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Assessment of Pre-Treatment of Mixed Agro-Food Industrial Wastewaters Using Advanced Chemical Oxidation Process

تقييم المعالجة المسبقة لمياه صرف صناعات زراعية غذائية مختلطة باستخدام عملية الاكسدة الكيميائية المتقدمة

A Master Thesis

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Thesis was prepared under the supervision of Prof. Dr. Rashed Al-Sa'ed and has been approved by all members of the Examination committee.

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The findings, interpretations, and conclusions expressed in this study do not necessary express the views of Birzeit University, the views of individual members of the MSc committee or the views of their respective employers.

إهداء

بسـمك اللهم أبدأ بفضـلك ولا بعد فضـلك أحد، لا قبلك احد انت الفرد الصـمد سـبحانك ربي كم من الليالي كنت وحدي ولم أجد غيرك مناجيا لقلبي، سبحانك يا كاتب المصير و واضع التدابير يا باعث الامل وموقد نار العمل لك الفضل حتى ترضى، ولك الفضل اذا رضيت، ولك الفضل بعد الرضى.

وبعد،،

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Abstract

Nablus municipality faces techno-economic and environmental challenges in finding environmentally sound and economically feasible alternatives for agro-food industrial wastewater treatment. The dairy and slaughterhouse lack pre-treatment systems, hence discharging industrial wastewater into Wadi Zaimer and Wadi Sajour without prior treatment. This practice results in non-compliance of agro-food industries with Cabinet Resolution (CR 16/2013), environmental and health impacts with increased annual operational expenditures for the industries and municipality. This research study aims at finding a technically reliable treatment option for the reduction of organic and solids loads from a mixed agro-food industrial wastewater (dairy and slaughterhouse) in Nablus city. For this purpose, bench scale Jar tests using an advanced oxidation process (AOP) were performed as a pretreatment stage. The classical Fenton's process was applied for mixed agro-food industrial wastewater samples with initial COD between was 15400-18200 mg/l. Initial tests revealed unsatisfactory results when Fenton reaction applied directly without prior treatment of mixed industrial wastewater. Hence, Fenton experiments preceded integration of partial treatments. Partial treatments of mixed samples included: sample "A" coagulant ($FeCl_3.6H_2O$) added, sample "B" settling (2h) allowed and the sample "C" lime $Ca(OH)_2$ flocculated. Obtained results showed that optimization of Fenton`s process was reached by partial treatment of mixed industrial wastewater. Compared with other partially treatments, sample (C), Fenton`s process lime preceded, was the most effective in the removal of organic (89% COD; 80% TKN) and inorganic loads (91% TSS; 62% TS) under H_2O_2/COD

(w/w ratio 2:1), H_2O_2/Fe^{+2} (w/w ratio 10:1) and acidic conditions (pH =3). Finally, our results comply with CR 16/2013; this encourages agro-food industries install onsite Fenton-based peroxidation systems to get connection permits to the public sewage networks.

الملخص

تواجه بلدية نابلس تحديات تكنولوجية واقتصادية وبيئية في إيجاد بدائل سليمة بيئياً ومجدية اقتصادياً لمعالجة مياه الصرف الصناعي الزراعي الغذائي. حيث تفتقر مصانع الألبان والمجازر إلى أنظمة المعالجة المسبقة، وبالتالي يتم تفريغ مياه الصرف الصناعية في وادي الزومر و وادي الساجور دون معالجة مسبقة. تؤدي هذه الممارسة إلى عدم امتثال هذه الصناعات الغذائية الزراعية مع قرار مجلس الوزراء لعام 2013 الخاص بربط المنشئات المنزلية والصناعية على شبكة الصرف الصحي العامة ، والآثار البيئية والصحية المترتبة على ذلك مع زيادة النفقات التشغيلية السنوية للصناعات والبلديات. تهدف هذه الدراسة البحثية إلى إيجاد خيار علاجي يمكن الاعتماد عليه تقنياً لتقليل الأحمال العضوية والمواد الصلبة من مياه الصرف الصناعي المختلطة الغذائية (الألبان والمجازر) في مدينة نابلس. لهذا الغرض ، تم إجراء اختبارات (Jar Tests) باستخدام عملية الأكسدة المتقدمة (AOP)كمرحلة المعالجة. وقد طبقت عملية فينتون الكلاسيكية على عينات مختلطة من المياه الصناعية المستعملة في الأغذية الزراعية باستخدام عينات يتراوح ال COD الأولي لها بين 18200-15400 ملغم/ لتر. حيث كشفت الاختبارات الأولية عن نتائج غير مرضية عندما تم تطبيق تفاعل فينتون مباشرة بدون معالجة مسبقة لمياه الصرف الصناعية المختلطة. ومن ثم ، فإن تجارب فينتون سبقت بعمل العلاجات الجزئية. تضمنت المعالجات الجزئية للعينات المختلطة: العينة الاولى "A" التخثير بواسطة ($FeCl_3.6H_2O$)، العينة الثانية "B" (الترسيب لمدة ساعتين)، والثالثة "C"عينة الجير $Ca(OH)_2$ الملبد. حيث أظهرت النتائج أن افضل عملية فينتون تم التوصل إليها هي عن طريق المعالجة الجزئية لمياه الصرف الصناعية المختلطة. مقارنة بالعلاجات الجزئية الأخرى، كانت العينة (C)، التي سبقت عملية فينتون هي المعالجة بالجير، هي الأكثر فعالية في إزالة الاحمال العضوية (COD; 80% TKN %89) والأحمال غير العضوية (TSS; %91 TS 62%)، تحت نسب H_2O_2/COD (w/w 2:1), H_2O_2/Fe^{+2} (w/w 10:1) وفي وسط

تفاعل حمضـي .وأخيرًا ، تتوافق نتائجنا مع قانون ربط المنشـآت لعام 2013؛ هذا يشـجع الصـناعات الغذائية الزراعية اسـتخدام أنظمة الاكسـدة المتقدمة فينتون في الموقع للحصـول على تصـاريح شـبك على شبكات الصرف الصحي العامة.

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AOPs	Advanced oxidation processes
AF	Anaerobic filter
APHA	American public health association
BOD	Biochemical oxygen demand
BZU	Birzeit university
°C	Celsius degree
COD	Chemical oxygen demand
CR 16/13	Cabinet resolution number (16) for the year 2013, "Bylaw on the House and Facilities' Connection System to the Public Sewage Network"
EPA	Environmental protection agency
KfW	Kreditanstalt für Wiederaufbau
nm	Nanometer
PADUCO2	Second Palestinian-Dutch Academic Cooperation Program
pH	Negative log of the activity of the hydrogen ion
Sample 1	Sample treated partially, then by Fenton reagent with pH =3 then terminated with pH=7.3
Sample 2	Sample treated by Fenton reagent directly
Sample 3	Sample treated partially, then by Fenton reagent without pH adjustment
Sample A	Coagulated by ferric chloride

Sample B	Sedimentary sample without coagulant (untreated wastewater)
Sample C	Flocculation with Lime $Ca(OH)_2$
SVI	Sludge volume index
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
UASB	Up flow anaerobic sludge blanket
UV	Ultraviolet light
WWTP	Wastewater treatment plant

1. Chapter One – Introduction

1.1 Background and Problem Definition

Beginning in 1994, with heavy focus since 2000, the Palestinian Authority has invested huge capital expenditures and put efforts, to enhance the quality of the water resources, to protect public health by upgrading and new erection of wastewater treatment facilities (Palestinian Water Authority, 2014).

Current water and environmental laws and water regulations, place national limits on industrial discharges and treated effluent from domestic and municipals dischargers, where Cabinet made Resolution Number (16) for the year 2013, “Bylaw on the House and Facilities’ Connection System to the Public Sewage Network". The resolution for item (16) focus on the specification of industrial wastewater, where the COD limit is 2000 mg/l in order to allow to the industry to connect to the public sewage system (Ministry of Local Government, 2013).

These limits primarily aim at the reduction of organic and inorganic pollution loads, which promote eutrophication and impair public sewers (Khan and Mohammad, 2014), treatment facilities, environment, and public health. Consequently, municipal by-laws and effluent discharge standards dictate the level of wastewater treatment required and call for pretreatment of industrial effluents before connection to public sewer networks (Ministry of Local Government, 2013).

Today, Palestinian communities and industrial firms face a critical crisis pertinent to sustainable wastewater management. Urban communities struggle with rehabilitating aged wastewater infrastructures, and upgrading overloaded wastewater treatment facilities, to meet increasingly stringent effluent discharge regulations of local and regional levels for guaranteeing sustainable operations of wastewater facilities, and to reach the original scope, which is ensuring that the protection of public health will be improved as much as possible.

Scientific advances in industry and food production have revolutionized quantity, and quality, for example, the horrendous increase in production using genetic engineering, many types of food products of animal or plant origin, and so on (Key and Drake, 2008). Here it has been noted that this progress included a large increase in the traditional industries and developed them. As well as, modern and non-traditional food industries. Such as inventions for the requirements of food industry technology, and methods of preparation, processing, transport, storage, distribution and else. In contrast, it was noted that many of those who have included this development in the field of food industry specifically resulted in many residues have caused a harmful impact on the environment. The impact is now the concern of many scientists and specialists, and it is not exaggeration. If we say that pollution of the environment, is one of the most important problems facing the governments of the world, without exception particularly in developed countries (Leonard, 1995).

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In this research, it has been focused on the most important agro-food industries wastewaters, which come from effluent of dairy factory and slaughterhouse in Nablus city. Due to high BOD levels from whey and blood, and its impact in the surrounding environment, and causes problems in operation of wastewater treatment plants.

This study provides specific mixed of Agro-Food industrial wastewater, which come from Al-Safa dairy wastewater, and municipal slaughterhouse of Nablus wastewater, these wastewater are classified in the list of food and agriculture, which contaminate the environment and harmful to human health (Environmental Quality Authority, 2015).

The wastewater of dairy factories and there are many and varied and have a harmful effect on the environment. The most important of these wastes is the water produced by the manufacturing process because of its content of proteins, fats, and salts (Kolhe et al., 2009). In addition, the remnants of the slaughterhouse due to the blood and the proudest wastewater from slaughtered animal (Technologien and Wirtschaftsberatung, 2001). Therefore, focus on disposal of these wastes in a proper manner so as not to reach the sewage or other of environmental problems.

In general, wastewater from dairies typically contains high BOD levels as well as fats. In addition, the wastewater from slaughterhouse contains high BOD levels as well as blood (EPA, 1971). The pollution of mixed of that wastewater will have reduced in a pretreatment process, which this thesis aims.

Based on the assumption and in reference to the literature reviews, the mentioned industrial facilities were considered as the main industrial pollutants, thus they were considered for pretreatment in this thesis. Advanced oxidation process (Fenton reaction) used in this study in order to reduce the contamination specially the organic loads of the wastewater in order to discharge it safely with acceptable specifications, at the public sewer network.

This research is one of the component project of Second Palestinian-Dutch Academic Cooperation Program (PADUCO2). The aim of this project is to promote applied integrated practices and technologies for sustainable industrial wastewater management in Palestine.

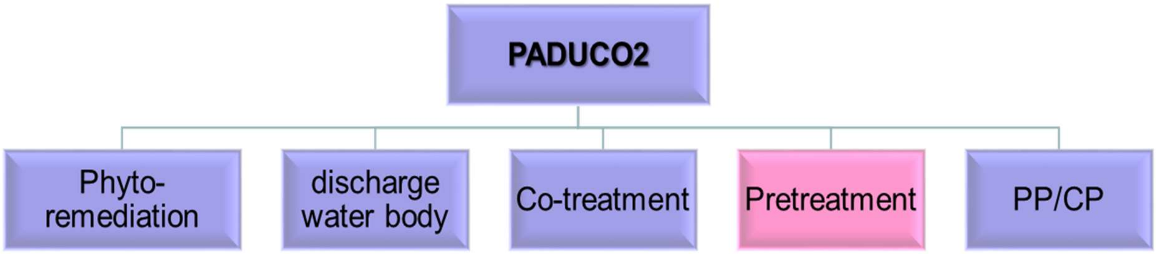

Figure 1: Components of PADUCO2 project.

1.2 Research Aim and Objectives

The main objectives of this research study are to:

- Conduct bench scale experiments, to explore the efficacy of chemical methods for the pretreatment of combined dairy and slaughterhouse effluents. Emphasis has been made on relevant physical and chemical characteristics of the mixed dairy and slaughterhouse wastewater.
- Operate and optimizes the pretreatment stages to produce effluent complying with Palestinian regulations for industrial wastewater discharge.
- Determine the influence of the AOP and evaluate the effectiveness of COD, TKN, and TSS removal.
- Limit the impact of the industrial pollution to reach acceptable level in order to meet the lower limits to those values, which mentioned in CR 16/13.
- Suggest a feasible management strategy for the dairies and slaughterhouses wastewater treatment, clarifying mixed effluents management.

1.3 Research Questions

1. What are the best practices of using chemical oxidation process to reduce the inorganic and organic contents in mixed of dairy and slaughterhouse effluents?

2. What are the feasible methods for AOP treatment, with partially treatment? Alternatively, directly treatment?

3. What is acceptable characteristic for the treated effluent to discharge at the municipal sewerage network, in reference to CR 16/13?

4. What are the operational costs achieved through envisaged pretreatment stage?

5. Which treatment strategy is feasible, onsite or combined treatment of industrial effluents?

2. Chapter Two - Literature Reviews

2.1 Background

According to the Ministry of Agriculture in 2015, especially in livestock sector strategy report. The Ministry reported that the livestock is the main economic source or income for the Palestinians. Where it is an important economic resource, many of the Palestinian, in different areas is owned large numbers of livestock, especially sheep, goats and cows, which is an important source of food and income. Although the Palestinians practiced various aspects of economic activities, such as trade and industry, agriculture and ranching were among the most important occupations (Ministry of Agriculture, 2015).

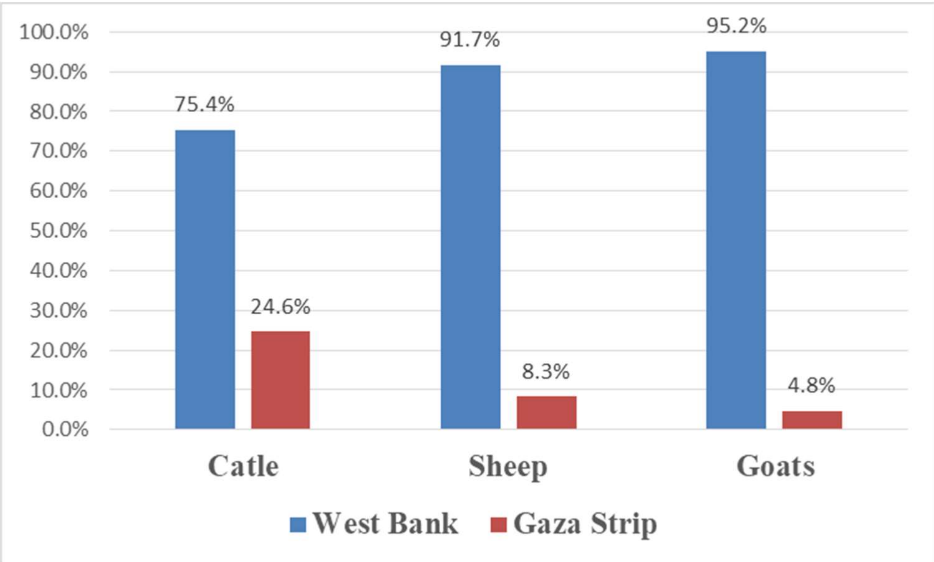

Figure 2: Distribution of livestock in Palestine (PCBS, 2012).

In reference to the FAO, (2011) cattle and poultry is almost 93% of the total meat production in the world. The production of slaughter process summarizing in, manure (inside of rumen and entrails), eaten blood parts such as liver, not eaten parts as hair, bones, teeth, and feathers, fat, and wastewater. However, with regard to the production of cow's milk, the percent is about 87%, and the rest comes from buffaloes, pigs, sheep, and goats.

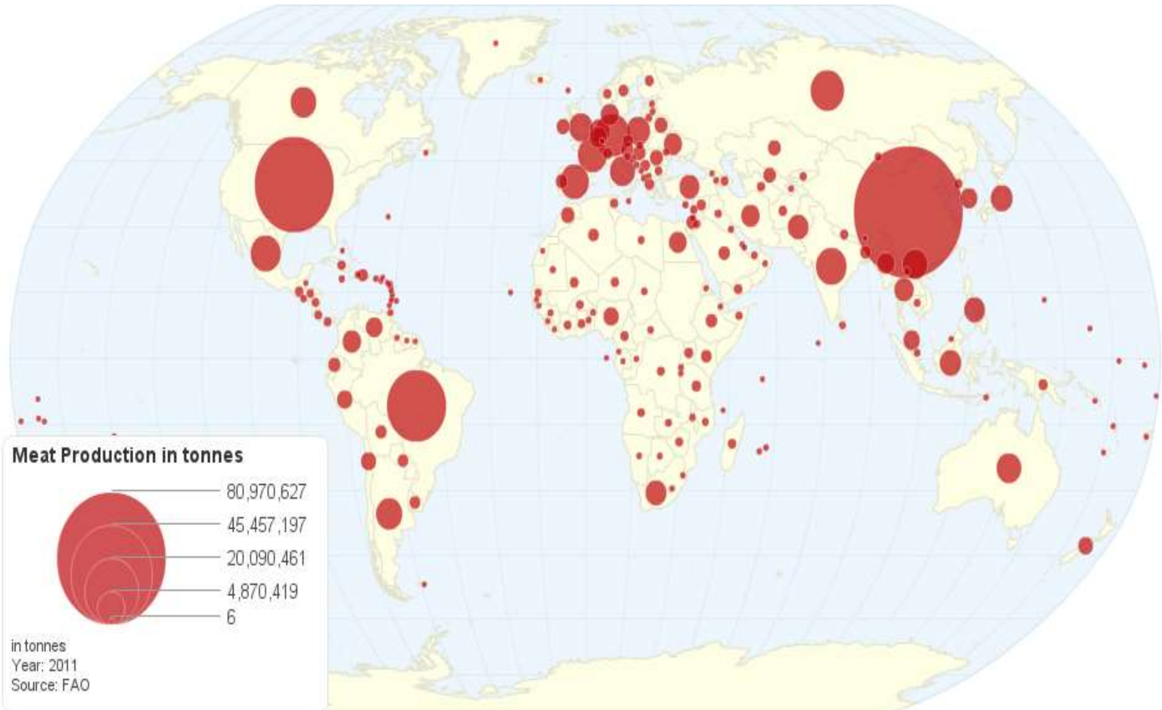

Figure 3: Meat production in the world according to FAO (2011).

In general, dairy wastewater contains lactose, proteins, fat, and salt (Ng, 2006). On the other hand, the waste of the slaughterhouse contains a lot of diluted blood, fat, grit, hair, flesh, grease, feather, manure, and undigested feed (Ng, 2006). The range of ratio

COD /BOD is among 1.5 to 2.2 for slaughterhouse wastewater, on the other hand the ratio for the dairy wastewater is 2.63 for BOD less than 450 mg/l, but for BOD more than 450 mg/l the value is 1.25 (EPA, 1971).

Agro-food industrial wastewater (e.g. dairy and slaughterhouses, breweries, distilleries, and olive oil mills) entails heavy organic and inorganic pollution loads, which can only be reduced using physical, chemical, and biological treatment processes (Chen and Pignatello, 1997).

Many treatment methods have been used in treating dairy wastewater. Reverse osmosis process to treat the generated efluent from dairy factory by Vourch et al., 2008. eleven factories had been included in the study, the results of treated effluent found in the recovry of wastewater which reached 95%, and the characteristics of the treated effluent is similar to vapour condensates, the quality of the effluent can be reused the process of the factory as cleaning, heating, and cooling.

On the other hand, Demirel et al., (2005), have conducted anaerobic treatment and combination of aerobic and anaerobic treatment for dairy wastewater, treatments have got practical and acceptable results through short period of time. These methods considered as traditional and known in treatments.

Also many treatment methods have been used in treating slaughterhouse wastewater. UASB (Upflow Anaerobic Sludge Blanket) as anearobic treatment has been used for wastewater generated from slaughterhouse and in an AF (Anaerobic Filter) the study choose this kind of wastewater among to high COD content due to blood. The result of this kind of treatment in 90% of COD removal for UASB reactor, and recommended in this reseach than AF (Ruiz et al., 1997).

Also combination of sludge blanket and filter arrangement in a single reactor have been recommended by Borja et al., 1998, in treatment of slaughterhouse wastewater, the result of this treatment in COD removal which reached 93% approximately.

The biological wastewater treatment is mostly used but these are usually slow, limited due to the presence of non-biodegradable contaminant, and sometime causes toxicity to microorganisms due to some toxic contaminants (Zelmanov and Semiat, 2008). So in this research advansed oxidation process has been used, to breakdown high pollution load in the short time as possible.

2.2 Current Status of Industrial Wastewaters in Nablus city

In 2015, Environmental Quality Authority reported the main sources of water pollution of water bodies:

- Industrial resources.
- Agricultural resources.
- Sewage sources.

Industrial waste contains 60% of all contaminants in seas, lakes, and rivers. Most of the pollutants are mainly sourced from factories such as tanning, lead, mercury, copper, nickel, paint, cement, glass, detergents, dairy factories, slaughterhouses, and sugar refineries. As well as pollution of hydrocarbons resulting from oil pollution (Environmental Quality Authority, 2015).

This research focus on dairy and slaughterhouse industries in Nablus city. According to the Palestinian Central Bureau of Statistics (PCBS, 2012), there are 17 slaughterhouses in Palestine, 11 in the West Bank and 6 in the Gaza Strip. On the other hand, the number of Palestinian dairy factories is 100 factories, 60 of them in west bank three of them are advanced, and in terms of quantity of production and these three factories have more than 70% of the share of the Palestinian market.

In Nablus city, several industries are the main contaminants of water sources, and mainly affect the operation of the Nablus West Wastewater Treatment Plant. These industries are according to the Environmental Control Unit in the Municipality of Nablus: municipal slaughter house Nablus East, Al-Safa dairy factory, stone cutting factories, tahini factories, jeans factories, olive mills, tannery, aluminum factory, veterinary, restaurants, and lead factory (Dalhem et al., 2017). Most factories do not comply with industrial discharge regulations, but dispose of industrial wastewater in an unsafe manner that affects water bodies (Environmental Quality Authority, 2015).

The table 1 below shows the summary of industries in Nablus city, and the strategy of Nablus municipality to reduce the pollution from those industries through KfW.

Table 1: Summary of industries in Nablus city, status, and solutions according to Environmental Control Unit of Nablus Municipality (Dalhem et al., 2017).

Industries of Nablus city	Current status	Nablus Municipality strategy
Stone cutting factories	Discharging to the Wadi	Pretreatment units will be implemented.
Tahini factories	Discharging to the Wadi and to the sewer network without treatment	Pretreatment units will be implemented/Sesame peeling machines
Jeans factories	Discharging to the Wadi and to the sewer network without treatment	Pretreatment units will be implemented/Install balance tank
Olive Mills	Discharging to the Wadi and to the sewer network without treatment	Zeibar will be transport to WWTP.
Slaughterhouse/ Nablus East	Discharging to the sewer network without treatment	Pretreatment units will be implemented/Install balance tank
Dairy/Nablus East	Discharging to the sewer network without treatment	Pretreatment units will be implemented/Install balance tank
Tannery	Discharging to the Wadi and to the sewer network without treatment	Pretreatment units will be implemented
Aluminum/ Nablus West		Pretreatment units will be implemented
Veterinary		Pretreatment units will be implemented
Restaurants		Grease trap will be installed
Chicken shops		Feather trap will be installed
Lead factory		Pretreatment units will be implemented

From table 1, the strategy of Nablus Municipality for both slaughterhouse and dairy wastewater is to install balancing tank. Then to transfer it to the Wastewater Treatment Plant, to be treated anaerobically in the digester of Nablus East Wastewater Treatment Plant (Dalhem et al., 2017). Therefore, this research suggest treating the previous wastewater on-site by Advanced Oxidation process, to connect those industries to the public sewer network.

2.3 Advanced Oxidation Processes

Treatment for water and wastewater were improved over the last few years by using method of advanced oxidation processes (AOPs) (Oturan and Aaron, 2014). Definition of AOPs found by Glaze et al., (1987), as the oxidation processes to breakdown the industrial waste.

Firstly, Fenton process substantive by Fenton in (1894), by using chemical oxidant mainly hydrogen peroxide (H_2O_2), in presence of ferrous ion (Fe^{+2}) to generate highly reactive radicals in aqueous solution. These free radicals mainly hydroxyl radical which was proposed by Haber and Weiss (1934) to be the hydroxyl radical (•OH) which are able to oxidize most of the organic compounds (Bossmann et al., 1998).

The hydroxyl radical ($^{\bullet}OH$) can be composed of H_2O_2 in a reaction that is catalyzed by Fe^{+2}. This reaction is called Fenton. The hydroxyl radical ($^{\bullet}OH$) is a very active molecule that can interact with proteins, nucleic acids, lipids and other molecules to change its structure and cause tissue damage (Walling, 1975). Design principle of the

Fenton in the following equation (Keenan and Sedlak, 2008, Walling and Goosen, 1973):

$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {}^{\bullet}OH + OH^-$…………..…………………………………..…. (1)

$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^+$………………………………….……......….(2)

The above equations (1) and (2) represents the basic reactions that is generated by the generation of hydroxyl radical, which begins immediately after their integration from a series of reactions to release organic compounds. In these reactions, hydrogen peroxide (H_2O_2) oxidized ferrous (Fe^{+2}) to ferric (Fe^{+3}), forming a hydroxyl radical (${}^{\bullet}OH$), and hydroxide ion (OH^-). Then ferric (Fe^{+3}) is reduced back into ferrous (Fe^{+2}) by another molecule of hydrogen peroxide (H_2O_2), forming hydroperoxyl radical ($HO_2^{\bullet}$) and proton (H^+). The equations also gives a primitive idea of the Fenton reaction, but in reality there is a competition between the items in the reaction media which ensure H_2O_2, Fe^{+2}, Fe^{+3}, ${}^{\bullet}OH$, OH^- (Haber and Weiss, 1934).

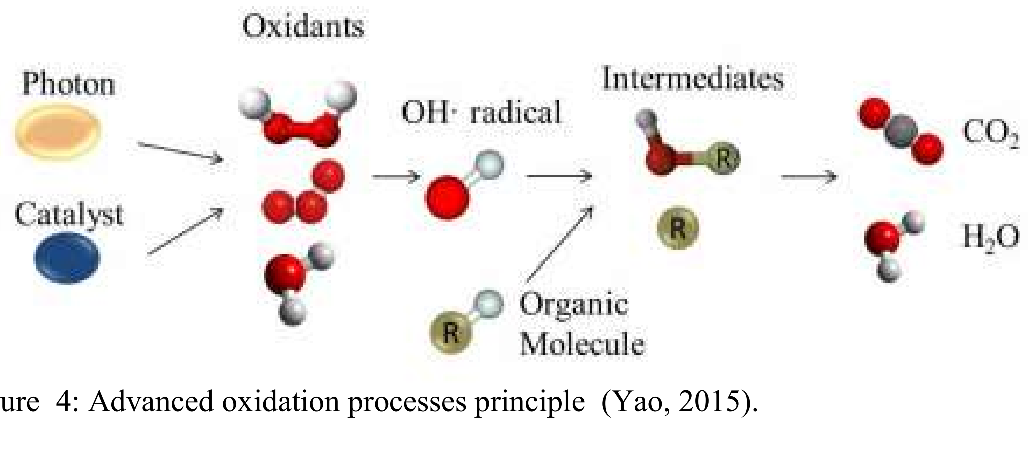

Figure 4: Advanced oxidation processes principle (Yao, 2015).

According to Huang et al., 1993, there are many systems listed under the definition of AOP, and the following Figure summarizes the types of advanced oxidation systems due to availability of light, as Non-photochemical and photochemical:

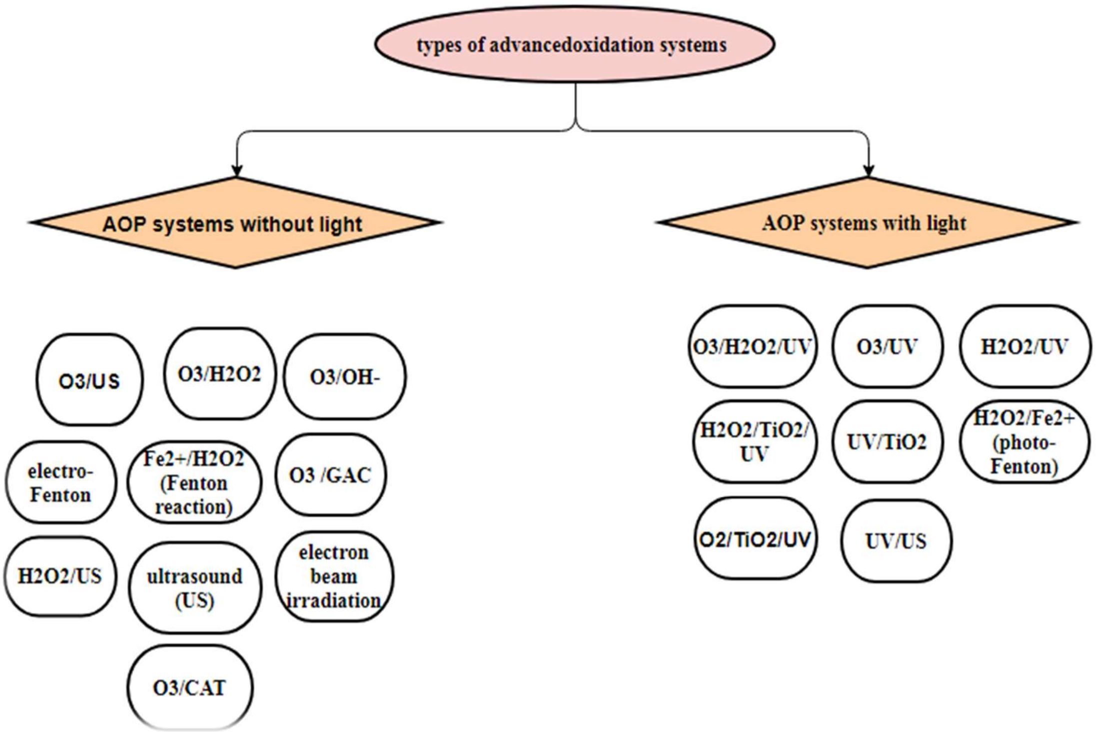

Figure 5: Types of AOP systems (Huang et al., 1993).

Non-photochemical oxidation processes (without light); there are many ways to generate hydroxyl radical without the use of photovoltaic energy, such as ozonation, ozonation with hydrogen peroxide, and Fenton processes (Huang et al., 1993).

Photochemical oxidation processes (with availability of light), in these ways organic compounds absorb light in the 200-300 nm range and disintegrate directly, or becoming more effectively with chemical oxidants. This chemical oxidation divided in to two types, homogeneous chemical oxidation processes, and heterogeneous optical oxidation processes (Ghaly et al., 2001).

These systems are high rates of contaminants removal, easy to deal with differences in water quality, and no need for large equipment's. The two main negative sides are high costs come from treatment itself and standards safety considerations due to the use of highly reactive chemicals (Kochany and Bolton, 1992),

According to Pereira et al., (2012), the general reaction of Fenton reaction is conducted by Fe^{+2} and Fe^{+3}, as catalyst added to the wastewater as aqueous solution,. to breakdown the industrial waste, the uses of this catalyst referring on its advantages as not high cost, numerous, it not harmful of the environment, it can be easily removed after treatment, and can work at variable values of pH and temperatures (Pereira et al., 2012).

Chemical oxidation has been found to be an important alternative to chlorination due to formation of toxic chlorinated organic compounds (Chen and Pignatello, 1997). Fenton and all concerning reactions are potentially valuable oxidation processes for breaking down toxic organic compounds in industrial wastewater. In these reactions, H_2O_2 is combined with Fe^{+2} or Fe^{+3} in the presence or absence of light to generate hydroxyl radicals (•HO). Therefore, chemical treatment by Fenton oxidization process warrants evaluation as a pretreatment process for agro-food industrial (Stefan, 2017).

Alaerts et al., (1982) evaluated the financial costs of using chemical oxidation and flocculation of industrial wastewater at large sewage quantity, where raw water characteristics play major roles in flocculants price, interest rates and local effluent requirements and sludge treatment facilities. Recent studies revealed that using oxidation and flocculation process enhanced the removal of organic, phosphorus, and pathogens (Bratby, 2006).

Advanced oxidation processes showed effectiveness in treating water and soil treatment, by generating the hydroxyl radical both in-situ and onsite remediation through ozonation, Photo-Fenton, and the Fenton reactions. In order to remove contaminations, especially toxic material (chemicals), also to improve biodegradation. Combination of H_2O_2 and ozone showed more degradation level and better in capital cost than other treatment methods (Goi, 2005).

Bench scale experiments (Elhalafawy et al., 2017) on treatment for mixed of domestic sewage and sugar industry were performed using Fenton reaction for removal of the organic pollutants. They found that pH, hydrogen peroxide dose, ferrous sulfate dose, initial dye concentration, and reaction time have impacts on the chemical reaction rates. Also Elhalafawy et al., (2017) reported that optimum conditions for the Fenton reaction were reached using 1.5 mg/l H_2O_2 dose for 20 minutes, achieving removal efficiency over 63.70%.

Complying with stringent effluent quality, the Coleshill Advanced Wastewater Treatment Facility opted for applying physical-chemical pretreatment option. The main pretreatment processes entailed physical chemical pretreatment such: coagulation with lime $Ca(OH)_2$, re-carbonation, ammonia stripping, and activated carbon treatment (Türkman and Uslu, 2012).

Using AOP in disinfecting slaughterhouse wastewater was showing effective results, after 8 minutes of adding 23.09 mg per min per litter from ozone. Effectiveness showed in disinfection of 99% removal of pathogens; however, it was found that the present of BOD and COD removal 23.09% and 10.70% respectively, moreover this process under this condition didn't improve the transmission of light and reducing of total suspended solids TSS (Wu and Doan, 2005).

On the other hand, when adding 110 mg/hr of ozone to the wastewater of the slaughterhouses, the result is that the removal rate of BOD and COD are 45% and 58% respectively, also removed the main contamination of organic matter was not reasonable (Millamena, 1992).

Hilles et al., (2016) studied application of the advanced oxidation treatment technology have by using combination of per sulfate and hydrogen peroxide in treating landfill leachate, where the study proved effective of treatment within two hours of time, where the removing results are 81% and 83% for COD and NH3-N respectively.

Advanced oxidation process UV/H_2O_2 was used to treat the organic pollutants present in cosmetic wastewater. Where the efficiency of the removal of the organic load in the reaction was reached 95.5%, under the following optimal standard conditions: pH 3, 1 ml/l H_2O_2 and 0.75 g/l Fe^{+2} and Fe^{+3} through 40 min (Ebrahiem et al., 2017).

In addition, Naumczyk et al. 2014 found AOP with coagulation for cosmetic wastewater; the COD removal reached approximately 94% with H_2O_2/Fe^{+2} ratios less than the ratio without coagulation.

Dulova and Trapido, (2011) find that to increase effectiveness of AOPs the pre-treatment of wastewater should be applied before Fenton reaction this result clear in treating food-processing wastewater in the removal rate of COD, which reach 79%.

Integration between advanced oxidation and biological processes has been recommended in optimum and adequate condition of these processes in treating slaughterhouse wastewater (Bustillo and Mehrvar, 2015).

Fenton reaction efficiency can be amended by using non-chemical materials such as ultraviolet light, electrified influx, and ultrasound. These methods referred to as expanded advanced oxidation (Stefan, 2017).

The process of Fenton is cost-effective, easy to apply and effective way to remove organic compounds (Lee and Shoda, 2008). Due to previous reasons, Fenton process has been chosen, instead of other methods in this research to be pretreatment method, in mixed agro-food wastewater.

Application of advanced oxidation processes reduces high organic load, but the classical method of advanced oxidation, the Finton reaction, has been adopted in this research. Because this type of treatment, is the cheapest and easiest in terms of use, and its results acceptable for slaughterhouse and dairy factory to be able to connect to the public sewer network.

3. Chapter Three – Materials and Methods

3.1 Background

This study focus on two mixed agro-food industrial wastewater. Slaughterhouse wastewater from municipal slaughterhouse of Nablus, and dairy wastewater from al-Safa dairy, which is the single commercial dairy operating in Nablus. Advanced oxidation treatment applied as pretreatment method.

The effects at pollution reduction from agro-food industries using adequate pretreatment processes, and complying with local guidelines for sewerage connection or full treatment with reclaimed water suitable for reuse and safe disposal. Decisions makers and industrial firms will follow an informed decision process by understanding the economic and environmental benefits of having industrial discharges pretreated onsite or treated combined with domestic wastewater.

3.2 Wastewater Characterization

3.2.1 Slaughterhouse

According to the meetings with environmental control unit in Nablus municipality and site visits for Municipal Slaughterhouse of Nablus, it has been found that the slaughterhouse of Nablus is only such industry in Nablus, and is actually owned by the Municipality.

Currently, an average of 25 cattle and 60 sheep are processed per day. Blood yields are 5 L per sheep and 20 L per cow for a total of 800 L/day. On the slaughter room floor, solids that are not carried into the drainage trench are collected to the municipal landfill.

An average of 50 m^3/d of city water is used to clean the floor and wash equipment. Blood from slaughtered animals is washed into the drain intermittently, and the carcasses are washed down to remove residual blood. The existing slaughtering process does not lend itself to easy separation of the blood from the wash water. Based on the reported slaughtering rate above, the average amount of blood collected each day would be 800 L. The average COD load would be 320 kg/d based on a blood COD of 400 g/L (Dalhem et al., 2017).

Figure 6: Municipal Slaughterhouse of Nablus.

In BZU lab, sample from slaughterhouse tested. It has been found that the COD value equal 7000 mg/l. COD test results according to Nablus Municipality, 2018, for slaughterhouse various samples showing in the following figure:

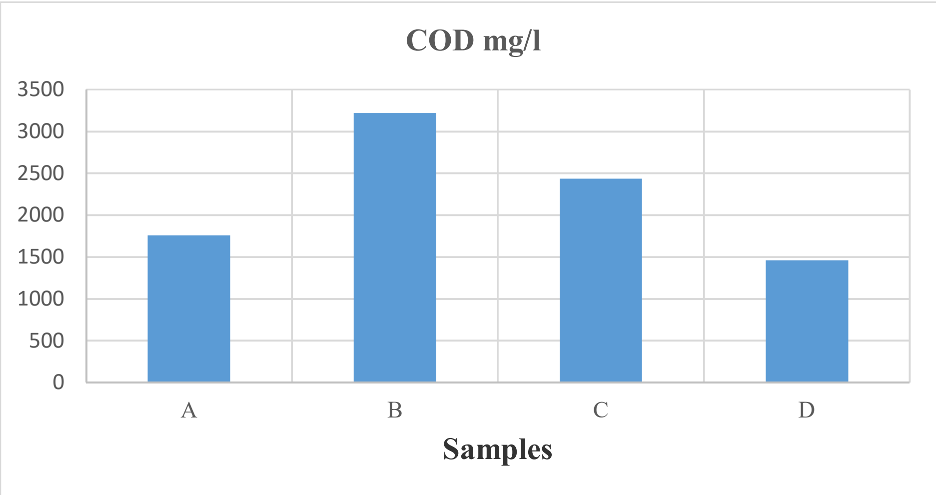

Figure 7: COD test results for various samples at various times (Nablus municipality, 2018).

Table 2: Typical characteristics of the slaughterhouse wastewater (Bustillo and Mehrvar, 2017)

Parameter	Range	Mean
BOD (mg/L)	150–8500	3000
COD (mg/L)	500–16,000	5000
TOC (mg/L)	50–1750	850
TN (mg/L)	50–850	450
TP (mg/L)	25–200	50
TSS (mg/L)	0.1–10,000	3000
K (mg/L)	0.01–100	50
Color (mg/L Pt scale)	175–400	300
Turbidity	200–300	275
pH	4.9–8.1	6.5

3.2.2 Dairy Wastewater

According to the meetings with environmental control unit in Nablus municipality and sites visits Al-Safa Dairy factory is the single commercial dairy operating in Nablus.

Figure 8: Al-Safa dairy factory.

The dairy production process is complex, but a partial process flow diagram is included in figure (9) below.

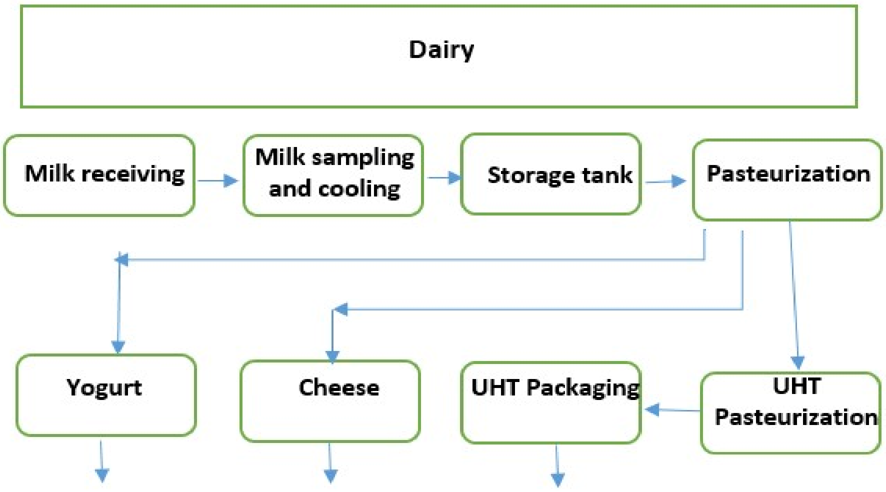

Figure 9: Partial process flow diagram of Al-Safa dairy factory.

The major products of this dairy are pasteurized milk and white cheese. The factory also produces small quantities of yogurt, thickened yogurt (lebnah), and sour cream. Plans for future products include adding flavoring to the yogurt and milk and production of fat free yogurt. Fat taken from the yogurt will be used in the sour cream. No chlorine is used to disinfect process equipment. Instead, a combination of caustic soda, phosphoric acid, and hot water (37-42 °C) are used for disinfection so as not to interfere with the taste of the final product. No preservatives are added to any of the final products.

Figure 10: Machines of Al-Safa dairy factory.

Based on data collected during the sites visits, the dairy employs 70 people and processes on average 4,200 m^3 of milk every year. This equates to 350 m^3/month, or 14 m^3/d. Cheese production consumes on average 460 m^3 of milk per year, or 11% of the total milk processed. Average monthly cheese production is around 52 m^3/month, with production varying from week to week depending on demand. Approximately 2 tons of milk is used to produce 300 kg cheese or about 6.5 kg milk for every 1 kg cheese.

The factory reported using on average 2,600 m^3 of water per month, which equates to 100 m^3/d. This is approximately 6.7 m^3 of water per m^3 of milk processed.

The Al-Safa factory is a very small dairy with very tight quality control measures. Each batch of milk delivered to the factory is tested before unloading, to ensure only the best quality milk is processed. Milk that is not meeting the dairy's standards is refused, and never enters the dairy. This procedure minimizes waste and reduces the amount of milk discharged to the sewer.

The majority of organic load in the dairy sewer appears to come from two sources:

- Flushing, rinsing and disinfecting of the process tanks and piping by sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4);
- Whey that is separated in the cheese making process.

A small additional load comes from the domestic wastewater, but this is a small percent of the total. Reported data suggests wastewater flow from a factory is around 50 L/person with a COD of 500 mg/L. Multiplied by 70 employees, the total domestic load is about 1.7 kg COD/day. Due to the small amount of domestic sewage compared to the industrial portion that includes the flushing rinsing and disinfecting process (Dalhem et al., 2017).

Based on site visits for the factories, it was estimated that no more than 2% of the processed milk is discharged into the municipal sewer network. The discharged water is discharged from different process steps in the factory. Flushing, rinsing, and disinfecting are considered as major process steps which is contributing the effluent discharge. The discharged effluent quantity and quality from the factory are 300 L/d and 200 g/L respectively. Milk has a typical COD of 200,000 mg/L, so the 300 L of discharged milk would create a load of approximately 60 kg COD/day (Dalhem et al., 2017).

Whey is represented as the main COD portion in the dairy wastewater. As mentioned before, the largest source of COD in dairy waste is typically whey, the byproduct from cheese making. At this dairy, milk used to produce cheese represents only 11% (4- year average) of the total milk processed, or about 1.5 m^3/d of milk on average. Typically, 90% of milk used to make cheese ends up as whey, or about 1.3 m^3/d on average. Whey COD typically ranges from 50,000 to 100,000 mg/L. By using the higher value, COD from the whey would amount to 130 kg COD /day, or 65% of the total COD load. If the whey is discharged to the sewer, the total COD load from milk and whey is estimated to be between 160 and 200 kg/day (Dalhem et al., 2017).

According to lab tests from Nablus municipality, 2018 the following table shows the results of raw dairy wastewater of Al-Safa factory :

Table 3: General characteristics of the dairy wastewater, according to the lab of Nablus west wastewater treatment Plant.

Parameters	Value and Results	Limits of CR 16/13
pH	12.4	5-9.5
Conductivity (μS/cm)	3130	-
COD (mg/l)	2212	2000
Suspended solid (mg/l)	210	600
Total dissolved solids (mg/l)	2307	-

From table 2, COD value equal 2212, due to presence of whey in the sample. The sample source is from flushing, rinsing, and disinfecting of the process tanks and piping.

In BZU lab, sample from Al-Safa dairy factory tested separately. It has been found that the COD value equal 26666 mg/l, due to whey.

Table 4: General characteristics of the dairy wastewater, according to various references.

Waste Type	COD	BOD	pH	TSS	TS	References
Milk and dairy products factory	10251.2	4840.6	8.34	5802.6		(Cristian, 2010)
Dairy effluent	1900-2700	1200-1800	7.2-8.8	500-740	900-1350	(Deshannavar et al., 2012)
Arab dairy factory	3383 ±1345	1941±864	7.9 ± 1.2	831±392		(Tawfik et al., 2008)
Dairy waste water	2,500- 3,000	1,300-1,600	7.2-7.5	72000-80000	8000-10000	(Qazi et al., 2011)
Dairy effluent	1120-3360	230-1750	5.6-8	28-1900		(Lata et al., 2002)
Whey	71526	20000	4.1	22050	56782	(Deshpande et al., 2012)
Bhandara co-operative dairy industry wastewater	1400 -2500	800- 1000	7.1-8.2	1045-1800	1100-1600	(Gotmare et al., 2011)
Cheese whey pressed	80,000-90,000	120000-135000	6	8000-11000		(Baroudi et al., 2012)
Aavin dairy industry wastewater	2500-3300		6.4 -7.1	630-730	1300-1400	(Sathyamoorthy and Saseetharan, 2012)
Dairy industry wastewater	2100	1040	7-8	1200	2500	(Arumugam and Sabarethinam, 2008)

3.3 Research Methodology

This section is describing the experiments, which have been conducted at laboratory of Birzeit University. Samples have been examined before adding any treatment materials to determine their physical, chemical, and biological properties. Then the three samples treated to choose the optimal condition in order to discharge it safely to municipal sewerage network.

3.3.1 Experimental and Analytical Methods

3.3.1.1 Analytical Methods

Physical parameters for mixed agro-food wastewater and treated wastewater were measured, pH measured by using (Metrohm-691). For TSS and TS parameters, those analyzed according to standard method.

For chemical parameters, which analyzed according to standard methods, Biological Oxygen Demand (BOD_5) 5210 B, Chemical Oxygen Demand (COD) - section 5220 D, Closed Reflux, Colorimetric Method-, Ammonia (NH_4-N) Nesslerization method, total kjeldahl nitrogen.

3.3.1.2 Mixed of Dairy and Slaughterhouse Wastewater

Samples of agro-food industrial wastewater have been collected from Al-Safa dairy factory, and municipal slaughterhouse of Nablus, and tested in the BZU lab. The mixed of the previous samples have been tested to determine their physical and chemical properties. All samples prepared according to APHA (2005).

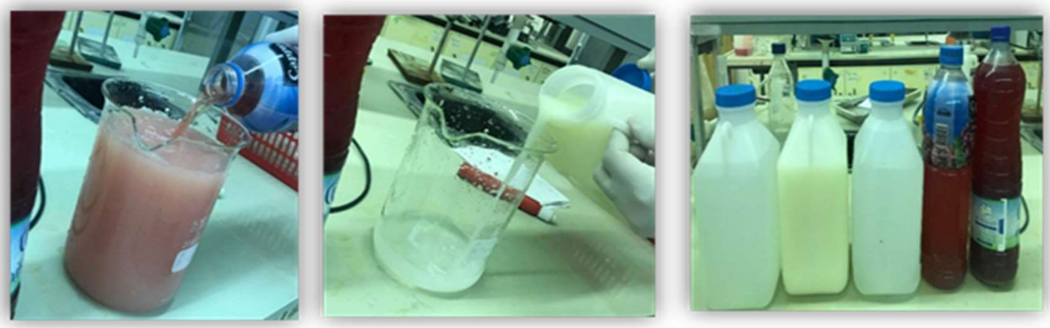

Figure 11: Raw of mixed dairy and slaughterhouse wastewater.

The dairy samples contain sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) with concentrations (2.8-3%), in addition to the whey, which is separated in the cheese making process. While the samples from slaughterhouse contain diluted blood, and wastewater produced from washing the slaughtered animals (manure, and undigested feed).

3.3.1.3 Experimental Procedure

Samples of mixed agro-food wastewater have been prepared. Number of samples treated partially then by AOP with deferent COD values. One sample treated directly by Fenton reagent. Other samples tested to find best dose and pH value for Fenton reaction.

Then three samples has been recommended in Fenton reaction to choose the feasible one (more organic load removal, lower cost).

Partially treatments were found before creating Fenton reaction, mainly to degrade high organics content as possible and to improve effectiveness of the Fenton process.

Note:

At the first time, treatment with Fenton reaction conducted directly without partially treatment, due to unacceptable results for it, partially treatment is recommended.

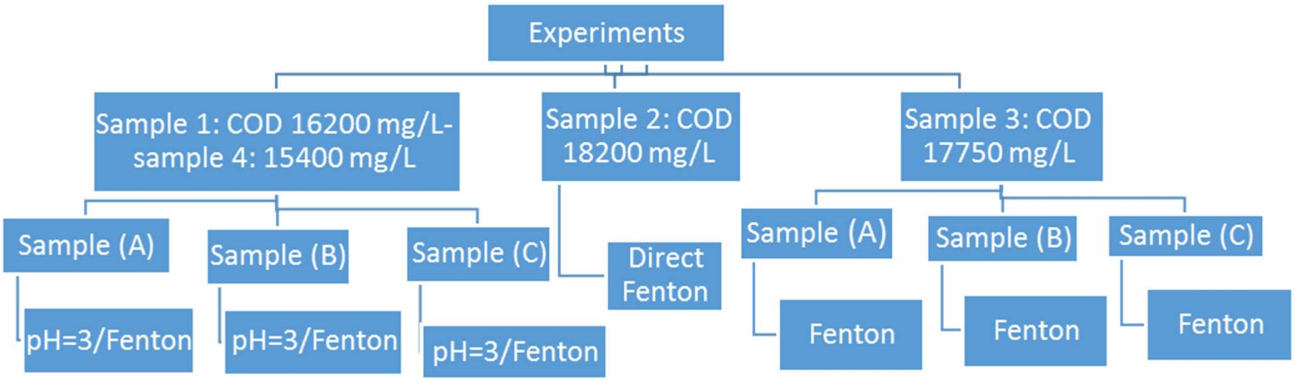

Figure 12: Experiments of samples by Fenton reagent.

- Sample (A): Coagulation with ferric chloride $FeCl_3.6H_2O$.
- Sample (B): Sedimentation without coagulant.
- Sample (C): Flocculation with Lime $Ca(OH)_2$.

3.3.1.3.1 Experimental Procedure of Partially Treatment samples

1. Sample (A) coagulation with ferric chloride $FeCl_3.6H_2O$: the sample of mixed raw dairy and slaughterhouse wastewater has been adjusted at room temperature (20±1 °C). Then in the jar test 1.0 L volume of the sample coagulated by using ferric chloride ($FeCl_3.6H_2O$) aqueous solution with dosage 1g/L, the aqueous coagulant added in rapid mixing at 300 rpm for 3 min, then 30 min in slow mixing at 40 rpm. Then two hrs of settling (Hossaini et al., 2013, Dennett et al., 1996).

Figure 13: Sample A coagulated with ferric chloride $FeCl_3.6H_2O$.

2. Sample (B) sedimentation without coagulant: 1 L of the initial untreated wastewater (at room temperature) at initial pH allowed settling for 2-4 h.

Figure 14: Sample B sedimentation (untreated sample).

3. Sample (C) flocculation with Lime $Ca(OH)_2$: One litter of initial wastewater has been mixed with raw lime $Ca(OH)_2$ by adding 1 g/l of and mixing it rapidly for creating flocculation (Hossaini et al., 2013, Leentvaar and Rebhun, 1982, Mo et al., 2013).

Figure 15: Sample C flocculation with Lime $Ca(OH)_2$.

3.3.1.4 Oxidation by Fenton Reagent

The Fenton oxidation process experiments carried out at lab of BZU. The test carried out for three samples in order to determine the most feasible and acceptable method in treatment, each treatment method has been evaluated separately:

i. Sample A: Coagulated by ferric chloride $FeCl_3.6H_2O$.
ii. Sample B: Sedimentary sample without coagulant (untreated wastewater).

iii. Sample C: Flocculation with Lime $Ca(OH)_2$.

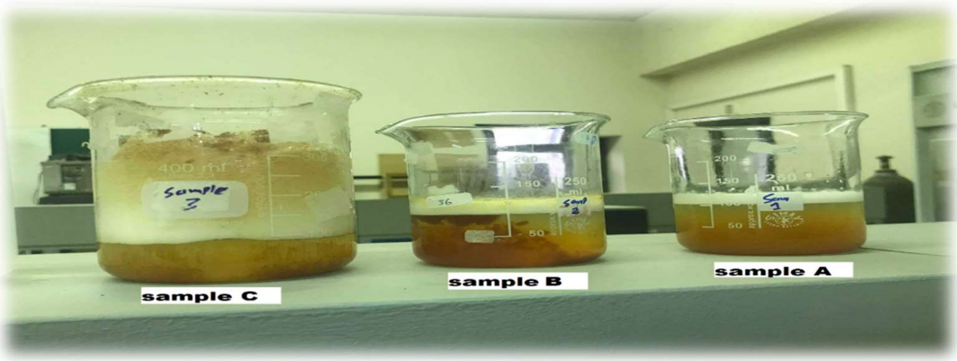

Figure 16: Samples through Fenton reagent by H_2O_2 and $FeSO_4$.

Fenton Reagent experiment:

1) 0.1 L of supernatant from all samples has been prepared to start reaction.
2) pH has been adjusted to acidic which equal 3 by adding acidic solution HCL.
3) Catalyst of Ferrous sulfate heptahydrate ($FeSO_4$•$7H_2O$; 5.2 mM Fe^{2+}) added to the pre-treated samples (supernatant) before adding hydrogen peroxide. The molar ratio of H_2O_2/Fe^{2+} w/w kept invariable at 10:1 and H_2O_2/ COD (w/w) kept constant at 2:1.
4) Three equal parts/or at once have been Added in 3 steps of H_2O_2 with wt. 30% (9.7 M) (density 1.11 g/cm^3).
5) Terminate oxidation by the adjustment of samples' pH to 5-9 by adding lime $Ca(OH)_2$.
6) Samples kept for a period of 2 hrs to allow the settling of solids.
7) Supernatant has been gotten to analyze.

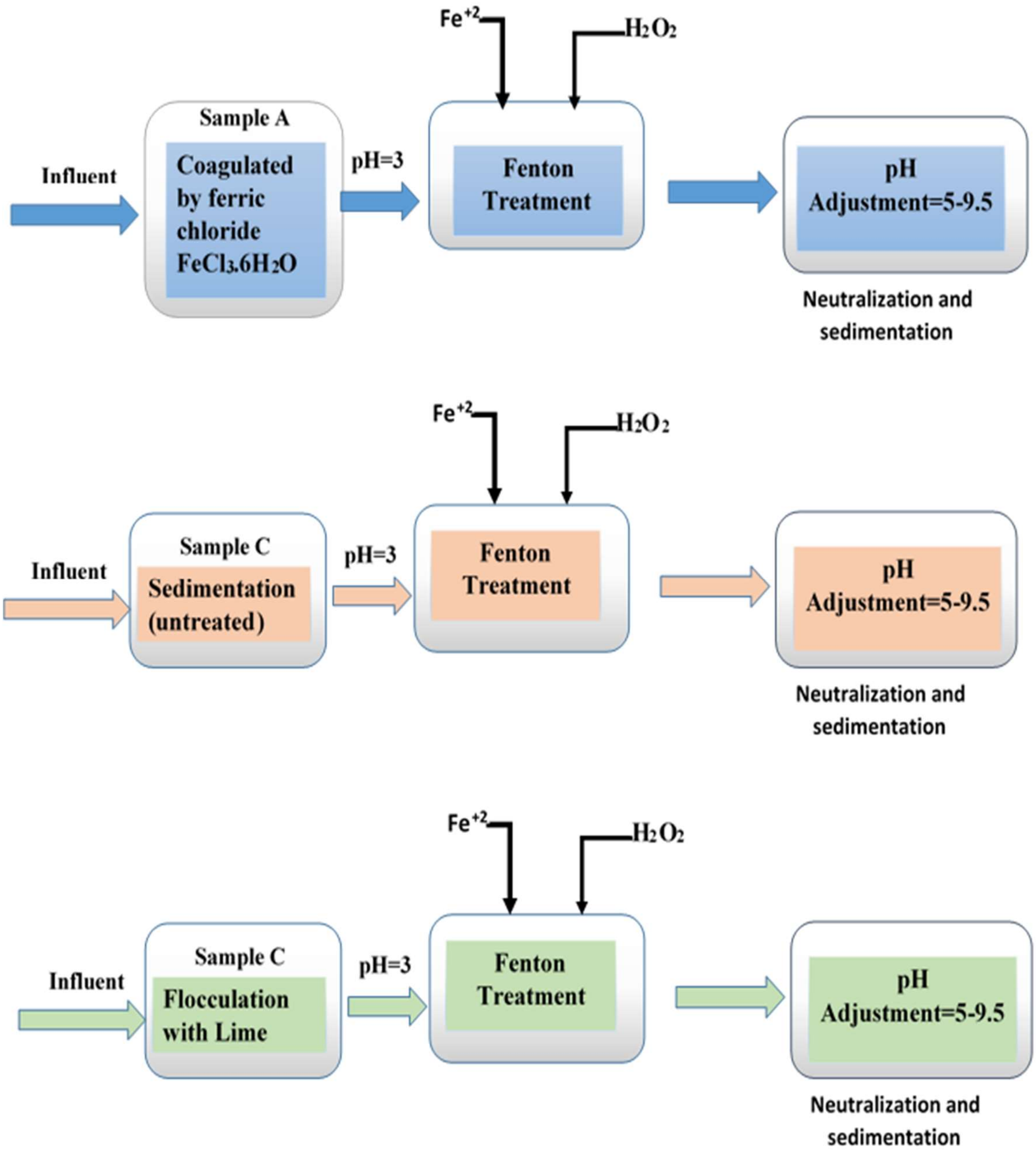

Figure 17: Steps of Fenton reaction experiment with pH adjustment for three recommended samples.

4. Chapter Four – Results and Discussion

The main objective of this study is to reduce the high organic load of the agro-industrial food wastewater, by AOP in order to reach the standard of Cabinet Resolution Number (16) for the year 2013, to discharge the wastewater into municipal wastewater network.

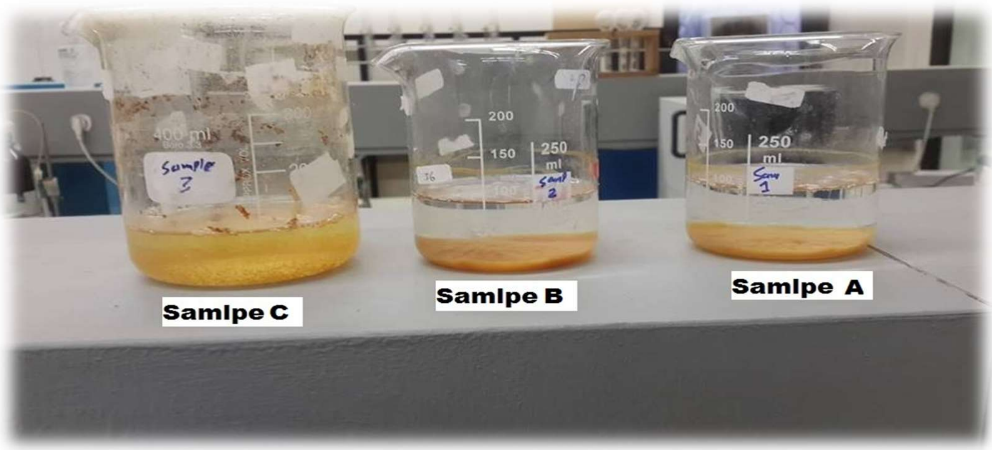

Figure 18: Samples after Fenton reaction complete.

4.1 Characteristics Of Mixed Agro-Food Industrial Wastewaters Sample.

The samples analyzed according to APHA (2005), table 5 shows general characteristics of the mixed agro-food wastewater for sample No.1, which recommended in partially treatment at pH=3:

Table 5: General characteristics of the mixed agro-food wastewater for recommended sample.

Characteristics	Results	Limits of CR 16/13
pH	6.96	5-9.5
COD (mg/l)	16200	2000
Total solid (mg/l)	3705	-
Total suspended solids (mg/l)	220	600
BOD_5 (mg/l)	7005	-
TKN (mg/l)	570	-

The above results show high in the results of organic load due to whey and blood mainly.

4.2 Results of Directly Treatment By Fenton Reagent

Many literatures used AOP directly, this led to use high dose of H_2O_2 and Fe^{+2}, to reduce high organic load. Mixed of mixed-agro food wastewater has been treated directly by Fenton reagent to sample No.2, which its COD value equal 18200 mg/l , the results are not sufficient for CR 16/13 due to COD 10,000 mg/l (45% removal) after treatment at H_2O_2/COD w/w ratio of 2:1 and H_2O_2/Fe^{+2} 10:1.

4.3 Pre-Treatment Results Before Creating Fenton Reaction for Three Samples

Advanced oxidation processes with coagulation had been conducted for various wastewater, which have high organic load (Naumczyk et al. 2014, Dulova and Trapido, 2011, Rizzo et al. 2008, Hossaini et al., 2013).

The first pre-treatment sample (1A) is coagulation with $FeCl_3.6H2O$. The treatment has been carried out to remove suspended compounds of wastewater through the formation of a solid precipitate (sludge) which will be treated by (Yoo et al., 2001). The treatment carried out with dosage 1g /L of $FeCl_3.6H_2O$ of wastewater. The removal rates for COD are (62%). This coagulant is also possible for TSS and TS removal (74%, 28%) respectively.

The second pre-treatment (1B) sample is sedimentation, it has been carried out to reduce the organic load, to improve mixed agro-food wastewater parameters (Dulova and Trapido, 2011), and to enhance the Fenton reaction. The result of pre-treatment in removal rates for COD (26%), this result is feasible to improve wastewater parameters but it's not effective as coagulation with $FeCl_3.6H_2O$ and flocculation with lime $Ca(OH)_2$ pre-treatments.

The third pre-treatment sample (1C) is flocculation with lime $Ca(OH)_2$ (Leentvaar and Rebhun, 1982, Mo et al., 2013). Results from this pretreatment showed more favorable values than the mentioned pretreatment and have been adopted in this research in the treatment of mixed agro-food wastewater before Fenton reaction. The result of pre-treatment in removal rates for COD (68%), TSS (58%), and in TS (19%).

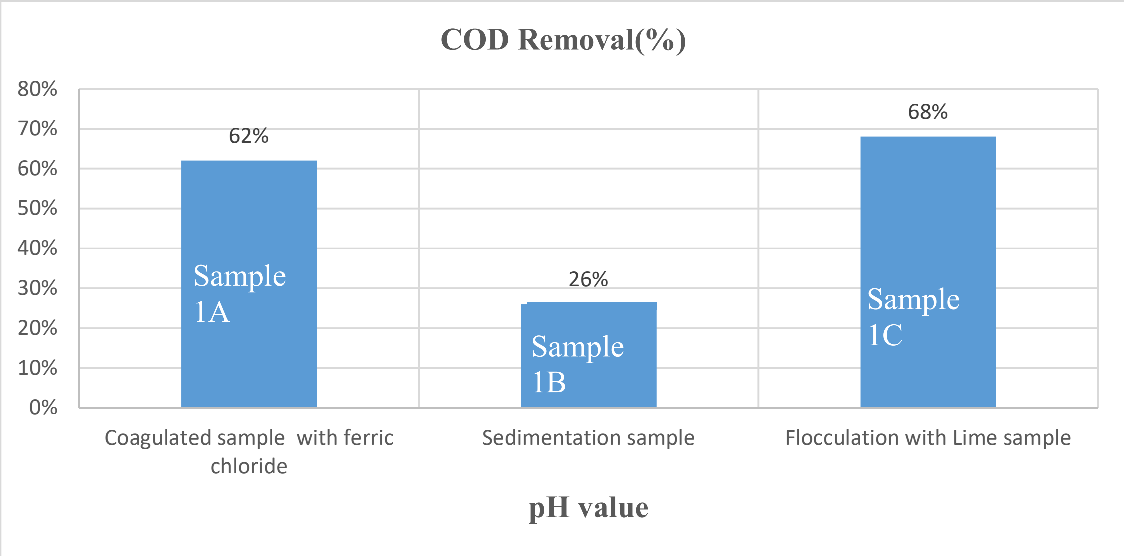

Figure 19: COD removal (%) for samples after partially treatment.

According to results of COD removal, Sample 1A and 1C recommended for further tests.

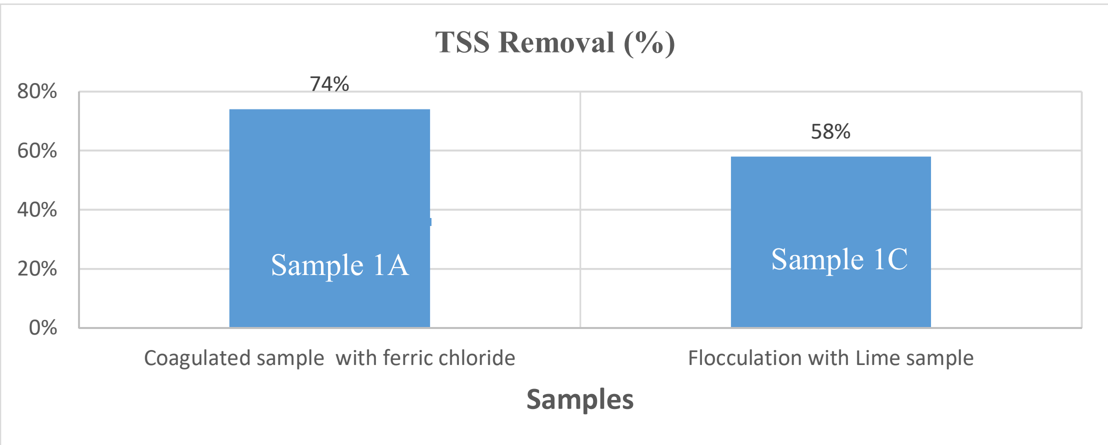

Figure 20: TSS removal (%) for samples after partially treatment.

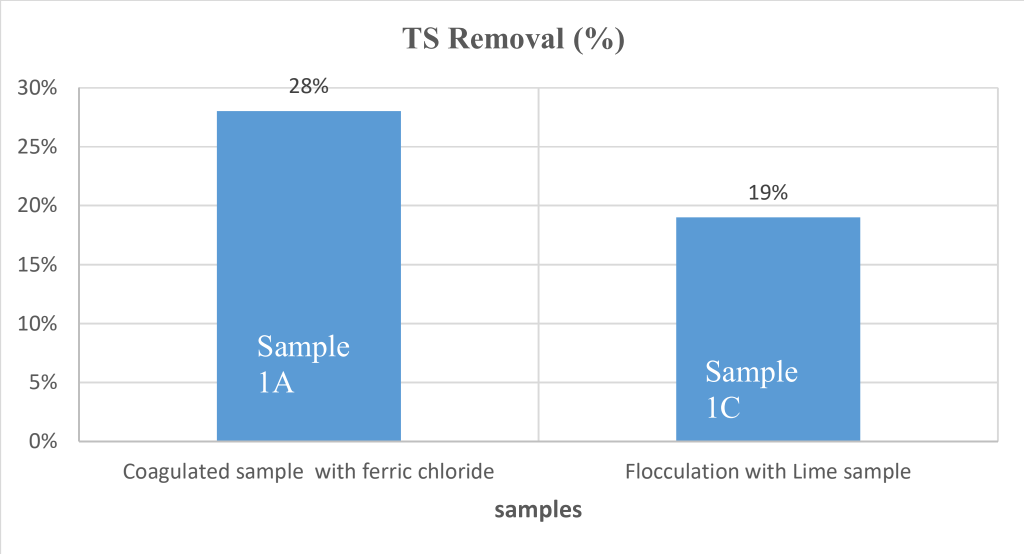

Figure 21: TS removal (%) for samples after partially treatment.

The table shows the result values of partially treated wastewater:

Table 6: Result values of partially treatment of mixed agro-food wastewater for sample No.1.

Parameters	Sample 1A (Coagulated by ferric chloride $FeCl_3.6H_2O$)	Sample 1B (Sedimentary sample without coagulant)	Sample 1C (Flocculation with Lime $Ca(OH)_2$)
COD (mg/l)	6080	11988	5150
Total solids (mg/l)	2685	3334.5	2988
Total suspended solids (mg/l)	56.2	178	93.5
BOD_5 (mg/l)	2920	5536	2780

4.4 Results of Fenton Treatment after Partially Treatment

4.4.1 Treatment by Fenton Reagent without pH Adjustment

At the first time, the pH left without adjustment to start Fenton reaction for samples:

i. Sample 3A: Coagulated by ferric chloride $FeCl_3.6H_2O$ at initial COD 17750.

ii. Sample 3B: Sedimentary sample without coagulant (untreated wastewater) at initial COD 17750.

iii. Sample 3C: Flocculation with Lime $Ca(OH)_2$ at initial COD 17750.

It was found from the experiments for the sample No.3 that done at BZU lab. That the best sample is the Lime $Ca(OH)_2$ flocculation sample (Sample 3C). It has been found that the COD removal reached 54% at pH value 11 with H_2O_2/COD w/w 2:1, and H_2O_2/ Fe^{2+} 10:1 (Dulova and Trapido, 2011).

while COD removal of coagulated by ferric chloride (Sample 3A) and sedimentation samples (Sample 3B) are equal 28% and 26% respectively at the same dosage of H_2O_2 and catalyst that used in treating lime $Ca(OH)_2$ flocculation sample, excepting pH values are equal 8 and 10.5 respectively. The performance of Fenton reaction in COD removal shown in the figure 22 for three samples:

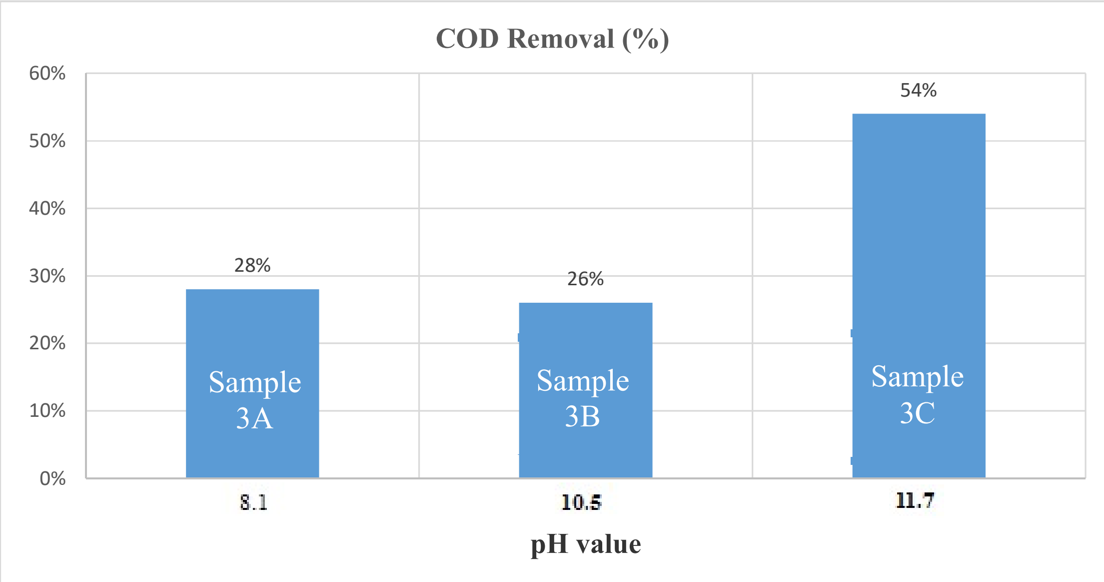

Figure 22: COD removal (%) for three samples at initial pH without adjustment.

The result value of raw wastewater in table below:

Table 7: General characteristics of the wastewater for sample No.3.

Parameters	Value and Results	Limits of CR 16/13
pH	9.66	5-9.5
COD (mg/l)	17750	2000
BOD_5 (mg/l)	8200	

The result value of treated wastewater without pH adjustment in table below:

By leaving the samples without pH adjusting, the COD removal efficiency is not satisfactory in order to achieve CR 16/13.

Table 8: Result value of treated wastewater without pH adjustment.

Parameters	Sample 3A (Coagulated by ferric chloride $FeCl_3.6H_2O$)	Sample 3B (Sedimentary sample without coagulant)	Sample 3C (Flocculation with Lime $Ca(OH)_2$)
pH	8.1	10.5	11.7
COD (mg/l)	12700	13200	8050
BOD_5 (mg/l)	6315	6544	4020

4.4.2 Treatment with pH Adjustment and Neutralization

An acidic solution (HCL) has been used to modify the pH value from basic to acid media in order to make adequate conditions to start reaction. It is found that the degradation efficiency increased rapidly, organic removal was significantly higher in acidic conditions at pH 3 than under alkaline conditions.

The optimum pH for the Fenton reaction is approximately 3 according to various literatures due to avoid precipitation of iron oxide-hydroxide which enhance the reaction (Fenton, 1894). It is the best case for the production of hydroxyl radicals, which is responsible for the breakdown of organic matter and responsible for oxidation reaction (Katsumata, et al., 2004), (Dulova, and Trapido, 2011). The ratio of H_2O_2/COD w/w kept 2:1 and H_2O_2/ Fe^{2+} 10:1.

The results of the experiments showed that the best sample in removal of organic load is the flocculation with lime $Ca(OH)_2$. It has been found that the removal rate for COD reached 70 % and for TSS and TS removal reached 65%, 47% respectively, and has been found that TKN reached 80% with the ratio of H_2O_2/COD w/w 2:1 and H_2O_2/Fe^{2+} 10:1, and at the room temperature and within 1 hour.

While COD removal of coagulated by ferric chloride sample (Sample 1A) is equal 52% and for TSS and TS removal reached 68% 48%. Moreover, it has been found that TKN reached 69% at the same ratios.

For the sedimentation sample (Sample 1B), the removal rate for COD reached 33%. The value of COD removal is low, and not accepted so this sample has been excluded for other results. After treatment. All samples have been neutralized at pH=7.3.

The performance of Fenton reaction in COD removal shown in figure 23, for treating three samples. By adjusting the pH, value for the three samples, the COD removal efficiency satisfactory for the sample which pre-treating by lime $Ca(OH)_2$, in order to achieve CR 16/13.

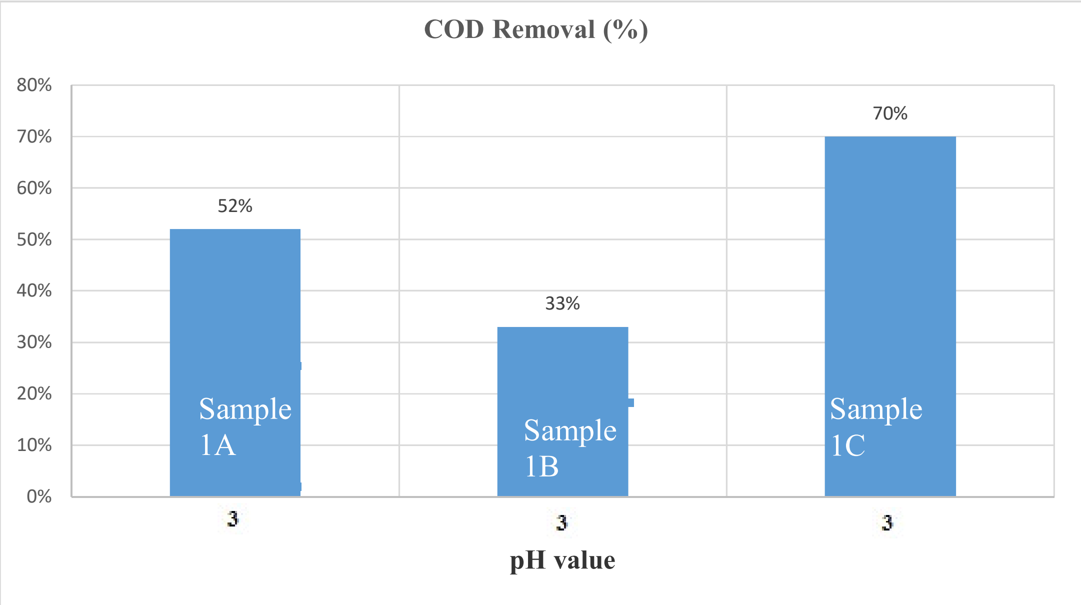

Figure 23: COD removal (%) for three samples at pH = 3.

According to results of COD removal, Sample A and 3 recommended for further tests.

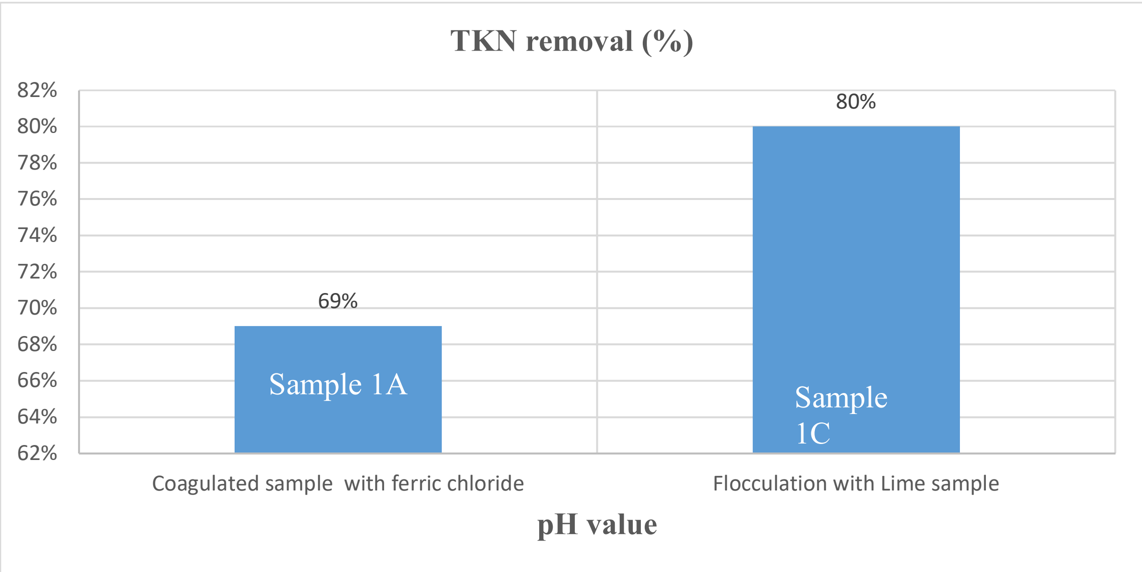

Figure 24: TKN removal (%) for samples after fenton process.

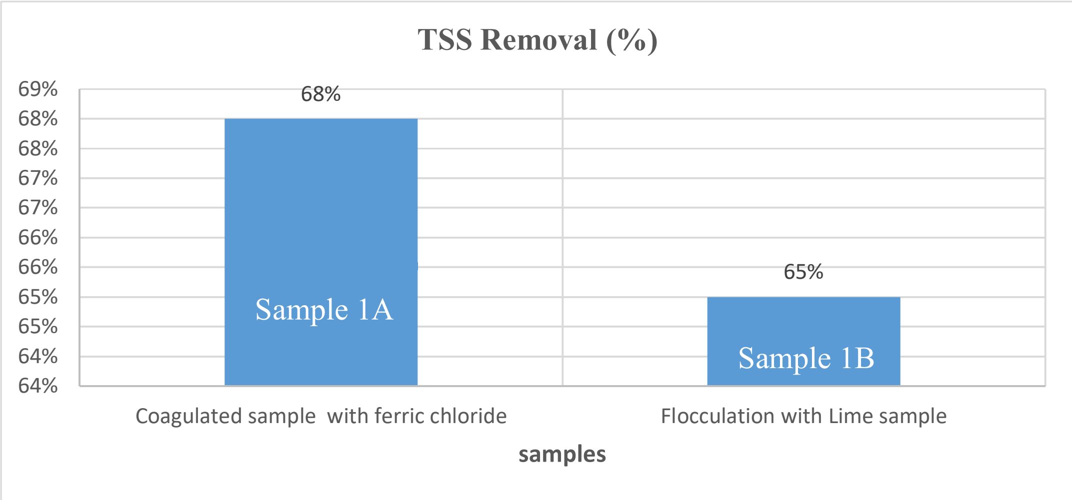

Figure 25: TSS removal (%) for samples after Fenton process.

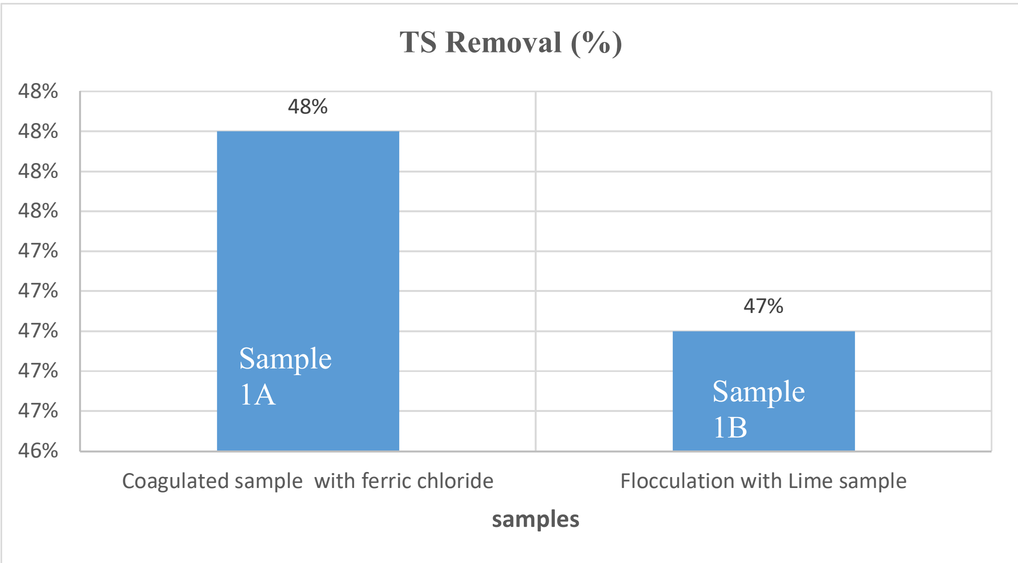

Figure 26: TS removal (%) for samples after partially treatment.

The result value of treated wastewater at pH=3, then neutralized at pH=7.3 in table below:

Table 9: Result value of treated wastewater at pH=3, then neutralized to pH=7.3.

Parameters	Sample 1A (Coagulated by ferric chloride $FeCl_3.6H_2O$)	Sample 1B (Sedimentary sample without coagulant)	Sample 1C (Flocculation with Lime $Ca(OH)_2$)
pH	7.3	7.3	7.3
COD (mg/l)	2889	1820	8032
Total Suspended solid (mg/l)	17.8	19.6	-
Total solids (mg/l)	1389	1415	-
BOD_5 (mg/l)	1380	968	-
TKN(mg/l)	123	113	-

4.5 Effect of H_2O_2 and Catalyst Dosage on Mixed Agro-Food Industrial Wastewaters Treatment Processes

In Fenton reaction process H_2O_2 is the main source of hydroxyl radical •OH which produced under catalyst, and has a key role in reducing the organic load of wastewater. The optimal dosage of hydrogen peroxide was determined experimentally and by calculations.

Insufficient dosage or little of hydrogen peroxide H_2O_2 led to decrease in COD removal of the organic load regarding to insufficiency hydroxyl radical •OH. In contrast an increasing in dosage of H_2O_2 specially in treating wastewater with high COD value to increase the efficacy of COD removal, the excessive dosage of H_2O_2 will affect the microorganisms which used in removing contaminant, also an excessive in the concentration of H_2O_2 will result in self-disintegration into H_2O and O_2 (Andreozzi and Marotta, 1999).

Experements repeted many times to finde the best dose of H_2O_2 and it has been found that the optimal ratio of the dose in tearm of H_2O_2/COD equal w/w 2:1.

Table 10: Example of calculation of H_2O_2 concentration in reference to COD (Dulova and Trapido, 2011).

Volume of H_2O_2	
COD, g/L (according to characteristic of wastewater)	6.08
Volume of wastewater sample, L	1
H_2O_2/COD, weight ratio (variable)	2.0
H_2O_2 conc., M	9.71
H_2O_2 30%, g/L	330
V(H_2O_2), mL, to add	36.85

For the dosage of $FeSO_4$ the increasing in the quantity of the catalyst it will affect the treated wastewater economically in removing excess Fe^{+2}, and if it is decrease the reaction will not get suffiant behavier to produce hydroxyl radical •OH.

Dosage of $FeSO_4$ calculated in term of H_2O_2 and COD concentration, $FeSO_4$ dose tested and it has been found that optimal ratio of H_2O_2/Fe^{+2} equal 10:1.

Table 11: Example of calculation of $FeSO_4$ concentration in reference to H_2O_2 (Dulova and Trapido, 2011).

Volume of Fe^{2+}	
Amount of H_2O_2, mol	0.358
H_2O_2/ Fe^{2+}, m/m	10
Amount of Fe, mol	0.0358
$FeSO_4.7H_2O$, g, to add	9.9426

Table 12 shows the summary of total removal rate for the contamination for three samples:

Table 12: Summary results of removal rate for contaminant in Fenton reaction

Sample	COD removal (%)	BOD removal (%)	TKN removal (%)	TSS removal (%)	TS removal (%)
Sample of Coagulated by ferric chloride $FeCl_3.6H_2O$	82%	80%	69%	92%	63%
Sample of sedimentary (without coagulant)	33%	29%	-	21%	15%
Sample of Flocculation with Lime $Ca(OH)_2$	88%	86%	80%	91%	62%

4.6 Cost Evaluation

In combined process of pre-treatment/AOP, the total costs mainly depend on pollution load and biodegradability of wastewater (Saritha et al, 2007).

According to various literature reviews advanced oxidation process by Fenton reaction is low cost technology for treatment and removing contamination (Goi, 2005). The following table summarizes the cost of used materials in this study and operation cost in reference to literatures:

Table 13: Cost of the used materials in this study.

Reagent	Unit	Cost ($)/unit according to BZU	Operating cost ($)/unit of the treatment methods	reference
$FeCl_3.6H_2O$	kg	1.3	0.223	(Kestioğlu et al, 2005)
NaOH	kg	2.4	0.224	(Kestioğlu et al, 2005)
H_2O_2	l	1	5.8	(Saritha et al, 2007)
$FeSO_4.7H_2O$	kg	1.5	2.67	(Kestioğlu et al, 2005)
$Ca(OH)_2$	kg	0.3	Available in Palestine by nature in large quantities, especially in stone cutting factories with cheap price (Ubeid, 2011).	

Total cost mainly consists from the summation of capital cost and operation and maintenance cost. To calculate the cost for a large-scale system depends on the flow rate and pollution load of the wastewater. Table (13) shows the cost evaluation for this study. This treatment is recommended because of the savings resulting from non-payment of fees due to excess organic load.

5. Chapter Five – Conclusion and Recommendations

5.1 Conclusions

This report provides for selected industries the final recommended pre-treatment process, to meet the discharge standards.

The current study has been conducted in order to evaluate the effectiveness of Pretreatment/Fenton reaction-hydrogen peroxide oxidation processes in the treatment of agro-food industrial wastewater.

Coagulation/flocculation $FeCl_3.6H_2O$/Lime $Ca(OH)_2$ have been used in this type of wastewater. The samples were coagulated/flocculated because this type of wastewater has a rapid response to these coagulants/flocculants and thus obtained satisfactory results (Carvalho and Rivas, 2013, Rodda, 1920).

AOP treatment of mixed of agro-food industrial wastewater resulted in major reduction of COD as indication of degradability amelioration. The dose of hydrogen peroxide and Fe^{+2} must be accurately optimized to create feasible treatment with low cost as possible because of increasing H_2O_2\COD ratio let to increase dose of Fe^{+2} which led to increase in sludge formation containing Fe which need costly further treatment.

It's found that the most feasible treatment is for the sample (3C) which partially treating by using lime $Ca(OH)_2$, after partially treatment finished COD removal and Nitrogen total removal are 88%, 80% respectively with H_2O_2\COD w\w 1:2 and H_2O_2\Fe^{+2} 10:1 also the results summarize in the following table:

Table 14: Summary results of total removal rate for contaminant in Fenton reaction for Sample of Flocculation with Lime $Ca(OH)_2$.

Sample	COD removal (%)	TKN removal (%)	TS removal (%)	TSS removal (%)
Sample (3C) of Flocculation with Lime $Ca(OH)_2$	88%	80%	62%	91%

5.2 Recommendations

According to the results of this research, various recommendations were summarized as follow:

1. Pre-treatment before Fenton process is recommended due to reduce pollution load as possible.
2. Using lime $Ca(OH)_2$ is highly recommended in order to the results that gotten by this material before and after Fenton reaction.
3. H_2O_2, and $FeSO_4$ dosages should be optimized carefully, in addition to pH media.
4. Scope of future look entails scale up of Fenton process using pilot plant
5. AOP recommended due to cost achievable, in nonpaying fees for the high pollution load.
6. AOP recommended achieving cabinet resolution number (16) for the year 2013.

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Annex (A): Part of the Regulations of Connecting Establishments to the Public Sewer Network

6. يلتزم مقدم خدمة المياه والصرف الصحي بفصل حسابات المياه والصرف الصحي عن الحسابات الأخرى، ويقوم بفتح حساب بنكي موحد لجميع الإيرادات العائدة من خدمات الصرف الصحي.

مادة (16)

البدلات الإضافية للصيانة والتشغيل

1. يستوفي مقدم خدمات المياه والصرف الصحي بدلات إضافية إلى تلك الوارد ذكرها في المادة (15) من هذا النظام من المنشآت التجارية والصناعية بعد إصدار الموافقة على ربطها بشبكة المجاري العامة، وذلك في حال تجاوز تركيز متطلب الأكسجين الكيماوي (COD) الحد الأعلى المسموح بتواجده في المياه العادمة المصرفة لشبكة المجاري العامة والبالغ 2000 (ملغم/لتر)، وذلك لتغطية ما يتكبده مقدم خدمات المياه والصرف الصحي من نفقات إضافية في عملية المعالجة.
2. تحدد البدلات الإضافية المخصصة لتغطية نفقات المعالجة وفق معادلة يقررها مقدم خدمات المياه والصرف الصحي ووفق معايير تتفق مع مبدأ "الملوث يدفع".
3. يتولى مقدم خدمات المياه والصرف الصحي إصدار المطالبات الخاصة بالبدلات الإضافية للمنشآت والمصانع التي تم ربطها بشبكة المجاري العامة.
4. يعتمد المتوسط الحسابي لتركيز متطلب الأكسجين الكيماوي (COD) لاحتساب البدلات الإضافية لتغطية نفقات المعالجة دورياً (كل ثلاثة أشهر)، على أن لا يقل عدد العينات التي يتم أخذها من المصنع عن عينة واحدة شهريا إذا كان ذلك ممكناً.

مادة (17)

واجب دفع بدلات الانتفاع

1. يقع واجب دفع بدلات الصيانة والتشغيل لمنظومة الصرف الصحي لمقدم خدمات المياه والصرف الصحي على عاتق مالك أو مستخدم العقار سواءً كان عداد المياه مسجلاً باسمه أم

دولة فلسطين
State of Palestine

دولـــــــــة فلســــــــطين

مجلس الوزراء

الملحق

تعليمات صرف المياه العادمة التجارية والصناعية والزارعية إلى شبكة المجاري العامة

مادة (1)

يمنع صــــرف المياه العادمة التجارية والصـــناعية الملوثة وغير الملوثة إلى شـــبكة المجاري العامة إلا بعد معالجتها والحصول على موافقة خطية من مقدم الخدمات وفقاً لهذه التعليمات.

مادة (2)

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

1. أية مواد صلبة أو سائلة بكميات أو بأحجام أو بخصائص بيولوجية أو كيميائية أو فيزيائية يمكن أن تؤدي إلى إعاقة التدفق في خطوط شبكة المجاري العامة أو تسبب ضرراً بالصحة العامة أو تؤدي إلى انبعاث المكاره أو تلحق ضـــرراً بشـــبكة المجاري العامة أو بالموظفين أو تتعارض مع أعمال صـــيانة وتشـــغيل محطات المعالجة أو مع عملية المعالجة فيها أو يمكن أن ينتج عنها مياه معالجة تهدد الصـحة والسلامة العامة، وعلى سبيل المثال لا الحصر، الرماد وبقايا الفحم المحترق والرمال والطين والقش والنشـــارة والمعادن والزجاج والخزف والريش والقار والبلاســـتيك والخشـــب والنفايات والدماء وأحشـــاء الحيوانات والســـماد الحيواني والشـــعر والأطباق الورقية والعبوات بمختلف أنواعها والدهون والشحوم والزيوت، والحوامض والكربون والأملاح المعدنية والبخار والغازات الحارة والأصباغ والمبيدات والمخلفات الســـائلة من معاصـــر الزيتون ومنتجات الألبان ودماء الحيوانات الناتجة من المسالخ.
2. أية مواد صلبة أو سائلة أو غازية تحتوي على مواد سامة أو عناصر معدنية أو معادن ثقيلة يمكن حســب رأي مقدم الخدمات أن تضـــر أو تتعارض مع عملية المعالجة أو يمكن أن تشكل منفردة أو نتيجة تفاعلها مع الفضلات الأخرى خطراً على الإنسان أو الحيوان أو النبات.

3. أية مواد يمكن أن تؤدي إلى:

أ. عدم إمكانية المعالجة خلال عملية المعالجة.

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

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

4. أية مياه عادمة خارجة من المنشأة يقل رقم الأس الهيدروجيني pH فيها عن (5.0) ويزيد على (9.5).

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

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

7. المياه العادمة التي تحتوي على الزيوت والشحوم والدهون النباتية والحيوانية أو الشمع بشكل مستحلب (Emulsified) وبتركيز يزيد على (100ملغم/لتر).

8. أية مياه عادمة أو مواد تحتوي على السيانيد أو مركباته بتركيز يمكن أن ينتج عنه (2) ملغم /لتر مقدرة على شكل سيانيد.

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

10. أية مياه عادمة أو مواد تحتوي على مركبات الكبريتيد بتركيز يزيد عن (2.0) ملغم/لتر مقدرة على شكل كبريتيد الهيدروجين.

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11. أية مياه عادمة أو مواد تحتوي المذيبات العضوية المكلوره (CHLORINATED ORGANIC SOLVENTS) .

12. أية مياه عادمة أو مواد تحتوي على المنظفات الكيميائية مقاسه كـ MBAS بتركيز يزيد عن (40) ملغم/لتر.

13. المياه العادمة التي تحتوي على الزيوت المعدنية من الات القطع والمقطرات بتركيز يزيد عن (20) ملغم/لتر.

14. أية اية مياه عادمة أو مواد تحتوي على مركبات السلفات (SO4) بتركيز يزيد عن عن (1000) ملغم/لتر.

15. أية مياه عادمة أو مواد تحتوي على مركبات الكلوريدات (Cl) بتركيز يزيد عن (500) ملغم/لتر.

16. أية مياه عادمة أو مواد تحتوي على مركبات الفلورايد بتركيز يزيد عن (60) ملغم/لتر.

17. أية مياه عادمة تحتوي على المواد الصلبة العالقة الكلية (TSS) بتركيز يزيد عن (600) ملغم/لتر.

18. أية مياه عادمة يكون الأكسجين الممتص كيماويا (COD) فيها يزيد عن (2000) ملغم/لتر.

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

مادة (3)

العناصر الثقيلة

يحظر صرف أية سوائل أو مواد تحتوي على عناصر ثقيلة أو سامة يزيد تركيز تلك العناصر فيها عند موقع الصرف على الحدود المبينة أدناه :

العنصر	التركيز (ملغم / لتر)
*كروم إجمالي	5
* نحاس	4.5
قصدير	10
بيريليوم	5

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Annex (B): Results

- Samples of raw mixed agro-food industrial wastewater with initial COD values.

Run No.	Sample No.	COD mg/L
1	Sample No. 1	16200
2	Sample No. 1A	16200
3	Sample No. 1B	16200
4	Sample No. 1C	16200
5	Sample No. 2	18200
6	Sample No 3	17750
7	Sample No 3A	17750
8	Sample No 3B	17750
9	Sample No 3C	17750
10	Sample No. 4	15400
11	Sample No 4A	15400
12	Sample No 4B	15400
13	Sample No 4C	15400

- Results for sample No. 1:

1. Raw mixed agro-food wastewater.

Wastewater sample of mixed agro-food wastewater from Al-Safa factory and municipal slaughterhouse of Nablus	
Parameters	Value and results
pH	6.96
COD (mg/l)	16200
Total solids (mg/l)	3705
Total suspended solids (mg/l)	220
BOD_5 (mg/l)	7008
TKN(mg/l)	570

2. Before Fenton.

Coagulated by ferric chloride		
Parameters	Value and Results	Removal Rate
COD (mg/l)	6080	62%
Total solids (mg/l)	2685	28%
Total suspended solids (mg/l)	56.2	74%
BOD_5 (mg/l)	2920	58%

Flocculation with lime $Ca(OH)_2$		
Parameters	Value and results	Removal rate
COD (mg/l)	5150	68%
Total solids (mg/l)	2988	19%
Total suspended solids (mg/l)	93.5	58%
BOD_5 (mg/l)	2780	60%

3. After Fenton

Coagulated by ferric chloride after Fenton			
Parameters	Value and results	Removal rate	Total removal rate
pH	7.3		
COD (mg/l)	2889	52%	82%
Total Suspended solid (mg/l)	17.8	68%	92%
Total solids (mg/l)	1389	48%	63%
BOD_5 (mg/l)	1380	53%	80%
TKN(mg/l)	176	69%	69%

Flocculation with lime $Ca(OH)_2$ after Fenton			
Parameters	Value and results	Removal rate	Total removal rate
Ph	7.3		
COD (mg/l)	1820	70%	88%
Total Suspended solid (mg/l)	19.6	65%	91%
Total solids (mg/l)	1415	47%	62%
BOD_5 (mg/l)	968	67%	86%
TKN(mg/l)	113	80%	80%

- Results for sample No. 2:

Sample	Initial COD (mg/l)	COD (mg/l) after Fenton treatment directly
Raw mixed agro-food wastewater	18200	10000

- Results for sample No. 3:

1. Raw mixed agro-food wastewater.

Parameters	Value and Results
pH	9.66
COD (mg/l)	17750
BOD_5 (mg/l)	8200

2. Results after Fenton.

Parameters	Sample 3A (Coagulated by ferric chloride $FeCl_3.6H_2O$)	Sample 3B (Sedimentary sample without coagulant)	Sample 3C (Flocculation with Lime $Ca(OH)_2$)
pH	8.1	10.5	11.7
COD (mg/l)	12700	13200	8050
BOD_5 (mg/l)	6315	6544	4020

- Results for sample No. 4:

Sample	Initial COD (mg/l)	COD (mg/l) after partially treatment	COD (mg/l) after Fenton treatment
Coagulated by ferric chloride $FeCl_3.6H_2O$	15400	6015	3500
Flocculation with lime $Ca(OH)_2$ after Fenton	15400	5020	1780
Sedimentary sample without coagulant	15400	10800	6080

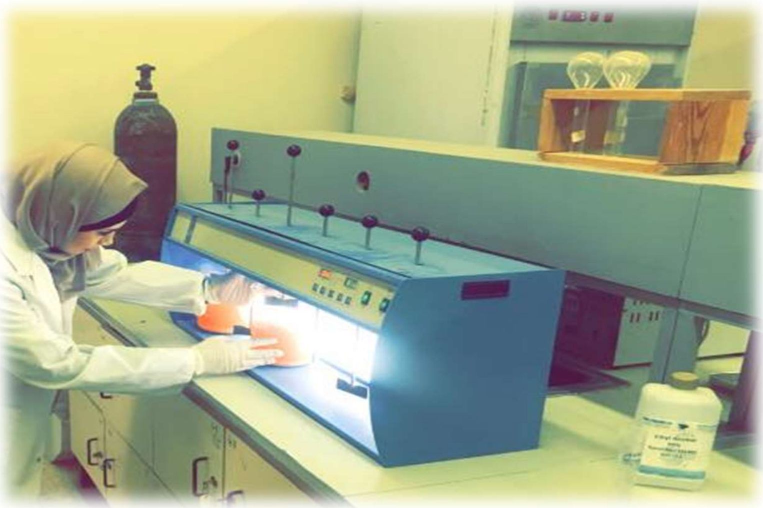
ANNEX (C): Photos from the Lab and Material Used

1. Photos and b while preparing mixed of agro-food wastewater.

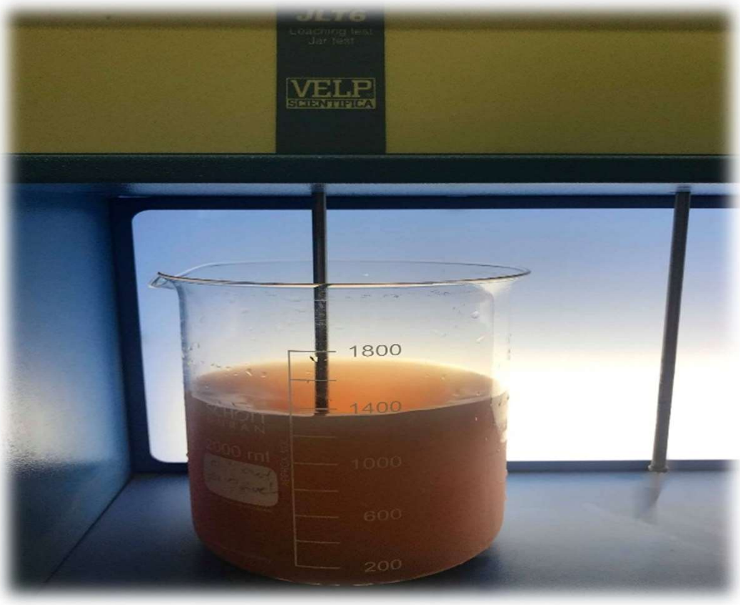
(a)

(b)

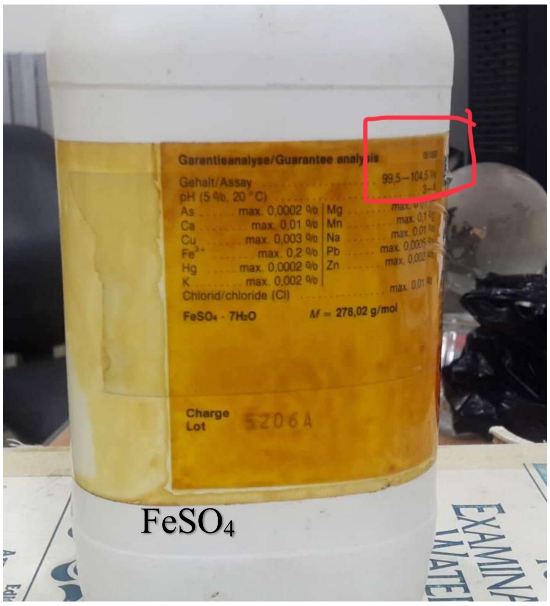
2. Photos c, d, and while using Jar test for coagulation by $FeCl_3.6H_2O$.

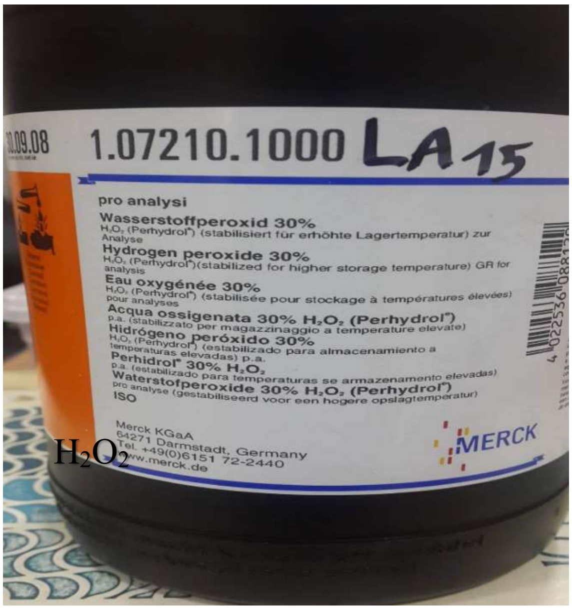


(c)



(d)

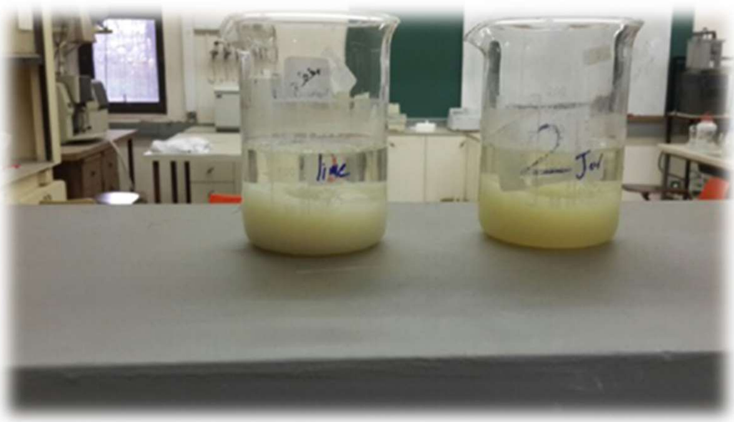




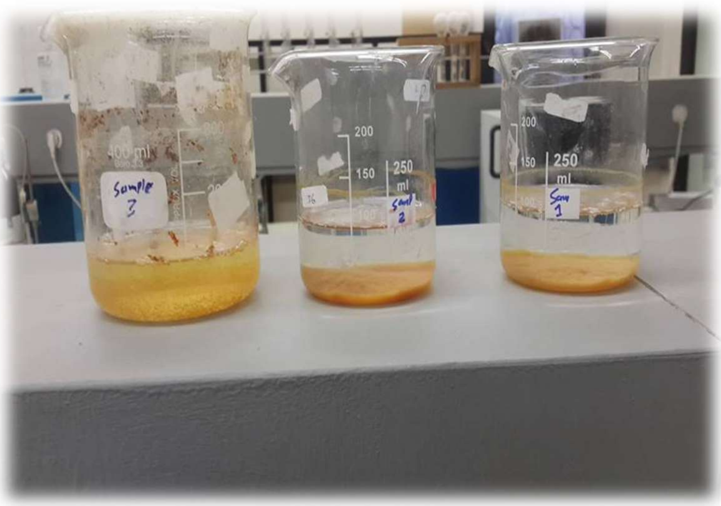
(e)

3. Photos e, f, and g while making Fenton reaction.

(f)



(g)



(h)