparticles were functionalized by methylene blue dyes. Figure 6.9 shows the adsorption isotherm of methylene blue onto γ -Fe₂O₃ nanoparticles.

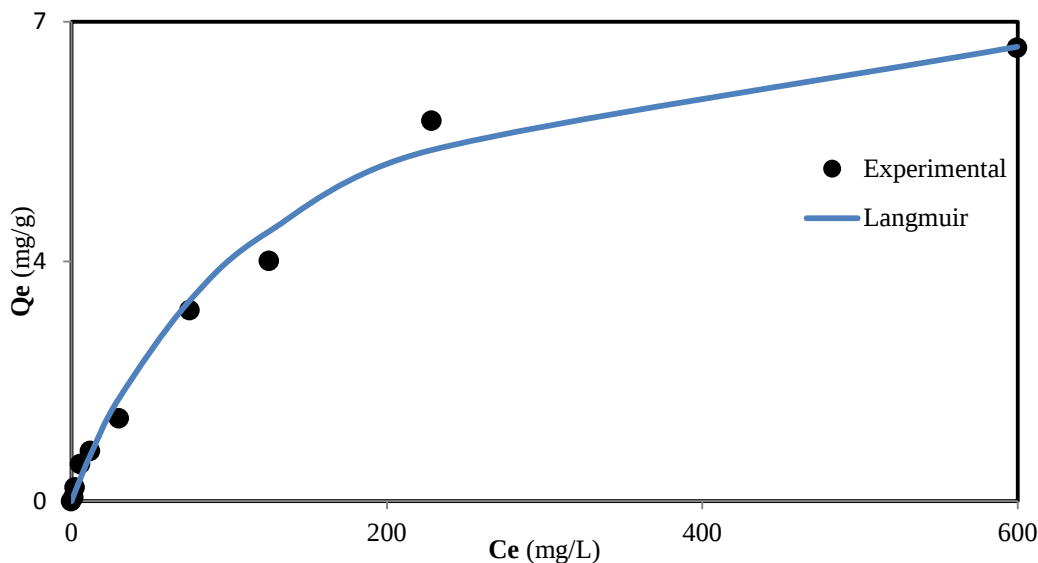


Figure 6.9: Adsorption isotherm of methylene blue dyes onto $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Points are experiments; solid line is the fitting to Langmuir model. Other experimental parameters are: pH=9, T=298K, mixing time is 24 h

As seen in Figure 6.9, and on the basis of the values in Table 6.6, the adsorption of methylene blue fits well to the Langmuir adsorption isotherm, which confirms the monolayer adsorption. Subsequently, functionalized $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with methylene blue dyes were exposed to OMW sample at different concentrations as seen in Figure 6.8, in the presence of MB, the adsorption isotherm curve was further shifted to the left, suggesting an increase in adsorption.

Table 6.6: Langmuir isotherm parameters obtained from the fitting of experimental data in Figure 6.9

$K_L(\text{L/mg})$	$Q_{max}(\text{mg/g})$	$Q_{model}(\text{mg/g})$	$Q_{e,exp}(\text{mg/g})$	χ^2
0.00755	8.0966	6.6324	6.6193	0.3386

The estimated values of q_{max} followed the order MB at $\text{pH}_9 > \text{pH}_3 > \text{pH}_7 > \text{pH}_{11}$. Consequently, K_l values followed the same order, suggesting that the adsorption affinity increases and the multilayer adsorption affected by MB molecule and solution pH.

6.2.5 Effect of Coexistent Contaminants

OMW contain a huge extent of various pollutants that may interfere in the removal efficiency of an individual one. As a result, the effect of coexisting pollutants should be addressed when conducting an adsorption study. This test should give us a good expression about the nature of the particles surface, and if it can effect on the adsorption itself. An OMW sample has been

tested for heavy metals and free ions contents before and after adsorption. Results are listed in Table 6.7.

Table 6.7: Result of OMW heavy metals and free ions contents before and after adsorption. The dosage of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles is 0.1 g per 10 ml sample. Other experimental parameters are: T=298K, pH=3, mixing time is 24 h

	OMW Supernatant	Treated OMW	% Removal
Iron (mg/L)	41.51	8.36	79.86
Cr⁺² (mg/L)	4.89	1.37	71.98
Cu⁺² (mg/L)	8.23	3.78	54.07
K⁺ (mg/L)	10162	5120	49.62
Ca⁺² (mg/L)	1520	850	44.08
Na⁺ (mg/L)	2213	805	63.62

As seen in Table 6.7, the adsorption was associated to the removal of many components efficiently. The removal of free ions ranged from 44 % of Ca^{+2} ions to approximately 64% of Na^{+} ions. While the removal of heavy metals was higher and ranged from 54 % of Cu^{+2} ions to approximately 80% of iron ions. This indicates that the nanoadsorbents surface is highly attractive to a large extent of OMW contaminants and multi adsorption would occur.

6.2.6 Packed Bed Column Decolourization of OMW

Phenolic compounds (i.e. phenol and poly phenols) are believed to be the coloring agent of OMW since it recorded to be the major pollutant contaminant (Ugurlu & Kula, 2007). Figure 6.10 shows a set of different samples obtained at different times from the packed bed column.



Figure 6.10: A photograph of a set of different samples obtained at different times from a packed bed column of a combination of 10 g of fine sand particles mixed with 1 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The height of the packing is 12 cm and the flow rate is 0.03 L/h. Other experimental parameters are: $T=298\text{K}$, $\text{pH}=3$. Photo taken by Laith Arar in March 2014

In this set of experiments, the time zero was considered after the first drop of water come out the packed bed column. As seen in Figure 6.10, the first sample at time $t=0$ is obviously very clear and colorless and more close to the pure water, After 30 min, the color becomes slightly pale yellow, and then after 60, 180 and 240 min it become obvious that the color become pale yellow; but it is very far in color comparing with the original sample. This is looking promising since the saturation time where the ratio C_e/C_i (ratio of exit concentration over initial concentration) will take a longer time to approach 1.

Due to lack of adequate measurement devices, one batch sample of supernatant with a volume of 10 ml of diluted OMW was treated with 0.1 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, and the removal of poly phenols was determined. Figure 6.11 and 6.12 shows the treated sample and the result of poly phenols removal test, respectively.



Figure 6.11: The change in color of a 10 ml 50 times diluted OMW sample treated with 0.1 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The sample to the right is the original sample before treatment. The sample to the left is the treated sample. Other experimental parameters are: $T=298\text{K}$, $\text{pH}=3$, mixing time 24 hr. Photo taken by Laith Arar in March 2014.

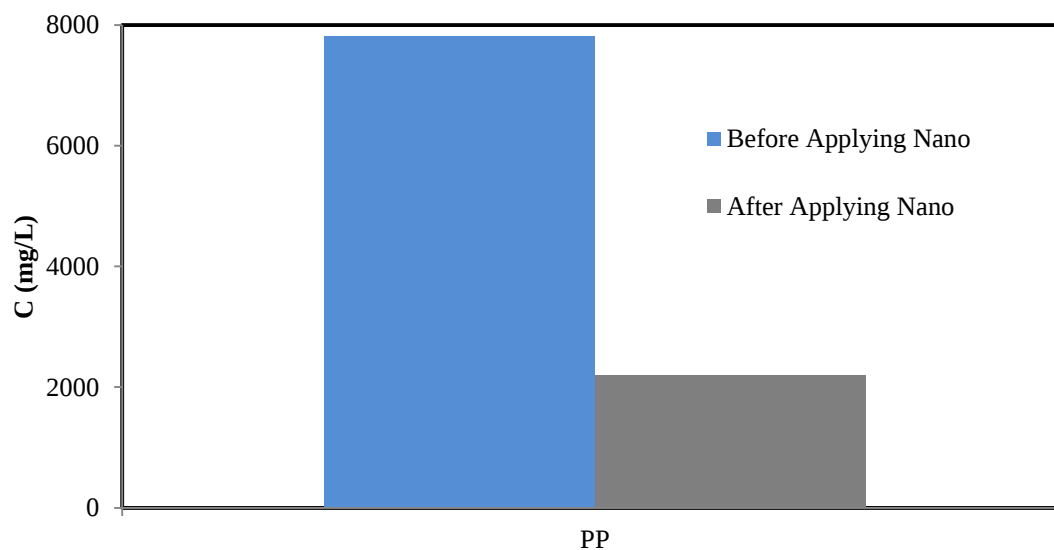


Figure 6.12: Adsorptive removal of poly phenols from a 10 ml 50 times diluted OMW sample treated with 0.1 g of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Other experimental parameters are: $T=298\text{K}$, $\text{pH}=3$, mixing time 24 h

As seen in Figure 6.12, the concentration of poly phenols in the original sample was 7800 mg/L, after treatment it becomes 2200 mg/L which mean that the removal is approximately 72%. This was for a batch sample shown in Figure 6.12. According to that and based on the photograph in Figure 6.12 and 6.11, it is expected to have a higher percentage removal of poly phenols in the packed bed column (i.e., continuous process). This would be very clear by comparing the treated sample in Figure 6.10 with those in Figure 6.11.

CHAPTER SEVEN

PRELIMINARY PROCESS DESIGN AND COST ESTIMATION OF NANOTECHNOLOGY APPLICATION IN OMW TREATMENT

This chapter introduces brief process design and cost estimation for applying nanoparticle technology in OMW treatment facilities.

7.1 Effluent Flow Rate

As reported in literature, 1 to 1.8 m³ of OMW is generated for every ton of olive fruit pressed (El-Gohary, et al., 2009). Thus, as the majority of olive presses in Palestine and worldwide working in a capacity of 3 tons of olive per hour, the estimated generation of OMW is approximately 3-5.4 m³/h (i.e., 72-130 m³/day). However, these numbers are affected by many factors, such as operating time, type of olive, type of olive presses, etc. Anyhow, 80 m³/h as effluent flow rate is safe to consider in this study.

7.2 Process Description

Figure 7.1 shows the typical block flow diagram of the suggested in-situ OMW treatment station.

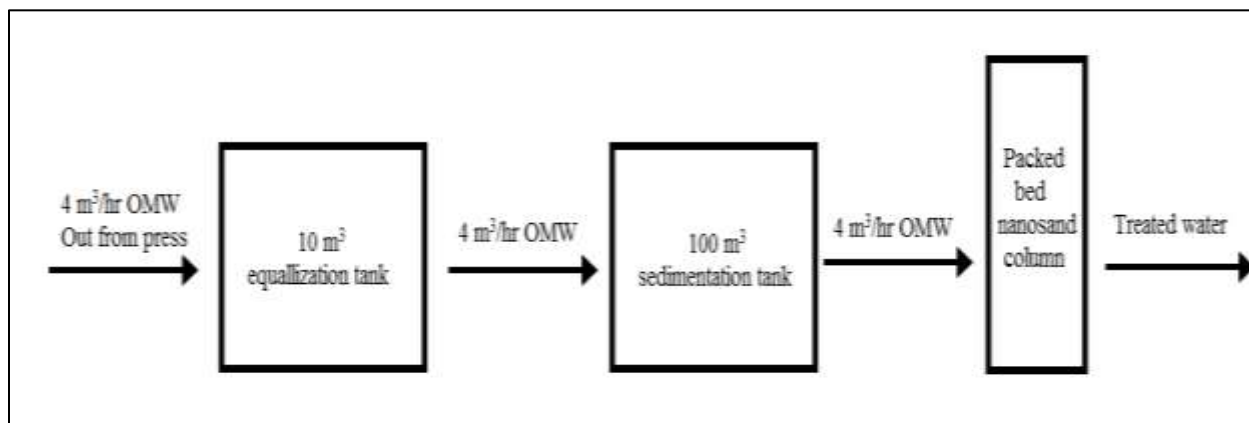


Figure 7.1: Block flow diagram of in-situ OMW treatment station

As seen, OMW effluent leaves the press to enter an equalization tank which is used to adjust the process conditions (e.g., pH, flow rate, concentration, etc.) to meet the treatment requirement. Then, the effluent leaves to enter a sedimentation tank for a residence time of 24 hours to allow big particles to settle down. Finally, the supernatant is withdrawn and pressurized to enter a

packed bed column that combines fine sand particles (i.e., less than 0.1 mm) with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

7.3 Equipments and Process Requirements

Figure 7.2 shows the process flow diagram of the in-situ OMW treatment station.

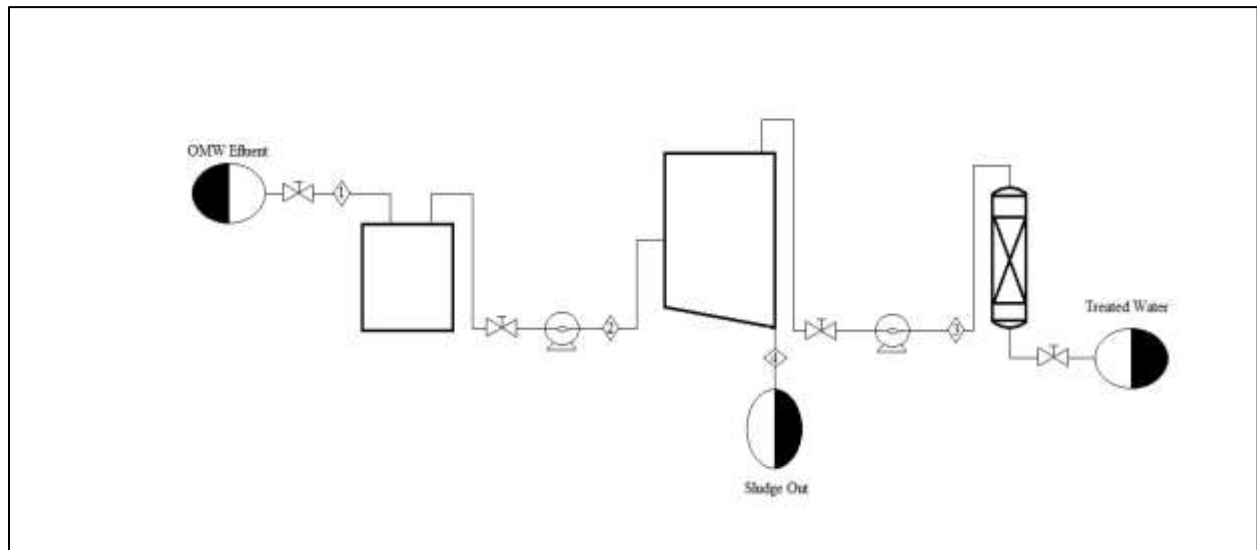


Figure 7.2: Process flow diagram of the in-situ OMW treatment station

As seen, three main equipment are used, which are mainly the equalization tank, inclined sedimentation tank and the nano-sand column. The other equipment are four manual gate valves and two centrifugal pumps. Table 7.1 shows the flow summary of the considered process. Details of each equipment is given below.

Table 7.1: Flow summary table of the considered process

Stream number	1	2	3
Temperature ($^{\circ}\text{C}$)	25 - 30	25	25
Volumetric flow rate (m^3/h)	3 - 4	4	4

7.3.1 Equalization Tank

The equalization tank is used mainly to regulate the flow and hold the effluent when the system is shutdown. Figure 7.3 shows the suggested design of equalization tank.

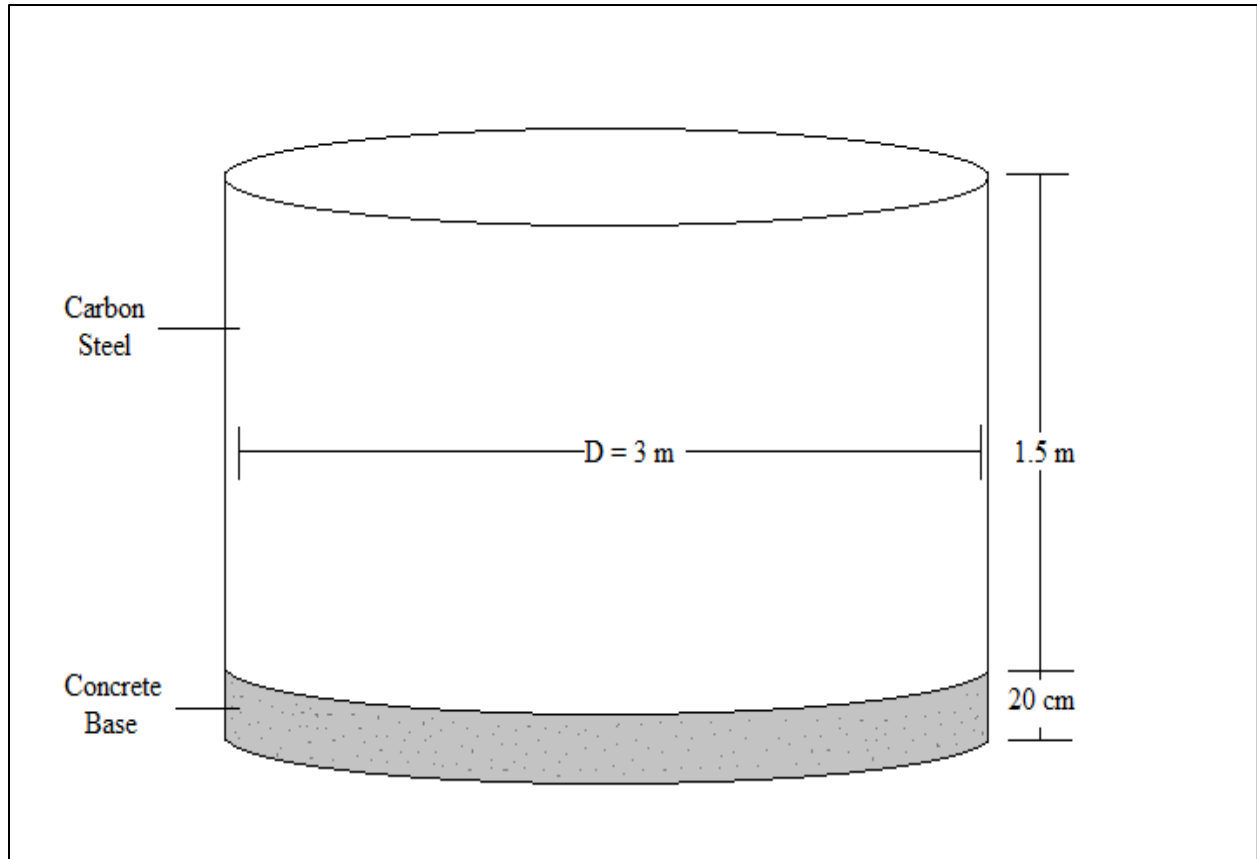


Figure 7.3: Equalization tank design

As seen, the shape of the tank is circular and constructed from carbon steel with dimensions of 3 m diameter and 1.5 m height. The tank is carried by a reinforced concrete base with 20 cm height.

7.3.2 Inclined Sedimentation Tank

The inclined sedimentation tank is used to hold the effluent to settle down and it allows withdrawing the sludge from the bottom of the tank through a manual gate. The tank is made of carbon steel and the total volume of the tank is 80 m^3 and the height is 4.1 m. Figure 7.4 shows the suggested design of inclined sedimentation tank.

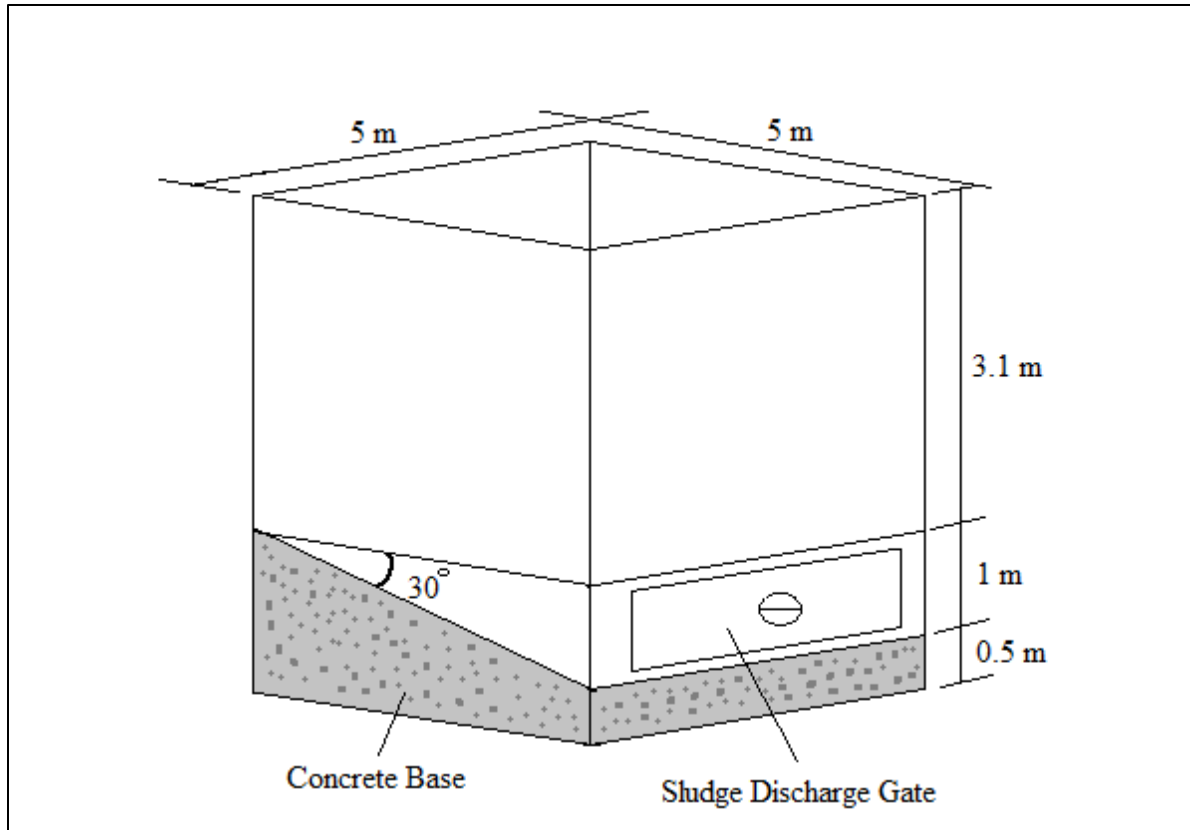


Figure 7.4: Inclined sedimentation tank design

As seen, the tank is inclined by 30° angle for self-cleaning and sludge removal. The total height of the rectangular tank is 4.1 m with a cross sectional area of 25 m^2 and total volume of 80 m^3 . The bottom of the tank hold a manual sludge discharge gate. The tank is carried by a concrete base ranged from 0.5 m from the inclined side to 1.5 m from the other side.

7.3.3 Nano-Sand Packed Bed Column

Sand filtration is the most common classical treatment technique in wastewater treatment. In this study, sand filtration is combined with nanoparticles adsorption in a packed bed column. Figure 7.5 shows the specifications of the nano-sand packed bed column.

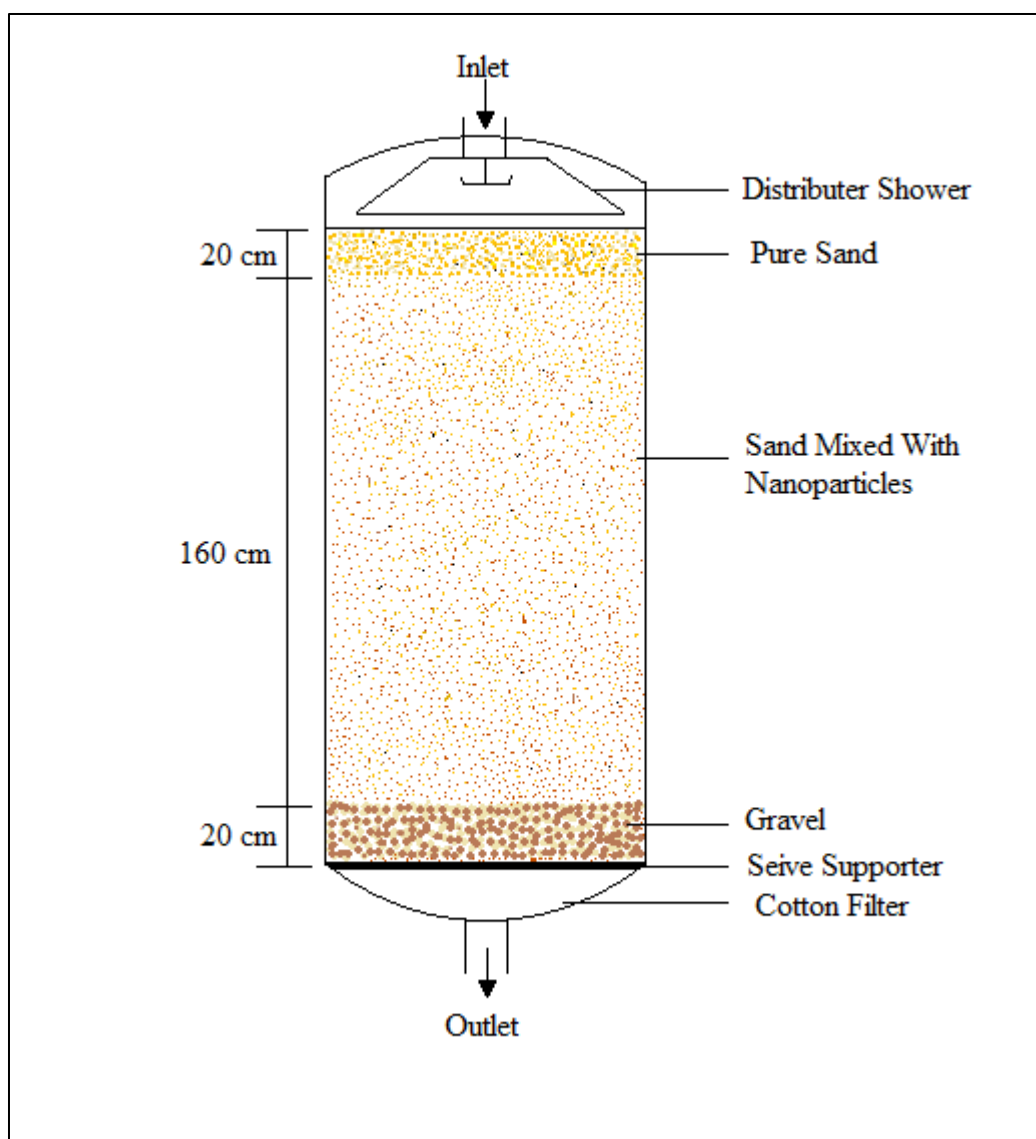


Figure 7.5: Nano-sand packed bed column design

As seen, the effluent enters the tower by a shower distributor to distribute the effluent and prevent channelling. The first layer is a virgin sand layer with a diameter less than 0.1 mm and the total height of the layer is 20 cm. The middle layer consists from the same type of sand mixed with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in a percentage of 10 % (w/w) (nanoparticles/sand). The total height of the middle layer is 160 cm. The lower layer is a gravel supporter with average diameter of 2 cm. The total height of the lower layer is 20 cm. Finally, the bottom of the tower is filled with a cotton layer in order to prevent the escape of nanoparticles or sand with the treated water out from the tower. The construction material of the bed is carbon steel and the bed is supported by a concrete base of 1 m height.

7.3.4 Piping System

The first important element in the piping system is the pumps. In this study, two centrifugal pump are selected to meet the process requirments. The selection and calculation of the pumps specefication are shown in section 7.4.5.

The total length of the pipes need is estimated to be 30 m of high density poly ethylene (HDPE). The four valves are manual gate valves.

7.4 Cost Estimation

The estimation of the process cost is based on the process requirments, types of construction materials, operating time and pressure drops. The capital cost of the project includes all the costs of construction materials, labor and installation, while the operating cost includes the cost of electricity only. As a preliminary estimation, the following assumptions are stated before calculating the capital cost:

- The average production of OMW is 4 m³/h.
- The average operating time is 20 h/day, because the operating time varies during the season.
- Olive pressing season runs 4 months yearly starting from mid-September and ending by the middle of January.
- The project lifetime is 15 years.
- 1 USD is equal to 3.5 New Israeli Shekel (NIS or ₪).
- The properties of OMW is the same as that for water at 25°C.
- Cost of labor and instalation are 10 % of total cost.
- Cost of materials fabrication is 15 % of raw materials cost.
- Cost of 1 KW electricity is 0.16 USD.
- Attainment is 92.5 %.
- Cost of one cubic meter of reinforced concrete is 172 USD.

7.4.1 Theory

This section introduces the main equations used in tank design and loss calculations.

7.4.1.1 Tanks Calculations

STEP 1: Finding the volume of the liquid in the equalization tank

$$VL = (Q_{in} - Q_{out}) \times \text{attainment} \times \text{storage time} \quad (7.1)$$

where; V_L : volume of the liquid in the tank (m^3)

Q_{in} : flow rate enters the tank (m^3/day)

Q_{out} : flow rate leaves the tank (m^3/day)

Working time: 7 days

Attainment: 92.5%

STEP 2: Finding the height of liquid in the tank

$$V_L = \frac{\pi}{4} \times D_i^2 \times H_L \quad (7.2)$$

where; V_L : volume of the liquid in the tank (m^3)

D_i : internal diameter of the tank (m)

H_L : height of liquid in the tank (m)

STEP 3: Finding the diameter of the tank

For mixing tanks

$$H_L = D_i \quad (7.3)$$

For non-mixing tanks

$$H_L = 2D_i \quad (7.4)$$

STEP 4: Finding the height of the tank

$$H_T = H_L + \frac{H_L}{3} \quad (7.5)$$

where; H_T : height of the tank (m)

STEP 5: Finding the bar pressure of the liquid in the tank

$$P_i = \rho \times g \times H_L \quad (7.6)$$

where; P_i : internal pressure of the liquid in the tank (Pa)

ρ : density of the liquid in the tank (Kg/m³)

g : standard acceleration of the gravity (9.81 m/s²)

STEP 6: Finding the thickness of the tank

$$t = \frac{P_i D_i}{2\sigma - P_i} \quad (7.7)$$

where; t : thickness of the tank wall (m)

D_i : internal diameter of the tank (m)

σ : maximum allowable stress of the steel (Pa)

STEP 7: Finding the thickness with corrosion allowance

$$t_{total} = t + CA \quad (7.8)$$

where; t_{total} : total thickness of the tank wall (m)

CA : corrosion allowance of steel (0.002 m)

STEP 8: Finding the external diameter of the tank

$$D_0 = D_i + 2t_{total} \quad (7.9)$$

where; D_0 : external diameter of the tank (m)

STEP 9: Finding the surface area of the tank

$$A_T = 2 \times \left(\frac{\pi}{4} D_0^2\right) + \pi D_0 H_T \quad (7.10)$$

where; A_T : surface area of the tank (m²)

STEP 10: Finding the total number of steel sheets required

$$No. Of sheets = \frac{A_T}{A_{sh}} \times \frac{t_T}{t_{sheet}} \quad (7.11)$$

where; A_{sh} : area of one sheet (m²) = 2 m²

t_T : thickness of the tank (m)

t_{sheet} : thickness of one steel sheet (m)

STEP 11: Finding the welding length vertically

$$L_V = H_T \left(\frac{\pi D_i}{3}\right) \quad (7.12)$$

where; L : total length of welding vertically (m)

STEP 12: Finding the welding length horizontally

$$L_H = \pi D_i \left(\frac{H_T}{1.5}\right) \quad (7.13)$$

STEP 13: Finding the number of welding tube

$$No. of welding tubes = \frac{L_H + L_V}{distance\ welded\ by\ one\ tube} \quad (7.14)$$

where; distance welded by one tube = 0.1 m

STEP 14: Finding the volume of concrete base

$$V_B = \left(\frac{\pi}{4} D_0^2\right) \times H_B \quad (7.15)$$

where; V_B : volume of the base (m³)

H_B : height of the base (m)

STEP 15: Finding the total cost of the tank

$$\text{Total cost} = \text{cost of steel sheets} + \text{cost of bases} + \text{cost of welding} + \text{installation cost} \quad (7.16)$$

where; total cost in New Israeli Shekel (₪)

Installation cost = 30 % from capital cost (₪)

7.4.1.2 Loss Calculations

STEP 1: Finding the internal diameter of the pipe

$$D_i = D_0 - 2 \left(\frac{D_0}{11} \right) \quad (7.17)$$

where; D_i : internal diameter of the pipe (m)

D_0 : external diameter of the pipe (m)

STEP 2: Finding the cross sectional area of the pipe

$$A = \frac{\pi D_i^2}{4} \quad (7.18)$$

where; A: cross sectional area of the pipe (m²)

STEP 3: Finding the velocity inside the pipe

$$v = \frac{Q}{A} \quad (7.19)$$

where; v: velocity inside the pipe (m/s)

Q: volumetric flow rate (m³/s)

STEP 4: Finding Reynolds number of the liquid

$$R_e = \frac{\rho \times V \times D_i}{\mu} \quad (7.20)$$

where; R_e : Reynolds number

ρ : density of the liquid (Kg/m³)

μ : viscosity of the liquid (Pa.s)

STEP 5: Finding the friction factor for turbulent flow

$$f = \frac{0.25}{\left[\left(\log \left(\frac{1}{3.7 \left(\frac{D}{\epsilon} \right)} + \frac{6.74}{(Re)^{0.9}} \right) \right) \right]^2} \quad (7.21)$$

where; f : friction factor

ϵ : roughness of the pipe

STEP 6: Finding the major loss in the pipe

$$h_{L \text{ major}} = f \times \frac{L}{D} \times \frac{V^2}{2g} \quad (7.22)$$

where; h_L : major loss inside the pipe

L : length of the pipe

g : standard acceleration of gravity (9.81 m/s²)

STEP 7: Finding the friction factor for fittings and valves for turbulent flow

$$f_T = \left(\frac{1}{2 \times \left(\log \left(3.7 \left(\frac{D}{\epsilon} \right) \right) \right)} \right)^2 \quad (7.23)$$

where; f_T : friction factor for fittings and valves

STEP 8: Finding the resistance coefficient

$$K = \left(\frac{L}{D} \right) \times f_T \quad (7.24)$$

where; K : resistance coefficient

STEP 9: Finding the minor losses

$$h_{L \text{ minor}} = K \times \left(\frac{V^2}{2g} \right) \quad (7.25)$$

STEP 10: Finding the total head loss

$$h_L \text{ total} = h_L \text{ minor} + h_L \text{ major} \quad (7.26)$$

STEP 11: Finding the head added by applying general energy equation

$$\left(\frac{P_1}{\gamma}\right) + \left(\frac{v_1^2}{2g}\right) + Z_1 - h_l + h_A = \left(\frac{P_2}{\gamma}\right) + \left(\frac{v_2^2}{2g}\right) + Z_2 \quad (7.27)$$

where; P_1 : pressure at point 1 (Pa)

P_2 : pressure at point 2 (Pa)

γ : specific weight (KN/m³)

V_1 : velocity at point 1 (m/s)

V_2 : velocity at point 2 (m/s)

h_A : head added to the pump (m)

STEP 12: Finding the output power of the pump

$$P = Q \times \gamma \times h_A \quad (7.28)$$

where; P : output power of the pump (W)

Q : volumetric flow rate (m³/s)

STEP 13: Finding the input power of the pump

$$P_{in} = \frac{P_{out}}{\epsilon} \quad (7.29)$$

where; P_{in} : input power of the pump (W)

ϵ : efficiency of the pump

STEP 14: Determining the annual operating cost

$$AOC = P_{in} \times \text{attainment} \times \text{operating time} \times \text{cost of electricity} \quad (7.30)$$

where; AOC : annual operating cost (₹/year)

Attainment (mostly 90 – 95%)

STEP 15: Determining the total capital cost

$$TCC = \text{cost of pipes} + \text{cost of fittings and valves} + \text{installation cost} \quad (7.31)$$

where; TCC: total capital cost (₪)

STEP 16: Determining the annual capital cost

$$ACC = \frac{TCC}{N} \quad (7.32)$$

where; ACC: annual capital cost (₪/year)

N: project life (year)

STEP 17: Determining the total annual cost

$$TAC = AOC + ACC \quad (7.33)$$

where; TAC: total annual cost (₪/year)

7.4.2 Cost of Equalization Tank

As described before, the equalization tank is 10 m³ volume with a diameter of 1.5 m and 3 m height. Table 7.2 shows the cost estimation of the equalization tank.

Table 7.2: Calculations of equalization tank cost

Volume of the tank (m³)	10
Internal diameter (m)	3
Height (m)	1.5
Pressure inside tank (KPa)	14.715
Thickness (m)	163×10 ⁻⁶
Total thickness (with corrosion allowance) (m)	2160×10 ⁻⁶
External diameter (m)	3.0043
Total surface area (m²)	28.32
Weight of steel needed (Kg)	459.5
Cost of steel +15% manufacturing (USD)	528
Dimensions of ready steel sheets (m)	2m×1m
Welding length vertically (m)	4.71
Welding length Horizontally (m)	9.42
Number of welding tubes	141.3

Cost of one welding tube (USD)	0.286
Cost of welding (USD)	40
Thickness of concrete base (m)	0.2
Volume of concrete base (m³)	1.4171
Cost of 1 m³ reinforced concrete (USD)	172
Total cost of concrete base (USD)	243
Installation cost (10% of total cost) (USD)	81
Total cost of equalization tank (USD)	893

As seen in Table 7.2, the corrosion allowance is 2 cm, and the cost of steel needed is estimated by calculating the mass of the raw steel and adding 15 % manufacturing cost. The cost of reinforced concrete is roughly estimated by the help of civil engineering experts. Finally, the total cost of equalization tank is 893 USD.

7.4.3 Cost of Inclined Sedimentation Tank

As shown in Figure 7.4, the inclined sedimentation tank is 80 m³ volume with a dimensions of 4.1 m height from the inclined side and 3.1 m from the normal side and with a 5 m length and width each. Table 7.3 shows the cost estimation of the equalization tank.

Table 7.3: Calculations of inclined sedimentation tank

Volume of tank (m³)	80
Dimensions of steel sheet (m)	1m×2m
Pressure (KPa)	40.221
Thickness (m)	745×10 ⁻⁶
Total thickness (with corrosion allowance) (m)	2745×10 ⁻⁶
Surface area (m²)	125
Weight of steel needed (Kg)	2573
Cost of steel +15% manufacturing (USD)	2960
Dimensions of steel sheets (m)	2×1
Total length of welding (m)	170
Number of welding tubes	1700
Cost of welding (USD)	486
Volume of concrete base (m³)	31.25
Cost of 1 m³ reinforced concrete (USD)	172
Total cost of concrete base (USD)	5357
Installation cost (10% of total cost) (USD)	587
Total cost of sedimentation tank (USD)	9,390

As shown in Table 7.3, the corrosion allowance is 2 cm, and the cost of steel needed is estimated by calculating the mass of the raw steel and adding 15 % manufacturing cost. Finally, the total cost of the inclined sedimentation tank is 9,390 USD.

7.4.4 Cost Estimation of Nano-Sand Packed Bed Column

As described in Figure 7.5, the height of the bed is 2 m with 1 m diameter, the effluent enters the column at flow rate of 4 m³/h. Hence, to keep the continuity of the process and maintain it in steady state, the effluent exit flow rate must be fixed to be 4 m³/h. Therefore, the pressure drop must be taken into consideration and the pump power must overcome the pressure drop. Further, it is important to take the internal pressure of the packed bed in consideration to ensure a suitable wall thickness. Typically, 2 cm wall thickness of the bed is enough to ensure the safety issues. Table 7.4 shows the calculations of the packed bed column cost.

Table 7.4: Calculations of the packed bed column structure cost

Volume of tank (m³)	1.57
Internal diameter (m)	1
Height (m)	2
Dimensions of ready steel sheet (m)	1m×2m
Thickness (m)	0.002
Total thickness (with corrosion allowance) (m)	0.004
External diameter (m)	1.008
Total surface area (m²)	1.62
Weight of steel needed (Kg)	48.6
Cost of steel +15% manufacturing (USD)	56
Welding length vertically (m)	1.57
Welding length Horizontally (m)	4.186
Total length of welding (m)	5.756
Number of welding tubes	57
Cost of welding (USD)	16
Volume of concrete base (m³)	1.595
Cost of 1 m³ reinforced concrete (USD)	172
Total cost of concrete base (USD)	273
Installation cost (10% of total cost) (USD)	35
Total cost of packed bed column (USD)	381

As seen in Table 7.4, the tank cost calculation was performed in a similar manner of equalization tank. The total cost of packed bed column structure is estimated to be 381 USD.

To estimate the cost of the sand and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, quick calculations could be performed assuming that the cost of 1 ton of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles to be 700 USD and the cost of 1 ton of sand to be 50 USD, the total amount of sand needed is the packing volume of the bed multiplied by the density of sand which is approximately 1700 kg/m^3 . Hence, the total weight of sand needed is 2770 kg with a cost of 134 USD. Therefore, at a base of 10 % (w/w) (nanoparticles/sand), the amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles needed is 277 kg and its cost is 159 USD.

Finally, the pressure drop inside the packed bed is calculated using Ergun equation (Bird, et al., 2001)

$$\frac{\Delta P}{h} = \frac{-G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left(\frac{150(1-\phi)\mu}{D_p} + 1.75G \right) \quad (7.34)$$

where; P: pressure (KPa)

ϕ : porosity or void fraction

g_c : conversion factor (1)

D_p : diameter of particle in the bed (m)

μ : viscosity of fluid passing through the bed (kg/m.s)

h : length down the packed bed bed of pipe (m)

u : superficial velocity (m/s)

ρ : fluid density (kg/m^3)

G : superficial mass velocity = ρu ($\text{kg/m}^2.\text{s}$)

Assuming the porosity to be 40%, the average diameter of particles is 0.1 mm, viscosity of OMW effluent is the same as that for water at 25 °C which is $8.9 \times 10^{-4} \text{ Pa.s}$, density is 996 kg/m^3 ,

superfacial velocity is 141×10^{-6} m/s. Substituting the values in Ergun equation yields a pressure drop $\Delta P = 2,142$ KPa. The power needed is calculated to be 2.38 KW which is equal to 3.2 hp.

7.4.5 Cost of Piping System

As shown in Figure 7.2, the system contain two main pipe streams, stream number 2 which is connecting the equalization tank with the sedimentation tank, while stream number 3 connecting the sedimentation tank with the packed bed column. Table 7.5 shows the specification of stream number 2.

Table 7.5: Specification of stream number 2

Number of 90° elbows	3
Number of gate valves	1
Number of transitions	1
Le/D gate	8
Le/D 90° elbow	30
K entrance	0.5
ϵ (roughness)	0.0002
K exit	1
Length (m)	10
Q (m³/s)	0.00011
Z₁ (m)	0.7
Z₂ (m)	2

Table 7.6 shows the losses and total capital cost calculations of stream number 2.

Table 7.6: Losses and total capital cost calculations of stream number 2

DN (mm)	40
D_i (m)	0.0327
A (m²)	0.0008
v (m/s)	0.1320
D/ϵ	164
R_e	3,324
f	0.0430
f_T	0.0323
K 90° elbow	0.9690
K gate valve	0.2584

h_L 90° elbow	0.0026
h_L gate valve	0.0002
h_L entrance	0.0004
h_L exit	0.0009
h_L minor	0.0041
h_L major	2.9453
h_L total	2.9494
Z_1-Z_2 (m)	1.3
h_A	4.2485
Power (hp)	0.2587
P_{in} (kW)	0.3216
Cost of 1 m pipe (USD)	1.732
Cost of 90° elbow (USD)	4.857
Cost of gate valve (USD)	11.14
Cost of piping (USD)	17.428
Cost of transition (USD)	10
Installation cost (USD)	16
Total capital cost (USD)	53.14

As seen in Table 7.6, the total capital cost of the stream 2 is approximately 53 USD. In fact, this is not surprising, since the stream is 10 m length only. All the prices above are supplied by Palestine Plastic Industrial Company (PPIC). Table 7.7 shows the specification of the stream number 3.

Table 7.7: Specifications of stream number 3.

Number of 90° elbows	6
Number of gate valves	1
Number of transitions	1
L_e/D gate	8
L_e/D 90° elbow	30
K entrance	0.5
ϵ (roughness)	0.0002
K exit	1
Length (m)	16.6
Q (m ³ /s)	0.00011
Z_1 (m)	3.6
Z_2 (m)	3

Table 7.8 shows the losses and total capital cost calculations of stream number 3.

Table 7.8: Losses and total capital cost calculations of stream number 3

DN (mm)	40
D_i (m)	0.0327
A (m²)	0.0008
v (m/s)	0.1320
D/ϵ	164
Re	3,324
f	0.0430
f_T	0.0323
K 90° elbow	0.9690
K gate valve	0.2584
h_L 90° elbow	0.0052
h_L gate valve	0.0002
h_L entrance	0.0004
h_L exit	0.0009
h_L minor	0.0067
h_L major	2.9453
h_L total	2.9520
Z_1-Z_2 (m)	0.6
h_A	3.5511
Power (hp)	0.2162
P_{in} (kw)	0.2688
Cost of 1 m pipe (USD)	1.732
Cost of 90° elbow (USD)	4.85
Cost of gate valve (USD)	11.15
Cost of piping (USD)	28.85
Cost of transition (USD)	10
Installation cost (USD)	23.7
Total capital cost (USD)	80

As seen in Table 7.6, the total capital cost of the stream 2 is approximately 80 USD. In fact, this is not surprising, since the stream is 16.6 m length only. All the prices above are supplied by Palestine Polymer Industrial Company (PPIC).

7.4.6 Cost of Pumps

In this project, pumps are the only source of power consumption (i.e., operating cost). Table 7.8 shows the pump calculations according to process requirements.

Table 7.9: Pump calculations according to process requirements

	Pump A	Pump B
Location	Between the equalization tank and the sedimentation tank	Between the sedimentation tank and packed bed column
Type	Centrifugal	Centrifugal
Power (hp)	0.5	4
Estimated Purchase cost (USD)	130	1000
Annual operating cost (USD)	132	344

As seen in Table 7.9, the two pumps are centrifugal pumps, the first pump is 0.5 hp, while the second is 4 hp because of the huge pressure drop occurs in the packed bed column plus the losses in stream number 3.

7.5 Summary

Table 7.10 shows a summary of all cost estimation of the suggested process.

Table 7.10: Summary of the whole process cost estimation

Element	Capital Cost (USD)	Annual Operating Cost (USD/yr)
Piping system	140	-
Equalization tank	893	-
Sedimentation tank	9,390	-
Nano-sand packed bed	380	-
Pump A	130	132
Pump B	1000	344
Sand	134	-
γ-Fe₂O₃ nanoparticles	159	-
Total	12,226	476

As seen, the capital cost of the entire project is 12,226 USD, this cost is relatively very low comparing with other techniques or conventional treatment stations. Also, the annual operating cost is very low comparing to the amount of water that will be treated and the environmental benefits.

CHAPTER EIGHT

CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

This chapter presents the conclusions of this study and highlights the recommendations for future work.

8.1 Conclusions

In this work, the adsorption mechanism by magnetic nanoparticles applied on model molecule (phenol) and OMW sample were employed successfully.

8.1.1 Application of $\gamma\text{-Fe}_2\text{O}_3$ Nanoparticles on Model Molecule (Phenol)

$\gamma\text{-Fe}_2\text{O}_3$ nanoadsorbents were employed successfully on the removal of phenol from wastewater. The adsorption rate was very fast and equilibrium was achieved within times of less than 10 min. The adsorption is highly dependent on the phenol concentration, while the pH has no significant effect. The adsorption increased with increasing initial concentration. The adsorption isotherm was also determined and was appropriately described by BET adsorption model; while the kinetics was appropriately described by pseudo second-order model.

8.1.2 Application of $\gamma\text{-Fe}_2\text{O}_3$ Nanoparticles on OMW

Same type of nanoparticles was applied on the OMW obtained from a local olive press in Nablus city. Again, the adsorption rate was very fast and equilibrium was achieved within times of less than 30 min. which is slightly higher than the model molecule. We refer this to the multicomponent in the OMW which contain coexisting contaminants. The adsorption is highly dependent on the OMW contaminants concentration and pH of the solution. Where the adsorption is favored at pH lower than 9. The adsorption fit very well to the BET adsorption model. Coating the surface of nanoparticles with methylene blue dyes enhance the adsorption process.

Coexisting contaminants are associated to the adsorption process. The removal of heavy metals, free ions such as iron, Cr^{+2} , Cu^{+2} , K^+ , Ca^{+2} , Na^+ was efficient and with high percentages up to 80%. Decolourization of OMW using packed bed column combine fine sand particles with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was achieved successfully.

Finally, this study confirms that $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles could be employed as an alternative technology for the removal of OMW pollutant contaminants. This nanoparticle technology is expected to be cost-effective as nanoparticles could be employed in-situ or can be easily incorporated with the conventional treatment technology.

8.1.3 Preliminary Process Design and Cost Estimation of OMW Treatment Facility

A preliminary plant design of OMW treatment process has been demonstrated successfully. The process capital cost (CC) was estimated to be 12,226 USD, while the annual operating cost (AOC) is estimated to be 476 USD/year.

This plant is expected to treat a typical flow rate of OMW of 80 m³/day. Therefore, the plant can be easily integrated with OMW process which will favor the economic value of the whole plant, reduce fresh water consumption and enhance water recyclability.

Finally, this study will provide valuable insight on the effect of nanoparticles toward the treatment and recyclability of olive mill wastewater, which is crucial for the local olive mill industry.

8.2 Recommendations for Future Work

- Preparation of nanoparticles in-situ (i.e., in the OMW sample) could be tested. This would favor the cost-effectiveness of the process.
- Coupling the adsorption with photo-catalysis could be an interesting future study as well. This would help in getting rid of the adsorbed contaminants and regeneration of the nanoparticles.
- Testing another type of nanoparticles could be advantageous for widen the application of nanoparticles.
- Testing another types of wastewater could be advantageous for widen the application of nanoparticles and helpful in solving the environmental problems related to wastewater locally and globally.
- Running the experiments in continuous flow mode (i.e., packed bed column) could provide more valuable results and better understanding of the future application on the integration of nanoparticle technology with the conventional wastewater treatment processes.

- Studying the suggested preliminary treatment process in a pilot plant could be useful to give a more accurate prediction of scaling-up.

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APPENDICES

APPENDIX A: CALIBRATION CURVES

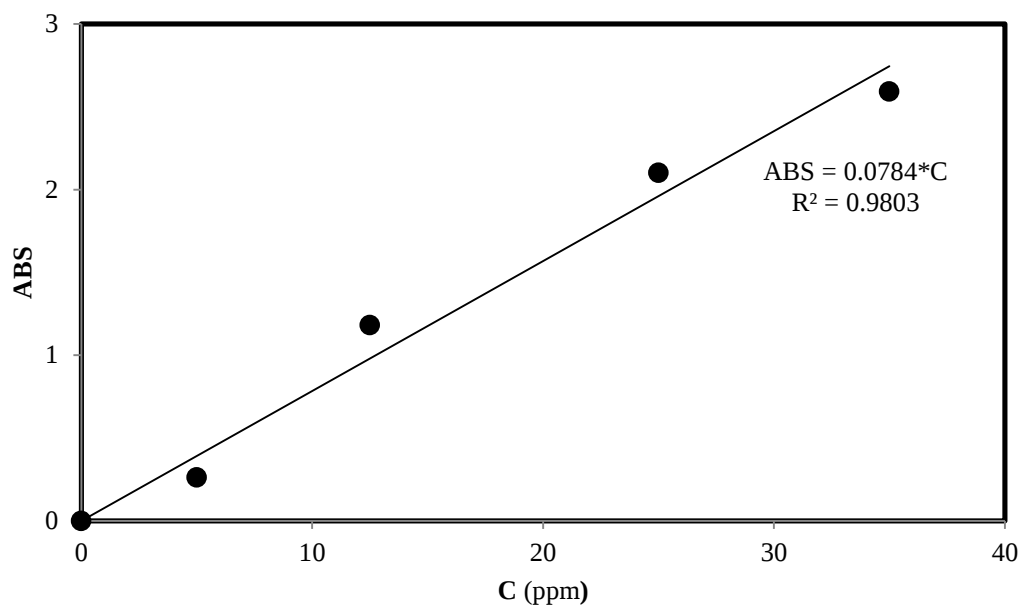


Figure A.1: Calibration curve of phenol

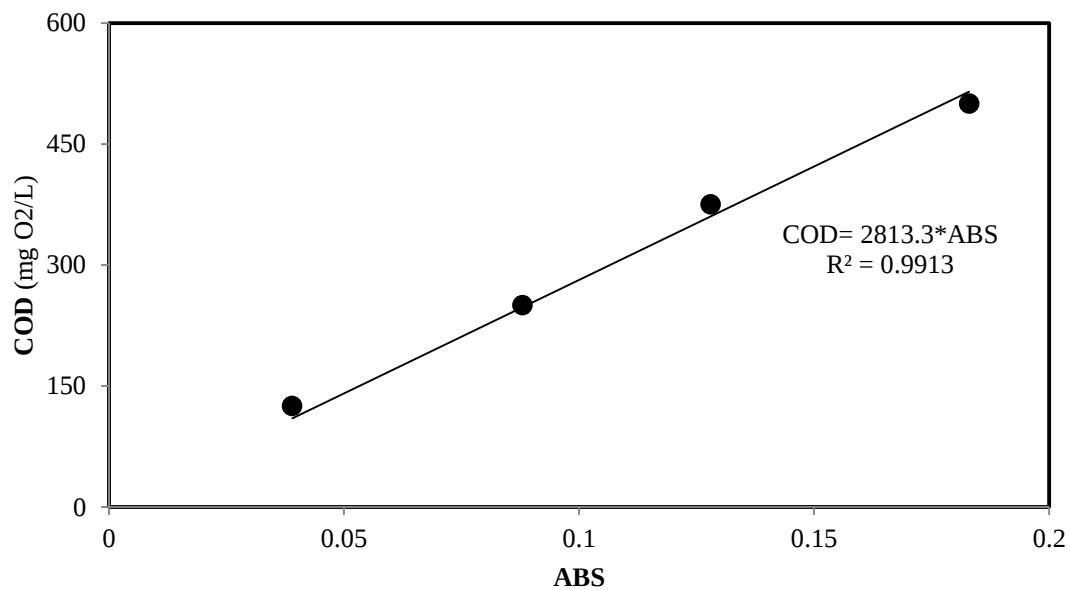


Figure A.2: COD calibration curve

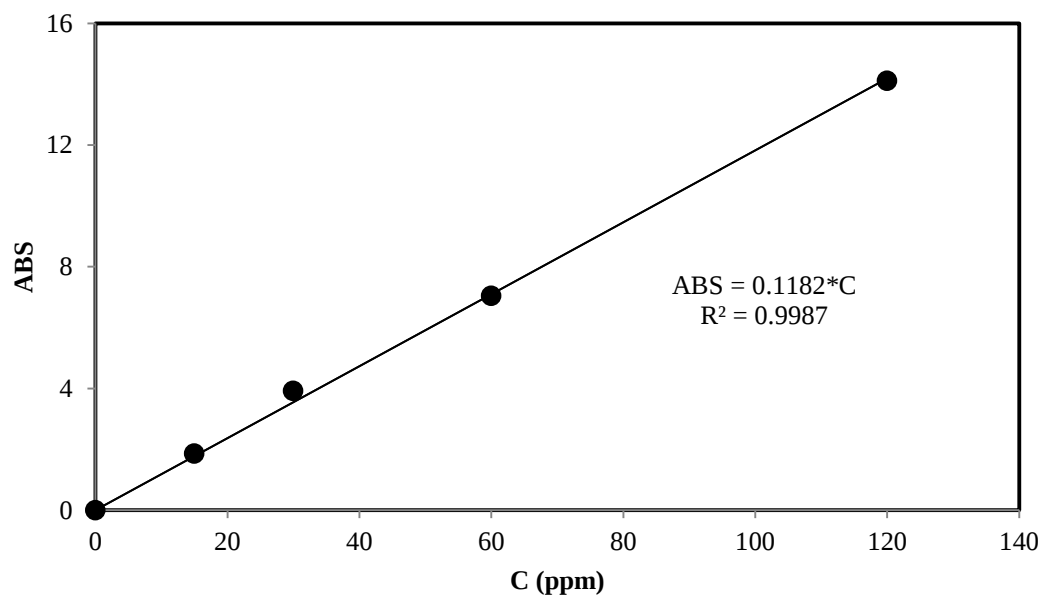


Figure A.3: Calibration curve of methylene blue dye

APPENDIX B: DEVICES AND INSTRUMENTS



Figure B.1: Aqua nova UV spectrophotometer



Figure B.2: Atomic absorption units



Figure B.3: COD test block reactor



Figure B.4: COD vials



Figure B.5: Conductivity and pH meter



Figure B.6: BOD test bottles



Figure B.7: UV spectrophotometer



Figure B.8: Density meter



Figure B.9: Oven



Figure B.10: Filter papers



Figure B.11: Balance



Figure B.12: Kjeldahl distillation unit



Figure B.13: TDS and TSS test



Figure B.14: Fresh OMW sample



Figure B.15: OMW in olive press station



Figure B.16: Rotary evaporator



Figure B.17: Water bath shaker



Figure B.18: The working team