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Al-Quds University

Characterization and Optimization of Olive Mill Wastewater Treatment by Coagulation Using Experimental Design Approach

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Thesis Approval

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Dedication

I dedicate this search To my beloved mother Mrs. Raja Zaitoon , who raised me when I was young and guided me and directed me towards all the best.

To my brothers Hamzah ,Omar and Imad ,who have been my source of joy , happiness and support at all times .

To my father's soul , May this work be a part of his good deed .

To the martyrs who are more generous than all of us, who watered the soil of this land with their blood in defense of its wealth.

To the prisoners, the lions behind bars, who spent the flower of their youth in the prisons of the occupation in defense of their land and their faith.

To them all: I offer this humble effort, I hope God Almighty to make it in the balance of my good deeds and all of them.

Thank you all

Sujood Abusabha

Declaration

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

Name: Sujood Faisal Khaleel Abusabha

Sign: سجود ابوصبحة

Date: 08/01/2022

Acknowledgment

My sincere gratitude to all my teachers those candles that stand tall, melting themselves to illuminate life for others, those hands that build the future and make minds and men. to my advisor Dr. Amer Marie Sawalha who was supportive and a respectful advisor . To all my teachers, Dr. Adnan Lahham, Dr. Mutaz Al-Qutb, Dr. Amer Kanaan and Dr. Jawad Shoqeir.

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Abstract

Olive Mill Wastewater (OMWW) are considered major environmental pollutants in the Mediterranean Basin, where for each produced liter of olive oil, about 4 liters of OMWW is produced. In the West Bank, the effluents are drained in the open environment. OMMW contains macro and micronutrients that could be useful for plants in case a reduction of phenols contents takes place.

The objective of this study is to propose a pre-treatment system using the coagulation technique, and select the best operating conditions by applying Design of Experiment software for optimum pollutants reduction. The proposed treatment aim to reduce pollutants of OMWW effluent including organic matter in term of COD, total suspended solids TSS, and phenolic compounds.

The principal operating parameters that have effects on coagulation process are pH, coagulant dose, and coagulant type. Two coagulant types' Aluminum sulfate (AlSO4) and Ferric Chloride (FeCl3) were used. The coagulant concentration ranges between 0.5 and 2 mg/L, and the pH values range between three and eight.

The number of samples and the level of each operating parameter were chosen based on experimental design methodology using Design Expert 13.0 software. For this, a 23 factorial design was used where the number of experiments proposed by the program was 18. Afterward, factorial regression analyses were used to analyze the results and chose the optimum combination of factors for treatment.

The efficiency of the treatment process was calculated based on the reduction percent in each pollutant concentration. The results indicate that the coagulation process can be used effectively for removing those three pollutants. The TSS, COD, and Total Phenols for the raw OMWW are 42, 60, and 6,7 g/L respectively. By using, the two coagulates salts, a reduction in TSS range between 90 and 96%, for COD between 53 and 73%, and for Total Phenols between 11 and 37%, in the other hand electrical conductivity increased from 12 mS/cm to about 20 mS/cm.

The statistical analysis of results was carried out using Design Expert 13.0 software following Pareto plot, graphical study of the effects, interaction diagrams, and 3D graphs. In addition to estimating the coefficients corresponding to the polynomial model for each response (b 0,1,2,3...bk). Moreover, Design Expert was used for analysis of variance (ANOVA), and the validity of models was checked by the correlation coefficient R2 and adjusted-R2, in Addition to F-value.

For TSS removal both coagulants have approximately the same efficiency 93.5 % and 93.7% average efficiency for AS and FC respectively. Aluminum sulfate best operational conditions were at pH 4.5 and 0.5g/l gave 96.4% efficiency. Ferric Chloride best operational conditions gave 96.9% were at pH 3 and 0.5 g/l.

The process leads to a great reduction in the solution turbidity. The original OMWW sample turbidity was measured at around 25,000± 305 NTU while the average turbidity in samples treated with AS was around 3300 and with FC was 4600 NTU.

For COD average removal efficiency was 63% and 58% for AS and FC respectively. For AS best operational conditions were at pH 4.5 and 2g/l concentration where the process had around 73% efficiency. FC best operational conditions were around pH 4.5 and 0.5 g/l concentrations where the process had around 60.9% efficiency.

Total Phenols reduction was 30% using AS and 14% using FC. Best conditions for, AS was pH4.5 at 2.0g/l conc. Giving 37.6% efficiency. And for FC at pH8 and 0.5 conc. Giving 24.1% efficiency.

تحديد خصائص الزبار واختيار افضل الظروف لمعالجته بتقنية التخثير باستخدام التصميم الاحصائي

إعداد: سجود أبو صبحه

إشراف: د. عامر صوالحة

الملخص

تعتبر المياه العادمة الناتجة عن معاصر الزيتون او كما تسمى (الزبار) من المشكلات الحقيقية التي تواجه مدن حوض البحر الأبيض المتوسط والذي يعد الأكثر شهرة في إنتاج زيت الزيتون . حيث يتم إنتاج حوالي 4 لترات من الزبار مقابل كل لتر من زيت الزيتون. في فلسطين والضفة الغربية غالبا ما يتم تصريف هذه المياه العادمة في شبكة المياه العادمة أو في البيئة المحيطة بدون اي معالجة.

يحتوي الزبار على العديد من العناصر المغذية من المغذيات الصغرى والكبرى والتي يمكن أن تكون مفيدة للنباتات في حالة تقليل تركيز البوليفينولات الضارة للنبات والبيئة قبل الاستخدام في للري. الهدف من هذه الدراسة هو اقتراح نظام معالجة أولي لهذا الزبار باستخدام تقنية التخثر، واختيار ظروف المعالجة المثالية من خلال استخدام برنامج تصميم التجارب (Design Expert) للحصول على أقصى معالجة وتقليل تركيز الملوثات. تهدف المعالجة المقترحة إلى تقليل ملوثات الزبار بما في ذلك المواد العضوية, إجمالي المواد الصلبة العالقة ، والمركبات الفينولية.

العوامل الأساسية التي تؤثر على عملية التخثر هي الرقم الهيدروجيني وجرعة المخثر ونوعه. في هذه الدراسة سيتم استخدام نوعين من مواد التخثر كبريتات الألومنيوم (4AlSO) وكلوريد الحديديك (3FeCl) ، ويتراوح تركيز مادة التخثر بين 0.5 و2 غم/لتر .

تم اختيار عدد العينات ومستوى كل عامل من العوامل المؤثرة على عملية التخثير على أساس منهجية تصميم التجارب باستخدام برنامج Design Expert 13.0 حيث كان عدد التجارب المقترحة من قبل البرنامج 18. بعد ذلك تم استخدام تحليلات معامل الانحدار لتحليل النتائج واختيار القيم الأمثل لكل عامل .

تم حساب كفاءة عملية المعالجة على أساس انخفاض النسبة المئوية في تركيز كل ملوث وتشير النتائج إلى أن عملية التخثر يمكن استخدامها بفعالية لإزالة هذه الملوثات الثلاثة: إجمالي المواد الصلبة العالقة و المواد العضوية والمركبات الفينولية حيث كانت قيمتها في الزبار غير المعالج كالاتي 42، 60 و 6,7 غرام/لتر على التوالي، باستخدام الملحين المخثرين كان هناك انخفاض واضح في تراكيز الملوثات حيث تراوحت تراكيز إجمالي المواد الصلبة العالقة بين 90 و 96٪، و المواد العضوية بين 53 و 73٪، وبالنسبة للفينولات بين 11 و 37٪، في ناحية أخرى زادت الموصلية الكهربائية من 12 mS/cm إلى حوالي 20 mS/cm.

تم إجراء التحليل الإحصائي للنتائج باستخدام برنامج Design Expert13.0 باستخدام الرسوم البيانية التي تبين تأثير كل عامل على عملية المعالجة والتفاعلات بين هذه المعاملات بالإضافة إلى الرسوم ثلاثية الابعاد التي توضح التغير في النتائج كل ما تنقلنا عبر القيم المختلفة للمتغيرات . وعلاوة على ذلك، تم استخدام برنامج التصميم لتحليل التباين (ANOVA) وتم التحقق من صحة النماذج من قبل معامل الارتباط R2 وR2 المعدلة ، بالإضافة إلى قيمة F .

في عملية ازالة المواد الصلبة العالقة كلا الملحين كان لهما أثر متقارب بكفاءة تصل الى 93.5٪ و93.7٪ لكبريتات الألومنيوم (4AlSO) وكلوريد الحديديك (3FeCl) على التوالي. حيث كانت أفضل الظروف التشغيلية لكبريتات الألومنيوم في pH 4.5 وتركيز 0.5 غم/لتر بكفاءة وصلت إلى 96.4٪. أما عن أفضل الظروف التشغيلية لكلوريد الحديديك أعطت نتائج 96.9٪ وكانت في pH 3 وتركيز 0.5 غم / لتر.

كما ادت العملية الى انخفاض كبير في العكورة حيث كانت حوالي 25،000 ±305 NTU في الزبار الخام في حين أن متوسط العكورة في العينات المعالجة مع كبريتات الألومنيوم كان حوالي 3270 ومع كلوريد الحديديك كان NTU 4600 .

بالنسبة لمتوسط كفاءة إزالة المواد العضوية كان 63٪ و 58٪ ل AS و FC على التوالي. بالنسبة لأفضل الظروف التشغيلية AS كانت في pH 4.5 وتركيز 2 غم / لتر كانت كفاءة العملية حوالي 73٪. وكانت أفضل ظروف تشغيلية FC حول pH 4.5 و تركيز 0.5 غم / لتر كانت العملية ذات كفاءة حوالي 60.9٪.

بالنسبة إلى إجمالي الفينولات كان الانخفاض بمقدار 30٪ باستخدام AS و 14٪ باستخدام FC . وكانت أفضل الظروف AS حول pH4.5 وتركيز 2.0 غم / لتر. وأعطت كفاءة 37.6٪. وبالنسبة ل FC حول pH8 وتركيز0.5 غم / لتر pH 8 بكفاءة 24.1٪.

List of Abbreviations

AS: Aluminum Sulfate

AOP: Advanced Oxidation Processes

BOD_5: 5 days Biochemical Oxygen Demand

Btw. : between

COD: Chemical Oxygen Demand

Conc. :Concentration

EU: European Union

FAO: Food and Agricultural Organization

FC: Ferric Chloride

IOC: International Olive Council

NTU : Nephelometric Turbidity Unit

MoA : Ministry of Agriculture

OMWW: Olive Mill Wastewater

rps: revolution per second

TP :Total Phenols

TSS : Total suspended solids

UTOMWW : Untreated Olive Mill Wastewater

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Chapter One

Introduction

1.1 Introduction

The olive oil production Industry is considered as an important economic activity among agro industrial sector for many countries in the Mediterranean regions . According to European Union report of market situation in the olive oil and table olives sectors the annual world production of olive oil reached about 3 million tons in 2020. Most of olive oil production comes from Mediterranean countries See Figure(1.1) (EU, 2020).

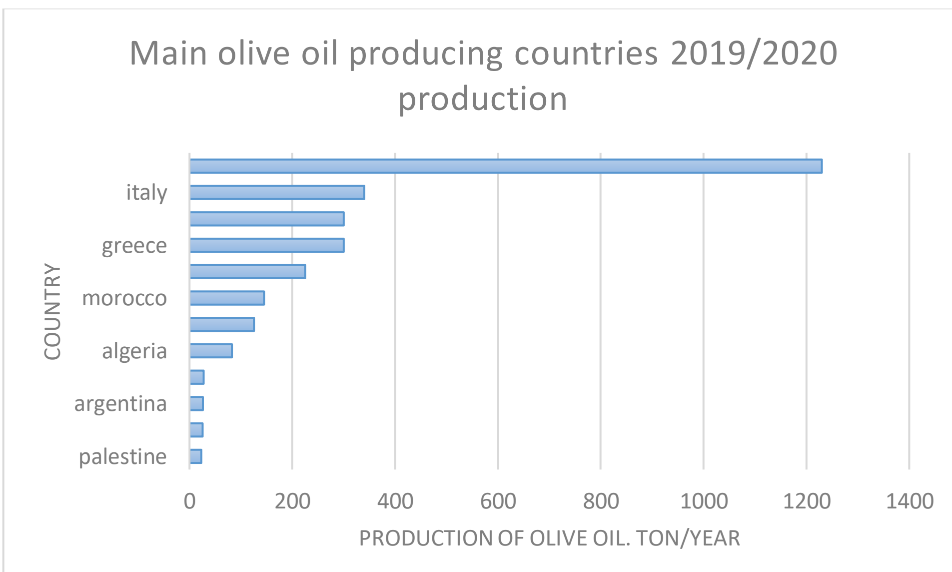


Figure1. 1 Main olive oil producing countries 2019/2020 production , adjusted from (IOC, 2019)

In Palestine, olive orchards cover more than 60 thousand dunum of Palestinian land and contribute to the economy through the food industry and other industries such as traditional soap production (Palestinian Central Bureau of Statistics, 2020). There are about one million olive trees in Palestine , and the olive subsector comprises 15 percent of the total agricultural income, this has a major role in mitigating unemployment and poverty in the Palestinian society by providing 3 to 4 million seasonal work days per year and by supporting 100,000 Palestinian families (Hanieh et al., 2020) .

he operations of these mills are spilt between modern and traditional methods , 275 of the working presses are fully automatic and 10 are half automatic or traditional presses(Palestinian Central Bureau of Statistics, 2020).

The amount of olive fruit produced during 2019/2020 season with the aim of pressing to extract oil was about 178 thousand ton, the amount of oil extracted reached about 40,000 ton .Figure(1.2) illustrates the percentage of oil extracted in Palestine for each provenance.

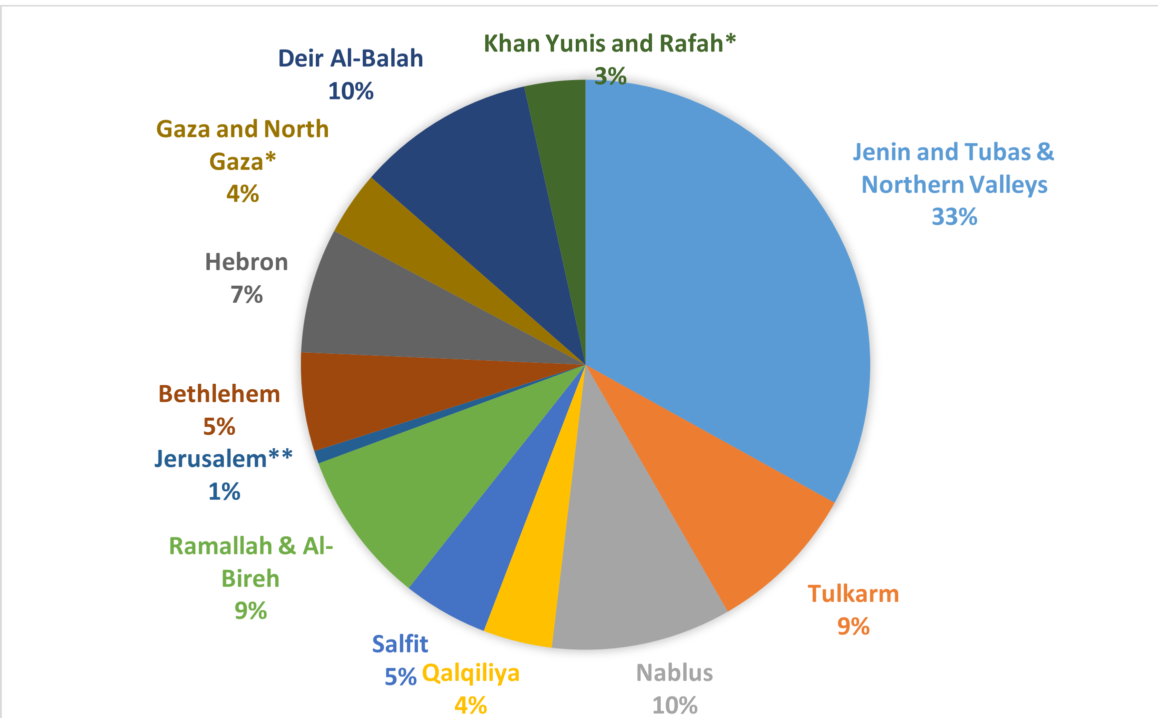


Figure1. 2:Quantity of oil extracted in Palestine for each provenance , source (Palestinian Central Bureau of Statistics, 2020).

Today there are three different processes used for olive oil production. These systems produce nearly the same amount of oil but differ to a large extent in the amount and the composition of the different byproduct fractions they produce (Camarsa et al., 2010). The first type is the traditional pressing method which has been used for many centuries now , Even though the traditional pressing is a relatively old fashioned technology, it is still in use for some olive oil producers . The second is the centrifugation method , this method has been adapted only few decades ago . These systems can be either three-phase or two-phase systems.

The three-phase system generates three fractions at the end of the process: a solid (olive husk or olive pomace) and two liquids (oil and wastewater).The centrifugation has many advantages compared to traditional method , including complete automation, better oil quality, smaller area needed . However, it also presents some problems such as greater water and energy consumption, higher wastewater production and more expensive installations.

In the two phase decanting processes the olive paste is separated into two fractions: an oil fraction and a wet pomace (humidity up to 65 %) called two phase olive mill waste that could be treated again to get a second of olive oil using solvents (Enaime et al., 2019).

The traditional press method typically generates about 50% of OMWW compared to the initial weight of the olives, whilst the continuous centrifugation process generates 80–110% of OMWW because the process is based on continuous washing of the olive paste with warm water before oil separation from the paste (Mantzavinos et al., 2005).

1.2 Problem Description

The highly valued oil and the large industry that relies on it doesn't come without a cost .The management and disposal of OMWW by traditional mills and modern centrifugation systems has become a great concern due to the effluent extremely polluting features and because they are generated in massive quantities in short periods of time (Roig et al., 2006). These large concentrations could cause a shock and a foul in the wastewater treatment system if disposed directly to the sewers without pretreatment .At this point ,agricultural land are the most commonly used OMWW management options (Komnitsas et al., 2012).

The OMWW effluent are characterized by high organic load , low pH , high load of phenolic compounds and suspended solids .Usually consists of (4–16%) organic matter , (83–92%)water, and (1–2%)minerals (Ramos-Cormenzana, 1986) .Organic substances found in OMWW include sugars, tannins, phenolic compounds, polyalcohols, pectins, and lipid (De Marco et al., 2007), about 10% of the organic matter is phenolic compounds (Ramos-Cormenzana, 1986).

The treatment of OMWW is extremely difficult due to its large volume and the high concentration of organic matter. Moreover , the olive oil manufacturing industries are small plants with a daily OMWW flowrate between 10 and 100 m^3 and are distributed over large areas (Mantzavinos et al., 2005). Moreover ,the high concentration of polyphenols is a major factor of problems imposed by the OMWW (Deeb et al., 2012).

The negative impacts on the environment are widespread to soil, water and air degradation. As for the soil, uncontrolled spreading of OMWW in fields can cause damage to the plants, if the wastes were not pretreated or in the case that they are spread in large quantities (Pierantozzi et al., 2012). Moreover, spreading of OMWW could be a reason for soil erosion (Mahmoud et al., 2010) . The uncontrolled spreading of OMWW on soils , evaporation ponds, the composting of liquid wastes or pruning residues in order to produce compost and the uncontrolled burning of pruning residues is responsible for high percent of pollutants emissions (Rana et al., 2003) .OMWW disposal also impose substantial environmental burden to the groundwater. The land spreading of olive mill wastewater is a serious hazard for groundwater pollution, which leads to biodiversity reduction and problems in potable water (Banias et al., 2017) .

Many solutions have been suggested for the treatment , management and disposal of OMWW but many factors should be taken into consideration when selecting the best method including total amount of effluents, investment costs, available land, industrial or agronomic environment, and most important local needs. That’s Why there is no unique, sustainable solution, since sustainability depends on the specific needs of the local area and each olive oil industry separately.

Most of olive oil producer countries in the Mediterranean area suffer from desertification, so the water and organic matter reuse would be beneficial to improve soil fertility and control the erosion processes. Also in organic agriculture, the use of treated OMWW as fertilizer could represent an important source of nutrients. Moreover , phenols of OMW are too valuable to be diminished or discharged to the environment. Therefore, the recovery of phenols accompanied with their reutilization in different products and markets should be considered .

In this context, researchers have been tirelessly proposing suitable treatments for these effluents, and several technologies have been proposed for removal of phenolic compounds and other pollutants like organic matter and suspended solids in OMWW based on thermal , biological, and physio-chemical processes including coagulation .Which if coupled with other environmentally friendly treatment processes such as adsorption could be sufficient to produce an effluent suitable for environmental applications .

Recently, factorial design experiment are employed instead of the conventional one-factor-at-a-time experiment. These programs and statistical approaches are used to find out most important process variables, which affect the treatments efficiency(Rathinam et al., 2011). The factorial experimental design involves changing all the variables from one experiment to next, as the individual variables can influence each other and the ideal value for one of them can depend on the values of others. Factorial design is employed to reduce the total number of experiments in order to achieve the best overall optimization of the system. It allow the simultaneous study of the effects that several factors may have on the optimization of a particular process. Although the statistical design of experiments is largely employed in the optimization of industrial process, it is rarely applied to wastewater treatment processes (Hamaidi-Maouche et al., 2009). To our knowledge there have been no local studies that have used experimental design for the optimization of coagulation treatment system . And this is what this research is aiming to tackle.

1.3 Research Objectives

The main objective of this study is to propose a pre-treatment system for olive mill wastewater using coagulation processes and select the pest operating conditions by means of design of experiment approach. The proposed treatment aim to reduce pollutants present in OMWW effluent including organic matter , Suspended Solids and phenolic compounds and produce an effluent suitable for land application or at least allow its safe disposal in unprotected evaporation ponds, thus minimizing the risk for soil, surface and groundwater contamination.

The following objectives serve the goal of this research, which are:

1. Proposing a pre-treatment system based on coagulation process .
2. Using the experimental design methodology (DOE), for determining optimal operating conditions for the proposed treatment to produce an effluent suitable for land application with low hazardous effect on the environment .

Chapter Two

Literature Review

2.1 Olive Pressing Processes

Presently , there are three different processes used for olive oil production. These systems produce nearly the same amount of oil but differ to a large extent in the amount and the composition of the different byproduct fractions they produce (Camarsa et al., 2010). The first type is the traditional pressing method which has been used for many centuries now , even though the traditional pressing is a relatively old fashioned technology, it is still used by some olive oil presses . The second is the centrifugation method , this method has been adapted only few decades ago, centrifugation systems can be either three-phase or two-phase systems, the difference between processes is shown in Figure(2.1) .

The three-phase system generates three fractions at the end of the process: a solid (olive husk or olive pomace) and two liquids (oil and wastewater).The centrifugation has many advantages including complete automation, better oil quality, smaller area needed . However, it also presents some problems such as greater water and energy consumption, higher wastewater production and more expensive installations. In the two phase decanting processes the olive paste is separated into two fractions: an oil fraction and a wet pomace (humidity up to 65 %) called two phase olive mill waste that could be treated again to get a second of olive oil using solvents (Enaime et al., 2019).The traditional press method typically generates about 50% of OMWW compared to the initial weight of the olives, whilst the continuous centrifugation process generates 80–110% of OMWW because the process is based on continuous washing of the olive paste with warm water before oil separation from the paste (Mantzavinos et al., 2005). The reduction of water dilution during the three phases process leads to increasing the phenolic concentration in the olive oil too. Therefore, new generation of three-phase water saving decanter centrifuges are designed for lower water consumption during the centrifugation process and consequently less generation of wastewater (Safa et al., 2017). Table(2.1) shows the approximate input and output data for two phase and three phase olive oil production systems.

The two phase continuous decanting system is currently the main olive oil production procedure used in several countries it’s frequently called “ecological” because of its minor water and energy requirements and reduced pollution load table . Although more olive oil producing countries are also slowly adopting the two phase technology, the three-phase extraction process is still ongoing in some areas where small olive oil enterprises resist switching due to the capital investment, especially where water economy is not a major consideration (Víctor-Ortega et al., 2016).

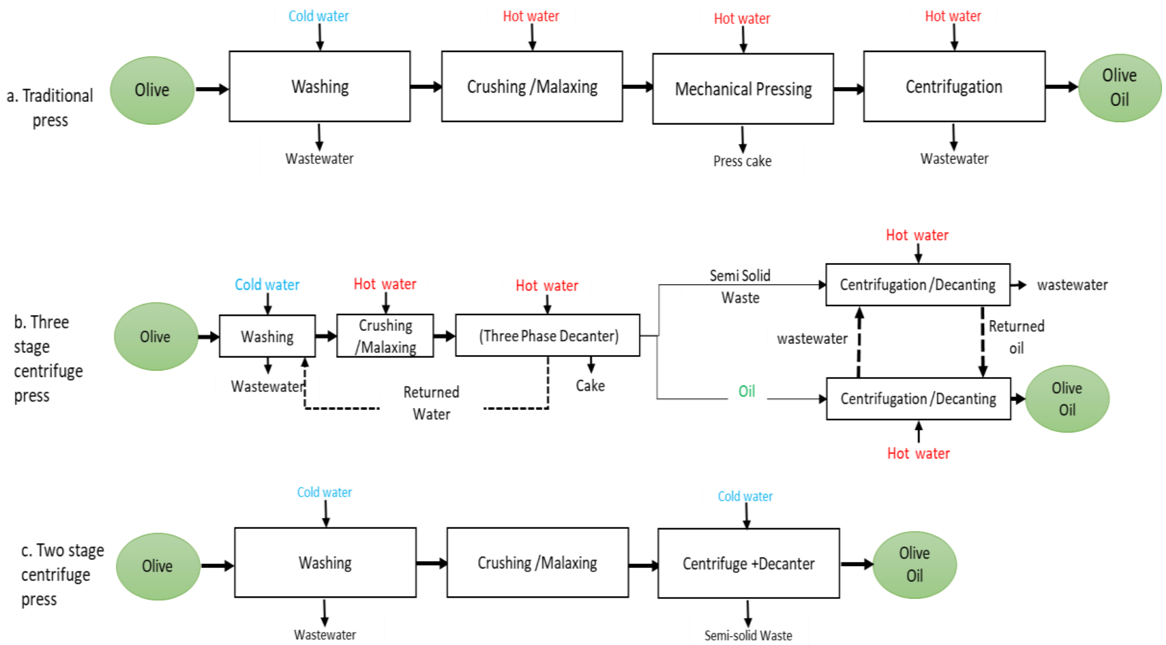


Figure2. 1 :A graph representing the different stages of olive oil pressing within the existing pressing systems a. Traditional b. Three phase c. two phase Adjusted from (Aladham, 2012)

Table 2. 1 : The approximate input and output data for two phase and three phase olive oil production systems.

Production Process	Input	Input Quantity	Output	Output Quantity (kg)
Three Phase	Olives	1 ton	Oil	200
	Wash Water	100 - 120 L	Solid Waste	500-600
	Fresh Water For Decanter	500-1000 L	Wastewater (94% Water +1%Oil)	1000-1200
	Water For Impure Oil Washing	10 L		
Two Phase	Olives	1 ton	Oil	200
	Wash Water	100 - 120 L	Solid Waste &Water Waste (60%Water+3%Oil)	800-950

2.2 Extraction Waste

Generally , olive oil extraction processes generate three main products : olive oil, solid residue and extremely high organic loaded aqueous waste called Zebar or Olive Mill Wastewater (OMWW),the amount of each byproduct depend mainly on the extraction procedure. In Palestine ,OMWW is typically disposed of in sewage systems or cesspools in addition to being discharged into water streams and valleys of the region (Al-Khatib et al., 2009) .

During olive processing, 3.5 L of water are consumed for every liter of olive oil produced, this process produces about 4.34 kg of OMWW and 2.07 kg of solid waste (olive cake) for every liter of olive oil produced (Avraamides et al., 2008). The majority of Palestinian presses distribute olive cake to farmers and small portion sell them for heating purposes ,while the OMWW is either discharged to wastewater network , or into Cesspit and a minority discharges the effluent directly to the environment . See Table(2.2).

Table 2. 2 :Number of olive presses in Palestine by governorate and methods used for waste disposal . (Palestinian Central Bureau of Statistics, 2020)

Waste type	Method of disposal	Number of Olive Presses in Palestine
Olive cake	Sell	53
	for Farmers	215
	Others	17
Wastewater	Tight Cesspit	95
	Sewage Network	47
	Porous Cesspit	136
	Others	7
Zebar	Tight Cesspit	111
	Sewage Network	43
	Porous Cesspit	118
	Others	13
Total No. of Operating Presses		**285**

2.3 Characteristics of Olive Mill Wastewater

Characteristics of olive waste are not constant, they vary significantly according to climate, olive fruit cultivation and oil extraction practices .On the first hand there are the olive fruit itself , The fruit consist mainly of Water ,Oil , nitrogen , sugar cellulose ,minerals , Poly phenols and other compounds , which explains the difference in Olives shapes, sizes and the various ratios between stone and pulp content . The majority of oil is contained in the pulp ,for this reason olive fruits with high pulp to stone ratio are preferred . (Iakovides et al., 2016) . On the other hand there is the OMWW effluent , it is considered a strong industrial wastewater; its composition is not constant. It varies according to cultivation soil, harvesting time, climatic conditions, use of pesticides, degree of ripening and olive oil extraction processes. This effluent is characterized by high organic load , low pH , high load of phenolic compounds and suspended solids . It usually consists of (83–92%)water, (1–2%)minerals and (4–16%) organic matter (Ramos-Cormenzana, 1986) .The organic substances found in OMWW include sugars, tannins, polyalcohols, pectins, and lipid (De Marco et al., 2007) and about 10% of the organic matter is phenolic compounds (Ramos-Cormenzana, 1986), which is about 150 times higher than the organic load of domestic wastewater, The organic load in OMWW is considered one of the highest concentrated effluents (Al-Khatib et al., 2009).

2.4 Environmental Impact of OMWW

OMWW are often disposed in evaporation ponds or various environmental receptors .The disposal of OMWW causes serious environmental problems during the olive harvest season. The negative impacts of olive mill wastewater on the environment are widespread to soil, water and air degradation., plants growth inhibition, soil contamination , natural streams pollution as well as severe effects to the aquatic fauna and to the ecological status.

2.4.1 Effect of OMWW on Soil

Spreading of OMWW in fields can cause damage to the top soil and plants, if the wastes were not pretreated or in the case that they are spread in large quantities (Pierantozzi et al., 2012).

Spreading of OMWW could be responsible for soil erosion (Mahmoud et al., 2010) . Researchers reported that the direct application of raw OMWW on plants causes leaf and fruit abscission (Aladham, 2012).

Uncontrolled disposal of OMWW may affect soil acidity, salinity, Nitrogen immobilization, microbial activity, nutrient leaching, lipids concentration, soil hydrophobicity, water retention capacity, infiltration rates and cause strong phytotoxic effects (Komnitsas et al.,

2012) . High OMWW application rates also affect the levels of exchangeable K and the content of N-NO3 in soils . Another major environmental concern is associated with P accumulation in soil and the long period required, up to 20 years, so that P content reduces again to acceptable levels for agronomic use (Rusan et al., 2016) .

2.4.2 Effect of OMWW on Air Quality

The uncontrolled spreading of OMWW on soils and evaporation ponds, in addition to composting liquid wastes or pruning residues in order to produce compost and the uncontrolled burning of pruning residues is responsible for high percent of pollutants emissions (Rana et al., 2003). In addition to strong odor nuisance.

2.4.3 Effect of OMWW on Water

The disposal and land spreading of OMWW also impose significant environmental burden on groundwater. which leads to reduction in natural biodiversity and problems in potable water (Banias et al., 2017) .

Discharge of OMWW even diluted in streams, rivers and other water bodies may severely affect macroinvertebrates, the entire ecological status of ecosystems and reduce the potential of self-purification mechanisms. Moreover, the effluent is rich in phosphorus that can cause serious environmental problems such as eutrophication if wasn't effectively removed (Iakovides et al., 2016). OMWW has poor biodegradability and high phytotoxicity due to the presence of phenolic compounds, in addition to the presence of reduced sugars that can stimulate microbial respiration and lower dissolved oxygen concentrations.

2.4.4 Effect of OMWW on Infrastructure

The suspended solids content can settle in the sewer system and cause clogging to the mills discharge pipes . Moreover ,Due to its acidic nature OMWW could be highly corrosive to sewer pipes .The sediments also undergo anaerobic fermentation and cause further increase the acidity content of wastewater which leads to disruption of biological activities in domestic wastewater ponds. This creates a strong and unpleasant odor due to aerobic digestion in open air systems (Al-Khatib et al., 2009) .

2.5 Treatment Processes of OMWW

Like all food processing wastes, olive mill wastewater have always been considered as a waste in need of treatment, minimization, and management due to the environmental effects induced by their disposal . Researchers have been tirelessly proposing suitable treatments for olive mill waste effluents .The difficulties of OMWW treatment are mostly related to its high organic loading, seasonal operation, high territorial scattering, and the presence of non-biodegradable organic compounds like long-chain fatty acids and phenols (Safa et al., 2017).

Several technologies have been proposed for removal of pollutants present in these effluents including phenolic compounds , organic matter and suspended solids , these treatments could be based on thermal , biological, and physio-chemical processes or a combination of these methods . In an attempt to categorize the proposed methodologies of OMWW treatment or processing, three categories can be given:

- Waste reduction through olive production systems conversion , for example conversion into two-phase instead of three-phase continuous systems ,
- Recovery or recycling of components from olive mill waste water ,
- And detoxification methods aiming at the reduction of impact of the pollution load to the recipient environment .These processes may include Physical , Thermal treatment , Biological treatment , or any combination of these processes .

2.5.1 Thermal Treatment

Thermal treatment can include several process such as Physio-thermal processes , Irreversible chemical-thermal and Lagooning :

- **Physio-thermal processes** : consist of evaporation and distillation of OMWW, where a concentrated solution and volatile stream consisting of water and vapor and volatile substances are produced , The main drawbacks of this processes is the high energy consumption , the odor problems. Moreover , the distillate has a low pH and cannot be discharged or reused to wash the olives before additional treatment since it would increase the degree of acidity of the pure olive oil (Aladham, 2012).
- **Irreversible chemical-thermal processes**: like combustion and pyrolysis

- **Lagooning**: Lagoons are large artificial evaporation ponds or storage lakes. The sun's energy is usually used to speed up the evaporation and drying process of OMWW.

2.5.2 Biological Treatment

Biological processes are the most environmentally friendly and least expensive wastewater treatment methods. Several studies have dealt with the efficiency of aerobic degradation concerning phenols and toxicity removal. Some studies Reported nearly complete removal of phenols after 20 days in batch fermenter (Aggelis et al., 2003) . Another study reported 69–76% removal of phenols after 12–15 days in shake flasks , and a reduction in Phytotoxicity (Tsioulpas et al., 2002).

Other studies suggested Co-digestion of OMWW with other effluents (Marques, 2001) , (Gavala et al., 1996) . Mixing and digesting OMWW with other effluents has several benefits including the reduction of feed COD and total phenols concentration, and this make it possible to run a year round treatment plant based on the digestion of seasonally generated effluents.

However , biological treatment methods has one major drawback , they cannot cope with the high organic load of OMWW that need to be diluted several times prior to biological treatment, thus introducing serious cost implications. In addition to this, the presence of some toxic compounds such as polyphenols and lipids makes OMWW inappropriate for direct biological treatment. (Mantzavinos et al., 2005).

2.5.3 Physio –Chemical Processes

This type of processes involves the use of chemicals or other materials for the purpose of neutralization, coagulation, flocculation, adsorption, chemical oxidation-ion exchange, and advanced oxidation processes (AOP) . Advanced oxidation processes (AOP) include ozonation, UV irradiation, photocatalysis, hydrogen peroxide/ferrous iron oxidation (the so called Fenton’s reagent), electrochemical oxidation, wet air oxidation as well as various combinations of the above. The problem with AOP processes they can only achieve partial decontamination even after prolonged treatment time, they also have high costs (Rahmanian et al., 2014)

Thermal processes target the condensation or destruction of the waste material, but they are ineffective due to the very high operating costs. physicochemical methods like neutralization, precipitation re relatively cheap. However, they require further treatment of the waste . Physical processes are typically applied as pre-treatment steps for the removal of solids. Therefore, combining more than one treatment processes has become preferable in recent years.

(Enaime et al., 2019) studied the efficiency of combining adsorption of raw olive mill wastewater (OMWW) on olive stone (OS) filters followed by a coagulation- flocculation. The filtration was found to be effective to remove TSS (82.5%) and Fatty Matter (73.8%) and presented an interesting performance to remove Total Phenols (11.3%) and COD (23.2%). (Jiang, 2015) stated that coagulation process if made as a prestep could enhance processes that follow like settling- flotation, filtration, adsorption, oxidation and disinfection.

2.5.3.1 Coagulation

Coagulation is an inexpensive, simple and easily applicable method for the treatment of olive mill wastewater. Coagulation is a physio-chemical water treatment process used to remove solids from water, by manipulating electrostatic charges of particles suspended in water. This process introduces small, highly charged molecules into water to destabilize the charges on particles, colloids, or oily materials in suspension which leads to combining small particles into a larger aggregates (flocs) and these impurities can be removed in subsequent solid/liquid separation processes (Jiang, 2015). Coagulation is a physio-chemical method that's widely used for the treatment of olive mill wastewater . The process relies on the effective decrease of the electrical charge of the suspended solids which allows particles to approach each other and form large clusters (Iakovides et al., 2016) .

Coagulation is one of the most economical and environmentally friendly and proper methods for treating OMWW, on the other hand its effectiveness is limited (up to 40–50% reduction of the initial COD values (Iakovides et al., 2016) hence if coagulation was made as a prestep it could enhance processes that follow like settling- flotation, filtration, adsorption, oxidation and disinfection (Jiang, 2015). Studies have also reported the ability of coagulation process to reduce the Phenolic compounds to a certain level (Enaime et al., 2019) .

Factors affecting coagulation process

Several chemicals were used in coagulation flocculation process to reduce pollutants including solids and organic load from the OMWW. The effectiveness of this process is mainly depended on the type and the added amount of these chemicals in addition to the experimental conditions used during the process including pH , the initial turbidity of the water that is being treated, and properties of the pollutants present (Iakovides et al., 2016) . Mixing conditions such as rapid mixing time, slow stirring speed is also important (Ma et al., 2012) . For Instance (Enaime et al., 2019) , studied the effect of different types and doses of coagulants along with pH levels to come up with an optimum combination for OMWW . Excessive coagulant addition can lead to the opposite results, which is re-stabilization of the suspended particles with opposite charge. Hence, the confirmation of the appropriate coagulant dosage is of highly important for the efficiency of the method.

Moreover , the selection of a right coagulant for a system or a treatment process will enhance the overall system performance . The coagulation process includes using primary coagulants and may include the addition of coagulant aids. The difference between these two is that Primary coagulants are used to cause destabilization of particles to begin to clump together (Spellman, 1999) .Commonly used coagulants of this type are aluminum salts such as aluminum sulfate($Al_2(SO_4)_3.18H_2O$) and Iron salts such as ferric chloride($FeCl_3$) because of their low cost and relative ease of handling (Brandt, Johnson et al. 2017) .In the other hand , enhanced coagulants and coagulant aids add density to slow settling floc and help maintain floc formation (Spellman, 1999). Organic polymers, like polyaluminum hydroxyl-chloride (PACl), in combination with a primary coagulant are usually used to enhance coagulation. Operational and fixed costs are the major aspects that define the sustainability of a treatment method. The cost for coagulation mainly comes from the amount and type of electrolytes or polyelectrolytes used in the proposed method.

A number of studies have been carried out regarding the selection of optimum electrolyte/polyelectrolyte for pollutants removal from OMWW . (Tsonis et al., 1989) and (Aktas et al., 2001) have used calcium hydroxide [$Ca(OH)_2$] and Aluminum sulfate (Al_2SO_4) to reduce the organic load of OMWW. Also (Jaouani et al., 2005) suggested the addition of lime (CaO) and ferric chloride ($FeCl_3$) as treatment to reduce the pollution load and the results were very promising. (Iakovides et al., 2016) studied coagulation/flocculation with respect to their removal efficiency in terms of chemical oxygen demand (COD), total suspended solids (TSS), Total solids (TS) and total phenols (TP) removal and by monitoring the zeta potential with electrolytes and polyelectrolytes , and found ferric chloride the most appropriate electrolyte with up to 43% COD removal. Aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) and ferric chloride($FeCl_3$) are two electrolytes proposed for treatment in our research .

Aluminum sulfate ,also called Alum , is a chemical compound with the formula $Al_2(SO_4)_3$. It is soluble in water and is mainly used as a coagulating agent in drinking water purification and wastewater treatment plants .AS comes in two forms , Anhydrous aluminum sulfate which is a white crystalline solid ,And 18-hydrate $Al_2(SO_4)_3.18H_2O$. Both of those forms are noncombustible , soluble in water, and nontoxic.

Aluminum sulfate reacts in different ways to achieve coagulation. Charge neutralization (destabilization) is the primary mechanism involved when used at relatively low doses (<5 mg/L), while at higher dosages, the primary coagulation mechanism is entrapment. In this case, aluminum hydroxide ($Al(OH)_2$) precipitates forming a “sweep-floc” that tends to capture suspended solids as it settles out of suspension.

Since solubility of the aluminum species in water is pH dependent ,the pH of the water plays an important role when alum is used for coagulation. If the water pH is between 4 and 5, alum is generally present in the form of positive ions (i.e., $Al(OH)^{2+}$, $Al_8(OH)^{4+}$, and Al^{3+}). However, optimum coagulation occurs when negatively charged forms of alum predominate, which occurs when the pH is between 6 and 8. When alum is used and charge neutralization is the primary coagulation mechanism, effective

flash mixing is critical to the success of the process. When the primary mechanism is entrapment, effective flash mixing is less critical.

The main advantages of Alum is availability and ease of use and it is inexpensive. However its main disadvantages that large amounts are often required. The dirtier the water, the more alum is needed. And It produces a lot of sludge, which is not very easy to dewater because it becomes very gelatinous.

Ferric chloride is an orange to brown-black solid, slightly water soluble ,noncombustible, and highly corrosive to most metals. It is used to treat sewage, industrial waste, and to purify water. Ferric chloride ($FeCl_3$) is the most common iron salt used to achieve coagulation. It’s reactions in the coagulation process are much like those of alum, but its relative solubility and pH range differ significantly from those of alum. The behavior of FC as a coagulant can be attributed to the adsorption , when FC is added to wastewater the insoluble ferric hydroxide, produced during the hydrolysis of FC, destabilizes colloidal particles by charge neutralization and allows small impurities to form large aggregates, which in turn provides a large available surface area to adsorb organic substances, which can be separated from pretreated wastewater by simple sedimentation (Kang et al., 2003) .

The main advantages of ferric chloride that there is no pH requirement ,hence it works over a broad pH range. And it’s very easy to use. However the main disadvantages of this salt that its expensive and the price can fluctuate. Moreover it is highly corrosive and Special stainless steel piping, storage equipment, and pumping equipment are required .

2.6 Reuse of Treated OMWW in Land Irrigation

Due to the scattered nature of small olive oil production units, evaporation in lagoons and disposal to agricultural land are the most frequently management options used for olive mill wastewater . Nevertheless , protection of soil and water quality as well as human health should be at all times considered as apriority before selecting any management option .

OMWW could be used effectively to minimize the pollution of the ecosystem and maximizing the use of the water and nutrients (Rusan et al., 2016). Using OMWW as fertilizer, due to its content in organic carbon, K, N and P, is often considered as a viable approach that restores soil fertility, keeping in mind that land application is controlled and also the soil type is suitable and not related to sensitive water resources and aquifers.

A study conducted by (Rusan, Albalasmeh et al. 2016) on maize planted in pot experiment. proved that irrigation with untreated olive mill wastewater increased soil salinity and reduced plant growth, while the treated OMWW via different technologies improved plant growth and produced lower soil pH .

(Mekki et al., 2006) studied the effects of Olive mill wastewater treated with white-rot fungi followed by anaerobic digestion . The effluent effect on seed germination, plant growth and soil fertility were studied on several plant types including tomato, chickpea, bean, wheat and barley . The treated plants showed an improvement in seed biomass, spike number, plant growth, and a similar or perhaps better dry productivity than plants irrigated with water. Moreover , an increase in soil organic matter content , its respiration potential ,and its enzymatic activities were enhanced.

Keeping in mind that although treated OMW enhances plant growth compared to untreated, the plant growth remains lower than using potable water with fertilizers, indicating lack of some essential plant nutrients . Although in most countries no specific guidelines exist, studies have shown that when OMWW are used as soil amendment, no more than 50 m^3 OMWW/ha should be spread in a single application (Defra,2009).

(Ayoub et al., 2014) recommended the application of 10 L OMWW/m^2 to improve soil fertility and olive plant performance after observing a significant increase in shoot growth, photosynthesis, fruit set, and fruit yield with no negative effects on oil quality parameters . in addition , the concentrations of K, organic matter, phenolic compounds, and total microbial count were significantly increased in OMWW-treated soil .

(Tamimi et al., 2016) suggested a safe strategy for OMWW disposal by application into soil in a controlled manner ,for example 140m^3 /ha or less ,and alternate the selected field annually . They also studied the mechanisms of OMWW - soil interaction affecting soil quality and their temporal dynamics and proved that OMWW disposal in spring had less negative effects compared to winter or summer .They stated that winter application has less impact on soil ,however poses higher risk of leaching into ground water .

(Ben Brahim et al., 2016) compared the effect of irrigating olive orchards with fresh water , OMWW and Treated wastewater and confirmed that there are no significant differences on oil quality indices and flavonoids between the three . However, the irrigation affected some aspects of olive oil composition like the reduction in palmitic acid and increase in linoleic acid and total phenols . The study suggested irrigating olive orchards with 100 m^3 /ha of OMWW for optimal olive oil quality and composition .

According to (Safa et al., 2017) OMWW application shows short-term negative effects on soil chemical and biological properties, but may be considered negligible after appropriate waiting period. Some studies recommended soil amendment with OMWW six months before maize sowing for toxicity mitigation .

Chapter Three

Methodology

This chapter describes in details sample collection and storage in addition to all analytical methods that have been used throughout the entire experiments which were applied in the characterization and treatment stages . Moreover the chapter go through the selection process of coagulants doses and design of coagulation experiment using Design Expert Software .The research Methodology followed these steps :

1. Sample collection.
2. Analyzing the sample to study its characteristics including pH ,Electrical Conductivity (EC), Turbidity , TSS ,COD .
3. An experiment to detect Change in OMWW Characteristics in 24 Hours Without Interference.
4. Designing coagulation process which included :
   - Selecting coagulants and selecting coagulants concentration
   - Designing coagulation process using design expert ,the program suggested 18 treatment sets
5. Conduction coagulation experiment in lab for all 18 sets .
6. Analyzing the experiment result by :
   - Analyzing all 18 treated samples for TSS ,Turbidity , COD, TP
   - Compare the results with the original sample to detect the percent change in the pollutants concentration ,hence detecting the treatment set efficiency
7. Statistical analysis for each pollutant results separately including
   - ANOVA
   - Graphical analysis of the model
   - Creating Polynomial model for each pollutant removal percent

3.1 Sample Collection & Storage

An olive mill wastewater sample was collected from a three-phase mill located in Hebron District in the West-Bank . The sample was collected in October 2020 and was preserved for 6 month before any lab experiment were conducted due to COVID19 lockdowns. The collected sample was tightly sealed and stored in the refrigerator at 4C and strongly stirred before use.

3.2 Analytical Methods

The following section intend to describe in detail all analytical methods that were applied for measuring the characteristics of OMWW which include: pH ,Electrical Conductivity (EC), Turbidity , TSS ,COD , Nutrients (N,P,K). A summary of all devices and methods used for measuring each parameter is illustrated in table Table(3.1) ,These methods were used for both the characterization and treatment stage of OMWW. All testing took place in the chemistry lab at Palestine Polytechnic University Hebron.

When needed, a pretreatment of OMW consists of filtering raw OMWW using filter papers (MN 615, average 90 mm, average retention capacity 4-12 m) at room temperature, which refers to 20-25 °C in order to remove solids to avoid interference while measuring the main characteristics of the raw OMWW .

Table3. 1 : Methods used for measuring each parameter related to characteristics of OMWW.

Parameter	Measuring method / device	Program number	wavelength	Reference
pH	pH/Cond340i handheld Mustimeter	-	-	-
Conductivity	pH/Cond 340i Handheld Mustimeter	-	-	-
COD	Hack spectrophotometer model DR7900 using the Hach kits with an effective range of 1-10000 mg/L	LCK014	605nm	According to kit Instructions
Turbidity	Hack spectrophotometer model DR7900	747	860nm	
Total suspended solids	Standard Methods for the Examination of Water and Wastewater (detailed in Annex 1.1)	-	-	(Baird et al., 2017)
Total phenols	Folin- Ciocalteu reagent method (detailed in Annex 1.2)	-	760 nm	(Maurya et al., 2010)

3.3 OMWW Treatment Using Coagulation Process

Coagulation processes for OMWW is suggested as treatment method to reduce the polluting load . There were two proposed coagulants which are ferric chloride(FC) and aluminum sulfate (AS) . The treatment was made on a number of samples using Jar test methodology . “Jar testing is a pilot scale test of the treatment chemicals used in a particular water treatment facility .It mimics the coagulation/flocculation process in a water treatment plant and helps the operator determine if the right amount of treatment chemicals is used , and thus, improves the process performance” (Satterfield, 2005) .

The principal operating parameters that have effects on coagulation process are pH , coagulant dose and coagulant type. By studying the effect of those factors on pollution removal and choosing the best combination we were able to reach to an optimal combination that provide the desired level of treatment . The number of samples and the level of each operating parameters were chosen based on experimental design methodology using Design Expert 13.0 software. afterwards factorial regression analyses was used to analyze the results and chose the optimum combination of factors for treatment .

Chemical Oxygen Demand COD , Total Suspended Solids (TSS) and Total phenolic compounds (PC) are the main parameters used as pollution indicators. The efficiency of treatment process was calculated based on the reduction percent in each parameter.

3.3.1 Change in OMWW Characteristics in 24 Hours Without Interference

Objective of this experiment was to detect the magnitude (if any) of changes that can occur on OMWW if it was left for 24 hours in ambient air conditions without any modification or interference . A 400 ml sample was put in a beaker and left to settle for 24 hours, every 4 hours a sample was taken from the surface of the beaker and preserved in a sealed container to prevent any oxidation, six samples in total were taken then COD & total phenols were measured for the samples , TSS was not measured since no actual change or settling was observed in the sample in those 24 hours Figure(3.1) .

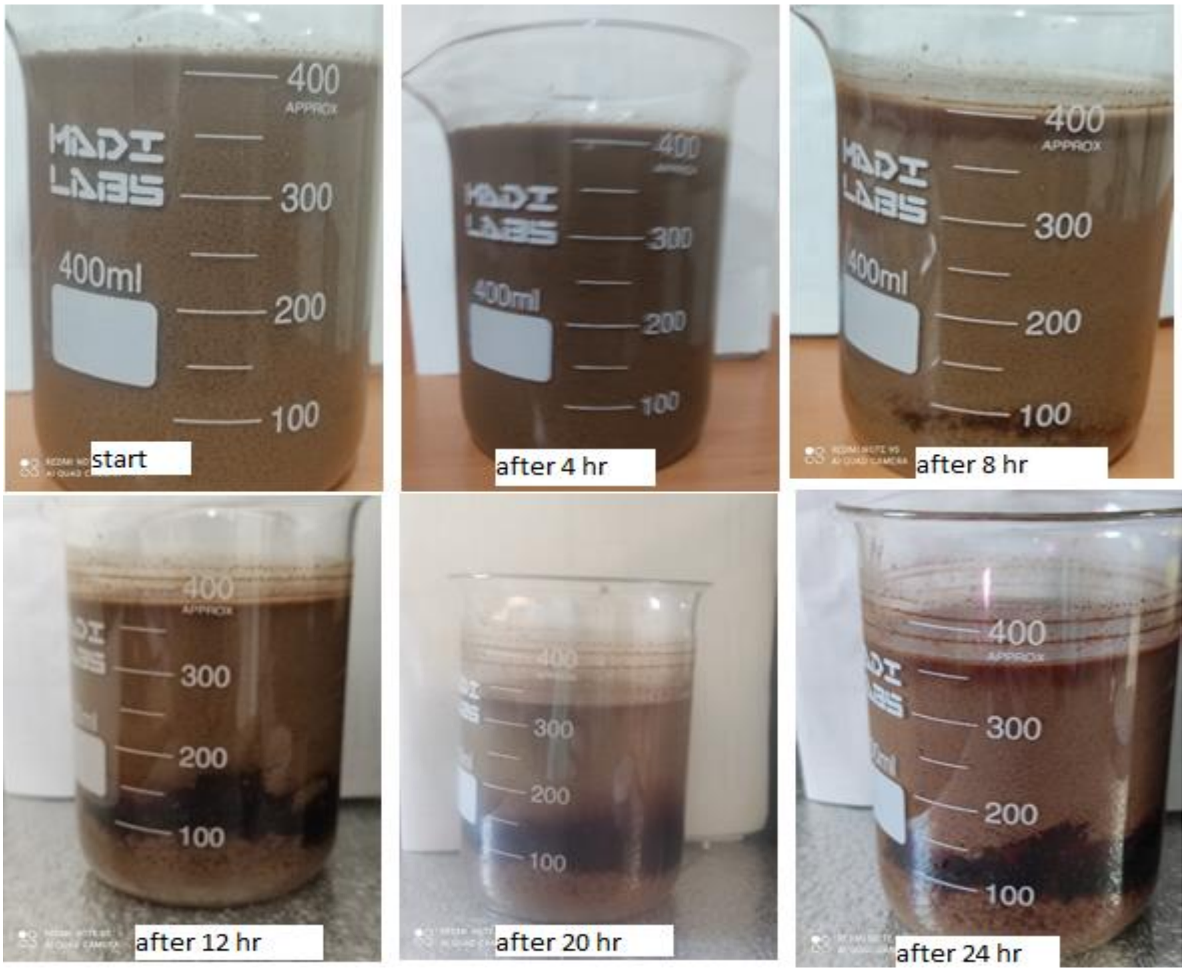


Figure 3. 1: Change in OMWW Characteristics in 24 Hours Without Interference

3.3.2 Selection of Coagulant Concentration

(Ginos et al., 2006) reported a Total Phenols reduction of 10% and a 50% COD reduction by performing coagulation with Fe(III) at 1.0 g/l . (Sarika et al., 2005) studied a variety of concentrations of FC from 0.67 to 8.3 g/l and reported that a complete removal of TSS was achieved at a relatively low coagulant concentration between 0.67 and 1.0 g/l while COD reduction did not exceed 20%. Increasing the FC concentration to 3.7 up until 8.3 g/l was accompanied with a sharp decrease of TSS removal and no COD reduction. In another study done by (Azbar et al., 2008) , researchers studied the performance of coagulation after acid cracking by varying $FeCl_3$ dosages from 0.5 to 6 g/l . They reported no significant change in the removal of both COD (24-27%) and TOC (31-35%) or total phenol concentrations (17-19%) with the increasing concentration of $FeCl_3.6H2O$. Nevertheless , higher concentrations of iron chloride resulted in coloration.(Vuppala et al., 2019) studied using Aluminum Sulfide as a coagulant among others with concentration ranging from 400 to 1,200 mg/L and found the concentration 800 mg/L to be an optimum choice with a reduction in phenols, COD and TOC, of about 62.89% , 57.16% and 16.76%, respectively . The variation in results could be due to the different experimental conditions used in those studies as well as to the different composition of tested OMWW .

In order to decide which concentrations range works best for the coagulation process, An experiment involved the following concentrations was conducted 0.5 , 1 , 2, 5 , 10 , 20 g/l . Six OMWW samples of 300 ml were prepared with the specified concentrations, the pH values were kept constant and equal to the natural pH of the wastewater which is 4.3 . All samples were stirred on magnetic stirrers for 2 min on high followed by 20 minute on low then left to settle for one hour. Results are discussed in the following chapter.

3.3.3 Design of Coagulation Experiment

3.3.3.1 Experimental Design

In the theory of optimization, an experiment is the series of tests in which the input variables are changed according to a certain order to identify the reasons for the changes in the output response . (Cavazzuti, 2012). Traditional univariate experiments study the effect of one factor at a time, keeping the rest of involved variables constant. This method is time consuming and require an excessive and unnecessary number of experiments to determine the optimum levels, they are usually unreliable. Moreover, the main drawback of these methods is that possible interactions among factors are not taken into consideration. These limitations can be eliminated by optimizing all the affecting variables simultaneously by means of experimental design (Víctor-Ortega et al., 2016) .

Experimental design or design of experiments (DOE), is the name given to the techniques used for guiding the choice of the experiments to be performed in an efficient way(Cavazzuti, 2012). The use of such design allows a simultaneous study of the effects that several factors may have on a process with fewer experiments, an estimation of which factor contributes more in the process and also an evaluation of the interaction between factors and how the effect of one factor varies as levels of other variables are changed. Benefits of factorial designs that it reveal whether the effect of each factor depends on the levels of other factors in the experiment. One factorial experiment can show interaction effects that a series of experiments each involving a single factor cannot do . It also provide excellent precision for the regression model parameter estimates that summarize the combined effects of the factors.

The first step when performing experimental design involves the selection of the experimental outcome to be optimized. The experimental outcome is normally the value for a certain property or a mathematical combination of several of them that represents a realistic measure of the process performance. Afterword's comes the selection of factors affecting the process and outcome results.

The second step is selecting all factors that affect the process .Experimental factors can be numerical variables, or categorical . Whether numerical or categorical the values of these factors are referred to as levels. The combinations of levels are normally called treatment combinations .An experimental run involves a specified level for each factor , each factor has two levels, minimum and maximum, normalized as -1 and +1, respectively .Sometimes in full factorial designs the central point of the design space is also added to the samples. The central point is the sample in which all the parameters have a value which is the average between their low and high level and noted as "m" (mean value) or "0".

A full factorial experiment consists of every combination of the levels of factors in the experiment. Thus, if we have k factors, each at two levels, the full factorial consists of the following treatment combinations:

$$\underbrace{2 \times 2 \times \cdots \times 2}_{k} = 2^k$$

The symbol 2k is used to represent this type of factorial design, not just as a calculation for the number of treatment combinations. The mathematical model representing the experimental response associated to a 2k factorial design (for k variables) is a linear polynomial model with interactions represented by following the equation :

$$y = b_0 + b_1X_1 + b_2X_2 + \ldots + b_kX_k \quad \ldots\ldots\ldots\ldots \text{ Equation 1}$$

Where

Y: The predicted response ,

Xi: Coded variable (-1 or +1)

b0: The constant term representing the average response in a factorial experiment

bi(i=1,2,3,4…k):Coefficient linked to the principal effect of the factor Xi for the response Y

In This research experiment , in order to evaluate the influence of coagulant type , pH and coagulant concentration on process efficiency and to define the optimum conditions allowing a maximum removal of TSS , COD and TP , a 2^3 factorial design was used. The original values of coded values of each factor and their corresponding levels are presented in Table(3.2). The design expert program produced a number of treatments . Each treatment was applied on an OMWW sample . All treatment sets are presented in Table(3.3). The treatment sets are expressed in actual values of the variables , coded values are available in Annex (2.1) .

Table3. 2 : Coded values of each factor and their corresponding levels

Factor	Name	Type	Min	Max	Coded Low	Coded High
A	pH	Numeric	3.0	8.0	-1	+1
B	Coagulant dose (g/L)	Numeric	0.5	2.0	-1	+1
C	Coagulant type	Categorical	Aluminum Sulfate	Ferric Chloride	-1	+1

Table3. 3 Suggested by design Expert program .

Sample number	Coagulant type	pH	Coagulant concentration(mg/l)
1	AS	8.0	1.0
2	AS	4.5	1.0
3	AS	4.5	2.0
4	AS	8.0	2.0
5	FC	8.0	0.5
6	AS	3.0	2.0
7	FC	3.0	1.0
8	FC	4.5	0.5
9	AS	3.0	0.5
10	FC	8.0	2.0
11	FC	8.0	1.0
12	AS	4.5	0.5
13	FC	3.0	0.5
14	FC	4.5	2.0
15	FC	3.0	2.0
16	AS	8.0	0.5
17	AS	3.0	1.0
18	FC	4.5	1.0

3.3.3.2 Conducting Coagulation Experiment in Lab

The coagulation experiments were conducted in a jar test. The OMWW sample was taken out of the refrigerator and allowed to come to room temperature and was stirred very well before use. The test included 18 beakers one for each treatment combination that was suggested by Design Expert , each beaker was filled with 200 ml OMWW and adjusted to a treatment set , first the pH was adjusted as needed using droplets of 7M NaOH and 3% HCL solutions , then the needed dose of each coagulant was added to the sample , the samples were then put on magnetic stirrers and stirred for 2 minutes on high speed (120rps)then for 20 minutes on low speed (20 rpm) (Satterfield, 2005). Then all samples were allowed to settle for 24 hours before collection . After 30 min of stirring there was a clear formation of two distinctive layers a dark dense layer of solid that started settling on the bottom and a lighter color liquid supernatant that started to collect on top . After settling for 24 hour the two layers were collected in separate containers and the top liquid supernatant was analyzed for TSS , COD and TP in order to study the coagulation process efficiency. The percent of removal efficiency of the contaminant species was defined as follows:

$$y\ \% = \frac{C0 - Ce}{C0} * 100\% \text{.............. Equation 2}$$

where C_0 and C_e are initial and final concentrations of each contamination indicator in(g/l)

Chapter Four

Results & Discussion

The results chapter includes four main sections :

1. Characteristics of OMWW

   This section discuss the characteristics of the raw OMWW that was collected for the purpose of treatment and comparing it with other local and worldwide values.

2. Results for the change in OMWW characteristics in 24 hours without interference

   This section discusses the effect of 24 hour settling time on changing OMWW characteristics ,mainly pollutants concentration .

3. Selecting coagulants concentrations

   This section discuss the selection processes of coagulants appropriate concentrations to be used in coagulation process .

4. Results of coagulation process in the lab

   This section discusses the effect of coagulation on the treated samples including :The change in pH and EC values and pollutants removal (TSS,COD,TP)

   Each of the three studied responses was studied and analyzed separately and the optimum combination for its best removal efficiency was allocated. The statistical analysis of results was carried out using Design Expert13.0 software following Pareto plot, graphical study of the effects, interaction diagrams and 3D graphs, in addition to estimating the coefficients corresponding to the polynomial model for each response (b 0,1,2,3..bk) . Moreover, Design Expert was used for analysis of variance (ANOVA) and the validity of models was checked by the correlation coefficient R^2 and adjusted-R^2, in Addition to F-value .

4.1 Characterization of Olive Mill Wastewater

OMWW characterization is the first step toward efficient and feasible treatment selection. To further study any olive mill waste water the first step must be to identify its existing characteristics . This section highlights the basic characteristics of OMWW in the study area . These main investigated characteristics include ;Total Suspended solids TSS , pH ,Electrical Conductivity (EC) ,Chemical Oxygen Demand (COD) ,Turbidity , and Total phenolic content(TP) . Three samples of untreated OMWW was analyzed and the average value obtained for each parameter were taken. Results for olive mill wastewater characteristics are summarized in Table (4.1) .

Average conductivity was 12 ± 0.30 ms/cm which is accepted to be within the normal range of OMWW conductivities. The pH value for our sample is 4.3 ± 0.20 which is slightly more acidic than reported values in Palestine(Al-Khatib et al., 2009) ,However it still remains within the reported values worldwide(Aladham, 2012) . Reported COD for OMWW in Palestine is in the range above 100 g/l , however our sample registered average values of 60±15 g/l , this slight decrees in COD value could be due to the long storage period before testing . BOD_5 was not measured in our experiments , according to (Aladham, 2012) special seeding must be taken into consideration for representative BOD5 results since BOD_5 in OMWW is low compared to COD due to the fact that total phenol inhibits biodegradation by the available microorganisms . Total Phenols concentration is 6.47 ± 0.40 , close range values were reported by Palestinian researchers (Al-Khatib et al., 2009) and much higher values were reported worldwide (Aladham, 2012) . Total suspended solids and turbidity were on average 42 ± 5.81g/l and 25,000 ± 305 respectively which is mainly due to cellulose material from the residues of olive husk pressing.

There are wide spatial and periodic variations in OMWW characteristics in Palestine. This is clearly shown in Table (4.1) comparing the OMWW characteristics in the study area with reported characteristics with other Palestinian researchers and some worldwide reported values. This variation is explained by annual and spatial variations in the quality of pressed olives. In addition, the regular modifications in the degree of automation and extraction techniques definitely affect the quality of generated OMWW.

Like any other industrial wastewater in Palestine, OMWW is subject to Palestinian standards for industrial wastewater discharge and need to be treated before discharge. The treatment degree depends on the fate of OMWW weather its wadies and streams with potential groundwater recharge or sewerage system. For instance , effluent discharged to sewer system need to have 2000mg/l ,3.0 mg/l and 500 mg/l for COD ,TP and TSS respectively (MEnA, 2000), For the collected OMWW sample as became evident after characterization measurements ,a considerable percent of around 97% , 89% and 99% for COD, total phenol, TSS respectively must be removed from this sample to meet the minimum standards for discharge to sewerage system.

Another suggestion is using treated effluent for irrigation, fruit trees in particular has tolerance for salinity and could be irrigated with treated OMWW if cleaned to a certain level. For instance olive date-palm is relatively salt tolerant and can be irrigated with waters with up to 4.5 ms/cm without any effect on its productivity. Olive orchards are moderately tolerant to salinity provided EC does not exceed 8 mc/cm, but EC of 4.5 mc/cm or less is preferred (Ayers et al., 1985).Which means , after sufficient treatment , our effluent could be mixed with fresh water and irrigated to trees .

Table4. 1: characteristics of OMWW compared to reported values in Palestine and Worldwide

Parameter	Unit	Measured value	Reported values in Palestine *	Reported values worldwide **
pH	--	4.3 ± 0.20	4.8 [b]	3-6
Conductivity	ms/cm	12.2 ± 0.30	10.8 [c]	5-41
COD	g/l	60 ± 15.0	138 [b]	40-220
Turbidity	NTU	25,000 ± 305	NA	NA
Total suspended solids TSS	g/l	42 ± 5.81	52 [b]	190
Total phenols	g/l	6.47 ± 0.40	3.7-4.6 [b]	5-80

*adjusted from a:**(Al-Khatib et al., 2009)** ,b: **(Aladham, 2012)** c:(Tamimi et al., 2016)
** adjusted from **(Aladham, 2012)**

4.2 Change in OMWW Characteristics in 24 Hours Without Interference

Drastic changes on the polluting load or OMWW characteristics takes long periods of time ,which can be reduced and cut much shorter with simple interference like treatments with coagulants . It is evident that leaving OMWW to settle without any interference does not change any of its pollutant characteristics including chemical oxygen demand and phenols See Figure (4.1) , which proves that any type of aid or interference to reduce the pollutant load in such short time is much better than discarding the pollutant into the environment without any handling or treatment first . Moreover, this step was made to make sure that 24 hour settling time did not have any effect on the final results of those test, since it's very important to be able the accurate and true values of these parameters due to the treatment itself .

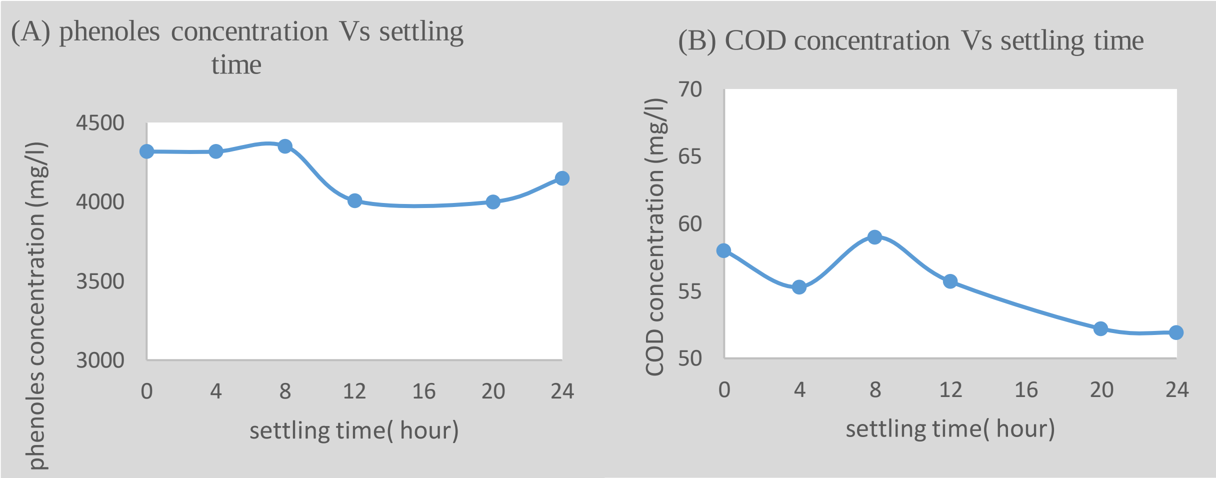


Figure4. 1: Change in (A) Phenols ,(B) COD concentration in OMWW in 24 hour settling time without interference

4.3 Selecting Coagulant Concentration

At 0.5- 2g/l concentrations, although the solution was slightly viscous, it still was easily manageable, while as concentration increased to 5 g/l and above the solution formed a gelatinous lumps and at concentrations greater than 10 g/l the solution turned virtually into a solid-like gel, See Figure (4.2). Filtration on filter paper and centrifugation were both used for the separation of those solids from the supernatant liquid and both were not successful. ,according to (Jaouani et al., 2005) higher coagulants concentrations can lead to an opposite effect and restablie charged particles as they reported that increasing coagulant concentration more than the optimum limit may lead to the restabilization of colloids. Concentrations of 2 g/l and lower , gave good separation results and produced two distinctive layers of a solid and a liquid supernatant layer on top , this correlates with previous researches (Ginos et al., 2006), (Sarika et al., 2005), (Azbar et al., 2008) and (Vuppala et al., 2019) . Concentrations of 2.0 g/l and less worked well, hence the next step is to decide which is the optimum concentration to use. The range of studied concentrations will be varied between 0.5 ,1 and 2 g/l .

Figure4. 2 Non effective treatment using coagulants concentration of 5g/l or higher

4.4 Results of Coagulation Process

4.4.1 Change in pH and EC Values

As shown in Table(4.2), most samples have experienced a slight decrease in pH values ,which can be related to the increase in hydrogen ions resulted from hydrolysis of the coagulation salts .According to the Palestinian standards the acceptable range for sewer and land discharge is between 6-8(MEnA, 2000). Another choice is using the discharge effluent for irrigation were lower pH is favorable .Either cases some action might need to be taken for pH adjustment .

The EC values increased slightly, this can be correlated to the addition of NaOH and HCl solutions for pH adjustment as well as the coagulation salts Figure (4.3) shows the increase in EC values with different coagulants .Given that high EC values cannot be tolerated by plants , in our analysis samples that have EC value below 15 ms/cm will be considered more favorable for trees irrigation after mixing with the right dilution amounts of fresh water .

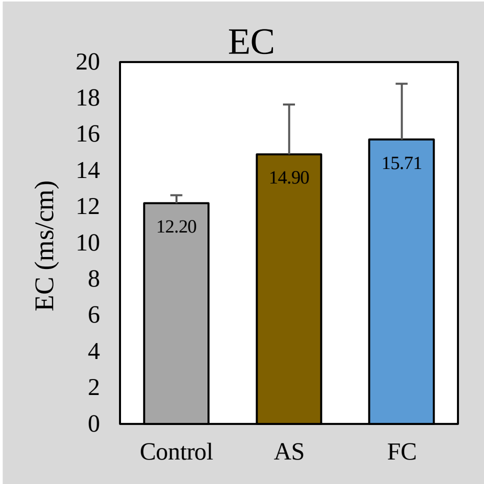


Figure4. 3: Average values of electrical conductivity over the different coagulants concentrations.

Table4. 2:EC and pH values for treatment sets before and after coagulation process .

Sample no.	Coagulant type	Coagulant conc.	pH before treatment	pH after treatment	EC (ms/cm)
UTOMWW (control)			4.30	4.30	12.20
1	AS	1.00	8.00	7.14	19.00
2	AS	1.00	4.50	4.75	12.70
3	AS	2.00	4.50	4.61	13.10
4	AS	2.00	8.00	7.25	20.00
5	FC	0.50	8.00	7.10	19.10
6	AS	2.00	3.00	3.25	15.00
7	FC	1.00	3.00	3.00	14.80
8	FC	0.50	4.50	4.50	12.30
9	AS	0.50	3.00	3.20	14.40
10	FC	2.00	8.00	6.64	20.10
11	FC	1.00	8.00	7.00	19.70
12	AS	0.50	4.50	4.70	12.80
13	FC	0.50	3.00	3.20	14.00
14	FC	2.00	4.50	4.50	13.20
15	FC	2.00	3.00	2.75	15.30
16	AS	0.50	8.00	7.22	12.70
17	AS	1.00	3.00	3.20	14.40
18	FC	1.00	4.50	4.50	12.90

4.4.2 Results of Pollutants Removal

A summary of the coagulation process results on Pollutant removal for all 18 samples and the control untreated olive mill wastewater (UTOMWW) sample in terms of mas reduction and change in actual values of Turbidity, TSS ,COD and Total are presented in Table(4.3). While Table (4.4) shows the process removal efficiency in percent for each treatment .

Each of the three studied responses was studied and analyzed separately and the optimum combination for its best removal efficiency was allocated. The statistical analysis of results was carried out using Design Expert13.0 software following Pareto plot, graphical study of the effects, interaction diagrams and 3D graphs, in addition to estimating the coefficients corresponding to the polynomial model for each response (b 0,1,2,3..bk) . Moreover, Design Expert was used for analysis of variance (ANOVA) and the validity of models was checked by the correlation coefficient R^2 and adjusted-R^2, in Addition to F-value .

An F statistic is a value obtained within ANOVA test or in regression analysis to find out if the means between two populations are significantly different. It’s much a like T-Test, A T-test says if a single variable is statistically significant and an F test will tell if a group of variables are significant jointly (Glen).

Pareto analysis give significant information about the influence of each factor on the studied response, where the horizontal t-value line represents the minimum statistically-significant effect magnitude, while the column lengths correspond to the significance of each variable. A positive value indicated that moving from low level to the high level is related to a favor or positive effect of factors improving the response, while a negative effect indicates an negative or unfavorable effect of a factor on the process**.**

The correlation coefficient (R^2) corresponding to a certain model should be at least 80% to provide a good fitting data, which indicates that obtained polynomial models represent adequately the relationship between responses and studied variables. However, the correlation coefficient may not evaluate adequately the model since it increases as variables increase, since even if they are not significant, they will still be added to the corresponding model. For more accuracy, the use of adjusted-R^2 can be better as it is adjusted to the number of variables used to generate the model (Enaime et al., 2019).

Table4. 3: Results of coagulation process results for all 18 treatments .

Sample no.	Coagulant type	pH	Coagulant conc.	Turbidity NTU	Weight after treatment (g/l)		
					TSS	COD	Total Phenols
UTOMWW (control)	--	--	--	25000	42	60	6.7
1	AS	8.0	1.00	7480	5.60	27.78	4.82
2	AS	4.5	1.00	2380	2.50	16.44	4.49
3	AS	4.5	2.00	1107	2.60	23.26	4.18
4	AS	8.0	2.00	6993	3.30	26.3	4.22
5	FC	8.0	0.50	8233	6.30	26.96	5.09
6	AS	3.0	2.00	1500	2.60	23.37	4.92
7	FC	3.0	1.00	2507	2.30	24.13	5.78
8	FC	4.5	0.50	2660	2.40	23.44	5.21
9	AS	3.0	0.50	787	1.60	23.84	4.65
10	FC	8.0	2.00	8893	1.80	28.41	6.53
11	FC	8.0	1.00	8033	5.20	27.91	5.9
12	AS	4.5	0.50	1880	1.50	23.79	5.08
13	FC	3.0	0.50	1767	1.30	24.05	5.23
14	FC	4.5	2.00	2140	1.60	25.67	6.05
15	FC	3.0	2.00	4560	1.60	21.38	5.9
16	AS	8.0	0.50	6060	2.30	27.91	5.12
17	AS	3.0	1.00	1253	2.70	18.4	5.01
18	FC	4.5	1.00	2553	1.40	24.32	5.92

Table4. 4:reduction efficiency for TSS, COD and TP for all samples compared to the control .

Sample no.	Coagulant type	pH	Coagulant conc.	Reduction %		
				TSS	COD	Total Phenols
1	AS	8.0	1.00	90.0	53.7	28.1
2	AS	4.5	1.00	94.0	72.6	32.9
3	AS	4.5	2.00	93.8	73	37.6
4	AS	8.0	2.00	92.1	56.2	37.0
5	FC	8.0	0.50	85.0	55.1	24.1
6	AS	3.0	2.00	93.8	70	26.6
7	FC	3.0	1.00	94.5	59.8	13.8
8	FC	4.5	0.50	94.3	60.9	22.3
9	AS	3.0	0.50	96.2	60.3	30.6
10	FC	8.0	2.00	95.7	52.6	10.0
11	FC	8.0	1.00	87.6	53.5	11.9
12	AS	4.5	0.50	96.4	60.4	24.2
13	FC	3.0	0.50	96.9	59.9	21.9
14	FC	4.5	2.00	96.2	57.2	9.8
15	FC	3.0	2.00	96.2	59.7	12.0
16	AS	8.0	0.50	94.5	53.5	23.6
17	AS	3.0	1.00	93.6	69.3	25.3
18	FC	4.5	1.00	96.7	59.5	11.6

4.4.2.1 Total Suspended Solids (TSS) and Turbidity Removal

Total suspended solids were measured for the raw OMWW sample, and the average TSS was found to be 42.10 ± 5.81 g/l after coagulation experiment TSS was measured for the liquid supernatant that formed as a top layer in the experiment beaker. Average TSS weight after treatment with Aluminum Sulfate was 2.74 ± 1.21 while for the samples treated using Ferric Chloride the average TSS value was reduced to 2.66 ±1.81 Figure (4.5(a)). Coagulation process was very successful in removing high percent of suspended solids from olive mill waste water. Both coagulants have approximately the same ability to reduce TSS with 93.5 % and 93.7 % average removal efficiency for Aluminum sulfate and ferric chloride respectively Figure(4.4). This correlates with data mentioned in literature , (Sarika et al., 2005) reported a 86% TSS removal using relatively low concentrations of ferric chloride between 0.67 and 1 g/L, However , increasing the dosage to 6.7 or 8.3 g/L had an adverse effect on the process as $FeCl3$ failed to cause separation .

The process also lead to a great reduction in the solution turbidity. The original OMWW sample turbidity measured at around 25,000± 305 NTU while the average turbidity in samples treated with AS was around 3300 and with FC was 4600 NTU. Even though FC had a higher ability to reduce suspended solids , samples treated with FC had higher turbidity Figure(4.5 (b)) . (Azbar et al., 2008) reported an increased coloration in solutions treated with FC compared with AS treatments.

There is also a positive correlation between total suspended solid removal and turbidity reduction as indicated in the best line fit equation in Figure (4.6).

TDS= (0.0005Turbidity) +1.1701 , where $R^2 = 0.5991$ ……Equation 3

This equation can be used as a quick indicator for TSS removal since Turbidity tests are much easier and time efficient than the standard TSS testing method.

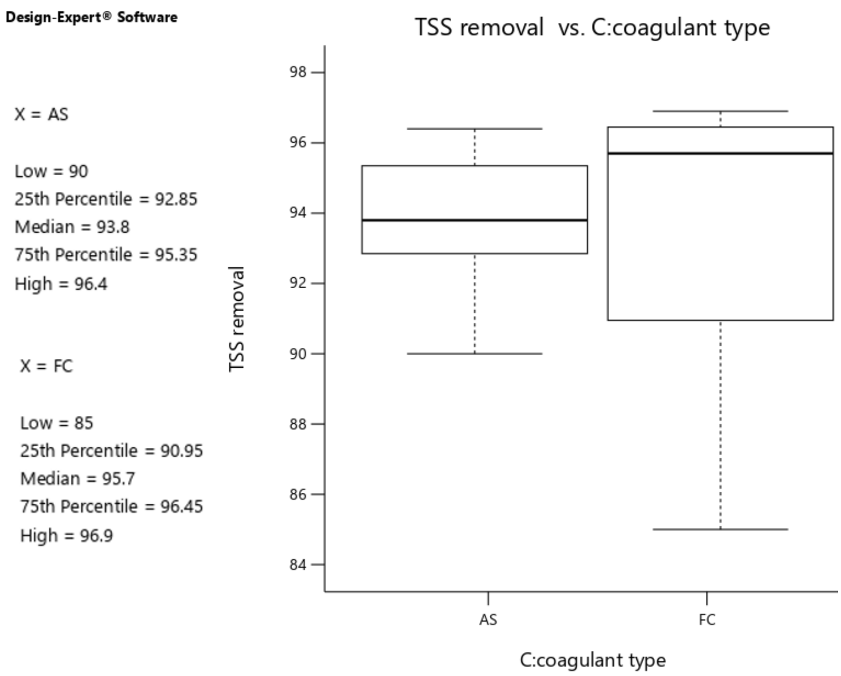


Figure4. 4: TSS removal efficiencies average values for Samples treated with AS and FC .

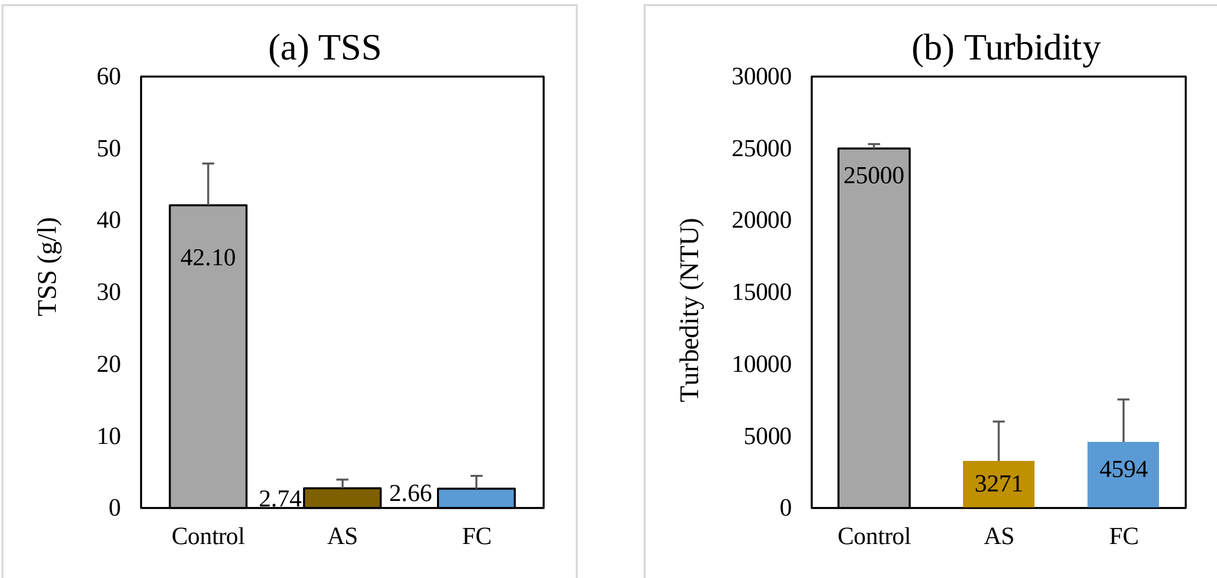


Figure4. 5 : TSS and Turbidity average values in g/l for Samples treated with Aluminum Sulfate and Ferric Chloride compared to UNOMWW.

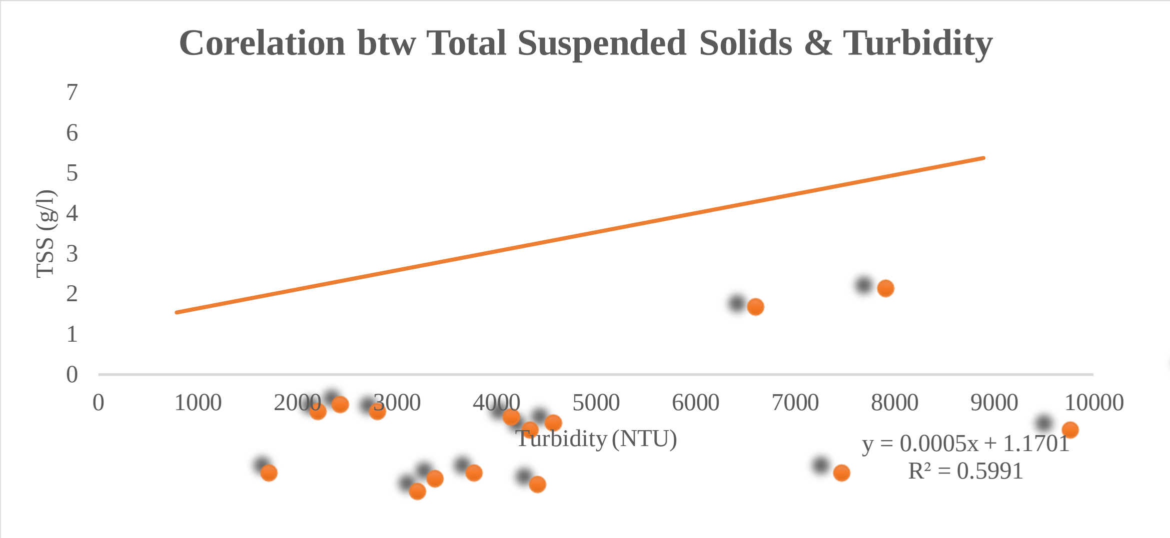


Figure4. 6 : Correlation between Total Suspended Solids & Turbidity

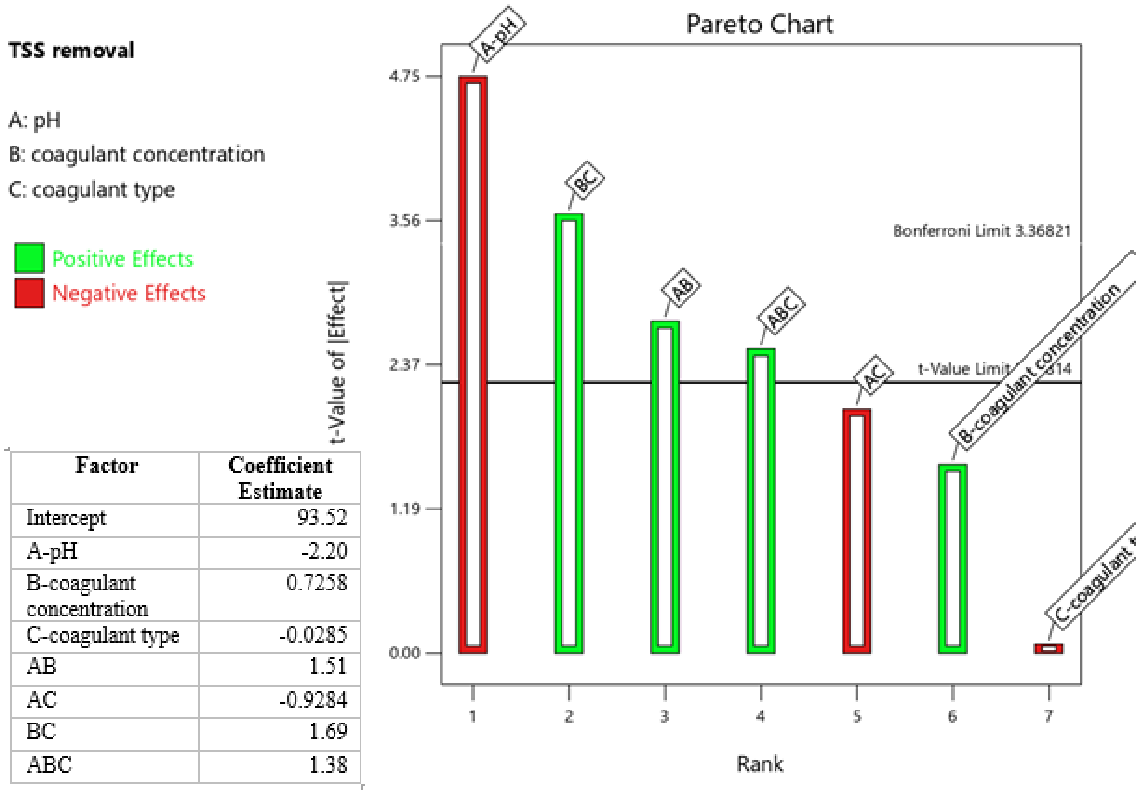
Pareto analysis give significant information about the influence of each factor on the studied response, where the horizontal t-value line represent the minimum statistically-significant effect magnitude ,while the column lengths correspond to the significance of each variable . A positive value indicated that moving from low level to the high level is related to a favor or positive effect of factors improving the response, while a negative effect indicates an negative or unfavorable effect of a factor on the process . Pareto plot for TSS removal is shown in Figure(4.7). It is evident that pH level (b= -2.2) was the only significant linear factor . Meaning that, pH has a major effect on TSS removal, at pH 3 , 4.5 and 8 the removal percentages were 95.20 , 95.24 ,and 90.28 respectively . It is noticed that the optimum removal was at the natural pH of the OMWW which is around 4-5 while alkaline media of pH 8 and higher reduced the process efficiency.

Evidently, coagulant type (b_C=- 0.029) had no significance in the model which indicates equal efficiency of both salts in the treatment process . which also applies on the studied range of coagulant concentrations (b_B=0.726) , the three tested concentrations had close range effect.

The interaction of coagulant type and coagulant concentration (b_{BC}=1.69) had a significant effect and was considered as the most influencing interaction on the investigated response . In case of Ferric Chloride increasing concentration from 0.5 to 2 g/l improved the TSS reduction by 5% (from 91 to 96%), while with Aluminum Sulfate the efficiency decreased by 2% (94.5 to 92.5) see Figure (4.8).

Interactions between pH and coagulant concentration(b_{AB}=1.51) is also significant. For AS at both High and low concentrations the process became less efficient as pH shifted from acidic (3-4.5) to alkaline conditions Figure (4.9(a)). Nevertheless, For FC at low concentration the process efficiency remained the same over the entire range of pH ,However at higher concentration the removal efficiency decreased significantly shifting towards alkaline conditions Figure(4.9(b)) . providing that best operational conditions would be around the natural pH of OMWW around 4-5 .

Interaction between the three studied factors (b_{ABC}=1.38) was also significant . The highest treatment obtained for FC was at 0.5g/l and pH 3 while for AS was at 0.5g/l and pH 4.5.



Factor	Coefficient Estimate
Intercept	93.52
A-pH	-2.20
B-coagulant concentration	0.7258
C-coagulant type	-0.0285
AB	1.51
AC	-0.9284
BC	1.69
ABC	1.38

Figure4. 7:Pareto chart for the standardized effects of variables affecting TSS removal .

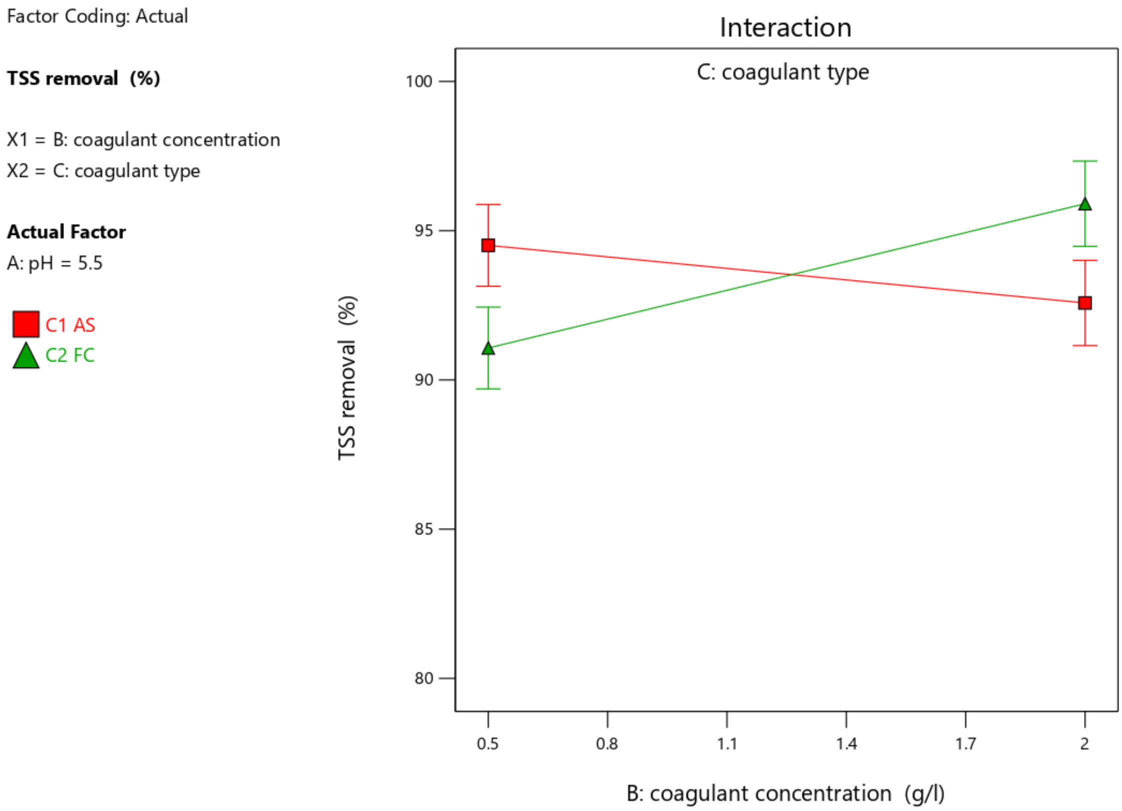
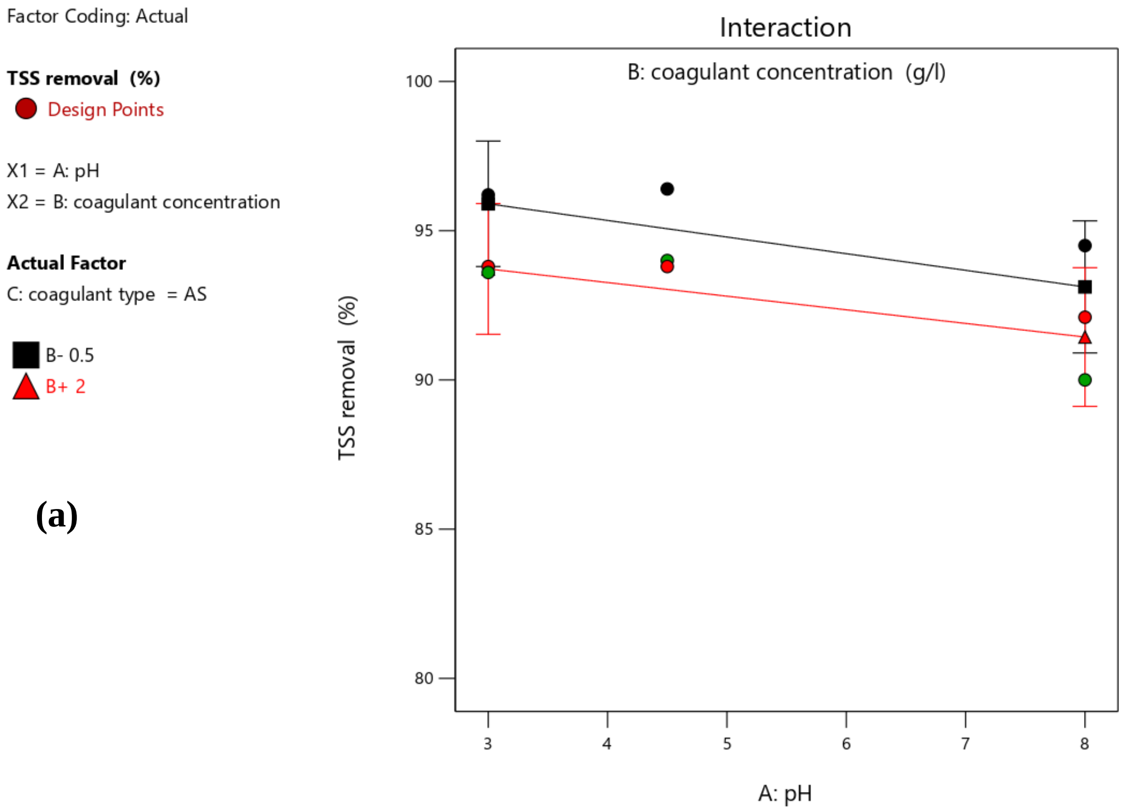
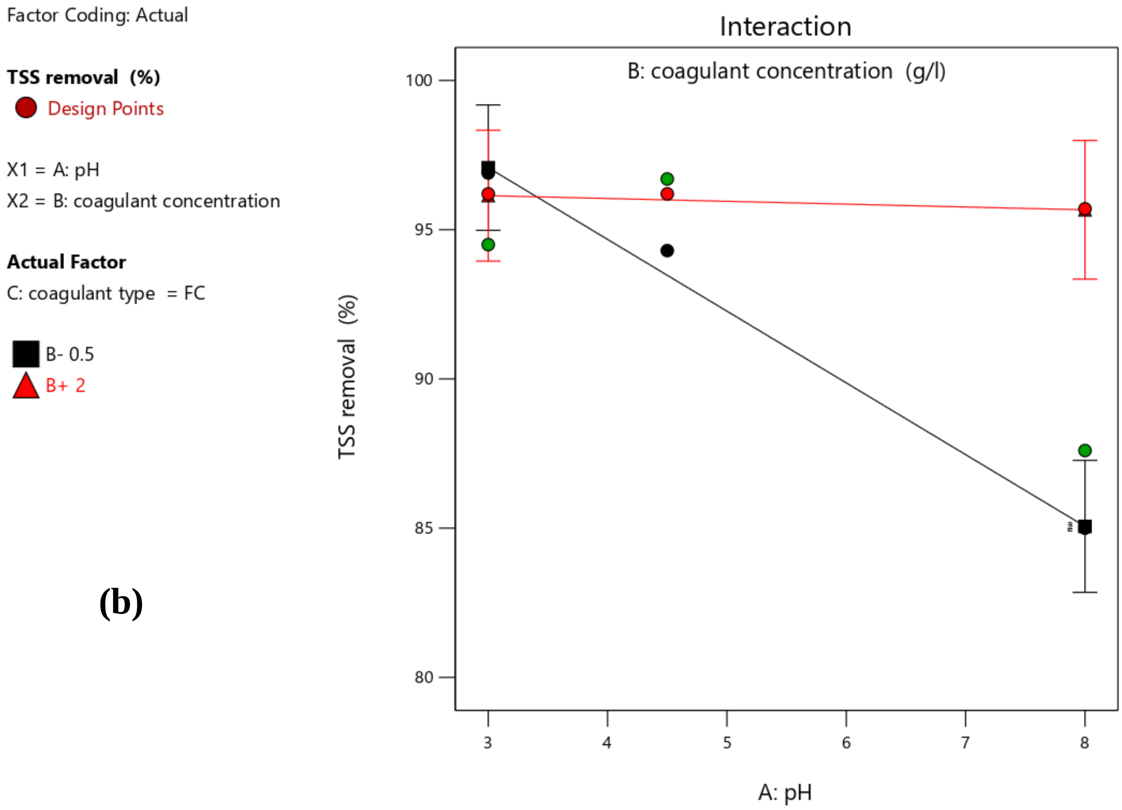


Figure4. 8: Interaction plot for TSS reduction % : interaction btw. coagulant conc. & type



(a)



(b)

Figure4. 9: Interaction plots for TSS reduction % : interaction btw. pH and coagulant concentration for (a)AS and (b)FC

Analysis of variance (ANOVA) was performed to obtain the coefficients of the final equation Table (4.5). Statistically, a factor is considered significant at a level of 95% (p-value <0.05) . All variables of the polynomial regression at a significance level of $P < 0.05$ were included in the model, In this case A, AB, BC ,ABC are significant model terms .

In addition, An F statistic is a value obtained within ANOVA test or in regression analysis to find out if the means between two populations are significantly different. It's much a like T-Test, A T-test says if a single variable is statistically significant and an F test will tell if a group of variables are significant jointly (Glen). The Model F-value of 8.26 implies the model is significant and there is only a 0.2% chance that an F-value this large could occur due to noise.

Most important, The correlation coefficient (R^2) corresponding to a certain model should be at least 80% to provide a good fitting data, which indicates that obtained polynomial models represent adequately the relationship between responses and studied variables. However, the correlation coefficient may not evaluate adequately the model since it increases as variables increase, since even if they are not significant, they will still be added to the corresponding model. For more accuracy, the use of adjusted-R^2 can be better as it is adjusted to the number of variables used to generate the model (Enaime et al., 2019). For our model, the R^2 values was 0.85 while the Adjusted R^2 is 0.75.

Table4. 5 Analysis of variance (ANOVA) results for TSS reduction factorial model.

Source	df	F-value	p-value
A-pH	1	22.53	0.0008
B-Coagulant conc.	1	2.41	0.1518
C- Coagulant type	1	0.0053	0.9434
AB	1	7.46	0.0211
AC	1	4.03	0.0725
BC	1	13.07	0.0047
ABC	1	6.27	0.0313
Model	**7**	**8.26**	**0.0018**
Model Std.	**1.63**		
Model Mean	**93.52**		

The linear polynomial model for predicting TSS reduction values is generated by Design expert and is as following:

TSS reduction %= 93.5157 + -2.19502 * A + 0.725791 * B + -0.0285488 * C + 1.50593 * AB + -0.928402 * AC + 1.69116 * BC + 1.38014 * ABC

Where

A:pH

B: Coagulant conc.

C: Coagulant type

The equation can be used to make predictions about the response for given levels of each factor. In substitution, the high levels of the factors are substituted as +1 and the low levels are substituted as -1. Annex3 contains an applied example for substitution in the model equation and how it is used for prediction. Substituting in this equation will give an exact value for the response . However, some factors are considered non-significant in this model, in this case with elimination of insignificant factors, the TSS reduction percent could be expressed using the following equation with a slight margin of error due to the eliminated factors.

TSS reduction %= 93.52 - 2.20pH+ 1.5 (pH * coagulant concentration) +1.69(coagulant concentration* coagulant type) + 1.38(pH*coagulant concentration coagulant type) ………………………………Equation 4

The relationships between the responses and the experimental variables were illustrated graphically with two-dimensional (2D) contour plots , For AS best operational conditions were around pH 4.5 and 0.5g/l concentration were the process had around 96.4% efficiency while the least efficiency observed was around pH 8 with 2.0 g/l concentrations of around 92 % Figure(4.10). While for FC , the best operational conditions were around pH 3 and 0.5 g/l concentrations were the process had around 70% efficiency in COD removal while the least efficiency observed was around pH 8 with 0.5 g/l concentrations of around 85% Figure(4.11).

In addition ,the cube Plot of TSS reduction % over the entire model variables is presented in Figure(4.12) . Moving around in the cube plot can give predicted removal efficiency for the TSS values at any specified level of all factors .

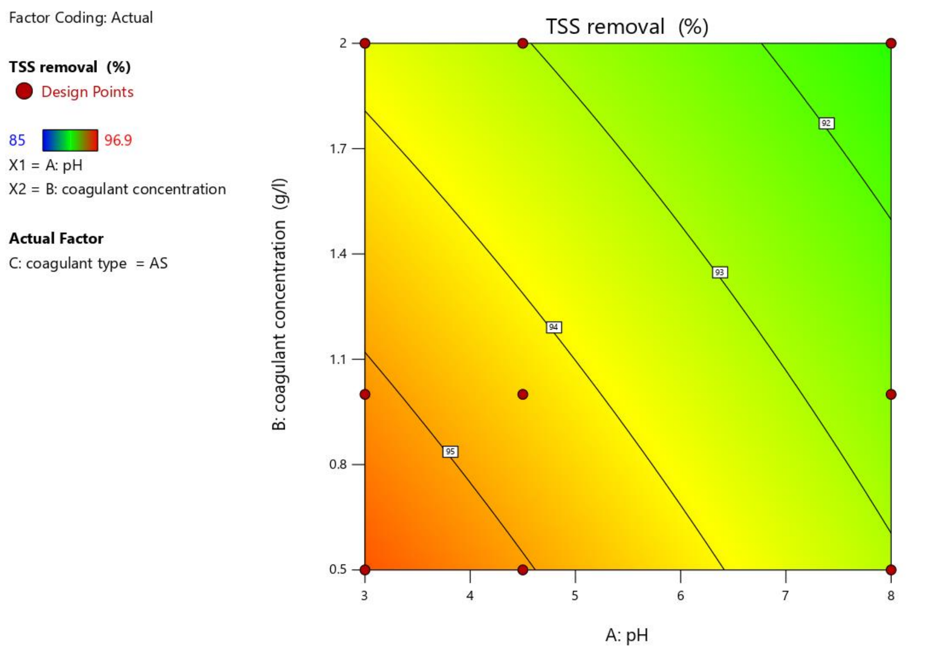


Figure4. 10:Contour Plots of TSS reduction % for Aluminum Sulfate.

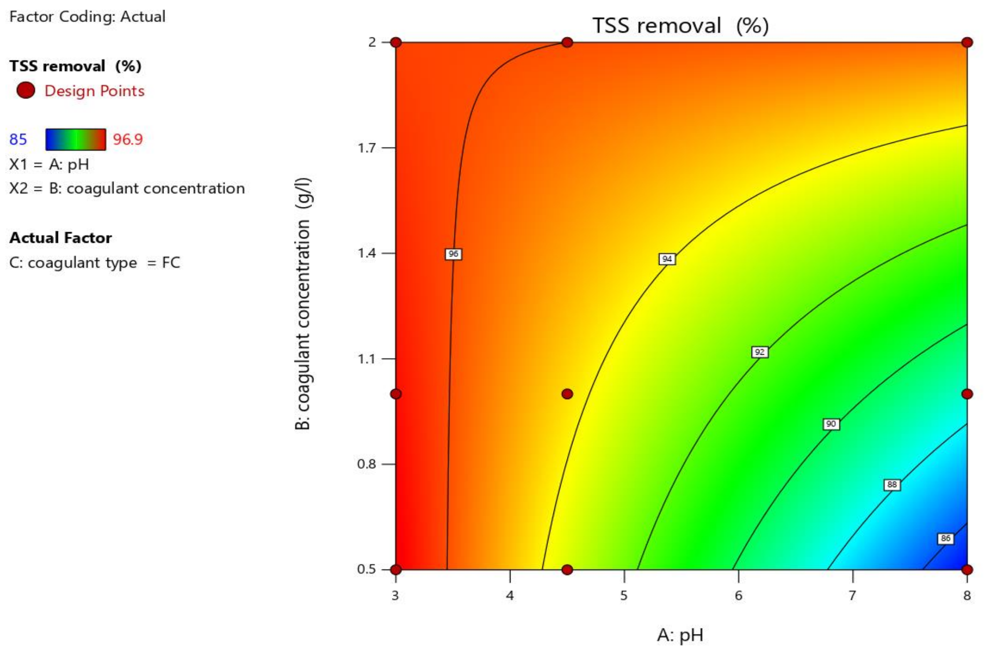


Figure4. 11:Contour Plots of TSS reduction % for Ferric Chloride.

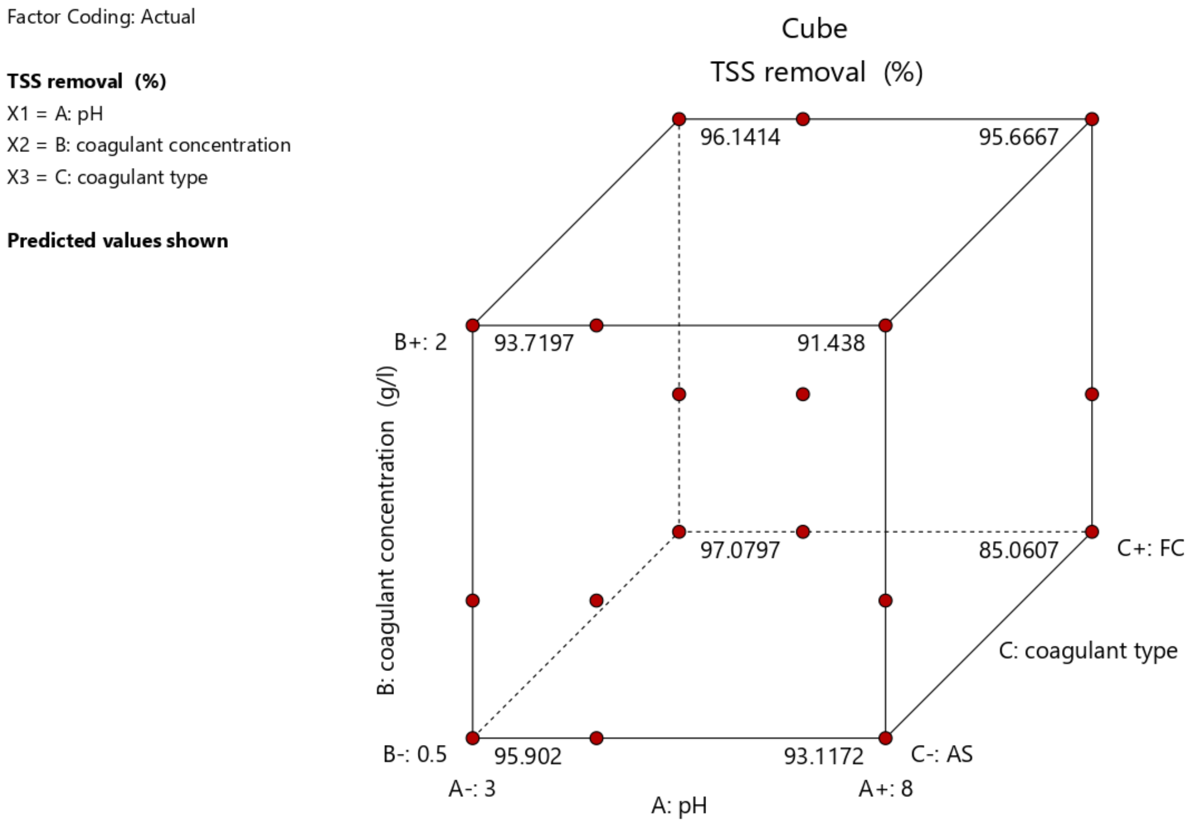


Figure4. 12: Cube Plot of TSS reduction % over the entire model variables.

4.4.2.2 Chemical Oxygen Demand (COD) Reduction

Chemical oxygen demand was found to be 60.00 ± 15.00 g/l for the raw OMWW sample. Average COD weight in samples treated using Aluminum Sulfate was 23.45 ± 3.90 g/l while for the samples treated using Ferric Chloride the average COD value was reduced to 25.14±2.29 g/l ,see Figure(4.13) . Coagulation process was very successful in removing high percent of COD from olive mill waste water. Removal efficiency was 63% & 58% for AS and FC respectively Figure (4.14).

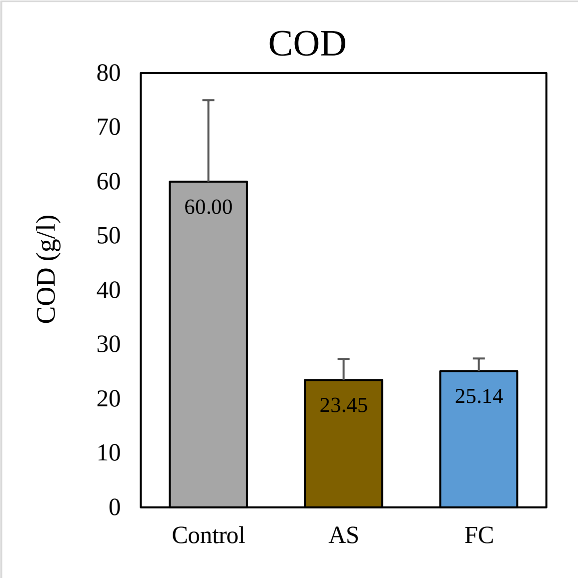


Figure4. 13: COD average values in g/l for Samples treated with AS and FC compared to UNOMWW.

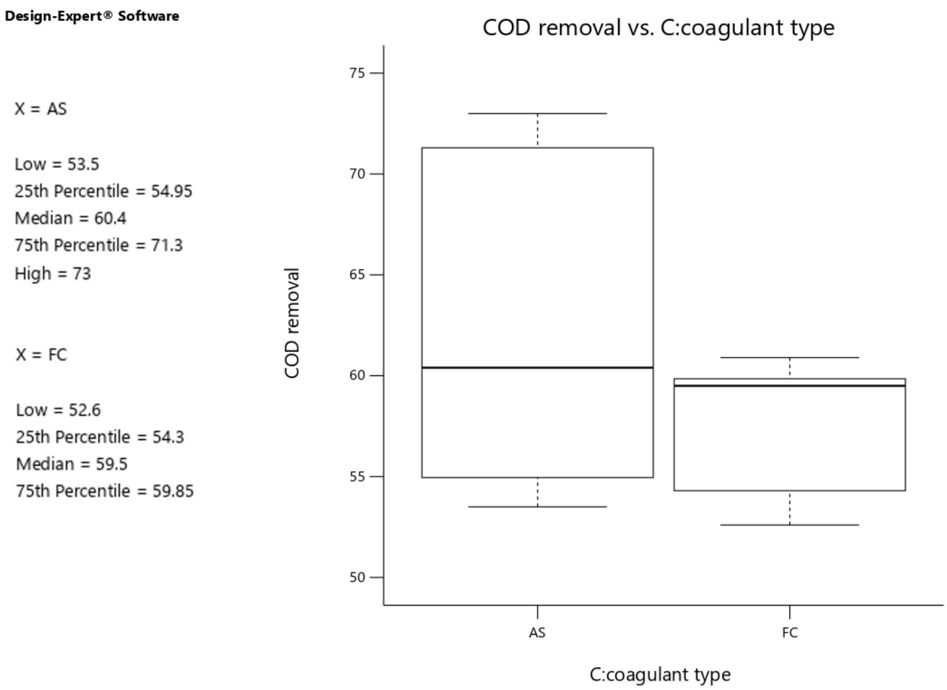


Figure4. 14: COD removal efficiencies average values for Samples treated with AS and FC.

As seen in the Pareto plot Figure (4.15), pH (b_A= -5.47) had the most significant effect ,it influence unfavorably on the COD removal , meaning that the increases or shift of pH from acidic values of 3 towards alkaline values around 8 reduces the removal efficiency Figure(4.17) & Figure(4.18) illustrates the shift in removal efficiency as pH shifts in values.

Coagulant type (b_C= -2.58) comes second in its effect indicating the use of AS is more effective than FC. While coagulant concentration (b_A= 1.55) had no significant, meaning that a concentration of 0.5 g/l has close range efficiency as the 2g/l regarding COD removal. Nevertheless, interaction between coagulant type and concentration (b_{BC}=-2.37) had a significant effect on the treatment process Figure (4.16).

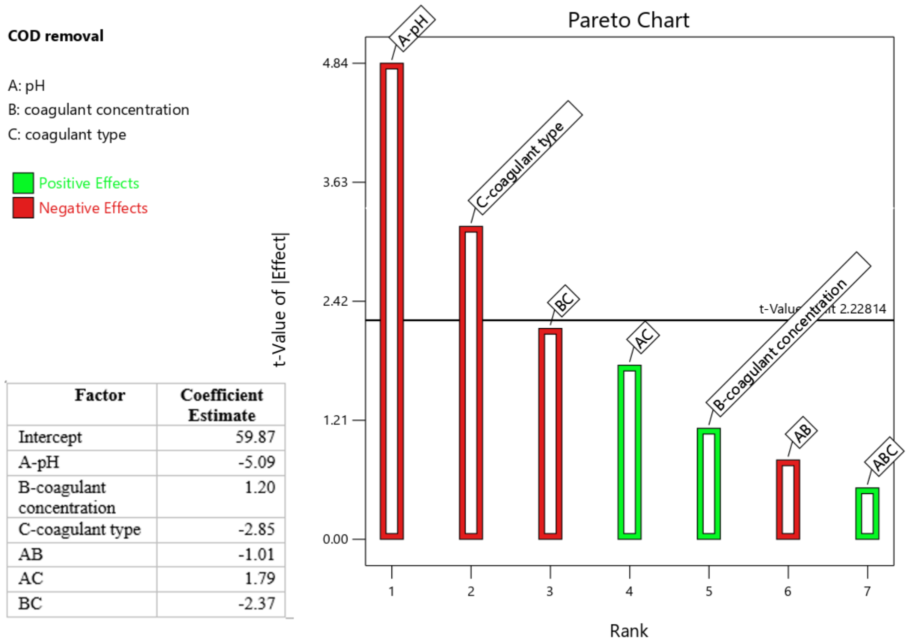


Figure4. 15: Pareto chart for the variables effects on COD removal.

Analysis of variance (ANOVA) was performed to obtain the coefficients of the final equation for better accuracy, Table (4.6). All variables of the polynomial regression at a significance level of P < 0.05 were included in the model, In this case pH(A) , coagulant type(C) and the interaction between coagulant type and concentration (BC) are significant model terms .In addition, The Model F-value of 7.78 implies the model is significant. There is only a 0.19% chance that an F-value this large could occur due to noise. The coefficient of determination (R^2) was generated to assess the adequacy of the model. The R^2 values was 0.81 while the Adjusted R^2 was 0.69.

Table4. 6 Analysis of variance (ANOVA) for COD reduction model.

Source	**df**	**F-value**	**p-value**
A-pH	1	25.11	0.0004
B-Coagulant concentration	1	1.36	0.2676
C-Coagulant type	1	10.93	0.0070
AB	1	0.6965	0.4217
AC	1	3.15	0.1034
BC	1	5.44	0.0397
Model	7	7.78	0.0019
Model Std.	3.7		
Model Mean	59.87		

After substituting the coefficients bi in the linear polynomial model by their corresponding values the final empirical model for COD reduction was expressed by the following equation , The equation can be used to make predictions about the response for given levels of each factor. In substitution , the high levels of the factors are substituted as +1 and the low levels are substituted as -1.

COD removal % =59.87 + -5.08691 * A + 1.19925 * B + -2.83718 * C + -1.01006 * AB + 1.85952 * AC + -2.27896 * BC + 0.653368 * ABC

Where

A:pH

B: Coagulant conc.

C: Coagulant type

After the elimination of insignificant factors the equation could be expressed as following :

COD removal % = 59.87 - 5.10 pH - 2.84 Coagulant type -2.28 (Coagulant type * coagulant concentration)………………Equation 5

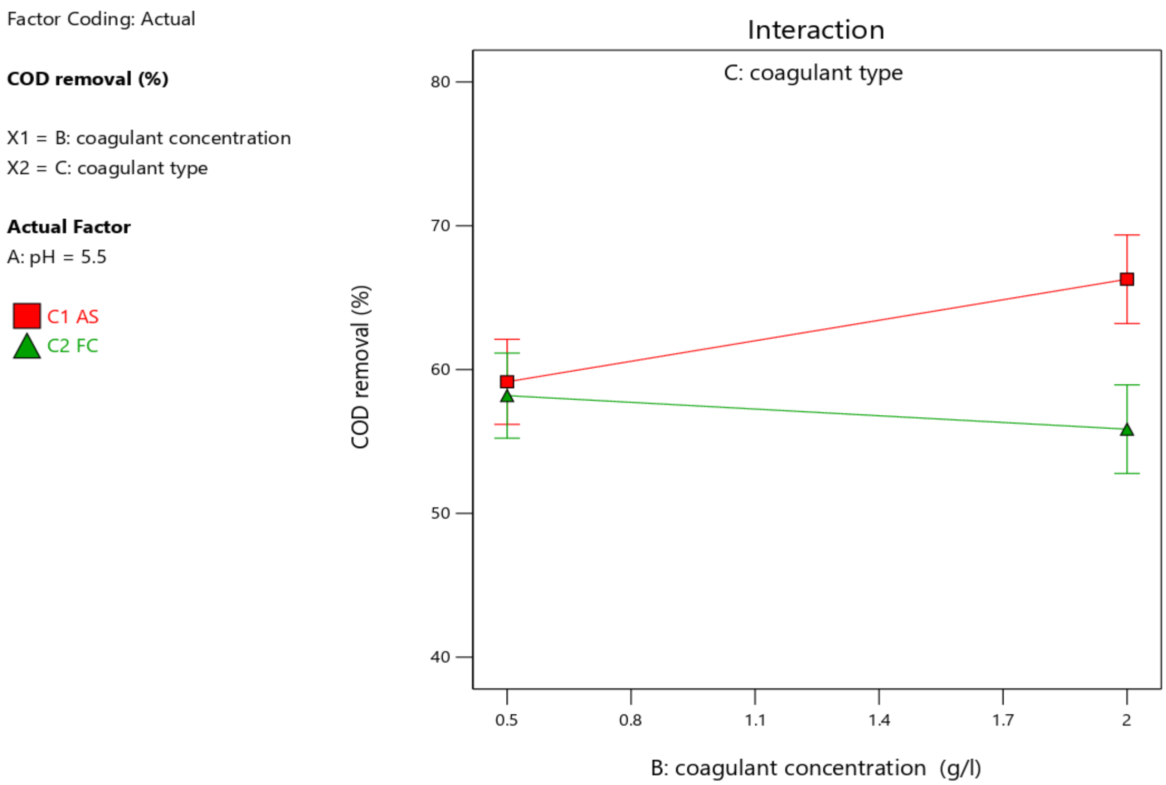


Figure4. 16:Interaction plots for COD reduction % ,interaction btw. coagulant conc. & type

.

Moreover, the relationships between the responses and the experimental variables were illustrated graphically with two-dimensional (2D) contour plots Figure(4.17&18) From those graphs it is shown that , For AS best operational conditions were around pH 4.5 and 2g/l concentration were the process had around 73% efficiency in COD removal while the least efficiency observed was around pH 8 with 0.5g/l concentrations of around 53% . As for FC , the best operational conditions were around pH 4.5and 0.5 g/l concentrations were the process had around 60.9% efficiency in COD removal while the least efficiency observed was around pH 8 with 2.0 g/l concentrations of around 53%.

In addition to the cube Plot of COD reduction % over the entire model variables Figure (4.19). Moving around in the cube plot can give predicted removal efficiency for the COD values at any specified level of all factors.

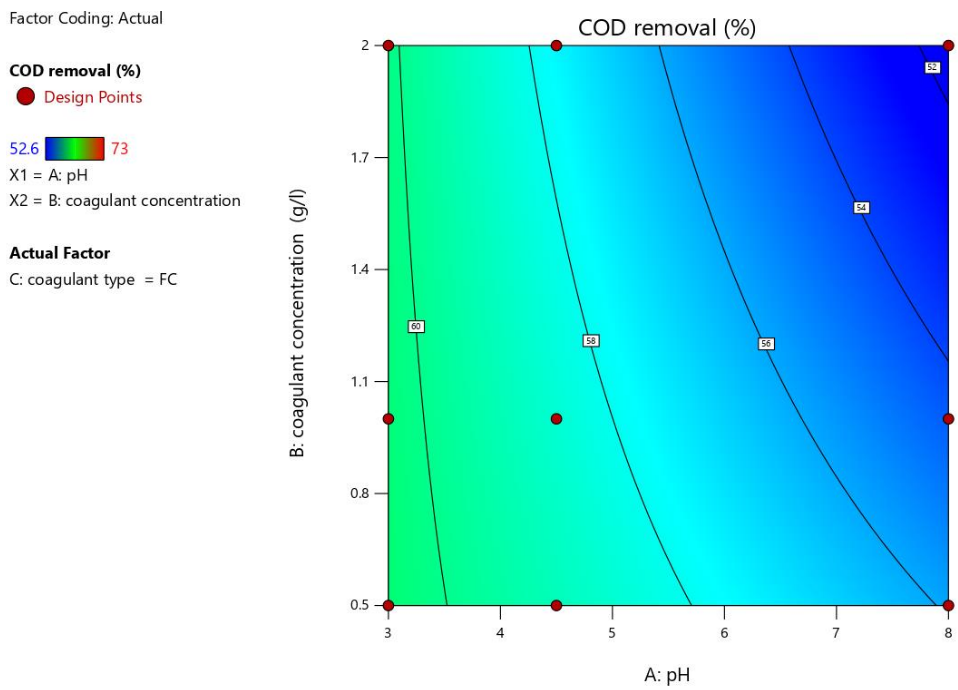


Figure4. 17: Contour Plots of COD reduction % for Ferric Chloride .

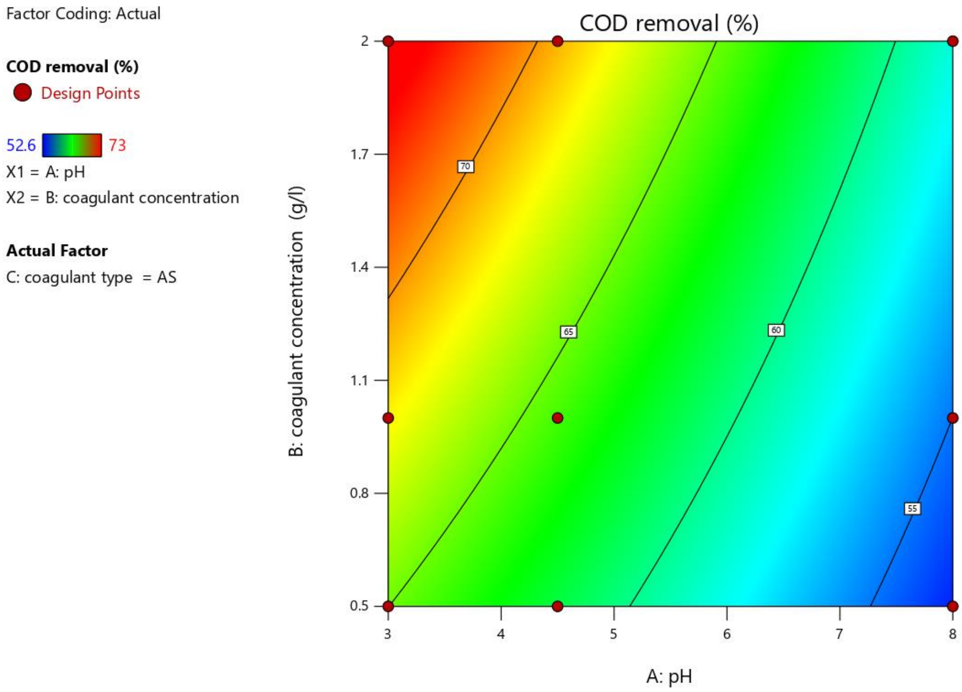


Figure4. 18:Contour Plots of COD reduction % for Aluminum Sulfate.

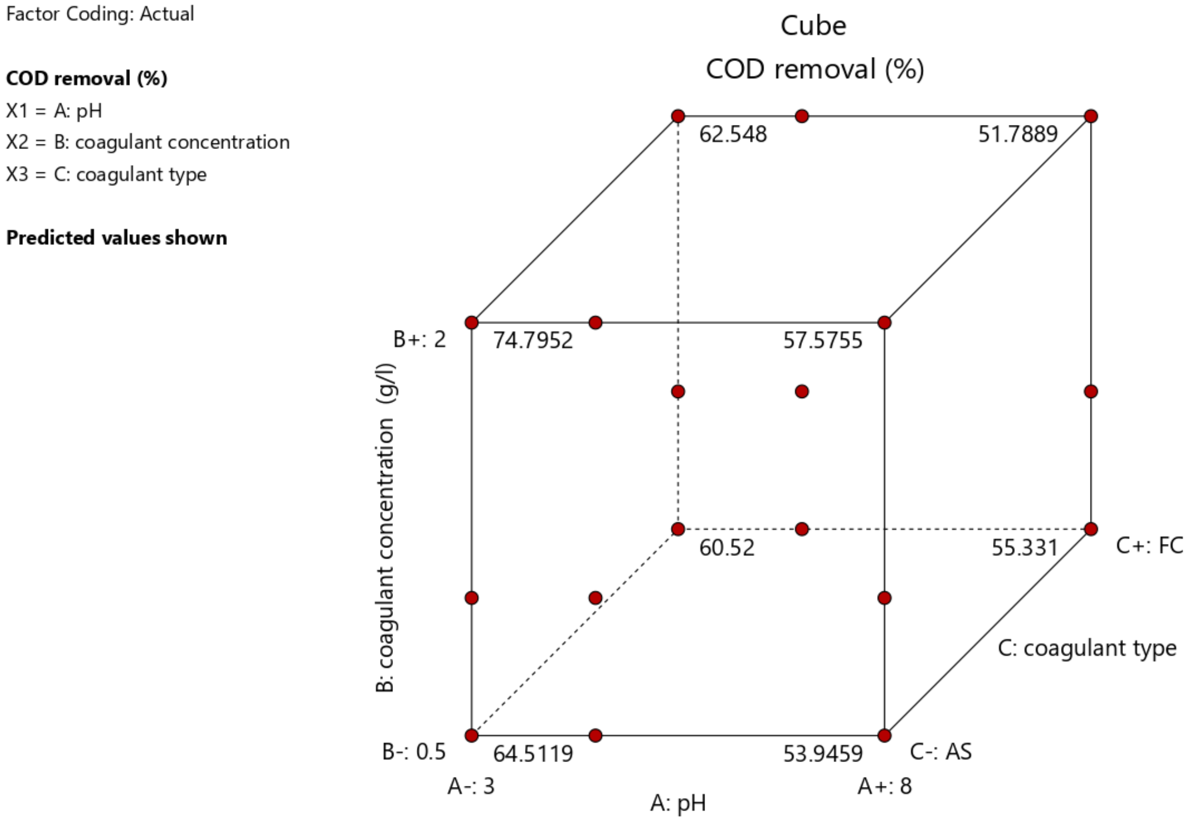


Figure4. 19: Cube Plot of COD reduction % over the entire model variables

4.4.2.3 Total Phenols Reduction

A. Effect of coagulants on phenols concertation

This experiment was conducted in order to identify if any of the coagulant impose any interference on the phenols measurement using the Folin-Ciocalteu method. Three 100 ml samples were prepared for the coagulants Aluminum sulfate and Ferric Chloride with 0.5 ,1.0 , and 2.0 g/l concentrations. Then the standard procedure for Folin-reagent method was followed for testing phenols reading in the samples. It is evident that the contribution of both coagulants to the phenols readings is negligible Table(4.7).

Table4. 7: Effect of adding coagulants AS and FC on phenols concentrations

solution concentration g/l	Coagulants	phenols Conc. (g/l)
0.5	FeCl	0.005
	$Al_2(SO_4)$	0.008
1	FeCl	0.006
	$Al_2(SO_4)$	0.013
2	FeCl	0.008
	$Al_2(SO_4)$	0.016

B. Results of TP removal via coagulation process

The average phenols concentration in UTOMWW was 6.47 ± 0.40 g/l while with the use of AS and FC, TP was reduced to 4.72 ± 0.36 and 5.73 ± 0.47 respectively. Correlating to 30% reduction using AS and 14% using FC . This reduction could be correlated to the amount of phenols precipitated in the solid part .See Figure(4.20 &21).

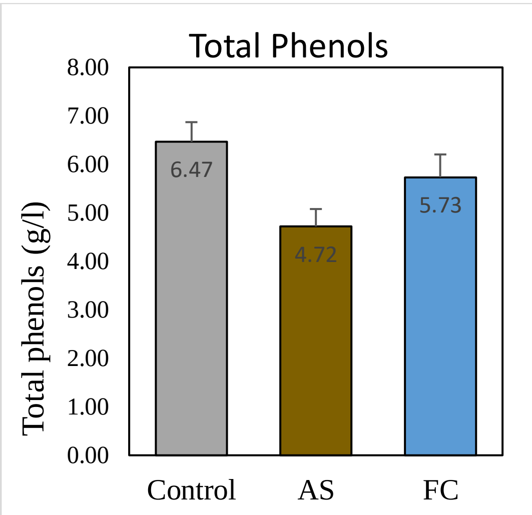


Figure4. 20:TP average values for Samples treated with AS & FC compared to UNOMWW

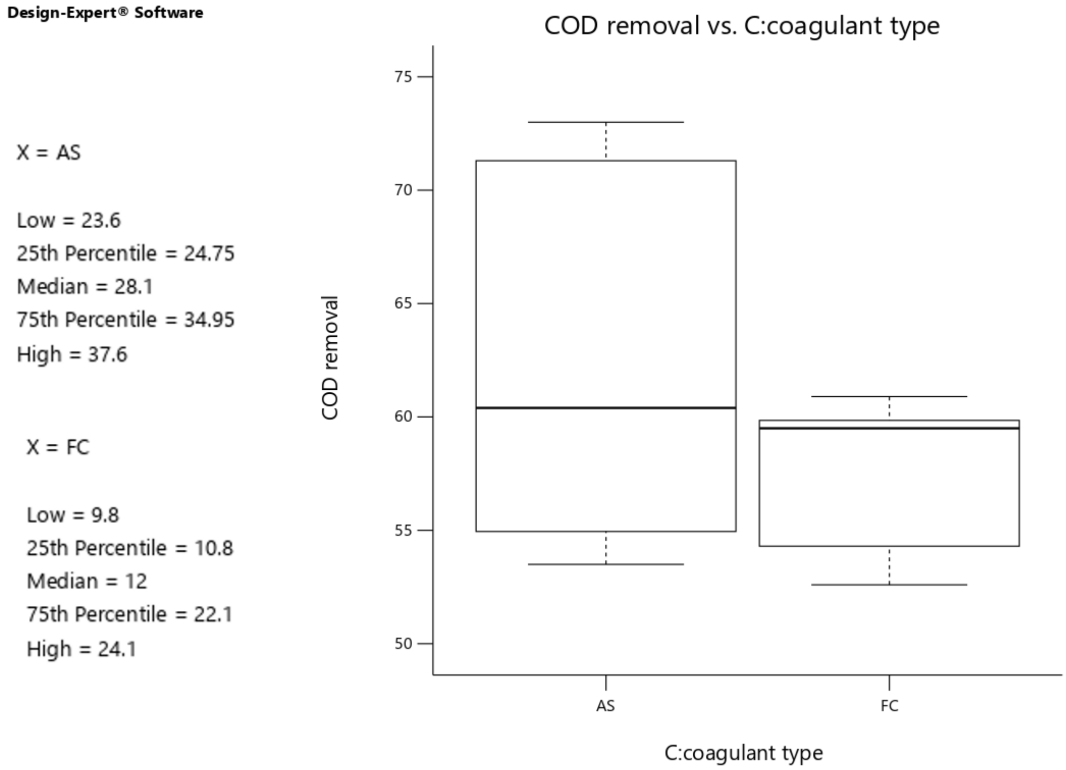


Figure4. 21: TP removal efficiencies average values for Samples treated with AS and FC .

As seen in the Pareto Chart Figure (4.22) ,pH (b_A=0.376) and coagulant concentration(b_B=-0.636) had insignificant effect on the treatment process in TP removal , while the coagulant type (C) was statistically significant (b_c= -7.73). It influence unfavorably on the TP removal , meaning that using AS is more vaporable and had higher removal efficiency than FC .

The interaction between coagulant type (C) and coagulant concentration(B) had a significant effect (b_{BC}= -4.89) and was considered as the most influencing interaction on the investigated response.

Figure(4.23) shows that with using AS increasing concentration lead to an increased efficiency in TP removal from 38% to 24% at 0.5 and 2.0 g/l respectively .In contrast to using FC where it showed better removal efficiency at low concentrations from 24% to around 10 % at 0.5 and 2.0 g/l respectively , this could be related several reasons including ; the fact that increasing FC dosage can lead to increased coloration of the solution (Enaime et al., 2019) , Moreover , one or more of the hydrolysis products of FC could react the same as total phenols with the Folin reagent , both reasons can affect the measurement method . In addition , (Jaouani et al., 2005) reported that there is a limit to coagulant dosage before a restabilization of the colloids occurs . The best treatment using AS was achieved at pH 4.5and conc. 2.0 g/l and with FC at pH 8 and conc.0.5g/l.

The interaction effect of all three factors, coagulant type, pH, and coagulant concentration (b_{ACB}=-2.15) , interactions between pH and coagulant type (b_{AC}=-1.40) and between pH and coagulant concentration (b_{AB}= 0.23) were non- significant .

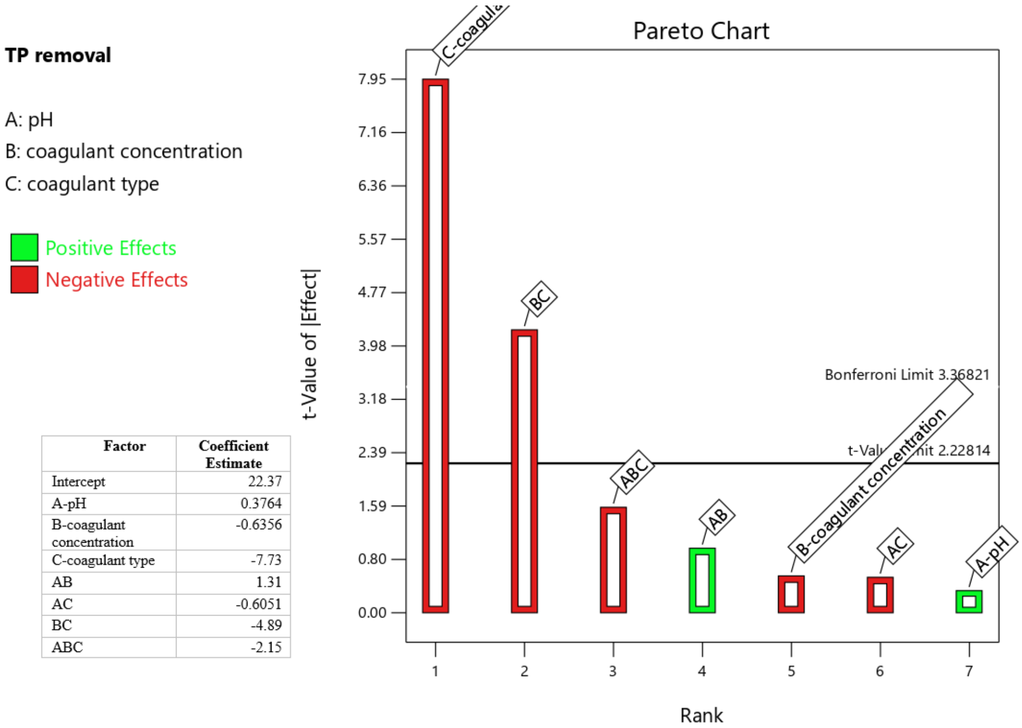


Figure4. 22 : Pareto chart for the variables effects on Total Phenols (TP) removal.

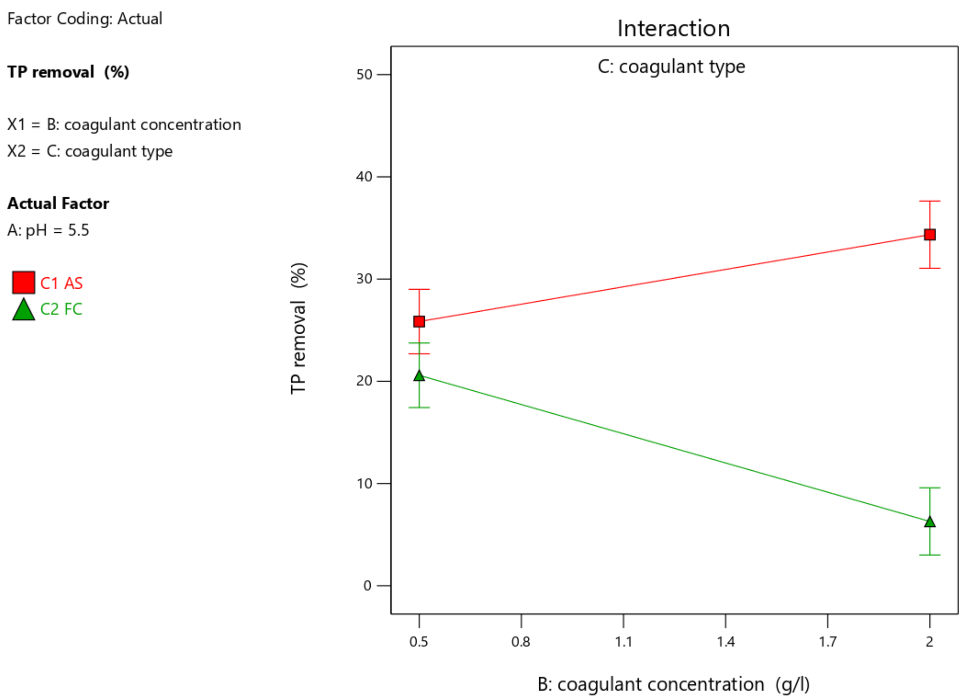


Figure4. 23: Interaction plot between coagulant type and dose on TP removal .

Analysis of variance (ANOVA) was performed to obtain the coefficients of the final equation for better accuracy, Table (4.8). All variables of the polynomial regression at a significance level of $P < 0.05$ were included in the model, In this case C, BC are significant model terms In addition, The Model F-value of 15.30 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The coefficient of determination (R^2) was generated to assess the adequacy of the model. The R^2 values was 0.88 while the Adjusted R^2 is 0.80

Table4. 8 Analysis of variance (ANOVA) for Phenols reduction model

Source	df	F-value	p-value
A-pH	1	0.1079	0.7493
B-coagulant concentration	1	0.3008	0.5954
C-coagulant type	1	63.22	< 0.0001
AB	1	0.9245	0.3590
AC	1	0.2788	0.6090
BC	1	17.77	0.0018
ABC	1	2.47	0.1472
Model	7	10.92	0.0006
Model Std.	4.04		
Model Mean	22.37		

After substituting the coefficients bi in the linear polynomial model by their corresponding values the final empirical model for TP reduction was expressed by the following equation, The equation can be used to make predictions about the response for given levels of each factor. In substitution, the high levels of the factors are substituted as +1 and the low levels are substituted as -1.

Phenols reduction % = 22.3657 + 0.376413 * A + -0.635601 * B + -7.73067 * C + 1.31335 * AB + -0.605052 * AC + -4.88619 * BC + -2.14642 * ABC

Where

A:pH

B: Coagulant conc.

C: Coagulant type

After the elimination of insignificant factors the equation could be expressed as following :

Phenols reduction % = 22.37 – 7.73* (coagulant type) – 4.89* (coagulant concentration * coagulant type) …………..Equation 6

Moreover, the relationships between the responses and the experimental variables were illustrated graphically with cube Plot of TP reduction % over the entire model variables Figure (4.24) .

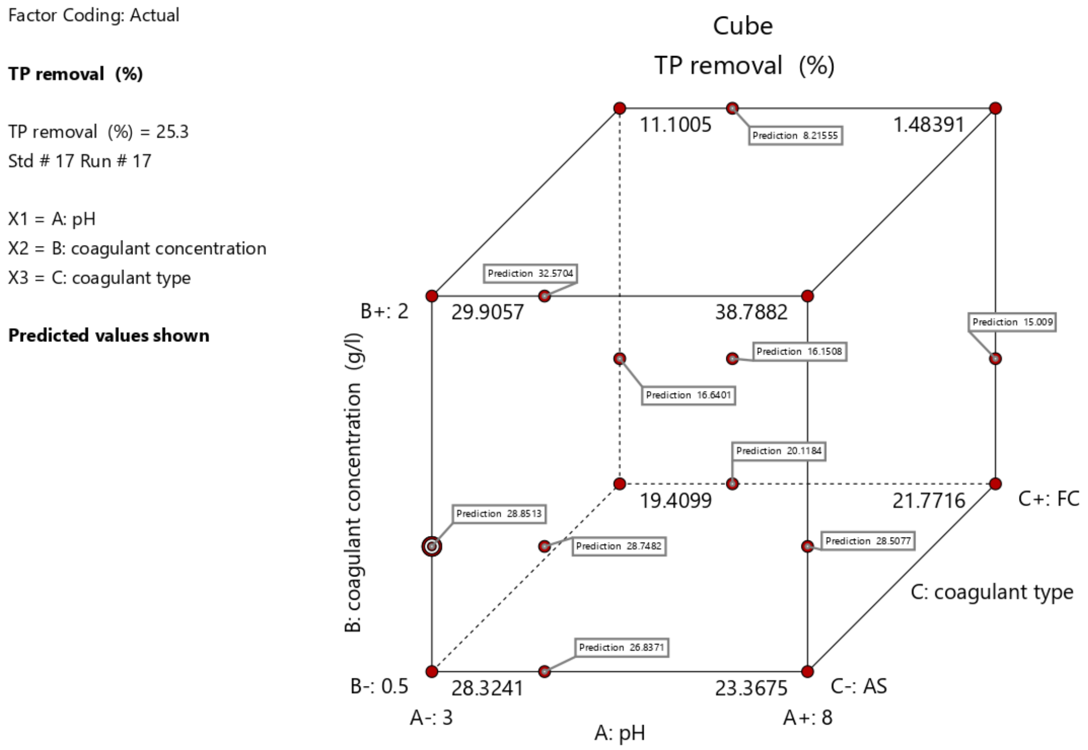


Figure4. 24 : Cube Plot of TP reduction % over the entire model variables .

C. Treatment with Calcium hydroxide

A further step have been made in this research for the treatment of TP using Calcium Hydroxide. Several studies reported the high ability of Calcium hydroxide in reducing phenols in wastewater generally and in OMWW in specific .(Beccari et al., 1999) proposed a process that combines pre-treatment by means of lime coagulation and adsorption on bentonite followed by anaerobic digestion. The Pretreatment was able to remove polyphenols and COD by 43% and 55%, respectively. In additional studies (Aktas et al., 2001) evaluated the impact of lime pre-treatment on total solids, COD and polyphenols removal for 17 different OMWW samples , Treatment with lime resulted in about 40–70% COD and color removal depending on the coagulant dosage employed . Some other studies reported the use of electrocoagulation over iron and aluminum electrodes (Inan et al., 2004) and lime coagulation coupled with the Fenton's reagent (Vlyssides et al., 2003) for OMWW treatment.

In this experiment the treated samples using coagulation were further treated by the addition of 0.5 g/calcium hydroxide. This process resulted in further reduction of phenols concentration from the OMWW.The average reduction over the entire sample population was 19% while a maximum reduction of 32% was obtained in some samples Table (4.9) . Combined with the reduced percent in the first coagulation step TP reduction percent can reach up to 60% in total.

Noticeably, the addition of Calcium hydroxide adjusted the pH of the samples to a great extent making them within the alkaline range. Although lime is readily available material and inexpensive, lime coagulation normally has several drawbacks, like the increase of solution pH and hardness, low COD removal capacity which typically varies between 20–40%, its need for large doses which leads to the generation of excessive amounts of sludge which is still quite phytotoxic and cannot be readily disposed of and need for coupling with flocculation to improve efficiency (Tatsi et al., 2003, Vlyssides et al., 2003), Hence our research propose the use of lime as a post coagulation treatment step to enhance the overall process but without the need for excessive amounts .

Table 4. 9: Effect of Calcium hydroxide addition to the treated OMWW samples as a further treatment step for TP removal.

Sample no.	pH Bbefore treatment	pH After treatment	Reduction % After treatment with coagulants First step	Reduction % After treatment with Calcium hydroxide Second step	Total reduction % in TP Combined first and second treatment steps
1	7.14	11.3	28.1	23	52
2	4.75	9	32.9	23	56
3	4.61	8.66	37.6	15	53
4	7.25	10.4	37.0	9	46
5	7.1	8.8	24.1	20	44
6	3.25	8.63	26.6	12	39
7	3	8.55	13.8	27	41
8	4.5	8.34	22.3	32	54
9	3.2	8.3	30.6	24	55
10	6.64	10.8	10.0	12	22
11	7	8.8	11.9	14	26
12	4.7	8.4	24.2	16	40
13	3.2	8.4	21.9	18	39
14	4.5	8.4	9.8	20	30
15	2.75	9.9	12.0	18	30
16	7.22	8.8	23.6	17	41
17	3.2	8.5	25.3	13	39
18	4.5	8.5	11.6	26	38
Avg.			**22**	**19**	**41**
Max			**38**	**32**	**56**
Min			**9.8**	**8.8**	**21.8**

In summary we can say the following:

1. Both coagulants have approximately the same ability to reduce TSS with 93.5 % and 93.7% average efficiency . For AS best operational conditions gave 96.4% efficiency were around pH 4.5 and 0.5g/l. For FC , the best operational conditions gave 96.9% were around pH 3 and 0.5 g/l .

2. The process lead to a great reduction in the solution turbidity. The original OMWW sample turbidity measured at around 25,000± 305 NTU while the average turbidity in samples treated with AS was around 3300 and with FC was 4600 NTU .

3. COD average removal efficiency was 63% and 58% for Aluminum sulfate and Ferric Chloride respectively. For AS best operational conditions were around pH 4.5 and 2g/l concentration were the process had around 73% efficiency. For FC , the best operational conditions were around pH 4.5 and 0.5 g/l concentrations were the process had around 60.9% efficiency .

4. Total Phenols reduction was 30% using AS and 14% using FC . Best conditions for AS was pH4.5 at 2.0g/l conc. Giving 37.6% efficiency .And for FC at pH8 and 0.5 conc. Giving 24.15 efficiency.

5. It is noticed that the optimum treatment for all tested pollutants was at the natural pH or the OMWW which is around 4-5 while alkaline media of pH 8 and higher reduced the process efficiency. In a study made by (Black et al., 1967) researchers showed that at pH 3 destabilization of colloids with Aluminum Sulfate is due to electrical double layer depression by un-hydrolyzed $(Al(H_2O)_6^{3+}$ species. While at pH 5, the destabilization is caused by adsorption of positively charged hydrolysis products. Upon increasing the pH value between 6-8 the formation of amorphous solid-state $(AlOH)_{3(s)}$ takes place, because the aluminum ions need sufficient alkalinity to form it. In this range of pH, the destabilization mechanism is a combined action of charge neutralization and precipitate enmeshment with $(AlOH)_3$ species (Wang et al., 2007) . This range of pH is reported as ideal for an effective coagulation using AS (Enaime et al., 2019)

6. While for Ferric ions**,** lower values of pH (< 3) are marked with a predominance of the hydrated aqua metal ions. Therefore, the mechanism of destabilization is almost totally due to double layer repression by ionic strength considerations. At pH > 4.5, the ferric ions can be hydrolyzed and precipitated as ferric hydroxide, insoluble in large range of pH, and so there is no particular upper pH limit for ferric coagulation (Akratos, 2016).

7. Although the process was highly effective in reducing large percent of pollution load, alone coagulation process was not enough to produce an effluent that complies with the Palestinian standards for wastewater network standards Table (4.10). Hence its recommended to couple it with a second stage of treatment.

Table4. 10:Comparison btw. This research results and the Palestinian stranded for wastewater discharge.

Parameter	**Unit**	**UTOMWW**	**AS Treatment**	**FC Treatment**	**Sewer system discharge**
EC	ms/cm	12.2± 0.20	14.90	15.70	-
COD	g/l	60.00 ± 15.00	23.50	25.14	2.0
Turbidity	NTU	25,000± 305	3270.00	4590.00	-
TSS	g/l	42.10 ± 5.81	2.74	2.66	0.5
Total phenols	g/l	6.47 ± 0.40	4.72	5.73	0.003

Conclusion

The results indicate that coagulation process using Aluminum Sulfate ($AlSO_4$) and Ferric chloride ($FeCl_3$) can be used effectively for removing Total Suspended Solids, Chemical Oxygen Demand , and Total Phenols from olive mill wastewater . The treatment reduced TSS by (90 -96%) and COD by (53 -73%) , and Total Phenols by (11-37%). The optimum weight of AlSO4, and FeCl3 are 0.5g/l.

Additional step was needed to reduce TP by using CaOH2 with optimum treatment dose of 0.5g/l , this increased the removal of TP up to 56%. With coagulation treatment a considerable amount of nutrients still remain in the effluent which could be of high advantage of wastewater management and reuse in supplementary irrigation tacking EC values into consideration and making the necessary dilutions with fresh water.

Recommendations for Future Studies

1. A second stage treatment applying Adsorption with Luffa cylindrica was intended for this research. However, due to time restrictions and COV-19 continuous lockdowns this step was not feasible. We recommend the Study of Adsorption process as a second stage for the final purification of the effluent to reach a level to be used in supplementary irrigation.
2. Further research could be conducted to study the possibility of phenols recovery from Calcium hydroxide.

3. Applying the effluent of coagulation process on chosen types of fruit trees and studying the effect on yield quantity and quality

Annexes

Annex 1 : Analytical Methods

Annex 1 .1 Measurement of Total Suspended Solid

Total suspended solid measurement Was conducted according to the standard Methods for the Examination of Water and Wastewater(Baird et al., 2017). The following is the detailed procedure:

1. The test was made in triplicate (3 samples)
2. Filter paper (90mm,615MN) was inserted in the filtration apparatus. & The filter was washed with three successive 20 ml portions of DI water. discard the washings.
3. The filter was removed and placed in a clean glass dish. Dried in an oven at about 100c until a constant weight was reached. The weight was registered (W_B)
4. Filter was Placed in the filtration apparatus. And Witted the filter with a small volume of DI water.
5. The sample then was stirred with a magnetic stirrer and while stirring. 20 ml sample was pipet onto the filter allowing complete drainage between washing. and continued suction for about 3 min after filtration.
6. Carefully removed filter from filtration apparatus and transfered to the same glass weighing dish.
7. Dried for at least 1hr 103 to 105c in an oven & Cooled in a desiccators to balance temperature and weight.
8. The cycle of drying. cooling. Was repeated three times until the difference in weight is less than 4% . and the final reading value was taken (W_A)
9.

$$\textbf{TSS (g/l)} = \frac{\mathbf{A-B}}{\boldsymbol{V}} \ \mathbf{*1000} \text{.............Equation 7}$$

Where: A: weight of filter +dried residue(g) B: weight of empty filter

V :sample volume in ml

Figure 3. 2 : Measurement of total suspended solids

Annex 1.2 Measurement of Phenolic compounds

The amount of total phenolic in extracts was determined with the Folin- Ciocalteu reagent method (Maurya et al., 2010). The Folin-Ciocalteu reagent is sensitive to reducing compounds including polyphenols, thereby producing a blue color upon reaction. This blue colour is measured spectrophotometrically, thus total phenolic content can be determined.

Standards and Chemicals

All chemicals were analytical-reagent grade and the water was distilled. The chemicals included

- 2 N Folin-Ciocalteu reagent (Dinâmica®, Diadema, Brazil)
- Anhydrous sodium carbonate (Synth®),
- Gallic acid (Sigma-Aldrich®, St. Louis, MO, USA),

Procedure

- Gallic acid was used as a standard and the total phenolic were expressed as mg/l gallic acid equivalents (GAE).
- 5 galic acid standards with Concentration of 10 ,20 ,30 ,40 , and 50 mg/l of gallic acid were prepared in distilled water .
- OMWW samples were diluted by 100 , using a volumetric flask by adding 0.5 ml of the sample and filling it with 50 ml of distilled water
- The 5 galic acid standard and the OMWW sample were introduced into test tubes and mixed with the following in the same oreder:
  - ✓ 1ml sample
  - ✓ 4ml of 7.5% sodium carbonate.
  - ✓ 5 ml of a 10 fold dilute Folin- Ciocalteu reagent

- The tubes were covered with parafilm and allowed to stand for 30 minutes at room temperature
- The absorbance was at read at 760 nm using DR3900 hack spectrophotometer
- All determination was performed in triplicate.

Calibration curve

Table3. 4 Gallic Acid standards that are used to create the calibration curve .

conc. (mg/l)	abs @760nm
10.8	0.094
21.6	0.192
32.4	0.323
43.2	0.45
54	0.602

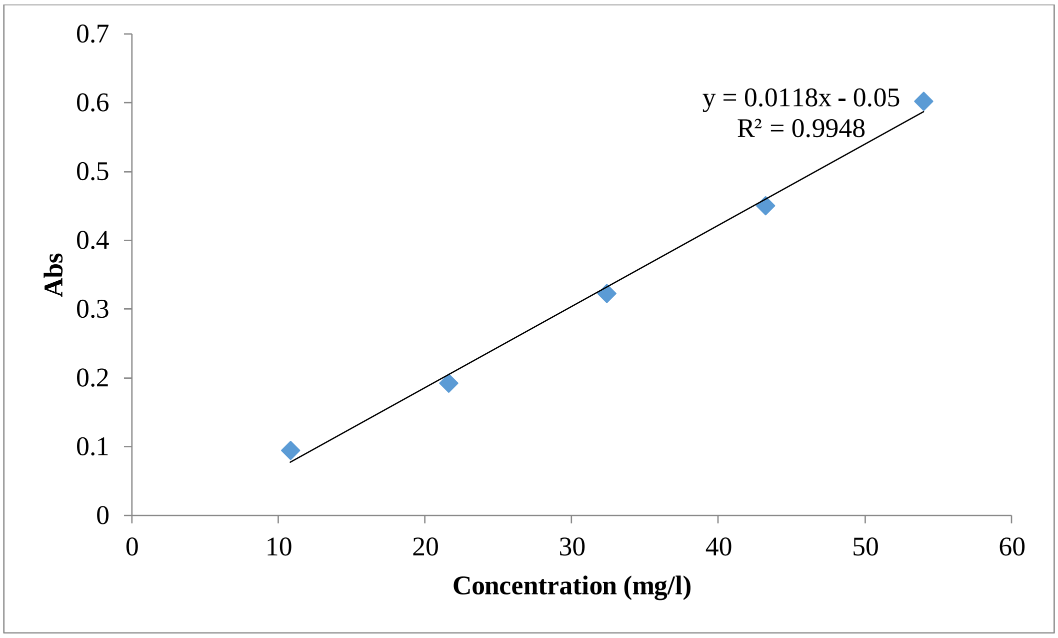


Figure 3. 3 : Gallic Acid calibration curve

Annex 2 : Design of Coagulation Experiment

Annex 2.1 : Coded values for the treatment sets proposed by Design Expert.

Sample number	Coagulant type	pH	Coagulant concentration(mg/l)
1	-1	1	-0.33
2	-1	-0.4	-0.33
3	-1	-0.4	1.00
4	-1	1	1.00
5	1	1	-1.00
6	-1	-1	1.00
7	1	-1	-0.33
8	1	-0.4	-1.00
9	-1	-1	-1.00
10	1	1	1.00
11	1	1	-0.33
12	-1	-0.4	-1.00
13	1	-1	-1.00
14	1	-0.4	1.00
15	1	-1	1.00
16	-1	1	-1.00
17	-1	-1	-0.33
18	1	-0.4	-0.33

Annex 3 : Practical Application For The Polynomial Equation For Predicting TSS Reduction Values .

TSS reduction % = 93.5157 + -2.19502 * A + 0.725791 * B + -0.0285488 * C + 1.50593 * AB + -0.928402 * AC + 1.69116 * BC + 1.38014 * ABC

Where

A:pH

B: Coagulant conc.

C: Coagulant type

In the equation all these actual values have to be converted to coded values in terms of +1&-1. The conversion is usually made automatically when Design expert program is used , However manually we can use the table in Annex 2 which contains coded values for the treatment sets proposed by Design Expert.

For example, if we chose a random sample for example treatment No 1 that has the following combination

sample lab no.		**A:pH**	**B: Coagulant conc.**	**C: Coagulant type**	**TSS reduction %**
1	Actual value	8	AS	1.00	90.0
	Coded value	-1	1	-0.33	Predicted by the equation

TSS reduction %= 93.5157 + -2.19502 *(-1) + 0.725791 * (1) + -0.0285488 * (-.33) + 1.50593 * (-1*1) + -0.928402 * (-1*-0.33) + 1.69116 * (1*-0.33) + 1.38014 *(-1*1*-0.33)

The predicted value for TSS reduction % is 94.5

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