STUDY ON THE ADSORPTION PROCESS OF MONOETHANOLAMINE (MEA) WASTEWATER USING ACTIVATED CARBON AND TREATED RICE HUSK

NORADLINNAINI BINTI MUHAMAD

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

STUDY ON THE ADSORPTION PROCESS OF MONOETHANOLAMINE (MEA) WASTEWATER USING ACTIVATED CARBON AND TREATED RICE HUSK

ABSTRACT

Monoethanolamine (MEA) is versatile bifunctional molecules compound which by the reaction it behaves like alcohol and Amine but Amine group usually exhibit the greater activity. MEA was always used as a gas stream scrubbing agent to remove carbon dioxide (CO_2) from flue gas known as stripping process. During the oil processing, some MEA with other wastes enter to industrial wastewater. This study was conducted to suggest the best method of treating the MEA wastewater in order to meet the potable quality standards and suited for reused of MEA.The method of treatment is by using adsorption process with two types of adsorbent which are treated rice husk, and activated carbon. Two parameters were manipulated to get the optimum value of removing oil, chemical oxygen demand (COD) and amine concentration that are adsorbent dosage and mixing speed. From the results we can see the oil residue and COD decreased while MEA concentration wastewater remains the same. Activated carbon became the most effective adsorbent for the adsorption process with up to 43.57% oil content removal and 66.81% COD reduction. Meanwhile, treated rice husk showed lower efficiency performance throughout this process with 37.83% oil removed and 53.32% COD reduction. MEA concentration remain constant for both adsorbent.

KAJIAN TENTANG PROCESS PENJEARAPAN AIR BUANGAN MONOETHANOLAMINE (MEA) MENGGUNAKAN KARBON AKTIF DAN SEKAM PADI TERAWAT

ABSTRAK

Monoethanolamine (MEA) adalah molekul sebatian dwi-fungsi serba boleh yang menunjukkan ciri-ciri seperti alkohol dan amine tetapi kumpulan Amine biasanya mempamerkan aktiviti yang lebih besar. MEA sentiasa digunakan sebagai ejen menapis aliran gas bertujuan untuk mengeluarkan karbon dioksida (CO2) dari serombong gas yang dikenali sebagai proses pelucutan. Ketika proses penulenan minyak dijalankan,sebahagian daripada MEA akan keluar bersam air sisa industri yang lain. Kajian ini dijalankan untuk mencadangkan kaedah terbaik merawat air sisa MEA dalam usaha untuk memenuhi standard kualiti yang dibenarkan dan sesuai untuk penggunaan semula MEA. Jenis rawatan adalah dengan menggunakan proses penjerapan dengan dua jenis penjerap iaitu sekam padi yang telah dirawat, dan karbon aktif. Dua parameter telah dimanipulasi untuk mendapatkan nilai optimum bagi mengeluarkan minyak, keperluan oksigen kimia (COD) dan mengekalkan kepekatan Amine iaitu dos penjerap dan kelajuan pergaulan. Dari keputusan kita dapat melihat sisa minyak dan COD menurun manakala kepekatan MEA dalam air sisa tetap sama. Karbon aktif menunjukkan prestasi yang terbaik dalam proses penjerapan dengan 43.57% pengeluaran minyak dan 66.81% pengurangan COD. Sementara itu, sekam padi yang telah dirawat menunjukkan prestasi yang kurang sepanjang proses berlaku dengan 37.83% pengeluaran minyak dan 53.32% pengurangan COD. Kepakatan MEA masih kekal sama untuk kedua-dua penjerap

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

MEA	Monoethanolamine
COD	Chemical Oxygen Demand
DOE	Department of Environment
RH	Rice Husk
RHA	Rice Husk Ash
ARH	Activated Rice Husk
^{o}C	Degree Celsius
G	Gram
Nm	Nanometer
mL	Mililiter
L	Litres
Rpm	Revolution per minutes
wt%	Weight percentage
mg/L	Concentration

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.0 RESEACH BACKGROUND

Monoethanolamine (MEA) is a clear, colourless with peculiar smell, soluble in water, alcohol, and benzene. MEA also known as MonoMethyl Ethanolamine,MMEA or N-Methyl Ethanolamine, 2-Methylaminoethanol (2-Hydroxyethyl) methylamine or Mono Methyl Amino Ethanol. It has many applications within various industries like dye stuff, lubricant, lacquer, coating, paint, pesticide, bactericide, personal care, whiting agent and gas treatment, etc. However MEA is largest utilized in textile, pharmaceutical, household and specialist industries. It is also used in manufacturing of surface active agent and wetting agent. MEA is versatile bifunctional molecules compound which by during reaction it behaves like alcohol and Amine but Amine group usually exhibits greater activity.

In the face of growing and expanding the economy, industrialization seems to be the best choice. But these growing industrial activities always lead to the environmental pollution especially water pollution which can affect health and environment. Aside from the environmental damage, human health is likely to be affected as the presence of pollutant beyond a certain limit (S.M Dal Bosco et al.,2006). The cost for the treatment was increased day by day due to the complexity of the treatment itself. Today, most of the industry tried to make collaboration with researchers on finding a way to manage their wastewater but at the same time can give some profit for them instead of just investing money for the treatment alone.

MEA was produced in huge volume by chemical industry as a wastewater. Recently studies showed that this wastewater can be treated to get the recycle MEA as its can be used as an agent for carbon dioxide (CO_2) removal in the refinery and other oil processing activities which will disturb the process for producing a good quality product. Besides, the CO_2 recovered from the process still can be used for other applications and sometimes it's also been sold to other company.

The natural gas is the most flexible of all primary fossil fuels and most of it must be purified in order to remove impurities particularly CO_2 before it can be used for other purpose (Binyam Seoyum.,2012). The release of CO_2 to the environment got a great concern among public since it can lead to the greenhouse effect (Kenji Nakao et al.,2012). Amine is the one of suitable chemical that can be used for this purpose. Researchers come out with a process called as adsorption used as an alternative process of MEA wastewater treatment that can separate Amine for CO_2 removal from processing plant and for other further usage.

1.1 PROBLEM STATEMENT

The disposal of MEA containing wastewater is a problem because MEA cannot be easily treated in wastewater in wastewater treatment systems due to its toxic effect and slow biodegrability. Low efficiency performance particularly when used on small concentration of removing oil, the necessity of using expensive chemicals in some methods are among the drawbacks of the conventional methods (D. Satapathy et at.,2006). Amine containing wastewater cannot be directly discharged to the surrounding water otherwise it can deplete dissolved oxygen in receiving water, stimulate aquatic plant growth, exhibit toxicity towards aquatic life and presence health hazards (Binyam Seyoum.,2012). So, researchers come out with the solution on which to treat this wastewater in order to removes the pollutants from it and also to sustain the Amine concentration for other usage that is known as adsorption process

This research is basically done to understand more on adsorption process and to finds out which adsorbent between activated carbon and treated rice husk can be used to properly treat the wastewater and at which conditions these two parameters that are adsorbent dosage and mixing speed shows optimum value of removing oil, chemical oxygen demand (COD) and amine concentration.

1.2 RESEARCH OBJECTIVE

The objective for this research is to suggest the best adsorbent and process condition in treating MEA wastewater via batch adsorption method by observing oil residue, amine concentration and Chemical Oxygen Demand (COD).

1.3 SCOPE OF STUDY

In achieving the objective stated, several scopes of work have been identified that are:

i. To compare the effectiveness of the treatment using different type of adsorbent that are activated carbon and treated rice husk in reducing oil residue and chemical oxygen demand (COD), and maintaining amine concentration.

ii. To examine the mechanism of adsorption process for each parameter those are adsorbent dosage and mixing speed.

CHAPTER 2

LITERATURE REVIEW

2.0 WASTEWATER

In many arid and semi-arid countries, water is becoming an increasingly scarce resource and planners are forced to consider any sources of water which might be used economically and effectively to promote further development. In general, we can categorize the wastewater source as residential, municipal, commercial, industrial or agricultural. Ujang Z et al, (2002), stated that this recent years the Malaysian Government has focused on improving and upgrading the existing sewerage system and facilities, which is inadequate in terms of treatment efficiency. In many cases, the effluent quality has not met the effluent standards required by the authority. Contaminant persisting in wastewater including heavy metals, inorganic compound, organic pollutant, and many other complex compound (Fatta et al.,2011; Li et al.,2011). Untreated and inadequate treatment of wastewater has been the major factor causing severe pollution of rivers and near-shore areas, which consequently increased the health risk for the public in Malaysia since the rapid industrialization and urbanization programmes in the 1980s. Some industries are abstract water from rivers and boreholes. Much of water used by industry is taken from public water supplies, and therefore been treated to potable quality standards.

2.1 CHARACTERIZATION OF WASTEWATER

Early research founds out that the source of the wastewater influences the characteristics of the waste stream. Wastewater from commercial sources such as restaurant, schools, supermarkets, hospitals, hotels, and convenience store with food services, car washes, beauty salons and other types of establishment can have characteristics specific to the wastewater generating activities conducted as part of the business . The article written by Rin Munter described some characteristic of wastewater that are:

2.1.1 Physical Characteristic

The total solids in a wastewater consist of the insoluble or suspended solids and soluble compounds dissolved in water. 40 and 65% of the solids in an average wastewater as suspended.

Colour is a qualitative characteristic that can be used to assess the general condition of wastewater. Wastewater that is light brown in colour is less than 6 hour old, while a light-to-medium grey colour is characteristic of wastewater that have undergone some undergone some degree of decomposition or that have been in the collection system for some time. Lastly, if the colour is dark grey or black, the wastewater is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions. The blackening of wastewater is often due to the formation of various sulphides, particularly ferrous sulphide. Colour is measured by comparison with standards.

The odour of fresh wastewater is usually not offensive, but varieties of odorous compound are released when wastewater is decomposed biologically under anaerobic condition. The principle odorous compound is hydrogen sulphide (the smell of rotten egg). Odour is measured by successive dilution of the sample with odour-free water until the odour is no longer detectable.

The temperature of wastewater is commonly higher than that of the water supply because warm municipal water has been added. The measurement of temperature is importance because most of wastewater treatment schemes include biological processes that are temperature dependent.

2.1.2 Chemical Characteristic

Inorganic chemicals such as heavy metals can produce toxic effects; therefore, determination of the amounts of heavy metals is especially important where the further use of treated effluent or sludge is to be evaluated. Many of the metals are also classified as priority pollutant.

Organic matters in wastewater include biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). Laboratory methods commonly used today to measure gross amount.

Volatile organic compounds (VOC) such as benzene, toluene,xylenes,dichloromethane and trichloroethane are common soil pollutant in industrialized and commercialized areas.

2.1.3 Biological Characteristic

Bacteria, viruses, and parasites make up the biological characteristics of wastewater. Wastewater contains vast quantities of bacteria and other organisms that originate in discharged wastes.

2.2 MONOETHANOLAMINE (MEA) WASTEWATER.

Monoethanolamine or also called as 2-aminiethanol is an amino alcohol that has basic properties. MEA is a clear, viscous, organic compound with a mild ammonia-like odour and can be prepared by the reaction between ethylene oxide and methylamine. It is used as a chemical intermediate in the wide range of heavy duty detergents and soaps, and in the neat form to purify refinery and natural gases. MEA is classified as corrosive chemical but it can steadily be control and do not pose a risk if the manufacturer's safety recommendations are followed. MEA wastewaters usually produce by petrochemical plants and other processing plant in huge volume.

The water or steam circulation system of nuclear power plants and thermal power stations uses anion-exchange resin column to capture MEA, and it is released into the wastewater through a resin regeneration process (Dong Jim Kim et al.,2010). The wastewater from the purged solution and the regeneration plant contains high concentration of MEA must be appropriately treated to meet the environmental discharge standard.

A substantial quantity of the amine released in the wastewater generated in a natural gas processing plant during periodic cleaning of the adsorption and stripping towers for carbon dioxide (CO_2) separation or during a process upset (Khodadoust. S et al.,2012). From the literature point of view, researches on MEA wastewater treatment were stil not sufficiently conducted. Indeed very little investment has been made in the past on treatment facilities, whilst water treatment and supply often received more priority than wastewater collection, treatment and reuse. Only some industries have their own wastewater treatment but the function and maintenance are not satisfactory enough due to the high cost (M.F.A Umuhoza et al.,2010). As for the MEA wastewater, the water was treated not only to remove residual oil and suspended solid but it is also to peoduce recycled MEA that can be used in the CO2 removal unit later (M.N Razali et al.,2010).

2.3 WASTEWATER TREATMENT

Many small communities begin the process of addressing wastewater treatment needs by thinking that all they need to do is find the ‘recommended’ treatment option and install it (Thitirat Chaosakul,2005). Heavy metal contamination is of great concern because of its toxic effect on plants, animals, and human beings, and its tendency for bioaccumulation even at relatively low concentration. Therefore, effective removal methods for all contaminant are extremely urgent and have attracted considerable research and practical interest (Chen et al., 2011). In recent years, the environmental impacts of a wastewater treatment plant have been analyzed and identified opportunities to improve its environmental performance. However, each situation is unique and there are numerous treatment technologies available.

2.3.1 Wastewater Treatment Technologies

In an effort to combat the problem of water pollution, rapid and significance progresses in wastewater treatment have been made including photocatalyic oxidation, adsorption or separation procession (Long F et al.,2011). An article written by Rein Munter stated that selection and design of treatment facilities is based on a study of the physical, chemical and biological characteristics of the wastewater, the quality that must be maintained in the environment to which the wastewater is to be discharged or for reuse of the wastewater and the applicable environmental standards or discharge requirement that must be met. Selection of the best method and material for wastewater treatment is highly complex task, which should consider a number of factors (Oller et al.,2011). Therefore, the following technologies that are treatment, flexibility and final efficiency, reuse of treatment agents, environmental security and friendliness, and low cost (Oller et al.,2011)

Methods of treatment in which the application of physical forces predominant are known as unit operations. The methods of treatment by which the contaminant removed chemically or biologically are called process unit. The unit operation and process unit are brought together to provide various treatment known as preliminary, primary, advanced primary, secondary and tertiary treatment. Figure below described these processes in more understandable view.

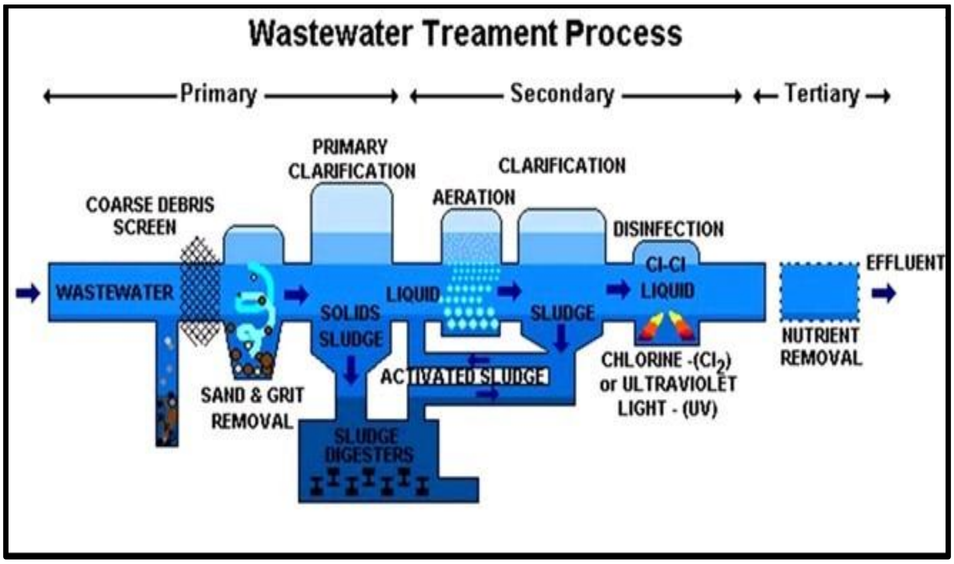

Figure 2.1 Wastewater treatment process

Source : Membranes Solution Company

2.4 ADSORPTION PROCESS FOR MEA WASTEWATER TREATMENT

During the process, some MEA with other wastes enter to industrial wastewater (J.C Garcia et al.,2003). High concentration of these pollutants in industrial wastewater causes negative effect on plant growth and development, environment and human health. The disposal of the MEA containing wastewater is a problem because MEA cannot be easily treated in other wastewater treatment system due to its toxic effect and slow biodegrability (S Bakalova.,2003). MEA is biodegraded by a process that involves the hydrolysis to ammonium and acetaldehyde (A.W.Ndegwa et al.,2004).

Activated sludge and pure culture have been used to compared with MEA degradation at different MEA concentration under aerobic conditions (J.T Hyun et al.,2007). Since MEA or other alkanoamine are difficult to biodegrade, this wastewater cannot be cleaned in the conventional activated sludge biological oxidation tank (Khodadoust. S et al.,2012). The toxicity of MEA and its effective level in the literature showed diverse result depending on the test methods and the organisms used in the experiments. Mrklas et al. (2004) reported that MEA could be degraded in 10 to 20 days depending on the availability of phosphorus. Other studies evaluate the flux and rejection of MEA solution across three different commercial reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membranes (S.Binyam et al.2009). this work shows that the membrane separation processes particularly reverse osmosis can be used to selectively remove MEA from artificial wastewater. However, adsorption is the most suitable to solve it (Mohammad Ajmal et al.,2003) and used economically in variety of separations in the chemical process . Adsorption is also a user-friendly technique and seems to be most effective method (B.H Rao et al,2007).

Adsorption is a process occur when a gas or liquid solute accumulate on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) (Aydin et al.,2008). Usually, the force is electrostatic and has the covalent bond or Van der Waals interaction between the molecules. There is also other stronger interaction involved such as direct electron transfer between sorbate and sorbent. The adsorption of organic contaminant took place via surface exchange reactions until the surface functional site are fully occupied, and thereafter contaminant could diffuse into adsorbent for further interactions with functional group (Hu et al.,2011).

The adsorbates are the substance that being removed from liquid throughout the process,while adsorbent is the material used to adsorpt these substance. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases. Chemisorption is a type of adsorption whereby molecules adhere to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

Among other methods, adsorption using low cost material is one of the viable solutions for the developing country. Adsorption by low-cost adsorbent have been reported by many researchers (Imran Ali and V. K Gupta.,2007,2008; Gupta et al.,2009,2011; Lu et al.,2011). Adsorption of wastewater onto low-cost adsorbet like activated carbon (Jusoh et al.,2011), fly ash (Singh et al.,2010), rice husk (Mubeena Akhtar et al. 2007; 2009). Many parameters can affect the adsorption process such as concentration, pH, contact time, and adsorbent doses. Earlier research shows that the adsorption pencent decreased as the initial concentration increased and after that adsorption percentage became constant. While the adsorption increased when contact time and pH were increased and at the same time the density decreased (Mohammad Ajmal et al.,2003).

2.5 CARBON DIOXIDE RECOVERY BY MEA

Lately, MEA become an important chemical in the industry since it can remove carbon dioxide (Harold et al.,2004). Carbon dioxide (CO_2) is used in the food industry in carbonated beverages, brewing, and flash drying. Its industrial uses include enhance oil recovery (EOR), welding, chemical feedstock, inert gas, fire fighting, and solvent extraction as a supercritical fluid.

MEA is one of the most widely used alkanolamine for removing sour gases such as CO2 from natural gas during refining in the so called ‘sweetening process’ (J.R Gallagher et al.,1995). Due to the ability of absorbing carbon dioxide from combustion gases, MEA has gained attention for the abatement of greenhouse gases (B.J Hwang.,2009).

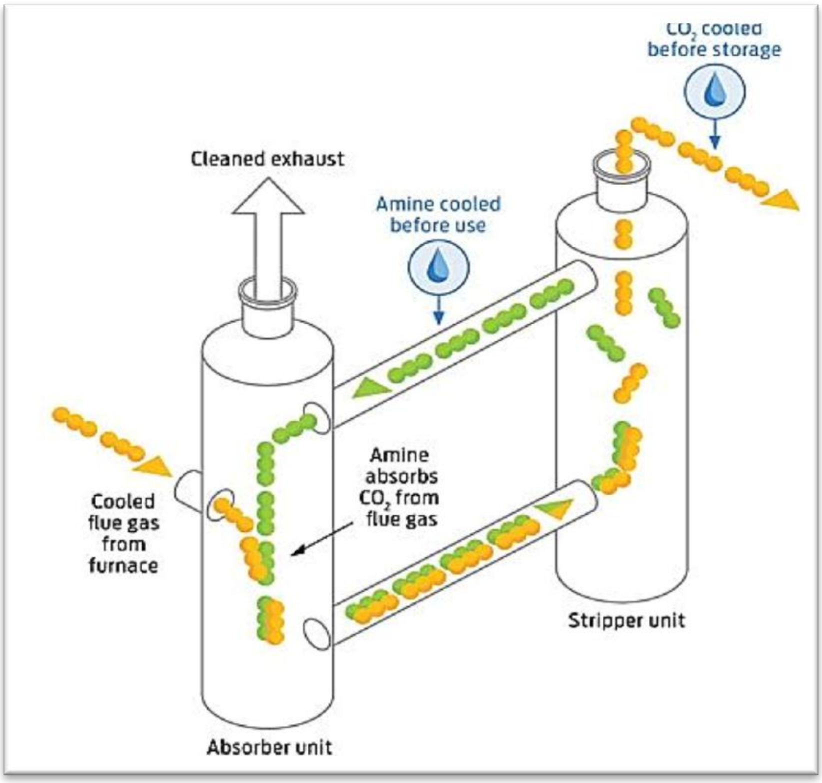

Figure 2.2 Carbon Dioxide recovery by MEA.

The Econamine FG process is today premier commercially proven process for the recovery of CO_2 from the flue gases using an inhibited 30wt.% MEA solution. It can recover 85 to 95% of the CO2 in the flue gas and produces a 99.95++% pure CO2 product (dry basis) (Dan Chaper et al.,1999). Since its introduction by Dow Chemical in the early-1980s,a lot of industry such as food and chemical process industry used this to recover their CO2 (M.T Sander and C.L Mariz.,1992).