ABSTRACT

Monoethanolamine (MEA) is a medium that is used for removing the carbon dioxide (CO_2) from the raw natural gas in gas processing plant. Foaming phenomena is formed in the absorber when heavy hydrocarbon component carried to the absorber with the feed gas. This phenomenon was reduce the effectiveness of MEA in CO_2 stripping and will affect the performance of the unit. This study was conducted to examine the best method to treat the MEA wastewater to gain back its effectiveness towards stripping CO_2. Adsorbent those are use in this research is rice husk and sugarcane bagasse. Two different variables that use in this research are adsorbent dosage and mixing time. The parameters that are going to be test in this research are amine concentration, oil and grease concentration and chemical oxygen demand (COD). Rice husk having the higher performance than sugarcane bagasse in removal of oil and chemical oxygen demand (COD).Rice husk achieve 71.11% of oil removal and 42.17% COD reduction. Whereas, sugarcane bagasse shower the lower performance with 46.46%.of oil and grease removal and 12.36% COD reduction. MEA concentration is maintained at 60-70 wt% for both adsorbent.

ABSTRAK

Monoethanolamine (MEA) adalah medium yang digunakan untuk menyingkirkan karbon dioksida (CO_2) dari gas asli mentah dalam loji pemprosesan gas. Fenomena pembuihan terbentuk dalam penyerap apabila komponen hidrokarbon berat dibawa ke penyerap dengan gas suapan. Fenomena ini telah mengurangkan keupayaan MEA dalam penyerapan CO_2 dan akan menjejaskan prestasi unit. Kajian ini dijalankan untuk mengkaji kaedah terbaik dalam merawat sisa buangan MEA dan mendapatkan kembali keberkesanannya untuk menyingkirkan CO_2. Penjerap yang digunakan dalam kajian ini adalah sekam padi dan hampas tebu. Dua pembolehubah yang berbeza yang digunakan dalam kajian ini adalah dos adsorben dan masa rawatan. Pembolehubah yang akan dianalisa dalam kajian ini adalah kepekatan Amine, minyak dan gris dan keperluan oksigen kimia (COD). Sekam padi yang mempunyai prestasi yang lebih tinggi daripada hampas tebu tebu dalam penyingkiran minyak dan tahap COD. Sekam padi mencapai 71,11% dalam penyingkiran minyak dan 42,17% dalam pengurangan COD. Manakala prestasi hampas tebu adalah 46.46% dalam penyingkiran minyak dan gris dan 12.36% dalam pengurangan COD. Kepekatan MEA tidak berubah pada 60-70 peratusan berat bagi kedua-dua adsorben.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	i
STUDENT'S DECLARATION	ii
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS	xii
LIST OF ABBREVIATIONS	xiii
LIST OF APPENDICES	xiv

CHAPTER 1 INTRODUCTION

1.1	Research Background	1
1.2	Problem Statement	4
1.3	Research Objective	8
1.4	Scope of Research	8

CHAPTER 2 LITERATURE REVIEW

2.1 Wastewater Treatment 9

2.2 Adsorption 11

2.3 Monoethanolamine (MEA) 12

2.4 Adsorbent 16

2.4.1 Rice Husk 17

2.4.2 Sugarcane Bagasse 19

2.5 Experiment Method 21

CHAPTER 3 METHODOLOGY

3.1 Research Design 23

3.2 Sample Preparation 24

3.3 Experiment Materials 25

3.4 Instrument and Apparatus 26

3.5 Amine Concentration Analyzing 28

3.6 Oil and Grease Method 29

3.7 Chemical Oxygen Demand (COD) Method 30

CHAPTER 4 RESULT AND DISCUSSION

4.1 Introduction 32

4.2 Characterization of Synthetic Monoethanolamine (MEA) Wastewater 33

4.3 Effect on Reduction of Residual Oil 34

4.4 Effect on Monoethanolamine(MEA) Concentration 37

4.5 Effect On Reduction Of Chemical Oxygen Demand (COD) 39

4.6 Comparison Of Rice Husk And Sugarcane Bagasse 41

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion 46

5.2 Recommendations 47

REFERENCES 49

APPENDICES 55

LIST OF TABLES

Table No.	Title	Page
1.1	Typical Standard of Recyclable MEA Waste	7
2.1	Parameter Limits of Effluent of Standards A and B	10
4.1	Characteristics of Synthetic Monoethanolamine Wastewater	33

LIST OF FIGURES

Figure No.	Title	Page
2.1	CO_2 initiated degradation of amine	14
2.2	The propagation degradation of amine	14
2.3	Rice husk	19
2.4	Sugarcane bagasse	21
3.1	Methodology and planning for research	24
3.2	The schematic drawing of the continuous experimental apparatus.	27
3.3	Flow diagram of experiment procedure	27
3.4	Flow diagram of Amine Concentration method.	29
3.5	Flow diagram of oil and grease method	30
3.6	Spectrophotometer HACH Model DR/2400 (HACH Company, USA).	31
3.7	Flow diagram of Amine Concentration method.	31
4. 1	Reduction of residue oil of adsorbent dosages versus time	35
4.2	Monoethanolamine(MEA) Concentration versus Time	37
4.3	COD reduction of adsorbent dosages versus time	40

4.4	The rice husk before and after the treatment	41
4.5	The sugarcane bagasse before and after the treatment	42
4.6	Oil Reduction versus Time	43
4.7	Monoethanolamine(MEA) Concentration versus Time	44
4.8	COD Reduction versus Time	45

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
H_2S	Hydrogen Sulphide
COD	Chemical Oxygen Demand
MEA	Monoethanolamine
PVC	Polyvinylchloride
Cd	Cadmium
Pb	Lead
Zn	Zinc

LIST OF APPENDICES

APPENDICES.	Title	Page
A	Experiment Results	55
B	Experiment Procedure	60

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Nowadays, increasing attention has been paid to the presence of emerging pollutants in surface and groundwater such as surfactants and pharmaceuticals that their sales are continuously increasing (C.G.Daughton, 2004). Then, improvement of the industrial waste must receive increasing attention where industry generates an amount of waste as a result of advance in processes and products. The petrochemical sector is a highly technological and capital intensive industry. The rapid growth of this industry is mainly attributed to the availability of oil and gas as feedstock, a well-developed infrastructure, a strong base of supporting services, the country's cost competitiveness. Refineries use large quantities of water. Wastewater production strongly depends on the process configuration. Uncontrolled discharge of refinery effluent is no longer possible. Furthermore the industry is well aware of her responsibility towards the environment. The industry has already taken several measures that reduce the water consumption, wastewater discharge and other emissions.

In petrochemical plant, raw natural gas which is contains carbon dioxide needs to be treated to remove the CO_2. This CO_2 is considerably as interference in the processing activities and would thwart the product quality (M.N.Razali, 2010). Monoethanolamine (MEA) is a medium that is used for removing the CO_2 from the raw natural gas. The process for removing CO_2 occurred by the exothermally reaction of CO_2 which is weak base with MEA which is weak acid and produce water soluble salt. This contaminated amine wastewater can be treat and reuse with the same efficiency as before it remove the CO_2 from the raw natural gas. 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.

Over the last few decades, adsorption was being an importance in industry and environmental protection for separation and purification process, especially for treating wastewater. Adsorption is a method which are high reliability, energy efficiency, design flexibility, and low in cost when use waste product as an adsorbent. Adsorption is a widely used as an effective physical method of separation in order to elimination or lowering the concentration of wide range of dissolved pollutants (organics, inorganic) in an effluent (M.Khah and R.Ansari, 2009). Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid (A.Mojiri,2011). Currently, several physical or chemical processes are used to treat dye-laden wastewaters. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. The adsorption process is one of the efficient methods to remove dyes from effluent (M.N.Rao et.al, 2011).

Chitosan, activated carbon risk husk and sugarcane bagasse are the example of adsorbent that usually use for adsorption treatment of wastewater. Chitosan, is a biocompatible and biodegradable polymer, has been widely tested in a variety of fields for the purpose of developing treatments as diverse as wound healing, lung surfactant additives, and tissue engineering (Yuan Y et.al, 2004). Activated carbon is a broad-spectrum agent that effectively removes toxic and bio-refractive substances such as insecticides, herbicides, chlorinated hydrocarbons, heavy metal ions, and phenols, typically present in many water supplies (M.Khah and R.Ansari,2009).

Rice husk is an agricultural waste material generated in rice producing countries, especially in Asia. The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk. Dry rice husk contains 70 – 85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane (N.A.Khan et.al., 2004) . Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch is composed largely of cellulose, pentosan, and lignin. (N.A.Khan et al,2004).Comparing all types of adsorbent, the chitosan and activated carbon is a high cost adsorbent, while rice husk and sugar cane bagasse is low cost adsorbent since it is agriculture waste which is abundantly available in this country.

1.2 PROBLEM STATEMENTS

Environmental problems have increased exponentially in recent decades mainly because of rapid growth in while technological development has improved the quality of life, on the other hand it has created the environmental and health problem too.MEA is the most commercial absorbent for CO_2 from raw natural gas compared to other physical or biological separation method. J.T.Cullinane, et. al.,2004 stated that, aqueous amines, is particularly important for removing acidic components (CO_2, H_2S) from gas streams. MEA is produce by the reaction between ethylene and ammonia. The disposal of the MEA containing wastewater is a problem because MEA cannot be easily treated in wastewater treatment systems due to its toxic effect and slow biodegrability (S.Bakalova et.al.,2003).

In the CO_2 absorption process, the reaction between MEA and CO_2 will produce some salt and increase the amount of suspended solids in absorber also contribute to the foaming problem. Result from foaming, the absorption efficiency will decrease, increased amine losses and reduced quality of product gas and MEA (M.N.Razali,2011) .Foaming is a problem that is widely encountered in gas treating plants and normally leads to serious consequences such as loss of absorption capacity, reduced mass transfer area and efficiency, and carryover of amine solution to the downstream plant (M.A.Abdi and. A.Meisen, 2000). Foaming can be induced by various chemical contaminants including condensed liquid hydrocarbon, fine particulates like iron sulfide, additives containing surface active chemicals, and amine degradation products CO_2 that containing in raw natural gas is need to remove because this CO_2 is considerably as interference in the processing activities and would thwart the product quality (M.N.Razali, 2010).

A significant problem with the MEA absorption technique in its current form is the degradation of the amine over time. The by products of MEA degradation are known to decrease the efficiency of CO_2 capture and have also been implicated in the corrosion of machinery8 In order to compensate for this degradation, current facilities include distillation of the amine to remove by products while continuously adding fresh amine to the system. Unfortunately, this leads to increased material and waste disposal costs. In addition, degradation processes have forced the use of lower concentrations of MEA(<20%) leading to larger overall equipment size, higher solvent circulation rate, and therefore increased energy requirements for CO_2 regeneration from the rich amine.

This increased energy requirement is especially significant since it increases the parasitic load on the power plant leading to increased fuel consumption, higher maintenance costs, and(ironically) increased CO_2 production relative to the power output of the plant (B.R.Strazisar,et.al.,2001).

Potassium in potassium carbonate solutions, overpower other components in small quantities, such as metals characteristic of corrosion, and their concentrations cannot be detected (G.T. Rochelle, et.al.,2004).Vanadium oxide is used as corrosion inhibitor (V.K.Bali,et.al.,2003).Corrosion inhibition of ferrous metals by aqueous potassium carbonate solutions in acid gas treating systems is effected by anions.

Petrochemical plant and other processing plant such as power plant were produce amine contaminated wastewater abundantly. For waste disposal handling is cost a lot of money. 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). Besides that, for buying the new MEA also the plant needs to spend a lot of money on it. Inversely if the MEA is treat and reuse as the CO_2 absorbent. Treating contaminated amine wastewater until it achieved its standard surely can bring a large benefit on the plant. Every petrochemical plant in Malaysian were produce 60-80 tones per upset cases and currently, this MEA wastewater were disposed to Kualiti Alam. This MEA wastewater is disposed have cost RM3000 per tones and the cost for replace the new absorber is RM 2760 per drum

(M.N.Razali,2010). So, in order to reduce cost for this process, the best method for MEA treatment until it achieves the standard was investigated. The typical Standard of Recyclable MEA wastes are as show in Table 1.1:

Table1.1 Typical Standard of Recyclable MEA Waste

Parameter	Standard Limits
MEA concentration Level	>15wt%
Oil ang Grease Concentration	<20mg/l
Foam Height	<4cm
COD	50 000 mg/l
Total vanadium	Min 0.70%
Potassium Carbonate	25-33 wt %

(M.N.Razali, 2011)

The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail (N.A. Khan et.al.,2004.) K.S.N. Kamarudin et. al., 2004 have state that, the adsorption characteristic of any adsorbent depends on adsorbent physicochemical properties, structure, and adsorbate physical properties.

1.3 RESEARCH OBJECTIVE

The objective of the research is:

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

1.4 SCOPE OF RESEARCH

i. To characterized the synthetic amine wastewater.
ii. To study the performance of rice husk and sugarcane bagasse as adsorbents.
iii. To compare the effectiveness of the treatment using the different type of adsorbents (Rice Husk and sugarcane bagasse) in reducing oil content and COD from MEA wastewater, maintaining amine concentration level.
iv. To study the effect of parameter which are adsorbent dosage, and contact time.

CHAPTER 2

LITERATURE REVIEW

2.1 WASTEWATER TREATMENT

Waste water is any water that has been adversely affected in quality by any anthropogenic influence. It therefore includes liquid waste discharged from domestic house, industrial, agricultural, or commercial processes. It does not include rain-water uncontaminated by human activities (M.N.Razali, 2010). Wastewater need to be treat before discharge to drainage system due the level of unsafe level of impurities that contained in the waste water like various of heavy metals and chemical substances..According to Malaysia's Environmental Law, Environmental Quality Act, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000, Standard A, as shown in the third column of the Third Schedule, into any inland waters within the catchment areas specified in the Fourth Schedule and Standard B, as shown in the fourth column of t h e Third Schedule into any other inland waters. Table 2.1 showed the parameter limits of effluent of standards A and B.

Table 2.1 Parameter Limits of Effluent of Standards A and B

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

(Malaysia's Environmental Law, Environmental Quality Act, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations.

Any discharge to impaired water must not exceed the Total Maximum Daily Load (TMDL), the maximum allowable amount of a pollutant that a particular body of water can receive and still meet water quality standards. States have the power to require lower effluent limits, as is the case in the Great Lakes region (E.K. Faulconer et. al., 2012).

2.2 ADSORPTION

Chemical absorption of acidic gases such as CO_2 and H_2S has been widely used in the industry for the treatment, purification of gaseous feed stocks. The acid gas absorption methods use aqueous solutions of alkanolamines or their mixtures as solvents; the most common alkanolamines used are monoethanolamine (MEA), diethanolamine (DEA) and N methyldiethanolamine (MDEA) (B.S.Ali et.al.,2012).Adsorption process has been proven one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water (A.Bhatnagar and M.Sillanpaa, 2010). Adsorption by a solid process need the solid has a very large surface area compared to its mass. The term adsorption refers to the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called 'adsorbate' and the solid on which adsorption occurs is 'adsorbent'.

A number of technologies are available with varying degree of success to control water pollution. Some of them are coagulation, foam flotation, filtration, ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, adsorption, electrolysis, microbial reduction, and activated sludge. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control (A.Bhatnagar and M. Sillanpaa, 2010). The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation (S.M.Kanawade et al ,2010).It over comes the problem of the water treatment techniques by taking advantage of an adsorbent's surface having an affinity for a particular molecular or ionic species coming onto contact with it. A further benefit is that adsorption can be very simple and offers sludge free operation. The evaluation of activated carbon for color removal has been extensive and effluent treatment systems using activated carbon have been successful. Some works of low cost, non-conventional adsorbents have been carried out which include, agricultural solid waste (N. Kanna et.al., 2012)

2.3 MONOETHANOLAMINE (MEA)

Monoethanolamine is a clear, colorless, viscous liquid. It is one of a class of organic compounds called ethanolamines. Ethanolamines have both properties of amines and alcohols. MEA is use as a chemical intermediate in the manufacture of cosmetics, surface-active agents, emulsifiers, pharmaceuticals, and plasticizing. Besides that, MEA is use for the absorption and removal of H_2S and CO_2 from refinery and natural gas streams. MEA solution is an important solvent in the CO_2 removal process because it reacts quickly with carbon dioxide for its primary amine characteristics. MEA undergoes moderate biodegradation and is not expected to be persistent in the environment. MEA is water soluble and biodegrades rapidly. It should not bioaccumulation or persists in the environment. However, large releases to wastewater-treatment facilities can result in poor treatment and toxic shock to biologically active species (R.Maceiras et.al., 2008).

MEA exhibits good temperature stability, but can react exothermically (producing heat) with many other materials, including strong oxidizing agents, strong acids, strong bases, aldehydes, ketones, acrylates, organic anhydrides, organic halides, formates, lactones, oxalates, and copper and zinc metals and alloys. It can also form an unstable crystalline complex called tris(ethanolamino)-iron when in contact with iron or steel, which can ignite when heated to 54–71°C (130–160°F) in the presence of air. Carbon capture from flue gas by absorption/stripping with aqueous amine will probably be an important technology with which to address global climate change. Aqueous monoethanolamine (MEA) at 7 m has been used at a smaller scale to remove CO2 from flue gas and represents an important baseline technology (Ross E. Dugas and Gary T. Rochelle, 2011).Since today, MEA wastewater is disposed to Kualiti Alam and replace with the new MEA to continue CO_2 removing process in the plant.