Enhanced Coagulation for Treatment of Wastewater from Acid Gas Removal Unit

by

Meylis Yazmyradov, 11080

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2012

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Enhanced Coagulation for Treatment of Wastewater from Acid Gas Removal Unit

by

Meylis Yazmyradov

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Usama Mohamed Nour Eldemerdash)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

MEYLIS YAZMYRADOV

ABSTRACT

Amine solutions which are widely used in the gas processing industry for the removal of acid gases frequently become contaminated with amine degradation products, heat stable salts, heavy hydrocarbons and particulates. Amine based gas purification plants generate large volumes wastewater which is the major issue that contribute to the water pollution problems. This is probably due to the fact that, industries consume high amount of process water and chemicals and at the same time, produce high amount of highly polluted discharge water. Due to its harmful effects towards the environment and living organisms, various researches have been carried out to treat these effluents. And there is a need to treat wastewater to suitable standards at relatively low cost without sophisticated advanced treatment processes which have high requirements [1].

There are many processes for wastewater treatment, like coagulation, adsorption and membrane separation. Highly water-soluble amines have not satisfactorily been removed by current physical or chemical treatment of water thus a new approach using coagulation and flocculation was investigated in this study. So, coagulation and Flocculation by being one of the most convenient physical and chemical treatments underlines more on how to make this process efficient in terms economic, residual water quality, and at the same time, to improve the produced sludge so that it will be easily treated or disposed later on.

Diethanolamine contaminated wastewater was treated using the enhanced coagulation method. The experiments had been carried out by varying few parameters like dosage of coagulant (Ferric Chloride), pH, temperature and effect of coagulant aids (lime and bentonite). Series of jar test had been conducted with 3 minutes of rapid mixing at 200 rpm, followed by 30 minutes of slow mixing at 45 rpm and 1 hour of settling process. Afterwards, the solution was tested for DEA level, Chemical Oxygen Demand (COD) and amount of sludge produced.

ACKNOWLEDGEMENT

Apart from the efforts of me, the success of any project depends largely on the encouragement and guidelines of many others. Thus, I would like to seize this opportunity to express my gratitude to the people who have been actively involved in the successful completion of this final year project.

My warmest appreciation falls to my supervisor, Dr. Usama Mohamed Nour Eldemerdash. The attention, guidance and concern shown by him are overwelming. I really appreciate his effort and facilitation as an advisor; to ease my understanding, make my attachment convenient, and thus call the research project an accomplishment. Above all and the most needed, he motivated me whenever I was down and supported in many ways.

Furthermore, thanks to the FYP Lab Technicians and other laboratory technicians. I am most grateful for all their kind effort in providing me with all the facilities and technical expertise in guiding me throughout the duration of the laboratory work to ensure the successfulness of the research work.

Heartfelt appreciation is next to Final Year Research Coordinator, Dr. Norhayati Mellon for her existence and assistance throughout the research work by providing kind arrangements especially seminar series.

Special thanks to my parents for the continuous support and courage they gave me, which always drives me to keep on going whenever I fall. Last but not least, I also want to thank everybody who have involved directly and indirectly in helping me along this project. Thanks again to all, your kindness and helps will always be remembered.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVATIONS AND NOMENCLATURES

DEA   **-**   Diethanolamine

COD   -   Chemical Oxygen Demand

AGRU   -   Acid Gas Removal Unit

UV   **-**   Ultraviolet

PV   **-**   Plastic viscosity

WWTP   **-**   Waste Water Treatment Plant

CHAPTER 1

INTRODUCTION

Nowadays, the acceleration in the rates and expansion of oil and gas operations observed is accompanied by engineering processes, hazardous chemicals, explosive and fire danger substances. The use of natural gas as an industrial and domestic fuel has become a prime source of energy generation. There are a number of processes utilized between the wellhead and the consumer to render the natural gas fit for consumption. These processes are vital for removal of contaminants within the gas stream which, if left in the gas, would cause problems with environmental, health and safety hazards. The final steps of gas conditioning are a combination of different processes to remove impurities such as elemental sulphur, solids, heavy hydrocarbons [5]. One of the gas processing units is Acid Gas Removal Unit (AGRU). Gas sweetening is one of the important purification processes which is employed to remove acidic contaminants from natural gases prior to sale. This includes removal of H_2S and CO2 from gas streams by using absorption technology and chemical solvents. So, to minimize foaming risk in operating AGRU, cleaning is recommended in vendor installation [6]. After cleaning AGRU system there will huge amount of wastewater drained to the environment from system which will contain amine. And there is a need to treat wastewater to suitable standards at relatively low cost without sophisticated advanced treatment processes which have high requirements [1]. Wastewater treatment is one of the most complicated environmental issues among all the industries. This is because of the characteristics of its wastewater, which consists of different highly stable chemical pollutants [4]. And there is many processes available for waste wastewater treatment but many of the available processes cannot be used on an industrial scale for technological and economic reasons [2]. It is shown that the advanced treatment processes became more cost effective for larger plants and enhanced coagulation is cheaper [1]. Enhanced coagulation will be used for treating amine from industrially polluted water.

1.1 Background

Gas processing plants is said to be one of the most complicated industries and considerable source of the environmental contamination. This is due to the nature of plant wastewater, which consists of various waste chemical pollutants and at the same time consumes a large amount of fresh water. Thus, throughout the experimental works, amine is selected as the pollutant. If these plant effluents are not well-treated, then it may cause various harm and damage to the living surrounding and people.

At present, there are numerous technologies which have been applied in treating the wastewater - biologically, physically and chemical methods. However, for this research, coagulation and flocculation has been chosen as the main process in determining the effectiveness of amine removal from the wastewater.

1.2 Problem statement

Although the acid gas-amine reactions are reversible, irreversible reactions may also occur, resulting in products from which the amines are not easily recovered. This phenomenon is called degradation [7]. Purification techniques of alkanolamine solutions fall into three major categories: treatment with adsorbers, reversal of degradation reactions and distillation. Amine removal is not suitable for bio degradation. By applying the coagulation and flocculation methods in treating these effluents which mainly focus on the amine, several parameters, value are required to be investigated. The parameters include temperature, pH, dosage of the coagulants and also the effect of coagulant aids. This is because the coagulation and flocculation process will react efficiently at optimal conditions only. The optimal operation conditions for different types of amine might be different from each other. In addition, optimization of these parameters will considerably improve and enhance the treatment process. Apart from that, mechanical flocculation and chemical coagulation are among the primary wastewater treatments. Thus, optimal conditions need to be achieved so that it will simplify the rest of treatment process (second and tertiary wastewater treatments) [2]. Besides, our major concern through the implementation of this method is to produce an efficiency and to produce sludge which can be easily utilized or eliminated later on [8].

1.3 Objectives and scope of work

The scope of the research mainly concentrates on the coagulation and flocculation method in eliminating amine, which is one of the major contaminants consumed in AGRU wastewater. In the meantime, the key objectives of conducting the research are:

1. To investigate the efficiency of coagulation and flocculation process as the first treatment in handling wastewater containing Diethanolamine.

2. To conduct a jar test on the test water in order to estimate an optimum dosage of coagulant (ferric chlorite) for the coagulation and flocculation process.

3. To conduct a jar test on the test water in order to estimate an optimum pH for the coagulation and flocculation process.

4. To conduct a julabo on the test water in order to estimate an optimum temperature for the coagulation and flocculation process.

5. To observe the effect of addition of coagulation aids (lime and bentonite material) during the coagulation and flocculation process and select better coagulant aid.

6. To analyze the initial and residual wastewater solution in terms of pH, and COD.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

In the early days whereby there are ample resources and negligible development, little attention has been given to environmental issues. However, rapid economic development through the urbanization industrialization and the other land-use activities later on arises to water, air and land pollution, which remain as severe environmental problems in Malaysia. Thus, the government during 1974 has moved a step ahead by introducing a law and regulation, which is namely as Environmental Quality Act 1974 which functions in order to preserve, abate and control pollution, and further enhancing the quality of the environment in the country. Pollution, as acknowledged in the legislation includes the direct or indirect alteration of quality of the environment or any part of it by means of a positive act or act of commmission [15].

According to the Environmental Quality (Sewage and Industrial Effluent), the efflluents from the wastewater treatment can be categorized into two, which are Standard A and Standard B (refer to appendix). Standard A criteria applies only to the area located upstream of drinking water supply off-takes and meanwhile, Standard B applies for inland water. In words, Standard A will be applicable if the downstream of the river is used for the human activities, and vice versa for Standard B. Thus, this explains on why the Standard A appears much stricter compared to the other one.

2.2 Physical and Chemical Properties of Diethanolamine (DEA)

Diethanolamine is produced by reacting ethylene oxide with ammonia. Diethanolamine exists as crystals or as a liquid and has a mild ammonia odor (Merck, 1983). Diethanolamine, usually shortened as DEA or DEOA. Diethanolamine in the

class of ethanolamine's. DEA is an organic compound with the formula HN(CH2CH2OH)2. DEA is a colorless liquid and it is polyfunctional, being a secondary amine and a diol. As other consisting organic amines, diethanolamine acts as a weak base. Reflecting the hydrophilic character of the alcohol groups, DEA is soluble in water, and is even hygroscopic. Amides usually prepared from DEA are often also hydrophilic. DEA among a lot of other applications it is mainly used in the production of agrochemicals, detergents and surfactants. DEA is used as a surfactant and a corrosion inhibitor. It is used to remove hydrogen sulfide and carbon dioxide from natural gas in the gas treatment plants.
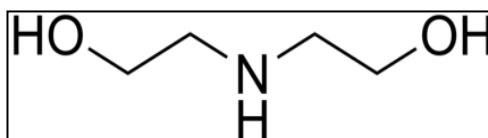
Figure 1: Structural and molecular formulae of DEA

2.3 Effects of DEA on Environment and Human Health

Diethanolamine and its derivatives in industrial effluents pose significant environmental risks due to slow degradability. Diethanolamine is used in a number of consumer products, such as shampoos, cosmetics, and pharmaceuticals. Short-term inhalation exposure to diethanolamine in humans may result in irritation of the nose and throat, and dermal exposure may irritate the skin.

Repeated skin applications of DEA-based detergents resulted in a major increase in the incidence of liver and kidney cancer (health-report.co.uk).

Exposures to DEA for humans can occur in the workplace, from environmental media, from contaminated drinking water or foodstuffs, or from use of consumer products containing DEA. Short-term effects reported include respiratory irritation, headaches, and burning eyes. Chronic effects of high exposures included weakness, muscle pain, anorexia, weight loss, and fatigue. Effects of long-term low-level exposures included increases in respiratory cancer, heart disease and effects on the immune system.

2.4 Types of Coagulants

Coagulant chemicals come in two main types - primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles in the water which causes the particles to clump together. Coagulant aids add density to slow-settling flocs and add toughness to the flocs so that they will not break up during the mixing and settling processes.

Primary coagulants are always used in the coagulation/flocculation process. Coagulant aids, in contrast, are not always required and are generally used to reduce flocculation time.
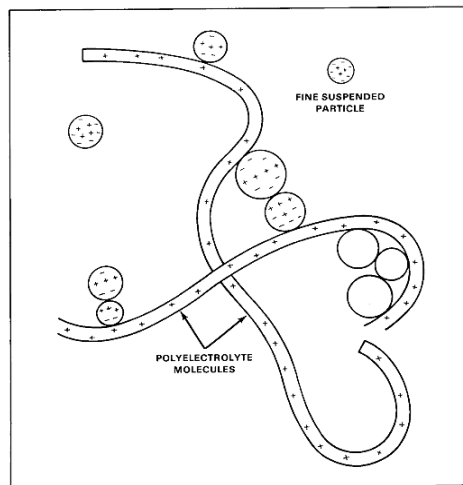

Figure 1-1. Forming a floc particle
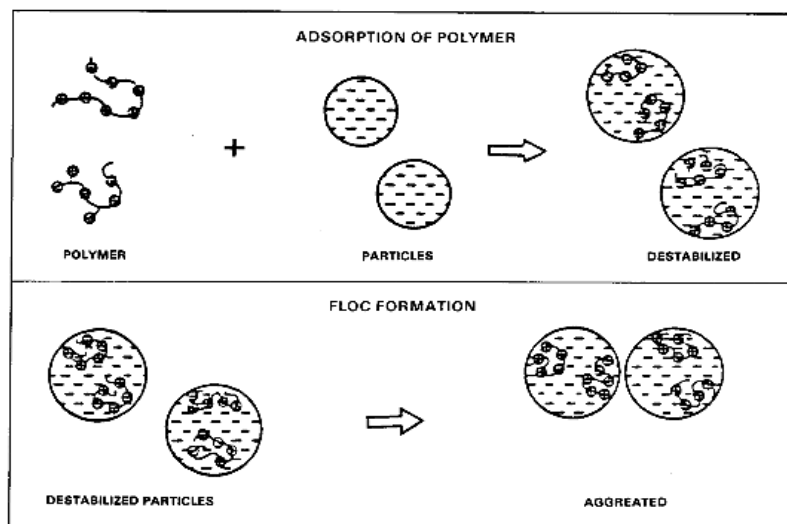
Figure 2: Forming a floc particle

Figure 1-2. Floc formation process

Figure 3: Floc formation process

Chemically, coagulant chemicals are either metallic salts (such as alum) or polymers. Polymers are man-made organic compounds made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged.) The table below shows many of the common coagulant chemicals and lists whether they are used as primary coagulants or as coagulant aids.

Table 1: Types of coagulant and coagunlant aids

Chemical Name	Chemical Formula	Primary Coagulant	Coagulant Aid
Aluminum sulfate (Alum)	$Al_2(SO_4)_3 \cdot 14\ H_2O$	X	
Ferrous sulfate	$FeSO_4 \cdot 7\ H_2O$	X	
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 9\ H_2O$	X	
Ferric chloride	$FeCl_3 \cdot 6\ H_2O$	X	
Cationic polymer	Various	X	X
Calcium hydroxide (Lime)	$Ca(OH)_2$	X*	X
Calcium oxide (Quicklime)	CaO	X*	X
Sodium aluminate	$Na_2Al_2O_4$	X*	X
Bentonite	Clay		X
Calcium carbonate	$CaCO_3$		X
Sodium silicate	Na_2SiO_3		X
Anionic polymer	Various		X
Nonionic polymer	Various		X

2.5 Coagulation Process

In industrial waste water different compounds are present like suspended solids, colloidal solids and dissolved solids. Suspended solids have a diameter larger than 10^{-6}m, colloidal solids between 10^{-9}m and 10^{-6}m and dissolved solids smaller than 10^{-9}m. This material must be removed prior to discharge. Because of the nature of the colloidal suspension these particles will not sediment or be separated with conventional physical methods (such as filtration or settling) unless they are agglomerated through coagulation

Coagulation process is a physicochemical used to separate suspended and colloidal solids from the waste water. Coagulation is the one of the most popular unit operations in water and waste water treatment units. (Zonoozi, Moghaddam, & Arami, 2008). Coagulation is frequently applied to process in the primary purification of industrial waste water and in some cases in secondary and tertiary treatment. (Mondal, 2008).It is the main component of wastewater treatment units and the applications include wastewater treatment, recycling and removal of pollutants (Gupta, Saleh, Nayak, & Agarwal, 2012)
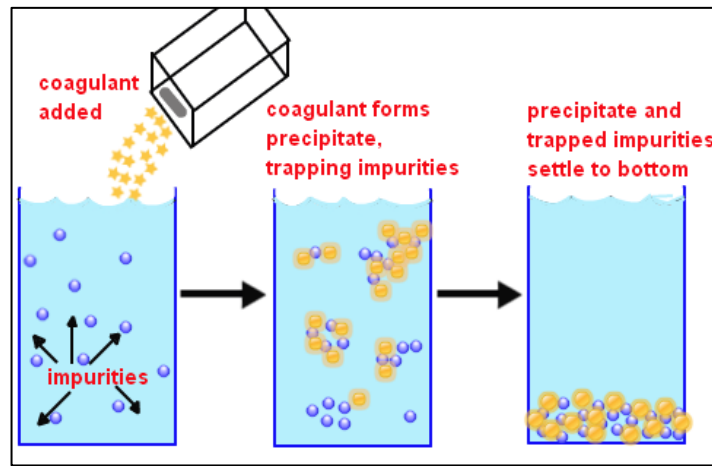

Figure 4: Coagulation Process

Coagulation, flocculation and clarification, followed by rapid gravity sand filtration, are the key steps in conventional waste water treatment systems. Conventional treatment (coagulation, sedimentation and sand filtration), as illustrated in Figure below, has several distinct stages.
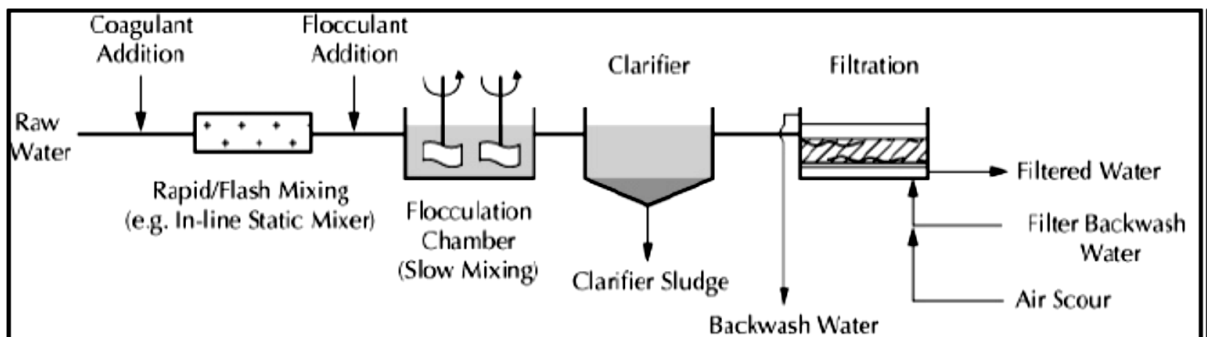
Figure 5: Conventional Coagulation, Sedimentation and Filtration

The coagulation process includes the dosing of a coagulant in water, resulting in the destabilization of water. It occurs in several steps intended to overcome the forces that stabilizes the suspended particles, allowing particle collusion and growth of floc.

The first step in the coagulation process is destabilizing the particle charges in the water. Coagulant of opposite charges added to neutralize the negative charge on the dispersed non-settable solids. Once the charge is neutralizes, the smaller particles are capable of sticking together to form a slightly larger particles. Rapid mixing after coagulant dosing is an important design parameter. It ensures the coagulant is properly dispersed in the water and promotes particle collision that is needed to achieve good coagulation.

Depending on the type of colloidal suspension that should undergo coagulation different destabilization mechanisms can be employed such as:

• Repression of the double layer

• Neutralization of colloid charge by adsorption of counter ions on the surface of the colloid

• Bridging of colloidal particles via polymer addition

• Entrapment of colloidal particles by sweeping floc

The addition of certain chemicals into the raw water causes particles to destabilize and allows agglomeration and floc formation to occur. The general terms for chemicals used for this purpose are:

✓ coagulants, which assist the destabilization of particles (particularly colloidal sizes)

✓ flocculants (also known as flocculant aids or coagulant aids), which assist in the joining and enmeshing of the particles together

2.6 Types of Coagulants

Figure below shows how the chemical coagulants works, these colloids are negatively loaded so they repel each other and they cannot make contact; it's the reason for the use of coagulants
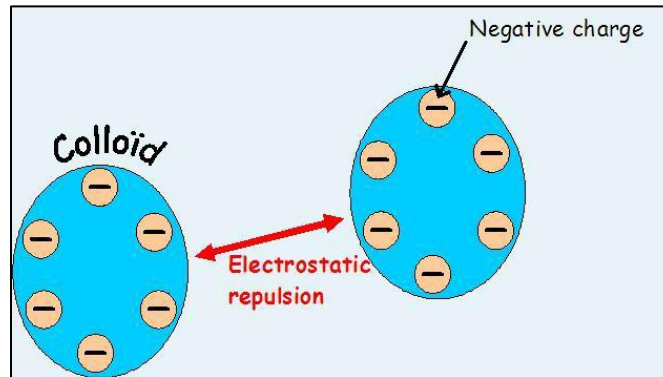
Figure 6: How Coagulants Works

There is vast selection of coagulant to choose from organic or inorganic types.

Coagulation is mainly induced by inorganic metal salts. The most common additives are aluminium sulphate (generally known as alum), ferric chloride and ferric sulphate (Renault, Sancey, Badot, & Crini, 2009). Using these chemical substances may have several environmental consequences such as:

i. an increase in metal concentration in water (which may have human health implications)
ii. production of large volumes of (toxic) sludge
iii. dispersion of acrylamide oligomers which may also be a health hazard

For these reasons, alternative coagulants have been considered for environmental applications. Natural or organic coagulants are more environmental friendly. Even the sludge produced is biodegradable thus there aren't any toxic sludge problem.

2.7 Coagulant Aid Types and Mechanisms

Coagulants aids add density to slow settling flocs as well as toughness to the flocs so that they will not break during the mixing and the settling process. Aggregation of suspended solids with coagulant aid mainly by either bridging or patch mechanism.

Destabilization by bridging occurs when segments of a polymer chain adsorb more than one particle, thereby linking the particles together. The coagulant aid will adsorb on the surface in a series of loops (segments extending in the solution) and trains (segments adsorbed on the surface).
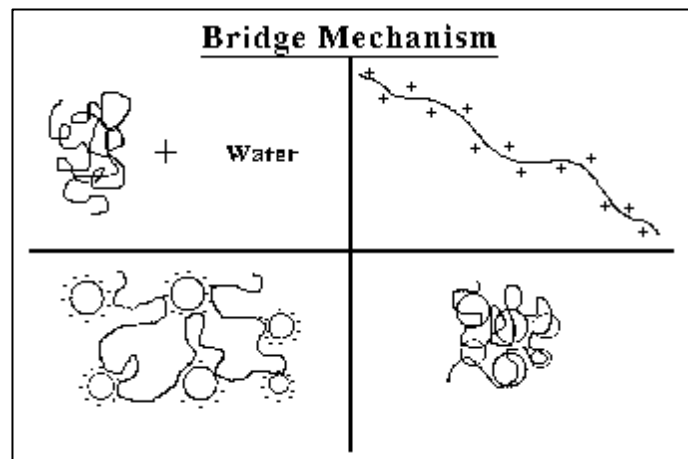
Figure 7: Bridge Mechanism

Several coagulant aids like bentonite and lime will be experimented and the results will be compared to choose the best type.

Bentonite consists essentially of clay minerals of the smectite (montmorillonite) group and has a wide range of industrial applications including clarification of edible and mineral oils, paints, cosmetics, and pharmaceuticals (Christidis, 1998). The abundance of bentonite in most continents of the world and its low cost make it a strong candidate as a coagulant for the removal of many pollutants from wastewaters. Research studies have shown its ability to bind and remove pathogenic viruses, pesticides, herbicides, and other toxins(Hartman & Martin, 1984). Other studies were carried out to investigate the possible use of natural bentonite as an effective adsorbent for the removal

of rare earth elements and heavy metals from aqueous solutions (Chegrouche, Mellah, & Telmoune, 1997). The aim of this work was to investigate experimentally, the potential of natural bentonite to act as coagulant aid to remove DEA in aqueous solution.

The use of lime in wastewater treatment was introduced long ago. Lime, as a general term, includes quicklime (CaO), hydrated lime [Ca(OH)2], and dolomitic lime as defined by the National Lime Association, NLA, 1999(Semerjian & Ayoub, 2003). Historically, lime has been used in treating wastewaters for a multitude of reasons. It has the inherent advantage of making no contribution to an increase in salinity, as is the case when alum or iron salts are employed. Moreover, apart from its positive economic impact in terms of chemical cost and energy requirements, lime effectively acts as a precipitant for phosphates, many trace metals, and bacteria, and as a coagulant for the removal of suspended and colloidal material in municipal wastewater. In this research work, lime (CaOH2) will be tested as coagulant aid for the removal of DEA.
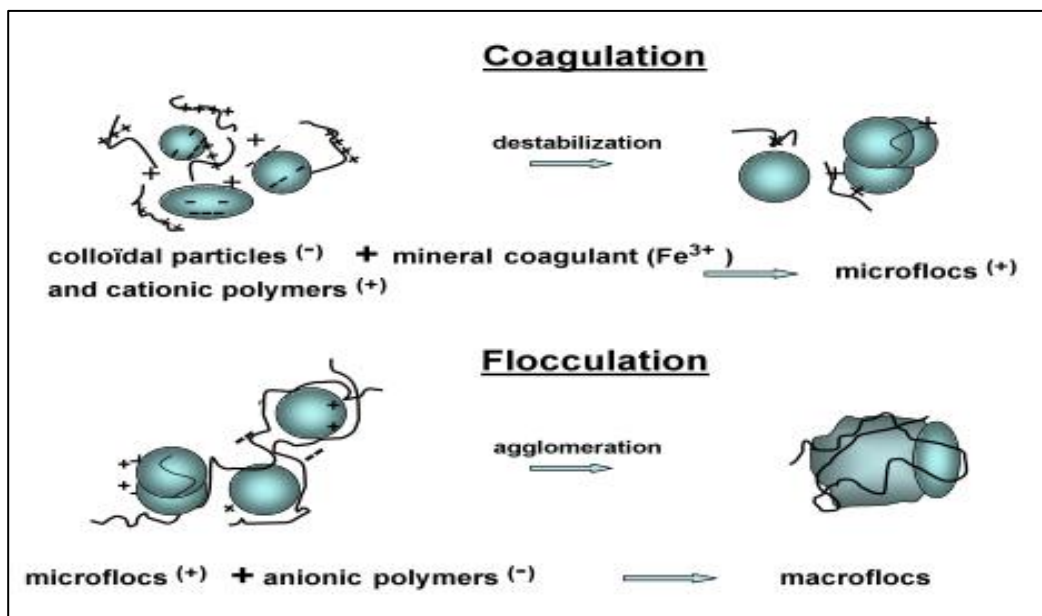
Figure 8: Coagulation and Flocculation processes

2.8 Factors Influencing Coagulation

In a water treatment, adjustments are often necessary in order to maximize the coagulation/flocculation process. These adjustments are a reaction to changes in the raw water entering the treatment flow. Coagulation will be affected by changes in the water's pH, alkalinity, temperature, time, velocity and zeta potential.

The effectiveness of a coagulant is generally **pH** dependent. Water with a color will coagulate better at low pH (4.4-6) with alum.

Alkalinity is needed to provide anions, such as (OH) for forming insoluble compounds to precipitate them out. It could be naturally present in the water or needed to be added as hydroxides, carbonates, or bicarbonates. Generally 1 part alum uses 0.5 parts alkalinity for proper coagulation.

The higher the **temperature**, the faster the reaction, and the more effective is the coagulation. Winter temperature will slow down the reaction rate, which can be helped by an extended detention time. Mostly, it is naturally provided due to lower water demand in winter.

Time is an important factor as well. Proper mixing and detention times are very important to coagulation.

The higher **velocity** causes the shearing or breaking of floc particles, and lower velocity will let them settle in the flocculation basins. Velocity around 1 ft/sec in the flocculation basins should be maintained.

METHODOLOGY

SUMMARY OF PROJECT WORKS:

3.1 GENERAL DESCRIPTION

Preparation of raw wastewater

(400ppm DEA)

→

Experiment 1: Varying the concentration of the coagulant (Ferric Chloride)

Note: pH 7 & room Temperature

Experiment 2: Varying the initial pH (3-12)

Note: Concentration of coagulant was fixed at the optimal point

→

Experiment 3: Varying the initial operating temperature.

Note: Concentration of coagulant and pH was fixed at optimal point

Experiment 4: Varying the dosage of lime and bentonite material

Note: Other parameters were kept at the optimal point.

→

Water Quality Measurements:
1. DEA removal
2. Sludge productions
3. COD removal

Figure 9: Experimental overall flow.

3.2 Experiment Procedure

The methodology of this project is mostly experiment that was conducted using the jar test apparatus.

The coagulation and floc formation process was simulated. The jar test apparatus consists of six paddle stirrers and 6 jars filled with sample as it is shown in figure below. To each jar a certain dose of coagulant was added during rapid mixing and coagulant aid was added during slow mixing. After rapid mixing at 200 rpm for 3 minutes, a slow stirring at 45 rpm for 30 minutes and a settling period of one hour, the sample was measured for Chemical Oxygen Demand (COD), DEA contaminant level and amount of sludge produced.

COD was measured using HACH Digital Reactor (DR 5000). DEA level was measured using UV-Vis Spectrophotometer. After settling period, Total Suspended Solid (TSS) apparatus was used to collect the sludge. The sludge was then dried in the oven at 106°C for 24 hours to remove the moisture content before being weighed.

There were several parameters that were manipulated in this experiment such as:
1) Optimum Coagulant Dose Ferric Chloride (500 - 2000ppm)
2) Optimum pH (pH3 - 12)
3) Temperature effect (30°C - 80°C)
4) Optimum Coagulant aid dose, Lime and Bentonite(250 - 2500ppm).

3.3 Raw Wastewater Preparation

Wastewater had to be prepared before conducting the experiment. According to literature, the standard DEA contaminant level in wastewater is in the range of 50ppm to 500 ppm. Throughout the experiment, 400ppm concentration of DEA was chosen to be the initial of concentration of wastewater. Wastewater was prepared by mixing 400 mg of DEA with 1L of distilled water to produce 400ppm DEA. This is because the main focus in this study is only on DEA removal in wastewater.

3.4 Optimum Coagulant Dose

To study the effect of coagulant dosage on DEA removal by dosing different amounts of Ferric Chloride ($FeCl_3$) solution into the wastewater sample. The sample at room temperature, initial modified pH 7 and with different dosage of coagulant was stirred in jar test at 200 rpm for 3minutes, then 30 minutes at 45 rpm and settling time for an hour. Initial pH7 was used because of operating pH range for Ferric Chloride is (3-9pH). It has flexible pH range. The sample water after test was tested for COD reduction, DEA removal percentage and amount of sludge produced. The coagulant dosage with the highest COD reduction and highest DEA removal percentage was chosen as optimum dosage. The following equations will be used:

$$COD\ Removal\ Rate = \left(\frac{Co - C}{Co}\right) \times 100$$

where;

C - final COD value

Co - initial COD value

$$DEA\ Removal\ Rate = \left(\frac{Co - C}{Co}\right) \times 100$$

where;

C - final DEA value

Co - initial DEA value

3.5 Optimum pH

pH plays an important role in the coagulation process. Thus pH must be controlled to establish optimum condition for coagulation. The pH was varied using 1M hydrochloric acid (HCI) and 1M sodium hydroxide (NaOH). The pH that was tested was between the ranges 3, 5, 7, 9, 11 and 12. The experiment was repeated at room ambient temperature ($25^{o}C$) with optimum coagulant dose. As in a previous section the pH with most COD reduction and highest DEA removal percentage was chosen as optimum pH.

3.6 Temperature Effect

Temperature control is vital in this experiment. Temperature effects the floc formation. Temperature was varied 30˚C, 40 ˚C, 50 ˚C, 60˚C, 70˚C and 80˚C at optimum coagulant dose and optimum pH. The temperature with most COD reduction and highest DEA removal percentage was chosen as optimum temperature.

3.7 Optimum Coagulant aid dosage

Different coagulant aids like lime and bentonite was experimented. Each coagulant aid was repeated using different dosage while keeping optimum coagulant dose, optimum pH, and optimum temperature constant. The coagulant aid with the most COD reduction and highest DEA removal percentage was chosen as the best coagulant aid at the optimum dose.

3.8 EQUIPMENTS

3.8.1 Jar Test

A standard jar test apparatus will implemented during the experimental works by varying few parameter, which namely as dosage of inorganic coagulants, and pH and all of them will be carried out at the ambient temperature (25°C). The jar test principally equipped with six paddle stirrer, together with six beaker apparatus.
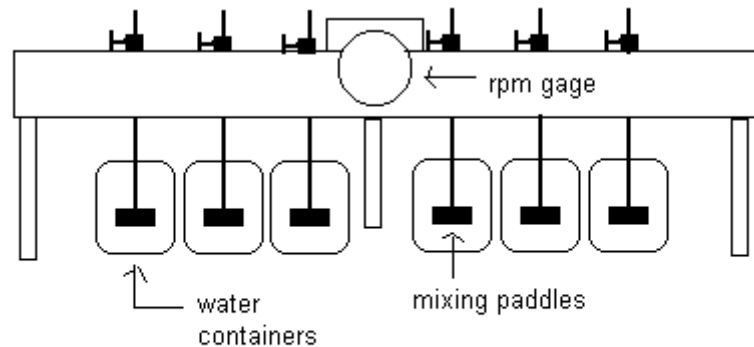
Figure 10: Jar test apparatus

3.8.2 Julabo

Apart from that, Julabo SW22 shaking water bath will also be implemented through the experimental works to determine the effect of various operating temperature (30-80°C) and dosage of coagulation aids, lime and biomass.

Figure 11: Julabo SW22

3.8.3 UV-Vis spectrophotometer

The UV/Vis spectrophotometer is an instrument that measures UV and visible light absorbed by a compound. Because the light absorbed by a compound may be used to determine how much of that compound is in a solution.

Figure 12: UV-Vis spectrophotometer.

3.9 Chemicals

1) 500-2500 ppm, Ferric Chloride ($FeCl_3$),

2) 1 M Sodium Hydroxide (NaOH), Merck

3) 1 M Hydrochloric Acid (HCI), Merck

4) 250-2500 ppm Lime, R&M Chemicals

5) 250-2500 ppm Bentonite, R&M Chemicals

6) 400 ppm DEA, Merck

CHAPTER 4

RESULT AND DISCUSSION

The research focuses on the optimum condition for the highest DEA removal percentage as DEA is the pollutant of main concern. In this study, coagulation method was tested on DEA contaminated wastewater. DEA contaminated wastewater is not visible to the eye because DEA is colorless. However, DEA concentration can be measured using UV-Vis Spectrophotometer. It measures the absorbance of DEA molecules in the wastewater. After each of the experiment the sample was tested for DEA removal percentage. The initial concentration of DEA throughout the research was 400ppm.

Chemical Oxygen Demand (COD) is a vital test for assessing the quality of effluents and wastewater prior to discharge. The COD test is commonly used to directly measure the amount of organic pollutants found in wastewater. The initial COD measurement for 400ppm DEA in wastewater is 603ppm. The regulation for discharge in Standard A and Standard B is 250 ppm respectively. Thus for each experiment the reduction in COD was also tested. A sample of waste water containing organic material is placed in contact with a very strong inorganic oxidant. The temperature is increased to the point of ebullition of the mixture which is at 150˚C, resulting in an increase of the oxidation rate. After 120 minutes (the standard duration of the test) oxidation of the organic compounds is virtually complete. Then the sample is tested in the HACH Digital Reactor, DR-5000 reactor for the COD level.

High production of sludge is undesirable in coagulation method. This is due to the difficulty in disposal of large amount of sludge. Throughout the research the amount of sludge produced was also measured.

4.1 Determination of Optimum Coagulant Dosage

During this research, Ferric Chloride (FeCl$_3$) was tested as a coagulant for removal of Diethanolamine in wastewater. Different dosage of Ferric Chloride between ranges (500-2000ppm) was added into the wastewater sample to determine the optimum dosage. The pH was changed so it was pH 7 as Ferric Chloride operating pH range (3-8) and experiment was conducted in room temperature. The dosage which gives highest DEA removal percentage and the most COD reduction will be chosen as the optimum dosage.

Table 2: Effect of Ferric Chloride Dosage at pH 7 & Room Temperature:

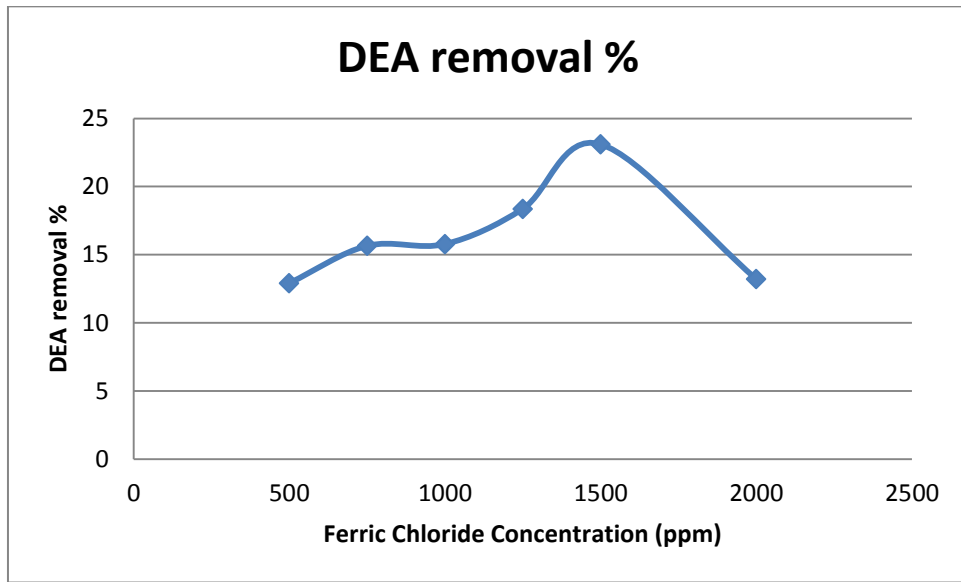| Ferric Chloride Concentration (ppm)	DEA concentration (ppm)		DEA removal %	COD (ppm)		COD removal %	Sludge amount (g)
	initial	final		initial	final		
500	400	348.3534483	12.91163793	603	374	37.97678	0.0004
750	400	337.4051724	15.6487069	603	370	38.64013	0.0002
1000	400	336.887931	15.77801725	603	385	36.15257	0.0006
1250	400	326.5431034	18.36422415	603	405	32.83582	0.0003
1500	400	307.5775862	23.10560345	603	364	39.63516	0.0009
2000	400	347.1465517	13.21336208	603	371	38.4743	0.0003

Figure 13: DEA Removal % vs. Ferric Chloride Concentration (ppm)
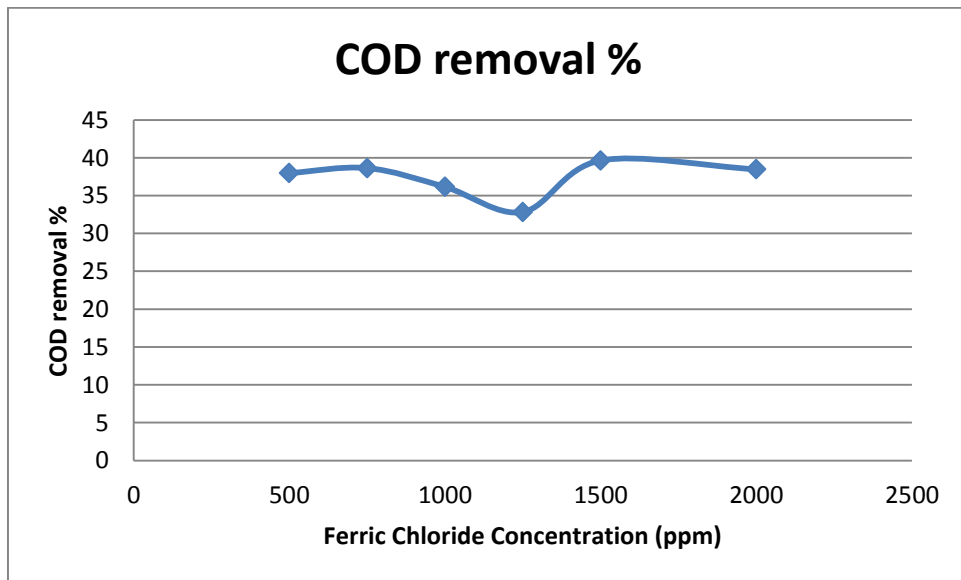

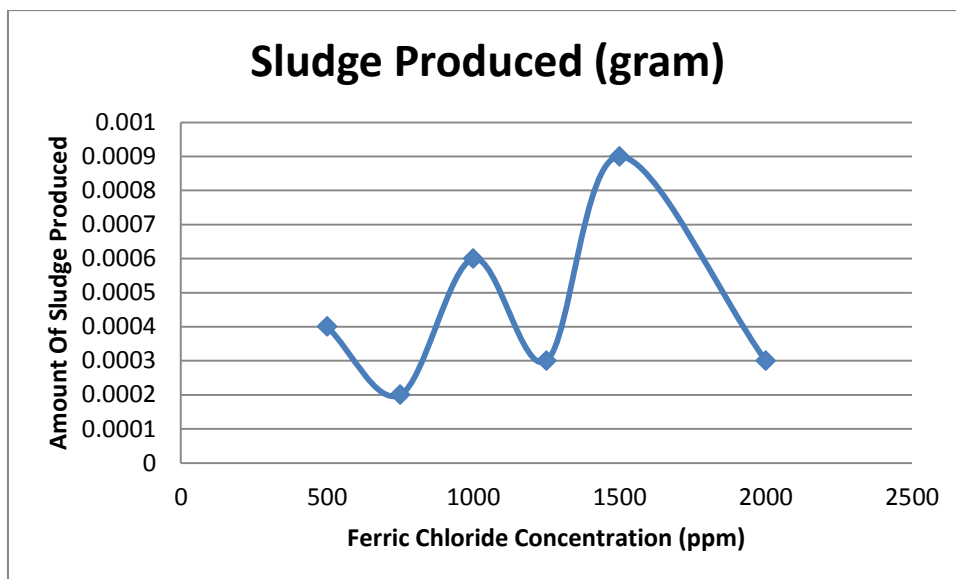**Figure 14: COD Removal % vs. Ferric Chloride Concentration (ppm)**

Figure 15: Sludge Produced vs. Ferric Chloride Concentration (ppm)

The optimum dosage will be the dosage of Ferric Chloride ($FeCl_3$) with the highest removal percentage of DEA and COD. In Figure 7 and Figure 8 at 1500 ppm concentration of coagulant, DEA and COD reduction was the highest which is 23.10560345 % and 39.63516 % respectively. Although the amount of sludge produced is high at 1500ppm but the amount is still manageable. Moreover 1500ppm is the minimum optimum dosage so the cost on coagulant will be the least. Thus the optimum Ferric Chloride dosage is 1500ppm at modified pH7 and at room ambient temperature ($25^{o}C$).

4.2 Determination of Optimum pH

As a matter of fact coagulation process is strongly pH dependent; the pH effect in coagulation unit was investigated. During this experiment focused on determining the optimum pH for the coagulation process with Ferric Chloride. The pH was varied between (3-12) pH ranges. To make the solution more acidic less than pH 7, drops of 1M of hydrochloric acid were added to achieve the desired pH. To make the solution alkaline droplets of 1M sodium hydroxide was added till desired pH was achieved. This experiment was conducted at ambient room temperature with optimum Ferric Chloride dosage 1500ppm.

Table 3: Effect of pH at Room Temperature & 1500ppm Ferric Chloride Dosage:

| pH range	DEA concentration (ppm)		DEA removal %	COD (ppm)		COD removal %	Sludge amount (g)
	initial	final		initial	final		
3	400	397.8362069	0.540948275	603	416	31.01160862	0.0006
5	400	339.387931	15.15301725	603	417	30.84577114	0.0003
7	400	315.4224138	21.14439655	603	385	36.15257048	0.0011
9	400	266.6293103	33.34267243	603	355	41.12769486	0.0024
11	400	369.8189655	7.545258625	603	449	25.53897181	0.0010
12	400	374.4396552	6.3900862	603	520	13.76451078	0.0004
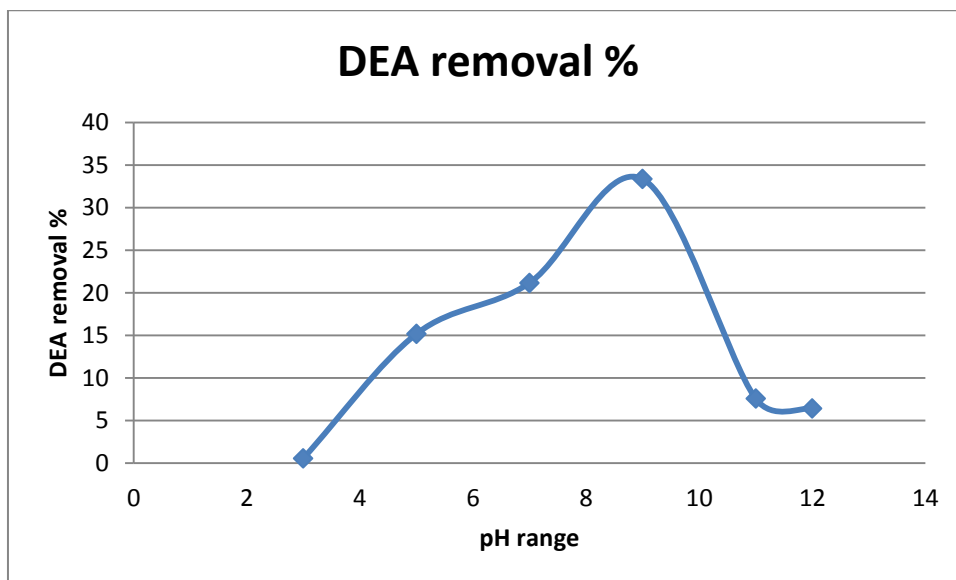
Figure 16: DEA Removal % vs. pH
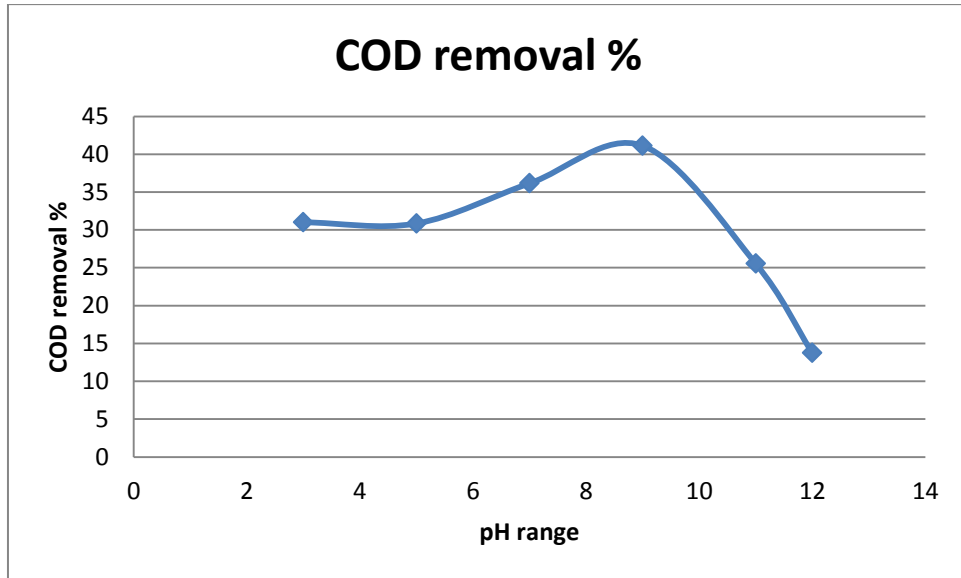
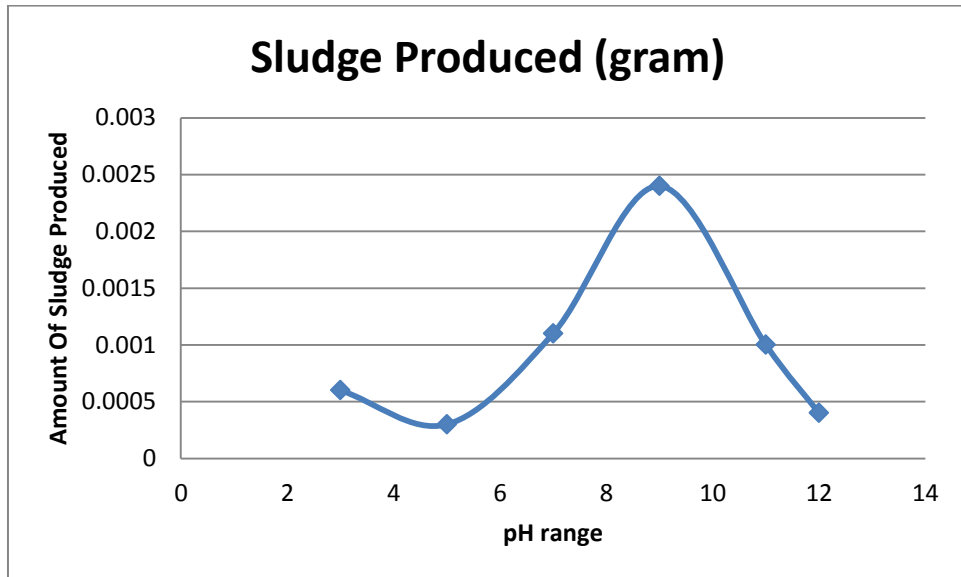**Figure 17: COD Removal % vs. pH**

Figure 18: Sludge Produced vs. pH

In coagulation process varying with pH range plays a major role. The pH will not only affect the surface charge of coagulants, but also the affects the stabilization of suspension (Hassan et al., 2009). The study of pH was essential to determine the optimum pH condition of the treatment. The stability of colloidal agglomeration depends on the forces that hold the particles in a suspension form. Even more, at the optimal pH, the coagulation process is more efficient since the pH is adjusted to the iso-electric point, which enables these colloids to stick together (Klimiuk, Filipkowska, & Korzeniowska, 1999).

So, the optimum pH will be the pH with the highest removal percentage of DEA and COD. In Figures above 10 and 11 at pH 9, DEA and COD reduction was the highest which is 33.34267243% and 41.12769486% respectively. Although the amount of sludge produced is highest at pH 9 but the amount is still manageable, it is only 0.0024g. At lower pH range, the efficiency of process was low this can be proved by observing Figure 10, 11 and 12. In Figure 10 and 11, at acidic condition the DEA removal percentage and COD reduction was the least which leads to lesser production of sludge because the colloids doesn't agglomerate and sediment. Thus the optimum pH is pH 9 at ambient room temperature with 1500ppm of Ferric Chloride optimum dosage as primary coagulant.

4.3 Determination of Optimum Temperature

For this experiment will be focusing on determining the optimum temperature for the coagulation process with Ferric Chloride. At the coagulation process as well as temperature taking big role too. The temperature was varied between 30˚C and 80˚C. To find optimum temperature this experiment was conducted at optimum pH, pH 9 and with optimum Ferric Chloride dosage 1500ppm.

Table 4: Effect of Temperature at (9pH & 1500ppm Ferric Chloride Dosage):

| temperature (°C)	DEA concentration (ppm)		DEA removal %	COD (ppm)		COD removal %	Sludge amount (g)
	initial	final		initial	final		
25(room)	400	266.6293103	33.34267243	603	355	41.12769486	0.0024
30	400	301.5431034	24.61422415	603	416	31.01160862	0.0020
40	400	344.3017241	13.92456898	603	519	13.93034826	0.0015
50	400	368.0603448	7.9849138	603	537	10.94527363	0.0014
60	400	376.2327586	5.94181035	603	548	9.12106136	0.0011
70	400	397.0948276	0.7262931	603	561	6.965174129	0.0007
80	400	399.5431034	0.11422415	603	587	2.653399668	0.0004
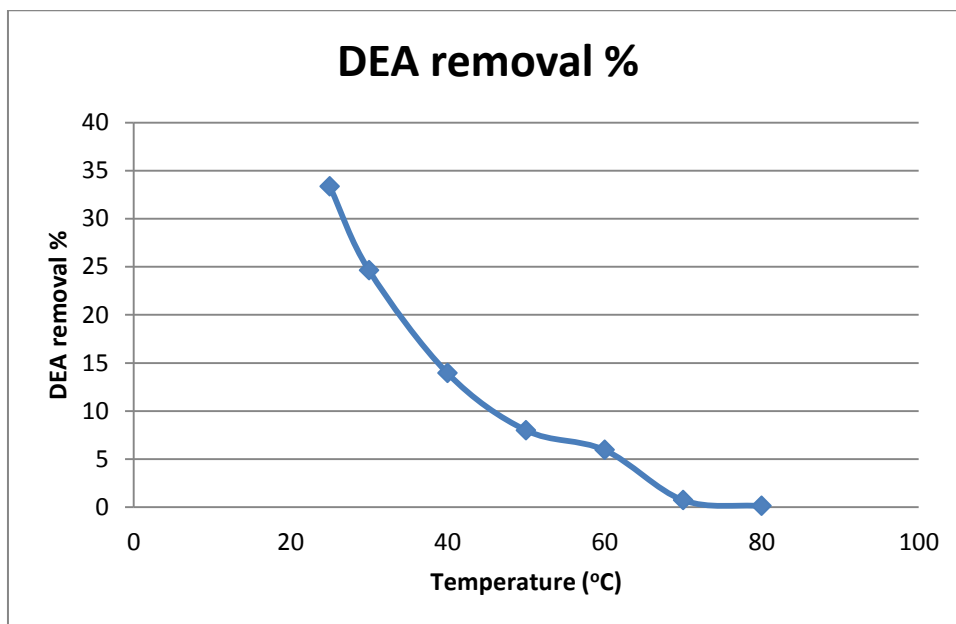
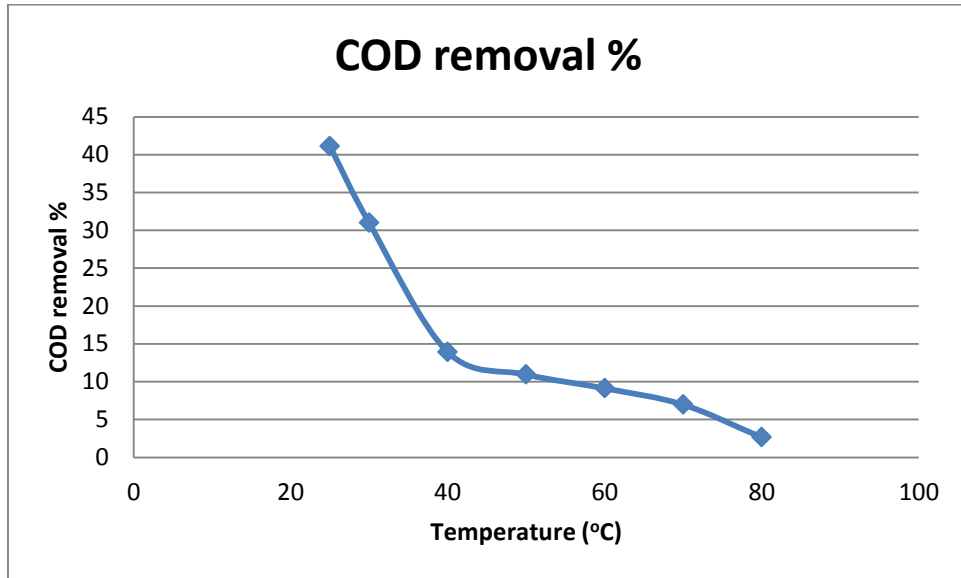**Figure 19: DEA Removal % vs. Temperature (°C)**

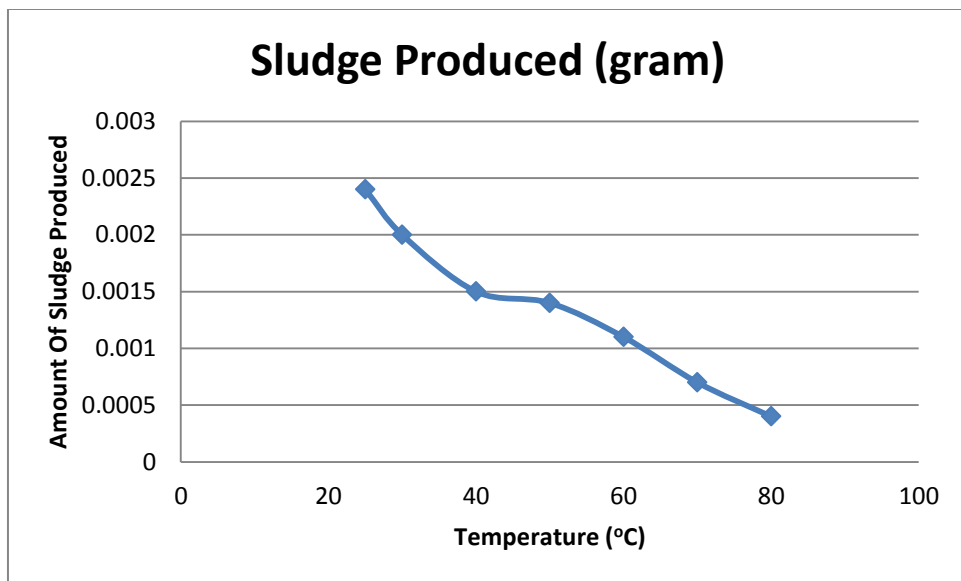**Figure 20: COD Removal % vs. Temperature (^{o}C)**

Figure 21: Sludge Produced vs. Temperature (^{o}C)

The figures above 13 and 14, shows that by increasing temperature from 30˚C to 80˚C, both the DEA and COD reduction percentage kept on decreasing. As an observation done during the experiment, the amount sludge forming at the bottom of the beakers were decreasing as the temperature increasing. It can be assumed that at higher temperature, there is a possibility that the formed precipitate re-dissolves in the solution. In figure 19 shows the amount of sludge produced at different temperatures. As temperature increasing, the amount of sludge produced kept decreasing. For temperature effects room temperature included in Table 3 for comparison.

The temperature effect may be due to the destabilization of charge on the suspended solids in wastewater. As the temperature of wastewater is increased with the addition of the coagulant, the floc particles size was smaller compare to the size of floc particles at the ambient room temperature of 25˚C. This might be due to the particle transport processes or particle collision rates and through the effect on viscosity (concentration) in wastewater. The floc strength becomes weaker with the increase of temperature and the 'macrofloc' can be easily broken (Othman, Bhatia, 2008). So as shown above in table and figures the optimum temperature is room temperature, 25˚C at pH 9 with 1500ppm of Ferric Chloride concentration as primary coagulant.

4.4 Determination of better Coagulant Aid and Optimum Dosage

As optimum values like pH and temperature obtained for coagulant Ferric Chloride, for further experiments focused on the best condition with the addition of coagulant aid. Coagulant aid was added during the slow mixing to add density to flocs and speed up the coagulation process by making the flocs agglomerate and settle faster. Coagulant aid also enhances the toughness and settleability of the floc during the experimental works. Therefore, throughout the study the choice of coagulant aid was lime and bentonite. The purpose of choosing these coagulant aids is because they are easily available.

4.4.1 Lime as Coagulant Aid

During this experiment, one of coagulant aids which is Lime was tested for removal of DEA in wastewater. Different dosage of lime was added into the wastewater sample to determine the optimum dosage. The pH used for solution was 9pH and experiment was conducted in room temperature (25°C). As in the previous experiments the highest DEA and COD reduction will be chosen as the optimum dosage for coagulant aid.

Table 5: Effect of Coagulant aid Lime at (9 pH , 25°C temperature & 1500ppm Ferric Chloride Concentration):

Lime coagulant aid (ppm)	DEA concentration (ppm)		DEA removal %	COD (ppm)		COD removal %	Sludge amount (g)
	initial	final		initial	final		
250	400	305.8534483	23.53663793	603	513	14.92537313	0.0028
500	400	246.9396552	38.2650862	603	497	17.5787728	0.0034
1000	400	194.7844828	51.30387931	603	456	24.37810945	0.0039
1500	400	147.5948276	63.1012931	603	398	33.99668325	0.0040
2000	400	73.1637931	81.70905173	603	296	50.91210614	0.0054
2500	400	119.5948276	70.1012931	603	345	42.78606965	0.0052
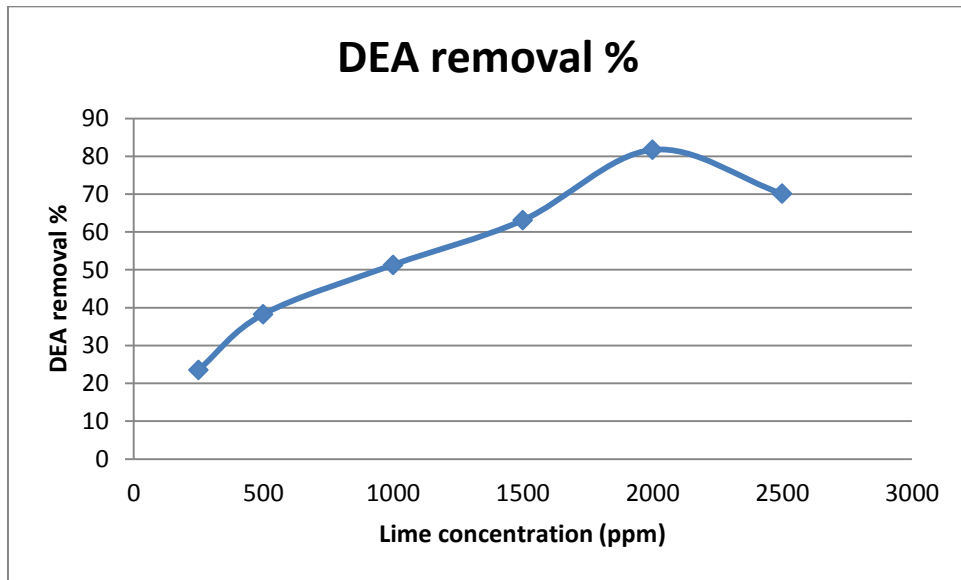
Figure 22: DEA Removal % vs. Lime concentration (ppm)
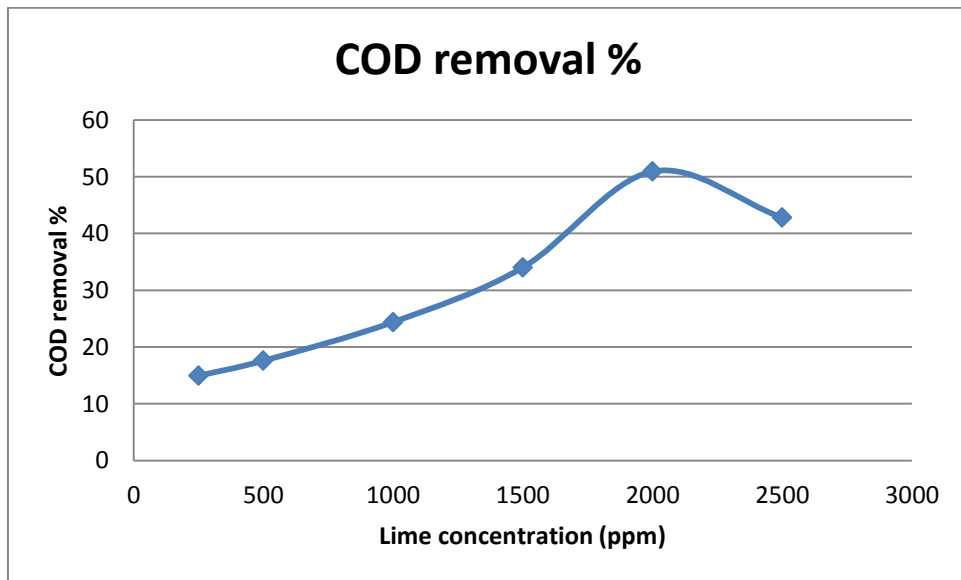
Figure 23: COD Removal % vs. Lime concentration (ppm)
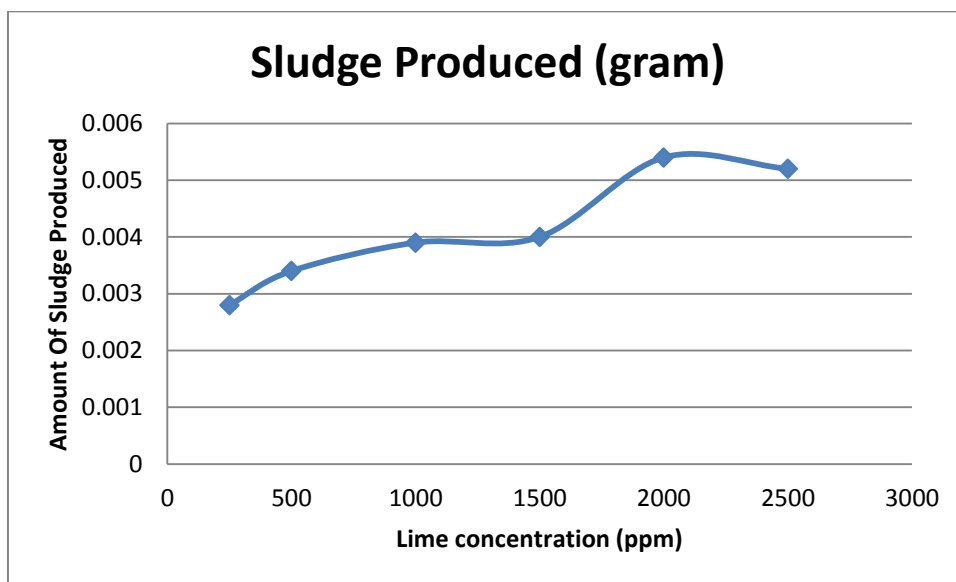
Figure 24: Sludge Amount vs. Lime concentration (ppm)

In Figure 16 and 17, it's clearly shown that at 2000ppm of lime as coagulant aid the DEA and COD reduction percentage was the highest. So the optimum coagulant aid lime dosage is 2000ppm at pH9, at room temperature with Ferric Chloride as primary coagulant at 1500ppm.

4.4.2 Bentonite as Coagulant Aid

During this experiment, bentonite was tested as a coagulant aid for removal of DEA in wastewater. Different concentrations of bentonite coagulant aid was added into the wastewater sample to determine the optimum dosage. The pH of the solution was pH9 as its optimum pH and experiment was conducted in room temperature. The dosage which gives highest DEA and COD reduction % will be chosen as the optimum dosage.

Table 6: Effect of Coagulant aid Bentonite at (9 pH , 25°C temperature & 1500ppm Ferric Chloride Dosage)

Bentonite coagulant aid (ppm)	DEA concentration (ppm)		DEA removal %	COD (ppm)		COD removal %	Sludge amount (g)
	initial	final		initial	final		
250	400	279.8189655	30.04525862	603	364	39.63515755	0.0041
500	400	298.2672414	25.43318965	603	398	33.99668325	0.0034
1000	400	324.2155172	18.9461207	603	487	19.2371476	0.0039
1500	400	345.4568966	13.63577585	603	516	14.4278607	0.0040
2000	400	354.6982759	11.32543103	603	551	8.623548922	0.0054
2500	400	362.9051724	9.2737069	603	597	0.995024876	0.0052
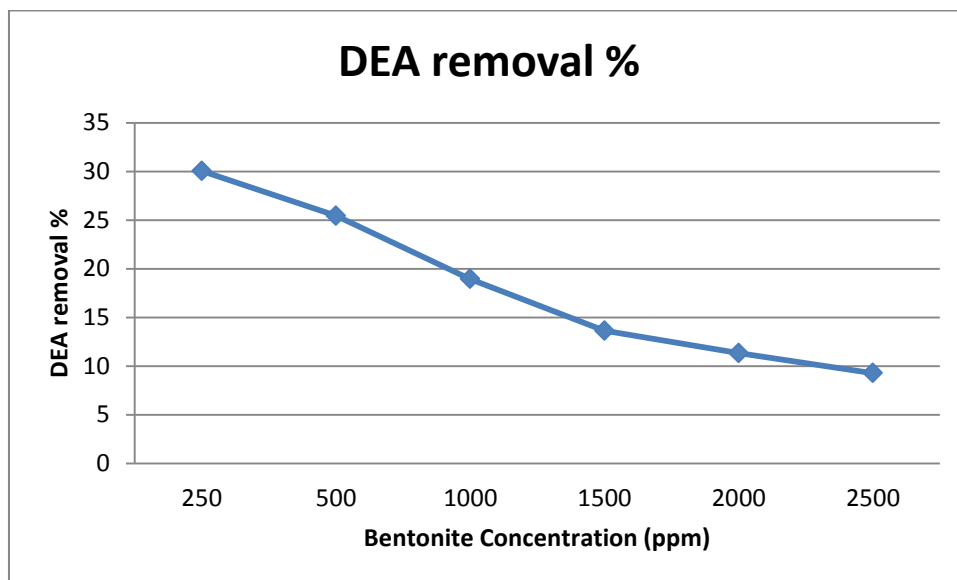
Figure 25: DEA Removal % vs. Bentonite concentration (ppm)
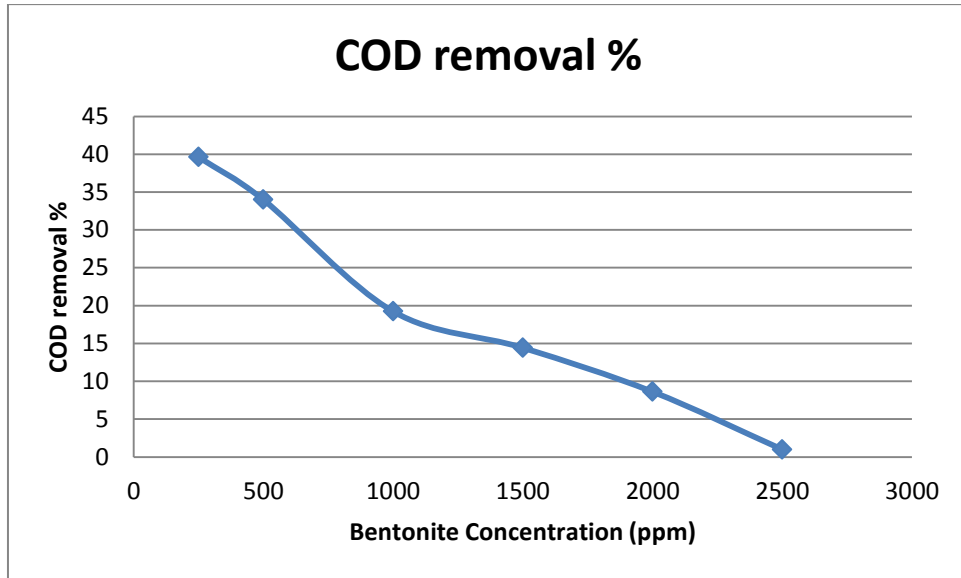
Figure 26: COD Removal % vs. Bentonite concentration (ppm)
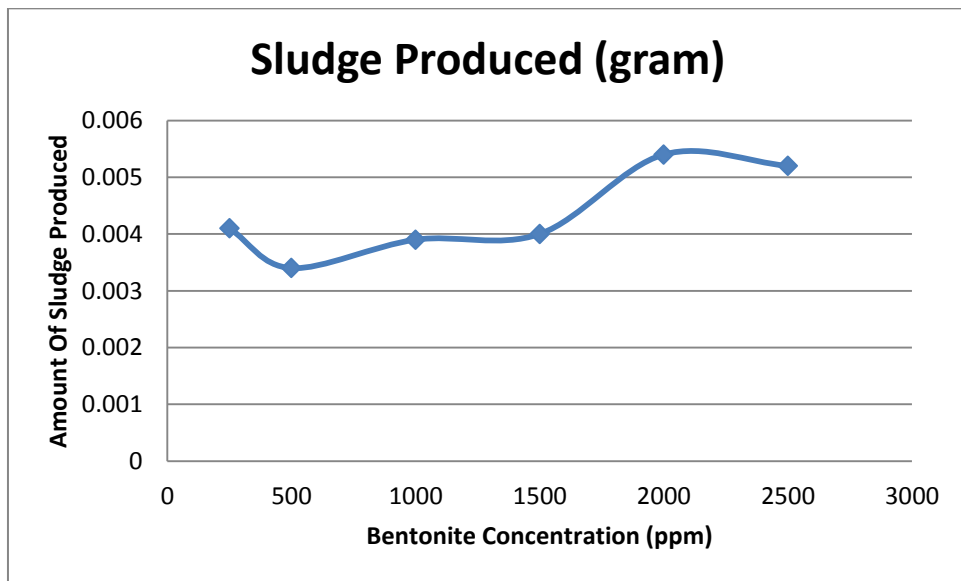
Figure 27: Sludge Amount vs. Bentonite concentration (ppm)

As its shown in the Figures above 19 and 20, it's clearly shown that at 500ppm of bentonite as coagulant aid the DEA and COD reduction percentage was the highest. So the optimum coagulant aid bentonite concentration is 500ppm at pH9, at room temperature with Ferric Chloride as primary coagulant at 1500ppm.

Comparison of Coagulant Aids Lime and Bentonite shown below:

DEA removal % Lime vs Bentonite
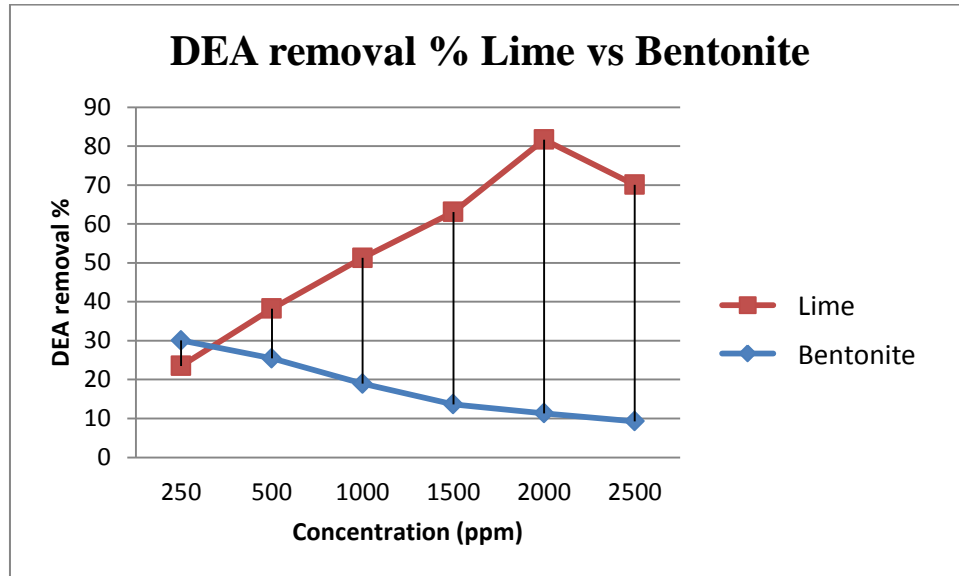
Figure 28: DEA removal % vs. Coagulant Aids concentration (ppm)

From the data above shown, can be concluded that lime is a better choice of coagulant aid with optimum concentration 2000ppm compared to bentonite in removal of DEA with Ferric Chloride as primary coagulant. The performance of these two coagulant aids depends on surface area as well as the exchange capacity.

Lime is a coagulant aid used to increase the alkalinity of the water. The increase in alkalinity results in an increase in ions (electrically charged particles) in the water, some of which are positively charged. These positively charged particles attract the colloidal particles in the water, forming floc. This helps the flocs to agglomerate and settle faster. Bentonite is a type of clay used as a weighting agent in water high in color and low in turbidity and mineral content. Perhaps that is the reason the performance of bentonite on DEA removal was poor. This type of water usually would not form floc large enough to settle out of the water. The bentonite joins with the small floc, making the floc heavier and thus making it settle more quickly.

CHAPTER 5

CONCLUSION

5.1 Conclusions

DEA is a priority pollutant in wastewater as it was pointed out in the earlier chapters. Industries such as oil refineries, gas treatments and petrochemicals contribute wastewater to the environment containing low or high concentration of DEA which treat harm. There are varieties of treatment methods to treat wastewater containting DEA. However, coagulation method is preferred compared to other methods because it is economically feasible, can handle large amount of wastewater and it is a continuous process. In any industry, cost plays a vital role thus every operation has to be cost effective. Despite the fact that coagulation process will produce sludge that needed to be treated later but if the coagulation process works efficiently at the optimum condition, it may ease the utilization or disposal of the sludge.

In summary, the coagulation and flocculation methods are only applicable at certain values of coagulant concentration, pH of solution, temperature and also effects of the coagulant aids. The optimum conditions are stated below:

i. The optimum concentration of Ferric Chloride as primary coagulant is 1500ppm
ii. The optimum pH of solution is at pH 9. The alkaline solution increases the number of ions in the solution; some of them are positively charged thus it aids the coagulation process.
iii. The optimum temperature is at room temperature is at 25˚C, that the floc re-dissolves at higher temperature. As temperature increasing, the amount of sludge produced keeps decreasing.
iv. Lime coagulant aid performed better as coagulant aid compared to bentonite clay. The optimum concentration of lime is 2000ppm.

Overall, the combination of 1500ppm of Ferric Chloride in pH 9, temperature of $25^{\circ}C$ as well as 2000ppm concentration of Lime coagulant aid contributes to approximately 81.7% DEA removal and 50.9% COD reduction and the amount of sludge produced is around 0.0054g which is considered a very small amount. These results suggest the coagulation method to be used to treat wastewater form AGRU using DEA as a solvent.

5.2 Recommendation

Through the research works, there are few recommendations which are proposed and can be applied for the future work undertaking. These recommendations are like the following stated below:

i. During the experiment for Lime(calcium hydroxide) coagulant aid, while applying Lime, the solution of the lime should be always thoroughly mixed to avoid any particle solids, calcium hydroxide from being settled down to the bottom part of the beaker.

ii. Further investigation should be on using different combination of natural and chemical coagulant as primary coagulant to improve the results. Chemical coagulants like Ferric Sulfate ($Fe_2(SO_4)_3$), Alum (aluminium sulfate) and others should be investigated for DEA removal efficiency.

Gantt Chart and Key Milestones:

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	▮	▮	▮	▮	▮	▮	▮									
2	Submission of Progress Report									● 5th NOV 2012							
3	Project Work Continues									▮	▮	▮	▮	▮			
4	Pre-EDX											● 26th NOV 2012					
5	Submission of Draft Report										3rd DEC 2012		●				
6	Submission of Dissertation (soft bound)										10th DEC 2012		●				
7	Submission of Technical Paper										10th DEC 2012		●				
8	Oral Presentation											19th – 25th DEC 2012		●			
9	Submission of Project Dissertation (Hard Bound)													By 11th JAN 2013	●		

Column heading in the break section: Mid-Semester Break

● Suggested milestone

▮ Process

REFERENCES

[1] D. Freese, D. J. Pryor, R. Rajagopaul, D. L. Trollip and R.A.Smith "Enhanced coagulation: a viable option to advance treatment technologies in the South Africa context", 2001 S. Water Science and Technology: Water Supply Vol 1, No 1, p33-41,

[2] Usama Eldemerdash, "Using Ceramic Materials for Enhanced Wastewater Treatment in Industrial Applications", 2011, Interceram.

[3] Nigel Graham, Fang Gang, Geoffrey Fowler, Mark Watts, "Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assesment", 2008. Volume 327, Issues 1–3 - ScienceDirect

[4] Usama Eldemerdash, "Evaluation of lime as an aid for coagulation-flocculation treatment of wastewater effluent" , 2012, Interceram.

[5]   http://hithaldia.academia.edu/smitra/Papers/649210/Gas_sweetening_process, 12.08.2012.

[6] W.S. Wan Ngah, M.A.K.M. Hanafiahocedure, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review", (2008), Bioresource Technology 99 3935–3948.

[7] Abdelaal, A. M. "Using a natural coagulant for treating wastewater, Eighth International Water Technology Conference", (2004), IWTC8 2004, Alexandria, Egypt, pp 781-792.

[8] S. Binyam, H. Mukhtar and K.K. Lau "Flux and Rejection of Methyldiethanolamine from Wastewater by Composite Reverse Osmosis Membrane", (2010), *Journal of Applied Sciences, 10: 3331-3336.*

[9] Shyh-Fang Kang, Chih-Hsaing Liao, Mon-Chun Chen "Pre-oxidation and coagulation of wastewater by the Fenton process", 2001. Chemosphere. Feb. 46(6):923-8.

[10] S D Freese, D J Nozaic, D L Trollip "Evaluation of process Chemicals", 2006, Water Research Commission (WRC).

[11] Fitzpatrick CS, Fradin E, Gregory J. "Temperature effects on flocculation, using different coagulants", 2011. Water Sci Technol. 2004; 50(12), p71-5.

[12] P Gebbie, "Using Polyaluminium coagulants in water treatment", 2001. *64th Annual Water Industry Engineers and Operators' Conference.*

[13] Ting Chen, Baoyu Gao, Qinyan Yue, "Effect of dosing method and pH on color removal performance and floc aggregation of polyferic chloride-polyamine dual-coagulant in synthetic dyeing wastewater treatment", 2010, Volume 355, Issues 1–3, 20 February 2010, Pages 121–129

[14] Elif Yilmaza, Shahabuddin Memonb, Mustafa Yilmaza, "Removal of direct azo dyes and aromatic amines from aqueous solutions usingtwo β-cyclodextrin-based polymers", 2010, Journal of Hazardous Materials 174 (2010) 592–597

[15] Abdullah, A. R. (1995). "Environmental pollution in Malaysia: trends and prospects". TrAC Trends in Analytical Chemistry, 14(5), 191-198.

[16] Chegrouche, S., Mellah, A., & Telmoune, S. (1997). :Removal of lanthanum from aqueous solutions by natural bentonite". Water research, 31(7), 1733-1737.

[17] Gupta, V. K., Saleh, T. A., Nayak, A., & Agarwal, S. (2012). "Chemical Treatment Technologies for Waste-water Recycling an Overview". RSC Advances,

[18] Hartman, W. A., & Martin, D. B. (1984). "Effect of suspended bentonite clay on the acute toxicity of glyphosate toDaphnia pulex andLemna minor". Bulletin of environmental contamination and toxicology, 33(1), 355-361.

[19] Mellah, A., & Chegrouche, S. (1997). "The removal of zinc from aqueous solutions by natural bentonite". Water research, 31(3), 621-629.

[20] Renault, F., Sancey, B., Badot, P. M., & Crini, G. (2009). Chitosan for coagulation/flocculation processes-An eco-friendly approach. European Polymer Journal, 45(5), 1337-1348.

[21]http://www.techneau.org/fileadmin/files/Publications/Publications/Deliverables/D5. 3.1A_Enhanced_coagulation_report.pdf

[22] Mellah, A., & Chegrouche, S. (1997). "The removal of zinc from aqueous solutions by natural bentonite". 1997, *Water research, 31*(3), 621-629.

[23] Lin, S. H., & Juang, R. S. (2009). "Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review". *Journal of Environmental Management, 90*(3), 1336-1349.

[24] Verma, A. K., Dash, R. R., & Bhunia, P. "A review on chemical coagulation/ flocculation technologies for removal of colour from textile wastewaters". *Journal of Environmental Management, 93*(1), 154-168.

[25] Zonoozi, M. H., Moghaddam, M. R. A., & Arami, M. (2008). Removal of Acid Red 398 dye from aqueous solutions by coagulation/flocculation process. *Environmental Engineering and Management Journal, 7*(6), 695-699.

[26] Semerjian, L., & Ayoub, G. M. "High-pH Magnesium Coagulation-Flocculation in Wastewater Treatment". (2003). *Advances in Environmental Research, 7*(2), 389-403.

[27] Renault, F., Sancey, B., Badot, P. M., & Crini, G. "Chitosan for coagulation/ flocculation processes-An eco-friendly approach". (2009). *European Polymer Journal, 45*(5), 1337-1348.

[28] Mondal, S. "Methods of dye removal from dye house effluent-an overview". *Environmental Engineering Science,* (2008). *25*(3), 383-396.

[29] Malakootian, M., & Fatehizadeh, A. "Color Removal From Water By Coagulation/caustic Soda And Lime". *Iranian Journal of Environmental Health Science & Engineering, 7*(3).

[30] Lipson, S. M., & Stotzky, G. "Specificity of virus adsorption to clay minerals". (1985). *Canadian journal of microbiology, 31*(1), 50.

[31] Klimiuk, E., Filipkowska, U., & Korzeniowska, A. "Effects of pH and coagulant dosage on effectiveness of coagulation of reactive dyes from model wastewater by polyaluminium chloride (PAC)". (1999). *Polish Journal of Environmental Studies, 8*, 73-80.

[32] Susan B. Peterson a, John M. Teal, "The role of plants in ecologically engineered wastewater treatment systems", (1996), Ecological Engineering 6 137-148.

[33] M.I. Aguilar, J. S!aez, M. Llorens, A. Soler, J.F. Ortuno, "Nutrient removal and sludge production in the coagulation–flocculation process", (2002), Water Research 36 2910–2919

[34] Joonghwan Mo, Jeong-Eun Hwang, Jonggeon Jegal, Jaephil Kim, "Pretreatment of a dyeing wastewater using chemical coagulants", (2007), Dyes and Pigments 72, 240e245

[35] James M. Ebeling, Philip L. Sibrell, Sarah R. Ogden, Steven T. Summerfelt, "Evaluation of chemical coagulation_/flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge", (2003), Aquacultural Engineering 29, p23_/42.

[36] Sajjad Haydar, Javed Anwar Aziz. "Coagulation–flocculation studies of tannery wastewater using combination ofalum with cationic and anionic polymers", (2009). Journal of Hazardous Materials 168, 1035–1040.

APPENDIX 1

Parameter Limits of Effluent of Standards A and B

Third Schedule

Environmental Quality Act 1974

Environmental Quality (Sewage & Industrial Effluent) Regulations 1979

(Regulation 8(1), 8(2), 8(3))

PARAMETER LIMITS OF EFFLUENT OF STANDARDS A AND B

Parameter	Unit	Standard A	B
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value		6.0 - 9.0	5.5 - 9.0
(iii) BOD5 at 20°C	mg/l	20	50
(iv) COD	mg/l	50	100
(v) Suspended Solids	mg/l	50	100
(vi) Mercury	mg/l	0.005	0.05
(vii) Cadmium	mg/l	0.01	0.02
(viii) Chromium, Hexavalent	mg/l	0.05	0.05
(ix) Arsenic	mg/l	0.05	0.10
(x) Cyanide	mg/l	0.05	0.10
(xi) Lead	mg/l	0.10	0.5
(xii) Chromium, Trivalent	mg/l	0.20	1.0
(xiii) Copper	mg/l	0.20	1.0
(xiv) Manganese	mg/l	0.20	1.0
(xv) Nickel	mg/l	0.20	1.0
(xvi) Tin	mg/l	0.20	1.0
(xvii) Zinc	mg/l	1.0	1.0
(xviii) Boron	mg/l	1.0	4.0
(xix) Iron (Fe)	mg/l	1.0	5.0
(xx) Phenol	mg/l	0.001	1.0
(xxi) Free Chlorine	mg/l	1.0	2.0
(xxii) Sulphide	mg/l	0.50	0.50
(xxiii) Oil and Grease	mg/l	Not detectable	10

APPENDIX 2

DEA Standard Calibration Curve Using UV-Vis Spectrophotometer