ABSTRACT

Monoethanolamine (MEA) is one of the most widely used alkanolamines for removing sour gases such as H_2S and CO_2 from natural gas for refining processes. MEA has gained attention for the abatement of greenhouse gases and the disposal of the MEA wastewater causing a problem as MEA cannot be treated easily due to its toxic effect and slow biodegradability. Foaming phenomena is formed in the absorber when heavy hydrocarbon component carried to the absorber with the feed gas that will leads to several problems such as increased amine losses, reduced gas adsorption efficiency and MEA feed back into the stripper as properties deterioration. This study was conducted to determine potential of continuous technique for treating MEA wastewater and to evaluate the potential of recycling on the treated MEA wastewater. Adsorption method was used for the treatment adsorbent of granular activated carbon with sugarcane bagasse as the comparison of these two adsorbents was investigated. Three parameters have being analysed which is the removal of oil content, amine concentration and COD level. The results showed that activated carbon was the best adsorbent for MEA wastewater treatment system. At the optimum condition, amine concentration is maintained and the residue oil reached its highest removal percentage of 91.72% and COD level reduction of 61.04% approximately via activated carbon adsorption treatment.

ABSTRAK

Monoethanolamine (MEA) merupakan salah satu alkanolamines yang digunakan secara meluas untuk menyingkirkan gas masam seperti H_2S and CO_2 daripada gas asli semasa proses penapisan. MEA telah mendapat perhatian bagi pengurangan gas rumah hijau dan pelupusan air sisa MEA mencetuskan permasalahan disebabkan MEA tidak boleh dirawat dengan mudah kerana kesan toksik dan biodegredasi yang perlahan. Fenomena pembuihan terbentuk dalam penyerap apabila komponen hidrokarbon berat dibawa ke penyerap dengan gas suapan yang akan membawa kepada beberapa masalah seperti kehilangan amine meningkat, keupayaan penjerapan gas berkurangan dan suapan MEA kembali masuk ke dalam penyerap kerana kemerosotan sifat. Kajian ini dijalankan untuk mengkaji potensi teknik berterusan untuk merawat sisa buangan MEA dan potensi kitar semula sisa buangan MEA. Kaedah penjerapan digunakan untuk merawat dengan dua jenis penjerap iaitu berbutir karbon aktif dan hampas tebu telah dikaji. Tiga pembolehubahan yang dianalisis seperti penyingkiran sisa minyak, kepekatan amine and tahap COD. Hasil kajian menunjukan bahawa berbutir karbon aktif merupakan penjerap terbaik dalam merawat sisa buangan MEA. Pada tahap optimum, kepekatan amine tidak terjejas dan penyingkiran tertinggi sisa minyak tercapai pada 91.72%, tahap COD berkurangan sebanyak 61.04% melalui rawatan penjerapan berbutir karbon aktif.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOL

%	Percentage
ml	Mililiter
N	Normal
g	Gram
t	Time
wt%	Weight Percentage
mg/l	Concentration
l	Litres

LIST OF ABBREVIATIONS

CO_2	Carbon dioxide
GAC	Granular Activated Carbon
PAC	Powdered Activated Carbon
H_2S	Hydrogen Sulphide
COD	Chemical Oxygen Demand
MEA	Monoethanolamine
PVC	Polyvinylchloride
SEM	Scanning Electron Microscope
Cd	Cadmium
Pb	Lead
Zn	Zinc

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Nowadays, extreme development of industrial world causes an increasing growth of new inventions technologies and also the accessibility of these technologies for humans. Unfortunately, lack of appropriate attention towards the fundamental and preliminary principles in planning or structuring a project may lead to inevitable problems, which can be considered as a major threat for humans and environment. The most important principles are environmental considerations due to establishment of an industry within a limited area, which will affect the surrounding environment. Petrochemical industry can be considered as one of the most important industries which were exposed to a great development due to specific-economic conditions of the country and increasing demand for petrochemical products during the last years. As the other industries, petrochemical activities result in many problems, most important amongst which is high environmental pollution (S.A. Mirbagheri et al, 2010).

A petrochemical refinery produces large amounts of wastewater (Coelho et al., 2006) originating from a variety of processes, including desalting, hydrocracking, hydroskimming and vapour condensates (Ahmadun et. al., 2006). In consequence, a wide variety of pollutants are present in petrochemical wastewater. Such wastewater is characterised by high chemical and biological oxygen demands (COD and BOD), and contains large amounts of suspended particulate matter, oil and grease, sulphides, ammonia, phenols (Diya'uddeen et al., 2011), benzene, toluene, ethylbenzene and xylenes (BTEXs), polycyclic aromatic hydrocarbons (PAHs)(Ahmadun et. al., 2006) and heavy metals (Perez et al.,2010).

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 further processing activities. This CO_2 is considerably as interference in the processing activities and would thwart the quality of product. In addition, the CO_2 recovered from the process ii often stored for other applications which useful for enhanced oil recovery application or in the chemical and food industries. For the other industries, CO_2 that has been removed from the flue gases is released to atmosphere through stack. The consequence from this action will minimize the greenhouse effect and generate revenue to the company by selling the recovered CO_2 (M.N.Razali et al, 2010). The 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 technologies are amine based CO_2 adsorption systems. The reasons being used widely are the system can used for dilute systems, low CO_2 concentration, easy to handle and can be retrofitted to any plants. Adsorption 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 (Abu-Zahra et. al., 2007). MEA (monoethanolamine) is widely used for the separation of carbon dioxide by the chemical absorption process (Park et. al., 2009).

1.2 PROBLEM STATEMENTS

Monoethanolamine (MEA) is one of the most widely used alkanolamines for removing sour gases (e.g., H_2S and CO_2) from natural gas during refining in the so-called 'sweetening process' (Gallagher et. al., 1995). As it can absorb CO_2 from combustion gases, MEA has gained attention for the abatement of greenhouse gases (Hwang et. al., 2009). Although MEA is recovered in the processes by stripping and distillation, irreversible degradation may also occur, resulting in products from which the MEA is not easily recovered (Dawodu et. al., 1994).MEA is often used for alkalinization of water in steam cycles of power plants, including nuclear power plants with pressurized water reactors to control corrosion of metals. The disposal of the MEA containing wastewater is a problem because MEA cannot be easily treated in wastewater treatment systems due its toxic effect and slow biodegradability (S. Bakalova et. al., 2003).

In CO_2 absorption process, foaming is formed in the absorber when heavy hydrocarbon component carried to the absorber with the feed gas. This is due to the reaction between MEA and CO_2 resulted in production of salt and increased the amount of suspended solids as well in the absorber. As the consequences from this phenomenon will leads to several problems such as increased amine losses, reduced quality of gas decreased adsorption efficiency and also cause MEA feed back into the stripper due to the properties deterioration and it has been removed as wastewater.

From the survey held on petrochemical industrial, every petrochemical plant in Malaysia were produced 60-80 tonnes per upset cases and this MEA wastewater were disposed to Kualiti Alam. The cost to dispose this wastewater was very expensive which 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 cost another RM 2760.00 per drum approximately. So, this MEA wastewater was contributed to increase disposal cost and influenced to the financial of the petrochemical companies itself (M.N.Razali et al, 2010).

This problem shows some potential outcomes in future since limited researchers studied on the treatment of MEA wastewater. The findings on effective methods to overcome the problem still limited. Approaches of adsorption process on separation of amine wastewater are based on physical, chemical and biological methods. The physical treatment method is being highlighted since several researchers have suggested the usage of adsorbents for the removal and recovery of the amine. Removal and recovery of amines emitted 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 (Boger et al**,** 1997; M.N.Razali et al, 2010).

The limitations of researcher's literature reviews on treatment of MEA wastewater from petrochemical plant are insufficiently conducted especially for the CO_2 recycling purpose. Moreover, no research has been done in literature for the treatment of MEA wastewater using activated carbon and sugarcane bagasse as the adsorbents. The real effluent usage is difficult to approach and as the alternative manner, these studies were done by using homemade synthetic effluent. The physical treatment methods would be the interesting research field due to simple, easy, short duration, economical to be commercialized, environmental friendly 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 on adsorption method were chosen, employed and explored in order to examine its ability in reducing the COD, suspended solid, oil concentration in the MEA wastewater and maintaining the amine concentration level at optimum limit. These parameters evaluation were very important in determining the treated MEA could be recycled or else. In the fact view of MEA wastewater is produced in a large amount from petrochemical plants and other processing plants for instance power plant and limited of researchers have been studied on the research.

1.3 RESEARCH OBJECTIVE

The objective of this research is:

i. To suggest the best adsorbent and process condition in treating MEA wastewater via continuous adsorption method.

1.4 RESEARCH SCOPES

In order to achieve the objectives mentioned above, there are several scopes of task have been discovered:

i. To characterise the Monoethanolamine (MEA) wastewater.
ii. To compare the effectiveness of the treatment using the different type of adsorbents (Granular Activated Carbon (GAC) and Sugar Cane Bagasse) in reducing oil content from MEA wastewater, chemical oxygen demand (COD) and maintaining amine concentration level.
iii. To examine the mechanism of adsorption for continuous technique in reducing measured parameters

CHAPTER 2

LITERATURE REVIEW

Literature reviews is one of important parts in a research that provide a guidance and concrete information to a specific topic from other researchers that related to this study. This chapter covers the subtopic on introduction on industrial wastewater treatment, Monoethanolamine (MEA) and adsorption theory.

2.1 INTRODUCTION ON INDUSTRIAL WASTEWATER TREATMENT

Industrial effluents such as wastewater constitute a major impact on the environmental condition of receiving bodies of water and ultimately human health. Therefore, it is the main concern to ensure that industries comply with effluent standards through technologies of wastewater treatment facilities that reduce the amount and concentration of harmful substances which cause water pollution. Today, under government's regulatory agencies, industries are able to handle and manage the pollutants found in their effluents before released to the environment. However, wastewater treatment plant operators and engineers still encounter operational problems due to uncertainties in influent characteristics and operational variations, which affect the quality of effluent (Ian Kit, 2008).

Industrial process wastewaters vary in terms of volume and pollutants present. The type of treatment applied prior to disposal will depend on these factors. The contaminants may be classified as suspended solids, dissolved solids, inorganic pollutants, organic pollutants, and pathogenic microorganisms. In general, the treatment of these water contaminants may be grouped into physical, biological, and chemical treatment methods (Henry and Heinke, 2000). For organic contaminants, biological treatment is applied that makes use of the ability of microorganisms to decompose organic matters present in wastewater.

As the other industries, petrochemical activities result in many problems, most important amongst which is high environmental pollution. This pollution can lead to several direct effects on social and environmental health and almost appears in three dimensions of water, soil and vibrations. The most considerable is water and soil pollution which had the most effect on local ecosystems. Release of the wastewater contaminated by ammonia and its derivatives into the ecosystems and fluid flow can be considered as water pollution. Release of these materials into the water flow changes the aquatic area and living organisms which have been studied in several literatures. Recently, a wide variety of research activities have been carried out on the reactions of biological settlement of wastewater contaminated by ammonia and its derivatives (S.A. Mirbagheri et al, 2010).

Compared to environmental systems or even industrial processes, wastewater treatment plants (WWTPs) have a high time variability of influent quality (Hong et al., 2003). The first step in wastewater purification involves physical treatment to remove oil fractions (Ahmadun et al., 2009), during which most of the heavier hydrocarbon fraction is removed (Stepnowski et al., 2002). The next step is chemical treatment, which removes macro size and colloidal suspended particles. An iron or aluminium salt or polymer coagulant is usually added to enhance the aggregation of particles for easier physical separation (Ahmadun et al., 2009). The last step is biological treatment, the main aim of which is to remove lighter hydrocarbons.

2.2 MONOETHANOLAMINE (MEA)

Monoethanolamine is one of a class of organic compounds called ethanolamines. Ethanolamines combine the properties of amines and alcohols. Monoethanolamine (MEA) is a clear, thick, colorless liquid with an ammonia-like smell. It is completely soluble in water. Monoethanolamine has a freezing point of 10.5°C (51°F), so it can become a solid at ambient temperatures. Monoethanolamine is one of a class of organic compounds called ethanolamines, which combine the properties of amines and alcohols and can undergo reactions common to both groups. They can react with acids to form salts or soaps and can also form esters (sometimes used as artificial flavourings and fragrances). Monoethanolamine is a primary amine – it has one chemical group and two hydrogen atoms attached to the nitrogen atom. This affects its reactivity with other materials. Monoethanolamine is available in a variety of grades, including low freeze grade (LF, 85%) and iron and chloride free (ICF,100%), as well as Gas Treating (GT)grades(Greiner et. al., 2009).

According to Monoethanolamine Safety Data Sheet (Dow, 2004), Monoethanolamine can cause burns to the eyes and skin. It is harmful and corrosive if swallowed. It is also harmful if inhaled or absorbed through the skin. It can cause lung damage if aspirated and repeated exposure may cause liver and kidney damage. Monoethanolamine is the most strongly basic material in the ethanolamine family, and it has the highest vapor pressure. It can react exothermically (to produce heat) with many other chemicals. Incompatible materials include strong oxidizing agents, strong acids, strong bases, aldehydes, ketones, acrylates, organic anhydrides, organic halides, formates, lactones, and oxalates. Although Monoethanolamine is not known to form nitrosamines, contact between ethanolamines and nitrosating agents (e.g., sodium nitrite) should be avoided. Contact between some amines and nitrosating agents can form nitrosamines, which are suspected cancer-causing materials. Monoethanolamine can form an unstable crystalline complex called tris(ethanolamino)-iron when in contact with iron or steel. This compound can ignite when heated to 54–71°C (130–160°F) in the presence of air. Stainless steel is recommended for any hot surfaces in contact with Monoethanolamine. Galvanized steel, copper, and copper-based alloys (e.g., brass or bronze) should not be used in contact with any ethanolamine contact. Monoethanolamine exhibits good temperature stability. However, at temperatures above 250°C (480°F), it can undergo a self-sustaining exothermic reaction, causing rapid decomposition. Contaminants such as caustic, alkali metals, or mineral acids can reduce the onset temperature of decomposition. Like many combustible liquids, Monoethanolamine can begin to self-heat when in contact with high-surface-area media, such as spill absorbents and metal-wire mesh. In some cases, this may lead to spontaneous combustion, and either smouldering or a flame may be observed. Materials contaminated with Monoethanolamine should always be washed or thoroughly wetted with water and then disposed of in closed, water-saturated containers, consistent with governmental requirements.

Monoethanolamine obtained from the reaction between ammonia and ethylene oxide. Monoethanolamine have a low volatility at room temperature, is hygroscopic, presents an ammoniac odour and can appear in solid or liquid form depending on the temperature and the purity grade. Monoethanolamine is a chemical that widely used in various application areas such as detergents, agrochemicals, treatments of gases and others. For detergents, monoethanolamine recommended as a component in detergent formulations for laundry and dishwashing, degreasers, multiple use detergents and disinfectants. Monoethanolamine can also be used as neutralizer agent in formulations of car wash shampoos, degreasers in general, and wax removers and as corrosion inhibitors. Meanwhile, monoethanolamine issued as neutralizer agent for anionic emulsifiers in agrochemicals processes. In treatment of gases applications, ethanolamines can be used to treat natural gas and petroleum residual gas in the absorption of carbon dioxide. In gas systems containing carbon dioxide, monoethanolamine can be used as a selective absorber, and plays an important role in the production of ammonia, liquid carbon dioxide and dry ice permitting regeneration in the latter cases. In addition, monoethanolamine recommended as synthesis intermediate for the manufacture of corresponding alkanolamides due to its reaction with fatty acid or coconut oil. As a consequence of its properties, this product can be used in various industrial segments such as detergents, lubricant oils, products for hygiene and personal care, flotation of minerals, etc. Ethanolamines can also be used in the formulation of pharmaceutical products, dispersing agents for glues, gums, latex and photographic developers, accelerators of rubber vulcanization, corrosion inhibitors, pH controllers, synthesis intermediates, lacquer, paint, wax and polisher wetting agents, polymerizing agents and catalysts for polyurethane resins (Arak, 2010).

Monoethanolamine storage condition is managed properly and carefully since this product is hygroscopic. Recommendation taken by provided the tanks with an inert atmosphere such as of nitrogen to reduce the absorption of water and to avoid darkening through contact with the air. Monoethanolamine is recommended storing by bulk in stainless steel 316 or 304 tanks, equipped with a water or vapour heating coil to maintain the products at a temperature above their solidification point (Arak, 2010).

Several researchers have modelled and studied the MEA absorption process (M. Vucaka et. al., 2002; Phairat Usubharatana, 2009; V. P. Carini et. al., 2010; Majeed S. Jassim, 2006; Ndegwa et. al., 2004), most of their conclusions focused on carbon dioxide capture by absorption. Climate change and the production of greenhouse gases have become important issues in many countries around the world. There has been a heightened awareness that carbon dioxide (CO_2) emission from fossil fuel combustion is the primary contributor to this phenomenon. One of the potential solutions to reducing CO_2 emissions is CO2 capture, a process whereby CO_2 is separated and collected from industrial gas streams, such as flue gases. Currently, there are many capture technologies for carbon dioxide. Among them, gas absorption into chemical solvents is the most promising technology due to its capacity to handle a large volume of flue gas. One of the keys to successful operation of CO_2 chemical absorption processes is the use of effective solvents. Aqueous solutions of alkanolamines are the most commonly used solvents for CO_2 and others acid gas removal. Nevertheless, aqueous alkanolamines do have shortcomings that make the process costly. Firstly, it quickly becomes chemically saturated, and secondly, significant energy is required for solvent regeneration (Phairat Usubharatana, 2009).

2.3 ADSORPTION

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). Note that adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

Adsorption at various interfaces has concerned scientists since the beginning of this century. This phenomenon underlies a number of extremely important processes of utilitarian significance. The technological, environmental and biological importance of adsorption can never be in doubt. Its practical applications in industry and environmental protection are of paramount importance. The adsorption of substrates is the first stage in many catalytic processes. The methods for separation of mixtures on a laboratory and on an industrial scale are increasingly based on utilising the change in concentration of components at the interface. Moreover, such vital problems as purification of water, sewages, air and soil are involved here too. On the other hand, many areas in which technological innovation has covered adsorption phenomena have been expanded more through art and craft than through science. A basic understanding of the scientific principles is far behind; in part because the study of interfaces requires extremely careful experimentation if meaningful and reproducible results are to be obtained.

In recent years, nanostructured solids are very popular in science and technology and have gained extreme interest due to their sorption, catalytic, magnetic, optical and thermal properties. Although the development of adsorption up to the 1918s has been following rather a zig-zag path, this arm of surface science is now generally considered to have become a well-defined branch of physical science representing an intrinsically interdisciplinary area between chemistry, physics, biology and engineering. Current