ADSORPTION TREATMENT OF MONOETHANOLAMINE (MEA) WASTEWATER FROM OIL AND GAS INDUSTRY

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Date : ……………………………..

ADSORPTION TREATMENT OF MONOETHANOLAMINE (MEA) WASTEWATER FROM OIL AND GAS INDUSTRY

MOHD NAJIB BIN RAZALI

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
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JUNE 2011

STUDENT'S DECLARATION

I declare that this thesis entitled "Adsorption Treatment of Monoethanolamine (MEA) Wastewater From Oil and Gas Industry" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ……………………………….
Name : Mohd Najib Bin Razali
Date :

The Almighty Allah, The Most Gracious and The Most Merciful

Special thanks to my family because of their love,
Pn Hjh. Rose Binti Hashim
Najihah Binti Razali
Muhammad Nazim Bin Razali
Nazirah Binti Razali

Lots of thanks to my friends, who guide and help me,
Last, but not least to my supervisor, thanks a lot

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ABSTRACT

Monoethanolamine (MEA) is commonly used in oil and gas industry as absorption medium to remove carbon dioxide (CO_2) from gaseous stream. Upon usage, the MEA solution is contaminated with hydrocarbon and suspended solids. Heavily contaminated MEA solution reduces its effectiveness in stripping the CO_2 gas and also causes foaming phenomenon in the CO_2 removal unit which further reduces the overall performance of the unit. There are many instances in which during operation, the solution overshoot and mix with condensed water in the knock-out drum. At this point, all the solution (the contaminated solution and the condensed water) is discharged as wastewater and replaced with fresh solution. It is common, in the range of 60 – 80 tons of MEA wastewater is generated per month. This study was conducted to examine the best method of treating the MEA wastewater for the best interest of the company. Characterization of the MEA wastewater suggested that the most rational way of treating the wastewater was to achieve quality suited for the purpose of recycling it back into the system. Adsorption method was used for the treatment with four different types of adsorbent, namely chitosan, activated carbon, alum and zeolite, were investigated. Five different variables, namely adsorbent dosage, pH, temperature, mixing time and mixing speed were varied to examine the effect on the parameters such as percentage of residue oil, suspended solids, MEA concentration and COD level. The results showed that chitosan was the best adsorbent in treating the MEA wastewater, followed by activated carbon, alum and zeolite. Adsorbent dosage was the main variable affecting the performance of the adsorbent in removing the residue oil, suspended solids and reducing the COD level. Chitosan indicated two mechanisms of adsorption in treating the MEA wastewater, in which at low adsorbent dosage chitosan functioned through chemical adsorption, while at high dosage, electrostatic adsorption started to accompany. In all adsorbents investigated in this study, MEA concentration was not affected by the adsorption treatment.

ABSTRAK

Monoethanolamine (MEA) digunakan secara meluas di dalam industri minyak dan gas sebagai medium penyerap gas karbon dioksida dari aliran gas. Setelah digunakan, MEA ini tercemar dengan hidrokarbon dan pepejal terampai. Larutan MEA yang tercemar teruk menjejas keberkesanannya untuk menyerap gas CO_2 dan mengakibatkan fenomena pembuihan di dalam turus penyerapan dan seterusnya mengurangkan prestasi keseluruhan turus penyerap CO_2. Di dalam banyak keadaan semasa operasi, larutan penyerap ini terlepas dari turus penyerap dan memasuki gelendung penampan dan bercampur dengan cecair pemeluwapan. Pada ketika itu, semua larutan tercemar ini di keluarkan dari sistem sebagai sisa buangan. Adalah kebiasaan antara 60 ke 80 tan sisa buangan MEA terhasil dalam sebulan. Kajian ini dijalankan untuk mengkaji kaedah yang terbaik untuk merawat sisa buangan MEA ini demi kebaikan industri yang terlibat. Pencirian sisa buangan ini menunjukkan bahawa kaedah yang terbaik untuk merawat sisa buangan ini adalah bagi mencapai kualiti yang menepati spesifikasi untuk dikitar semula ke dalam sistem penyerapan tersebut. Kaedah penjerapan digunakan untuk merawat dengan empat jenis penjerap iaitu chitosan, karbon aktif, alum dan zeolite telah dikaji. Lima pembolehubah yang berbeza iaitu dos penjerap , pH, suhu, masa percampuran dan kepantasan percampuran divariasikan untuk menguji kesan pengurangan kepada parameter seperti peratusan sisa minyak, pepejal terampai, kepekatan MEA dan tahap COD. Keputusan kajian menunjukkan bahawa chitosan memberikan keputusan yang terbaik dalam merawat sisa buangan MEA, diikuti oleh karbon aktif, alum dan zeolite. Jumlah dos penjerap yang digunakan semasa rawatan merupakan faktor utama yang mempengaruhi prestasi untuk menurunkan sisa minyak, pepejal terampai serta mengurangkan COD. Chitosan menunjukkan dua mekanisma penjerapan dalam merawat sisa MEA, di mana pada dos rendah, chitosan berfungsi melalui jerapan kimia manakala pada dos yang tinggi, tambahan jerapan secara elektrostatik akan berlaku. Di dalam kesemua jenis penjerap yang dikaji, kepekatan MEA tidak terjejas oleh proses penjerapan yang berlaku.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

MEA	Monoethanolamine Wastewater
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TS	Total Solids
SS	Suspended Solids
WSP	Waste Stabilization Ponds
DOE	Department of Environment
%DA	Degree of Deacetylation
^{o}C	Degree Celsius
mL	Milliliter
G	Gram
Min	Minute
Nm	Nanometer
mPa·S	mili pascal-second
w/w.	(an abbreviation for "by weight") the concentration of a substance in a mixture or solution
L	Litres
Rpm	Revolutions per minutes
wt%	Weight Percentage
mg/L	Concentration

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

In petrochemical industry, especially in natural gas processing plant, raw natural gas which contains carbon dioxide needs to be treated to remove the CO_2 prior to further processing activities. This CO_2 pose as interference in the processing activities and would thwart the product quality. Additionally, the CO_2 recovered from the process is often stored for other applications. For instance it can be used for enhanced oil recovery application or in the chemical and food industries. In other industries, CO_2 also has been removed from the flue gases before releasing the flue gases to atmosphere through stack. This is done to minimize the greenhouse effects and circuitously generate revenue to the company by selling the recovered CO_2. Technologies to separate CO_2 from flue gases are based on absorption, adsorption, membranes or other physical and biological separation methods. The most commercially used technology is amine based CO_2 absorption systems. The reasons being used widely are the system can be used for dilute systems and low CO_2 concentration, easy to use and can be retrofitted to any plants. Absorption processes are based on thermally regenerable solvents, which have a strong affinity for CO_2. The solvent is regenerated at elevated temperature, thus requires thermal energy for the regeneration (Paul *et al.*, 2007). Currently, aqueous monoethanolamine (MEA) is widely used for removing carbon dioxide and hydrogen sulfide from flue gas streams (Harold *et al*, 1998). It has been used in the Flour Daniel technology's Econamine FG^{TM} and Econamine FG Plus^{TM} (Mariz, 1998) and the ABB Lummus Global technology (Barchas, 1992).

The conventional MEA flow sheet is shown in Figure 1.1 The flue gas containing CO_2 enters the absorber and contacts an aqueous solution of MEA flowing counter currently to the flue gas stream. CO_2, a weak base, reacts exothermically with MEA, a weak acid, to form a water soluble salt. The 'rich' MEA stream exits the absorber at the bottom of the column. It is then preheated in a heat exchanger by the lean MEA stream leaving the stripper and enters the stripper where, with the further addition of heat, the reaction is reversed. The chemical solvent is regenerated in the stripper at elevated temperatures (100-140^{o}C) and a pressure not much higher than atmospheric. Heat is supplied to the reboiler using low-pressure steam to maintain regeneration conditions. This leads to a thermal energy penalty because the solvent has to be heated to provide the required desorption heat for the removal of the chemically bound CO_2 and for the production of steam, which acts as stripping gas. Steam is recovered in the condenser and fed back to the stripper, after which the produced CO_2 gas leaves the condenser. The 'lean' MEA is then recycled back to the absorber (Alie *et al.*, 2005).

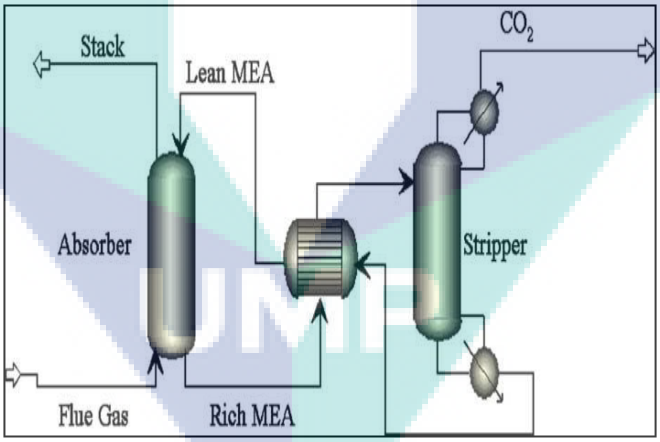


Figure 1.1: Basic MEA CO_2 capture process flow sheet

1.2 PROBLEM STATEMENT

MEA is an organic chemical compound which has both primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group). Like other amines, MEA acts as a weak base, toxic, flammable, corrosive, colorless and viscous liquid with an odor similar to ammonia. MEA is produced by reacting ethylene oxide with ammonia (Harold *et al*, 1998). By heating the aqueous solution, the covalent bonding between MEA and CO_2 will break and releases CO_2 as gaseous state. As the MEA left in aqueous solution, any treatment methods imply would be ease due to ions mobilisation in the solution.

Focusing on the CO_2 absorption process, the heavy hydrocarbon component could be carried over to the absorber with the feed gas which caused sudden foaming in the absorber. The reaction between CO_2 and MEA will produce some salt and increased the amount of suspended solids in absorber also contributed to the foaming problem. This foaming phenomenon give a number of different problems such as decreased absorption efficiency, increased amine losses, reduced quality of product gas and MEA somehow is not appropriate to feed back into the stripper due to properties deterioration and thus give difficulties in optimizing the absorption processes and it has been removed as wastewater.

Once the MEA wastewater entering the wastewater treatment plant (WTP), it will upset the WTP by increasing the loading and significantly increase the chemical oxygen demand (COD), oil contents and suspended solids which complicates the effective treatment of such wastewater. In many occasions, the concentration of amine in the wastewater triggers the COD to exceed the 200,000 ppm level and not possible to be sent to the wastewater treatment plant. The MEA wastewater then has to be stored for disposal and conversely, it costs a lot of money for waste disposal handling, to buy fresh MEA and thus, minimizes the profit margin. From the industrial survey, every petrochemical plant in Malaysia were produce 60-80 tonnes per upset cases and currently, this MEA wastewater were disposed to Kualiti Alam. Furthermore, this MEA wastewater were classified as scheduled waste, so the cost to dispose this wastewater was very expensive approximately RM 3000.00 per tonne. Besides that, the petrochemical plants need to buy new fresh MEA to replace the MEA wastewater at the CO_2 absorber system which is very costly approximately RM 2760.00 per drum. So, this MEA wastewater was contributed to increase disposal cost and influenced to the financial of the petrochemical companies.

Several researches have been conducted and suggested a few methods to treat MEA wastewater. The researches were not limited to aliphatic amine but up to aromatic amine used as targeted sample. Generally, the treatment methods to separate amine from wastewater are based on physical, chemical and biological separation methods. Wang *et al.* (2007) has illustrated that biological treatment of isolating strain bacteria by using activated sludge of a complex bio-denitrification system (CBDS) for treating petrochemical wastewater in Northeastern China capable of degrading pentyl amine up to 82%. For maximum degradation efficiency, the strain required a neutral pH, full aeration of 6 mg O_2/L and temperature of 30^oC. Under such conditions, two stage treatment systems is required to reach 99% degradation of pollutant representing the required standards for surface water discharge. On the other hand, when the oil refinery activated sludge was inoculated with the strain bacteria, 93% of pentyl amine was degraded. Nevertheless, several disadvantages were identified for instance, it takes longer time (24 hours) and inadequate to degrade high concentration of pentyl amine in petrochemical wastewater. In addition, further research needs to be carried out to clarify and demonstrate the limitation and findings.

In chemical treatment method, several researchers have suggested the conversion of amine into their corresponding acetates in excellent yields. Das and Thirupathi (2007) have illustrated the treatment of amine (aliphatic and aromatic) with acetic anhydride at room temperature using $NaHSO_4.SiO_2$ as heterogeneous catalyst affords the corresponding acetates in excellent yields. Meanwhile, Joseph *et al.* (2007) has proposed the conversion of amine into acetates using acetic anhydride and Alumina supported MoO_3 as heterogeneous catalyst and found that about 90% yield was attained. They also found that the catalyst indicating the recyclability and reusability without loss of reaction activity. Both researchers have not mentioned the used of MEA wastewater as studied subject and intentionally focusing on virgin amine solvent for the preparation of bioactive natural products. In the physical treatment method, several researchers have suggested the usage of adsorbents for the removal and recovery of the amines. Boger *et al*. (1997) has demonstrated that the removal and recovery of amines emmited from foundry can be performed by an adsorptive process. Activated carbon and hydrophobic zeolite can be used as adsorbents. However, in both cases a loss in capacity due to chemisorption is found. Moreover, the studies has shown that the adsorbent can be regenerated by adding small amounts of a purge gas and at condition of 100 mbar vacuum conditions.

The potential of using chitosan as alternative adsorbent for the treatment of MEA wastewater is becoming a research interest field in the near future. It has been proven that this adsorbent has the capability to adsorb metal ions, oil and grease and improve wastewater quality (Ahmad *et al*, 2006). Chitosan also has potential as an adsorbent for removal of reactive dyes from textile wastewater because it can adsorb reactive dyes over wide pH range and at high temperatures. The effect of initial pH, elution studies, and the thermodynamic parameters demonstrated that the reactive dye was probably adsorbed onto chitosan by both physical and chemical adsorption. In addition, the adsorption mechanism under acidic conditions was chemical adsorption, while under caustic conditions was both physical and chemical adsorption. However, the ATR-FTIR spectra confirmed that the amines on chitosan polymer tend to be effective functional groups for dye adsorption under acidic conditions, while the hydroxyl group tended to be the effective functional group for dye adsorption under caustic conditions (Niramol et al, 2005). The literature on the interaction of chitosan with those contaminations has been discussed elsewhere (Guibal, 2004; Evans *et al*, 2002). Due to chemisoption and structure properties of chitosan, the adsorbent is believed capable to treat MEA wastewater tremendously.

From the literatures point of view, researches on treatment of MEA wastewater from petrochemical plant are insufficiently conducted especially for recycle purpose. In view of the fact that, no work has been done in the literature regarding the treatment of MEA wastewater using chitosan, activated carbon, alum and zeolite. Furthermore, not many studies were been done using real effluent, whereby these studies were done using homemade synthetic effluent. Besides that, this research was also evaluating the potential of recycling the treated MEA wastewater and reuse in the CO_2 removal unit. The physical treatment methods would be the interesting research field due to simple, easy, shorter time, economically viable to be commercialized and widely used in wastewater treatment plant.

Based on industrial survey, four types of adsorbents commonly used in wastewater treatment industries which are chitosan, activated carbon, alum and zeolite based adsorption method were selected, employed and explored in order to examine its feasibility in reducing the COD, suspended solid, oil concentration in the MEA wastewater and at the same time maintaining the level of amine concentration at acceptable limit. These parameters evaluation were very crucial in determining the treated MEA could be recycled or else. In view of the fact that the MEA wastewater is produced abundantly from petrochemical plants and other processing plants for instance power plant, and the lack of researches have been carried out to date, the research needs is significantly important in order to find alternative route methods for treating MEA wastewater which is inexpensive, simple, economically viable and environmental friendly. Due to this, chitosan is believed to be the best natural adsorbent to reduce COD, suspended solid and remove oil from MEA wastewater rather than other adsorbents.

1.3 OBJECTIVES

The objectives of this research are:

1. To suggest the best adsorbent and process condition in treating MEA wastewater from the petrochemical processing plants via adsorption method.

2. To study the potential of recycling the treated MEA wastewater and to reuse the treated MEA wastewater based on typical standard MEA usage in the CO_2 removal unit.

1.4 SCOPE OF THE STUDY

In achieving the objectives stated above, several scopes of work have been identified:

1. To characterise the Monoethanolamine (MEA) wastewater produced from petrochemical plant.

2. To compare the effectiveness of the treatment using the different type of absorbents (Chitosan, Activated Carbon, Zeolite, Alum) in reducing COD, suspended solid, oil content from MEA wastewater, and maintaining amine concentration level.

3. To examine the mechanism of adsorption for each technique in reducing the measured parameters.

4. To study the influence of dosage, pH, temperature, mixing time, mixing speed, performance of Chitosan flake and powder for treatment process of MEA wastewater.

1.5 THESIS OUTLINE

The organisation of the thesis reflects the sequence of the objectives as discussed previously and entails five chapters. Chapter 1 serves as general introduction and is intended to provide the background, the objectives and the scopes.

Chapter 2 presents the literature reviews. Chapter 3 contains materials and methods of the research. All materials, experimental procedures and analytical methods used throughout this study in this chapter.

In order to achieve the objectives and scopes of this study, Chapter 4 elaborates them. Finally, Chapter 5 presents the conclusion of the study. Future work and recommendation on this study was also being suggested.

1.6 SIGNIFICANCE OF RESEARCH

The main aim of this study was to study a feasible method, investigate the potential and effectiveness of chitosan, activated carbon, alum and zeolite in removing oil, suspended solid and reducing COD from MEA wastewater. The research was also evaluating the potential of recycling the treated MEA wastewater and reuse in the CO_2 removal unit. This study concentrated on raw samples of MEA wastewater from oil and gas industry.

1.7 CHAPTER SUMMARY

In this chapter, detailed explanations of the early step in the process of designing the research have been presented. This explanation will be helpful in supporting this research work. Thus the objectives of the research will be in proper guidelines to be achieved. The literature review will be explored in the next chapter.

CHAPTER 2

LITERATURE REVIEW

Literature reviews provide a handy guide and a solid background to a particular topic. This chapter explores the subtopic of introduction of wastewater treatment, monoethanolamine (MEA) wastewater, adsorption theory, mechanism and types of adsorbents. This discussion concerns the works of the previous researches that related to this research.

2.1 INTRODUCTION OF WASTEWATER TREATMENT

Wastewater is any water that has been adversely affected in quality by any anthropogenic influence. It therefore includes liquid waste discharged from domestic houses, industrial, agricultural or commercial processes. It does not include rain-water uncontaminated by human activities.

In water and wastewater treatment processes, substances which cause troubles in the systems utilizing water and pollute the environment are removed from water. Removed suspended solids through water and wastewater treatment processes are discharged as sludge with high water content. Sludge treatment is carried out to prevent the sludge from causing the environmental pollution and the other problems again. As water includes many kinds of dissolved solids and suspended solids, suitable water treatment methods have to be selected according to the water quality to be treated (Kurita, 1999).

Wastewater treatment methods are generally classified into three categories which are:

- i. mechanical treatment
- ii. chemical treatment
- iii. biological treatment

2.1.1 Mechanical Treatments

Mechanical wastewater and sludge treatment methods are classified as shown in Figure 2.1.

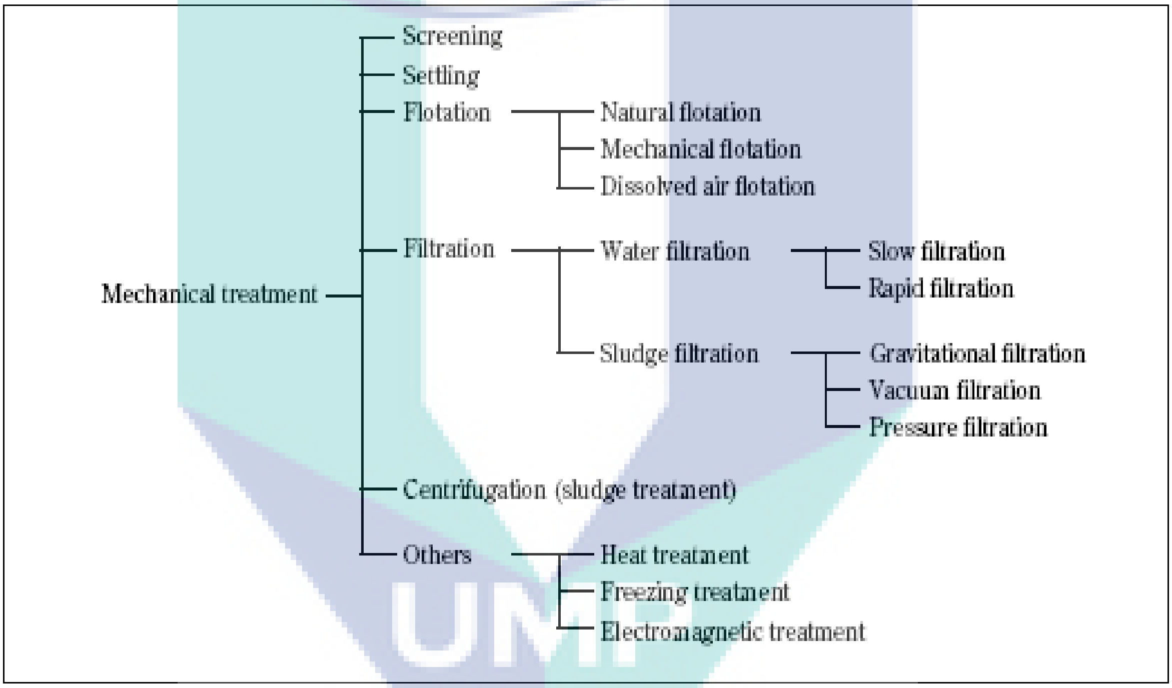


Figure 2.1: Classification of mechanical wastewater and sludge treatment methods (Kurita, 1999)

2.1.1.1 Screening

Screening is the first step of water and wastewater treatment to remove large matter by using screening bars or net to protect downstream structures, such as pumps, pipings and filters. Generally, the screening effectively removes the matter of large size and low specific gravity such as pieces of wood, plastics and papers.

2.1.1.2 Settling

Suspended solids having larger densities than that of water are settled to separate from water. Factors which determine the settling velocity of suspended solids are mainly the diameter and density of particles, and the viscosity of solution. The suspended solids of small size and colloids which are hardly settled under natural conditions are settled after forming their flocs through coagulation and flocculation treatment by using coagulants and flocculants.

2.1.1.3 Flotation

Substances having the almost same or lower densities than that of water, such as oils and fats, are separated from water by flotation. The flotating velocity of particles is also expressed in the Stokes' equation. Therefore, particles which have the large size and small density are easily floated under natural conditions. Mechanical flotation and dissolved air flotation are applied to increase the flotating velocity of particles. In those processes, fine airbubbles are generated in water. Then the adhesion of bubbles with particles and the upward-flow of bubbles improve the flotation efficiency. Generally, the pressurizing of water and its releasing are applied to generate microbubbles efficiently.

2.1.1.4 Filtration

Slow filtration applies to purify surface waters without prior coagulation or settling. The filtration rate is generally lower than 1 $m^3/m^2 \cdot day$. Rapid filtration uses to treat drinking water, industrial water and wastewater. Generally, it applies after coagulation or flotation process. It is also used for the filtration of in-line coagulated water. The filtration rate is in the range of 4 to 50 $m^3/m^2 \cdot day$. For sludge filtration, many kinds of vacuum filters and pressure filters are applied.

2.1.1.5 Centrifugation

Centrifugation is a separation method which utilizes centrifugal force to accelerate the settling of particles in a liquid-solid mixture. This method usually uses for dewatering of sludges or for treating wastewater including high concentration of suspended solids (Kurita, 1999).

2.1.2 Chemical Treatment

Chemical treatment is generally applied to carry out mechanical treatment, such as settling, flotation and filtration, more efficiently. It is also used for treating waters which are difficult to treat sufficiently by mechanical treatment only. Figure 2.2 shows the classification of chemical treatment methods and the kinds of typical chemicals to be applied (Kurita, 1999).

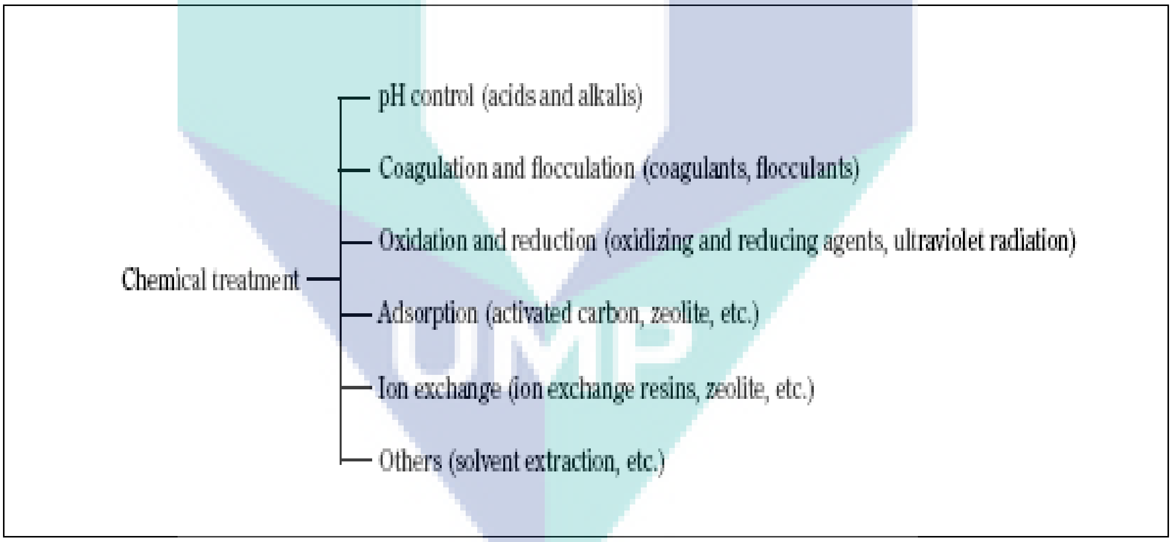


Figure 2.2: Classification of chemical water and wastewater treatment methods (Kurita, 1999)

2.1.2.1 pH control

The solubilities of some substances in water are remarkably changed by the pH change. For example, the solubility of ferric ion or aluminum ion is sufficiently reduced to form the hydroxide precipitate in a specified pH range. This method often applies to separate metallic ions from water and wastewater. The pH control of water is also an important measure to carry out coagulation, flocculation, oxidation, reduction treatments and so on efficiently.

2.1.2.2 Coagulation and flocculation

Coagulation and flocculation treatment is a method to aggregate fine particles and colloids dispersed stably in water and to make their large flocs which are easily separated from water through settling, flotating processes and so on. Ferric salts and aluminum salts are usually used as coagulants. High molecular weight synthetic polymers are used as flocculants. Coagulants neutralize the surface electrical charges of particles and break their stable dispersion in water. Flocculants combine with neutralized particles and form large flocs. Thickeners, flotators, filters, etc. are used for separating those flocs from water.

2.1.2.3 Oxidation and reduction

Oxidation treatment is applied to decompose cyanides, nitrites and various organic substances to harmless substances. It is also used for oxidizing ferrous ion in underground water to ferric ion which is easily precipitated as the ferric hydroxide. The pH and temperature of water should be adjusted within the suitable ranges for proceeding the oxidation and reduction processes efficiently.

2.1.2.4 Adsorption

Activated carbon adsorbs various organic substances in water. Recently, special adsorbents which selectively adsorb specified heavy metal ions, etc., are also used for water and wastewater treatment. Usually, adsorbants are filled in fixed-bed or fluidizedbed, and water to be treated passes through the bed. In a batch treatment, adsorbants are added into water and are separated by settling or filtration after the completion of adsorption. The adsorbants after used are regenerated or disposed after making them harmless by solidification, etc.

2.1.2.5 Ion exchange

In ion exchange process, ions in solution are exchanged with those of ion exchanger such as ion exchange resin. The ion exchanger approaching the full capacity is regenerated and reused. In water treatment, ion exchangers are largely utilized for removing hardness from water (softening) and producing demineralised water. In wastewater treatment, they are applied for removing toxic substances, such as heavy metals, and recovering valuable materials from wastewater.

2.1.3 Biological Treatment

Biological treatment is a means of decomposing organic substances in wastewater by utilizing the functions of microorganisms. Biological treatment is largely divided into aerobic and anaerobic treatments as shown in Figure 2.3.

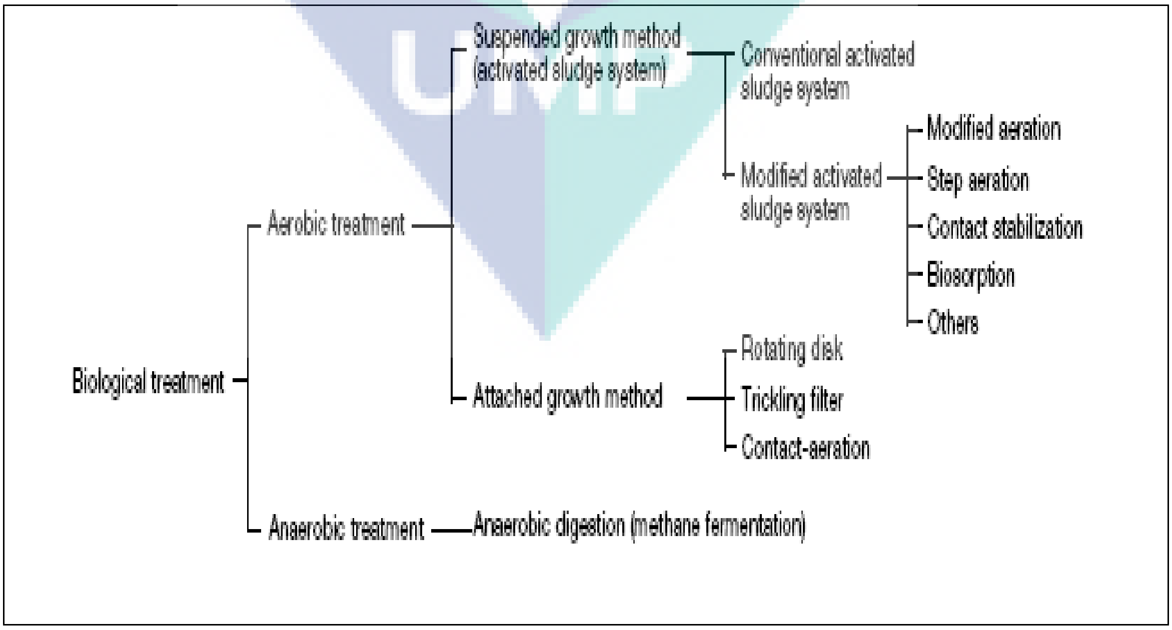


Figure 2.3: Classification of biological wastewater treatment methods (Kurita, 1999)

2.1.3.1 Aerobic treatment

Aerobic treatment is a way of oxidizing and decomposing organic substances in wastewater by using aerobic or facultative anaerobic bacteria. It is also called biological oxidation. Organic substances are oxidized and decomposed by enzyme reactions of microorganisms and produce energy. Microorganisms multiply using a portion of the energy and organic substances. The excess of microorganisms grown must be separated and disposed as the excess sludge. In activated sludge system, wastewater is mixed with microbial flocs (activated sludge) in the aeration tank to decompose the organic substances by supplying air (oxygen) to the mixed liquor. The mixed liquor is separated in the sedimentation tank and the precipitated activated sludge is returned to the aeration tank (Kurita, 1999).

The supernatant water is discharged as treated water. In activated sludge treatment, it is the most important thing to maintain a suitable environment for the activity of microorganisms. When the environment becomes an improper and the microbial activity is decreased, the efficiency of removing organic substances is reduced or an insufficient separation of sludge from water (bulking) may occur. The suitable operation conditions of activated sludge system are generally as follows;

i. pH = 6–8
ii. Temperature = 15–30^{o}C
iii. Dissolved oxygen= more than 0.5 mg/l
iv. BOD load = 0.2–0.6 kg BOD/kg MLSS·day

2.1.3.2 Anaerobic treatment

This treatment method is also called anaerobic digestion or methane fermentation, and utilizes anaerobic bacteria to decompose organic substances. Wastewater or sludges are introduced into a closed tank which is kept under anaerobic conditions and sometimes warmed to enhance the digestion. The retention time in the tank is from several days to several tens of days. Anaerobic treatment is generally suitable for the treatment of wastes containing high concentrations of organic substances.

2.1.4 Flowsheet of Wastewater and Sludge Treatments

Various pollutants are contained in wastewaters. Therefore, mechanical, chemical and biological treatment methods are usually combined to treat them depending on the quality and quantity of the water. Figure 2.4 shows a typical flowsheet of wastewater and sludge treatments including the applicable chemicals (Kurita, 1999).

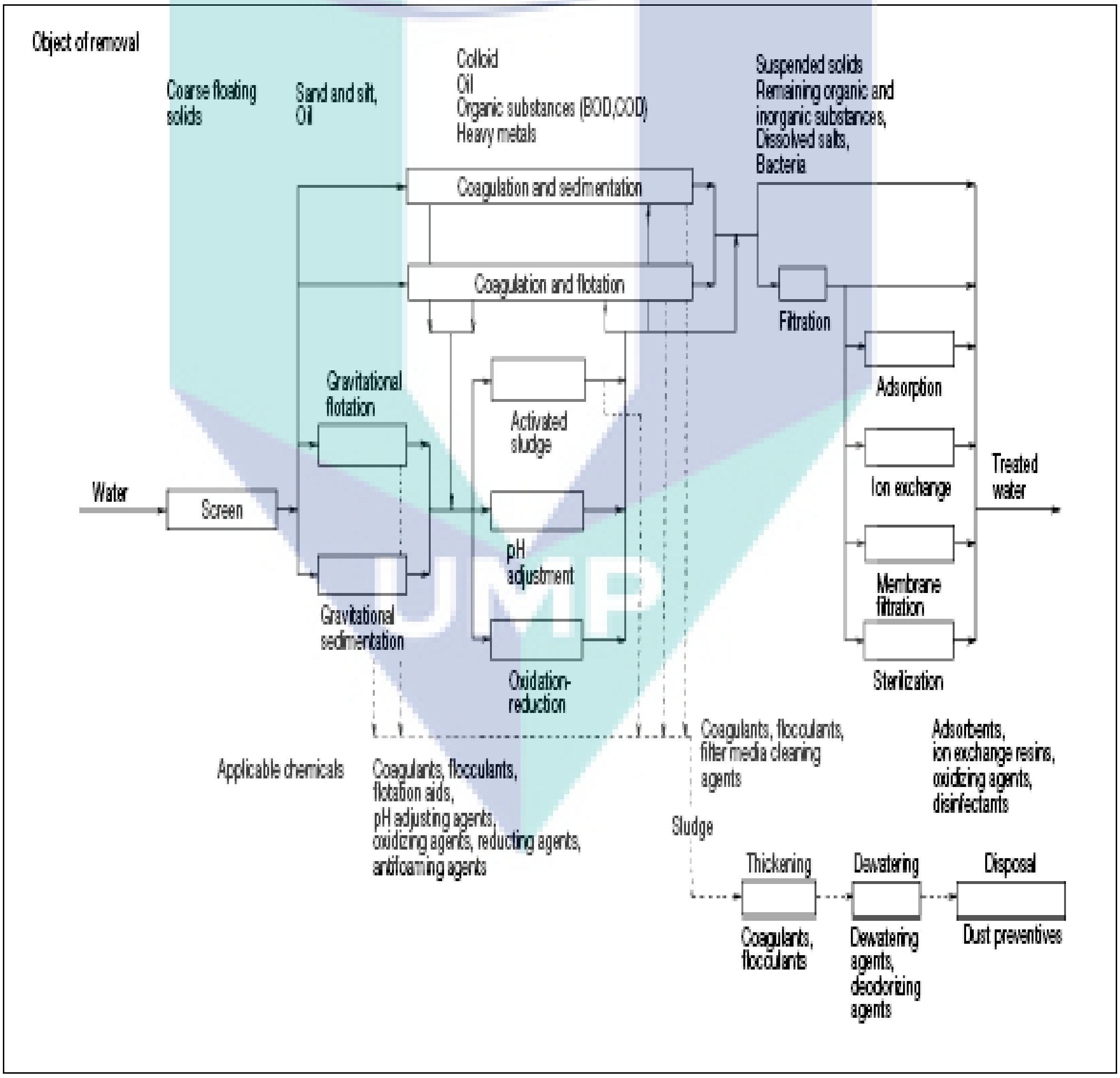


Figure 2.4: Example of wastewater treatment processes and chemicals to be applied (Kurita, 1999)

2.1.5 Effect of wastewater to the environment.

There has been a widespread awareness for a cleaner environment. The major sources of pollution can be from water and air. Toxic chemicals, harmful bacteria, unwanted solid waste and most of these can be classified as organic & inorganic waste. When organic waste enters into the stream, it will stimulate bacterial growth that affects aquatic life forms by depleting the quantity of oxygen level in the water.

The stream becomes septic due to bacteria undergoing anaerobic metabolism, producing odors and darkening the water appearance. The inorganic wastes such as copper, nickel, lead, when entered into the stream, are basically toxic substances that cannot be further broken-down by the bacteria and can be poisonous to human health & aquatic life forms. There is some common type of pollution effected by wastewater:

i. Total Solids is the sum of suspended solids and dissolved solids.

ii. Suspended solids are those that can be removed by filtration.

iii. Biodegradable organic. Those that can be broken down by micro- organism to form stable compounds such as CO_2 and water.

iv. Effluent is the liquid product discharged or emerging from a process.

v. COD (Chemical Oxygen Demand) - It is the amount of oxygen (usually measured in mg/1 (milligram per litre) required to oxidize both organic and oxidizable inorganic compounds.

vi. BOD (Biochemical Oxygen Demand) - It is the amount of oxygen (mg/1) required by micro-organism to consume biodegradable organic in waste-water.

2.1.6 The principle of commercialize waste water treatment

Wastewater treatment is the process that removes the majority of the contaminants from waste-water or sewage and produces both a liquid effluent suitable for disposal to the natural environment and sludge. To be effective, sewage must be conveyed to a treatment plant by appropriate pipes and infrastructure and the process itself must be subject to regulation and controls. Other wastewaters require often different and sometimes specialized treatment methods. Figure 2.5 shows a typical wastewater treatment plant flow.

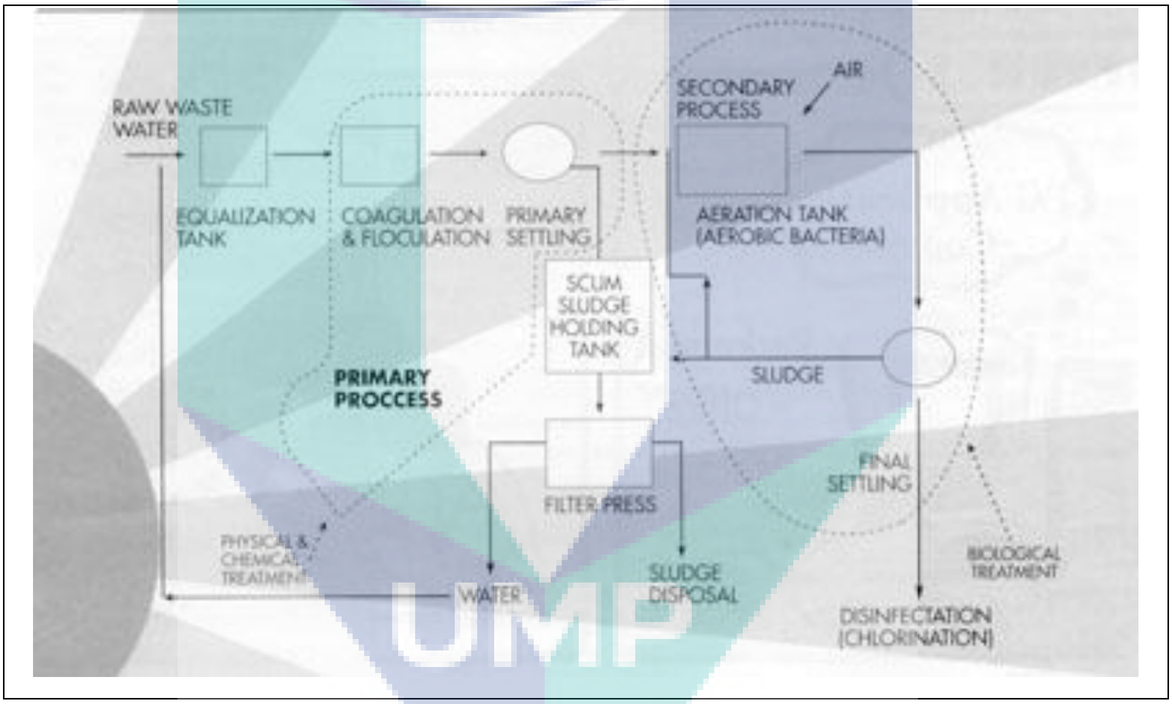


Figure 2.5: Typical Wastewater Treatment Plant Flow (Kurita, 1999)

Firstly for commercialize waste water treatment raw wastewater will flows into the equalization tank then into the primary process (Physical Chemical Treatment). This process will basically involve in two chemicals. A coagulant, usually an inorganic substance, is used to destabilize the electrostatic repulsive forces which tend to keep colloidal and soluble suspension particles apart and prevent them from gathering together.

After that, the flocculants, usually organic in nature, must be added to combine the particles into bigger flocs, which can then be more easily floated or settled. In a well-designed system there should have proper flowrate that allows the coagulant to have sufficient time to destabilize the repulsive forces before the flocculant is added. In the aeration (Biological Treatment) basin, organic matter will acts as food supply for bacteria to metabolize the waste solids resulting in absorbing oxygen (BOD) and releasing CO_2. The process removes organic matter from solution by synthesis into microbial cells. Then it will transfer to a clarifier for separation of the sludge and effluent.

The sludge is pollutants then converted into concentrated form. This sludge has to be further treated in order to prevent further pollution of waterways. The basic aim of sludge treatment is to reduce the volume and destroy or stabilize sludge solids before final disposal. The chlorination of water and wastewater is to disinfect & destroy Pathogens and control microorganisms. Chlorine is also used for oxidation where the oxidant used is iron and manganese. In general when the water appeared to be cloudy as a result of many suspended particles floating & the electrical repulsive charge is actually holding the particles in suspension. After that, the next process occur called coagulation and flocculation process.

2.2 MONOETHANOLAMINE (MEA)

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as MEA), is an organic chemical compound, which is both a primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group). Like other amines, monoethanolamine acts as a weak base. Ethanolamine is a toxic, flammable, corrosive, colourless, viscous liquid with an odour similar to ammonia. Refractive index of ethanolamine is 1.4539. Ethanolamine is commonly called monoethanolamine or MEA to distinguish it from diethanolamine (DEA) and triethanolamine (TEA). Monoethanolamine is produced by reacting ethylene oxide with ammonia. Further treatment with ethylene oxide can yield DEA and/or TEA. Ethanolamine is the second most abundant head group for phospholipids, substances found in biological membranes (Harold *et al.*, 2004).

Ethanolamine also refers to a class of antihistamines containing an ethyl-amine group attached to a diphenyl structure. Examples of drugs within this class include diphenhydramine (Benadryl), phenyltoloxamine (Percogesic), and doxylamine (Unisom Sleep Tablets). They are one of the oldest classes of antihistamine drugs, yet remain the most effective for treating allergy symptoms, even exceeding the effectiveness of new OTC and prescription antihistamines such as loratadine (Claritin) and Fexofenadine (Allegra). However, all ethanolamines are extremely sedating, even more so than many barbiturates. For this reason, they are not always desirable drugs for treatment, and less-effective drugs are indicated to avoid the substantial drowsiness inherent in ethanolamines. On the other hand, they are such effective sedatives that they are marketed as over-the-counter sleep-aids in addition to anti-allergy medications (Harold *et al.*, 2004).

2.2.1 Production of Monoethanolamine (MEA)

Monoethanolamine is produced by reacting ethylene oxide with aqueous ammonia; the reaction also produces diethanolamine and triethanolamine. The ratio of the products can be controlled by changing the stoichiometry of the reactants (Klaus *et al.*, 2003). Figure 2.6 shows the reaction between ethylene oxide and ammonia.

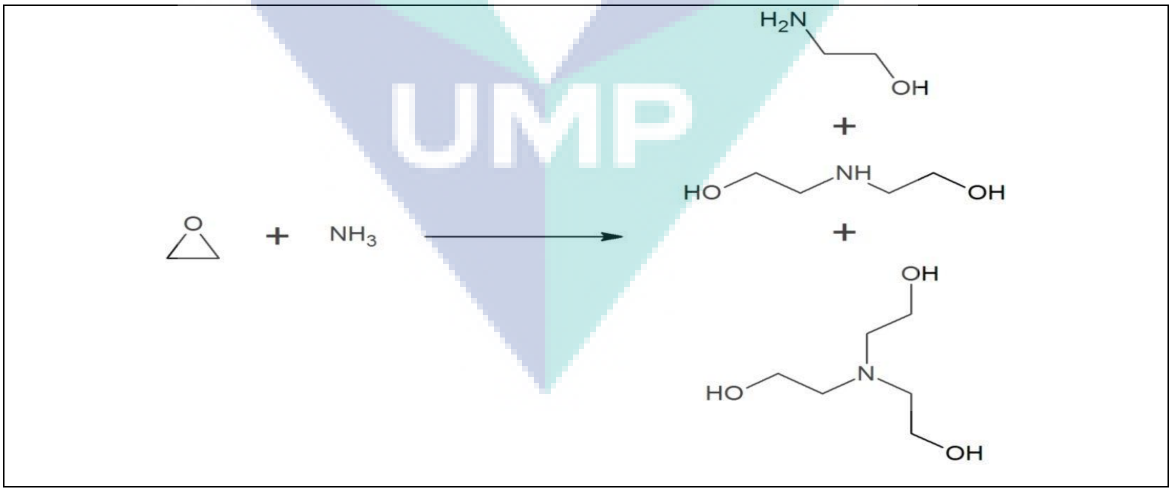


Figure 2.6: Reaction between Ethylene Oxide and Ammonia

2.2.2 Application of Monoethanolamine (MEA)

MEA is used in aqueous solutions for scrubbing certain acidic gases and is also used in surface active agents, emulsifiers, polishes, pharmaceuticals, corrosion inhibitors, chemical intermediates. In pharmaceutical formulations, MEA is primarily used for buffering or preparation of emulsions (Klaus *et al.*, 2003).

Aqueous solutions of MEA (solutions of MEA in water) are used as a gas stream scrubbing liquid in amine treaters. For example, aqueous MEA is used to remove carbon dioxide (CO_2) from flue gas. Aqueous solutions can weakly dissolve certain kinds of gases from a mixed gas stream. The MEA in such solutions, acting as a weak base, then neutralises acidic compounds dissolved in the solution to turn the molecules into an ionic form, making them polar and considerably more soluble in a cold MEA solution and thus keeping such acidic gases dissolved in this gas-scrubbing solution. Therefore, large surface area contact with such a cold scrubbing solution in a scrubber unit can selectively remove such acidic components as hydrogen sulfide (H_2S) and CO_2 from some mixed gas streams. For example, basic solutions such as aqueous MEA or aqueous potassium carbonate can neutralize H_2S into hydrosulfide ion (HS^-) or CO_2 into bicarbonate ion (HCO_3^-). H_2S and CO_2 are only weakly acidic gases. An aqueous solution of a strong base such as sodium hydroxide (NaOH) will not readily release these gases once they have dissolved. However, MEA is rather weak base and will re-release H_2S or CO_2 when the scrubbing solution is heated. Figure 2.7 shows the typical CO_2 adsorption system in oil and gas industry.

Figure 2.7: CO_2 adsorption system

Therefore, the MEA scrubbing solution is recycled through a regeneration unit which heats the MEA solution from the scrubber unit to release these only slightly acidic gases into a purer form and returns the regenerated MEA solution to the scrubber unit again for reuse (Klaus *et al.*, 2003).

2.3 ADSORPTION

Adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbate accumulates. The adsorption process has not been used extensively in wastewater treatment, but demands for better quality of treated wastewater effluent, including toxicity reduction and has led to an intensive examination (Metcalf and Eddy, 2003).

The driving force for adsorption is unsaturated forces at the solid surface which can form bonds with the adsorbate. The forces are typically electrostatic, covalent bonding or van der Waals interactions (reversible). Stronger interactions involve direct electron transfer between sorbate and the sorbent (irreversible). The strength of this interaction dictates the relative ease or difficulty in removing (desorbing) the adsorbate for adsorbent regeneration and adsorbate recovery. Figure 2.8 shows the adsorption phenomenon in the suspensions.

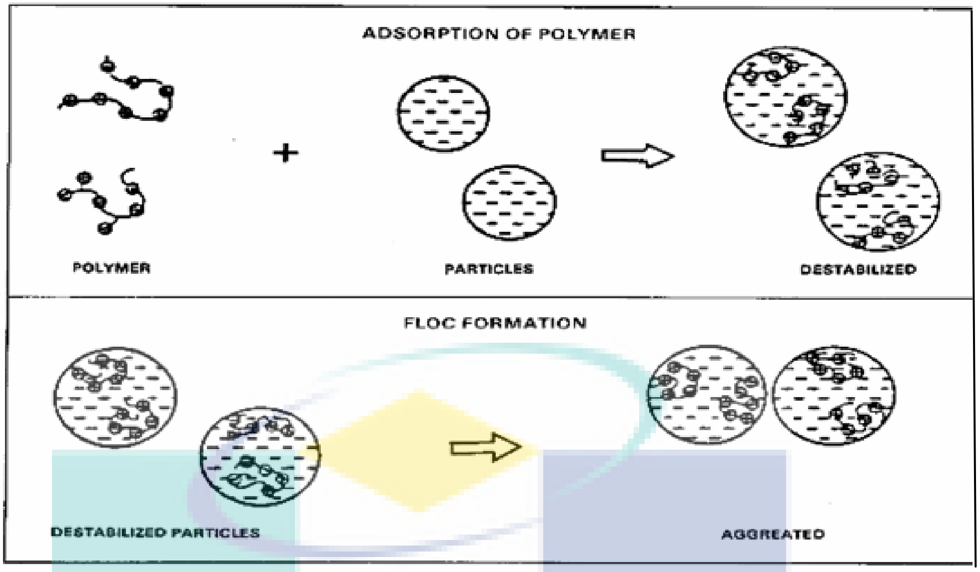


Figure 2.8: Adsorption phenomenon

The selective nature of the adsorbent is primarily due to the relative access and strength of the surface interaction for one component in a feed mixture. The solid is the mass-separating agent and the separating mechanism is the partitioning between the fluid and solid phase. An energy separating agent, typically a pressure or temperature change, is used to reverse the process and regenerate the sorbent (Richard and Patricia, 2004). Adsorption processes are used economically in a wide variety of separations in the chemical process industries. Activated carbon is the most common adsorbent with annual worldwide sales estimated at $380 million (Keller, 1995). One common adsorption process is dehydration for the drying of gas stream.

2.3.1 Adsorption Mechanism

Adsorption occurs when molecules diffusing in the fluid phase are held for a period of time by forces emanating from an adjacent surface. The surface represents a gross discontinuity in the structure of the solid, and atoms at the surface have a residue of molecular forces which are not satisfied by surrounding atoms such as those in the body of the structure. These residual or van der Waals forces are common to all surfaces and the only reason why certain solids are designated “adsorbents” is that they can be manufactured in a highly porous form, giving rise to a large internal surface. In comparison the external surface makes only a modest contribution to the total, even when the solid is finely divided. Iron oxide particles with a radius of 5 µm and a density of 5000 kg/m3 have an external surface of 12,000m^2/kg. A typical value for the total surface of commercial adsorbents is 400,000m^2/kg (Richardson *et al.*, 2002).

The adsorption which results from the influence of van der Waals forces is essentially physical in nature. Because the forces are not strong, the adsorption may be easily reversed. In some systems, additional forces bind absorbed molecules to the solid surface. These are chemical in nature involving the exchange or sharing of electrons, or possibly molecules forming atoms or radicals. In such cases the term chemisorption is used to describe the phenomenon.

This is less easily reversed than physical adsorption, and regeneration may be a problem. Chemisorption is restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules (Richardson *et al.*, 2002). Figure 2.9 shows the adsorption formation process.

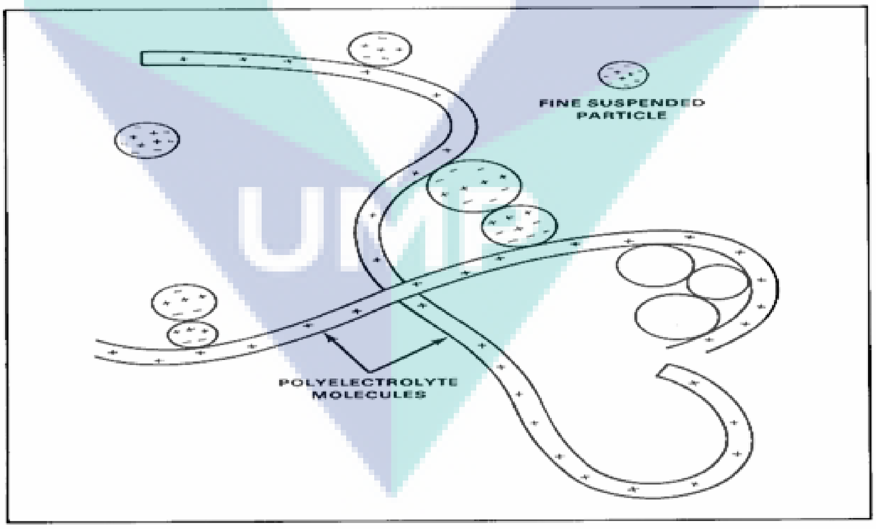


Figure 2.9: Adsorption formation process

When molecules move from a bulk fluid to an adsorbed phase, they lose degrees of freedom and the free energy is reduced. Adsorption is always accompanied by the liberation of heat. For physical adsorption, the amount of heat is similar in magnitude to the heat of condensation. For chemisorption it is greater and of an order of magnitude normally associated with a chemical reaction. If the heat of adsorption cannot be dispersed by cooling, the capacity of the adsorbent will be reduced as its temperature increases (Richardson *et al.*, 2002). Table 2.1 shows the summary of typical of commercial adsorbents used in the oil and gas industry.

Table 2.1: Typical applications of commercial adsorbents

Type	Typical applications
Silica gel	Drying of gases, refrigerants, organic solvents, transformer oils; desiccant in packings and double glazing; dew point control of natural gas.
Activated alumina	Drying of gases, organic solvents, transformer oils; removal of HCl from hydrogen; removal of fluorine and boron-fluorine compounds in alkylation processes.
Carbons	Nitrogen from air; hydrogen from syn-gas and hydrogenation processes; ethene from methane and hydrogen; vinyl chloride monomer (VCM) from air; removal of odours from gases; recovery of solvent vapours; removal of SO_x and NO_x; purification of helium; clean-up of nuclear off-gases; decolourising of syrups, sugars and molasses; water purification, including removal of phenol, halogenated compounds, pesticides, caprolactam, chlorine.
Zeolites	Oxygen from air; drying of gases; removing water from azeotropes; sweetening sour gases and liquids; purification of hydrogen; separation of ammonia and hydrogen; recovery of carbon dioxide; separation of oxygen and argon; removal of acetylene, propane and butane from air; separation of xylenes and ethyl benzene; separation of normal from branched paraffins; separation of olefins and aromatics from paraffins; recovery of carbon monoxide from methane and hydrogen; purification of nuclear off-gases; separation of cresols; drying of refrigerants and organic liquids; separation of solvent systems; purification of silanes; pollution control, including removal of Hg, NO_x and SO_x from gases; recovery of fructose from corn syrup.
Polymers and resins	Water purification, including removal of phenol, chlorophenols, ketones, alcohols, aromatics, aniline, indene, polynuclear aromatics, nitro- and chlor-aromatics, PCB, pesticides, antibiotics, detergents, emulsifiers, wetting agents, kraftmill effluents, dyestuffs; recovery and purification of steroids, amino acids and polypeptides; separation of fatty acids from water and toluene; separation of aromatics from aliphatics; separation of hydroquinone from monomers; recovery of proteins and enzymes; removal of colours from syrups; removal of organics from hydrogen peroxide.
Clays (acid-treated and pillared)	Treatment of edible oils; removal of organic pigments; refining of mineral oils; removal of polychlorobiphenyl (PCB).

2.3.2 Chemical Bonding

The number of electrons in the outer, or valence, shell determines the relative activity of the element. The arrangement of electrons in the outer shell explains why some elements are chemically very active, some are not very active, and others are inert. In general, the fewer electrons an element must lose, gain, or share to reach a stable shell structure, the more chemically active the element is. The likelihood of elements forming compounds is strongly influenced by the completion of the valence shell and by the stability of the resulting molecule. The more stable the resulting molecules are, the more likely these molecules are to form. For example, an atom that "needs" two electrons to completely fill the valence shell would rather react with another atom which must give up two electrons to satisfy its valence.

In the case of $H^+ + Br^-$, this is likely to take place because the exchange would satisfy the needs of both atoms. Although there is far more to consider than just the number of valence electrons, this is a good rule of thumb.

If the atom needed two electrons and only picked up one, it would still actively seek out an additional electron. The reaction of $H^+ + Te^{-2}$ is far less likely to take place because the resulting molecule would still have an incomplete valence shell. Of course, the combining of two atoms, when both want to release or gain electrons, may take place (for example; H_2 or O_2) but is less probable when other atoms are available.

Atoms are joined or bonded together through this interaction of their electrons. There are several types of chemical bonds that hold atoms together; three will be discussed, ionic, covalent, and metallic (Kurita, 1999)

2.3.2.1 Ionic Bond

An ionic bond is formed when one or more electrons is wholly transferred from one element to another, and the elements are held together by the force of attraction due to the opposing charges. An example of ionic bonding is shown in Figure 2.10 (A) for sodium chloride.

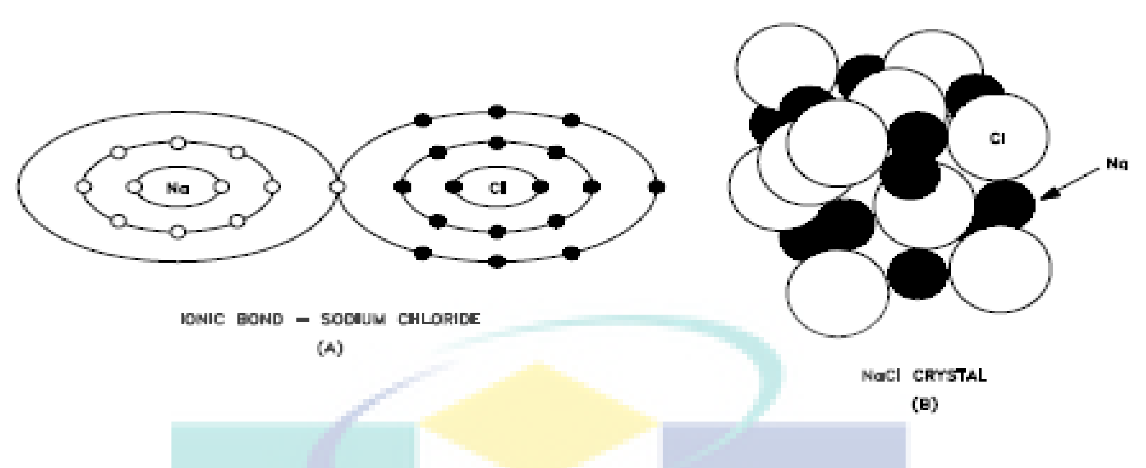


Figure 2.10: Ionic Bond, sodium chloride

The sodium atom loses the one electron in its outer shell to the chlorine atom, which uses the electron to fill its outer shell. When this occurs, the sodium atom is left with a +1 charge and the chlorine atom a -1 charge. The ionic bond is formed as a result of the attraction of the two oppositely-charged particles. No single negatively-charged ion has a greater tendency to bond to a particular positively-charged ion than to any other ion. Because of this, the positive and negative ions arrange themselves in three dimensions, as shown in Figure 2.10 (B), to balance the charges among several ions. In sodium chloride, for example, each chloride ion is surrounded by as many sodium ions as can easily crowd around it, namely six. Similarly, each sodium ion is surrounded by six chloride ions. Therefore, each chloride ion is bonded to the six nearest sodium ions and bonded to a lesser extent to the more distant sodium ions. Accordingly, the ionic bond is a force holding many atoms or ions together rather than a bond between two individual atoms or ions. (Kurita, 1999)

2.3.2.2 Covalent Bond

A covalent bond is formed when one or more electrons from an atom pair off with one or more electrons from another atom and form overlapping electron shells in which both atoms share the paired electrons. Unlike an ionic bond, a covalent bond holds together specific atoms. Covalent bonding can be single covalent, double covalent, or triple covalent depending on the number of pairs of electrons shared. Figure

2.11 shows the bonding that occurs in the methane molecule, which consists of four single covalent bonds between one carbon atom and four hydrogen atoms (Kurita, 1999).

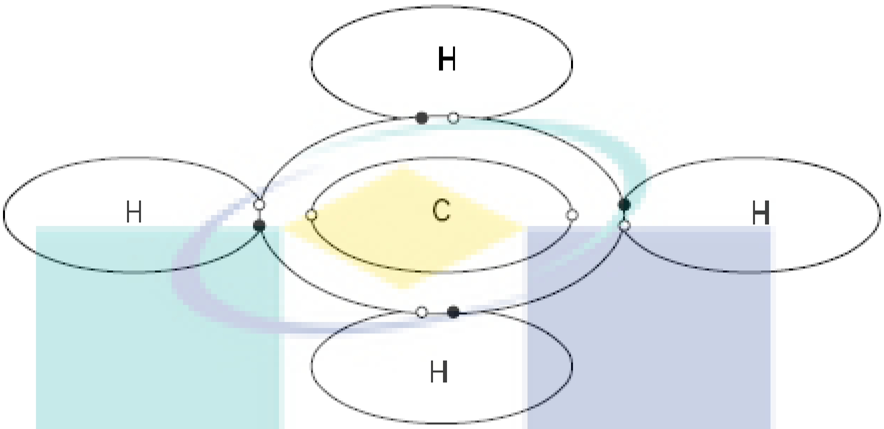


Figure 2.11: Covalent Bond, Methane CH_4

Two double covalent bonds result when carbon dioxide, which consists of one carbon atom and two oxygen atoms, is formed. Four pairs of electrons are shared by the carbon atom, two from each of the two oxygen atoms as shown in Figure 2.12. A combination of two electrons forms a combination of lower energy than their energy when separated. This energy difference represents the force that binds specific atoms together.

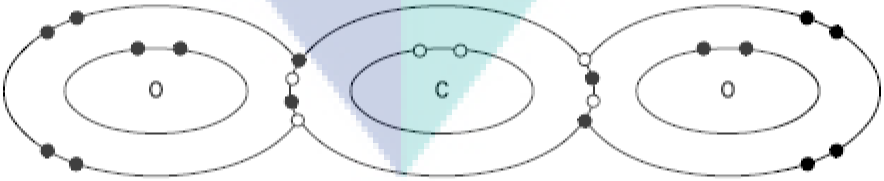


Figure 2.12: Formation of the Carbon Dioxide Molecule

When both shared electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Although both shared electrons come from the same atom, a coordinate covalent bond is a single bond similar in properties to a covalent bond. Figure 2.13 illustrates the bonds of the negatively-charged chlorate ion. The ion consists of one chlorine atom and three oxygen atoms with a net charge of -1, and is formed with two coordinate covalent bonds and one covalent bond. The chlorine atom has effectively gained an electron through the covalent bond, which causes the overall negative charge.

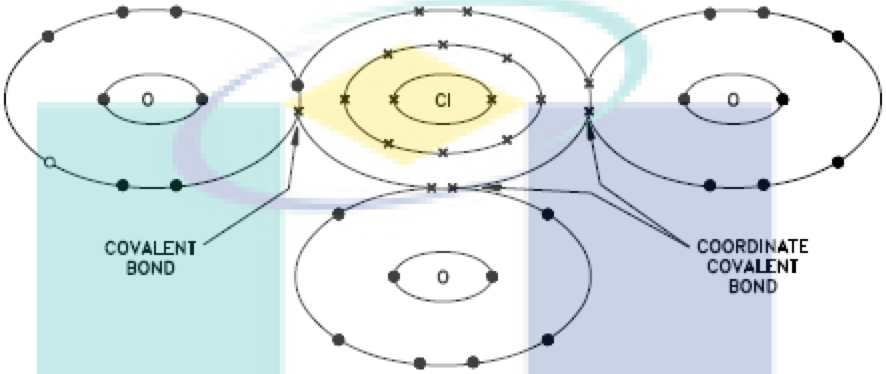


Figure 2.13: Coordinate Covalent Bond, Chlorate Ion ClO_3

Covalent bonds can be either polar or nonpolar. When the shared pair of electrons is not shared equally, one end of the bond is positive, and the other end is negative. This produces a bond with two poles called a polar covalent bond. Molecules having polar covalent bonds are called dipolar or polar molecules. Water is an example of a polar molecule. When two atoms of the same element share one or more pairs of electrons (such as H or N), each atom exerts the same attraction for the shared electron pair or pairs. When the electron pairs are distributed or shared equally between the two like atoms, the bond is called a nonpolar covalent bond. If all the bonds in a molecule are of this kind, the molecule is called a nonpolar covalent molecule (Kurita,1999).

2.3.2.3 Metallic Bond

Another chemical bonding mechanism is the metallic bond. In the metallic bond, an atom achieves a more stable configuration by sharing the electrons in its outer shell with many other atoms. Metallic bonds prevail in elements in which the valence electrons are not tightly bound with the nucleus, namely metals, thus the name metallic bonding. In this type of bond, each atom in a metal crystal contributes all the electrons in its valence shell to all other atoms in the crystal.

Another way of looking at this mechanism is to imagine that the valence electrons are not closely associated with individual atoms, but instead move around amongst the atoms within the crystal. Therefore, the individual atoms can "slip" over one another yet remain firmly held together by the electrostatic forces exerted by the electrons. This is why most metals can be hammered into thin sheets (malleable) or drawn into thin wires (ductile). When an electrical potential difference is applied, the electrons move freely between atoms, and current flows (Kurita,1999).

2.3.2.4 Van Der Waals Forces

In addition to chemical bonding between atoms, there is another type of attractive force that exists between atoms, ions, or molecules known as van der Waals forces.

These forces occur between the molecules of nonpolar covalent substances such as H_2, Cl_2, and He. These forces are generally believed to be caused by a temporary dipole, or unequal charge distribution, as electrons constantly move about in an atom, ion, or molecule. At a given instant, more electrons may be in one region than in another region, as illustrated in Figure 2.14.

The temporary dipole induces a similar temporary dipole on a nearby atom, ion, or molecule. Every instant, billions of these temporary dipoles form, break apart, and reform to act as a weak electrostatic force of attraction known as van der Waals forces.

It is important to note that van der Waals forces exist between all kinds of molecules. Some molecules may have these forces, as well as dipole or other intermolecular forces. Van der Waals forces, however, are the only intermolecular bonds between nonpolar covalent molecules such as H_2, Cl_2, and CH_4. The number of electrons in a substance increases as the gram molecular mass (mass in grams of one mole of compound) increases. Therefore, the strength of the van der Waals forces between substances increases with increasing gram molecular mass.

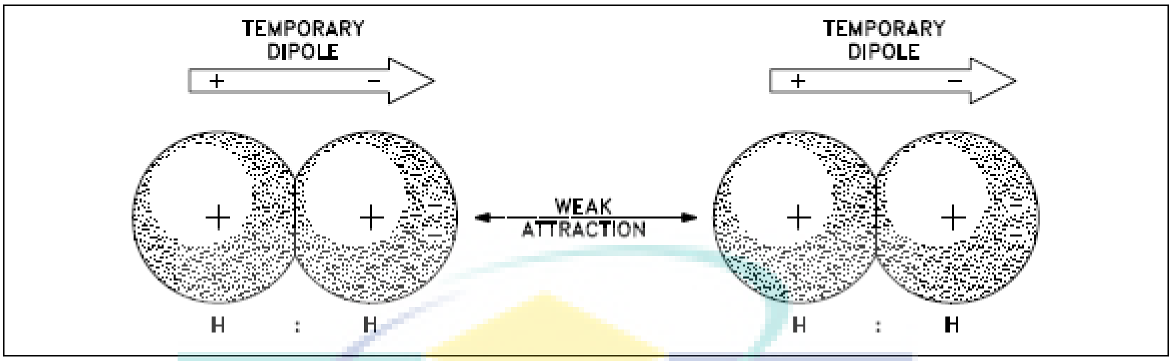


Figure 2.14: Van Der Waals Forces

Van der Waals forces are small compared to the forces of chemical bonding and are significant only when the molecules are very close together (Kurita, 1999).

2.3.3 The Nature of Adsorbents

Adsorbents are available as irregular granules, extruded pellets and formed spheres. The size reflects the need to pack as much surface area as possible into a given volume of bed and at the same time minimise pressure drop for flow through the bed. Sizes of up to about 6 mm are common.

To be attractive commercially, an adsorbent should embody a number of features:

(a) It should have a large internal surface area.

(b) The area should be accessible through pores big enough to admit the molecules to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules which it is desired not to adsorb.

(c) The adsorbent should be capable of being easily regenerated.

(d) The adsorbent should not age rapidly, that is losing its adsorptive capacity through continual recycling.

(e) The absorbent should be mechanically strong enough to withstand the bulk handling and vibration that is a feature of any industrial unit.

There are four types of adsorbent which are used in this research:

1. Chitosan
2. Activated Carbon
3. Alum
4. Zeolite

2.4 INTRODUCTION OF CHITOSAN

Chitosan is one of the natural products that are potentially can be used as adsorbents. Chitosan is cationic biodegradable biopolymer produced by the extensive deacetylation of chitin obtained from shrimp shell wastes. Moreover, chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is produced commercially by deacetylation of chitin, which is the structural element in exoskeleton of crustaceans (origin from crabs, shrimp, etc) (Shahidi and Synowiecki, 1991). Chitosan, poly (D-glucosamine) a natural deacetylated marine polymer has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry, and biomedical (Majeti, 2000). Chitosan has excellent properties such as biodegradability, hydrophilicity, insoluble in water, biocompability, adsorption property, flocculating ability, polyelectrolisity, antibacterial property and its capacity of regeneration in a number of applications (Feng *et al*, 2000). Its largest use is as non-toxic adsorbents in the treatment of organic polluted wastewaters and as a chelating agent for toxic (heavy and reactive) metals (An *et al*, 2001).

Chitosans are polysaccharides that result after the N-deacetylation of chitin (Figure 2.15), (Hirano, 2000; Hudson and Smith, 1998). Chemically they are derivatives of cellulose with 2-acetamido-groups instead of 2-hydroxy groups. They consist of β-(1-4)-D-glucosamine. The process of N-deacetylation of chitin can be controlled in its conditions, and according to the conditions different deacetylated chitosans result (40%-98%) (Pavlath *et al.*, 1996). Furthermore, the products vary in their degree of polymerization. Chitosan powders have been determined to be crystalline up to 71% deacetylation, further deacetylation leads to a strong decrease in crystallinity and starting from 89% deacetylation crystallinity increases (Luyen and Huong, 1996).

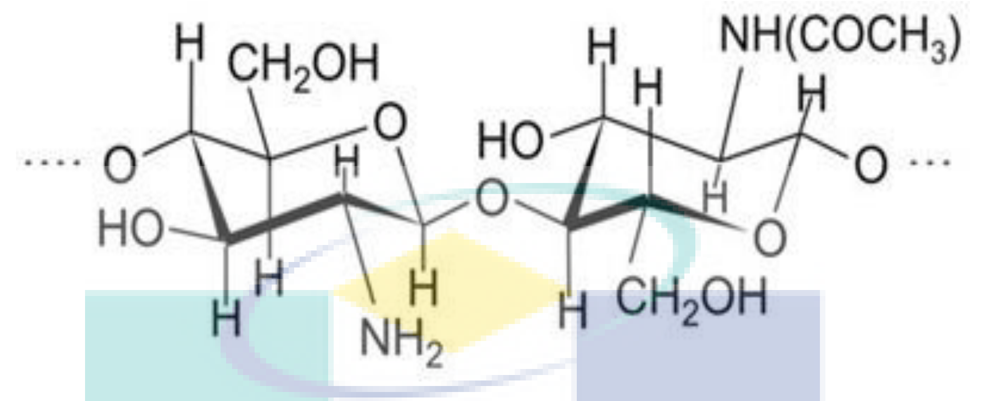


Figure 2.15: Chemical structure of chitosan

Chitin is the second most common polymer and is naturally present in crustacean shells and fungi. The shells of crab, shrimps, and lobster are waste products of the food industry and can be used to produce chitosans (Hudson and Smith, 1998).

Chitosans are nontoxic, biocompatible, and biodegradable and have been widely used for pharmaceutical purposes, and for other purposes such as clarification of waste water, in food products, in feed ingredients, and as a wet strength additive in the paper industry (Hudson and Smith, 1998; Paul and Sharma, 2000).

Chitosan is a white amorphous solid which is insoluble in water but soluble in very dilute acids such as acetic, formic, etc. However, its solutions undergo slow biodegradation (Chihpin *et al.*, 2000). It is second only to cellulose in abundance. Moreover, chitosan is a fiber-like substance derived from chitin, a polysaccharide found in the exoskeletons of crabs, shrimp and other shellfish. It possesses a positive ionic charge, which gives it the ability to chemically bond with negatively charged fats, lipids and bile.

2.4.1 Manufacture and Properties

Chitosan has the highest sorption capacity for several metal ions (Deshpande, 1986) among the many other low cost absorbents identified (Olin *et al*. 1996; Bailey *et al.*, 1997, Bailey *et al.*, 1999). Chitin (2-acetamido-2-deoxy-β-Dglucose-(N-acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps (Deshpande, 1986; Chen and Chang, 1994; Ilyina *et al.*, 1995).

Worldwide, the solid waste from processing of shellfish, crabs, shrimps and krill constitutes large amount of chitinaceous waste. Chitosan (2-acetamido-2-deoxy-β-D-glucose-(Nacetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution as shown in Figure 2.16. The degree of deacetylation (%DA) can be determined by NMR spectroscopy, and the %DA in commercial chitosans is in the range 60-100 %.

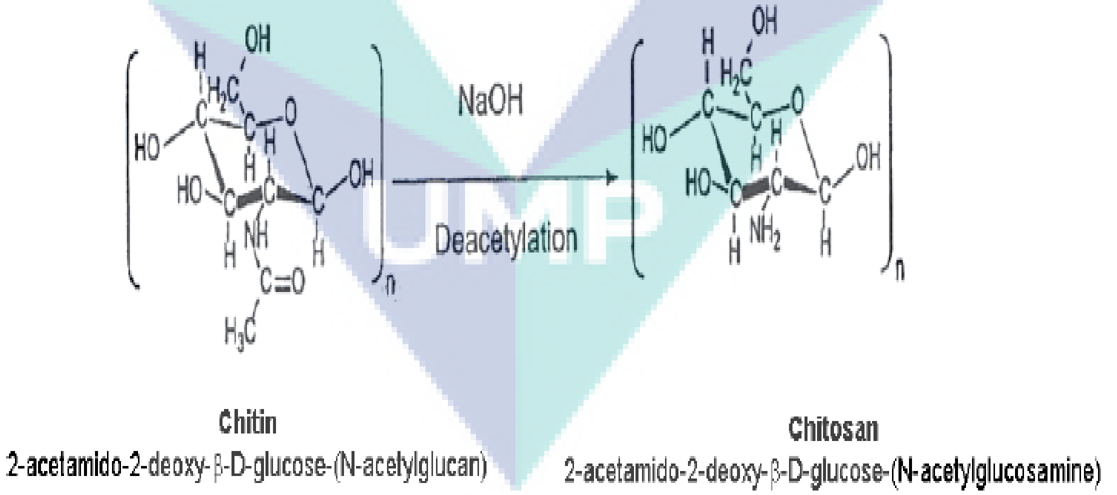


Figure 2.16: Conversion of chitin to chitosan by deacetylation

Chitosan chelates five to six times greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin (Yang and Zall, 1984). The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value. In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes. Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosans are available for biomedical applications.

Besides, the biosorbent material, chitosan, is slightly soluble at low pH and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions. In addition, the active binding sites of chitosan are not readily available for sorption. Transport of the metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications.

2.4.2 Characteristics of Chitosan

Chitosan is a non toxic, biodegradable polymer of high molecular weight, and is very much similar to cellulose, a plant fiber. This can be proof by refer to the figure 2.17.

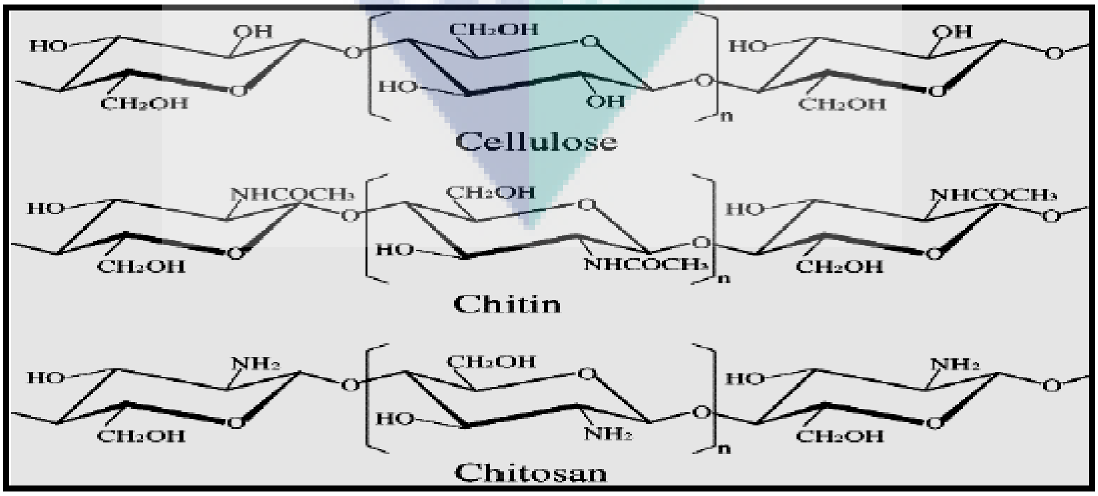


Figure 2.17: Structures of Cellulose, Chitin, and Chitosan

As seen in Figure 2.17, the only difference between chitosan and cellulose is the amine (-NH2) group in the position C-2 of chitosan instead of the hydroxyl (-OH) group found in cellulose. However, unlike plant fiber, chitosan possesses positive ionic charges, which give it the ability to chemically bind with negatively charged fats, lipids, cholesterol, metal ions, proteins, and macromolecules (Tolaimate *et al.*, 2000). In this respect, chitin and chitosan have attained increasing commercial interest as suitable resource materials due to their excellent properties including biocompatibility, biodegradability, adsorption, and ability to form films, and to chelate metal ions.

A few characteristics of chitosan that makes it a more environmental friendly coagulant to be use in waste water treatment are as follow:-

i. Chitosan wastewater treatment products are organic and biodegradable.
ii. Chitosan is not soil/water specific. The only water chemistry variables are pH, water temperature, and chitosan dose rate (which depends on turbidity).
iii. Capable of large flow rates.
iv. Capable of continuous treatment operations.
v. Chitosan treatment may help remove other contaminants such as heavy metals which adhere to sediment particles.

2.4.3 Usage of Chitosan

Chitosan is used primarily as a plant growth enhancer, and as a substance that boosts the ability of plants to defend against fungal infections. It is approved for use outdoors and indoors on many plants grown commercially and by consumers. The active ingredient is found in the shells of crustaceans, such as lobsters, crabs, and shrimp, and in certain other organisms. Given its low potential for toxicity and its abundance in the natural environment, chitosan is not expected to harm people, pets, wildlife, or the environment when used according to label directions.

Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. Chitosan also removes phosphorus, heavy minerals, and oils from the water. Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone while the Chitosan with sand filtration removes up to 99% turbidity (Alan, 2002).

Chitosan is also useful in other filtration situations, where one may need to remove suspended particles from a liquid. Chitosan, in combination with bentonite, gelatin, silica gel, isinglass, or other fining agents is used to clarify wine, mead, and beer. Added late in the brewing process, chitosan improves flocculation, and removes yeast cells, fruit particles, and other detritus that cause hazy wine. Chitosan combined with colloidal silica is becoming a popular fining agent for white wines, because chitosan does not require acidic tannins (found primarily in red wines) to flocculate with.

2.4.4 Preparation of Chitin and Chitosan

The quality of chitosan produced from shrimp shell depends on the conditions of the chemical extraction process, including the concentration of chemicals used, the soaking time and the sequence of the treatments for deproteination, decalcification and deacetylation. The results show that 4% NaOH is a suitable concentration for removal of protein at room temperature (25°C). When the process started with deproteination, decalcification with 4% HCl for 2 hour is sufficient to get chitin with low ash content. For the production of chitosan with high viscosity, the decalcification should precede the deproteination. Chitosan with a high degree of deacetylation can be obtained by multiple deacetylations at 40°C (Lertsutthiwong *et al.*, 2002).

Chitosan was prepared by two different treatments in which deproteination and decalcification were applied in either sequence. Other method to prepare chitin and chitosan from crustaceans shell is the freeze-dried Alaska king crabs were crushed manually. The particle size fraction between 1-2 mm was sieved out for further processing. The decalcification of chitin was carried out according to the method suggested by Muzzarelli (1973). Chitosan samples with different DDA were obtained by hydrolyzing chitin in concentrated NaOH solutions (10% to 40% (w/w)) at a temperature of 90-12^{o}C for 5-120 minutes. A sample with DDA ~100% was obtained by successive alkali treatments (Zhang and Schiewer, 2006).

In this study, only the process of producing chitin from shrimp shell is done according to the standard procedure. After chitin is produce, the process to produce chitosan was modified by varying the molar percentage of NaOH added at different temperature and time range to produce chitosan with different degree of deacetylation as in Figure 2.18.

2.4.5 Deacetylation of Chitin

Deacetylation is the process to convert chitin to chitosan by removal of acetyl group. It is generally achieved by treatment with concentrated sodium or potassium hydroxide solution (40-50%) usually at 100^{o}C or higher for 30 minutes or longer to remove some or all of the acetyl groups from the polymer (No and Meyers, 1995). The N-acetyl groups cannot be removed by acidic reagents without hydrolysis of the polysaccharide, thus, alkaline methods must be employed for N-deacetylation (Muzzarelli, 1977).

Depending upon the production sequence, deacetylation can be achieved by reaction of demineralized shells or crawfish chitin with 50% NaOH (w/w) solution at 100^{o}C for 30 minutes in air using a solid to solvent ratio of 1:10 (w/v) (No *et al.*, 1989). There are several critical factors that affect the extent of deacetylation including temperature and time of deacetylation, alkali concentration, prior treatment applied to chitin isolation, atmosphere (air or nitrogen), ratio of chitin to alkali solution, density of the chitin, and particle size. Considering all these necessary conditions, the ideal purpose of deacetylation is to prepare a chitosan that is not degradable and is soluble in dilute acetic acid in minimal time. Figure 2.8 shows the flow of the production of chitosan.

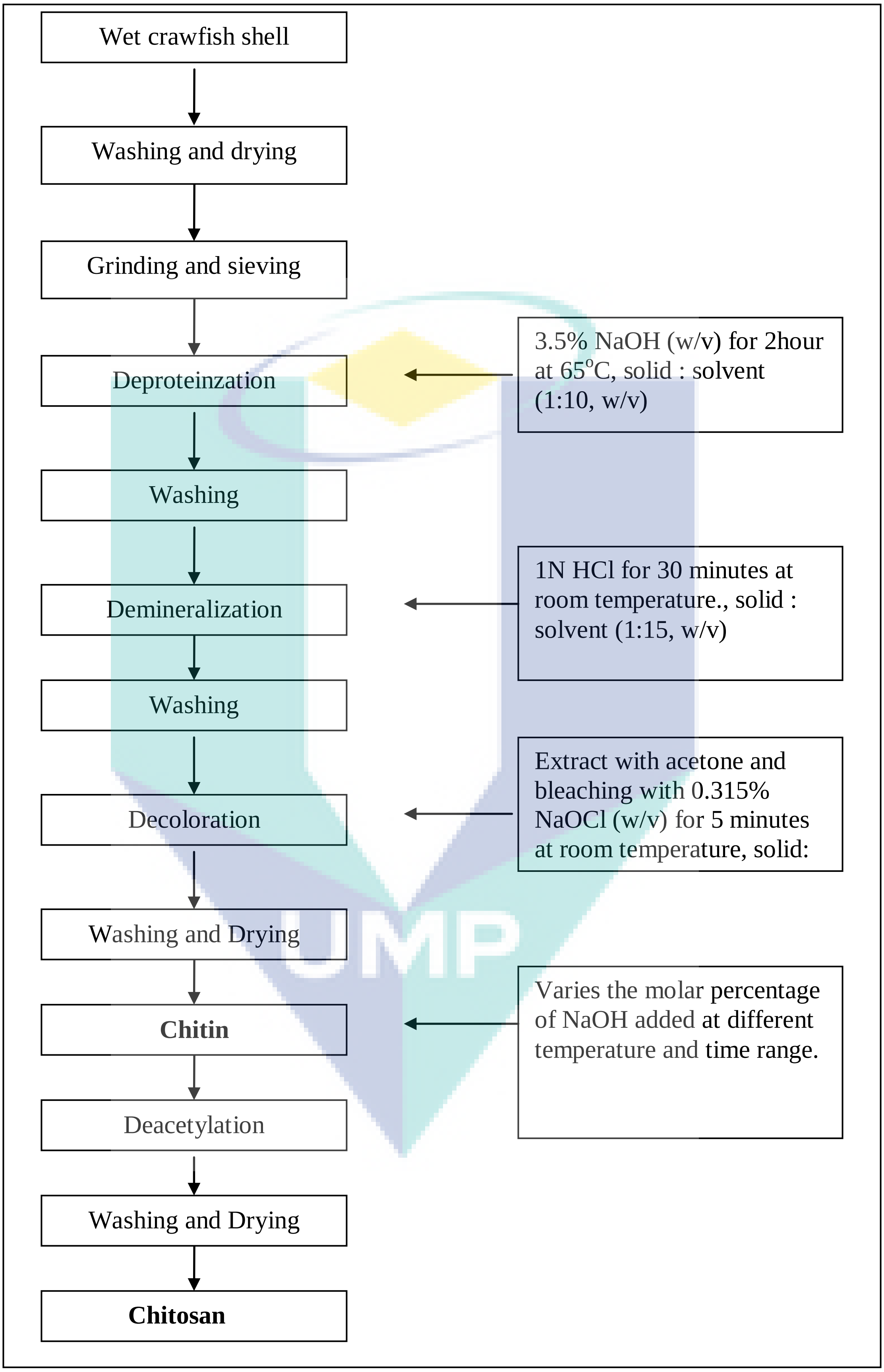


Figure 2.18: Flow of the production of chitosan

A new process for treating chitin under high concentrations of sodium hydroxide with microwave energy was proposed by Peniston and Johnson (1980) to accelerate the deacetylation of chitin within 18 minutes with 50% NaOH at a mean temperature under 80°C. Chitin was deacetylated with concentrated aqueous NaOH in the presence of water-miscible organic solvents such as 2-propanol, 2-methyl-2-propanol or acetone (Batista and Roberts, 1990).

Although it is difficult to prepare chitosan with a degree of deacetylation greater than 90% without chain degradation, Mima *et al.* (1983) developed a method for preparation of chitosan having a desired degree of deacetylation of up to 100%, without serious degradation of the molecular chain. This was achieved by intermittently washing the intermediate product in water two or more times during the alkali treatment for less than 5 hr in 47% NaOH at 110°C.

A simple and inexpensive technique for deacetylation of chitin has been developed in which Alimuniar and Zainuddin (1992) produced chitosan by treatment of prawn chitin with strong sodium hydroxide at ambient temperature (30°C) without heating in an inert atmosphere or without the addition of other additives to control the reaction. With 50% NaOH, the acid-soluble chitosan with 87% degree of deacetylation could be formed in a single day using 560 mL of the solution for 10 g of chitin, two days using 420 mL, three days using 280 mL and six days using 140 mL.

For a large-scale preparation of chitosan, the process of deacetylation needs to be optimized. No *et al.* (2000) used autoclaving conditions (15 psi/121°C) to deacetylate chitin to prepare chitosan under different NaOH concentration and reaction times. Effective deacetylation was achieved by treatment of chitin under an elevated temperature and pressure with 45% NaOH for 30 minutes with solid to solvent ratio of 1:15. Treated chitosan showed similar content, degree of deacetylation, and molecular weight, but significantly higher viscosity value than those of commercial chitosan.

In another process, after 3 days of deacetylation at 40°C, over 70% of the acetyl groups in the chitin were removed (as shown on figure 2.19). When the process of deacetylation was extended, the DDA did not increase much any more. After 8 days of deacetylation, the DDA obtained was about 80%. A higher degree of deacetylation, such as 85-90%, can not be achieved at low temperature in one step. Chitosan with 88% DDA could be reached when the deacetylation is carried out twice. The results are in agreement with those of Roberts (1997), and Chinadit *et al.*, (1998) who concluded that a multi-step process was required to obtain a high degree of deacetylation at a low temperature. However, deacetylation at high temperature can reach high DDA in one step as well. For instance, the deacetylation of chitin with 50% NaOH at 90°C for 5 hr gave a chitosan product with 88% DDA (Chinadit *et al.*, 1998).

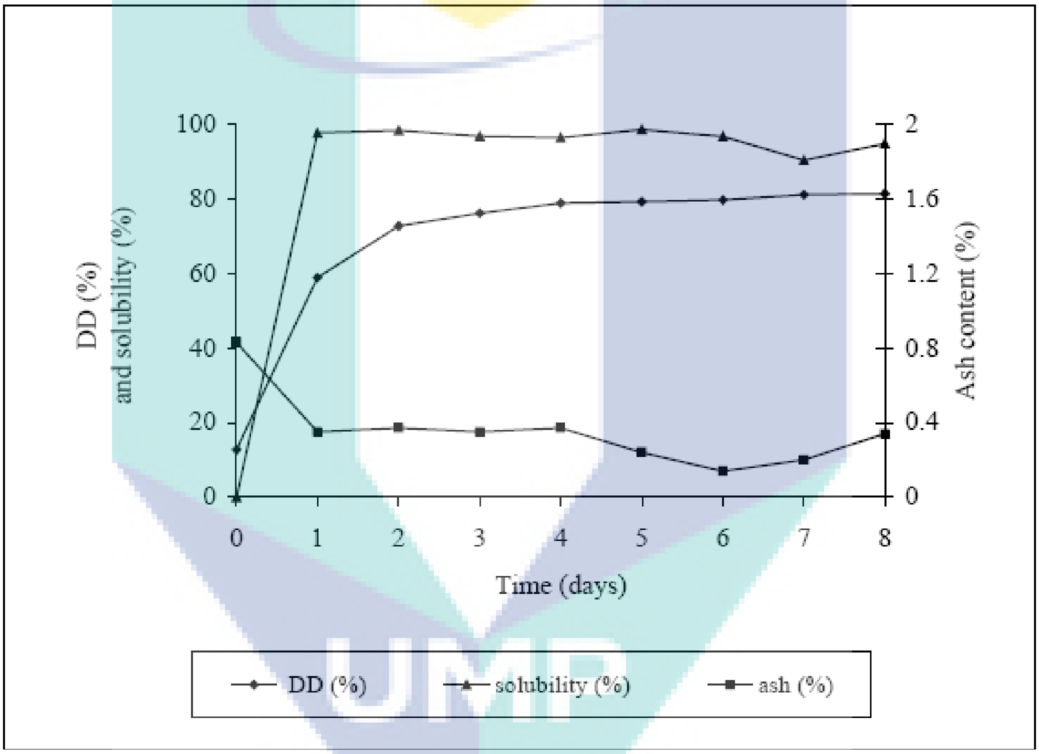


Figure 2.19: Effect of deacetylation time on the characteristics of chitosan.

2.4.6 Degree of Deacetylation (DDA)

The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree chemical reactive amino group ($-NH_2$). This makes the degree of deacetylation (DDA) an important property in chitosan production as it affects the physicochemical properties, hence determines its appropriate applications (Rout, 2001). Deacetylation also affects the biodegradability and immunological activity (Tolaimate *et al.*, 2000).

A sharp nomenclature border has not been defined between chitin and chitosan based on the degree of *N*-deacetylation (Rout, 2001). In an earlier study by Rudall (1963), he reviewed evidences suggesting that approximately one in every six to seven residues in the chain has a proportion of free amino groups that manifests some histochemical properties. In any case, the degree of deacetylation can be employed to differentiate between chitin and chitosan because it determines the content of free amino groups in the polysaccharides. In fact there are two advantages of chitosan over chitin. In order to dissolve chitin, highly toxic solvents such as lithium chloride and dimethylacetamide are used whereas chitosan is readily dissolved in diluted acetic acid. The second advantage is that chitosan possesses free amine groups which are an active site in many chemical reactions (Knaul *et al.*, 1999).

The degree of deacetylation of chitosan ranges from 56% to 99% with an average of 80%, depending on the crustacean species and the preparation methods (No, 2000; No and Meyers, 1995). Chitin with a degree of deacetylation of 75% or above is generally known as chitosan (Knaul *et al.*, 1999). Various methods have been reported for the determination of the degree of deacetylation of chitosan. These included ninhydrin test, linear potentiometric titration, near-infrared spectroscopy, nuclear magnetic resonance spectroscopy, hydrogen bromide titrimetry, infrared spectroscopy, and first derivative UV-spectrophotometry (Khan *et al.*, 2002).

The followings are some baselines proposed for the determination of the degree of deacetylation of chitosan:

$$1.\ \mathrm{DDA} = 100 - \left[\frac{\left(\frac{A_{1655}}{A_{3450}}\right)\times 100}{1.33}\right]$$

Domszy and Roberts (1985)

$$2.\ \mathrm{DDA} = 97.67 - \left[26.486\times\left(\frac{A_{1655}}{A_{3450}}\right)\right]$$

Sabnis and Block (1997)

$$3.\ \mathrm{DDA} = 100 - \left[\left(\frac{A_{1655}}{A_{3450}}\right)\times 115\right]$$

Baxter *et al.*, (1992)

$$4.\ \mathrm{DDA} = 118.883 - \left[40.1647\times\left(\frac{A_{1655}}{A_{3450}}\right)\right]$$

Rout, (2001)

2.5 INTRODUCTION OF ACTIVATED CARBON

Activated carbon is a crude form of graphite, the substance used for pencil leads. It differs from graphite by having a random imperfect structure which is highly porous over a broad range of pore sizes from visible cracks and crevices to molecular dimensions. The graphite structure gives the carbon it's very large surface area which allows the carbon to adsorb a wide range of compounds. Activated carbon can have a surface of greater than 1000 m^2/g. This means 5g of activated carbon can have the surface area of a football field (Cheremisinoff, 2002).

Activated carbon, also called activated charcoal or activated coal, is a general term which covers carbon material mostly derived from charcoal. For all three variations of the name, "activated" is sometimes substituted by "active". By any name, it is a material with an exceptionally high surface area. Just one gram of activated carbon has a surface area of approximately 500 m^2, typically determined by nitrogen gas adsorption, and includes a large amount of microporosity. Sufficient activation for useful applications may come solely from the high surface area, though often further chemical treatment is used to enhance the absorbing properties of the material.

Activated carbon is used as adsorbent in many industrial applications as an economic mass separation agent to raise the final product quality. Drinking water, wastewater treatment processes, food and chemical industry processes are typical examples (Ahmad *et al*, 2006). Activated carbon is the most common adsorbent due to its large surface area per unit mass (300 to 1500 m^2/g). The surface of activated carbon is non polar or only slightly polar as result of the suface oxide groups and inorganics impurities. Most other commercially available sorbents are polar in nature. This difference has some very useful advantages. Activated carbon does not adsorb water very well. So, it does not require any pretreatment to remove water prior to use and is very useful as a selective sorbent for aqueous system (Richard and Patricia, 2004). Despite of its prolific use, activated carbon is still assumed as an expensive material and not much work has been done in order to adsorb residual oil (Guibal, 2004).

Adsorption is the process by which liquid or gaseous molecules are concentrated on a solid surface, in this case activated carbon. This is different from absorption, where molecules are taken up by a liquid or gas. Activated carbon can made from many substances containing high carbon content such as coal, wood and coconut shells. The raw material has a very large influence on the characteristics and performance activated carbon (Cheremisinoff, 2002).

The term activation refers to the development of the adsorption properties of carbon. Raw materials such as coal and charcoal do have some adsorption capacity, but this is greatly enhanced by the activation process. There are three main forms of activated carbon.

i. Granular Activated Carbon (GAC) - irregular shaped particles with sizes ranging from 0.2 to 5 mm. This type is used in both liquid and gas phase applications.

ii. Powder Activated Carbon (PAC) - pulverized carbon with a size predominantly less than 0.18mm (US Mesh 80). These are mainly used in liquid phase applications and for flue gas treatment.

iii. Pelleted Activated Carbon - extruded and cylindrical shaped with diameters from 0.8 to 5 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

Activated carbon has the strongest physical adsorption forces or the highest volume of adsorbing porosity of any material known to mankind. Activated carbon is also available in special forms such as a cloth and fibres. Activated Charcoal Cloth (ACC) represents a family of activated carbons in cloth form. These products are fundamentally unique in several important ways compared with the traditional forms of activated carbon and with other filtration media that incorporate small particles of activated carbon. Developed in the early 1970's Activated Charcoal Cloth products are carbon. This gives the products the same high capacity for adsorption of organic compounds and other odorous gases as the more traditional, pelletised, granular and powder forms of activated carbon. As with the traditional forms of activated carbons, Activated Charcoal Cloth products can be impregnated with a range of chemicals to enhance the chemisorption capacity for selected gases. By being constructed of bundles of activated carbon filaments and fibres in a textile form, several important advantages are imparted to Activated Charcoal Cloth. The diameter of these fibres is approximately 20 mm, so the kinetics for Activated Charcoal Cloth products is similar to that of a very tine carbon particle. Gases and liquids can flow through the fabric and the accelerated adsorption kinetics mean that the Activated Charcoal Cloth can retain the advantages of mass transfer zones associated with deeper filter beds. Faster adsorption rates mean smaller adsorption equipment and up to twenty times less carbon on line (Cheremisinoff, 2002). Figure 2.20 shows the common activated carbon in the market.

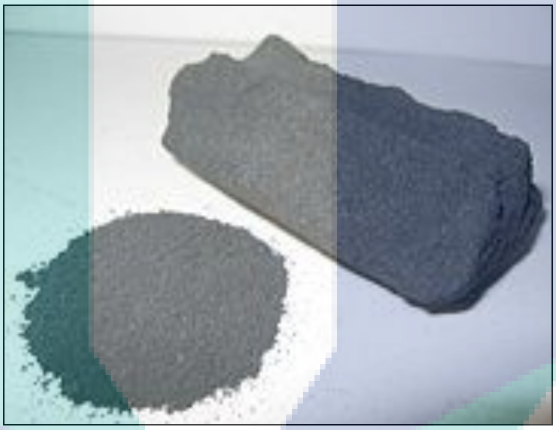


Figure 2.20: Activated Carbon

Adsorption is the process where molecules are concentrated on the surface of the activated carbon. Adsorption is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London Dispersion Forces are extremely short ranged and therefore sensitive to the distance between the carbon surface and the adsorbate molecule. They are also additive, meaning the adsorption force is the sum of all interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any material known to mankind. All compounds are adsorbable to some extent. In practice, activated carbon is used for the adsorption of mainly organic compounds along with some larger molecular weight inorganic compounds such as iodine and mercury. In general, the adsorbability of a compound increases with:

i. Increasing molecular weight
ii. A higher number of functional groups such as double bonds or halogen compounds
iii. Increasing polaris ability of the molecule. This is related to electron clouds of the molecule.

2.5.1 Properties of Activated Carbon

A gram of activated carbon can have a surface area in excess of 500 m², with 1500 m² being readily achievable. For comparison, a tennis court is about 260 m². Carbon aerogels, while more expensive, have even higher surface areas, and are used in special applications.

Under an electron microscope, the structure of activated carbon looks a little like ribbons of paper which have been crumpled together, intermingled with wood chips. There are a great number of nooks and crannies, and many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behaviour are usually done with nitrogen gas at 77 K under high vacuum, but in everyday terms activated carbon is perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of an atmosphere. Physically, activated carbon binds materials by Van der Waals force or London dispersion force.

Activated carbon does not bind well to certain chemicals, including alcohols, glycols, ammonia, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does absorb iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is used as an indication of total surface area.

Activated carbon can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulphide (H_2S), ammonia (NH_3), formaldehyde (HCOH), radioisotopes iodine-131 (^{131}I) and mercury (Hg). This property is known as chemisorption.

2.5.2 Application of Activated Carbon

Activated carbon is used in gas purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and filter masks, filters in compressed air and many other applications.

One major industrial application involves use of activated carbon in metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. Variety of organic chemicals are added to plating solutions for improving the deposit qualities and for enhancing its properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to a desired optimum level.

2.6 INTRODUCTION OF ALUM

Alum (aluminum sulfate) is a compound derived from aluminum, one the earth's most abundant metals. Alum has been part of our lives ever since the time of early Egyptians, who used it in dyeing and purification. Today, it is one of the most widely used and versatile industrial chemicals.

Alum, $[Al_2(SO_4)_3.nH_2O]$ is a adsorbent used extensively in wastewater treatment. When added to water, aluminium ions are hydrated, producing amorphous aluminium hydroxide in the form of large, positively charged molecules with aluminium ions at their centre.

High surface area per unit mass alumina, either amorphous or crystalline, which has been partially or completely dehydrated, is termed activated alumina. This material is very hydrophilic and is often used for drying or dehydration of gases and liquids. Environmental applications would include water removal from acid gas or organic solvent streams. The surface area per unit mass of this material is usually in the range of 200-400 m^2/g (Richard and Patricia, 2004).

2.6.1 Uses of Alum

Most of the alum produced today is used in the pulp & paper industry as well as water and wastewater treatment. It is inexpensive and effective for a broad range of treatment problems because it can function as a coagulant, flocculant, recipitant and emulsion breaker. As a coagulant and flocculant, alum removes turbidity, suspended solids and colloidal color, reduces biochemical oxygen demand (BOD) and clarifies potable, process and wastewater. Table 2.2 shows the summary of the uses of alum in the industry.

Table 2.2: Uses of Alum (Richard and Patricia, 2004)

Cellulosic insulation	Additive to cellulosic insulation
Clay manufacturers	China clay beneficiation
Dyes	Mordant for dyes
Grease manufacturers	Manufacture of aluminum soaps and greases
Industrial wastewater treatment	Sewage and industrial wastewater treatment, emulsion breaking
Manufacture of alumina trihydrate and printing inks	Manufacture of alumina trihydrate for lakes and color extenders
Municipal wastewater treatment	Clarification and phosphorus removal
Potable and process water treatment	Color and turbidity removal
Pulp and paper mills	Process water and mill effluent treatment. Paper sizing

Soap manufacturers	Manufacture of glycerin from soap lyes
Swimming pools, oil well operators, manufacturers	Water treatment
Tanneries	Tanning furs and white leathers
Zeolite and catalyst manufacturers	Manufacture of zeolites and aluminosilicate catalysts and carriers

2.7 INTRODUCTION OF ZEOLITE

Zeolites are nanoporous oxide crystalline structures, typically aluminosilicates. The aluminum in the structure has a negative charge that must be balanced by a cation, M. This ionic structure leads to the hydrophilicity of the zeolite. Zeolites have uniforms pore sizes that typically range from 0.3 to 0.8 nm. Zeolites can selectively adsorb or reject molecules based on their size, shape, or sorption strength. The molecular sieving effect is a common term associated with zeolites and refers to selectivity based on size or shape exclusion. Zeolites can also provide separations based on competitive sorption. This situation can lead to reverse selectivity where a larger molecule can be selectively sorbed and separated from a smaller molecule. For example, most zeolites are polar adsorbents and will preferentially adsorb polar species (water) over non polar species (organics) of comparable size (Richard and Patricia, 2004). Figure 2.21 shows the typical of zeolite.

Figure 2.21: Zeolite

Zeolites are minerals that have a micro-porous structure. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite.

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. They are basically hydrated alumino-silicate minerals with an "open" structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite. An example mineral formula is: $Na_2Al_2Si_3O_{10}$-$2H_2O$, the formula for natrolite. Figure 2.22 shows the micro-porous molecular structure of a zeolite, ZSM-5.

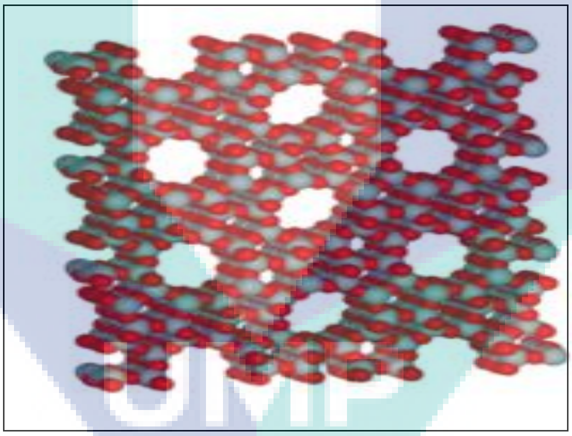


Figure 2.22: The micro-porous molecular structure of a zeolite, ZSM-5

Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves". The term molecular sieve refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical.

2.7.1 Sources of Zeolite

Conventional open pit mining techniques are used to mine natural zeolites. The overburden is removed to allow access to the ore. The ore may be blasted or stripped for processing by using tractors equipped with ripper blades and front-end loaders. In processing, the ore is crushed, dried, and milled. The milled ore may be air-classified as to particle size and shipped in bags or bulk. The crushed product may be screened to remove fine material when a granular product is required, and some pelletized products are produced from fine material. Producers also may modify the properties of the zeolite or blend their zeolite products with other materials before sale to enhance their performance.

Currently, the world’s annual production of natural zeolite is about 4 million tons. Of this quantity, 2.6 million tons are shipped to Chinese markets to be used in the concrete industry. Eastern Europe, Western Europe, Australia, and Asia are world leaders in supplying the world’s demand for natural zeolite. By comparison, only 57,400 metric tons (source: U.S. Geological Survey, 2004) of zeolite (only 1% of the world’s current production) is produced in North America; only recently has North America realized the potential for current and future markets.

There are several types of synthetic zeolites that form by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. One of the important processes used to carry out zeolite synthesis is sol-gel processing. The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as the templates used. In sol-gel process, other elements (metals, metal oxides) can be easily incorporated. The silicalite sol formed by the hydrothermal method is very stable. Also the ease of scaling up this process makes it a favorite route for zeolite synthesis.

Synthetic zeolites hold some key advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Finally, zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature. Disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts.

2.7.2 Application of Zeolite

2.7.2.1 Commercial and Domestic

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed.

Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include: noble gases, N_2, freon and formaldehyde. However at present, the true potential to improve the handling of such gases in this manner remains unknown.

2.7.2.2 Petrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) is powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. Catalytic cracking uses a furnace and reactor. First crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor the crude meets with a catalyst such as zeolite. It goes through this step three times, each time getting cooler. Finally it reaches a step known as separator. The separator collects recycled hydrogen. Then it goes through a fractionator and becomes the final item.

2.7.2.3 Nuclear Industry

Zeolites have uses in advanced reprocessing methods, where their micro-porous ability to capture some ions while allowing others to pass freely allow many fission products to be efficiently removed from nuclear waste and permanently trapped. Equally important are the mineral properties of zeolites. Their alumino-silicate construction is extremely durable and resistant to radiation even in porous form. Additionally, once they are loaded with trapped fission products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form, closing the pores and trapping the waste in a solid stone block. This is a waste form factor that greatly reduces its hazard compared to conventional reprocessing systems.

2.7.2.4 Agriculture

In agriculture, clinoptilolite (a naturally occurring zeolite) is used as a soil treatment. It provides a source of slowly released potassium. If previously loaded with ammonium, the zeolite can serve a similar function in the slow release of nitrogen. Cuban studies in the emerging field of "zeoponics" suggest that some crops may be grown in 100% zeolite or zeolite mixtures in which the zeolite is previously loaded or coated with fertilizer and micronutrients. Zeolites can also act as water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under plant demand. This property can prevent root rot and moderate drought cycles.

A potting soil with 12% clinoptilolite was shown to harvest morning dew and return it to the plant roots for reuse. The same bed was able to grow a Jerico strain of leaf lettuce in a sub tropical climate without external water and daytime temperatures exceeding 85 °F. This produce did not bolt and went full term before setting seeds. It also has been shown that certain zeolites can reduce nitrates and nitrites to more plant usable free nitrogen by ion exchange.

2.7.2.5 Medical

Zeolite-based oxygen generation systems are widely used to produce medical grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air, in a process involving the absorption of undesired gases and other atmospheric components, leaving highly purified oxygen and up to 5% argon. Zeolite is also the active component in QuikClot, an emergency coagulant.

2.7.2.5 Heating and refrigeration

Zeolites can be used as solar thermal collectors and for adsorption refrigeration. In these applications, their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability is exploited. This hygroscopic property coupled with an inherent exothermic reaction when transitioning from a dehydrated to a hydrated form (heat adsorption), make natural zeolites effective in the storage of solar and waste heat energy.

2.8 ZETA POTENTIAL

Zeta potential is a scientific term for electrokinetic potential in colloidal systems. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta, hence *ζ-potential*. From a theoretical viewpoint, zeta potential is electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

A value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly-charged surfaces. The significance of zeta potential is that its value can be related to the stability of colloidal dispersions (e.g. a multivitamin syrup). The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles (the vitamins) in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e. the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table (ASTM, 1985). Table 2.3 shows the effect of Zeta Potential to colloids.

Table 2.3: Effect of Zeta Potential to Colloids (ASTM, 1985)

Zeta potential [mV]	**Stability behavior of the colloid**
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

Zeta potential is widely used for quantification of the magnitude of the electrical charge at the double layer. However, zeta potential is not equal to the Stern potential or electric surface potential in the double layer. Such assumptions of equality should be applied with caution. Nevertheless, zeta potential is often the only available path for characterization of double-layer properties. Zeta potential should not be confused with electrode potential or electrochemical potential (because electrochemical reactions are generally not involved in the development of zeta potential).

2.9 CHAPTER SUMMARY

This chapter has presented a detailed explanation of the topic. The previous works and researches have been provided to relate with this research, thus this research will be more relevant and supported. The research methodology will be discussed in the next chapter.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the materials, equipment, and methods followed to solve the problem of this study. To accomplish the objectives and scopes of this research, this study was carried out by conducting adsorption treatment batch process. The experimental methods involve the procedure for collection of monoethanolamine (MEA) wastewater, experimental-set-up for adsorption batch treatment, oil content, suspended solids, monoethanolamine (MEA) concentration and chemical oxygen demand (COD) analysis. Details of the experimental are discussed below.

3.1 SAMPLE SELECTION

Samples of MEA wastewater were collected from oil and gas industry at Terengganu. The collected samples were then placed in a thermal resistant plastic container, sealed tight and labelled, before transported to the laboratory. For preservation, samples were refrigerated at about 4°C in order to prevent the wastewater from undergoing biodegradation due to microbial activities. A portion of the samples were analyzed for their characteristic.

Freshly discharged MEA wastewater is black in colour and oily with obnoxious odour. MEA wastewater characteristics may different for each sample depending on the gas processing plant failure. This might due to the foaming phenomenon cause by heavy hydrocarbon content and suspended solids. Although the characteristics of MEA wastewater could vary in order to minimize the effect of different characteristics of MEA, the experiments were repeated with same samples of MEA wastewater to obtain average results. Sampling was carried out every problem occur at the gas processing plant and five bottles of 5 L samples were taken and transported to laboratory. Figure 3.1 shows the Monoethanolamnie (MEA) wastewater used in this research.

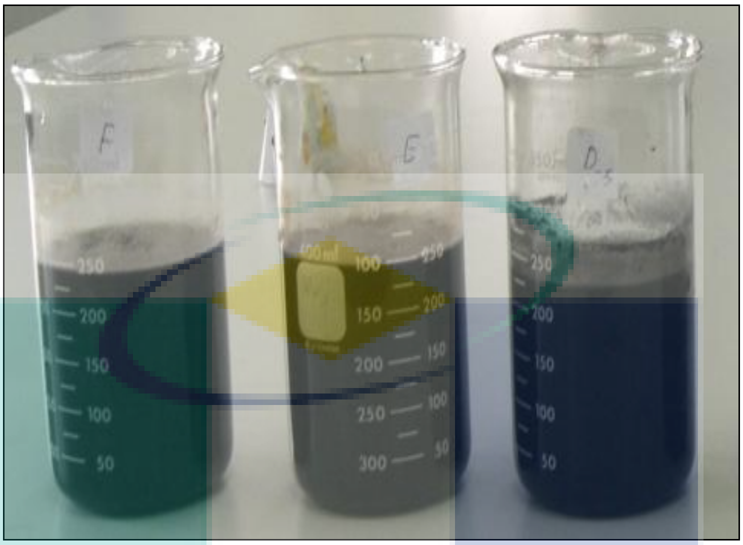


Figure 3.1: Monoethanolamine (MEA) wastewater

3.2 EXPERIMENT MATERIALS

Chitosan was supplied by Mathani Chitosan Pvt. Ltd. (India) in off-white flakes and powders form with viscosities and DDA are about 30-3000 mPa·S (at 25 ^{o}C) and 85% - 98% respectively were used for the monoethanolamie (MEA) wastewater treatment. Activated carbon was supplied by Scharlau Chemie S.A (Spain), Zeolite was supplied by Fluka Biochemica with a mesh size less than 45 µm and Alum was supplied by Merck.

Distilled water was used to dilute hydrochloric acid solution (Merck, Germany) and dissolve sodium hydroxide pellets (Merck, Germany) to obtain solution of 5 M. These solutions were used for pH adjustment during the treatment process. N-hexane (Merck) was used as the solvent for oil extraction in the residue oil analysis.

3.3 INSTRUMENTATION AND APPARATUS

To accomplish this study, there were a few equipments used in this study to complete both adsorption treatment process and chemical oxygen demand (COD) test. In adsorption treatment process, a conventional jar test apparatus (JLT6 Jar Test, VELP Scientifica) was used in the experiment. The COD test was performed by colorimetric method using Spectrophotometer HACH Model DR/2400 (HACH Company, USA). Figure 3.2 shows the jar test apparatus used in this experiments.

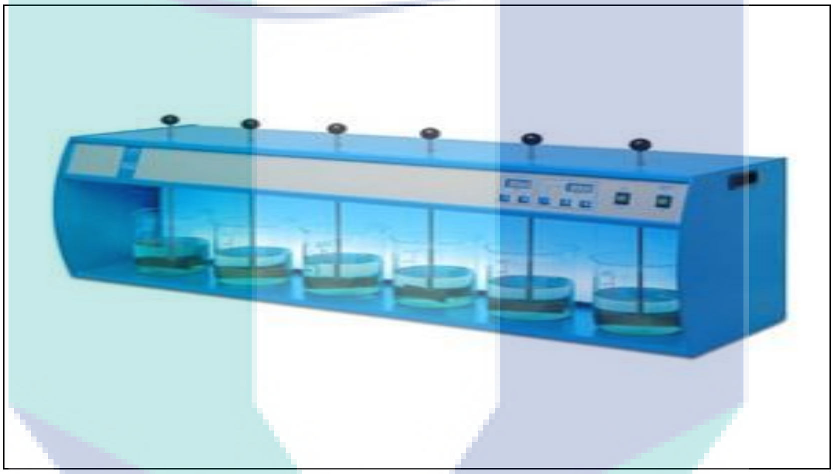


Figure 3.2: Jar Test Apparatus

. The particle size was measured using Malvern Mastersizer 2000 for solids and Malvern Hydro 2000G for liquids as shown in figure 3.3.

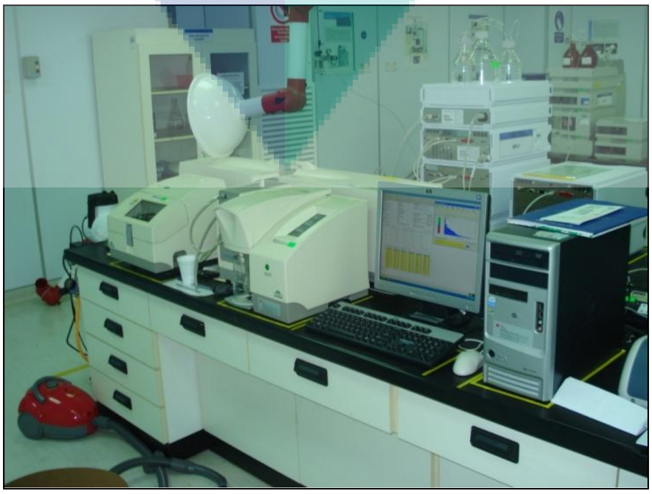


Figure 3.3: Malvern Particle Size Analyzer

3.3.1 Scanning Electron Microscopic Analysis

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The untreated and pretreated samples were closely analyzed by scanning electron microscope model Philips SL40, Holand, which generated high resolution images of shapes of object. A small amount of sample was coated under argon atmosphere with gold prior to analysis and examined under SEM at 30kV for range magnifications between 100 to 1000 times. Figure 3.4 shows a typical SEM instrument with the electron column, sample chamber, EDS detector, electronics console, and visual display monitors.

Figure 3.4: A typical scanning electron microscope instrument

3.4 EXPERIMENTAL PROCEDURES

From the industrial survey, there were four parameters which were oil content, suspended solids, amine concentration and chemical oxygen demand (COD). These parameters evaluation were very crucial in determining the treated MEA could be recycled or else. Whereas, Chemical Oxygen Demand (COD) was also analyzed and this evaluation would provide information to the alternative treatment via wastewater treatment plant if the treated MEA was not possible to be recycled.

A conventional jar test apparatus (JLT6 Jar Test, VELP Scientifica) was used in the experiments to treat MEA wastewater with the adsorbents. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. The samples were mix homogeneously before fractionated into the beakers containing 250mL of suspension each. Prior to the test, the samples were measured for COD, suspended solid, residue oil and amine concentration for representing an initial concentration. After the desired amount of adsorbents was added to the suspension, the beakers were agitated at identical speed (100 rpm) for 1 hour. A sample was withdrawn using a pipette from the top inch of supernatant for analysis, representing the final concentration.

The pH of samples was also determined. The COD, residue oil, suspended solid and amine concentration were determined for each sample of MEA wastewater both before and after experiment. Three replicates of each test were undertaken with the mean value obtained being calculated from the replicates. All tests were performed at an ambient temperature in the range of 26-30°C. Thus, the optimum experiment parameters needed to achieve maximum removal residue oil, suspended solid and COD was determined.

The whole processes were then repeated by studying effect of using several different parameters which include:

i. Types of adsorbents which are chitosan, activated carbon, alum and zeolite.
ii. Adsorbent dosages (from 1 wt%, 2 wt%, 3 wt%, 4wt% and 5 wt %)
iii. pH (from pH 3, pH 5, pH 7, pH 9 and pH 11)
iv. Temperature (from 30^oC, 40^oC, 50^oC, 60^oC, 70^oC and 80^oC)
v. Mixing time (from 0 min, 10 min, 20 min, 30 min, 40 min, 50 min and 60 min)
vi. Mixing speed (from 0 rpm, 50 rpm, 100 rpm, 150 rpm, 200 rpm, 250 rpm and 300 rpm)
vii. Comparison of chitosan powder and chitosan flake.

Figure 3.5 shows the process flow of the experimental works in this research.

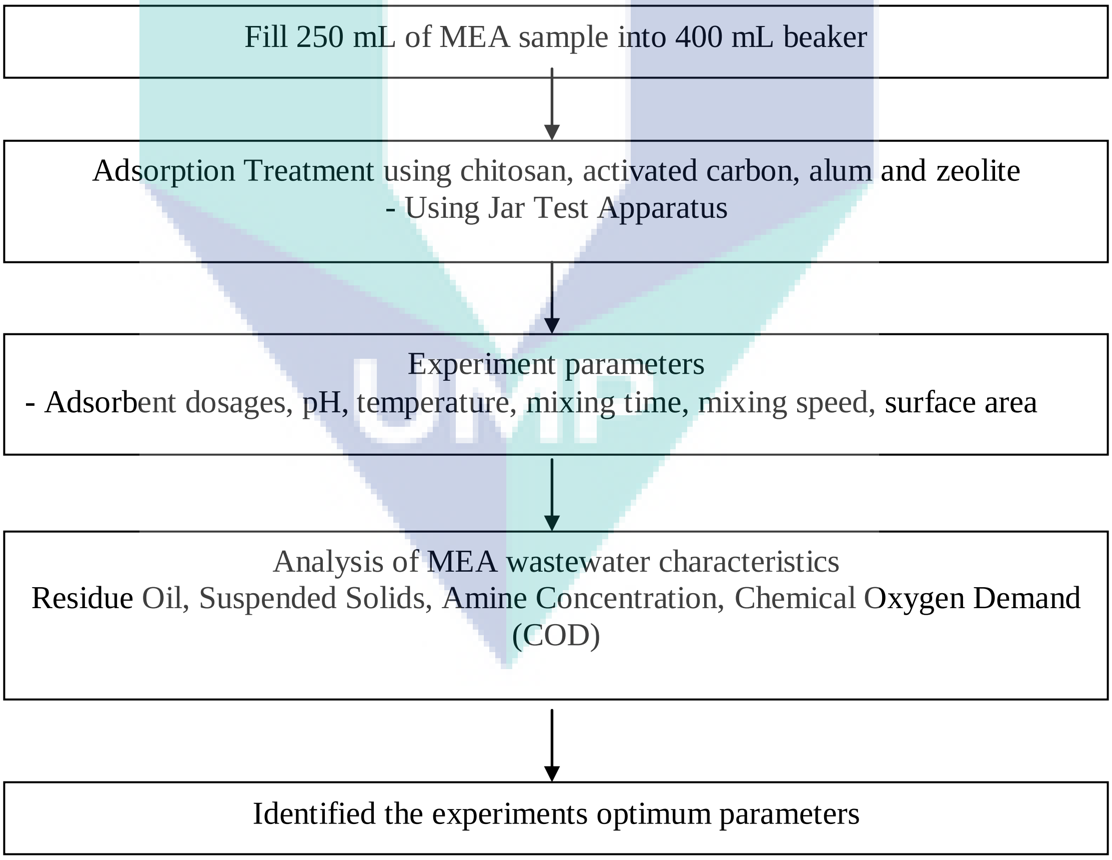


Figure 3.5: Flow diagram of experimental work

3.4.1 Oil and Grease Method

The residue oil content was measured by using the oil and grease method recommended by APHA method (Apha, 1992), with n-hexane being used as the oil-extraction solvent. The residue oil content in the suspension was determined for each sample of MEA wastewater both before and after each experiment. 100 mL of upper aliquots liquid of sample was transferred into a separating funnel. Then, 2.5 mL of 50% sulfuric acid, H_2SO_4 was added to re-active the sample. After that, 30 mL of n-hexane were added into the separating funnel to collect the oil content.

The contents were shaken vigorously for 2 minutes and 3 mL of 2-propanol were added to expel the existed bubbles. The samples were allowed to separate into layers for 5 minutes and the aqueous layer was drip drained into second separating funnel. Extraction was repeated twice with two more portions of 30 mL n-hexane. Then, the all the surface layers were collected and 2 scoops of anhydrous sodium sulphate were added to expel the water in the layers. The samples of extracted residual oil with n-hexane were transferred into round bottom flask and the samples were heated to remove n-hexane. The initial weight was measured and the drying and cooling were repeated until the weight becomes constant in every 1 hour. Figure 3.6 shows the flow diagram of oil and grease method.

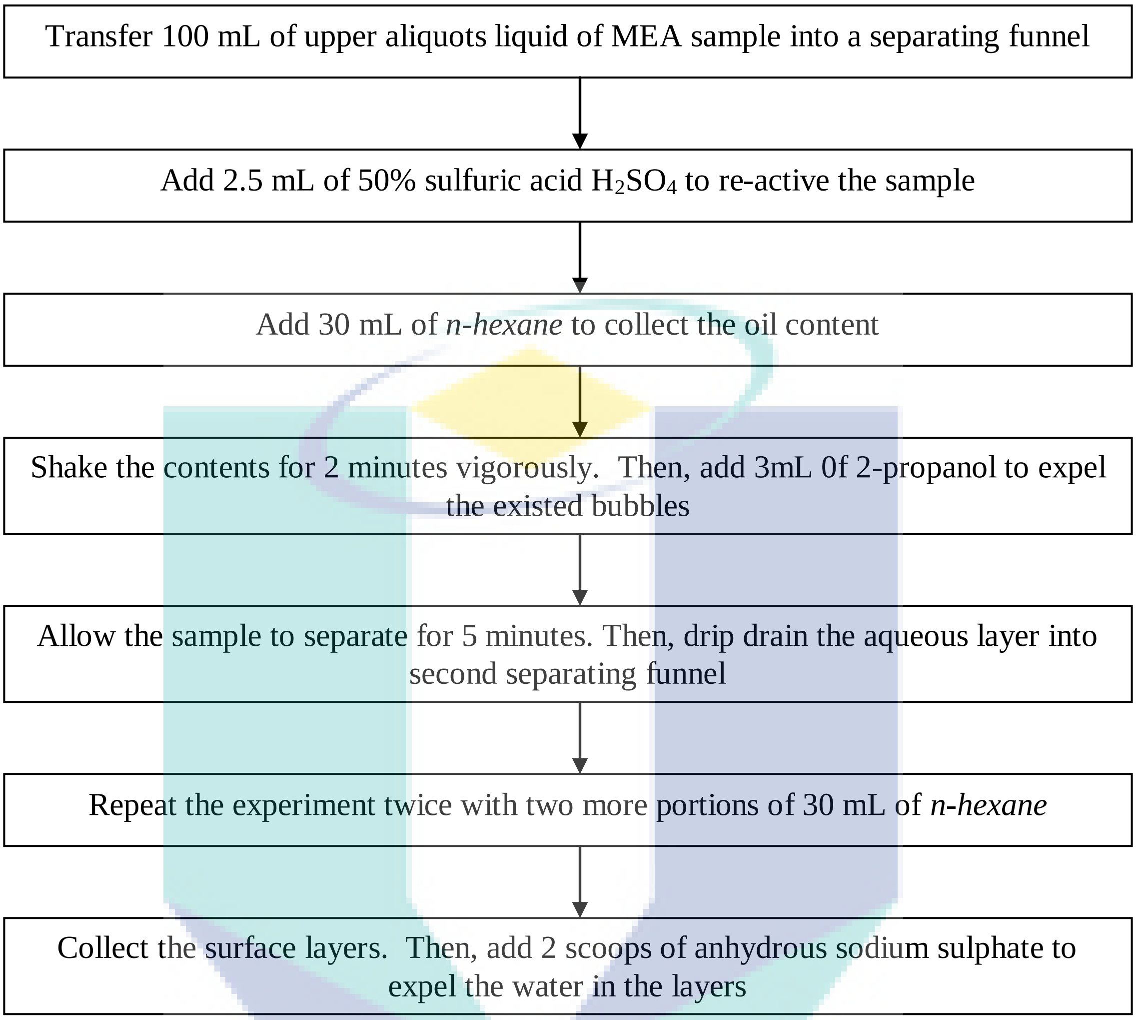


Figure 3.6: Flow diagram of oil and grease method

3.4.2 Suspended Solids Method

A gravimetric method recommended by APHA method (Apha, 1992) was used to determine the suspended solid. With the aid of vacuum filtration apparatus, a retained solid on the filter was recorded after heating. The details about the procedure were included in appendix B. Figure 3.7 shows the flow diagram of suspended solids method used in the experiments.

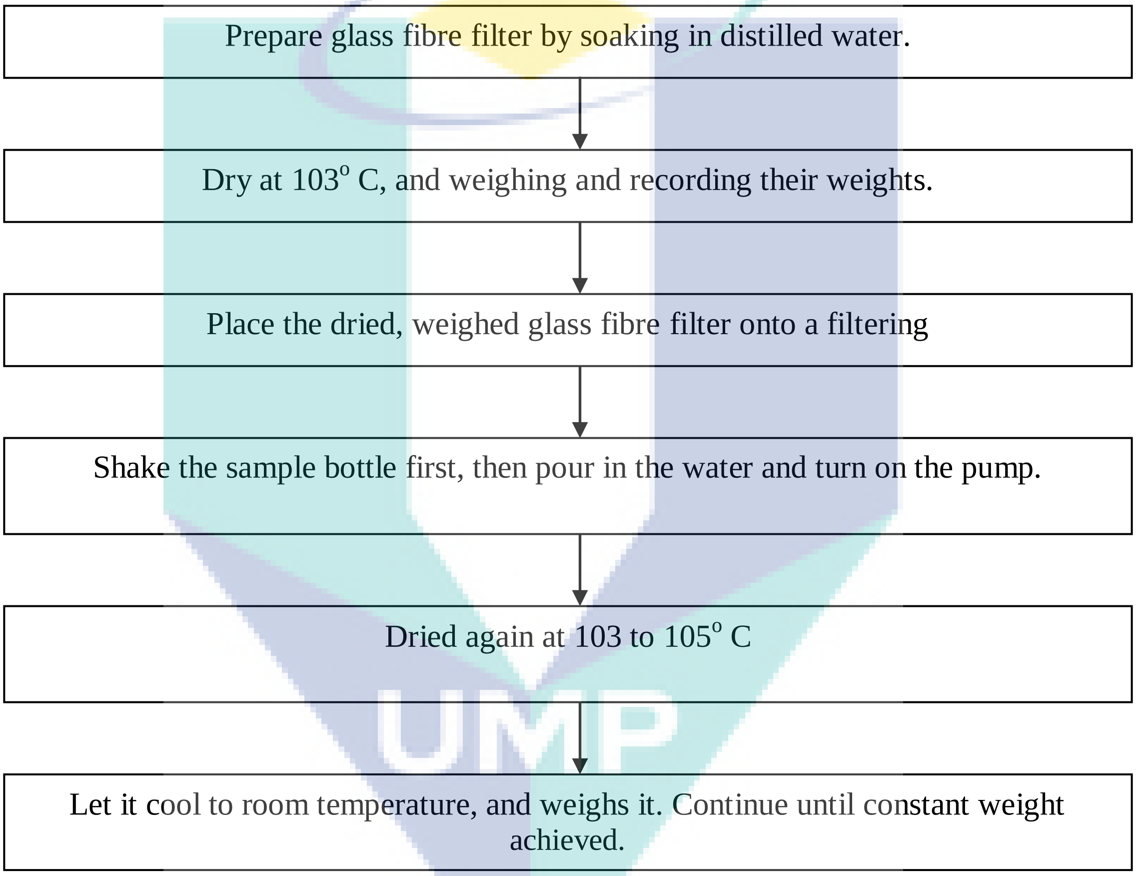
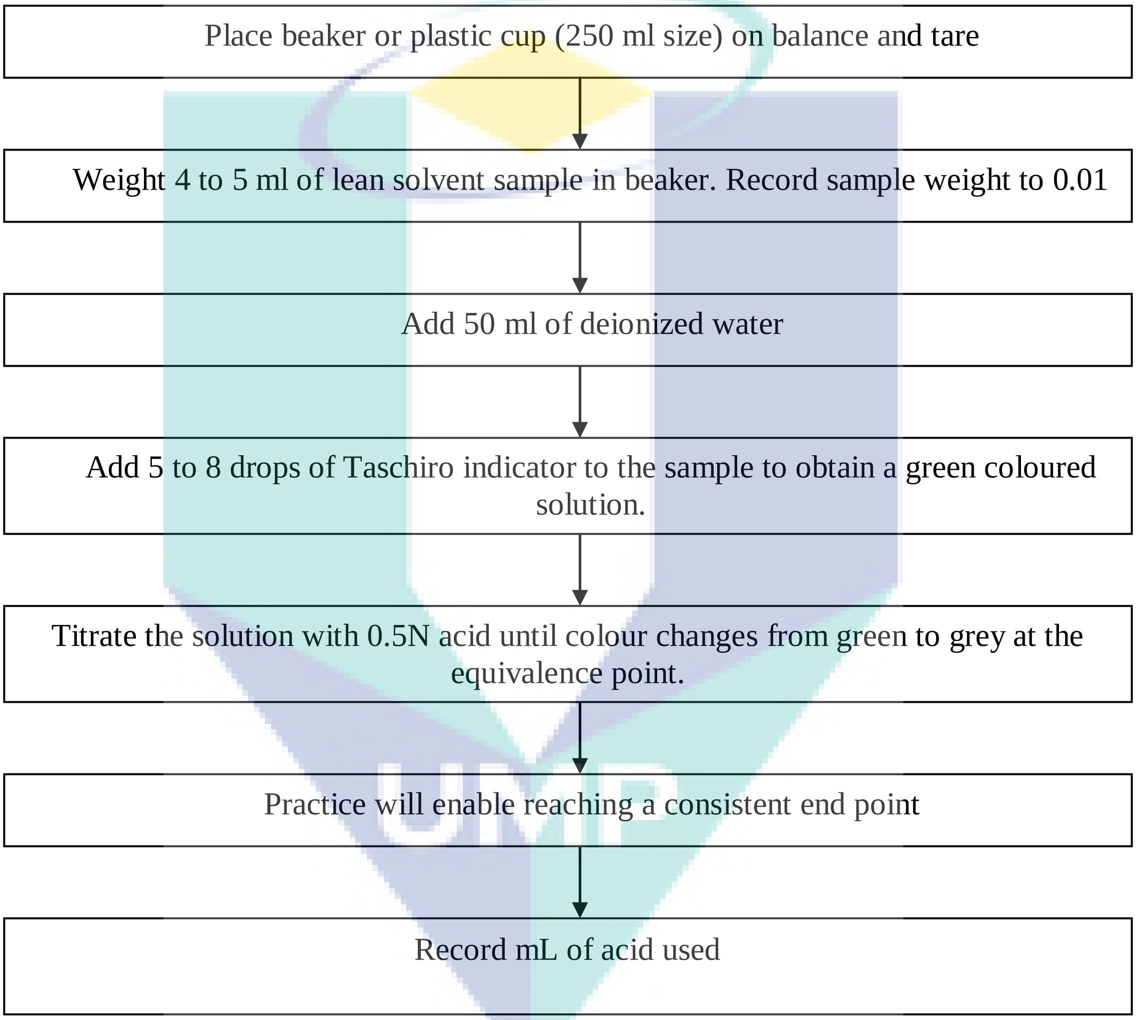


Figure 3.7: Flow diagram of suspended solids method

3.4.3 Amine Concentration Method

The amine concentration was measured by using titration method recommended by APHA method which Taschiro indicator used as amine indicator. The details about the procedure were included in appendix B. Figure 3.8 shows the flow diagram of amine concentration method.



Place beaker or plastic cup (250 ml size) on balance and tare

Weight 4 to 5 ml of lean solvent sample in beaker. Record sample weight to 0.01

Add 50 ml of deionized water

Add 5 to 8 drops of Taschiro indicator to the sample to obtain a green coloured solution.

Titrate the solution with 0.5N acid until colour changes from green to grey at the equivalence point.

Practice will enable reaching a consistent end point

Record mL of acid used

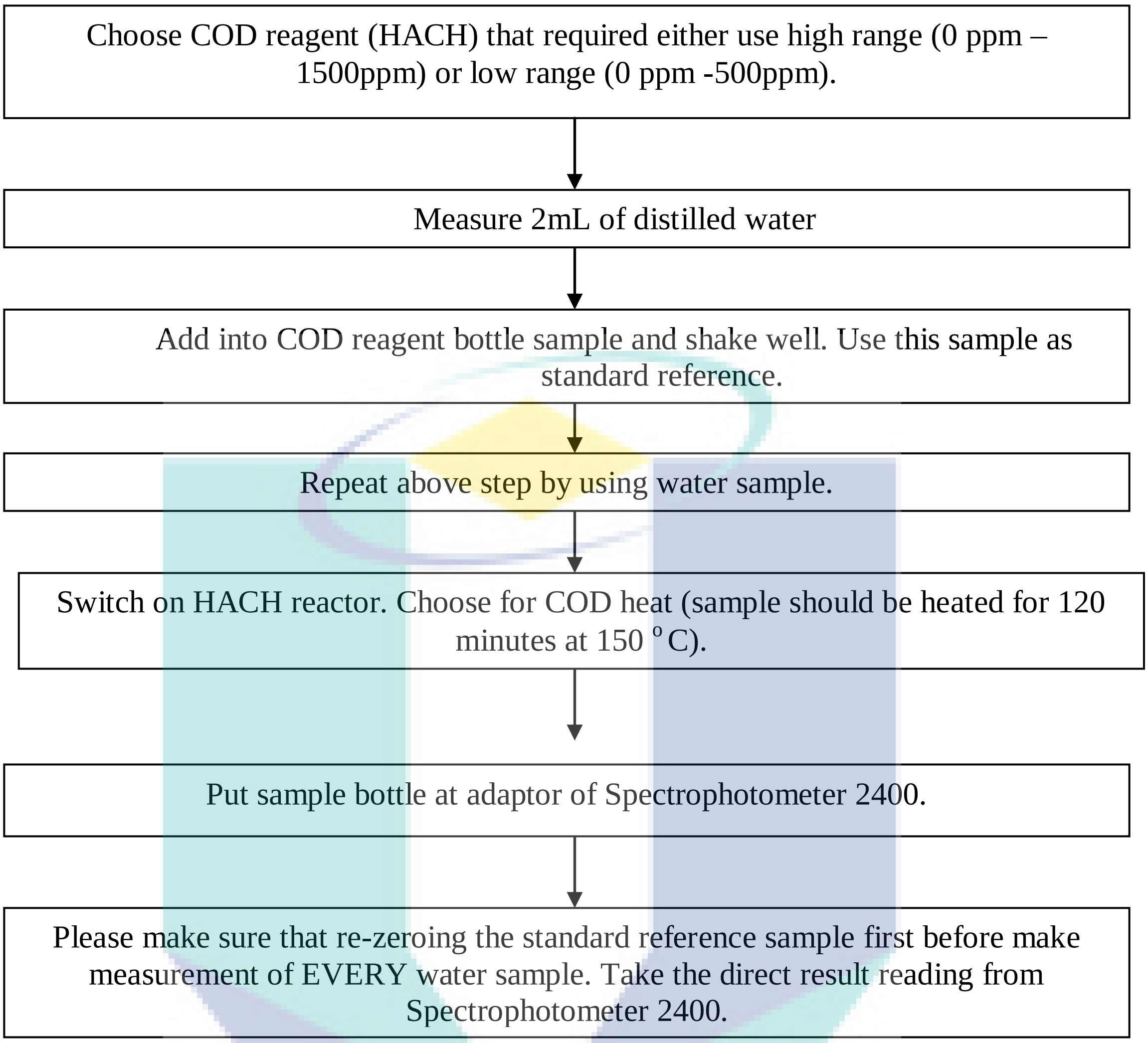
Figure 3.8: Flow diagram of amine concentration method

3.4.4 Chemical Oxygen Demand (COD) Method

The COD test was performed by colorimetric method using Spectrophotometer HACH Model DR/2400 (HACH Company, USA). It measures the amount of oxygen (O_2) required for complete oxidation of organic matter using strong oxidation agent, i.e. dichromate ion ($Cr_2O_7^{2-}$). The details about the procedure were included in appendix B. Figure 3.9 and 3.10 shows the portable spectrophotometer analyzes water quality and Hach reactor equipment used in the COD experiments while figure 3.11 shows flow diagram of COD method.

Figure 3.9: Portable Spectrophotometer Analyzes Water Quality

Figure 3.10: Hach Reactor Equipment



Choose COD reagent (HACH) that required either use high range (0 ppm – 1500ppm) or low range (0 ppm -500ppm).

Measure 2mL of distilled water

Add into COD reagent bottle sample and shake well. Use this sample as standard reference.

Repeat above step by using water sample.

Switch on HACH reactor. Choose for COD heat (sample should be heated for 120 minutes at 150 °C).

Put sample bottle at adaptor of Spectrophotometer 2400.

Please make sure that re-zeroing the standard reference sample first before make measurement of EVERY water sample. Take the direct result reading from Spectrophotometer 2400.

Figure 3.11: Flow diagram of COD method

3.5 Chapter Summary

This chapter presented a detailed explanation of the research methodology according to which conducted this research. It utilised the chemicals, materials and instruments available in the lab in order to make this research be successful. The experiments were repeated several times to give the best and significant results. In later chapter, it will revisit the action research methodology, analysing it, and discussing its appropriateness for this type of research.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

In order to give a clear understanding of the research work, the results and the respective discussion were grouped and arranged accordingly in the following manner: The first part of the chapter focused on the typical standard to be complied before recycling MEA wastewater. Then, discussion was focused on treatment performances of adsorbents, namely chitosan, activated carbon, alum and zeolite in reducing the residue oil, suspended solids and chemical oxygen demand (COD) in the MEA wastewater and at the same time maintaining the level of MEA concentration at acceptable limit. These evaluations of parameters were very crucial in determining whether the treated MEA could be recycled or otherwise.

Experiments were performed to find out the influence of adsorbents dosage, pH, temperature, mixing time, mixing speed, comparison of chitosan flake and chitosan powder for treatment process of MEA wastewater. In this research, chitosan was chosen as the main adsorbent to be evaluated for its potential to treat and to recycle the MEA wastewater compared to other adsorbents based on the reasons elaborated in chapter 1. Finally, optimization process was performed using a response surface methodology (RSM) with central composite design in order to attain maximum dosage of chitosan to get optimum condition of the removal rate of residue oil, suspended solids, and COD level of MEA wastewater using chitosan. In order to ensure the reliability of the data, each experiment was conducted for a minimum of 3 times with degree of acceptable error within +/- 10%.

4.2 CHARACTERISATION OF MONOETHANOLAMINE (MEA) WASTEWATER

Characterizing the monoethanolamine (MEA) wastewater is important to be conducted before further investigation can be performed in order to understand the nature and behaviour of the sample. It was also important as it would enable to explain the reasons behind its response towards specific treatment adopted in this study. To date, no data was available on the characteristics of the MEA wastewater from the industry generating the scheduled waste. Hence, study was conducted to examine seven critical parameters of the wastewater as shown in Table 4.1. The table showed the typical characteristics of Monoethanolamine (MEA) wastewater measured in the laboratory for several samples.

Table 4.1: Characteristics of Monoethanolamine Wastewater

Parameters	MEA Wastewater	Standard B DOE*
pH	10.0-12.0	5.5-9.0
Amine Concentration Level	30-50 wt%	-
Oil and Grease Concentration	500-2,000 mg/l	10.0 mg/l
Biochemical Oxygen Demand (BOD)	500-3,000 mg/l	50 mg/l
Chemical Oxygen Demand (COD)	200,000 – 300,000 mg/l	100 mg/l
Suspended Solids	60,000-80,000 mg/l	100 mg/l
Turbidity	30,000-50,000 NTU	-

** Third Schedule, Environmental Quality Act (Sewage and Industrial Effluents) Regulations 1979*

Based on the readings indicated in Table 4.1, it was obvious that the scheduled waste was far from acceptable to be released as effluent. All the parameters measured exceeded the limits of standard B effluent discharge act imposed by the Department of Environment, Malaysia. In order to discharge the wastewater, it requires thorough and comprehensive treatment to comply with standard B. Even, if the waste MEA is to be sent to the wastewater treatment plant of the company, the COD level for example, needs to be below 50,000 mg/l for it will disrupt the ecosystem of aerobic and anaerobic microbes in the treatment plant should the COD is above 50,000 mg/l limit. Hence, it makes more sense to treat the waste MEA for the purpose of recycling it back into the system. This approach will enable the industry to save cost of disposing the scheduled waste and at the same time reduce the cost to buy new MEA solution. This study is hence focused on rejuvenating the MEA solution for the purpose of recycling.

4.2.1 Typical Standard for Recycling of MEA Wastewater

Petroleum and petrochemical industry have set certain standard for waste MEA to be recycled back into the process systems. The standard was set to ensure that the recycled MEA able to function according to its purpose without creating further problem to the process system. Table 4.2 shows the typical standard of recyclable MEA waste.

Table 4.2: Typical Standard of Recyclable MEA waste

Parameters	Standard Limits
MEA Concentration Level	> 15 wt%
Oil and Grease Concentration	< 20 mg/l
Foam Height	< 4 cm
COD	< 50,000 mg/l
Total Vanadium (V_2O_5)	Min 0.70 %
Potassium Carbonate (K_2CO_3)	25 – 33 wt%

Among the six parameters listed in Table 4.2, MEA concentration is the most important criteria to be fulfilled by the MEA waste before any treatment method is to be employed. MEA concentration must be above 15.0 wt% for it to have sufficient strength to be recycled as CO_2 and H_2S absorbent in the absorption tower. Typically, in the absorption process, when MEA concentration in the solution is low, it requires higher temperature to absorb the CO_2 and H_2S contaminants in the gaseous stream.

The oil and grease concentration of the waste MEA also need to be below 20 mg/l for it to be recycled. This parameter is very crucial because hydrocarbon content greater than 20 mg/l will cause serious foaming in the absorber during operation, and this will reduce the efficiency of the absorption tower dramatically. In relation to this, the waste MEA is also subjected to measurement of foam height. Foam height of less than 4 cm is a necessity to ensure that its formation will not affect the performance of the absorption tower. Suspended solid is another parameter of concerned which may contribute to the formation of foam in the absorption tower, even though it is not highlighted in the typical standard of recyclable MEA waste mentioned above. Based on practical experiences of various professionals in the oil and gas industry, and findings from literature on the nature of suspended solids in liquids, it is strongly believed that high concentration of suspended solids in the MEA together with the presence of oil and grease can trigger the formation of foam in the tower.

This research work focused on treating the waste MEA so as to recycle it back into the system. Various adsorbents were examined for the treatment of waste MEA. The finding and data gathered from the experimental works were discussed thoroughly and the discussion was encapsulated on the removal efficiency of the adsorbents in term of oil and grease concentration, suspended solid and reduction of amine concentration. These parameters evaluation were very crucial in determining whether the treated MEA could be recycled or to be sent to wastewater treatment plant. Whereas, COD was also analyzed and this evaluation would provide information for the alternative treatment via wastewater treatment plant if the treated MEA was not possible to be recycled. Based on the objective of this research, four parameters were selected for the study, namely removal of residue oil, suspended solid, amine concentration level and COD.

4.3 EFFECT OF ADSORBENTS DOSAGE

Adsorbent dosage is one of the independent variables varied in this study to examine the performance of adsorbents in treating the waste MEA. The effect of varying the dosage on the degree of removal of residue oil, suspended solid, MEA concentration level and reduction of COD were examined and discussed in this section.

4.3.1 Effect on Removal of Residue Oil

The effects of adsorbent dosage (wt%) on the removal of residue oil from MEA wastewater was analyzed by varying the weight percentage of adsorbents at 100 rpm of mixing rate and 30 minutes of mixing time and at temperature of 30°C. Tests were carried out at original pH of the sample, i.e. 11.21. The pH value needs to be in the range of pH 11 to adhere with requirement and operating condition of the CO_2 removal system. Figure 4.1 shows the removal percentage of residue oil from MEA wastewater using chitosan, activated carbon, alum and zeolite. From the figure, it can be seen that at the highest adsorbent dosage (5 wt%), chitosan showed the highest removal of residue oil compared to other absorbents. Chitosan managed to remove 95 % of residue oil while activated carbon removed 87%, alum removed 64% and zeolite removed 46% of residue oil at the maximum dosage. Based on the results, Chitosan proved to be the best adsorbent in removing residue oil from MEA wastewater compared to activated carbon, alum and zeolite, within 5 wt% of adsorbent dosage.

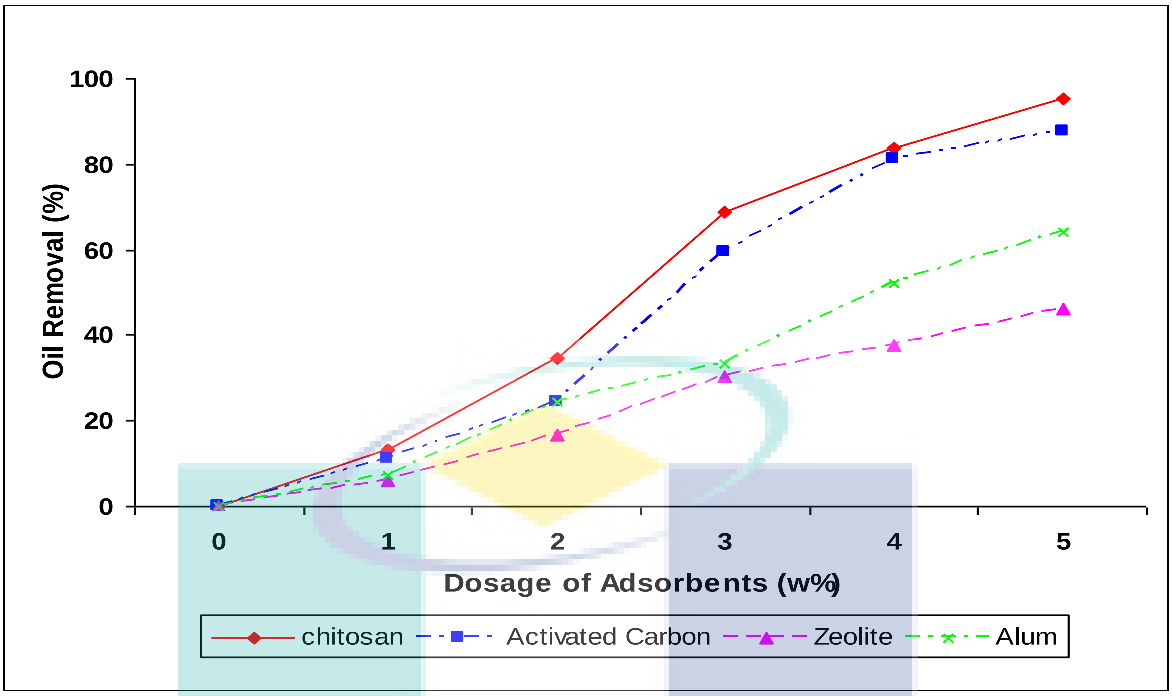


Figure 4.1: Percentage of residue oil removed versus dosage of adsorbents

The figure indicated that alum and zeolite behaved linearly within the range of adsorbent dosage investigated in this study. Chitosan and activated carbon, on the other hand shows two distinct phases of behaviour where at low dosage (1-2 wt%), slow progressive increase of oil removal was observed, while at high adsorbent dosage (above 2 wt%), high percentage of oil removal was experienced.

The main reason for the different behavior observed in the usage of various adsorbents mentioned above is due to the difference in mechanism of adsorption taking place in the systems. The linear relationships observed in alum and zeolite systems indicated that only one single mechanism of adsorption took place during the treatment process. Alum, a typical flocculating agent in water treatment plant, mainly adsorbed residue oil droplets through chemical adsorption. Zeolite, on the other hand, mainly adsorbed the residue oil droplets through physical adsorption.

The two distinct phases observed in Figure 4.1 in chitosan and activated carbon systems suggesting more than one mechanism of adsorption involved in each of the system. Chitosan, a well known biopolymer adsorbent, removed the residue oil droplets through chemical adsorption. Further increasing the dosage of the adsorbent increased the electrostatic field of the system significantly and contributed to the increase in the percentage of oil removal through electrostatic adsorption. On the same note, activated carbon, having large area/volume ratio, adsorbed residue oil droplets through physical adsorption and at high adsorbent dosage also showed significant contribution of electrostatic adsorption taking place.

Chemical adsorption took place as a result of the presence of hydroxyl groups and charge density on the adsorbent. In addition to this, residue oil in the MEA wastewater is negatively charged. Alum contained positive charge Al^{3+} which attracted the negatively charged residue oil in MEA wastewater to its surface. However, the charge density of alum is less than that of chitosan, hence, the degree of chemical adsorption in alum is less than that of chitosan.

Zeta potential measurement was therefore conducted to measure the charge density of chitosan and alum in the MEA solution. The measurement showed that zeta potential of chitosan system revealed a reading of ZP = -13.02 mV while alum system revealed a reading of ZP = -34.41mV. High negative value of ZP indicates a more stable suspension system (Sis and Birinci, 2009). Hence, the lower negative value of ZP in chitosan system indicated a more readiness of the system to be affected by the adsorbent, as compared to the alum system with a higher negative value. The finding is consistent with the explanation on the chemical adsorption given above. This can be noticed especially at low adsorbent dosage (for instance at 2 wt%) where chitosan removed 34 wt% oil as compared to 24 wt% removed by alum. Chitosan has a high charge density compared to other adsorbents (Ahmad *et al*, 2006). Chitosan is a cationic biopolymer adsorbent and possesses a positive ionic charge, with the ability to chemically bind with the negatively charged residue oil in the MEA wastewater. The deprotonation of the hydroxyl group occurred under alkaline conditions makes the chitosan positively charge (Niramol *et al*, 2005). The hydroxyl groups in the chitosan polymer adsorbed residue oil ions by ionic and covalent bonding. The strong alkaline condition aggravates MEA wastewater to break the oil droplets.

Activated carbon and zeolite mainly adsorbed residue oil through physical adsorption. BET measurement conducted on the adsorbents confirmed this finding. The

BET specific surface area for chitosan, activated carbon, alum and zeolite were measured via N_2 adsorption isotherms. It was found that the BET specific surface area for chitosan was 7.02 m^2/g, activated carbon was 1042.62 m^2/g, alum was 2.85 m^2/g and zeolite was 104.49 m^2/g respectively. The readings tally with the findings presented above. The relatively high values of BET for activated carbon and zeolite reflected the mechanism of physical adsorption in removing the residue oil. Similarly, the low values of BET for chitosan and alum supported the suggestion that chemical adsorption was the main mechanism in removing residue oil for both of the systems.

Activated carbon is a common type of adsorbent used for the removal of color and organic compounds in wastewater and water treatment plant and up to date there is no research conducted on the usage this adsorbent in removing residue oil, especially in the MEA contaminated wastewater. Activated carbon can be used to adsorb residue oil due to its highly porous nature of the solid and its large surface area to volume ratio . Much of this surface area is contained in micropores and mesopores. Due to its high degree of porosity, through physical adsorption, activated carbon removed more residue oil as compared to zeolite. This can be seen especially at low adsorbent dosage (below 2 wt%), where activated carbon removed 24 wt% of residue oil as compared to zeolite, 16 wt%. In physical adsorption, attraction of residue oil to the surface of activated carbon and zeolite was mainly due to the relatively weak van der Waals forces between the ions.

At pH 11, electrostatic attraction occurred between hydroxide ions of residue oil in MEA wastewater and the activated carbon surface to perform physical and electrostatic adsorption (Ensar and Bulent, 2005), but the attraction was much weaker than the chemical adsorption as in chitosan. This can be seen in Figure 4.1 where removal of residue oil was lower than the removal achieved in chitosan system. Furthermore, the zeta potential readings also indicated that the activated carbon possessed lower charge density (ZP = - 16.19 mV) as compared to chitosan (ZP = - 13.02mV).

The mechanism of adsorption by zeolites was mainly through ion-exchange (Chojnacki *et al*, 2004 and Erdem *et al*, 2004). The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. Zeolites also contain various types of cationic sites. The overall negative charge of the anions is balanced by cations that occupy the channels within the structure, and can be replaced with heavy metal ions (Chojnacki *et al*, 2004).

MEA wastewater contained various negative and positive charge ions of residue oil. Based on chemical nature of zeolite, the dominating mechanism of sorption was ion exchange in which cations in MEA wastewater bind to negatively charged groups on the zeolite surface. However, zeolite, having lower adsorption capacity (i.e. lower BET value than activated carbon) and the fact that ion exchange was weaker attraction than physical and chemical adsorption, removed less residue oil as compared to chitosan, activated carbon and alum, in treating the MEA wastewater. Furthermore, the zeta potential readings also indicated that the zeolite possessed lower charge density (ZP = - 38.22 mV) as compared to chitosan (ZP = - 13.02mV), activated carbon (ZP = - 16.19 mV) and alum (ZP = - 34.41 mV).

4.3.2 Effect on Removal of Suspended Solid

Figure 4.2 demonstrates the effect of adsorption on the percentage of suspended solid removal in MEA wastewater. In general, all adsorbents used in this study managed to reduce the suspended solids in the liquid sample. The untreated MEA wastewater was opaque and black in nature, having average suspended solids of 83,000 ppm. Prior to adsorption treatment, the MEA wastewater was pre-filtered with 0.45 μm ceramic filter. The purpose of this pre-filtration was to remove the coarse particles (> 0.45 μm) in the waste water since preliminary study showed that directly adsorbing the suspended solids before pre-filtering the sample resulted in fluctuation of readings, making it difficult to interpret the curve. This suggested that the presence of coarse particles affected the stability of the newly formed flocs or agglomerates, reflected by the fluctuation of the collected data. Upon pre-filtration, the concentration of suspended solids dropped to 69,000 ppm.

Figure 4.2 indicated that the percentage of suspended solids removal was a function of adsorbent concentration. The result showed that the suspended solid decreased progressively with the incremental increase of adsorbent from 1 wt% to 5 wt%. The result is analogous to the removal of residue oil from MEA wastewater. The graph shows that chitosan was the best adsorbent to remove suspended solid compared to activated carbon, alum and zeolite. The performance of suspended solids removal was similar to residue oil removal, i.e. chitosan > activated carbon > alum > zeolite.

Figure 4.2 showed the first instance of introducing the adsorbent gave the highest impact on the removal of suspended solids. Region 0 to 1 wt% of adsorbents dosage showed the most dramatic effect, with removal of solids achieving 40% using chitosan, followed by activated carbon (28%), alum (24%) and zeolite (20%). Percentage of solids removal continued to increase slowly in response to the increase of adsorbent concentration until reaching the maximum concentration of 5 wt%. At maximum dosage of adsorbents application, 5 wt% Chitosan managed to remove 57 % of suspended solid (29,000 ppm) while activated carbon was 49%, alum was 43% and zeolite was 38% (42,000 ppm) respectively.

It is interesting to note that without addition of adsorbent, even after a prolonged standing time of 7 days, no changes were observed on the condition of the MEA wastewater. As adsorbent was applied onto the sample, coagulation started to occur and upon filtration, concentration of suspended solids was reduced significantly. However, it was also noticed that there was no change in colour appearance of the sample. As the treated sample was left standing further for 7 days, clear sample was observed, indicating further settling of fine particles at the bottom of the container.

The observation indicated the presence of emulsifying agent in the residue oil within the vicinity of the wastewater which encapsulated the solid particles and prevented the particles to flocculate. As adsorbent was added into the wastewater, the emulsifier was adsorbed, leaving the particles to coalesce and settled at the bottom of the container. Another supporting point was the fact that the original wastewater sample contained suspended solids with a range of particle sizes, ranging from large to fine particles. Leaving the sample standing for several days did not change the appearance of the sample. Even after pre-filtering the wastewater sample before treating with adsorbent, the sample still appeared opaque and black in colour, after further standing for seven days.

Hence, it is obvious that adsorbent was more attracted to oil than solid particles. This was evident from the results obtained showing high percentage of oil residue removed from the system for all types of adsorbents as compared to the percentage of solids removed from the wastewater. The trends of removal observed were similar for both residue oil and suspended solids. Thus, it can be concluded that most of solid particles were removed together with the residue oil. Upon filtration of the treated sample, the wastewater was still appeared unchanged (opaque and black). Analysis of the wastewater showed almost all residue oil was removed while up to 57% of suspended particles were removed, leaving final solids concentration of 29,000 ppm (in the case of chitosan).The opaque and black nature of the wastewater indicated the presence of fine solid particles suspended in the liquid medium. The absence of emulsifier in the wastewater after being adsorbed by the adsorbent (chitosan, alum, activated carbon, zeolite) allowed the fine suspended solids to settle with time, resulting in a clear liquid after seven days standing.

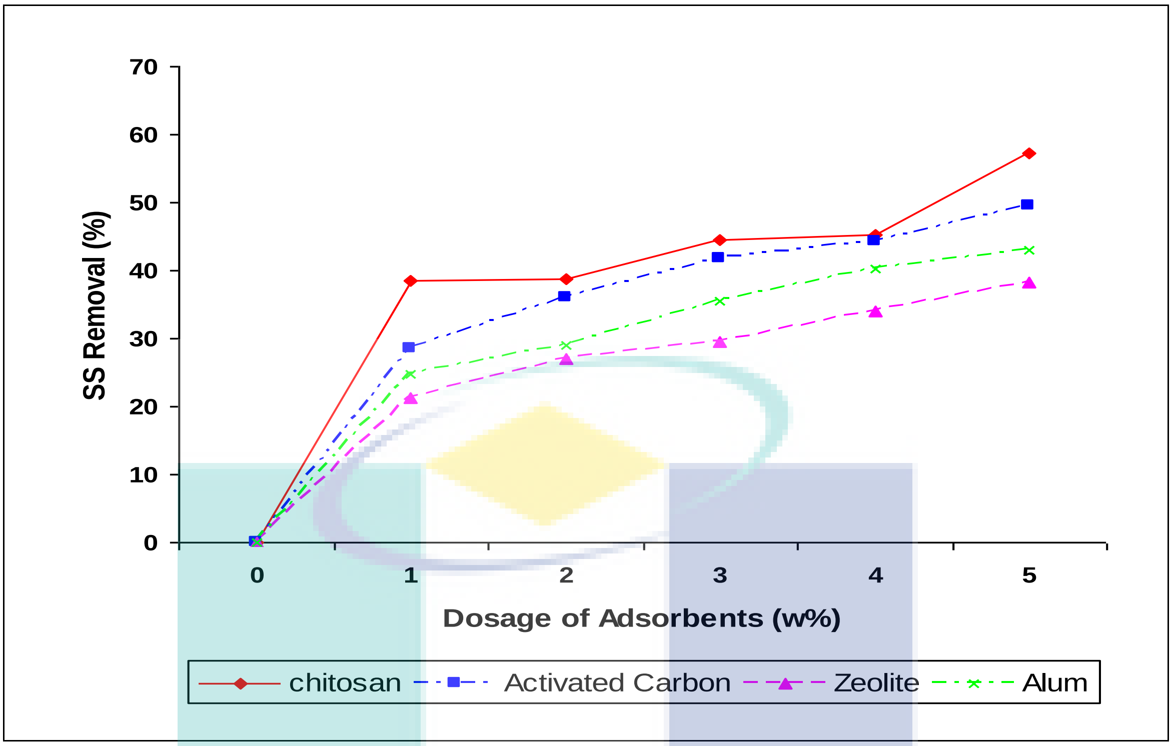


Figure 4.2: Percentage of suspended solids removal vs dosage of adsorbents

As compared to the performance of residue oil removal in MEA wastewater, these four types of adsorbents showed poor performance to remove the suspended solids. This happened due to suspended solids in the MEA waste was not 100% ionic. Some component such as potassium, vanadium and heavy metals were present in the MEA wastewater. These heavy metals could not be adsorbed by the adsorbents due to the selectivity and competition occurred in the MEA wastewater. In this case, the surface area of chitosan and other adsorbent preferred to adsorb the ionic charge particles compared to heavy metals. Therefore, after the adsorbents reached the maximum adsorption capacity, it was unable to adsorb heavy metals. Furthermore, the concentration of suspended solids in MEA wastewater was 60,000 – 80,000 mg/l while concentration of residue oil was 500 – 2,000 mg/l. It showed that the selectivity of residue oil adsorption was about 120 times greater than suspended solid adsorption. So, the adsorbents were not capable to adsorb all the particles in the suspension.

There were also differences in the nature of solids and liquids interactions. The strength of adsorption interaction was different involving solid-solid and solid-liquid attractions. The surface tension and surface contact between particles in MEA wastewater with adsorbents were much weaker than residue oil ions with adsorbents. The interaction between suspended solids with adsorbents involving Van Der Waals interaction was not stable and easily to break off into the suspensions.

However, the results also verified that adsorption of suspended solid on chitosan, activated carbon, alum and zeolite was insignificant at strong alkaline condition (pH 11). This is because at this pH condition, chitosan loses its cationic nature (Ahmad *et al*, 2005), whereas activated carbon, alum and zeolite were very unstable. Particularly for alum and zeolite, it was an extreme case, because alum and zeolite charges are very unstable at these alkaline conditions. Furthermore at this pH, the adsorption process itself is very unstable due to the characteristics of MEA wastewater. It needs to be mentioned that adsorbents were introduced once into the MEA wastewater and observation was conducted to see its effect on all the parameters

4.3.3 Effect on MEA Concentration

Figure 4.3 shows the effects of varying the dosage of adsorbents (chitosan, activated carbon, alum and zeolite) on the MEA concentration in the treatment of MEA wastewater. As observed in the graph, no significant reductions of amine concentration were observed in the waste water. Hence, it can be concluded that all the different types of adsorbent used in this study did not adsorb amine molecules in the waste water during treatment, even upon increasing the dosage of the adsorbents. The results indicated that in general, the adsorbents were effective in reducing the residue oil and suspended solids and at the same time the adsorbents were inert to the amine group. This was due to the fact that the amine group itself functioned as an absorber to capture CO_2 and H_2S in the gas stream during absorption tower operation. This implied that the amine group consisted of relatively big molecules to function as an absorber. Thus, adsorption treatment of the MEA waste water would not be able to capture the amine molecules. This scenario indicated that adsorption method of treating the waste MEA solution is suitable and can be explored further so as to rectify the proposed method of treatment.

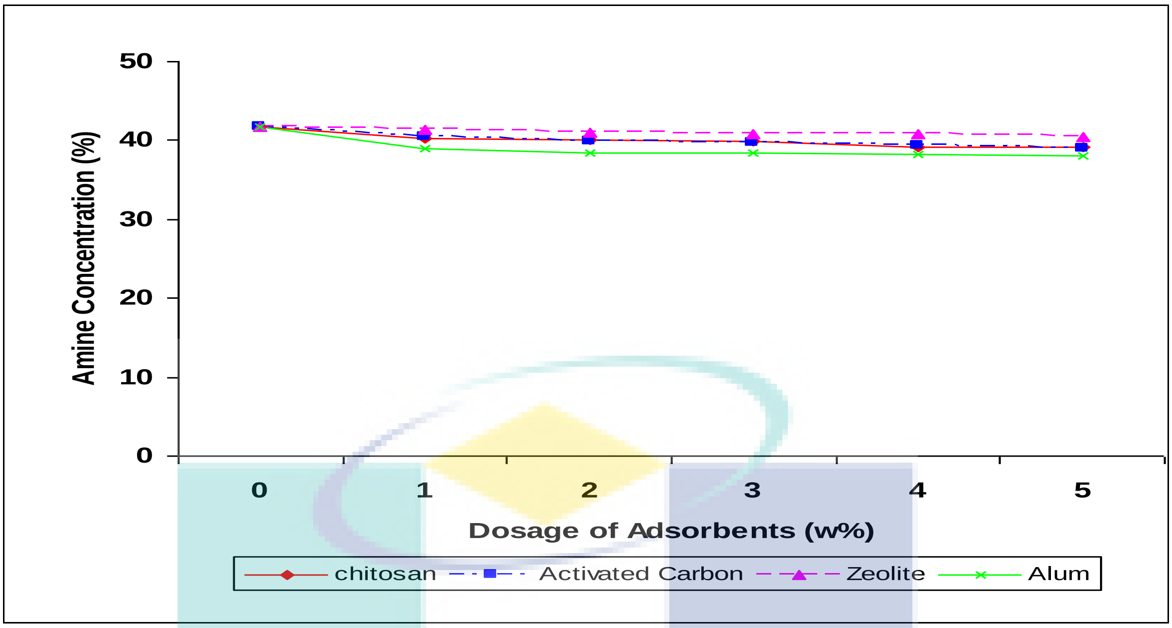


Figure 4.3: MEA concentration (MEA) vs dosage of adsorbents

4.3.4 Effect on Reduction of Chemical Oxygen Demand (COD)

For recycling purposes of MEA waste solution into the absorption process system, COD reading is not a parameter of concern to be monitored. However, if the solution is to be discharged to the wastewater treatment plant, then COD reading is the almost important parameter to be monitored since waste water having COD value exceeding 50,000 ppm will destroy the microorganism activities in the treatment plant.

Study was conducted to measure the COD reading of waste water sample before and after adsorption treatment to examine the effectiveness of the absorbents in reducing the COD. This COD reading would show either the wastewater can be recycled or not. Figure 4.4 shows the COD readings as a function of adsorbent dosage for the four types of adsorbents investigated in this research. The initial COD reading of the untreated MEA waste solution was 230,000 ppm. Based on the study, all of the investigated adsorbers showed effect of COD reduction especially upon increasing the adsorbent dosage. Chitosan managed to reduce 83 % of the COD reading to 38,500 ppm, while activated carbon treatment reduced the reading by 80% to 44,000 ppm. Alum reduced the COD reading by 73% to 62,000 ppm while zeolite by 71% to 66,000 ppm, respectively. All the readings were recorded at adsorbent dosage of 5wt%. At this dosage, only chitosan and activated carbon were able to reduce the COD reading below the requirement limit of the wastewater treatment plant (i.e. 50,000 ppm). Looking at the trend of the curves in Figure 4.4, it was expected that increasing further the adsorbent dosage greater than 5 wt%, will eventually able to reduce the COD below 50,000 ppm for alum and zeolite.

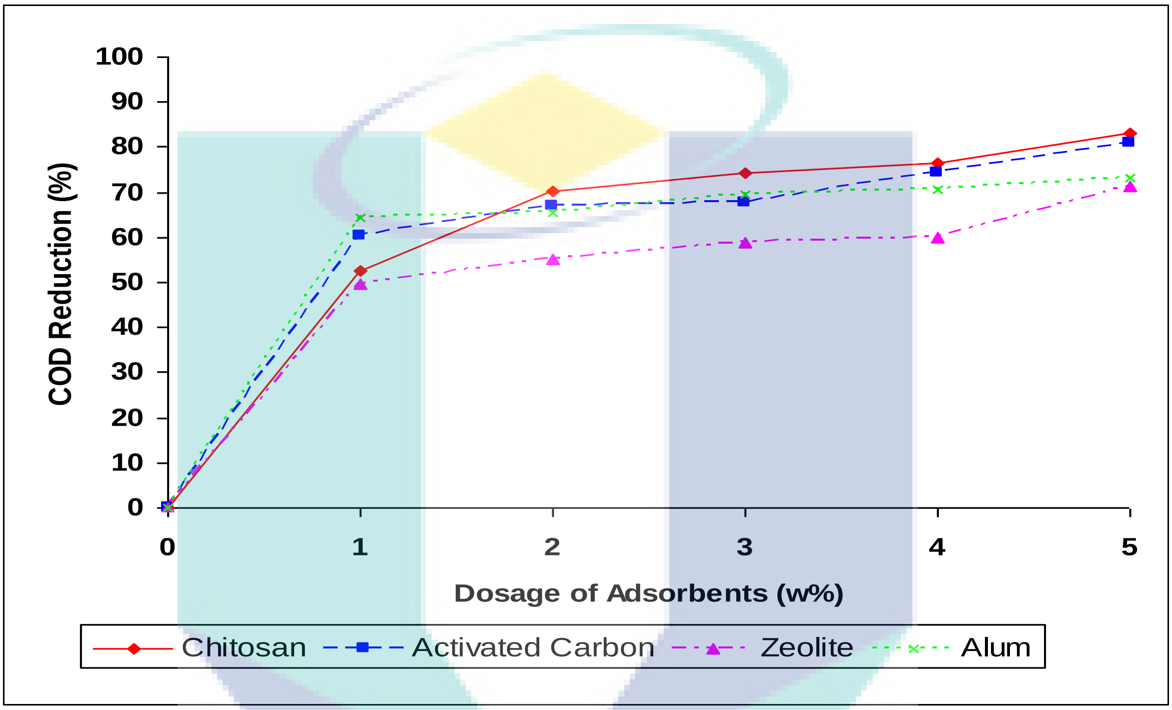


Figure 4.4: Percentage of COD reduction vs dosage of adsorbents

COD of MEA wastewater was high because it contained high organic material and heavy metals, especially heavy hydrocarbon contaminated from the gas processing. The heavy hydrocarbon consists of long carbon chain which is difficult to degrade. Removal of oil and grease as well as the suspended solids by the adsorption treatment contributed to the reduction of COD value significantly. Hence, it can be concluded that chitosan showed the best adsorbent in reducing the COD level effectively, followed by activated carbon and alum, while zeolite showed the least effective adsorbent for the reduction of COD, within the scope of this study.

4.4 EFFECT OF pH

Effect of varying the pH of the MEA waste water on the monitored parameters were conducted at optimum adsorbent dosage (5 wt%), 100 rpm of mixing rate, 30 minutes of mixing time and at 30°C of temperature.

4.4.1 Effect on Removal of Residue Oil

The effect of pH was investigated by varying the pH value between pH 11 and pH 3 using dilute HCl solution. pH of wastewater is known to influence the performance of adsorption process since it generally affects the surface charge of adsorbents, and in some instances affects the degree of ionization and adsorption of residual oil during reaction.

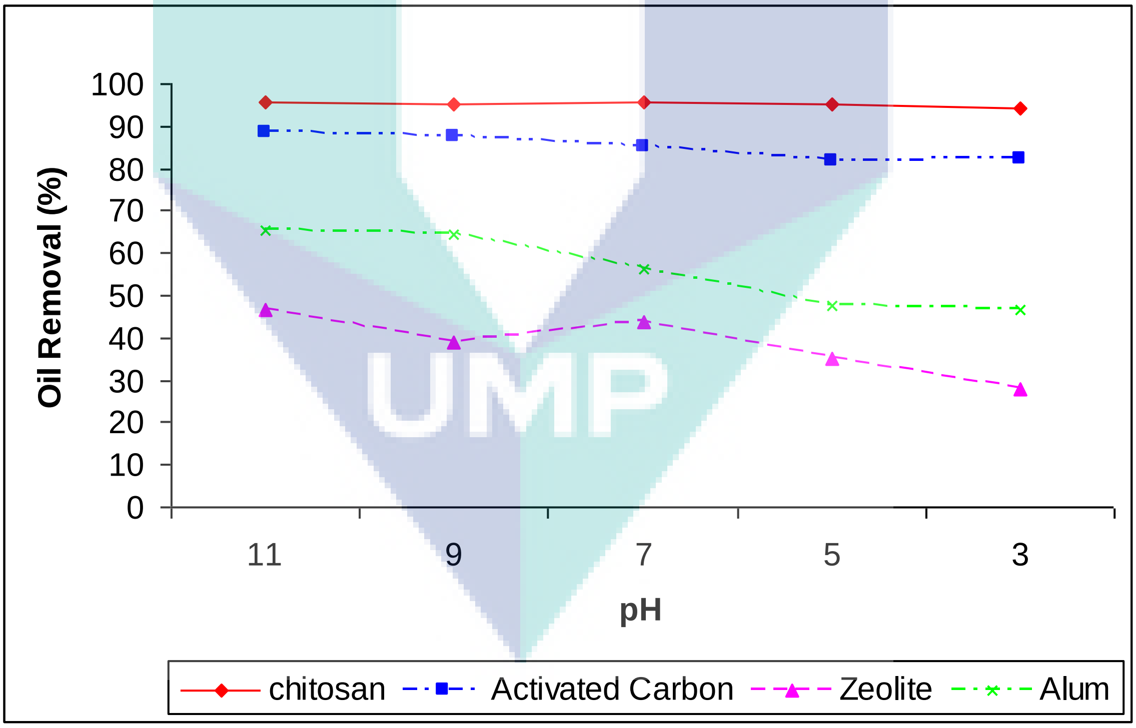


Figure 4.5: Percentage of residue oil removed versus pH

Figure 4.5 showed the effect of pH on the performance of adsorption processes in reducing oil and grease from MEA wastewater. From the figure, in general, it can be safely suggested that the performance of chitosan as oil and grease remover was unaffected by the pH variation of the MEA wastewater (maintained at 95% oil removal). Activated carbon showed only a slight drop in percentage of oil removal when the pH was brought down progressively, from 88% at pH 11 to 82% at pH 3. On the other hand, alum and zeolite showed significant drop in percentage of oil removal as the pH progressively decreased, from 65% and 46% at pH 11 to 46% and 27% at pH 3 respectively.

The result indicated that application of chitosan was not influenced by the pH of the solution, neither acidic nor basic condition. The high percentage of oil removal (95% oil removal) indicated the strong affinity of oil towards chitosan surface, irrespective of the surrounding environment. The hydrophobicity nature of chitosan in addition to its adsorptive characteristics surpassed any barrier imposed by the surrounding medium. This phenomenon was attributed to chitosan structure. Every unit of chitosan contained one amine group, one primary hydroxyl group ($-CH_2OH$) and two secondary hydroxyl group ($-OH$). Therefore the residual oil ions tend to react preferentially with the primary hydroxyl group of the chitosan (Gurusamy et al, 2007) at high pH 8 to 11. Meanwhile, at lower pH (pH 6 to pH 3), amino groups became active components to adsorb oil. At this stage, more protons were available to protonate amine groups of chitosan molecules to form NH_3^+ groups, thereby increasing electrostatic attractions between negatively charged residual oil and positively charged adsorption sites, and causing high degree of residual oil adsorption.

Activated carbon normally worked best in acidic environment since activated carbon is generally being activated in acidic condition. Looking at the trend of the curve, it showed that activated carbon performed better in alkaline as compared to acidic environment, contradicted with the general expectation. The trend dropped slightly at pH 5 downward as HCl acid was added to the suspension. Alum and zeolite, with relatively low adsorption ability, showed significant drop in percentage of oil removal as the wastewater pH was progressively reduced to acidic condition via HCl addition, with both systems dropped by 19% respectively.

Addition of HCl solution reduced the pH of the MEA wastewater to acidic condition and produced hydroxyl and hydrogen peroxide ions which acted as reacting agents in transforming the amine into NH_3 ions. In addition, the acid also reacted with metal particles to produce metal chlorides. The changed in the MEA wastewater characteristics did not affect the performance of chitosan in adsorbing the residue oil since oil has strong affinity towards chitosan and the characteristics of chitosan with its hydroxyl group in basic solution and the role of amino group in acidic condition which has been elaborated earlier.

Activated carbon, being less adsorptive than chitosan, was affected by the change in characteristics of the wastewater. The relatively high degree of adsorptivity of activated carbon was due to its high area/volume ratio and the presence of electrostatic interaction. As more HCl was added into the system, more Cl^- ions were available and posed competition with the negatively charged residue oil droplets to interact with the activated carbon. Hence, a slight drop in percentage of oil removal was noticed in application of activated carbon as adsorbent to treat the MEA wastewater.

Alum and zeolite, having relatively low adsorptivity, were affected significantly by the changes brought about by the acidity of the MEA wastewater. Al^{3+} ion in alum has tendency to bind with Cl^- ion from the HCl added into the system. Hence, as more HCl was added into the system to reduce further the pH of the wastewater, more Cl^- ions were available for Al^{3+} ions in Alum to react. As a result, significant drop in percentage of residue oil removal at low pH was observed in Figure 4.5 for alum. Zeolite, on the other hand, adsorbed residue oil through ion exchange mechanism. Zeolite contained Si^{4+} and Al^{3+} ions which tended towards Cl^- ions presence in the wastewater due to the HCl addition. The competition of this additional ion to bind with zeolite significantly reduced the percentage of residue oil removal observed in Figure 4.5 at low pH values.

4.4.2 Effect on Removal of Suspended Solid

Figure 4.6 shows the effect of pH on the suspended solid removal using chitosan, activated carbon, alum and zeolite from MEA wastewater. All adsorbents showed similar pattern of decreasing percentage of particle removal in the event of decreasing the pH value from pH 11 to pH 3. From the results, it appears that at pH value of 11.0 (actual pH of MEA wastewater), the removal of suspended solids was at maximum with 61% for chitosan, 49% for activated carbon, 42% for alum and 38% for zeolite.

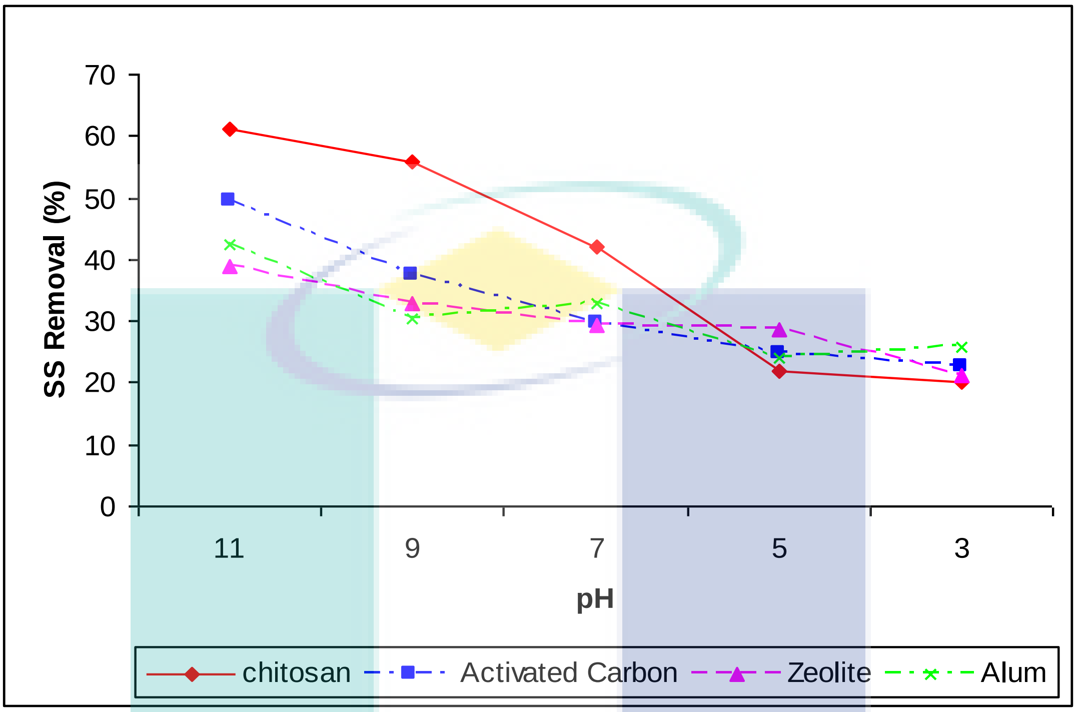


Figure 4.6: Percentage of suspended solids removal vs pH

Figure 4.6 showed that adsorption of suspended solids via chitosan was most affected by the increase in competition for adsorption in the system as a result of HCl addition. The removal of suspended solids dropped by 31% as the pH decreased progressively from pH 11 to pH 3, contrasting to residue oil removal, in which chitosan did not show any drop in the percentage of oil removal. Zeolite showed the least affected with 14% decrease in suspended solids removal.

The main reason for the observed drop in performance of all the adsorbents in removing the suspended solids was due to the effect of Cl^- ion presence in the system as a result of HCl addition. Cl^- ion reacted with heavy metals to produce metal chlorides or metal salts. As more HCl was added, concentration of Cl^- ion increased accordingly and led to more neutralization reaction occurring. Metal salts were less prominent to be adsorbed by the adsorbents as compared to the positively charged metals. At the same time, Cl^- ion also competed with the suspended solids to interact with the adsorbent.

These two factors contributed most in the decrease of suspended solids removal by the adsorbents in the event of decreasing the pH, as observed in Figure 4.6.

4.4.3 Effect on MEA Concentration

Figure 4.7 shows that increasing the pH significantly affected the MEA concentration in the wastewater. As elaborated in section 4.3.3, chitosan, activated carbon, alum and zeolite did not alter the MEA concentration in the wastewater during adsorption. On that note, it can be concluded that the decrease in MEA concentration in the wastewater in the event of progressively decreasing the pH of the wastewater occurred due to the HCl addition which degraded the amine solution.

As observed in Figure 4.7, as the pH progressively decreased from pH 9 to pH 3, the level of MEA concentration decreased and reduced from 41 wt% to 15 wt% for all the adsorbents. These happened due to amine deterioration and degradation after the addition of hydrochloric acid to adjust the pH of the samples. Sabtanti and Dutta, (2009) reported that the degradation of high concentration amine depended on the concentration of hydrogen peroxide and Fe^{2+} at acidic condition. This hydrogen peroxide was the source materials for generation of strong oxidizing radicals such as hydroxyl and hydroperoxyl in solution. Since MEA contained the elements C, H, O and N, oxidation of amine by hydroxyl radical is expected to transform the organic nitrogen into NH^{4+}, NO^{2-} and NO^{3-}. Klare et al (2000) presented a possible mechanism of amine degradation by hydroxyl radical which identified NH_3 as product in partially amine. The hydrochloric acid was the reacting agent to produce hydroxyl and hydroperoxyl ions in the MEA that became active compound to degrade amine. Based on the result, it can be concluded that the decreasing of pH by addition of hydrochloric acid increased the amount of hydroxyl and hydroperoxyl group to degrade amine. Naturally, all the adsorbents did not adsorb MEA since MEA molecules are big. The drop in the MEA concentration was purely due to degradation of MEA as a result of the reaction with HCl.

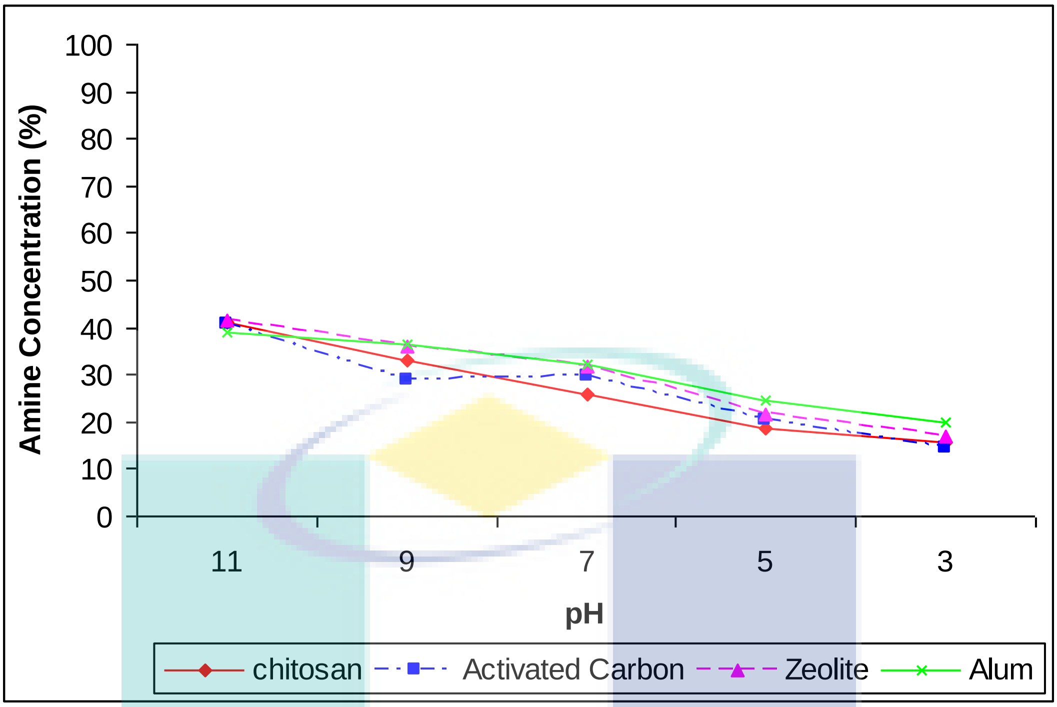


Figure 4.7: MEA concentration (MEA) vs pH

4.4.4 Effect on Reduction of Chemical Oxygen Demand (COD)

The result in Table 4.3 and graphically illustrated in Figure 4.8 showed the effect of pH on COD of MEA wastewater as a result of adsorption via chitosan, activated carbon, alum and zeolite, respectively. The figure appears that decreasing the pH of the MEA wastewater gave negative effect on the performance of the adsorbents in reducing the COD. At pH 11 (the original pH of the wastewater), 5 wt% of chitosan managed to reduce the COD from its original value of 230,000 mg/l to 38,500 mg/l, while activated carbon reduced to 44,000 mg/l, alum to 62,000 mg/l and zeolite to 66,000 mg/l, respectively. As the pH of the wastewater was reduced progressively via addition of HCl solution, COD values in all the adsorption experiments conducted showed increasing trend, as observed in figure 4.8. As mentioned in the above section, addition of HCl acid caused reaction to occur with amine group, producing NH^{4+}, NO^{2-} and NO^{3-}. As pH was reduced further by increasing the dosage of HCl acid, more reaction took place. This phenomenon resulted in the increase of COD of the wastewater and overshadowed the role of adsorbents in decreasing the COD values, as observed in figure 4.8.

Table 4.3: Effect of pH on COD level

	Chitosan	Activated Carbon	Zeolite	Alum
pH	COD (mg/l)	COD (mg/l)	COD (mg/l)	COD (mg/l)
11	38500	44000	66000	62000
9	76000	86500	99500	90300
7	109000	164600	176000	170500
5	Out of range	Out of range	Out of range	Out of range
3	Out of range	Out of range	Out of range	Out of range

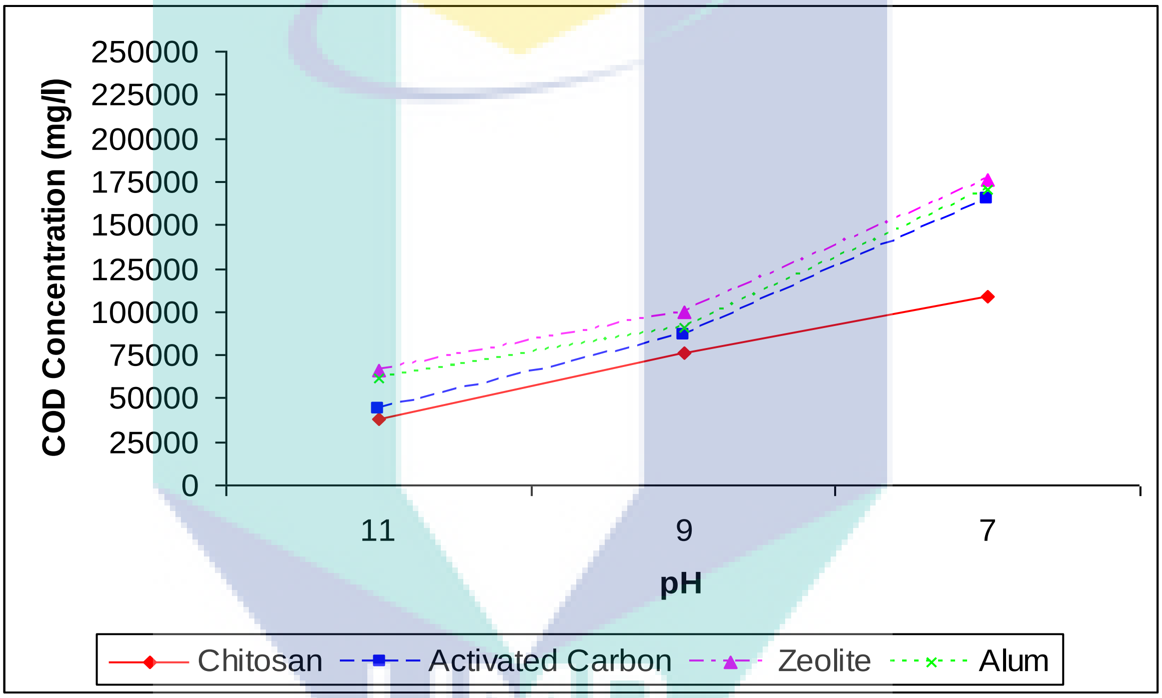


Figure 4.8: COD Concentration vs pH

4.5 EFFECT OF TEMPERATURE

Effect of temperature was investigated since temperature typically affects the performance of processes. Hence, understanding its influence on the process will enable one to improve and optimize the overall process of the system.

4.5.1 Effect on Removal of Residue Oil

Influence of temperature on adsorption performance using chitosan, activated carbon, alum and zeolite was studied in relation to removal of residue oil. Figure 4.9 shows the effect of temperature on percentage of residue oil removal in the adsorption process. As observed, increasing the temperature of the system showed insignificant effect on the adsorption behavior. Within the temperature range of 30 to 80^{o}C, no significant change on the percentage of oil removed was observed for all types of adsorbents used in this study. Hence, it can be concluded that supplying heating energy into the system did not influence the adsorption behavior, neither increased nor decreased the performance of the adsorbents. On another aspect, affinity of adsorbents toward residue oil exceeded the influence of temperature increase in the system. Thus, increasing the temperature did not affect the percentage of residue oil removal.

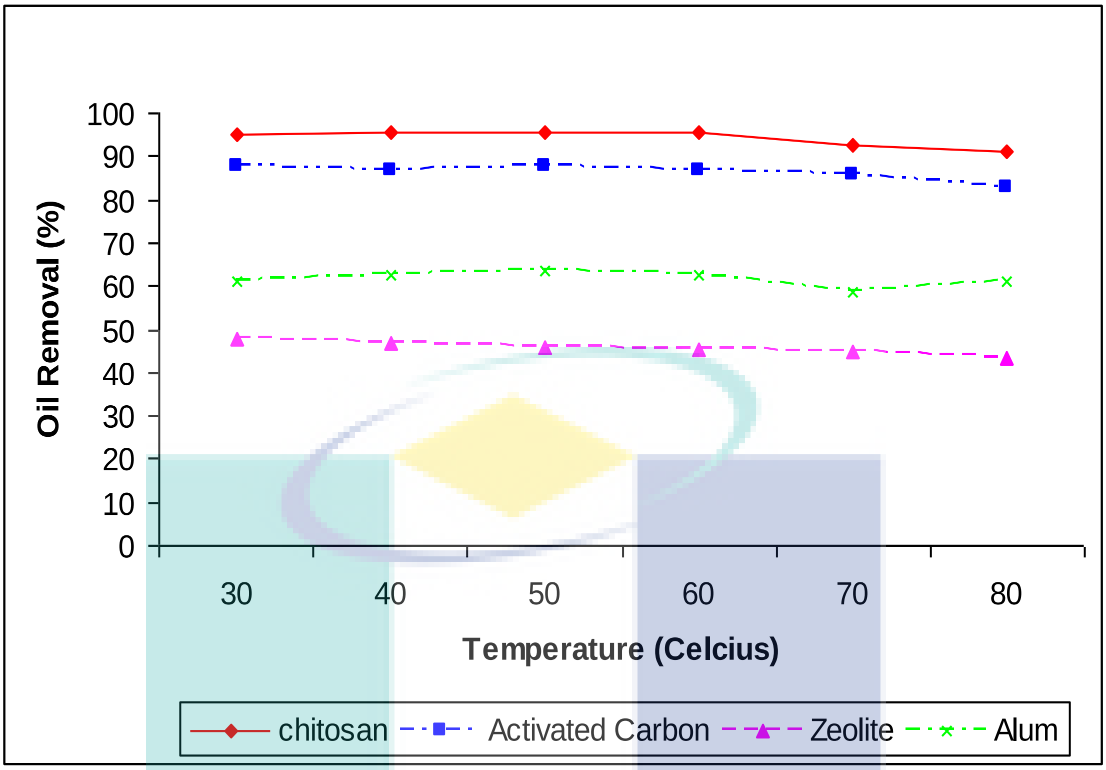


Figure 4.9: Percentage of residue oil removed versus temperature

4.5.2 Effect on Removal of Suspended Solid

Figure 4.10 showed the effect of temperature on the removal of suspended solid by adsorbents. In general, the figure showed that increasing the temperature of the system in the range of 30 to 80°C gave either least or no significant effect on the removal of suspended solid. Chitosan indicated a slight drop in the percentage of suspended solid removal (dropped from 60% to 52% as the temperature exceeded 60°C). At this temperature, chitosan lost its cationic nature, in which positive charges on chitosan surface reduced slightly and affected chemical adsorption process. The drop in its cationic nature affected the adsorption of suspended solid. Nevertheless, removal of residue oil was not affected since affinity of oil towards chitosan exceeded the decrease of the ionic strength.

Alum, on the other hand, showed a slightly positive response towards temperature increase. An increase of 5% was observed in the suspended solid removal as the temperature exceeded 50°C. The slight increase in suspended solid removal was due to heat absorption of the metal content in Alum. This energy absorption increased the reactivity of Alum to further react with anions. This was reflected through the slight increase of solid removal in the system. Activated carbon and zeolite performances were, on the other hand, not affected by the temperature increase. This indicated that in general, removal of suspended solids via adsorption was unaffected by temperature variation.

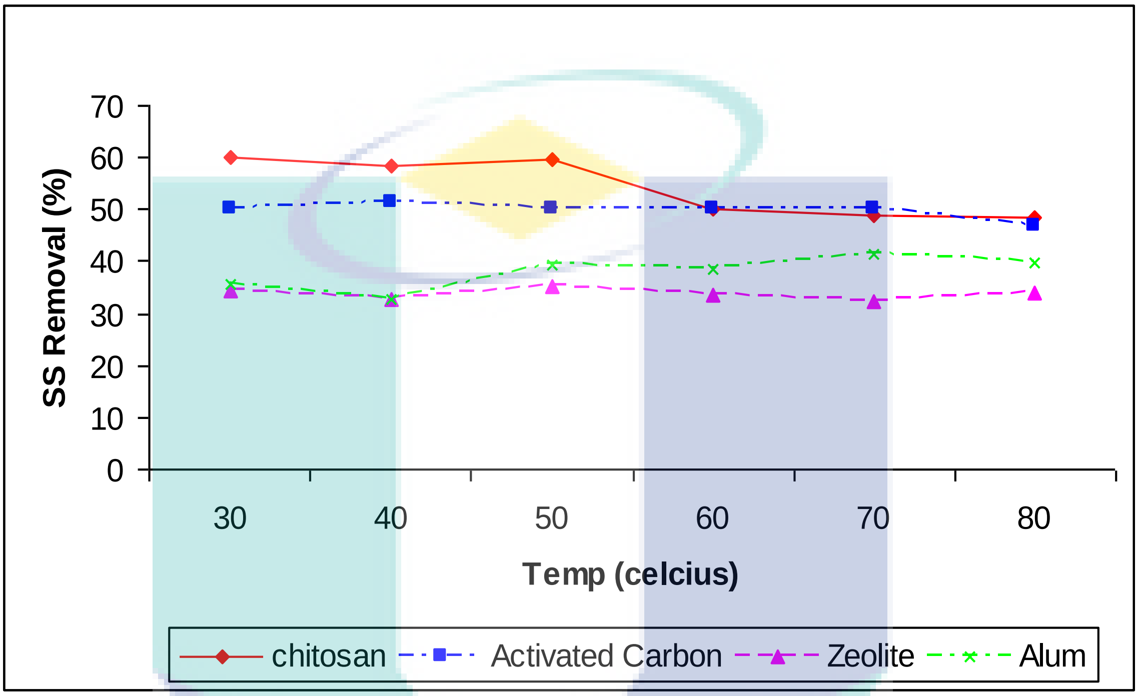


Figure 4.10: Percentage of suspended solids removal versus temperature

4.5.3 Effect on MEA Concentration and Chemical Oxygen Demand (COD)

Figure 4.11 and 4.12 showed the effect of temperature increase on MEA and COD reductions through adsorption, respectively. As observed in the figures, obviously there was no reduction of MEA or COD occurring in the adsorption process. Varying the temperature in the range of 30 to 80^{o}C also did not alter the performance of the adsorption process.

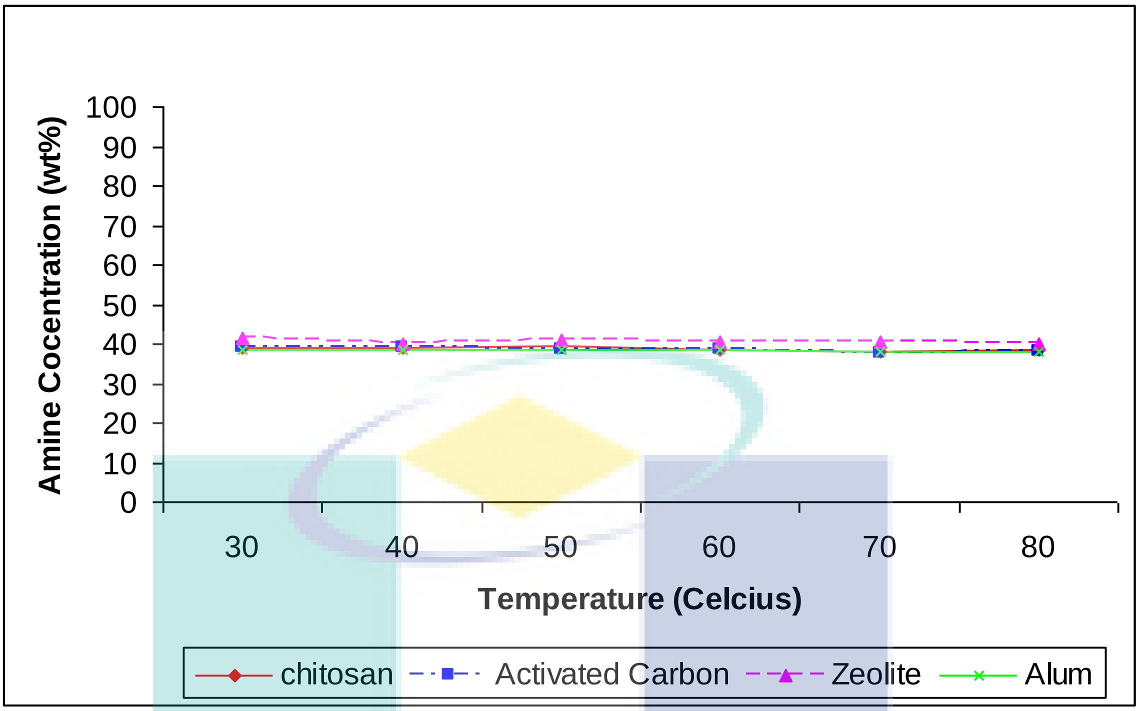


Figure 4.11: MEA concentration (MEA) versus temperature

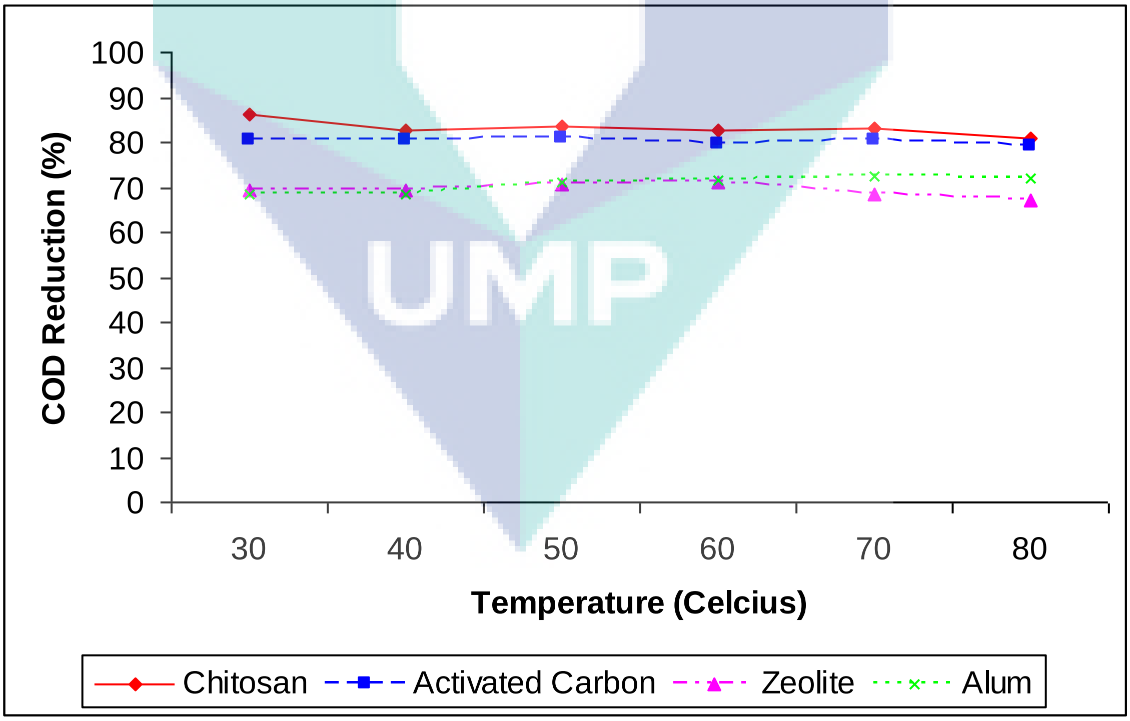


Figure 4.12: Percentage of COD reduction versus temperature

4.6 EFFECT OF MIXING TIME

4.6.1 Effect on Removal of Residue Oil

Figure 4.13 shows the effect of mixing time on the removal of residue oil. The adsorption was conducted at mixing speed of 100 rpm, pH 11 and temperature of 30°C, with adsorbent dosage of 5%wt. Based on the results presented in Figure 4.13, it clearly showed that there must be a minimum duration of mixing required for a specific type of adsorbent to achieve its maximum removal of residue oil. Similar to the discussion presented earlier, the order of performance in descending manner for all the adsorbents investigated in this study was as followed: Chitosan>Activated carbon>Alum>Zeolite. In general, percentage of residue oil removed by the adsorbent increased accordingly as the mixing time was increased until it reached its maximum achievable percentage of oil removed upon which increasing further the mixing time would not exceed the maximum percentage of oil removed. In some occasion, such as in Alum and Zeolite, further increasing the mixing time in fact gave adverse effect on the performance of the adsorbents.

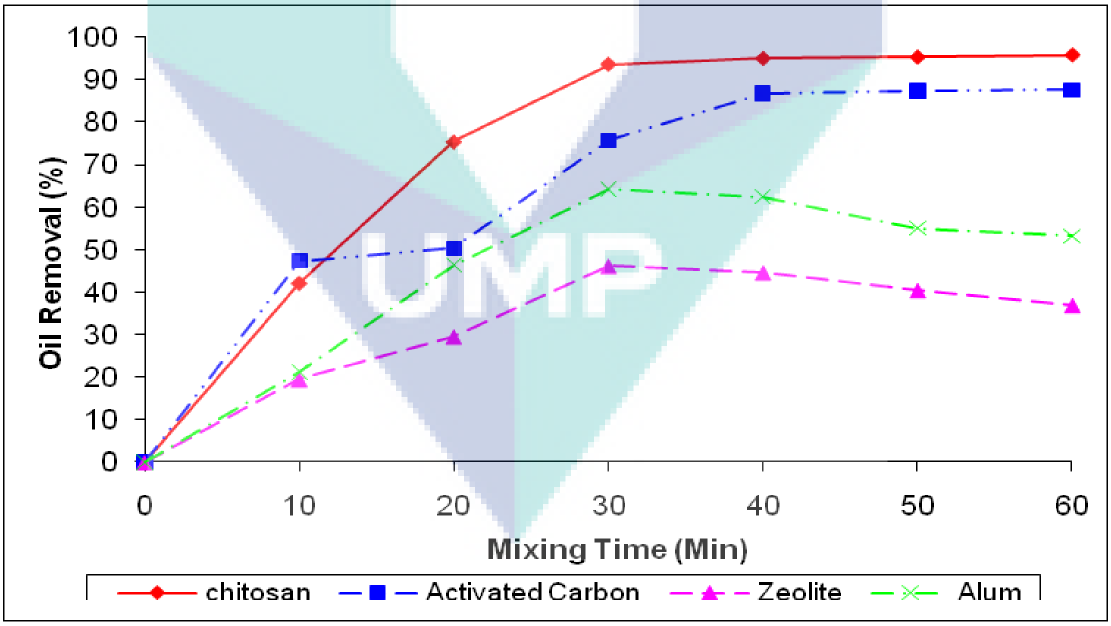


Figure 4.13: Percentage of residue oil removed versus mixing time

Chitosan achieved its maximum percentage of oil removed (95%wt) at 30 minutes mixing time. Exceeding further the mixing time did not show any improvement on the percentage of oil removed. Activated carbon, on the other hand, took 40 minutes to achieve highest percentage of residue oil removed (83%) while alum and zeolite took

30 minutes of mixing time to achieve 64% and 46% of residue oil removal respectively. Chitosan, alum and zeolite were faster to adsorb the residue oil compared to activated carbon. Mixing action helped increase the interfacial contact area of oil droplets by breaking them into smaller droplets and at the same time dispersed the droplets in the continuous water phase to increase the chance of coalescing and contacting with the adsorbents (Ahmad et al, 2005).

Chitosan adsorption in MEA wastewater was dominated by the strong chemical adsorption mechanism and required only 30 minutes to achieve its maximum adsorption capacity. Figure 4.13 also showed similar duration of mixing required by alum and zeolite to achieve the maximum adsorption capacities. On the other hand, for activated carbon, residue oil was mainly adsorbed via physical adsorption mechanism, and hence, required longer duration of mixing (40 minutes) to achieve its maximum adsorption capacity.

Meanwhile, it was observed that when the mixing time was increased further, beyond the optimum duration for alum and zeolite, the percentage of oil removed dropped slightly. Alum adsorbed residue oil mainly via weak chemical adsorption which required less time to adsorb in comparison to physical adsorption. However, since the chemical bonding in alum was weak, extended duration of mixing caused breakage of bond and eventually released some of the residue oil back into the water phase. Zeolite, on another instance, adsorbed residue oil via ion exchange mechanism, which behaved relatively similar to the weak chemical bonding explained above.

4.6.2 Effect on Removal of Suspended Solids

Figure 4.14 showed that mixing time influenced the removal of suspended solids in the sense that minimum duration of mixing was required to achieve the maximum removal of suspended solids, in which exceeding this duration showed a plateau condition. As discussed earlier in the previous sections, most of suspended solids were mainly removed together with the residue oil. Hence, the percentage of suspended solids removed was influenced by the degree of oil removed. The effect of mixing time was conducted at mixing speed of 100 rpm, pH 11 and temperature of 30^{o}C, with adsorbent dosage of 5%wt. Figure 4.14 showed a minimum of 30 minutes mixing time was required for chitosan to achieve its maximum removal of suspended solids (62%wt), while activated carbon, alum and zeolite needed 40 minutes to achieve the highest percentage of suspended solids removed.

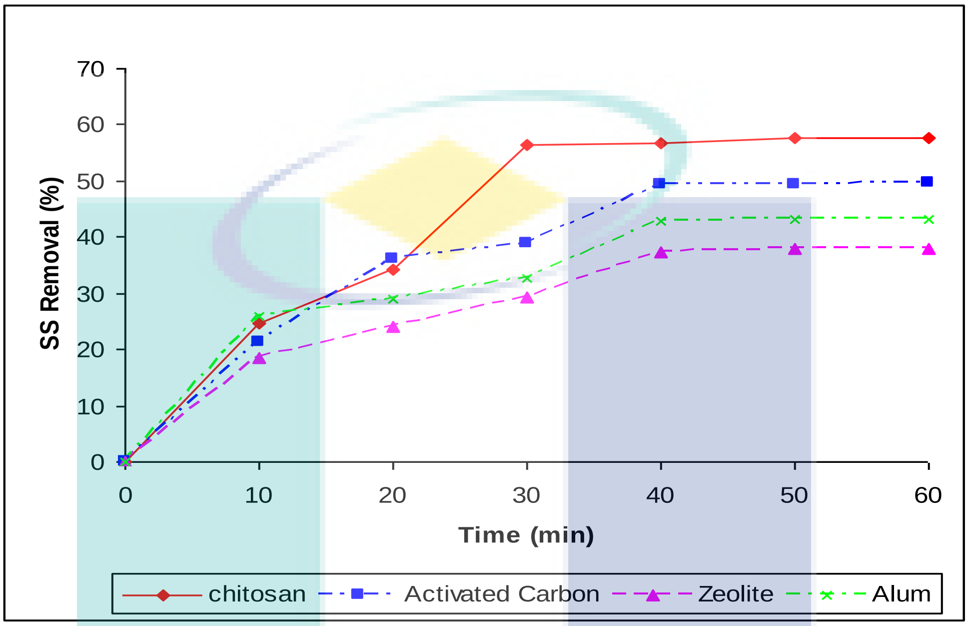


Figure 4.14: Percentage of suspended solids removal versus mixing time

Consistent with all the findings discussed above, chitosan showed the best adsorbent in removing the suspended solids, followed by activated carbon, alum and zeolite, respectively.

4.6.3 Effect on MEA Concentration

Figure 4.15 showed further confirmation that MEA concentration was not affected by the addition of adsorbent in the MEA wastewater. Hence, the figure clearly showed that mixing time has no influence on the performance of adsorbent in reducing the MEA concentration.

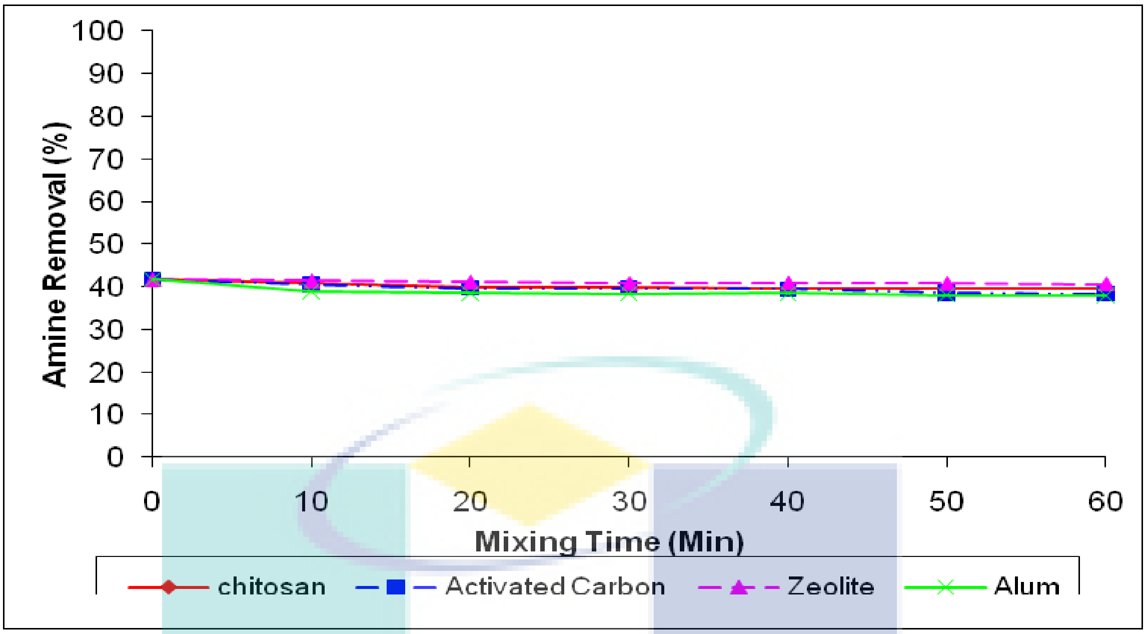


Figure 4.15: MEA concentration (MEA) versus mixing time

4.6.4 Effect on Chemical Oxygen Demand (COD)

Figure 4.16 showed the effect of mixing time on the COD reduction by chitosan, activated carbon, alum and zeolite as adsorbents. The figure showed that increasing the mixing time below the optimum duration, increased the percentage of COD reduction by 10 to 20%. Chitosan managed to reduce 83 % of COD while activated carbon reduced 80%, alum by 73% and zeolite by 71% respectively. Upon reaching the optimum mixing time, increasing further the mixing duration showed no further increase in the COD reduction. 20 minutes of mixing time was required by chitosan to achieve its maximum COD reduction. On the other hand, 40 minutes was required by activated carbon, alum and zeolite to achieve similar objective. Hence, it can be concluded that mixing time has least influence on the performance of adsorbents investigated in this study, especially after approaching the optimum mixing time.

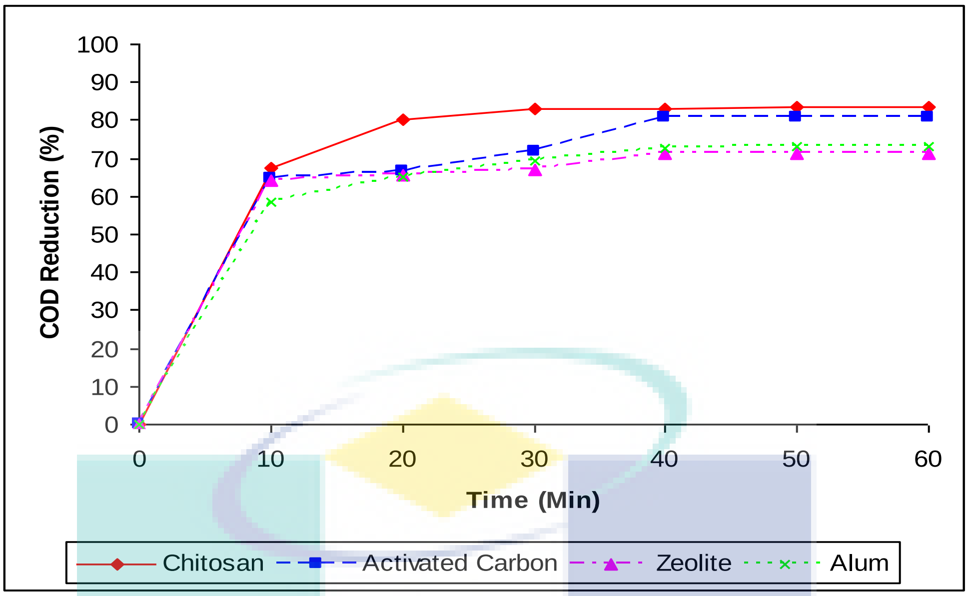


Figure 4.16: Percentage of cod reduction versus mixing time

4.7 EFFECT OF MIXING SPEED

4.7.1 Effect on Removal of Residue Oil

The effect of mixing speed was conducted by varying the mixing speed at 30 minutes of mixing time, pH 11 and at temperature of 30^{o}C. Dosage of chitosan, activated carbon, alum and zeolite was set at the maximum value (5%wt) as discussed earlier in Section 4.3. Figure 4.17 shows that effect of mixing speed was noticed only up to 100 rpm. Exceeding this mixing speed showed no further increase in residue oil removal. The maximum achievable percentage of residue oil removal was similar to what has been discussed earlier where chitosan managed to adsorb 95%wt of residue oil, followed by activated carbon (87%wt), alum (64%wt) and zeolite (46%wt) respectively. Agitation increased the incidence of adsorbent getting into contact with residue oil. At low mixing speed, less incidence of adsorbent contacting the residue oil, resulting in low removal of residue oil for all adsorbents examined in this study. Increasing the mixing speed directly increased the contact between adsorbent and residue oil, hence increased the oil adsorption (Ahmad et al., 2005). Figure 4.17 indicated that optimum mixing speed to be employed was 100 rpm in which exceeding this rpm showed no further increase in residue oil removal. In other word, 100 rpm of mixing speed was sufficient to achieve the maximum achievable percentage of residue oil removal by adsorbents.

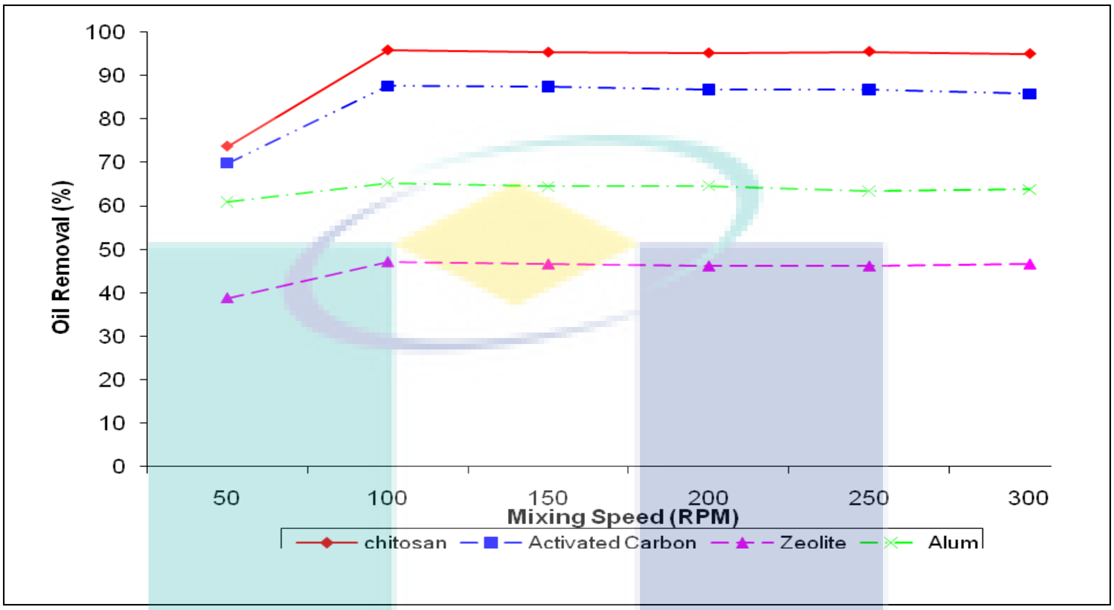


Figure 4.17: Percentage of residue oil removed versus mixing speed

4.7.2 Effect on Removal of Suspended Solids

Removal of suspended solids also showed similar trend of result in which increasing the mixing speed enhanced the adsorption and flocculation of suspended solids, up to its maximum achievable percentage. Figure 4.18 shows that at mixing time of 30 minutes, pH 11 and at temperature of 30°C, maximum achievable percentage of suspended solids removal was analogous to previous findings discussed earlier in section 4.3.2. Chitosan and activated carbon achieved the maximum suspended solids removal at 100 rpm mixing speed, at 57%wt and 50%wt respectively. Alum, on the other hand, achieved its maximum percentage of suspended solids removal (42%wt) at 200 rpm mixing speed, while zeolite achieved its maximum removal (35%wt) at 150 rpm. The hierarchy of adsorbent effectiveness also followed similar trend as other results discussed above, i.e. chitosan>activated carbon>alum>zeolite.

Alum and zeolite, having low zeta potential, required external factor such as mixing, to enhance the interaction between the adsorbent and the suspended solids. Hence, alum and zeolite required higher mixing speed (>100 rpm) to reach the maximum percentage of suspended solids removal as compared to chitosan and activated carbon which possessed relative high zeta potential.

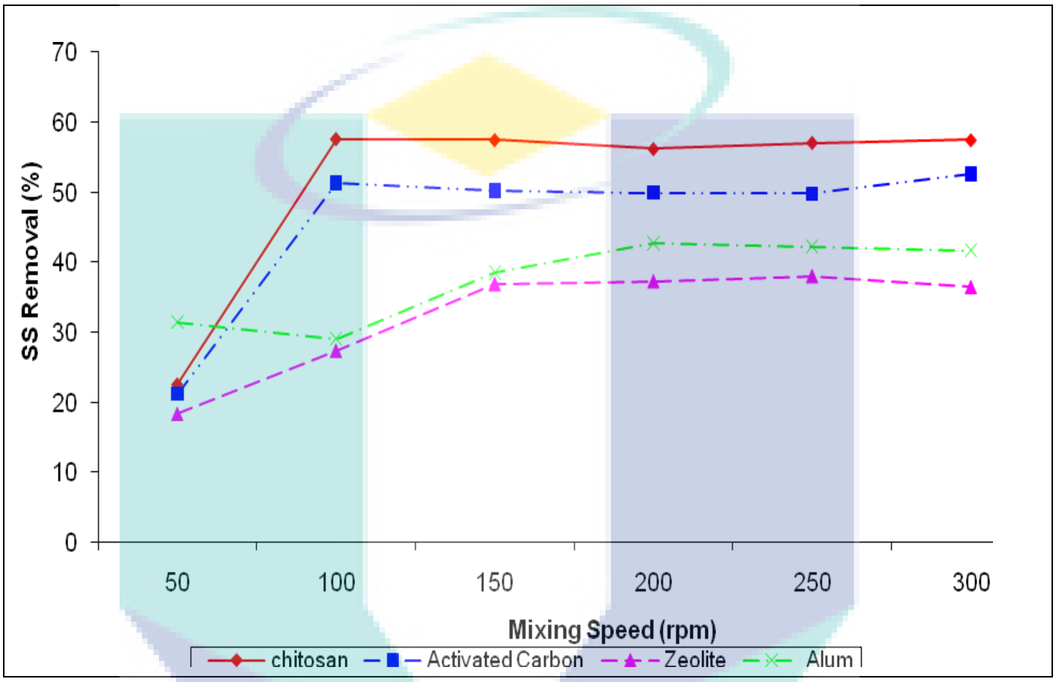


Figure 4.18: Percentage of suspended solids removal versus mixing speed

4.7.3 Effect on MEA Concentration and Chemical Oxygen Demand (COD)

Figure 4.19 and 4.20 showed that application of adsorbents (chitosan, activated carbon, alum and zeolite) did not affect the MEA concentration and COD concentration even when the mixing speed was increased. Hence, the adsorbents were not capable to adsorb amine molecule in the MEA even upon increasing the mixing speed up to 300 rpm.

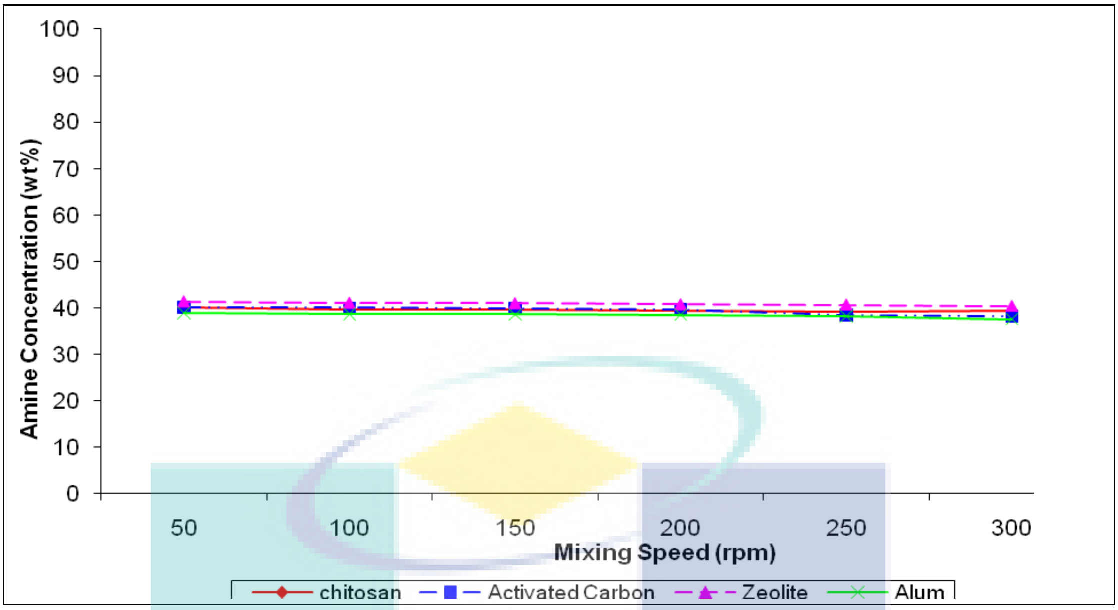


Figure 4.19: MEA concentration (MEA) vs mixing speed

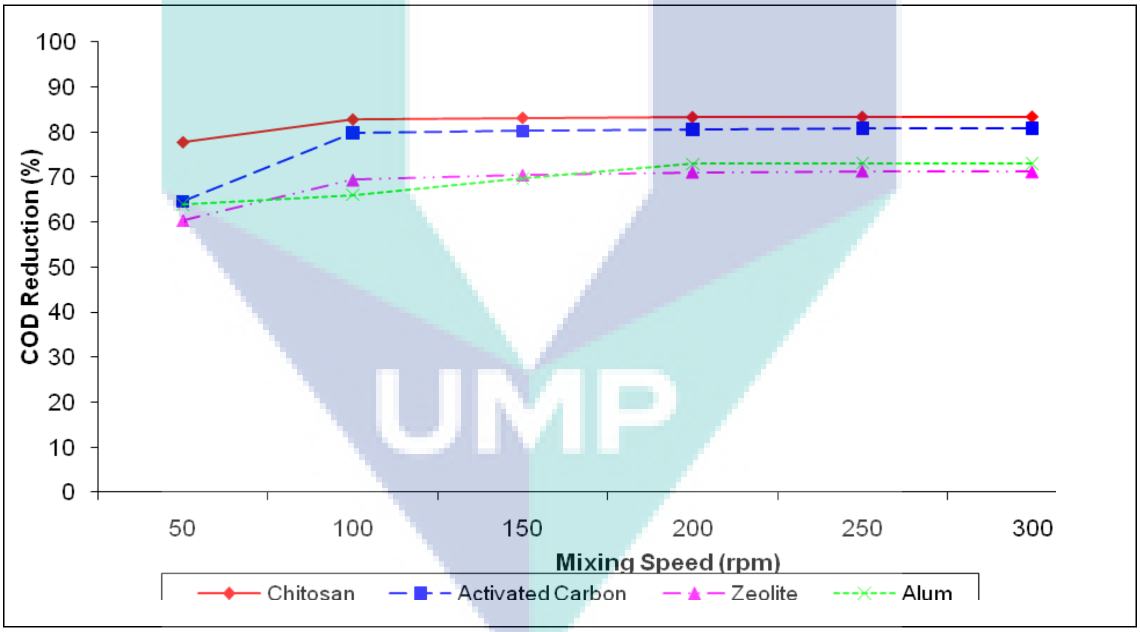


Figure 4.20: Percentage of COD reduction versus mixing speed

4.8 COMPARISON OF CHITOSAN FLAKE AND CHITOSAN POWDER

Overall results indicated that chitosan was the best adsorbent in treating the MEA wastewater. Hence, a study was further conducted to examine the effect of chitosan's physical appearance, particularly its form, flake and powder, on the degree of effectiveness in treating the MEA wastewater.

Experiments were conducted with the two forms of chitosan at operating conditions of 100 rpm mixing speed, 30 minutes mixing time, 30^oC and at pH of 11.21 (actual pH of CO_2 removal system). Figure 4.21 shows the removal percentage of residue oil from MEA wastewater using chitosan powder and chitosan flake, while Figure 4.22 shows the comparison between the chitosan forms in removing the suspended solids. Figure 4.23, on the other hand, shows the performances of the two forms of chitosan in reducing the COD.

The main conclusion that can be drawn from all the figures is the fact that chitosan powder performed better than the chitosan flake. This was mainly due to the larger surface area of the powdery chitosan as compared to the flaky type. In the removal of residue oil, chitosan powder performed around 5 to 6% better than the chitosan flake, whereby the powdery form removed up to 97% residue oil as compared to the flaky type which managed to remove up to 91% oil. In removing the suspended solids, chitosan powder performed up to 4% better than the flake type, with a maximum removal of 61% versus the 57% achieved by the flake type of chitosan.

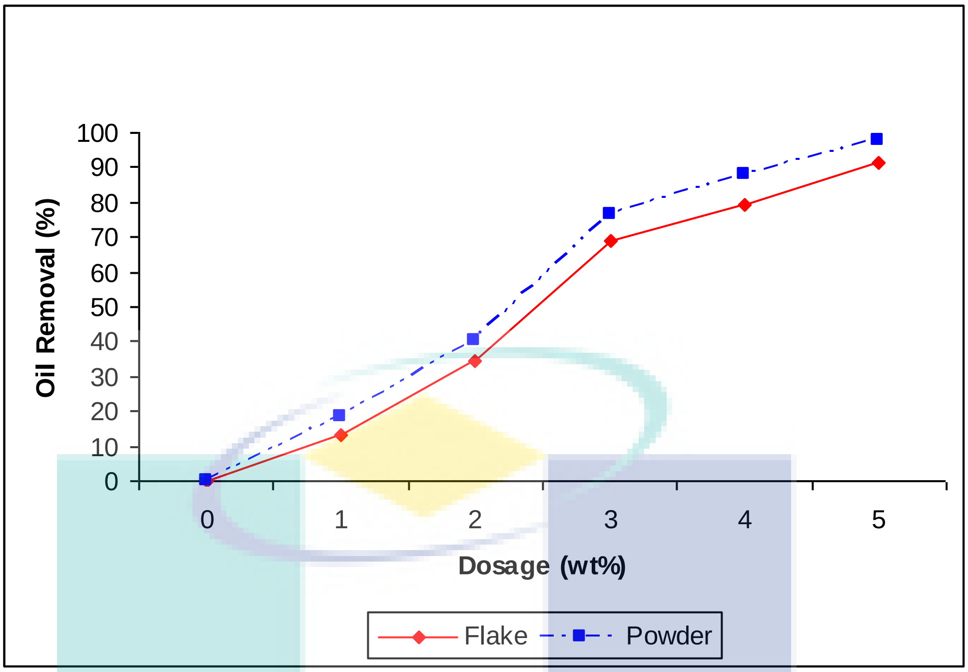


Figure 4.21: Percentage of residue oil removed versus dosage of adsorbents

In reduction of COD, similar trend was observed, in which the powdery chitosan performed better than the flake type of chitosan by 2%. Chitosan powder managed to reduce the COD by as much as 85% while the flaky chitosan only managed to reduce up to 83%.

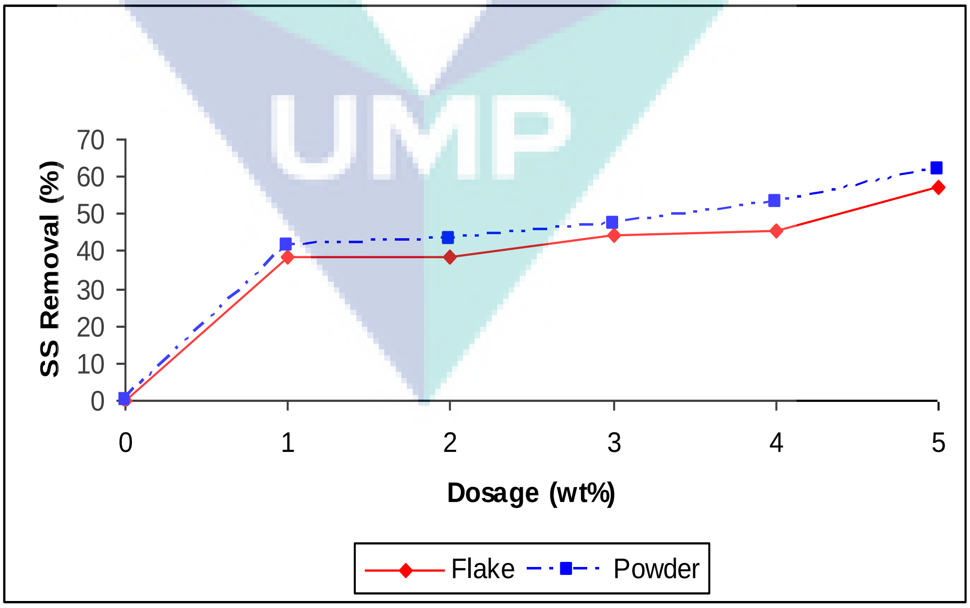


Figure 4.22: Percentage of suspended solids removal versus dosage of adsorbents

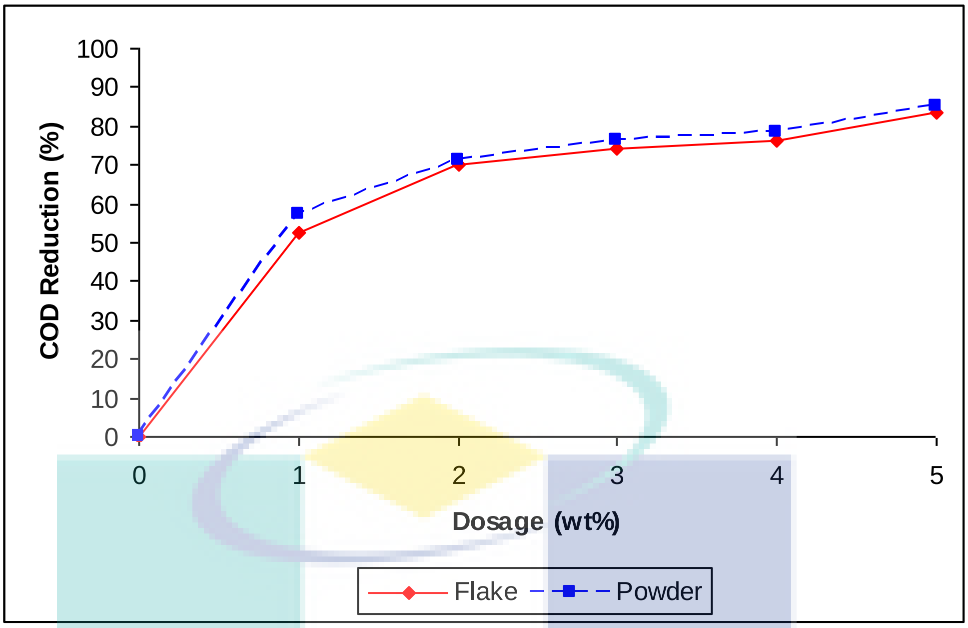


Figure 4.23: Percentage of COD reduction versus dosage of adsorbents

4.8.1 Scanning Electron Microscope (SEM) Analysis

SEM photographs were taken to examine closer the chitosan flake and powder, before and after residue oil adsorption. SEM photographs were taken with 500 magnifications. SEM photographs of chitosan flake and powder before adsorption were shown in figure 4.24a and figure 4.25a, respectively. Figure 4.24b and 4.25b, on the other hand, showed the SEM photographs of chitosan flake and powder after residue oil adsorptions, respectively. Chitosan flake shows a very clear and bumpy layer of pores which are arranged homogenously. Whereas, chitosan powder has patchy type of particle distribution and its pores are widely scattered and uneven in size. However, this is not the case after oil adsorption for both types of chitosan.

Figures 4.24b and 4.25b showed significant changes of structure and appearance on chitosan flake and powder. The SEM photographs reveal that most of the chitosan areas were covered with muddy-like substance and this is the adsorbed residue oil. The surface of chitosan flake was spread and covered with a muddy-like or rough surface with crater like pores due to the oil molecules which covered the flake. For chitosan powder, it shows a rather well exhibited bubble form of blobs on the surface. These globules are the residue oil adsorbed onto the powder. These images prove that, oil was adsorbed by chitosan into its pores and developed a layer of oily substance on the surface.

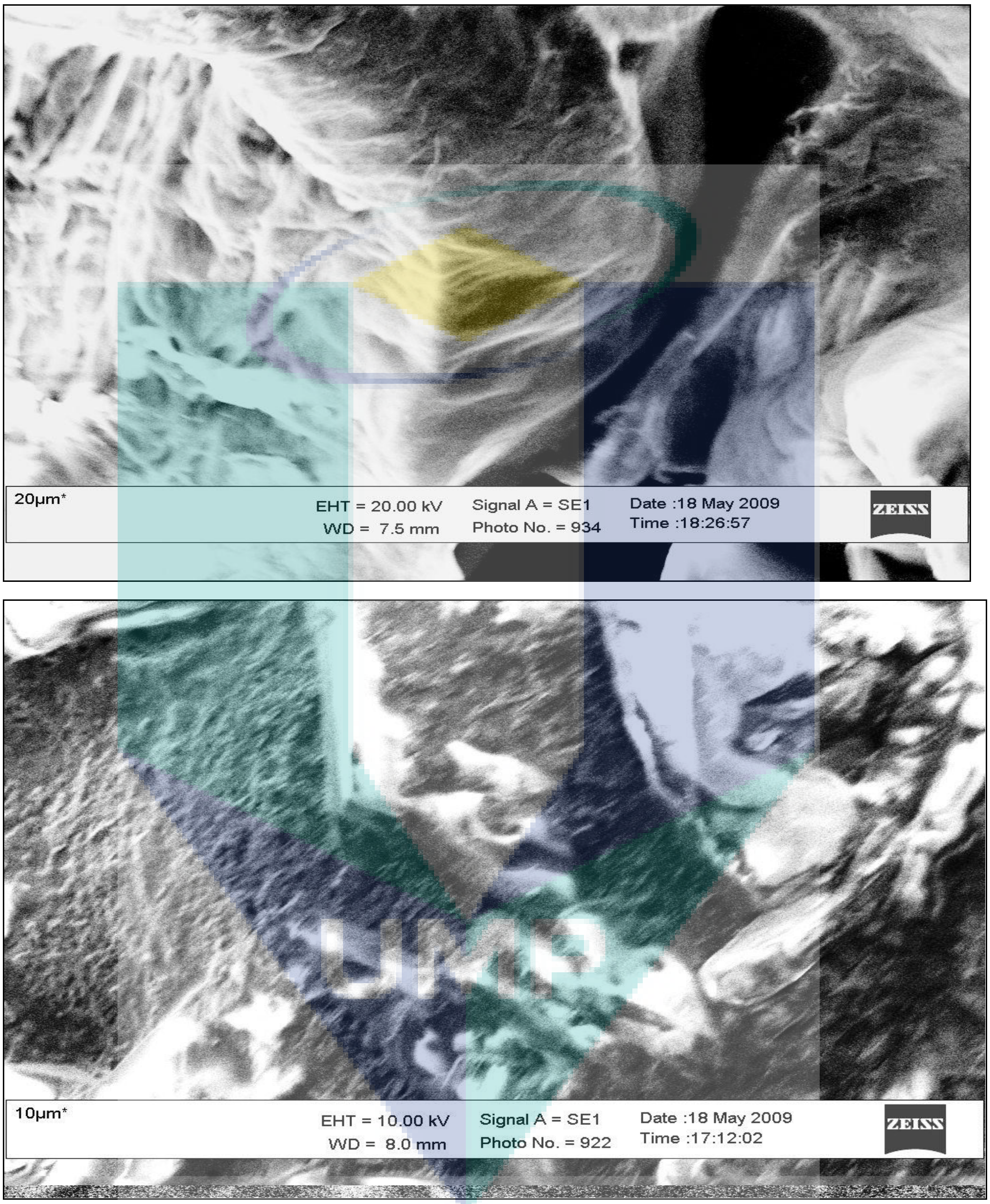


Figure 4.24: Electron microscopic photographs of chitosan flake (a) before and (b) after residue oil adsorption (500X)

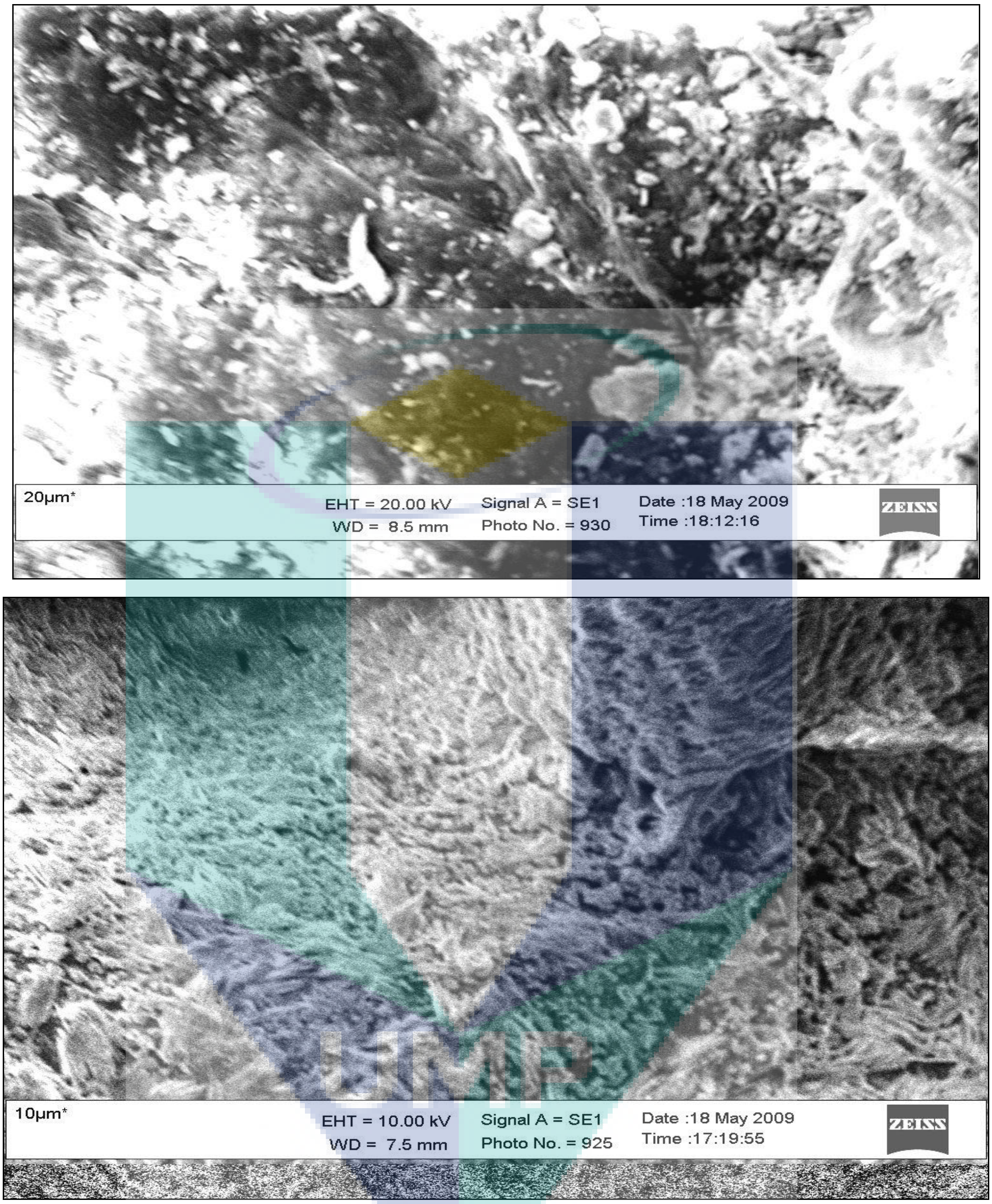


Figure 4.25: Electron microscopic photographs of chitosan powder (a) before and (b) after residue oil adsorption (500X)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

From the discussion elaborated in chapter 4, some conclusions were drawn and listed as below:

1. The characterization study of MEA wastewater indicated the readings were obviously far from acceptable limit for the wastewater to be released as effluent and required thorough treatment even for the purpose of sending to the wastewater treatment plant of the company. Since high MEA concentration was measured in the wastewater, it makes more sense to treat the waste MEA for the purpose of recycling it back into the system rather than disposed it to Kualiti Alam.

2. Adsorption technique using Chitosan, Activated Carbon, Alum and Zeolite were selected since these adsorbents did not react with MEA concentration. Chitosan showed the best performance as an adsorbent to remove residue oil, suspended solid and reducing COD level compared to activated carbon, alum and zeolite. Chitosan and activated carbon systems showed more than one mechanism of adsorption involved in each of the system. Chitosan functioned through chemical adsorption at low dosage, while further increasing the dosage increased the electrostatic field of the system significantly and contributed to the increase in the percentage of removal through electrostatic adsorption. Activated carbon, having large area/volume ratio, adsorbed residue oil droplets through physical adsorption and at high dosage also showed significant contribution of

electrostatic adsorption taking place. Alum and zeolite systems indicated that only one single mechanism of adsorption took place during the treatment process. Alum, a typical flocculating agent in water treatment plant, mainly adsorbed residue oil droplets through chemical adsorption. Zeolite, on the other hand, mainly adsorbed the residue oil droplets through physical adsorption.

3. The lower negative value of zeta potential in chitosan indicates its readiness to accept particles and oil droplets as compared to activated carbon, alum and zeolite which have relatively higher zeta potential values.

4. The high values of BET for activated carbon and zeolite confirmed the suggestion that adsorption of residue oil by these adsorbent were mainly through physical adsorption. Similarly, the low values of BET for chitosan and alum supported the suggestion that chemical adsorption was the main mechanism in removing residue oil for both of the systems.

5. The experimental results showed that adsorbent dosage was the most influential factor affecting the removal of residue oil, suspended solids and COD level compared to other factors such pH, temperature, mixing time and mixing speed. Increasing the adsorbent dosage showed positive impact in reducing the residue oil, suspended solids and COD level.

6. Overall results indicated that chitosan was the best adsorbent in treating the MEA wastewater. Hence, a study was further conducted to examine the effect of chitosan’s physical appearance, particularly its form, flake and powder, on the degree of effectiveness in treating the MEA wastewater. It was found that chitosan powder performed better than the flake and this was mainly due to the larger surface area of the powdery chitosan compared to the flaky type.

5.2 RECOMMENDATIONS FOR FUTURE WORK

Recommendations are made to suggest for future work which can be performed to give better understanding and improvement on the treatment and recycling of MEA wastewater. Below are some recommendations for future work:

1. Combination of adsorbents to treat MEA wastewater
   From this research, chitosan and activated carbon were found to be the best two adsorbents in treating the wastewater. Combination of chitosan and activated carbon as adsorbents may give better result since the two adsorbents functioned differently in treating the MEA wastewater.

2. Performance of recycled MEA solution after treatment should be conducted to study its effectiveness in removing CO_2 from the exhaust gas via absorption process. This study will enable to conclude the feasibility of recycling the MEA wastewater commercially.

3. Pilot scale study of the MEA wastewater treatment system should be conducted to evaluate the performance of the system and to rectify any weaknesses of the treatment system before detail design can be proposed.

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APPENDIX A

Experiment Results

1.1 Effect of Adsorbents Dosage

Experiment Condition

Mixing Rate 100 rpm, Mixing Time 30 min, pH 11, temperature 25 – 30^{o}C

A. Effect on Removal of Residue Oil

	Chitosan		Activated Carbon		Zeolite		Alum	
% weight	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	596	0.00	596	0.00	596	0.00	596	0.00
1	518	13.09	531	10.91	561	5.87	552	7.38
2	390	34.56	450	24.50	497	16.61	451	24.33
3	186	68.79	243	59.23	415	30.37	398	33.22
4	96	83.89	112	81.20	372	37.58	284	52.35
5	28	95.30	75	87.42	321	46.14	213	64.26

B. Effect on Removal of Suspended Solid

	Chitosan		Activated Carbon		Zeolite		Alum	
% weight	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	69370	0.00	69000	0.00	69000	0.00	69000	0.00
1	42580	38.61	49370	28.45	54320	21.28	52000	24.63
2	42530	38.70	44170	35.99	50300	27.10	48970	29.03
3	38520	44.47	40130	41.84	48690	29.43	44520	35.48
4	37930	45.32	38440	44.29	45610	33.90	41200	40.30
5	29310	57.31	34880	49.45	42670	38.16	39290	43.06

C. Effect on MEA Concentration

	Chitosan		Activated Carbon		Zeolite		Alum	
wt%	Conc (wt%)	% remove	Conc (wt%)	% remove	Conc (wt%)	% remove	Conc (wt%)	% remove
0	41.69	0.00	41.69	0.00	41.69	0.00	41.69	0.00
1	40.24	3.48	40.36	3.19	41.31	0.91	38.98	6.50
2	40.02	4.01	39.87	4.37	41.07	1.49	38.47	7.72
3	39.95	4.17	39.63	4.94	40.85	2.01	38.42	7.84
4	39.23	5.90	39.29	5.76	40.74	2.28	38.16	8.47
5	39.15	6.09	38.91	6.67	40.53	2.78	38.07	8.68

D. Effect on Reduction of Chemical Oxygen Demand (COD)

	Chitosan		Activated Carbon		Zeolite		Alum	
% weight	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%
0	230000	0.00	230000	0.00	230000	0.00	230000	0.00
1	109000	52.61	91500	60.21	115500	49.78	82000	64.35
2	68500	70.22	76500	66.73	103500	55.00	79500	65.43
3	59500	74.13	74000	67.82	95000	58.70	70500	69.35
4	54000	76.52	59500	74.13	92500	59.78	68000	70.43
5	38500	83.26	44000	80.86	66000	71.30	62000	73.04

1.2 Effect of pH

Experiment Condition

Mixing Time 30 min, Mixing Speed 100 rpm, Temp 25-30°C, Adsorbents Dosage 5 wt%

A. Effect on Removal of Residue Oil

	Chitosan		Activated Carbon		Zeolite		Alum	
pH	mg/l	%	mg/l	%	mg/l	%	mg/l	%
11	596	0.00	596	0.00	596	0.00	596	0.00
11	26	95.64	69	88.42	319	46.48	206	65.44
9	28	95.30	74	87.58	365	38.76	213	64.26
7	27	95.47	89	85.07	335	43.79	262	56.04
5	29	95.13	110	81.54	387	35.07	311	47.82
3	33	94.46	105	82.38	430	27.85	318	46.64

B. Effect on Removal of Suspended Solid

	Chitosan		Activated Carbon		Zeolite		Alum	
pH	mg/l	%	mg/l	%	mg/l	%	mg/l	%
11	69000	0.00	69000	0.00	69000	0.00	69000	0.00
11	26790	61.17	34760	49.62	42130	38.94	39750	42.39
9	30450	55.87	43170	37.43	46300	32.90	47970	30.48
7	40030	41.99	48500	29.71	48690	29.43	46420	32.72
5	53800	22.03	51970	24.68	49310	28.54	52400	24.06
3	55200	20.00	53400	22.61	54320	21.28	51290	25.67

C. Effect on MEA Concentration

	Chitosan		Activated Carbon		Zeolite		Alum	
pH	Conc (wt%)	% Remove	Conc (wt%)	% Remove	Conc (wt%)	% Remove	Conc (wt%)	% Remove
11	41.69	0.00	41.69	0.00	41.69	0.00	41.69	0.00
11	40.96	1.76	40.48	2.90	41.41	0.67	38.88	6.74
9	33.01	20.81	28.66	31.25	36.08	13.45	36.49	12.47
7	25.97	37.71	29.63	28.92	31.74	23.86	32.41	22.27
5	18.76	55.00	20.53	50.75	21.49	48.45	24.49	41.26
3	15.54	62.72	14.56	65.07	16.79	59.72	20.01	52.00

D. Effect on Reduction of Chemical Oxygen Demand (COD)

	Chitosan		Activated Carbon		Zeolite		Alum	
pH	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%
11	230000	0.00	230000	0.00	230000	0.00	230000	0.00
11	38500	83.26	44000	80.87	66000	71.30	62000	73.04
9	76000	66.96	86500	62.39	99500	56.74	90300	60.74
7	109000	52.61	164600	28.43	176000	23.48	170500	25.87
5	Overange	0.00	Overange	0.00	Overange	0.00	Overange	0.00
3	Overange	0.00	Overange	0.00	Overange	0.00	Overange	0.00

1.3 Effect of Temperature

Experiment Condition

Mixing Time 30 min, Mixing Speed 100 rpm, pH 11, Temp 25-30°C, Adsorbents Dosage 5 wt%

A. Effect on Removal of Residue Oil

	Chitosan		Activated Carbon		Zeolite		Alum	
Temp	mg/l	%	mg/l	%	mg/l	%	mg/l	%
30	596	0.00	596	0.00	596	0.00	596	0.00
30	28	95.30	73	87.75	310	47.99	232	61.07
40	26	95.64	80	86.58	316	46.98	223	62.58
50	27	95.47	74	87.58	324	45.64	216	63.76
60	26	95.64	78	86.91	326	45.30	224	62.42
70	43	92.79	84	85.91	328	44.97	247	58.56
80	54	90.94	103	82.72	338	43.29	231	61.24

B. Effect on Removal of Suspended Solid

	Chitosan		Activated Carbon		Zeolite		Alum	
Temp °C	mg/l	%	mg/l	%	mg/l	%	mg/l	%
30	69000	0.00	69000	0.00	69000	0.00	69000	0.00
30	27450	60.22	34300	50.29	45320	34.32	44410	35.64
40	28790	58.28	33600	51.30	46320	32.87	46370	32.80
50	27750	59.78	34440	50.09	44670	35.26	41920	39.25
60	34560	49.91	34560	49.91	45810	33.61	42500	38.41
70	35330	48.80	34430	50.10	46720	32.29	40370	41.49
80	35460	48.61	36700	46.81	45680	33.80	41540	39.80

C. Effect on MEA Concentration

	Chitosan		Activated Carbon		Zeolite		Alum	
Temp	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%
30	41.69	0.00	41.69	0.00	41.69	0.00	41.69	0.00
30	39.01	6.42	39.12	6.15	41.43	0.62	38.68	7.22
40	38.79	6.95	38.98	6.49	40.15	3.68	38.64	7.30
50	39.42	5.45	38.38	7.94	40.86	1.99	38.43	7.81
60	38.69	7.19	38.43	7.81	40.61	2.58	38.48	7.69
70	37.81	9.29	37.42	10.25	40.46	2.95	38.10	8.62
80	38.43	7.81	38.22	8.33	40.18	3.62	37.89	9.11

D. Effect on Reduction of Chemical Oxygen Demand (COD)

	Chitosan		Activated Carbon		Zeolite		Alum	
Temp	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%
30	230000	0.00	230000	0.00	230000	0.00	230000	0.00
30	31400	86.35	44500	80.65	71000	69.13	73000	68.26
40	39400	82.87	45100	80.39	70500	69.35	72100	68.65
50	38000	83.48	43600	81.04	67000	70.87	66900	70.91
60	39400	82.87	46700	79.70	66500	71.09	65400	71.57
70	43500	83.26	45300	80.30	73000	68.26	63500	72.39
80	44400	80.70	48100	79.09	75400	67.22	64200	72.09

1.4 Effect of Mixing Time

Experiment Condition

Mixing Rate 100 rpm, pH 11, Temp 25-30^{o}C, Adsorbents Dosage 5 wt%

A. Effect on Removal of Residue Oil

	Chitosan		Activated Carbon		Zeolite		Alum	
time (min)	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	596	0.00	596	0.00	596	0.00	596	0.00
10	345	42.11	314	47.32	480	19.46	470	21.14
20	147	75.34	296	50.34	420	29.53	320	46.31
30	38	93.62	145	75.67	321	46.14	213	64.26
40	30	94.97	79	86.74	330	44.63	224	62.42
50	28	95.30	75	87.42	355	40.44	268	55.03
60	25	95.81	74	87.58	376	36.91	279	53.19

B. Effect on Removal of Suspended Solid

	Chitosan		Activated Carbon		Zeolite		Alum	
Time	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	69000	0.00	69000	0.00	69000	0.00	69000	0.00
10	52010	24.62	54370	21.20	56320	18.38	51200	25.80
20	45320	34.32	44170	35.99	52300	24.20	48970	29.03
30	30040	56.46	42230	38.80	48690	29.43	46420	32.72
40	29800	56.81	34970	49.32	43310	37.23	39400	42.90
50	29310	57.52	34880	49.45	42810	37.96	39290	43.06
60	29270	57.58	34700	49.71	42780	38.00	39130	43.29

C. Effect on MEA Concentration

	Chitosan		Activated Carbon		Zeolite		Alum	
time (min)	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%
0	41.69	0.00	41.69	0.00	41.69	0.00	41.69	0.00
10	40.96	1.76	40.48	2.90	41.41	0.67	38.88	6.74
20	40.01	4.02	39.66	4.86	41.08	1.46	38.49	7.67
30	39.99	4.08	39.63	4.94	40.74	2.27	38.41	7.87
40	39.63	4.94	39.45	5.37	40.89	1.91	38.49	7.68
50	39.45	5.38	38.56	7.50	40.79	2.15	38.03	8.77
60	39.43	5.41	38.33	8.06	40.65	2.49	37.88	9.13

D. Effect on Chemical Oxygen Demand (COD)

	Chitosan		Activated Carbon		Zeolite		Alum	
Time	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%
0	230000	0.00	230000	0.00	230000	0.00	230000	0.00
10	75400	67.22	81500	64.57	82000	64.35	95000	58.70
20	46000	80.00	76500	66.74	79500	65.43	80300	65.09
30	39000	83.04	64600	71.91	76000	66.96	70400	69.39
40	38600	83.22	45000	80.43	66500	71.09	63000	72.61
50	38500	83.26	44200	80.78	66000	71.30	62000	73.04
60	38400	83.30	44300	80.74	66000	71.30	62200	72.96

1.5 Effect of Mixing Speed

Experiment Condition

Mixing Time 30 min, pH 11, Temp 25-30°C, Adsorbents Dosage 5 wt%

A. Effect on Removal of Residue Oil

	Chitosan		Activated Carbon		Zeolite		Alum	
RPM	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	596	0.00	596	0.00	596	0.00	596	0.00
50	157	73.66	180	69.80	365	38.76	233	60.91
100	25	95.81	74	87.58	315	47.15	207	65.27
150	28	95.30	75	87.42	318	46.64	212	64.43
200	29	95.13	79	86.74	321	46.14	211	64.60
250	27	95.47	79	86.74	321	46.14	218	63.42
300	30	94.97	85	85.74	318	46.64	216	63.76

B. Effect on Removal of Suspended Solid

	Chitosan		Activated Carbon		Zeolite		Alum	
RPM	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0	69000	0.00	69000	0.00	69000	0.00	69000	0.00
50	53450	22.54	54370	21.20	56320	18.38	47310	31.43
100	29230	57.64	33600	51.30	50120	27.36	48970	29.03
150	29340	57.48	34350	50.22	43570	36.86	42420	38.52
200	30210	56.22	34570	49.90	43310	37.23	39500	42.75
250	29610	57.09	34650	49.78	42810	37.96	39870	42.22
300	29350	57.46	32700	52.61	43880	36.41	40230	41.70

C. Effect on MEA Concentration

	Chitosan		Activated Carbon		Zeolite		Alum	
RPM	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%	Conc (wt%)	%
0	41.69	0.00	41.69	0.00	41.69	0.00	41.69	0.00
50	40.01	4.02	40.12	3.76	41.35	0.81	38.95	6.57
100	39.71	4.74	39.98	4.10	41.05	1.53	38.69	7.19
150	39.64	4.92	39.86	4.39	40.94	1.79	38.58	7.46
200	39.41	5.46	39.67	4.84	40.72	2.32	38.49	7.67
250	39.20	5.97	38.41	7.86	40.65	2.49	38.15	8.50
300	39.40	5.49	38.21	8.34	40.38	3.14	37.59	9.83

D. Effect on Chemical Oxygen Demand (COD)

	Chitosan		Activated Carbon		Zeolite		Alum	
RPM	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%	COD (mg/l)	%
0	230000	0.00	230000	0.00	230000	0.00	230000	0.00
50	51400	77.65	81500	64.57	91000	60.43	83000	63.91
100	39800	82.70	46500	79.78	70500	69.35	78100	66.04
150	39000	83.04	45600	80.17	68000	70.43	69900	69.61
200	38600	83.22	44800	80.52	66500	71.09	62400	72.87
250	38500	83.26	44200	80.78	66000	71.30	61900	73.09
300	38400	83.30	44100	80.83	66400	71.13	62200	72.96

1.6 Comparison of Chitosan Flake and Chitosan Powder

Experiment Condition

Mixing Rate 100 rpm, Mixing Time 30 min, pH 11, Temp 25-30°C

A. Effect on Removal of Residue Oil

	Chitosan Flake		Chitosan Powder	
dosage (wt%)	mg/l	%	mg/l	%
0	596	0.00	596	0.00
1	518	13.09	487	18.29
2	390	34.56	355	40.44
3	186	68.79	142	76.17
4	122	79.53	73	87.75
5	50	91.61	14	97.65

B. Effect on Removal of Suspended Solids

	Chitosan Flake		Chitosan Powder	
Dosage (wt%)	mg/l	%	mg/l	%
0	69370	0.00	69000	0.00
1	42580	38.61	40370	41.49
2	42530	38.70	39170	43.23
3	38520	44.47	36560	47.01
4	37930	45.32	32490	52.91
5	29310	57.31	26420	61.71

C. Effect on MEA concentration

	Chitosan Flake		Chitosan Powder	
Dosage (wt%)	Concentration (wt%)	%	Concentration (wt%)	%
0	44.81	0.00	44.81	0.00
1	43.76	2.34	43.56	2.79
2	42.35	5.49	42.34	5.51
3	42.89	4.28	41.75	6.83
4	41.65	7.05	40.87	8.79
5	41.93	6.43	41.35	7.72

D. Effect on Reduction of Chemical Oxygen Demand (COD)

	Chitosan Flake		Chitosan Powder	
Dosage (wt%)	COD (mg/l)	%	COD (mg/l)	%
0	230000	0.00	230000	0.00
1	109000	52.61	98500	57.17
2	68500	70.22	66500	71.09
3	59500	74.13	54000	76.52
4	54000	76.52	49500	78.48
5	38500	83.26	34000	85.22

APPENDIX B

A. O & G – Oil and Grease Procedure

DOE Method (1985) 2^{nd} Edition 1995

1.0 REAGENTS

1.1 50% Sulphuric Acid (to re-active sample).

1.2 N-Hexane (to collect oil content).

1.3 2-Propanol (to expel bubble).

1.4 Sodium Sulphate (to expel water).

2.0 PROCEDURE

2.1 2 units separating funnel.

2.2 1 unit round bottle flask (dry 2 hours before begin the experiment).

2.3 Pour known volume (mL) sample into separating funnel.

2.4 Add 2.5 mL 50% H_2SO_4.

2.5 Add 30 mL N-Hexane. Cover the mouth and shake well for 2 minutes.

2.6 Add 3 mL 2-propanol.

2.7 Transfer the bottom layer into 2nd separating funnel. Repeat (2 times) step 2.5 and 2.6.

2.8 Collect all surface layers, then add 1 scoop Sodium Sulphate.

2.9 Transfer into round bottom flask and heat (reflux) the sample (to remove N-Hexane). Measure the initial weight and repeat the drying and cooling until the weight becomes constants in every 1 hour.

3.0 CALCULATION

$$\text{Oil and Grease, mg/L} = \frac{(A-B) \times 1\,000\,000}{S}$$

Where:
A = Weight of round flask + Oil (g)
B = Weight of empty flask (g)
S = Volume of Sample (mL)

Tested by : ______________________________
Date : ______________________________
Remarks : ______________________________
____
____

No.	**Sample Name**	**Empty Flask (g)**	**Flask + Oil (g)**	**Flask + Oil (g) after 1 hour**	**Flask + Oil (g) after 2 hour**	**Flask + Oil (g) after 3 hour**	**Flask + Oil (g) after 4 hour**

B. SS – Suspended Solid Procedure

DOE Method (1985) 2nd Edition 1995

1.0 REAGENTS / APPARATUS

1.1 Glass fiber filter paper

1.2 Vacuum pump

1.3 2 pieces filter set

2.0 PROCEDURE

2.1 Measure known sample

2.2 Weighing filter paper with dish (dry for 1 hour at 105 °C)

2.3 Put filter paper on top of 2 pieces filter

2.4 Pour known sample (make it duplicate)

2.5 Weighing again filter paper + dish + residue

2.6 Measure the initial weight and repeat the drying and cooling until the weight becomes constants in every 1 hour

3.0 CALCULATION

$$\text{Suspended Solid, mg/L} = \frac{(A-B) \times 1\,000\,000}{S}$$

Where:
A = Weight of dish+ residue (g)
B = Weight of empty dish (g)
S = Volume of Sample (mL)

Tested by : ______________________________
Date : ______________________________
Remarks : ______________________________
____
____

No.	**Sample Name**	**Empty dish (g)**	**Dish + Residue (g)**	**Dish + Residue (g) after 1 hour**	**Dish + Residue (g) after 2 hour**	**Dish + Residue (g) after 3 hour**	**Dish + Residue (g) after 4 hour**

C. COD –Chemical Oxygen Demand Procedure

HACH Spectrophotometer 2400

100ppm (Standard B limit)

1.0 REAGENTS

1.1 Choose COD reagent (HACH) that required either use high range (0 ppm – 1500ppm) or low range (0 ppm -500ppm). Depend to type of sample used.

2.0 PROCEDURE

2.1 Measure 2mL of distilled water and add into COD reagent bottle sample and shake well. Use this sample as standard reference.

2.2 Repeat step 2.1 by using water sample.

2.3 Switch on HACH reactor. Choose for COD heat (sample should be heated for 120 minutes at 150 ^{o}C).

2.4 After that, put sample bottle at adaptor of Spectrophotometer 2400. Choose the wanted program either use high range (0 ppm – 1500ppm) or low range (0 ppm -500ppm).

2.5 Please make sure that re-zeroing the standard reference sample first before make measurement of EVERY water sample.

3.0 CALCULATION

Remarks: No calculation. Take the direct result reading from Spectrophotometer 2400.

D. Determination of Total Amine Solvent Concentration

1.0 Reagents

1. 0.5N (0.5 Normal0 hydrochloric (HCl) or sulphuric (H2SO4) acid.
2. Taschiro indicator [1]

2.0 Apparatus

1. Burrette
2. Electronic Balance
3. pH meter
4. Magnetic Stirrer

3.0 Procedure

1. Place beaker or plastic cup (250 ml size) on balance and tare.
2. Weight 4 to 5 ml of lean solvent sample in beaker. Record sample weight to 0.01 gram.
3. Add 50 ml of deionized water.
4. Add 5 to 8 drops of Taschiro indicator to the sample to obtain a green coloured solution.
5. Titrate the solution with 0.5N acid until colour changes from green to grey at the equivalence point. Practice will enable reaching a consistent end point [2].
6. Record quantity (mL) of acid used.

[1] Other indicators having an approximate pH range of 3.0 to 5.0 maybe substitute.

[2] An alternate method is to use a pH meter and titrating the solution to a pH of 4.5. Be sure to calibrate the meter with pH 5 & 7buffers before use.

4.0 Calculations

Total Amine Solvent Concentration, wt%

$$\mathbf{Wt\% = \frac{N\ acid\ X\ ml\ acid\ x\ 9.76}{Sample\ weight}}$$

Note: Most indicators can be purchased through a chemical supply company