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ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAIT)

SCHOOL OF CHEMICAL AND BIO ENGINEERING

EVALUATING PENTIANTIAL OF "SUPHE" SOIL AS A COAGULATING AGENT IN PRIMARY TREATMENT OF ASELLAMALT FACTORY WASTE WATER

A Thesis submitted to the school of Chemical and Bioengineering Addis Ababa Institute of Technology in partial fulfillment of the requirement for degree of Master of Science in Chemical Engineering under Environmental Stream.

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Addis Ababa, Ethiopia

October, 2018

ADDIS ABABA UNIVERSITY

INSTITUTE OF TECHNOLOGY

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This is to certify that the thesis prepared by: Arega Getaneh Moges, entitled: Evaluating Treatment Efficiency of “Suphe” Soil as a Pretreatment Agent in Biological Treatment Method for Malting Factory Waste Water and submitted in partial fulfillment of the requirement for the degree of Master of Science in environmental engineering (Chemical and Bio Engineering) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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ABSTRACT

Malt industries generate large amounts of wastewater effluent which contains a high concentration of biodegradable and non-biodegradable organic compounds which are poisonous to the environment and to eco system if discharged untreated. In this study, treatment performance of "Suphe" soil was evaluated first by treating composite malting waste water samples collected from different stages of production process at three different doses which were, 50mg/l, 500mg/l, 1000mg/l of "Suphe" soil in order to remove COD, BOD, TSS, then it was followed by adjusting the pH of waste water at acidic (pH 5), neutral (pH 7) and basic (pH9) medias. Sodium Hydroxide (NaOH) 0.1N and Sulfuric acid (H_2SO_4) 0.1 N were used for adjusting the pH at the desired levels and the removal efficiency of "Suphe" soil was best recorded at pH of 7 and coagulant dose of 50 mg/l. Design-Expert 7.0.0 three-level-three-factor Box-Bhenken Design (BBD) was applied for experimental design and statistical analysis of results. Coagulant dose, pH of wastewater, and settling time had a significant effect on treatment process of malting wastewater samples process. For this treatment system, a set of experiments was performed to investigate removal of COD, BOD and TSS at different experimental phases. From these analyses, Results on overall efficiency had COD and BOD removal performance of 94.3% and 94.4 % for the first wet steep; 97.7%and 97.1% for the second wet steep and 96.3% and 96.1% for the composite treated effluent respectively. Andthe turbidity removal efficiency of the "Suphe" soil coagulant was 98.76%, 99% and 99.83% respectively for first wet steep, second wet steep and finally treated composite effluent at coagulant dose of 50 mg/l and pH of 7 On the other hand at the same pH level in which "suphe" soil was used, Alum turbidity removal efficiency was 96.2%, 96.6%and 99.4% respectively as mentioned above. Therefore, "Suphe" soil is found to lay a significant malting wastewater pretreatment agent which has the potential to replace the hydrated aluminum sulphate.

Key words: Biodegradable, wastewater, "Suphe" soil, coagulant, malting

ACKNOWLEDGMENTS

There is an African proverb that says "A great thinker will always appreciate the importance of thanks giving". First and foremost, I give all glory and honor to the God of all ages, the source of all wisdom, knowledge and understanding. I thank Him and praise Him for giving me life and wisdom to achieve this feat. To Him alone I give all the glory.

The completion of this thesis work will not be possible without the excellent guidance of my advisor Dr/Eng Abubeker Yimam so, I acknowledge all his encouragements and valuable time given to me with deep gratitude and appreciation. I wish to thank all the great people whose contributions have made my thesis a success; whether or not I address all of them in this short acknowledgement.

I would like to thank all my fellow graduate students in the chemical and bio engineering department for the assistance they provide me throughout my studies in the past two years; especially I would like to thank environmental engineering group members who made this journey interesting and exciting. I want to thank all my family for they stood behind me through difficult time as every man goes through ups and downs, but the difference between those that succeeds and those that fails lies within the voice of the people around them. They always had been the voice of reason and encouragement that feeds my energy to succeed and my deepest gratitude also goes to a PhD student Hana Melese, who helped me to be here today with everything I was in.

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LIST OF ACRONYMS

AMF	Assela malt factory
ANOVA	Analysis of variance
APHA	American Public Health Association
ASTM	American society testing for material
BBD	Box Bhenken design
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EPA	Environmental Protection authority
EU	European Union
H_2SO_4	Sulfuric acid
NaOH	sodium hydroxide
pH	Potential of Hydrogenation
TN	Total nitrogen
TSS	Total suspended solids

LIST OF APPENDIXES

1. INTRODUCTION

Assela and Gonder Malt Factories are enterprises that process malting barley in Ethiopia and they supplies one of the most important raw materials for brewery industries of the country. Alemayehu Hailemicael (2010), reported that the wastewater generated by Assela Malt Factory is disposed freely and join the nearby water body mainly wolkesa river without any treatment. Communities downstream of Assela Malt Factory and students of the nearby elementary school use the water from the river in which the effluent is part, for a variety of purposes such as drinking, livestock watering, irrigation, and other purposes and the bad odor released from the wastewater canal has created also caused huge discomfort to the nearby communities. Water pollution is serious global problem; which involves the discharge of dissolved or suspended substances into groundwater, streams, rivers, lakes and oceans. A major source of pollution especially in developing countries is industrial activities and this has gradually increased the problem of waste disposal. In most developing countries, industries dispose their effluents without adequate characterization, quantification and pretreatment due to economic and technological constraints. These effluents are the main source of direct and continuous input of pollutants into the aquatic ecosystems (Sweeney *et al*., 1995).

The wastewater generation and mismanagement in beverages and malt industries become a serious threat to freshwater bodies, aquatic biota and human health. The continuous discharge of effluents into streams and rivers raises the level of trace and toxic metals, which have considerably adverse effect on fresh water bodies. Untreated wastewater from most of industries discharged into inland water bodies resulting to stench, discoloration and a greasy oily nature of such water bodies. These wastes pose a serious threat to associated environment, including human health risks. Thus there is need to control the pollution of surface and ground water since the public health and well-being of the people have a direct link with the availability of adequate quantity of good quality water (Ipeaiyeda and Onianwa,2009).the malting and brewing industries use a large volume of water and discharge more than 70% of the intake as effluent with a high organic contamination. The malt beverage brewing industry is one of the largest industrial users of water, but its effluent is characterized by high levels of organic contaminants which require remediation before reuse. It generates large amounts of wastewater effluent which are discharged directly into a waterway (oceans, rivers, streams, or lakes), directly into a municipal sewer system, and into the waterway or municipal sewer system. Malting effluents usually contains a high concentration of biodegradable and non-biodegradable organic compounds and therefore they must be subject to different ways of wastewater pretreatment to prevent pollution. In cases where the malt industry does not discharge to the municipal sewer, then primary and secondary treatment of the effluent is required (Isaac and Anderson, 1973).

The disposal of untreated (or partially treated) malting wastewater into water bodies can constitute potential or severe pollution problems to the water bodies since the effluents contain organic compounds that require oxygen for degradation. The main characteristics of environmental concern that can be associated with malt industry wastewater include; Biochemical Oxygen Demand (BOD) or Chemical Oxygen Demand (COD) concentration, TSS concentration, pH, nutrients (nitrogen and phosphorus) concentration and temperature (Driessen and Vereijken, 2003).

Untreated malt industry effluents are known to have, high biological oxygen demand (BOD), high chemical oxygen demand (COD) and high concentrations of suspended solids (SS). Malt effluents, having chemical (with very high organic contents) and microbial contaminants, results in a rather chaotic layout of utilities such as water supply, irrigation and laundry of the receiving river. High concentration of these parameters indicates a nutrient-rich wastewater, one which promotes the growth of algae and bacteria if discharged into a river. The presence of these microorganisms creates a situation of oxygen deficiency in water and subsequently the death of marine life.Studies have been performed characterizing dissolved organics present in wastewater and have reported that these contents are highly heterogeneous with compounds of a variety of different molecular weights, ranging from simple structures to very complex polymers (Janhom*et al*., 2010).The disposal of untreated (or partially treated) malting wastewater into water bodies can constitute potential or severe pollution problems to the water bodies since the effluents contain organic compounds that require oxygen for degradation. The main characteristics of environmental concern that can be associated with malt industry wastewater include; Biochemical Oxygen Demand (BOD) or Chemical Oxygen Demand (COD) concentration, TSS concentration, pH, nutrients (nitrogen and phosphorus) concentration and temperature (Driessen and Vereijken, 2003).

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According to EPA (2003), the majority (90%) of existing industries in Ethiopia discharge untreated effluents into nearby water bodies, streams and open land, For instance, malting industry in Ethiopia generates about 70% effluent of wastewater resulting in water pollution on nearby rivers and when released directly on the ground, the pollutant will infiltrate into the ground water resulting ground water pollution. Most of the industries in Ethiopia are also established very close to rivers and the most polluting sources are sugar factories followed by textile and tannery factories (Seyoum Leta *et al*., 2010). Treatment performance of Bioprocess for BOD, COD and nutrient removal was evaluated and it is effective method for treating Assela Malt factory malting wastewater with careful application of pretreatment, thus this study aims to evaluate the efficiency of “Suphe” soil coagulant as a pretreatment to treat waste water of Assela malt factory and to compare the treatment efficiency of “Suphe” soil with commonly used chemical coagulants (alum), so as to reduce the amount of sludge produced as much as possible and to reduce difficulty removing sludge and season dependability of microorganisms.

1.1. Statement of the Problem

Among the food processing industries, the malting industry produces significant volumes of liquid effluents, typically with high nutrient load. Malt industry effluents are generally characterized by a high content of biodegradable pollutants and suspended substances (Alemayehu Hailemichael*et al*., 2010). The usual practice of wastewater discharge from malt industry has included four options. These are listed as, directly into a river; directly into a municipal sewer system; into a river or municipal system after pre-treatment; and into the malt factories own waste water treatment plant. Each of these approaches has some limitations and threats to aquatic life. They also have high treatment cost and chronic as well as acute effect on human health (Fergus *et al*., 2006).

AMF malting wastewater is released untreated with high organic content in the effluent which threatens the ecology of the receiving water body and this malting wastewater is being used by ARDU MIRT ZER agricultural organization which is found besides of AMF for irrigation purpose without any attempt to treat the malting waste water and also communities downstream of Assela Malt Factory and students of the nearby elementary school use the water from the river in which the effluent is part, for a variety of purposes such as drinking, livestock watering, irrigation, and other purposes. Thus, this study attempts to address the issue through evaluating pretreatment efficiency of "Suphe" soil coagulant in malting wastewater treatment process of AMF, which have low possibility of producing toxic by-products and regenerating usable water from waste effluent.

1.2. Research Objectives

1.2.1. General Objective

To evaluate Evaluating Potential of "suphe" soil as a coagulating agent in primary treatment of Asella malt factory waste water (AMF).

1.2.2. Specific Objectives

- ✓ to measure COD, BOD, TSS and amount of chemical contents of malting waste water
- ✓ to prepare "Suphe"soil coagulant to improve its coagulating effect.
- ✓ perform jar test in order to determine effective dose of "Suphe" soil coagulant for treatment
- ✓ to determine the effect of pH, Retention time and Dose on performance of "Suphe"soil coagulant
- ✓ to determine COD, BOD and TSS removal efficiency of "Suphe" soil
- ✓ to determine contaminant chemical removal efficiency of "Suphe" soil
- ✓ to compare the treatment efficiency of "Suphe" soil with alum and the specified standards

1.3. Significance of the Study

The effluents from different industries are becoming huge headache in front of today's world by affecting the socio economic aspect and more over having healthy aquatic environment is becoming far dream to new and existing generation. Primary reasons for wastewater reuse being an uncommon practice in malting industry includes, public perceptions and the possible product quality deterioration. As the shortage of water is becoming an increasingly serious global and even local problem day by day, the momentum of malting wastewater reuse is inescapable (Belgiorno*et al*., 2007). Therefore, world is in a big need of clean and secure of water resource, which shows every community should collaborate to achieve what is needed.

The concept of water treatment for reuse by other organizations has been shown in the literature recently, as the regulations regarding wastewater disposal have become more rigorous alongside a rising cost for intake water. The associated cost of discharging untreated or partially treated wastewater into municipal sewer systems or in rivers is quite high. AMF discharge 70% of incoming water as effluent; a quantitative analysis showed about 5 m^3 of water was used as intake per each ton of malt produced whereas 3.33 m^3 of waste water effluent was generated per a single ton of malt produced in most cases, malting effluent disposal costs are much higher than water supply costs (Alemayehu *et al*., 2010).

To maintain the quality of natural ecosystems, it is crucial to build eco-friendly strategies into every industry and a prime concern of environmental engineer today, is how to lower the coagulants and flocculants cost and at the same time to improve the characteristics of the produced sludge to be safely utilized and if this study is implemented in larger scale, it attempts to use natural soil as a pretreatment agent found in East Arsi with a small amount of chemical initiators to treat Assela malt factory waste water effluent.

2. LITERATURE REVIEW

Assela Malt Factory, the first enterprise that process malting barley in Ethiopia, is located in Oromia administrative region, Arsi Zone 167 kms South East of Addis Ababa, near Assela town. The surrounding highlands and planes of Arsi and Bale, which are generally 2300 meters above sea level, are long known for their best suitability for growing barley. Assela Malt Factory was established in 1984 GC at Assela. The factory was installed with annual production capacity of malt for use by breweries locally. It has annual production capacity of 200,000qts. AMF's share of malt supply now stands at 56% and the rest is met through import (IPS, 2005).

2.1. Traditional Industrial Wastewater Treatment methods

Wastewater impurities consist of a mixture of organic materials characterized by its ability to be biologically degraded and non-organic suspended or dissolved materials carried in the water (Jaiyeola and Bwapwa, 2016). It also contains microorganisms that help to dissolve and ferment these materials, as well as a large quantity of mineral ions and some industrial wastes (heavy metals, chemical solutions, industrial effluents) that would otherwise be discharged into public sewers. It is readily possible to treat wastewaters and obtain clean water that does not harm humans or animals using different technologies based on scientific advancements (Sponza*et al*., 2006). According to UNEP (2009), commonly used traditional wastewater treatment methods include the following processes which are carried out either separately or jointly.

2.1.1. Physical Treatment: This is a primary treatment, and includes operations like the use of bar screens to protect the treatment plant from large debris or other materials in the incoming wastewater that may halt or interfere with the wastewater treatment plant operation so that screens with graded diameters are used for this purpose and primary settling which is operated at the settling basin to remove floating materials from the wastewater.

2.1.2. Physico-chemical Treatment: This is kind of secondary waste water treatment which involves coagulation followed by sedimentation to remove suspended materials in the wastewater that did not settle in the first stage by using coagulants. This treatment can also remove some other elements and chemicals (heavy metals, phosphate) from the wastewater.

2.1.3. Biological Treatment: Biological waste water treatment is a secondary treatment method by using bacterial action to remove all biologically-degradable material from the wastewater. It is based on establishing “biological farms” containing large groups of microorganisms and single- and multiple-cell microscopic organisms. These microorganisms grow and reproduce as the wastewater is passed over them, using the biodegradable materials in the wastewater as a food and energy. Biological treatment is carried out in two stages:1) relatively rapid removal of the BOD of suspended and colloid materials, because of their adhesion and absorption on the solid surfaces containing the microorganisms and2) slower removal of the BOD of the remaining materials by the biological mass (the mass of all organisms in the medium) by the microorganisms that feed and reproduce at their expense. The first stage removes approximately 80% of the initial BOD in the wastewater, with the remaining BOD removed in the second stage (Akpor and Muchie, 2010).

2.1.4. Sludge Treatment and Drying: This treatment method is used essentially to dry the sludge material removed from the wastewater as a result of the above-noted wastewater treatment stages. Following the above primary and secondary treatments, a tertiary treatment must be used to remove the remaining non-biodegradable materials in the wastewater based on the need of treated effluent which means that based on the purpose of treated water.

2.1.5. Tertiary Treatment: It is used to reduce the concentrations of biochemical oxygen demand (BOD) and any remaining suspended materials, remove phosphate, facilitate denirification, and facilitate chlorination. With the use of these treatment process, virtually all materials in the wastewater that represent human health hazards are removed, including organic and chemical contaminants, heavy metals and pathogenic microbes and viruses. Any smell, color or turbidity also will be removed using tertiary treatment system.

2.2. Waste Water Treatment Using Coagulation/flocculation processes

Coagulation and flocculation process is considered as a non-expensive and effective method to reduce organic and inorganic content of industrial wastewaters. Coagulation and flocculation are used to separate the suspended solids portion from the water where Suspended particles are known by varied in source, charge, particle size, shape, and density therefore correct application of coagulation and flocculation process depends upon these factors (Zagklis*et al*., 2012).

Coagulation and flocculation occurs in successive steps, allowing particle collision and growth of floc; and this is then followed by sedimentation. If coagulation is incomplete, flocculation step will be unsuccessful, and if flocculation is incomplete, sedimentation will be unsuccessful. Flocculation, a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. Microfloc particles collide, causing them to bond and produce larger, visible flocs called pinflocs. Floc size continues to build with additional collisions and interaction with added inorganic polymers (coagulant) or organic polymers (coagulant). Macroflocs are formed and high molecular weight polymers, called coagulant aids, may be added to help bridge, bind, and strengthen the floc, add weight, and increase settling rate. Once floc has reached it optimum size and strength, water is ready for sedimentation (Prakash*et al*., 2014).Wastewaters often contain pollutants that are present is colloidal form. In such cases the colloidal suspension may contain organic materials, metal oxides, insoluble toxic compounds, stable emulsions and material producing turbidity. The primary purpose of the coagulation followed by flocculation process is the removal of turbidity from the water. In addition to removing turbidity from the water, coagulation and flocculation process removes many bacteria which are suspended in the water and can be used to remove color from the water (Gregory*et al*., 1981).

2.2.1. Coagulation

In the area of wastewater treatment, clarification of water with coagulating agents has been practiced since ancient times, using a variety of substances the most notable among them being crushed seeds. The commonly used metal coagulants fall into two general categories: those based on aluminum and those based on iron. The most widely used metal coagulant is probably the aluminum sulfate ("alum"), which has been used for water treatment. The application of simple metal coagulants (conventional) is widespread, especially due to the relatively low cost and the simpler application route. However, they exhibit several disadvantages, such as the need for pH adjustment before or after treatment, the sensitivity to temperature changes, the need for higher dosages, because the charge neutralization is not usually sufficient, the sensitivity to sample specific characteristics and composition, as well as the excessive sludge production (Prakash*et al*., 2014). The Egyptians, as early as 2000 BC, used almonds smeared around a vessel to clarify river water. The early Romans were also familiar with alum, though it may not have been for water treatment Nevertheless; its use of a coagulant by the Romans, alum was used as a coagulant in water treatment in England, and more formally for the treatment of public water supplies in 1881(Bratby, 2006). In modern wastewater treatment, coagulation followed by flocculation is still essential step in the waste water treatment processes. The process of coagulation is one of the most important physicochemical operations used in water, and wastewater treatment can be achieved by chemical and electrical means. It has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation targets the colloid particles of size 10^{-7} to 10^{-14}cm in diameter. The colloid particles exhibit Brownian movement through the water where their surface is negatively charged so they repel one another, and they form a stable dispersed suspension (Bache *et al*., 1999).

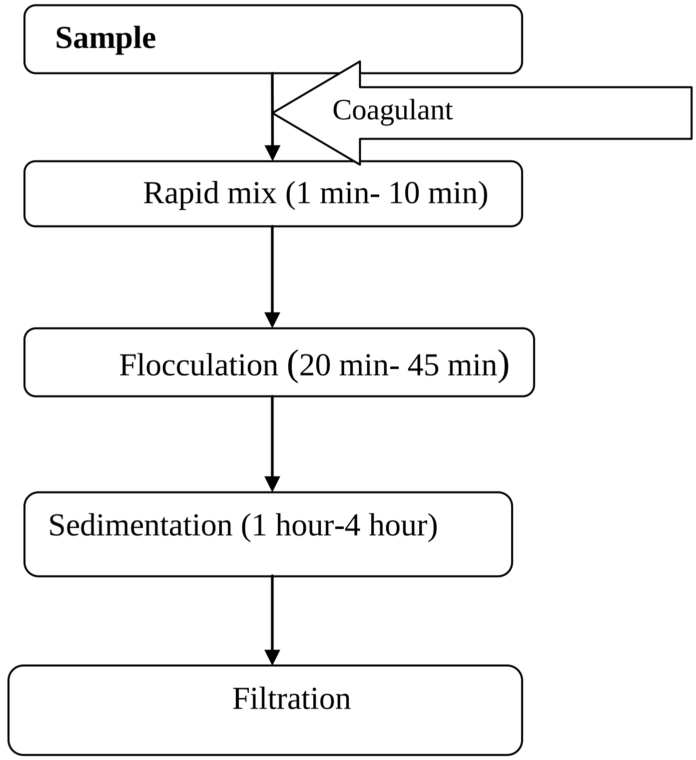


Figure 2.1: Steps of coagulation process

As the figure 2.1 clearly shows, the chemical is added to wastewater and that is followed by the second step, where the solution is mixed rapidly in order to make certain which means that the chemicals are evenly and homogeneously distributed throughout the wastewater. In the third step, the solution is mixed again, but this time in a slow fashion, to encourage the formation of insoluble solid precipitates, the process known as "coagulation" and the final step is the process of removing coagulated particles by way of filtration or decantation (Yılmaz*et al.*, 2007).

Effective coagulation is a function of many factors, where the complete list of factors which are detailed in Table (2.1) as sited by luu. Some of the most important factors influencing the effectiveness of coagulation to treat waste water are coagulant type, dosage, pH of waste water, mixing intensity, coagulant addition point, proper coagulant feed and mixing times. There is a range of optimum dosages for a coagulant at which maximum settling and removal of suspended particles is most efficiently and effectively achieved. Below this range, the amount of coagulant added is insufficient to adequately destabilize the particles and above this range, the coagulant essentially serves as a chemical coating which re-stabilizes the particle. The window of acceptable dosages varies with every coagulant and with many of these factors, making some less sensitive to imprecisely measured dosages (Kim, 2000).

Table2.1 Factors affecting effective coagulation

Coagulant Characteristics	Physical Characteristics	Raw Water Characteristics
Coagulant type	settling time	Suspended solids
Coagulant dose	mixing intensity	Temperature
Proper solution makeup and dilution	mixing time	pH
Proper coagulant age	Coagulant addition Point	Alkalinity
Proper coagulant feed		Ionic constituents

Source: - Murcott and Susan (2011)

2.2.2. Flocculation

It is the process of intending to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of larger particle commonly called floc, coagulation and flocculation occur in successive steps where Flocculation is the physical process of agglomerating small particles into larger ones which are called and that can be more easily removed from suspension. It is always used in conjunction with, and preceded by coagulation in which during the coagulation process the repulsive forces between solids particles are reduced even almost eliminated (Hussain*et al*., 2013).The coagulation process brings the destabilized particles into contact with one another to form micro flocks which is turned into visible flock masses and these larger particles are more readily removed from the water in subsequent processes mainly by sedimentation (Pernitsky and Edzwald, 2006).

2.2.3. Wastewater Treatment using Chemical Coagulant

In modern water treatment, coagulation and flocculation are still essential steps in the treatment processes. Coagulation in water and wastewater treatment can be achieved by chemical and electrical means where Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and which causes growth of floc. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization (Pernitsky*et al*., 2006).

Coagulation targets the colloid particles of size 10^{-7} to 10^{-14} cm in diameter and the colloid particles exhibit Brownian movement through the water while their surface is negatively charged so they repel one another, and they form a stable dispersed suspension (Bache *et al*., 1999). If colloid particles or ions of positive electric charge are added it neutralizes the electric negative charge. Flocculation refers to the successful collision that occurs when destabilized particles are driven toward each other by the hydraulic shear force in the rapid mix and flocculation basin. It agglomerates of a few colloids then quickly bridge together to form microflocs which is turned into visible floc masses (Gregory *et al*., 2006).

Coagulant chemicals come in two main types which are primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles into the water which causes the particles to clump together (Schulz *et al*., 1984). Chemical coagulants are either metallic salts (such as alum) or polymers. Polymers are man-made organic compounds (“Suphe” soil coagulant) made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged). Chemical coagulation has been in practice for several decades to precipitate the soluble heavy metals present on the waste water, as hydroxides and facilitate their removal by physical separations through the sedimentation process. Basically, coagulants are divided among four categories, according to their application and nature specifically listed as, Aluminum salts (alum), Ferric and ferrous salts, Lime Polymers and Natural coagulants (Cohen and Hannah, 1971).

2.2.3.1. Coagulation with Aluminum Salts

The most common and economical salt of aluminum is alum (Al_2 (SO_4).nH2O) and widely used as a coagulant in the water treatment (Table 2.2). The aqueous chemistry of aluminum is complex and upon addition of an aluminum coagulant in water treatment, multiple reaction pathways are possible. The mechanism by which aluminum salt functions depend on the factor which aluminum species react to remove dissolved or colloidal contaminants. Destabilization involving aluminum monomers is referred to as charge neutralization or coagulation of colloidal particles in the presence of Al $(OH)_3$ is termed as enmeshment or sweep floc. Dissolved organic can be removed by adsorption on aluminum precipitation (Benschoten*et al*., 1990).

From the numerous reviews of the fundamental theory and mechanisms of coagulation, various mechanisms for destabilizing contaminants using chemical coagulants have been identified. These mechanisms include double layer compression, adsorption charge neutralization, sweep coagulation and inter particle bridging. The type of inter actions between the chemical coagulant and contaminants determine the mechanism of coagulation. The predominance mechanisms observed during conventional coagulation with metal coagulants are adsorption charge neutralization and sweep coagulation. For aluminum salts, the mechanism of coagulation is controlled by the hydrolysis speciation (Dennett *et al*., 1996).

Coagulations with iron salt: Iron compounds possess pH coagulation ranges and floc characteristics similar to aluminum sulfate. The cost of iron compounds may often be less than that of alum. However according to research conducted by Alemayehu Hailemichael (2010), the iron compounds are generally corrosive and often present difficulties in dissolving, and their use may result in high soluble iron concentration in process effluents. The iron salts most commonly used as coagulants include ferric sulfate, ferric chloride and ferrous sulfate. These compounds often produce good coagulation when conditions are too acidic for best results with alum. Sometimes the particles are best removed under acidic conditions, and iron compounds give better results, therefore, there is a need to regulate the pH of waste water to treat by iron salts. Mahesh *et al*. (2006)studied many hydrolysis products are cationic and these can interact strongly with negative colloids, giving demineralization and coagulation, under the correct conditions of coagulant dosage and waste waterpH. Excess dosage can give charge reversal and restabilisation of colloids.

2.2.3.2. Coagulation with Natural Anionic Polymers

Many sulfated polysaccharides are available as natural biopolymers or their derivatives, some examples being heparin, dextran sulphate, mannansulphate and chondroitin sulphate, but the applications are mainly medical. One proposed for use in the water industry is the modified natural polymer lignin sulphonate, made by sulfonating low MW kraft pine lignin. Certain of these polymers are equivalent in performance to cationic PAMs for the dewatering of sludge(Rice *et al*. 1964).

Table 2.2.Common chemical coagulants used to treat wastewater (Meister and Li, 1990).

Common name	Chemical formula	Comments
Aluminum sulfate (alum)	$Al_2(SO4)_3.14H_2O$	used with cationic polymers
Ferric sulfate	$Fe_2(SO4)_3$	often used with lime softening
Ferrous sulfate	$FeSO_4.7H_2O$	less pH depended than alum
Sodium aluminate	$Na_2Al_2O_4$	used with alum to improve coagulation
Sodium silicate	$Na_2O.(SO_4)_x$	ingredient of activated silica coagulant aids
Aluminum polymer	-	Include poly aluminum chloride and sulfate

2.2.4. Wastewater Treatment using Soil Coagulants

Sewages which are produced from oil refining, water mines, petrochemical plants, organics of synthesizing plants, coke-chemical, malt industry wastes, brewery industry effluents etc. contains different amounts of harmful and toxic matters and which are the major sources, and wasting our environment. The most harmful pollutants of these sewage matters are mainly in oxidizing processes, owing to degradation of water oxygen, which is one of the water contents and this lead to increasing the biochemical oxygen requirements and that can be expressed by BOD (biochemical oxygen demand) index of water or COD (chemical oxygen demand) in mg/l. In addition, it was recognized that, treating industrial sewages and wastewater by using coagulants and flocculants at different types and dosages reduces toxic matters from these wastes But the big problem is the chemicals cost and the toxic sediments that produced from the process and its polluting effects on the water resources, especially when the sediments contain high levels of toxic matters as COD, phenols, oils, heavy metals etc. (Kebede *et al*., 2017).

Many organic materials are used to absorb contaminants from wastewater and among them Clay-based treatment products are available at a low cost, typically Bentonite clay modified with various polymers and chemicals. Bentonite clay can treat oil, sulfate, phosphate, and metals and is extremely effective at removing certain cationic components from wastewater. It has a remarkable affinity for metals, particularly heavy metals in solution and it is also used frequently in treating waters containing heavy color, high turbidity. In addition to its weighting action, also benefit obtained from the known ability of clays to adsorb organic compounds. Furthermore, the addition of clay to low turbidity water provides increase opportunity for particle collisions, resulting in rapid formation of settable floc. The resulting mass or floc is a complex mixture of encapsulated contaminants and clay solids held together by Vander Waals and electrostatic forces. The contaminants are microencapsulated and surrounded by a barrier of clay particles making it nonreactive to external leaching (Tripathy*et al*., 2006).

Clay soil material is one of soil types which have played an important role in the environmental protection. These minerals have been used in the disposal and storage of hazardous chemicals as well as for remediation of polluted water. The use of clay mineral as the adsorbents for the adsorption of various hazardous substances (heavy metals, dyes, antibiotics, biocide compounds, and other organic chemicals) has been widely studied by a large number of researchers. Clay soil has been studied for its coagulation activity and coagulant aid ability and study on clay soil performance effectiveness and optimum working condition on two soil types called Shendi and Sinja soil coagulants by which local people in Sudan who live nearby Blue Nile are using. Both soil coagulants has performed properly in wide range of pH ranging from 3-10 at coagulation dosage of 300-400 mg/Lwhereas the optimum settling time is 30 minutes for Sinja and one hour for Shendi the removal efficiency was 92.2 % and 87.3 % for Shendi and Sinja respectively (Mohammed *et al*., 2013). Apart from sole use of clay soil coagulant in oily waste water, clay coagulation improves the coagulation and flocculation with alum as coagulant aid. Moreover the locally available low cost material has important practical implications for removal of dyes from textile waste water (Bizuneh*et al*., 2011).

2.3. Malt Industry Wastewater Treatment

Food industry effluents are generally characterized by a high content of biodegradable pollutants and Suspended substances constitute a large part of these pollutants, in addition to the high BOD and COD concentrations of the effluents. Among the food processing industries, the malting industries produces significant volumes of liquid effluents, typically with high COD and BOD load. If the wastewater is released untreated, the high organic content would threaten the ecology of the receiving water body and human health (Rustrian*et al*., 1997).

Most of the time, in order to describe malt industry wastewater quality; biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solid (TSS) have been reported. High concentration of these parameters indicates that nutrient-rich wastewater, one which promotes the growth of algae and bacteria if discharged into a river (figure 2.2). The presence of these microorganisms creates a situation of oxygen deficiency in water and subsequently the death of marine life. According to AlemayehuHailemicael (2010), Studies have been performed characterizing dissolved organics present in wastewater and have reported that these contents are highly heterogeneous with compounds of a variety of different molecular weights, ranging from simple structures to very complex polymers. Malt wastewater has high levels of DOC (Dissolved Organic Content) and an absorbance at UV254 indicating that a high level of organic content with aromatic structures (Janhom*et al*., 2009).

Fig2.2:Untreated effluent discharge of AMF to the nearby river and its effect on aquatic lives.

2.3.1. Malting Process Description

Malt is derived from a cereal grain, usually barley, after being germinated for a limited period and then dried. As it is generated from cereal grain, it is rich in carbohydrate, degraded proteins, various vitamins B's and inorganic materials. Malting serves the purpose of converting insoluble starch to soluble starch, simplifying proteins, generating nutrients for yeast and the development of enzymes. In other words, malting is the process of modifying the grain in order to make the sugars trapped inside the kernel available for mashing which is gained by force germinating (Figure 2.3). There are three main steps of the malting process are steeping, germination, and kilning (Kelly*et al*., 2011).

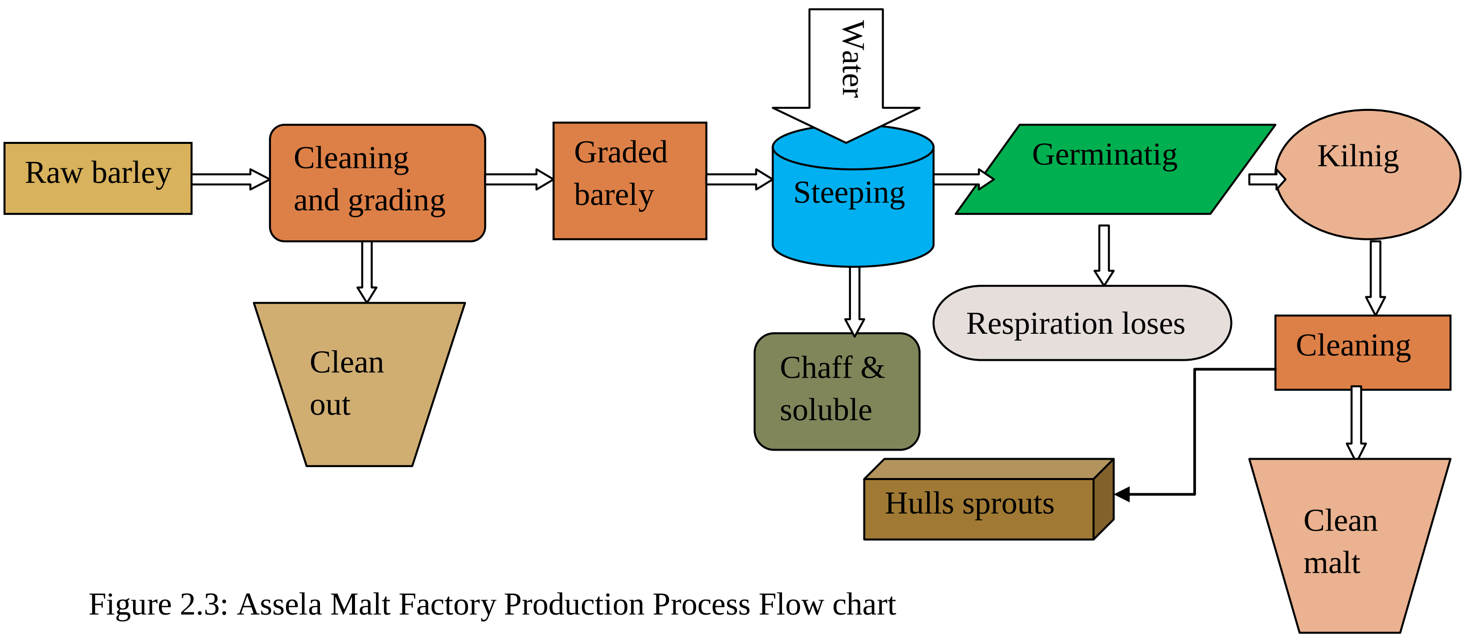


Figure 2.3: Assela Malt Factory Production Process Flow chart

2.3.1.1. Steeping

The purpose of steeping is to evenly hydrate the endosperm in the raw barley kernel. Steeping will raise the moisture content of the grain from approximately12% to 45% which will help in the promotion of germination (fig. 2.4). The steeping process typically will take about 36-48 hours depending on the moisture content of cereal grain going into steep (Kelly*et al*., 2011).

Fig 2.4: steeping process of AMF

2.3.1.2. Germination

After steeping takes place, the kernels are spread out on a false bottom which is called bottom bed so that the grains can comfortably sprout or start germinates (fig. 2.5). Germination bed can be either pneumatic type of germination beds or traditional floor malting methods but, regardless of the method, the germinating grain must be aerated periodically, by hand or by machine(Valta*et al.*, 2015). Floor malted beds are aerated by hand while Pneumatic beds are mechanized to "walk" the grains along a track and this motion automatically aerates the grain and prevents the rootlets from twining together. The malt's protein modification and enzyme content is set over the next three to six days as the grain's rootlets develop but the longer the germination period, the more highly modified the malt and finally Post germination, pre-kilned barley is called "green malt"(Bolto and Gregory, 2007).

Fig 2.5: Germination bed of AMF

2.3.1.3. Kilning

The moist, sprouted malt or “green malt” from the germination step is moved to the kiln to be dried (fig. 2.6). This step arrests further modification of the kernel and the main goal is to dry the malt as much as possible at lower temperature around 33 ^{0}C which helps preserve the enzymes in the malt. The first drying period typically takes about 24 hours and the second drying period which typically last about 12 hours will be at a slightly higher temperature around 49°C. The third and final “curing” process will occur over the next 24-48 hours atapproximately 82-105°C. The curing process influences the malt taste, aroma and stability. The malt style determines the temperature and length of the kilning and the roasting process to follow (Thamer *et al, 2007*).

Fig 2.6: kilning process of AMF

2.4. Factors Affecting Coagulation

2.4.1. Coagulant Dosage

The concentration of coagulant required for waste water treatment coagulation should be proportional with the concentration of an organic matter present in solution or in the waste water, and it was stated that before turbidity became settled, the coagulant must be added in sufficient amount to destabilize the organic matter. Apparently, these substances react with the coagulants before the coagulants can destabilize clay suspensions. Coagulant dosage is proportional to the pH of the sample which means that, the dosage decreases with decreasing pH because more carboxylic groups become prorogated and do not interact with coagulant.As current researches state that, there is no reliable formula to determine the effective dosage However, a jar test is the most reliable method to determine both the effective type of coagulant and their proper dosage (Kawamura *et al*., 1996).

Proper coagulation is essential for good clarification and filtration performance and for the control of pathogens and disinfection by-products. Improper coagulation can cause high residual, coagulant residuals in treated water and post-treatment precipitation of particles causing turbidity, deposition and coatings of pipes in the distribution system. Minimizing of solids residuals from coagulation has also become a more important part of utility operations due to increased disposal costs and land filling restrictions (Pernitsky, and Edzwald, 2006).

2.4.2. Alkalinity

Alkalinity refers to the acid neutralizing capacity of water, and is a general indication of water's buffering capacity. Alkalinity and pH are closely related which means that higher alkalinity waters will have higher pH. Metal coagulants are mostly known to be acidic, andas a result, coagulant addition consumes alkalinity and from this point we can say that for low alkalinity waters, coagulant addition may consume all the available alkalinity, depressing the pH to values too low for effective treatment. High alkalinity waters (highly buffered) may require elevated coagulant additions to depress the pH to values favorable for coagulation. Alum and ferric chloride are more acidic than PACls, and therefore, they results in greater alkalinity consumption after addition. For PACls, alkalinity consumption is related to basicity it means that, higher basicity PACls will consume less alkalinity than low or medium basicity ones (Voycheck and Tan, 1993).

2.4.3. Temperature

Temperature has different effects on waste water treatment process like the following points; it affects the solubility of the metal hydroxide precipitate and the rate of formation of the metal hydrolysis products. Low temperature affect's coagulation and flocculation processes by altering coagulant solubility, increasing water viscosity, and retarding the kinetics of hydrolysis reactions and particle flocculation. Higher coagulant doses, the addition of flocculation or filter aids, longer flocculation times, and lower flotation, sedimentation, and/or filtration rates are often required to produce low turbidity treated water and Sedimentation processes are most affected. In full-scale plants, processes are sometimes operated at subordinate hydraulic loading rates in the winter due to decreased water demands and this tends to compensate for the lesser settling rates (David and PernitskyS, 2003). Cold-water temperatures often cause decreased performance for sedimentation and make proper coagulant selection more important. High-basicity PACl is reported to be less affected by cool temperatures than alum and the presence of sulphate in a PACl resulted in a better settling floc (Dempsey *et al*., 1974).

As Edzwald and Bunker (1994), mentioned chilled water decreases the solubility of alum and PACl coagulants, increases water viscosity, and retards the kinetics of hydrolysis reactions and particle flocculation. Thus, higher coagulant dosages and additional flocculation time are required at a low temperature. Low water temperatures decrease the rates of coagulant dissolution, precipitation, cell enmeshment and floc formation, mainly when alum was used (O'Connor and Brazos, 1990). Warm water often causes an increased level of algae and other organic matter in raw water. Temperature also significantly affects turbidity and particle counts during coagulation (Braul*et al*., 2001).However, dissolved organic carbon (DOC) and colour removal are not sensitive to temperature (Knocke*et al*., 1986).The negative effect of temperature tends to be greatest with dilute suspensions. Direct filtration and DAF processes are much less affected by cold-water temperatures than sedimentation (Pernitsky and Edzwald, 2006).

2.4.4. Mixing

Rapid mixing after coagulation is an important design parameter in which the coagulant must be uniformly mixed in the waste water. In case mixing is indigent local under and overdosing occurs, resulting in unhappy performance during the process. The parameter expressing mixing intensity is called the velocity gradient or G-value (s^{-1}). Recommended G-value for rapid mixing is minimally 1500 s^{-1} (Hanson and Cleasby, 1990; Randtke, 1998). As Chichuan*et al*.(2002)and Licsko*et al*.(1996) stated,mixing intensity and time has the significant effect of the mechanisms involved in the following process of coagulation Between the hydrolysis of the coagulant in water and the development of large flocs, short-lived water soluble aluminum and iron(III) hydroxide complexes, metal hydroxide solutions are formed, which also carry a positive charge. These latter two metal hydroxide types (which also exist for a brief period - a few seconds-only) are the ones capable of destabilizing the dispersion and adsorbed on the surfaces. The bond between the suspended solids to be removed and the metal hydroxide solutions and water soluble metal hydroxide complexes must be established within this short period. Quick mixing of the coagulant will ensure rapid hydrolysis of the coagulant, contact between the sols and the suspended solids and will retard the development of large flocs which are inactive in destabilizing the dispersion and removing of a pollutant.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Chemicals

Hydrated aluminum sulfate (alum) ($A1_2\ (SO_4)_3{\cdot}18H_2O$): used in order to compare the efficiency of "Suphe" soil coagulant with the treating efficiency of most common coagulant agent hydrated aluminum sulfate. Sulfuric acid (H_2SO_4): was used as "Suphe" Soil coagulant activator and were collected from Hawash melkasa sulfuric acid factory."Suphe" Soil coagulant is the main pretreatment agent in this research and was collected from East Arsi zone, Honkolo Wabe woreda, Bole and BadiKalu districts.

3.1.2. Instruments

Materials needed for malt industry waste water treatment were, glass bottles for collecting samples, thermometer to measure the temperature of Assela malt factory (AMF)malting waste water, pH meter to measure pH value of malt waste water and potassium dichromate to measure COD of the waste, DO meter (Membrane Electrode), jars to perform jar test and dark incubator to measure BOD_5.

3.2. Methods

3.2.1. Data Collection

Composite samples were collected from AMF malting process wastewater streams. Wastewater samples were taken for four months for every two weeks. From the period of taking malting wastewater sample for four months, the first two months were sample collection period for characterization purpose which was performed every two weeks with sample size of two liters at every four sites of malting process of AMF, which was eight liters of total sample size. This was made by taking samples at different steps of the malting processes which are stated as, treated raw inlet water, first wet steep, and second wet steep and effluent (outlet).

After the samples were collected, necessary preservation techniques were applied; and analysis of samples was made within appropriate times which were five days of maximum. Samples collected from AMF were analyzed for chemical oxygen demand (COD),biological oxygen demand (BOD), ammonia-nitrogen ($NH4^{+}$-N), total nitrogen (TN), total phosphorus, ortho-Phosphate, sulphide, sulphate were done using Hack spectrophotometer.

3.2.2. Data Analysis

Triplicate and quadruple data were collected for analysis from the four different sites of the production process of Assela malt factory (AMF) and labs-scale treatment process for characterization, performance evaluation, regression analysis and evaluation of the statistical significance of the data collected were subjected to mean (average) value. Statistical software Design Expert (version is 7.0.0) and “R” software were used for drawing graphs.

3.2.3. Wastewater Characterizing Method

To characterize the malting waste water samples collected from AMF, different parameters like pH, conductivity, Total suspended solid, COD, BOD and different chemical contents of the composite sample were measured in Laboratory for both raw waste water sample and zero treated waste water.

3.2.3.1. pH Determination

500 mL of AMF composite malting waste water sample was filled into a 1000mL beaker and the relative concentration of f H^{+} ion and OH^{-} measured using an electronic pH meter, whereas pH test was carried out to determine the optimum range of the pH value which gives the highest turbidity removal using the “Suphe” soil coagulant. Sodium Hydroxide (NaOH) 0.1N and Sulfuric acid (H_2SO_4) 0.1 N would be used for adjusting the pH at the desired levels if the pH of waste water of AMF were beyond the desired levels but the average pH measured from the malting waste water effluent were relatively at a desired level to be treated by organic coagulant, but constant pH’s were used for comparison purpose and to take action the treatment operation for acidic, neutral and basic media purpose which are 5, 7, and 9 while the treated pH’s of malting waste water were slightly different.

3.2.3.2. Biochemical Oxygen Demand (BOD) Determination

Biochemical oxygen demand (BOD) is an empiric laboratory assay which measures the amount of organic matter contained in a water sample. This assay is the most widely used method for the assessment of water quality. The equation which describes the biochemical process behind the BOD assay is given by according to the following equation.

$$\textbf{Organic matter + microorganism + } O_2 \textbf{ + nutrients} \longrightarrow CO_2 + H_2O \textbf{ + microorganism}$$

Biochemical oxygen demand (BOD) is in fact, a measure of the amount of oxygen consumed by microorganisms for the biochemical oxidation of organic and inorganic matter (autotrophic or nitrogenous BOD). Hence, the BOD value is expressed in mg/L and the higher the organic matter in water malt waste water the higher BOD value (Schulz *et al*., 2004).

$$\text{BOD (mg/L)} = \frac{D_1 - D_5}{P} \qquad (3.1)$$

Where

D_1 = initial DO;

D_5 = DO at day 5; and

P = decimal volumetric fraction of wastewater used.

To measure the BOD of malting waste water, half a litter volume of AMF waste water sample was putted in a recipient sealed with manometer and in constant agitation in dark conditions. The manometer measures the decline of pressure inside the recipient caused by oxygen consumption. Once the volume is measured, and then it was introduced into the recipients. To ensure that we were fall within a valid range, three different volumes which were 100ml, 250ml and 500m were used for each sample and at point nitrification inhibitor were added and finally sodium hydroxide was added into plastic enclosure located within manometric cap and next the bottles were firmly closed to guarantee an airtight environment inside. Then manometric caps are calibrated to start measuring from afresh and once that done, all recipients containing samples were introduced in the magnetized tray which was already located inside incubator at 20^{o}C in dark conditions and after five days of samples in the incubator, measurements were taken from the manometric caps and using the above equation stated to measureBOD_5, AMF waste water Biological oxygen demand (BOD_5) was calculated.

3.2.3.3. Total Suspended Solid (TSS) Determination

In a laboratory, to measure total dissolved solids in waste water, the following materials were used sample, pre-weighed filter and aluminum dish, marker, vacuum flask, filtration apparatus such as reservoir or filter support, tweezers, pipette, DI water, oven, timer, desiccators, and analytical balance. After all the materials were got ready, the tray will be labeled with sample number and liquid at the 5 ml volume then the filter was placed on a reservoir and filter apparatus was closed immediately. Then the vacuum was turned on and the sample were agitated to ensure that it was mixed well and then using a pipette the sample was distributed evenly on filter and then reservoir was rinsed with DI water and the liquid was left to drain and then the vacuum was turned off and the filter was removed and transferred to a tray and moved on to a calibrated oven which means that itwas at the correct temperature which should be103 – 105^{0}C and waited for about an hour and after an hour the filter was removed using tweezers and placed in desiccators for about 30 minutes then the samples were weighed and the results were recorded, finally to calculate TSS in mg/L, equation below was used.

$$TSS\ (mg/L) = \frac{[\text{final weight (g)} - \text{original weight (g)}] \times 1{,}000{,}000}{\text{Sample volume (mL)}} \quad (3.2)$$

3.2.3.4. Chemical Oxygen Demand (COD) Determination

COD is an empiric laboratory assay which measures the amount of inorganic matter contained in a water sample, which means in other words, COD measures the amount of oxygen consumed for the oxidation of total organic matter. Thus, amount of COD is given by mg oxygen equivalent per liter as the following.

$$[COD] = mg\ O_2\ /L \quad (3.3)$$

COD is related to biochemical oxygen demand (BOD), which is another standard test for assaying the oxygen demanding strength of waste waters. However, whereas BOD is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions, COD does not differentiate biologically available and inert organic matter and it is a measure of total quantity of oxygen require oxidizing all organic material into carbon dioxide and water. In this way, the COD values of a water sample can be typically related to its BOD values in a more or less constant ratio. COD values are always greater than BOD values but, COD measurements can be made in a few hours while BOD measurements take at least five days. Since the COD test can be performed rapidly, it is often used as a rough approximation of the waters BOD, even though the COD test measures some additional organic matter which is normally not oxidize by biological action (Pipes and Zmuda, 1997).

Chemical oxygen demand (COD) is the amount of oxygen necessary to oxidize the organic carbon completely to CO_2, H_2O, and ammonia. Chemical oxygen demand is measured via oxidation with potassium dichromate ($K_2Cr_2O_7$) in the presence of sulfuric acid and silver and is expressed in mg/L. Thus, COD is a measure of the oxygen equivalent of the organic matter as well as microorganisms in the wastewater. If the COD value is much higher than the BOD value, then the sample can be explained as, it contains large amounts of organic compounds that are not easily biodegraded (Sawyer and McCarty, 1967).

In this research, COD of AMF waste water was measured using colorimetric method based on spectrophotometric determination which involved actions like, Strong oxidant ($K_2Cr_2O_7$) was added to the water sample after (H_2SO_4) was added to make the solution in acidic condition and silver (Ag) was used as a catalyst to prepare the solution . Then the sample was digested for 2 hrs at 150^oC, and its determination was done by using a spectrophotometer.

$$\text{Organic matter} + k_2Cr_2O_7 + H_2SO_4 + Ag \longrightarrow CO_2 + H2O + Cr^{3+}$$

First of all dry block heater was switched on in order to achieve 150^oC on time, while preparing the water samples for digestion. The water samples were blended and mixed before pouring any volume into digestion vessels so that suspended solids were not excluded from any aliquot. Three replicates for each sample were prepared in order to reduce error by eliminating outliers. Then 2.5 mL of water sample was poured into a digestion vessel after that, the reagents were incorporated into each digestion vessel. Since a very exothermic reaction was occurred it was done in the fume hood.

First of all, 1.5 mL of digestion solution ($k_2Cr_2O_7$) was introduced to each of digestion vessel then 3.5 mL of sulfuric acid was introduced and then each cap tube were closed tightly and mixed completely, then the tubes placed in the dry-block digester preheated at 150^oC and the timer was set for 2 hours. After that the tubes were removed from the dry-block digester and left cap tubes cool down. Once samples were cooled, colored vessels were observed which shows the darker orange color the greater the COD value and, therefore, the larger the amount of organic matter in the water sample. Before measuring the absorbance of each tube, reaction vessels were mixed completely and then the spectrophotometer was seated at a wavelength of 600 nm and then proceeded to measure the absorbance of each water sample and were noted down the absorbance value of each replicate.

3.3. Experiments and Design of Experiments (DOE)

The experimental data were analyzed using statistical software Design Expert software version 7.0.0.and "R" software for regression analysis and for the evaluation of the statistical significance of the equations developed. Design of experiments (DOE) is defined as a statistical technique or approach that is used for the design and the analysis of experiments. The use of DOE is required in designing experiments in order to draw valid and accurate conclusions about any set of experiments. In DOE, a series of tests are made where certain changes are imposed to the input factors, so that the causes of the main changes in the output or response are identified. DOE is a statistical tool used to explore new processes and gain understanding of the existing processes. This helps researchers to optimize such processes. DOE is all about following a particular pattern of experiments in order to generate a great deal of information about a certain process while using the absolute minimum of actual experiments or runs needed to get this information. In most research areas, the majority of experiments are designed by studying the effects of two or more inputs on the output or the response variable rather than the effect of the individual factors. A full factorial design study is about studying the effect of each of the selected factors on the desired response variable or output. For full factorial designs, three levels of each factor are studied. The use of factorial design is more advantageous than studying the effects of individual factors or the one-factor-at-a-time analysis approach (John Wiley and Sons, 2005). The experimental design selected for this study was response surface methodology, three-level-three-factor Box-Behnken Design (BHD) and the response variable measured was the percentage of conversion (Table 3.1).

Table 3.1: Table Independent variables and levels use in the BHD for coagulation process

Variable	Unit	LEVELS		
		-1	0	+1
pH	_	5	7	9
Dose	(mg/l)	50	500	1000
Chemical(“suphe” soil)	(g/l)	0.75	1.50	2.25

3.3.1. Jar Test

The purpose of the laboratory jar test is to select and quantify dose of treatment materials (chemicals) to a treatment program in removal of suspended solids, BOD, or COD from waste stream. Jar tests were conducted on six-place gang stirrer, which can be utilized to simulate mixing and settling conditions in a clarifier. Jars (beakers) with different treatment programs or the same product at different dosages was run side-by-side, and the results were compared to an untreated jar, or one treated with the current program (John Wiley and Sons, 2005).In this set-up, four samples with different doses of coagulant added were treated simultaneously or separately as required in the beaker of 1000ml capacity. 500 ml of the composite sample in each beaker was flocculated by individual stirrer rotated by a common driving shaft connected to a variable speed electric motor. The mixing and settling time was adjusted to find out the optimum turbidity removal for a specified coagulant dose by measuring it using turbidity meter. The coagulation, flocculation, sedimentation and filtration processes was done for both Alum (hydrated aluminum sulfate) and the soil coagulant as well as their respective pH and conductivity measures were recorded by pH and conductivity meter for the two coagulants respectively. The jar testing equipment was programmed using the ASTM International standard jar testing sequence of 120 revolutions per minute (RPM) for 1 minute (min), 50 RPM for 20 min and 15 min in settling cone, simulating a coagulation time of 1 min, a flocculation time of 20 min, and a settling time of 15, 30, and 45 min and for the two coagulant

Comparison at the desired pH value of (5, 7and 9) levels (ASTM, 2003). The other experimental run was varying the settling time to determine the best (most preferable) settling time and in this experimental run Batch sludge settling was performed following a similar method to that found in research conducted previously which means that Jar tests were dosed and conducted as described in the previous section. However, immediately following the flocculation sequence, water from each jar is carefully transferred into one-liter graduated cylinders which are inverted once, and allowed to settle. The inversion step is performed to re-suspend flock particles and minimize interference from transferring the water. The sludge interface height was recorded carefully over time and used to compare the settling time of the solids and settling velocities for each coagulant dose (15 min, 30 min, and 45 min) but, the constant time for mixing were 30 ins and mixing speed of 120 RPM.

Figure 3.1.Jar test set up to determine dosage of coagulants

4. RESULTS AND DISCUSSION

4.1. Wastewater Composition Analysis

4.1.1. PH

The average pH value was nearly neutral for the inlet water (6.67$\pm$0.12), first wet steep (5.17$\pm$0.21) and second wet steep (6.14$\pm$0.15) and finally become slightly acidic in the effluent (outlet) (5.29$\pm$0.25) as shown in (Table 4.1).

Table 4.1: pH value of Waste Water samples taken at different sites of production process.

samples	Treated in let water	First wet steep water	Second wet steep water	Effluent(composite)
Sample 1	6.8	4.8	6.3	5.00
Sample 2	6.6	5.8	5.5	5.30
Sample 3	6.5	4.9	6.6	5.98

4.1.2. Total Suspended Solid (TSS)

There was no average suspended solid in the first wet steep but, it reached the maximum level in the first wet steep (169.67$\pm$13.20) and still with larger value in the second (121.33$\pm$12.01) and effluent (outlet) (139.67$\pm$27.15) as shown in (Table 4.2).

Table 4.2: profile showing TSS content of AMF samples at different sites of the production process.

TSS	Treated in let water	First wet steep	Second wet steep	Composite effluent (out let)
Sample 1	-	158	122	143
Sample 2	-	167	109	165
Sample 3	-	184	133	111

4.1.3. Chemical Oxygen Demand (COD)and Biological Oxygen Demand (BOD)

In addition to TSS and pH, the laboratory result shows that, the inlet water was found to have small amount of chemical oxygen demand (74±7.12) and extremely less biological oxygen demand (4.85±0.34). Maximum values for COD and BOD were recorded in the first and second wet steep with a mean value of (2617±9.96) and (3251±5.34)for COD; as shown in (Table 4.3) and (886.97±4.94) and (1107.77±8.61) for BOD (Table 4.4)respectively and finally, the amount of COD and BOD for the effluent (outlet) was (1190.75±7.99) and (397.42±1.29), respectively.

Table 4.3: COD value of AMF samples taken at different sites of production process

COD in mg/l	Treated in let water	First wet steep	Second wet steep	Effluent (composite)
Sample 1	66	1410	1496	605
Sample 2	80	2720	6692	2202
Sample 3	70	2502	2582	502
Sample 4	80	3842	1942	1462

Table 4.4: BOD value of samples taken at different stages of production process

BOD in mg/l	Treated inlet water	First wet steep	Second wet steep	Effluent
Sample 1	4.4	507	774.5	362
Sample 2	5.2	1222	1302.5	538.67
Sample 3	4.8	1512	2197	438
Sample 4	5	315	165	257

4.1.4. Analysis of Chemical Compositions for Malting Wastewater

Laboratory analysis was done to know the amount of chemical compositions in waste water and treated inlet water of AMF and the results were listed as follows.

4.1.4.1. Nitrogen (N)

High proportion of average total nitrogen (28$\pm$4) was observed in the first wet steep, (12.67$\pm$7.77) in the second, (11.07$\pm$2.10) in the effluent (outlet) and almost absent in the inlet water.

4.1.4.2. Ammonia Nitrogen (NH_3-N)

The average NH_3-N has reached its highest value in the first wet steep (7.24 $\pm$3.48), medium in the second wet steep (4.6 $\pm$0.96) and minimum in the effluent (outlet) and inlet with (2.53 $\pm$1.82) (0.427 $\pm$0.34) values, respectively.

4.1.4.3. Phosphate Ion (PO_4^{3-})

The result showed that the wastewater originated from first wet steep was found to have an average PO_4^{3-} value of (55.92 $\pm$ 21.57) which was the maximum of the phosphorus source. However, it became reduced in the second wet steep and effluent (outlet) with a value of (13.54 $\pm$ 1.63) and (2.74 $\pm$0.78), respectively.

4.1.4.4. Sulphate Ion (SO_4^{2-})

Unlike the Ions listed above, the average amount of sulphate was found to be high in the inlet water (219mg/l $\pm$ 5.8) and persist there at different stages of the production process with (126.25$\pm$ 8.75) (445.75$\pm$ 2.66) (38.25$\pm$5.75) values for first wet steep, second wet steep and effluent (outlet) respectively.

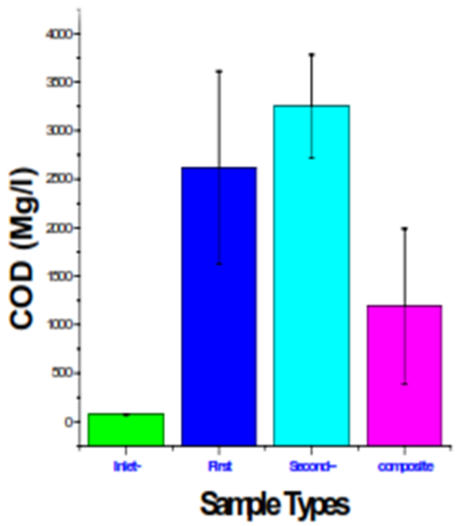
4.1.4.5 Sulphide (S^{2-})

The sulphide content was less in different stages of the production process with (0.04 $\pm$ 0.02), (0.70$\pm$ 0.17), (0.46$\pm$ 0.04), (0.2 $\pm$ 0.11) for inlet water, firstand second wet steep and effluent (outlet), respectively.

Table 4.5: Mean characteristics of the effluent wastewaters for the various wastewater streams.

Parameters	Wastewater Streams			
	In let water	First wet steep	Second wet steep	Effluent(outlet)
pH	6.67±0.12	5.17 ±0.21	6.14 ±0.15	5.29 ± 0.25
COD	74 ± 7.12	2617 ±9.96	3251 ± 5.34	1190.75±7.99
BOD	4.85 ± 0.34	886.97±4.94	1107.77± 8.62	397.42 ±1.29
Total N	0.59 ± 0.46	28 ±4.00	12.67 ±7.77	11.07 ± 2.10
NH_3-N	0.427 ±0.34	7.24 ±3.48	4.6 ± 0.96	2.53 ±1.82
PO_4^{3-}	0.43 ± 0.20	55.92 ± 21.57	13.54 ± 1.63	2.74 ± 0.78
NO_3^- -N	23.5 ± 3.11	125 ± 11	24.5 ± 4.51	12.5 ± 2.89
SO_4^{2-}	219 ± 5.80	126.25± 8.75	445.75 ± 2.66	38.25 ± 5.75
S^{2-}	0.04 ± 0.02	0.70 ± 0.17	0.46 ± 0.04	0.2 ± 0.11
TSS	–	169.67 ±1.32	121.33 +12.01	139.67 ± 27.15

The graphical representation for COD, BOD, PO_4^{3-}, NH_3-N, NO_3^--N, SO_4^{2-}, S^{2-}, TSS and pH composition and values of the various wastewater streams from AMF are shown in Figures 3-9.



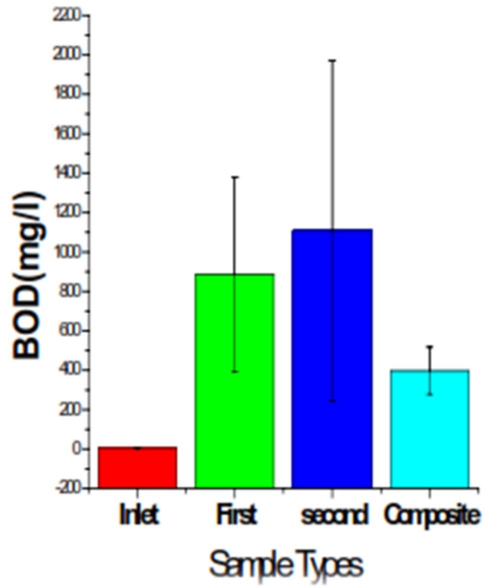


Fig: 4.1 Average COD and deviation of samples taken at Different Stages of production process

Fig: 4.2 Average BOD and deviation of samples taken at different stages

The result obtained from different source (wastewater stream) revealed the existence of huge variation within the samples taken at same periods. For instance, deviation from their respective mean values as 2617 $\pm$ 9.96, 3251 $\pm$ 5.34 and 1190.75$\pm$7.99 for COD values; and 886.97$\pm$ 4.94, 1107.77$\pm$ 8.61, 397.42 $\pm$ 1.29 for BOD of first wet steep, second wet steep, and effluent (outlet), respectively, were observed. For COD and BOD values equitable results were observed in first and second wet steeps with COD value of 2617, 3251 and BOD of 886.97, 1107.77 while the wastewater from effluent (outlet) was comparably lower having a COD value of 1190.75, and BOD of 397.42.

The values for sulphide and ammonia-nitrogen were very less which are recorded as 0.2 $\pm$ 0.11and 2.53 $\pm$1.82 in the effluent (outlet), respectively. This is expressed graphically in figure 7and 9 where the bars for this waste stream got highly reduced when compared with other two which are first and second wet steep.The result in Table A-11 of the appendix section indicate that, the COD: BOD ratio for various waste stream range between 2-3 for the first wet steep, second wet steep and effluent (outlet) waste streams, respectively, and are expressed graphically in Figures 7and 8.

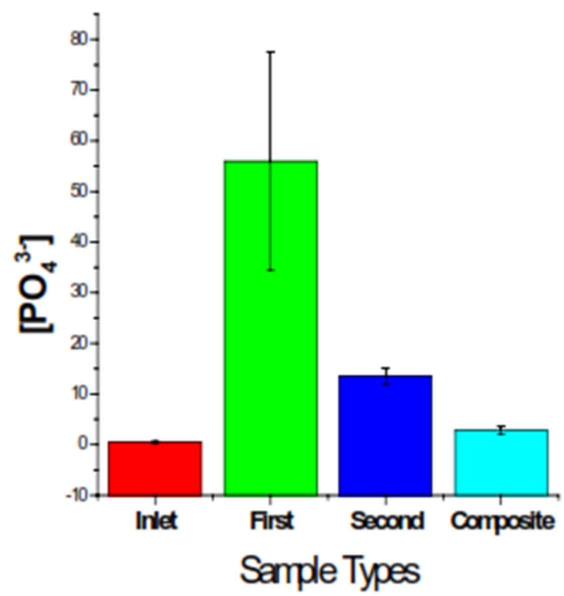


Fig 4.3 Avarege PO_4^{3-} and deviation of samples taken fromdifferent sites

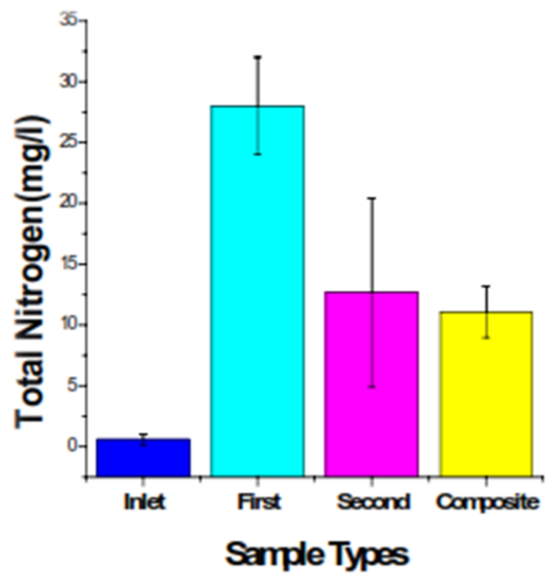
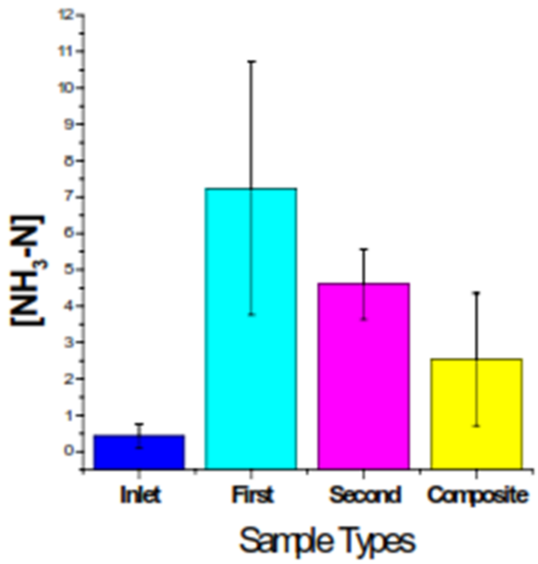


Fig 4.4 Avarege TN and deviation of samples taken from different sites



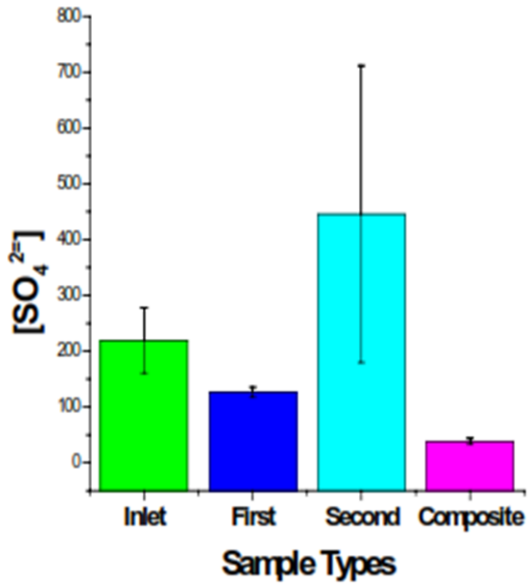
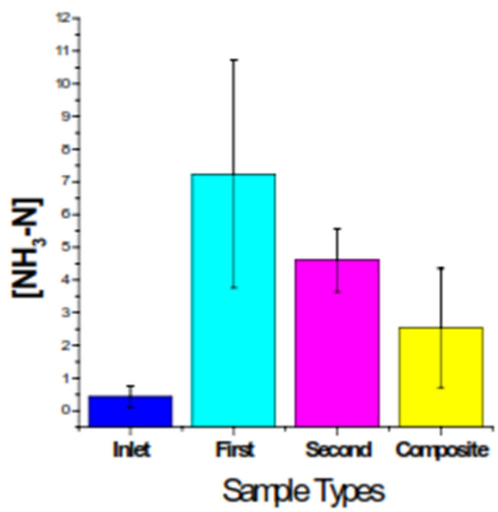


Fig 4.5: Deviation and average “NH_3-N” of Fig 4.6: Deviation and average “SO_4^{2-}” of

Samples taken at different sitessamples taken at different sites



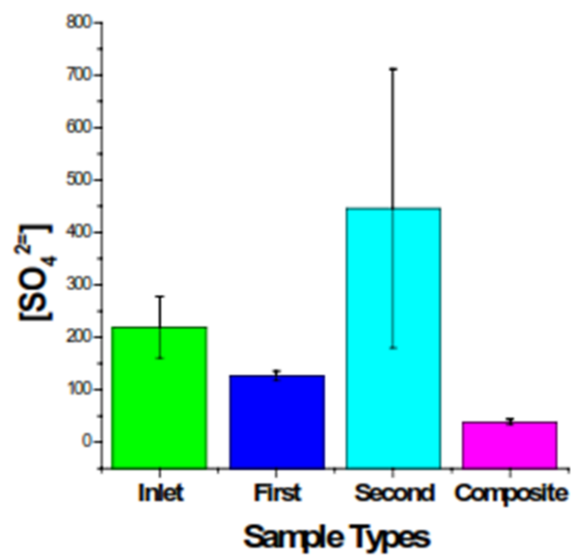


Fig4.7: Average “S^{2}”$^{-}$and deviation of

Samples taken at different sites

Fig4.8: Average “NO_3-N” and deviation of

samples taken at different sites

4.2. Characteristic Analysis of “Suphe” Soil

In addition to Assela Malt Factory waste water quality parameters, grain and silicate analyses of soil were examined in this research and have compared the “Suphe” soil coagulant with popular chemical coagulant which is alum. Though the test results of the raw soil gradation show 6% clay soil, the crushed, sieved and prepared soil for treatment is clay soil as confirmed by texture test (Table 4.6). A chemical analysis of coagulant was performed using a complete silicate analysis method by Geo-Chemical Laboratory (GCL) which is found in Addis Ababa, Ethiopia and the result is shown in the following table .The major chemical constituents in the sample soil are Silicon oxide, calcium oxide, aluminum oxide and iron oxide, by weight and the loss on ignition (LOI) was found to be 20% by weight.

Table 4.6: “Suphe” soil coagulant silicate analysis

Chemical constituents	Percent (wt. %)
MnO	< 0.01
K_2O	< 0.01
Na_2O	0.40
H_2O	0.45
TiO_2	1.07
MgO	2.28
Fe_2O_3	4.66
Al_2O_3	9.98
CaO	23.94
SiO_2	38.92
LOI	19.99

4.3. Turbidity Removal Analysis of "Suphe" Soil

Turbidity removal potential of the "Suphe" soil was tested in the laboratory using jar tester. Primarily the process noticed of turbidity removal efficiency by considering the three treatment parameters which are initial pH of waste water, dose of coagulant, and settling time. The data obtained from over 81 jar tests for each coagulants ("Suphe" soil and Alum) conducted throughout the study have been provided in Appendix (B). The statically tests has portrayed that settling time after 15 min of sedimentation for the treated water after flocculation is not by itself significance (p-value =0.26) to the process of turbidity removal of AMF wastewater as showed in appendix . As result settling time is omitted from interpretation and comparison due its insignificancy. The results were selected to be represented by a box plot shown in Figures below through Figure (4.1 up to 4.16). The laboratory results have been presented in this chapter using graphical representations and it is was found proper if they are presented by a box plot. So that Box plots were developed to depict the percent removals of turbidity, the results of pH and EC of treated wastewater up on the application of the coagulants. The star shown on those box plots of graphical expression was set to display the mean turbidity removal performance and the dark bold line stands for the median. The Figures Through 4.1 - 4.4 attempts to show the turbidity removal efficiency along with different initial pH points and dose levels of soil coagulant. The pH points during the jar testswere 5.17, 6.14 and 5.29 labeled pH_1, $pH_3$and pH_2 respectively on the box plot in order to represent the different samples taken from streams of process operation sites of malting wastewater and which are treated by the "Suphe" soil. On the other hand dose levels are 50 mg/l, 200 mg/l, 500mg/l and 1000 mg/l labeled D_1, D_2, D_3 and D_4 respectively. pH and dose denotation remain the same to the entire document.

4.3.1. Effects of Jar Test Parameters on Turbidity Removal

Turbidity removal based on coagulation can be affected due to number of factors as tried to mention in table 2.1. Different coagulants chose specific pH conditions while others are effective in extensive ranges of pH levels for the process of coagulation. The figure below shows the turbidity removal efficiency of the soil coagulant considering pH levels of 5, 7 and 9.

Turbidity removal at 5pH was 95.3 %, 98.5 at 7pH 97.2% at 9 pH. As shown in figure 4.1 at pH 7 (pH_2) and (pH_3) the “Suphe” soil performed better turbidity removal from the malting waste water in which this result can extend if pH adjustment is combined with dose adjustments and this result of removal might show extended variance among pH levels, if initial turbidity of the wastewater was smaller than the one used for this study. So bearing in mind that higher initial turbidity for all pH levels of turbidity removal using soil coagulant has showed significance turbidity removal efficiency. According to Mohammed et al., 2013, highly acidic coagulants may drive the pH down and consequently decrease the efficiency of the coagulation as the solution became more acidic. However, “Suphe” soil coagulants work efficiently in wide range of pH which is from3 to 10with different treatment efficiency and therefore can be used for wastewater treatment without adjusting the pH of waste water. So we could use this “Suphe” soil coagulant in wide range of pH (3-10). Even though it would be more efficient to use the “Suphe” soil coagulant at around pH range of 5.29and 6.13, otherwise may need pH adjustments on the malting waste water if it is beyond this range.

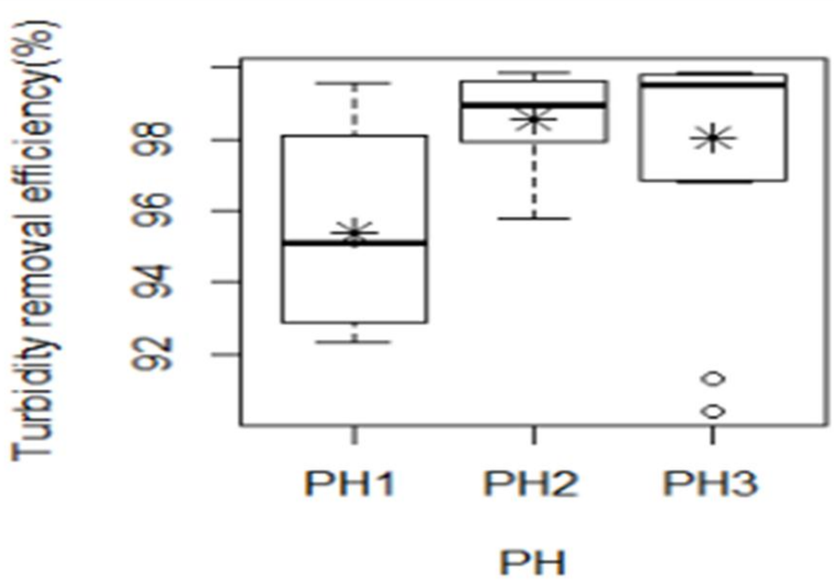


Figure 4.9.Turbidity removal efficiency of “Suphe” soil at different pH,

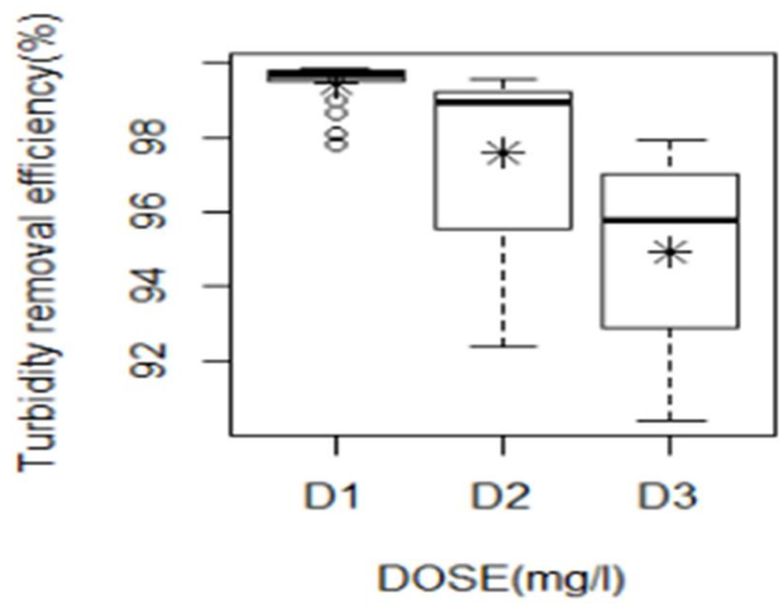


Figure4.10. Turbidity removal efficiency of “Suphe” soil at different dose level

The above two figures shows the turbidity removal efficiency of “Suphe” soil coagulant at different dose levels; where D_1, D_2 and D_3 stands for 50 mg/l, 500mg/l and 1000 mg/l respectively(Table 4.7). Removal efficiency of “Suphe” soil coagulant at 50 mg/l was 99.43%, 97.57% at 500 mg/l and 93.92% mg/l at 1000 mg/l of dose levels.

Table 4.7: Turbidity removal efficiency of “Suphe” soil coagulant at different doses.

Dose (mg/l)	Turbidity removal efficiency (%)
50	99.43
500	97.57
1000	93.92

Amount of coagulant added to wastewater affect highly the coagulation activity of turbidity removal efficiency. According to the experiment done, increasing the dose could not necessarily increase the turbidity removal efficiency of the "Suphe" soil coagulant, instead it increases soil coagulant resulted in turbidity removal decrement with an extended range of difference while going from lower dose level to higher this can give a generalization of selecting appropriate amount of dose for treatment purpose is curtail which was found to be 50 mg/L for the "Suphe" soil coagulant case for the malting waste water of AMF.

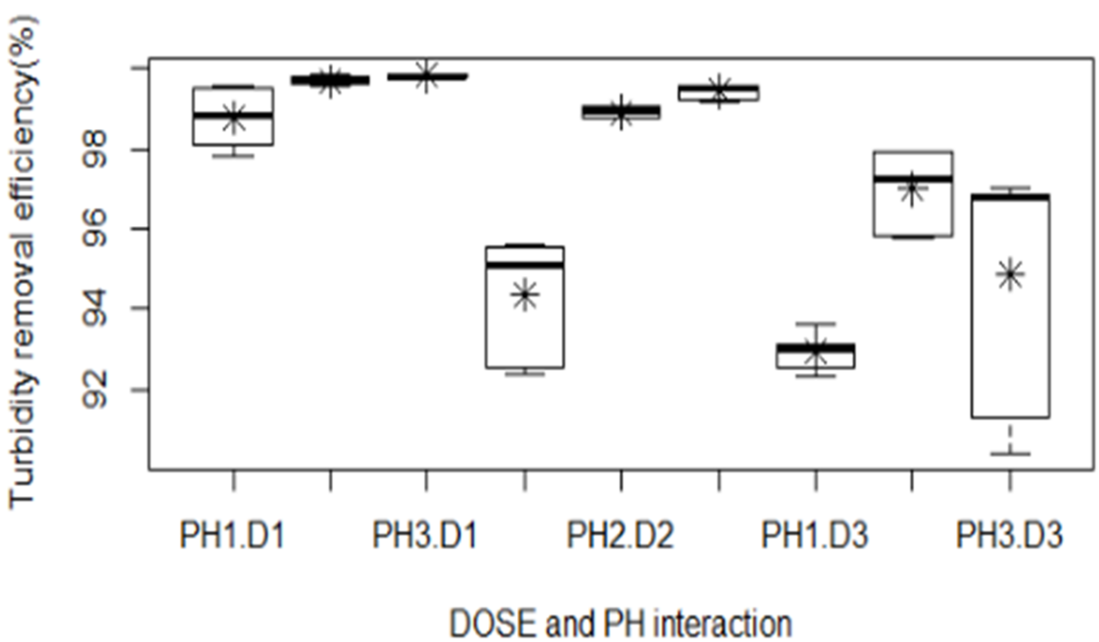


Figure 4.11.The combined effect of pH and Dose of "Suphe" soil turbidity removal efficiency

Combination of the two factors, which are DOSE and pH have great impact on the removal efficiency was analyzed. So as it is shown in the figure 4.3 above. By the treatment that combines minimum dose of 50 mg/l with pH levels of 5.17, 5.29 and 6.14(D_1:pH_1, D_1:pH_2, D_1:pH_3) the turbidity removal efficiency of the "Suphe" soil coagulant was 98.76%, 99% and 99.83% respectively. Similarly for medium dose of 500 mg/l of those PH combinations (D_2:pH_1, D_2:pH_2, D_2:pH_3) removal efficiency was 94.36%, 96.91% and 99.43 and for maximum dose which was 100mg/l, the analogs combination (D_3:pH_1, D_3:pH_2, D_3:pH_3) turbidity removal was 92.92%, 95.9% and 96.86% respectively. As it shows on the figure and result taken, turbidity removal has decreased with increasing dose and decreasing pH. However it has known from the statistical tastings and the figure above that dose has more significant impact than pH. If it is considered in the plot though it is said decrease in removal with decreasing pH for generality, the dose has up lifted the removal efficiency with its decreasing out performance and yet the pH is not capable to have the comparable impact in its increasing. Nonetheless the removal efficiency of the “Suphe”soil coagulant is still better at around pH level of 5, if the dose was 50 mg/l only. Therefore, from the experiment it is possible to conclude that the soil has optimum coagulation effect when it is coagulated dominantly with 50 mg/l, which is the lower dose and higher pHs which are 5.29 and 6.14 conditions.

From the best performing pH circumstances pH 6.14 has lower margin of giving efficient turbidity removal. And the turbidity removal resulted minimum at conditions where Dose is higher and pH is lower (i.e. 1000 mg/l and 5 pH). Therefore even if the soil executed well in those all conditions of the experiment, it is better to use 50 mg /l “Suphe” soil coagulant from Honkolo Wabeworeda around at pH of 5 -7for AMF waste water condition to have promising turbidity removal efficiency.

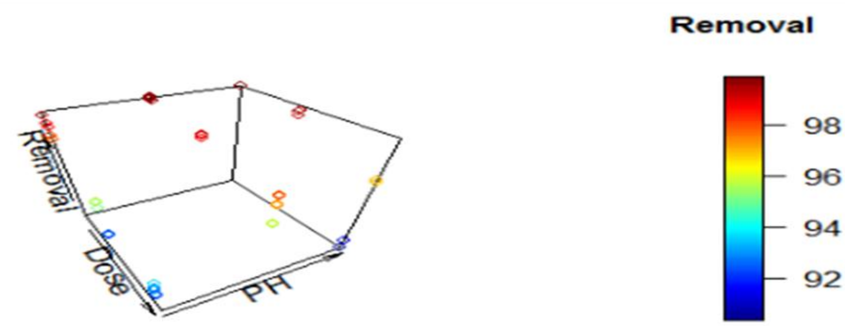


Figure 4.12 show of combined effect of Dose and pH

Figure 4:12above clearly shows circumstances of turbidity removal efficiency alongside dose and pH and it represents the more efficient with darkened red and the minimums with darkened blue from the spectrum of colors. In most the conditions 50 mg/l has good performance particularly with higher pHs. The removal efficiency goes down when dose level is increasing and pH is decreasing.

Generally, it is preferable to select the combination of the minimum dose with higher pH for effective turbidity removal processes. In addition from the laboratory experiment and statistical analysis, for this study it is found that the "Suphe" soil coagulant has turbidity removal efficiency of 97.31% which has extended up to 99.86 to the maximum and 90.39 to the minimum for AMF waste water.

4.4. Untreated Effluent Comparison

Effluent characterization of AMF indicates that, the effluent discharged did not meet the requirements for discharge of such effluents as stated in effluent discharge standard (Tables 4.8 and 4.9).When the wastewater composition of AMF is compared with standard for brewery and malt industries waste effluent discharge, the values are found to be beyond the standard.

Table 4.8: Comparison of AMF Effluent with malting Effluent Discharge limits (Source: World Bank,1997)

Parameters	Maximum value (standard)	AMF effluent
pH	6-9	5.67 - 6.6
COD	250	1191 ± 800 - 3251 ± 530.5
BOD	50	397 ± 119 - 1108 ± 861
TSS	50	121 ± 12 – 170 ±13
Ammonia-Nitrogen	10	2.7 ± 0.9 - 55.9 ± 21.6
Phosphorus	5	2.7 ± 0.9 - 55.9 ± 21.6

Table-9: Indicative discharge standards in the EU (Source: Drissen, *et al*., 2003)

Parameters	Maximum limits (mg/L)
COD	125
BOD5	25
TSS	35
N (Nitrogen)	10-15
P (phosphorus)	1-2

Setting standards or guidelines should be considered local conditions and the socioeconomic level of a particular situation and based on this basis; the quoted standards of developed countries (like USA, Belgium etc) should be applied with caution in the absence of Ethiopia specific standards.Based on this idea, indicative discharge limits are generally applied in the EU council directive and other relevant discharge standards for receiving surface water bodies could be taken for comparison purpose (EPA, 2000).

4.5. “Suphe” Soil Treatment Efficiency Comparison with Alum

4.5.1. COD and BOD Removal Efficiency

Results on overall efficiency had COD and BOD removal performance at pH of 7 and coagulant dose of 50 mg/l of 94.3% and 94.4 % for the first wet steep, 97.7%and 97.1% for the second wet steep and 96.3% and 96.1% for the third composite effluent respectively and at the same pH and dose as that of “Suphe” soil was used, the removal potential for Alum is 91.6% and 92.3% for first wet steep,95.0% and 94.8% for second wet steep and 95.4% and 96.0 for the treated composite effluent and This increased in efficiency might be attributed to familiarization of the “Suphe” soil coagulant to effectively act on the wastewater constituents as it has been used for tannery waste water treatment process.

4.5.2. Comparison for Turbidity Removal Efficiency of "Suphe" Soil with Alum

4.5.2.1. Dose Comparison

Dose consumption is crucial method for selecting appropriate coagulant amounts which would be feasible in the field of wastewater treatment. Removal efficiency of "Suphe" soil at a constant pH of 7 was 50 mg/l was 99.43%, 97.57%at 500 mg/l and 94.92%mg/l at 1000 mg/l of dose levels. On the other hand at the same pH level in which "Suphe" soil was used, alum turbidity removal efficiency was 99.2%, 96.6%and 99.4% for dose1 (D_1), dose2 (D_2), and dose3 (D_3) respectively.

As shown in the figure below, the turbidity removal for "Suphe" soil coagulant from HonkoloWabe is adequately comparable even better at D1 and D2 dose levels with alum coagulant. The coagulation activity was very good while feeding the turbidity removal process with the lower dose of 50 mg/l. The higher dose levels of 500 mg/l and 1000 mg/l has lowest performance.

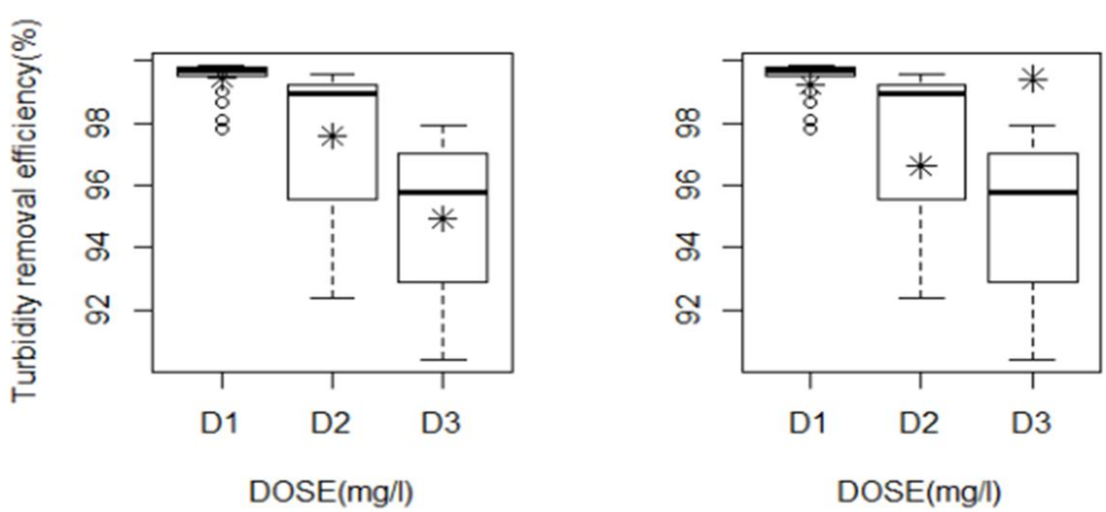


Figure 4.13Turbidity removal efficiency comparison of alum (A) and "Suphe" soil (B) at different dose levels respectively

4.5.2.2. pH Comparison

The pH of water affects the solubility of many toxic and nutritive chemicals, and it determines favorability of aquatic environment. Turbidity removal of “Suphe” soil for waster at pH of 5 was 95.35%, 98.54% at pH of 7 and 98.04%at pH of 9. On the other hand alum coagulant removal efficiency is 96.24 for waste water at PH of 5, 99.55%at pH 7 and 99.44% at pH 9. Like that of dose, both coagulants effective pH level was similar for the “Suphe” soil and Alum.

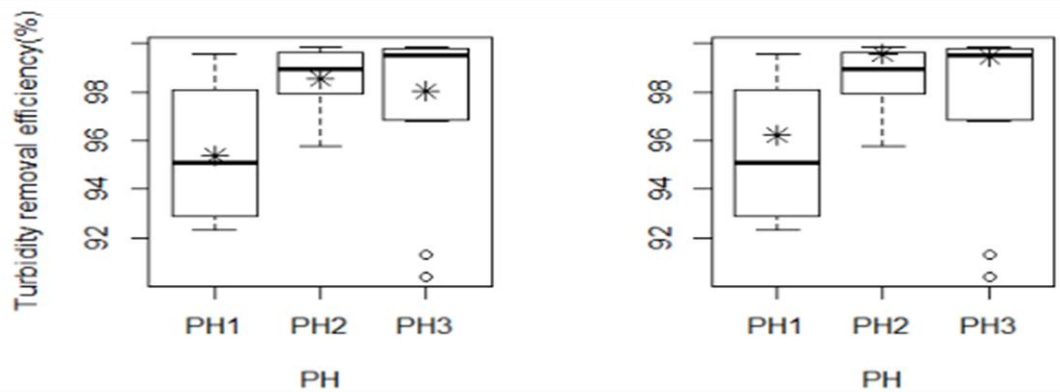


Figure 4.14 Alum (A) and “Suphe” Soil (B) turbidity removal efficiency with different pH levels

As it is shown in the Figure 4.15 below, it combines minimum dose of 50 mg/l of alum with pH levels of 5, 7 and 9 (D_1pH_1, D_1pH_2, D_1pH_3) the turbidity removal efficiency of the alum coagulant was 98.11%, 99.77 % and 99 .72% respectively similarly for medium dose of 500 mg/l of those combinations (D_2pH_1, D_2pH_2, D_2pH_3) removal efficiency is 91.26%, 99.55% and 98.99% and for maximum dose of 1000mg/l the analogs combination (D_3pH_1, D_3pH_2, D_3pH_3) turbidity removal is 98.94%, 99.32% and 99.60% respectively.

For “Suphe” soil by the treatment that combines minimum dose of 50 mg/l with pH levels of 5, 7 and 9(D_1pH_1, D_1pH_2, D_1pH_3) the turbidity removal efficiency of the soil coagulant for 50 Mg/l was 98.76%, 99.7 % and 99.83% respectively similarly for medium dose of 500 mg/l of those combinations (D_2pH_1, D_2pH_2, D_2pH_3) removal efficiency was 94.36%, 98.91% and 99.43 and for maximum dose 100mg/l the analogs combination (D_3pH_1, D_3pH_2, D_3pH_3) turbidity removal was 92.92%, 96.99% and 94.86% respectively.

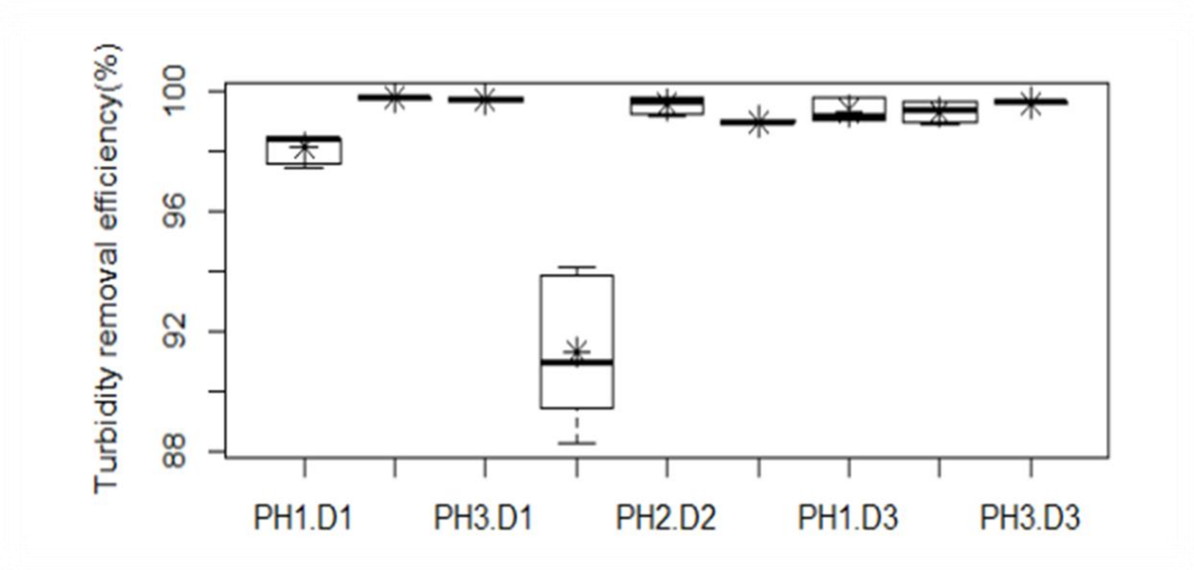


Figure 4.15 The combined effect of PH and Dose on Alum turbidity removal efficiency

As shown on the box plot, the combination of the two factors has better performance on those combinations of initial pH conditions of waste solution paired with 50 mg/l dose of soil coagulant. On the contrary each dose levels including the smaller D_1 (50 mg/l) is decreasing in Removal efficiency while going from smaller pH (5) to higher. Moreover the larger pH circumstances (7 and 9) have performed well for both alum and soil. On both cases of coagulants D_1 has pH tolerating performance consistency is showed in the pH conditions whereas D_2 especially D_3 has larger variation of turbidity removal efficiency.

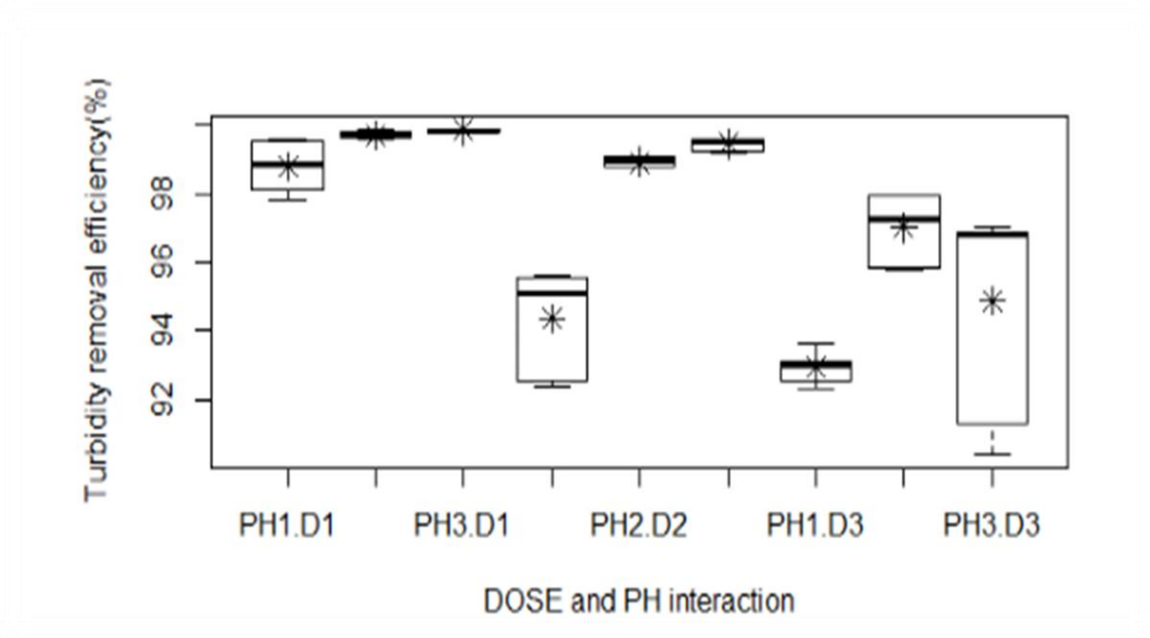


Figure 4.16The combined effect of pH and Dose on “Suphe” soil turbidity removal efficiency

4.5.2.3. Resultant pH

The resulting pH of the treated waste water may find pH adjustment if the used coagulants cause extreme acidity and alkalinity to the effluent waste water in order to release nearly neutral, pH conditioned effluent. As shown on Figure 4.16 the amount of pH change up on application of coagulants from initial pH levels of 5, 7 and 9 was (-0.99), (+0.79),`(-0.67) for “Suphe”soil and on the other hand (-0.81), (-2.37) and (-2.62) for alum respectively. The negative signs on the values of pH change are meant to say decrease in pH while plus is increase. The mean pH after using “Suphe” soil coagulant was 6.07 and it was 5.12for alum.

Alum coagulant changed the pH of the waste water 1.87 to the negative which means that it is acidic condition caused by consuming alkalinity. On the other hand “Suphe” soil changed the pH with 0.77, which it shows it is 0.53 to negative and particularly for pH 7 it changed the pH 0.24 to the positive which clearly shows it is basic. Therefore using “Suphe” soil coagulants resulted relative calm to the pH of the treated wastewater to the initial pH value than alum does. From the ”Suphe” soil of pH 7 and 9 conditions showed better stability and finally, figures through 4.16-4.19 of below tried to show the pH consequence of the coagulants on treated waste water.

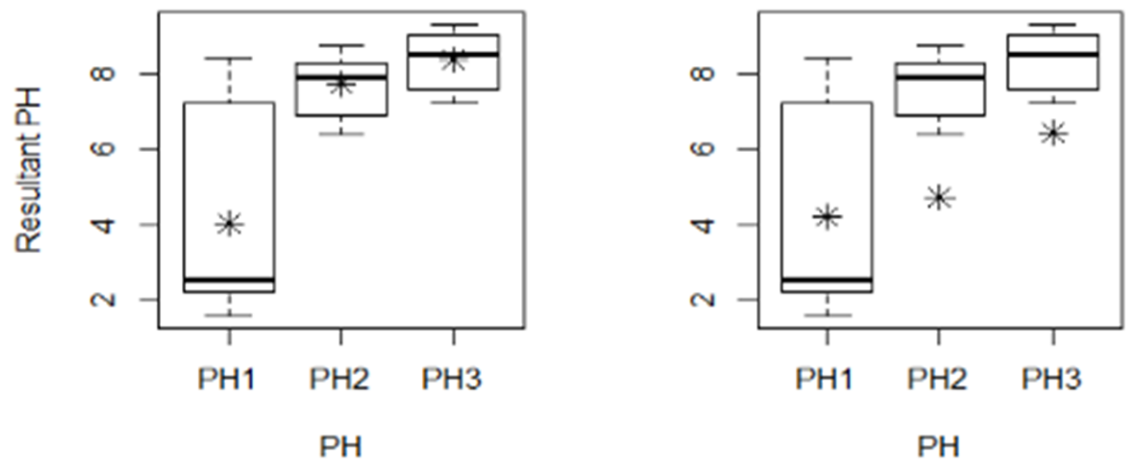


Figure4.17. Alum (B) and “Suphe” soil (A) resultant pH with different initial pH levels

Figure 4.18 below shows the pH change up on application of coagulants with different dose levels of 50mg/l, 500 mg/l and 1000 mg/l was 8.6,6.6 and 5.7 for “Suphe” soil coagulant and 8.04, 4.31 and 3.01 for alum coagulant respectively. As the result clearly shows it is known that decreasing application of dose end with increasing in the resulting pH. So adding more coagulant per volume of malting waste water may result acidic discharge. However as mentioned earlier in this chapter, the minimum dose that is 50 mg/l has performed better, therefore need to adding more coagulant is basically nothing. Both of the coagulants reduced the pH, even though, the alum coagulant relatively pulls the pH towards acidic state than the “Suphe” soil and also “Suphe” soil coagulant has closer pH resultant than alum to the neutral pH condition.

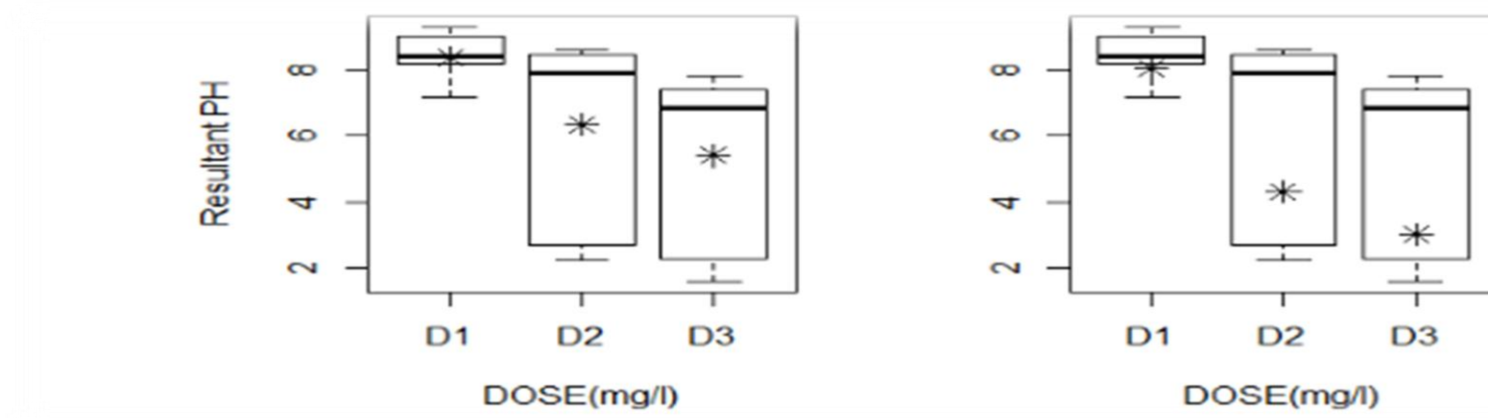


Figure 4.18.pH of Alum (A) and “Suphe” soil resultant (B) with different dose levels

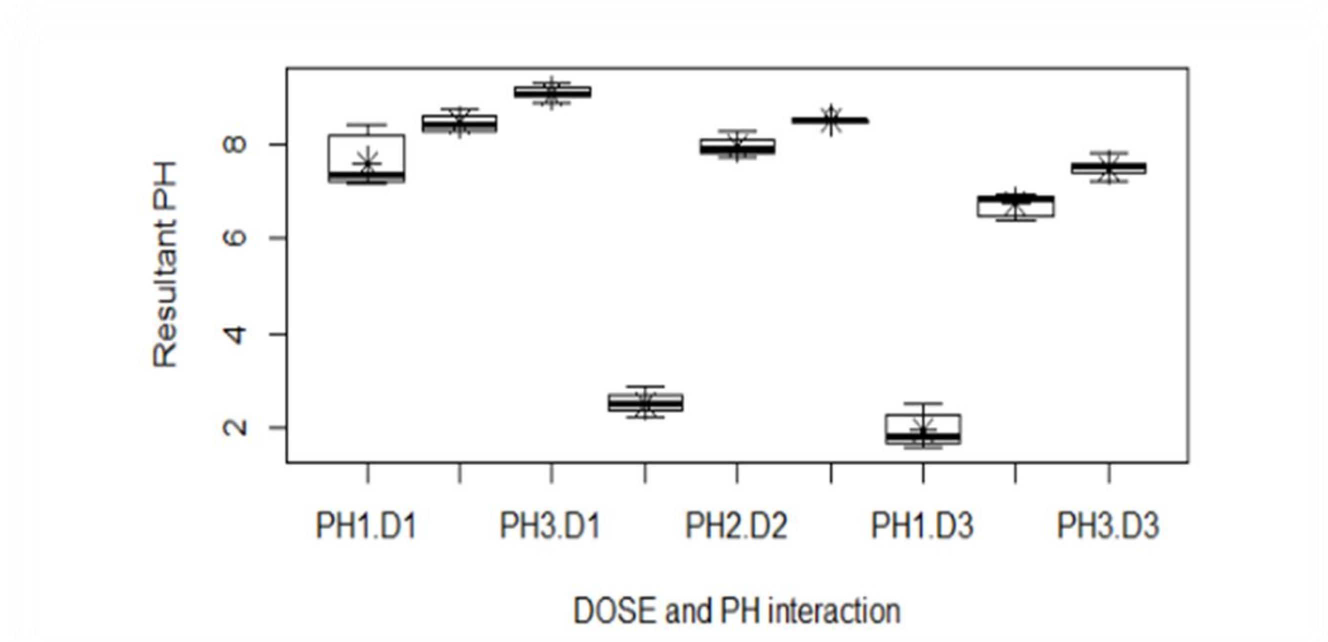


Figure 4.19. The combined effect of pH and Dose on “Suphe” soil resultant pH

For the “Suphe”soil coagulant, the treatment that combines minimum pH of 5 with dose levels of 50 mg/l, 500 mg/l and 1000 mg/l (D_1:pH_1, D_2:pH_1, D_3:pH_1) the resultant pH of the treated waste water is 7.72, 8.65 and 9.38 respectively. Similarly for medium dose of 500 mg/l of those combinations (D_2:pH_1, D_2:pH_2, D_2:pH_3) resultant pH is 2.74, 7.99 and 8.65. Finally for maximum dose 100mg/l the analogs combination (D_3:pH_1, D_3:pH_2, D_3:pH_3) resultant pH is 2.05, 6.57 and 7.92 respectively. On the other hand the resultant pH changes from the initial pH of malting waste water.

So as it is shown in last figure of 4.20 that combines minimum dose of 50 mg/l of alum with pH levels of 5, 7 and 9(D_1:pH_1, D_1:pH_2, D_1:pH_3), the resultant pH of the alum coagulant treated malting waste water was 6.57, 8.80 and 9.39 respectively. Similarly for medium dose of 500 mg/l of those combinations (D_2:pH_1, D_2:pH_2, D_2:pH_3) the resultant pH is 2.65, 2.00 and 7.14 and for maximum dose of 1000mg/l the analogs combination (D_3:pH_1, D_3:pH_2, D_3:pH_3) resultant pH is 4.42, 2.16 and 2.77 respectively.

The resultant pH of alum treated malting waste water was altered 1.54 towards the basic when using 50 mg/l (D_1), 2.98 to the acidic when using 500 mg/l (D_2) and 4.09 when using 1000 mg/l(D_3) of alum coagulant. On the contrary resultant pH of “Suphe” soil treated malting waste water was altered 1.42 towards the basic when using 50 mg/l (D_1), the initial pH changes 1.13 which was 1.09 to the acidic and 0.32 to the basic when using 500 mg/l (D_2) and 1.60 to acidic state when using 1000 mg/l (D_3). The minimum change on pH was noticed at D_1 combination with pH_3 which was dose 50mg/l and pH 9 which had a magnitude of 0.09 for alum and 0.08 for “Suphe” soil. In both cases of coagulants, the pH resultant change is greater tending towards acidic when using bigger quantities of coagulants which extend up to 6.63at D_3:pH_3 and 3.04 at D_3:pH_1 for alum and “Suphe” soil respectively.

Generally the mean value of resultant pH using “Suphe” soil coagulant was 6.707 and 5.124 using alum coagulant. Moreover the “Suphe” soil impacts a pH change of 1.42 and 2.6 pH change from the initial malting waste water for alum, dominantly to the acidic condition in the case of alum. This clearly shows alum coagulant needs more pH adjustment before discharge to the nearby river by using adjustment chemicals like lime or calcium carbonate which cause additional cost.

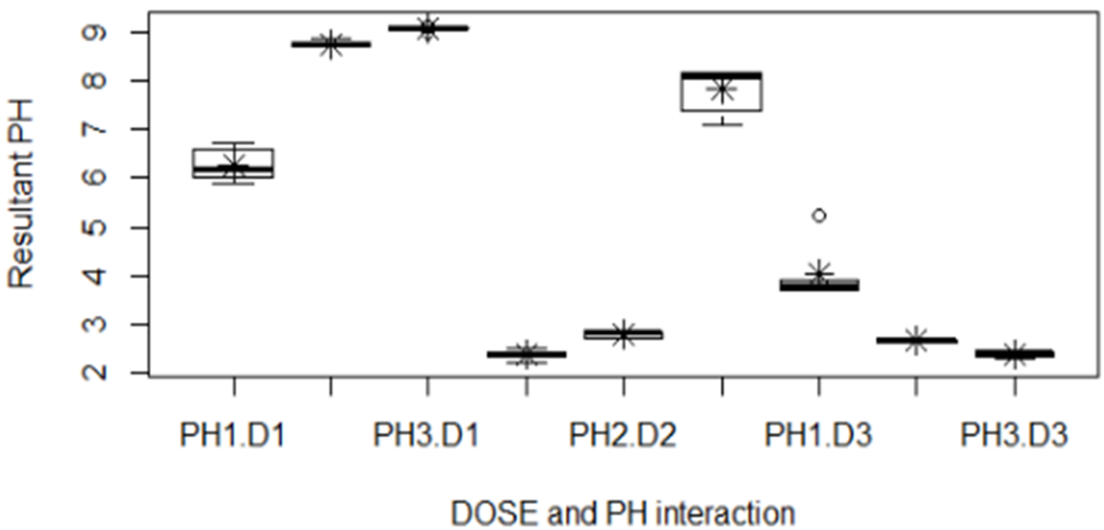


Figure 4.20.The combined effect of pH and Dose on Alum resultant pH

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

To investigate the coagulation potential of “Suphe” soil and compare it with the widely used Alum coagulant, a coagulation experiment was done for both Alum and “Suphe” Soil coagulant using a jar test. Wastewater treatment factors influencing the process of coagulation majorly were determined to be type of the coagulant, pH condition of the solution and settling time of wastewater after gentle mixing. There is a significant variation in composition of effluents released from individual process steps in terms of organic matter (COD and BOD), nitrogen, phosphorus, sulphide and sulphate composition. This could be for the reason that, the wastewater generated at different steps of the production process such as first wet steep, second wet steep, spray water of germination box released at different times separately with no continuous flow. The amount of phosphate released during the first wet steep was high as it released from washing and cleaning of grains. The functional treated raw water used for various purposes contain reasonable amount of sulphate.

Suspended solid contains huge amount of spent grains and remains of deculming (roots and shoots grown during germination). Turbidity of the raw waste water discharge, as it was possible to now from the characterization experiment was high. This high turbidity result might have presented inflated removal result. Nevertheless almost all of the turbidity removal readings of Alum and “Suphe”Soil coagulant are far more efficient than the zero (blank) wastewater treatment mean turbidity reading. Beside to this the soil coagulant material has performed better when pH condition is relatively neutral and minimum dose levels. Alum coagulant also performed better on those conditions of pH and dose levels, Nevertheless the impact of dose was higher, even on the lower pH minimum dose levels scored good turbidity removal efficient. Relatively to Alum coagulant the “Suphe”soil coagulant doesn’t as such change the initial wastewater pH. Instead Alum altered the initial pH of the waste water towards lower pH which causes more acidity of water and this shows treating the waste water using “Suphe” soil coagulant may not need pH adjustment chemicals after malt industry waste water treatment that could have increased the expense of the treatment process.

This study has found the “Suphe”soil coagulant has comparable potential even improved in some circumstance with Alum coagulant in its efficiency of total suspended solid removal from malt industry wastewater.

The “Suphe”soil coagulant has increasing and decreasing patterns with the treatments of selected influencing conditions of dose and pH levels nearly similar to that occurs with alum coagulant provided for comparison. Both of these coagulants experience pleasing turbidity removal, due to their coagulation activity. Dose has to be one of the factors predetermined in order to perform effective coagulation activity. Even though the remaining amounts (500mg/l and 1000) of coagulant added for treatment throughout the study has satisfactory result, for this paper purpose the study found 50 mg/l is the most effective dose level for both of the coagulants. Finally, the “Suphe” soil from HonkoloWabeworeda, East Arsi is potential coagulant which has promising efficiency to remove malt wastewater turbidity. Moreover the soil coagulant could be effective and economical due to its abundance and inexpensiveness. Plus to that it might be an additional source of income for the local community.

5.2. Recommendations

- Detail soil research have to be done on the enhancing probabilities for the “Suphe”soil coagulating capacity
- The effluent released at different steps of the production process of periodically taken samples show high total suspended solid in the form of spent grains, germules during deculming and some skimmed materials. These constituent of the wastewater can be greatly reduced by physical screening and sorting spent grains. These activities not only reduce the amount of wastewater requiring disposal but also reduce the level of COD in the effluent. This would in turn bring the COD: BOD ratio to within the required range. Optimal efficiency in treatment could be achieved by incorporating screens before the coagulation tanks
- Standardization of the cleaning processes through integrated water management techniques can also help to reduce the amount of water used. The use of CIP (clean in place) systems and water jets would significantly reduce the wastewater load adjacent to end of pipe treatment
- The efficiency of the lab-scale treatment plant shows directive information indicating that the effluent is amenable to biological treatment. The anoxic stage of the treatment process has

shown the ability to reduce the organic load more than 90% and, to polish the remaining organic load to a desirable discharge limit the anaerobic process has to be followed by aerobic or other small aerated lagoon depending on cost effectiveness and available space

- For the sake of simplification, scope and limitation this study was restricted to certain factors which were thought to be crucially influencing the process of coagulation therefore, broader studies capable of considering multi factors which would have effect in the process have to be researched with more spectrum of levels. Example the effluent released at different steps of the production process of periodically taken samples show high total suspended solid in the form of spent grains, germules during deculming and some skimmed materials could be a treatment factor which would have impact on the process.
- "Suphe" soil is a new coagulant product which is therefore crucially need toxicity test for the treated waste water.

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7. APPENDIXES

Appendix A: Calculations of Physical and Chemical Properties

Table A-1: A profile showing the COD value of samples at different sites of the production process

COD in mg/l	Treated Inlet water	First wet steep water	Second wet steep water	Composite Effluent (Outlet)
Sample 1	66	1408	1494	603
Sample 2	80	2720	6990	2200
Sample 3	70	2500	2580	500
Sample 4	80	3840	1940	1460
Average	74± 7.12	2617±9.94	3251±5.34	1190±7.99
Percentage of COD	1%	44%	54.7%	

Table A-2: A profile showing the BOD value of samples at different sites of the production process

BOD in mg/l	Treated inlet water	First wet steep	Second wet steep	Composite Effluent (Outlet)
Sample1	4.4	505	772.5	360
Sample2	5.4	1220	1300.5	536.67
Sample3	4.8	1510	2195	438
Sample4	5	312.87	163.07	255
Average	4.85± 0.34	886.97±4.94	1107.77 ± 8.61	397.42 ±1.29
Percentage of BOD	.02%	44.3%	55.4%	

Table A-3: A profile showing the PO4 3- value of samples at different sites of the production process

PO_4^{3-} in mg/l	Treated inlet water	First wet steep water	Second wet steep water	Composite Effluent (Outlet)
Sample 1	0.22	23.57	15.98	1.62
Sample 2	0.62	76.19	11.63	3.91
Sample 3	0.45	68	13	2.7
average	0.43± 0.2	55.92 ±21.57	13.54±1.63	2.74±0.78
Percentage of PO_4^{3-}	0.6%	80.01%	19.37%	

Table A-4: A profile showing the SO_4^{2-} content of samples at different sites of the production process

SO_4^{2-} in mg/l	Treated inlet water	First wet steep	Second wet steep	Composite Effluent (Outlet)
Sample 1	230	130	670	40
Sample 2	250	140	540	48
Sample 3	262	125	513	35
Sample 4	134	110	60	30
average	219$\pm$58.18	12625$\pm$8.75	445.75$\pm$ 2.66	38.25$\pm$5.75
Percentage of SO_4^{2-}	27.7%	16%	56.3%	

Table A-5: A profile showing the S^{2-} content of samples at different sites of the production process

S^{2-}in mg/l	Treated inlet water	First wet steep	Second wet steep	Composite effluent(outlet)
Sample1	0.013	0.95	0.39	0.04
Sample2	0.05	0.46	0.52	0.34
Sample 3	0.06	0.68	0.47	0.22
average	0.014$\pm$ 0.02	0.70$\pm$017	0.46$\pm$0.04	0.2$\pm$0.11
Percentage of S^{2-}	3.4%	58%	3%	

Table A-6: A profile showing the Total Nitrogen content of samples at different sites of the production process

Total nitrogen	Treated inlet water	First wet steep	Second wet steep	Composite effluent (outlet)
Sample 1	0.06	24	4	9
Sample 2	0.9	32	19	13.2
Sample 3	0.8	28	15	11
average	0.59$\pm$0.46	28$\pm$4	12.67$\pm$7.77	11.07$\pm$2.1
Percentage of total nitrogen	1.4%	67.8%	30.7%	

Table A-7: A profile showing the Nitrate -N content of samples at different sites of the production process

Nitrate-N	Treated inlet water	First wet steep	Second wet steep	Composite effluent(out let)
Sample 1	20	103	18	9
Sample 2	25	132	25	13
Sample 3	27	135	27	16
Sample 4	22	130	28	12
average	23.5±3.11	125±11	24.5±4.51	12.5±2.89
Percentage	13.6%	72.3%	14.1%	

Table A-8: A profile showing Ammonia-N content of samples at different sites of the production process

NH_4-N	Treated inlet water	First wet steep	Second wet steep	Composite effluent (outlet)
Sample 1	0.72	4	5.7	3.35
Sample 2	0.06	10.91	3.9	0.45
Sample 3	0.5	6.8	4.2	3.8
average	0.43±0.34	7.24±3.48	4.6±0.96	2.53±1.82
percentage	3.5%			

Table A-9: A profile showing Total suspended solid content of samples at different sites of the production process

TSS	Treated inlet water	First wet steep	Second wet steep	Composite effluent(outlet)
Sample 1	-	158	122	143
Sample 2	-	167	109	165
Sample 3	-	184	133	111
average	-	169.67±13.2	121.3±12.01	139.67±27.15
percentage		58%	41.95%	

Table A-10: A profile showing PH value of samples at different sites of the production process

pH	Treated inlet water	First wet steep	Second wet steep	Composite effluent(outlet)
Sample 1	6.8	4.8	6.3	5.000
Sample 2	6.6	5.8	5.5	5.3
Sample 3	6.5	4.9	6.6	5.98
average	6.633	5.1666667	6.13333	5.286667
Standard deviation	$\pm$0.152753	$\pm$0.208167	$\pm$0.152753	$\pm$0.251661

Table A-11: A profile showing the COD: BOD ratio of Assela malt Factory Effluent

Sample type	COD in mg /l	BOD in mg/l	COD:BOD ratio
First wet steep	2617	886.97	2.95
Second wet steep	3251	1107.77	2.93
Composite effluent(outlet)	1190.75	397.42	2.99

Appendix B: "Suphe" Soil Efficiency Evaluation with respect to Acidic, Neutral and Basic Media of Samples

Table B_1: treatment efficiency evaluation of "Suphe" soil (SS) at pH of 5.

Sample site	Dose (mg/l)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)
First wet steep	50	1367	244	169
	500	1385	249	192
	1000	2600	486	203
	Mean value	1404$\pm$ 49.3	249.3$\pm$5.5	188.3$\pm$16.8
Second wet steep	50	76	32	68
	500	130	40	73
	1000	169	110	121
	Mean value	125$\pm$46.7	29$\pm$16	68$\pm$6
effluent	50	53	23	17
	500	96	27	22
	1000	148	39	139
	mean value	99$\pm$47.6	23$\pm$5	67.3$\pm$4.5
	50	28	8	4
Finallytreated	500	81	16	7
composite effluent	1000	131	20	11
	Mean value	80$\pm$51.5	14.7$\pm$6	7$\pm$4

Table B_2: treatment efficiency evaluation of "Suphe" soil at pH 7.

Sample site	Dose (mg/l)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)
First wet steep	50	1170	558	221
	500	1180	563	228
	1000	1267	786	262
	Mean value	1205.7$\pm$53.4	636$\pm$130	237$\pm$22
Second wet steep	50	119	50	59
	500	122	55	68
	1000	119	67	87
	Mean value	128.12$\pm$13.621	57$\pm$9	71$\pm$14
effluent	50	41	16	14
	500	64	21	16
	1000	68	26	23
	Mean value	58$\pm$14.7	21$\pm$5	18$\pm$5
Final treated outlet	50	15	13	12
	500	29	16	15
	1000	36	20	21
	Mean value	26.7$\pm$11	16$\pm$5	16$\pm$5

TableB$_3$: treatment efficiency evaluation of "Suphe" soil at pH 9.

Sample site	Dose (mg/l)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)
First wet steep	50	1305	595	215
	500	1370	625	244
	1000	1485	690	267
	Mean value	1387±91	638±49	242±26.2
Second wet steep	50	340	123	167
	500	386	140	189
	1000	455	172	205
	Mean value	394±58	145±143	187±19.1
effluent	50	48	25	108
	500	67	31	134
	1000	75	38	189
	Mean value	63±14	31±7	144±41
Final treated composite outlet	50	32	17	21
	500	55	22	27
	1000	68	35	33
	Mean value	52±18	25±9.3	27±6