STUDY ON BATCH ADSORPTION PROCESS OF MONOETHANOLAMINE (MEA) WASTEWATER TREATMENT USING RICE HUSK AND BANANA PEELS

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ABSTRACT

An experimental study was performed in treating Monoethanolamine (MEA) wastewater using bananas peels and rice husk. The main objective of this research is to study the potential of adsorbent usage in treating Monoethanolamine (MEA) wastewater treatment using bananas peels and rick husks. In order to attain maximum result of MEA wastewater treatment, batch process analyses were being done completely. Two important parameters were selected which affected the removal rate of wastewater which are mixing times and adsorbents dosage. From the equipment, it showed that the best potential of adsorbent showed rice husk was better than bananas peels with term percentage of residue oil and reduction of chemical oxygen demand (COD). At 5 wt% (maximum dosage), rice husk removed 43.47% while banana peels removed 41.48% of residue oil of the MEA wastewater. For COD reduction, rice husk manage to reduce 53.32%, while banana peels manage to reduce 49.86% only. At the highest mixing times in 50 minutes, rice husk achieved the highest percentage of oil removal at 78.9% while 76.65% of banana peels. Furthermore, the highest reduction of COD with 52.57% for banana peel and 61.92% reduction for rice husk. Besides, in term of MEA concentration, both adsorbent was not affected by the addition of adsorbent in the MEA wastewater in range below 6% of amine reduction.

KAJIAN MENGENAI PROCES “BATCH ADSORPTION” TERHADAP SISA BUANGAN MONOETHANOLAMINE (MEA) MENGGUNAKAN KULIT PISANG DAN SEKAM PADI

ABSTRAK

Satu kajian telah dilakukan dalam merawat sisa buangan Monoethanolamine (MEA menggunakan kulit pisang dan sekam padi. Dalam kajian ini, objektif utama adalah untuk mengkaji potensi penyerap dalam merawat sisa buangan Monoethanolamine (MEA). Dalam usaha untuk mencapai hasil yang maksimum rawatan sisa buangan MEA, analisis secara berkelompok telah dijalankan sepenuhnya. Terdapat dua pembolehubah yang dipilih bagi mengesan kadar pembuangan sisa kumbahan iaitu perubahan masa dan dos agen penyerap. Melalui proses yang telah dijalankan, sekam padi menunjukkan potensi penyerap yang lebih baik daripada kulit pisang. Pada sukatan 5% berat (dos maksimum), sekam padi mengurangkan 43.47% manakala kulit pisang megurangkan 41.48% minyak dari sisa buangan MEA. Bagi pengurangan COD, sekam padi berpotensi mengurangkan sebanyak 53.32%, manakala kulit pisang berpotensi mengurangkan 49.86% sahaja. Pada masa 50 minit pencampuran, sekam padi mencapai peratusan tertinggi penyingkiran minyak pada 78.9% manakala 76.65% daripada kulit pisang. Tambahan pula, 52.57% pengurangan COD untuk kulit pisang dan 61.92% pengurangan untuk sekam padi. Selain itu,kedua-dua penyerap tidak mempengaruhi perubahan kepekatan MEA dalam smerawat sisa buangan dengan nilai kurang dari 6% pengurangan Amine.

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INTRODUCTION

1.1 Research Background

Natural gas is a primary energy source, which is also used as a raw material for many chemical and petrochemical industries. It consists of both hydrocarbon as well as non-hydrocarbon gases, in which methane contribute to about 70–90% of its total composition. The non-hydrocarbon contaminants namely, carbon dioxide (CO_2), hydrogen sulphide (H_2S) and nitrogen (N_2) are considered important for deciding the quality of natural gas for pricing. The presence of CO_2 reduces the fuel value of natural gas, whereas the presence of H_2S increases the toxicity. The presence of these acid gases (CO_2 and H_2S) not only makes the natural gas acid, but also leads to corrosion problem in the pipelines and equipments used for natural gas processing.

During the burning of natural gas, the emission of CO_2 causes serious environment concern. The greenhouse effect might also leads to a rise in global temperature. Therefore, the removal of CO_2 from natural gas prior to its processing is of commercial importance. This compelling need to reduce these greenhouse gas emissions has brought increasing attention among the researchers, towards the development of new absorbents for CO_2 capture and appropriation (Taib *et al.*, 2012).

Moreover, 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 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 (Razali *et al.*, 2010). Presently, aqueous monoethanolamine (MEA) is widely used for removing carbon dioxide and hydrogen sulfide from flue gas streams (Harold *et al*., 2004).

Furthermore, MEA is very important also for removing CO_2 as a function of combustion of fuel. Based on the theory of combustion, it releases CO_2 to the surrounding. On the research of combustion, the combustion of fossil fuel which is responsible for 85% of the world's energy supply. It is also the most significant source of carbon dioxide (CO_2) emissions worldwide. Because of concern about the effect of CO_2 emissions on the global climate, as well as the world's great dependence on fossil fuels, the development of strategies for the reduction of CO_2 emissions has become increasingly important (Herzog, 1997).

In chemical treatment method, the method that has been most widely used on an industrial scale is chemical absorption using an aqueous solution of monoethanolamine (MEA) as a solvent. In this method, MEA absorbs CO_2 through chemical reaction in an absorber column. Because the reaction is reversible, the CO_2 can be driven off by heating the CO_2 rich amine in a separate stripper column. The MEA may then be recycled through the process. For the low CO_2 partial pressure that is present in flue gas, alternative methods of CO_2 removal are less efficient and more expensive than chemical absorption (Herzog, 1999).

1.2 Problem Statement

Overview about amine, Monoethanolamine (MEA) is a clear viscous, liquid organic compound with mild ammonia like odour, derived from ethylene oxide and ammonia. Besides, it is a chemical intermediate used in the production of a wide range of heavy duty detergents and soaps, and in the orderly form to purify refinery and natural gases. By heating the aqueous solution, the covalent bonding between MEA and CO_2 will break and release CO_2 as gaseous phase. Based on the theory of absorption process, when reaction occurs between CO_2 and MEA, it will produce salt and increased the amount of suspended solid in absorber also contributed to foaming problem. The effect of this reaction, MEA give difficulties in optimizing the absorption processes and it has been removed as wastewater.

Focusing on treatment of MEA, when the amine contaminated wastewater entering the wastewater treatment plant (WTP), it will upset the WTP by increasing the loading and significantly increase the COD and BOD which complicates the effective's treatment of such wastewater. Because of this reason, the amine contaminated wastewater has been stored for disposal rather than permits to enter the WTP. On the other hand, it costs a lot of money for waste disposal managing and minimizes the profit scope.

Monoetanolamine (MEA) aqueous solution is commonly used in oil and gas industry as absorption medium to remove carbon dioxide (CO_2) from gaseous stream. Upon regenerating the MEA solution, some of MEA is carried over into the condensate and contaminate the wastewater. In many occasions, the concentration of amine in the wastewater triggers the COD to exceed the 200, 000 ppm level. In Malaysia, amine contaminated wastewater is sent to Kualiti Alam for disposal, with a cost of around RM2900 per ton of waste (Razali, *et al*., 2010). Since, lots of money is spent by oil and gas to dispose the wastewater, it is rationale to conduct research in order to find a feasible method to treat amine contaminated wastewater.

Adsorption method is chosen due to its direct application, simple, easy and widely used in wastewater treatment plant. 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). In the proposed study, adsorption method is to be explored to examine its feasibility in reducing the amine concentration, suspended solid and oil removing from MEA in the wastewater. The bananas peel and rice husk are selected as absorbent for this study. Then, rice husk will show the best performance in treating the amine contaminated wastewater than bananas peels.

Moreover, chitosan also as adsorbent and shows good performed in treating wastewater. Actually, 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 proved that this adsorbent has the capability to adsorb metal ions, oil and grease, and improve wastewater Quality (Razali et al., 2010). 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. However, bananas peels and rick husk also have a potential as adsorbent to treats wastewater.

1.3 Research Objective

The main objective of this research is to study the potential of adsorbent in treating Monoethanolamine (MEA) wastewater treatment using bananas peels and rick husk.

1.4 Scope of research

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

i. To characterize the amine contaminated wastewater.
ii. To study the effluences of adsorbent dosage and mixing times for oil removal, COD and amine concentration for treatment process of MEA.
iii. To compare the effectiveness of the treatment using different type of absorbents (rice husk and bananas peels) in reducing COD, oil content from MEA wastewater, and maintaining amine concentration level.

CHAPTER 2

LITERATURE REVIEW

This topic explores the subtopic of introduction of wastewater, monoethanolamine (MEA), adsorption theory, performance of adsorbents, and type of adsorbent (bananas peel and rice husk).

2.1 Introduction of wastewater

Wastewaters are usually classified as industrial wastewater or municipal wastewater. Industrial wastewater with characteristics compatible with municipal wastewater is often discharged to the municipal sewers. Many industrial wastewaters require pretreatment to remove noncompatible substances prior to discharge into municipal system. Characteristic of industrial wastewater vary greatly from industry and consequently treatment processes for industrial wastewater also vary, although many of the processes used to treat municipal wastewater are also used in industrial wastewater treatment (Peavy *et al.*, 1998). Wastewater also can be defined as the flow of used water discharged from homes, businesses, industries, commercial activities and institutions which are directed to treatment plants by a carefully designed and engineered network of pipes.

Sewage is the wastewater released by residences, businesses and industries in a community. It is 99.94 percent water, with only 0.06 percent of the wastewater dissolved and suspended solid material. The cloudiness of sewage is caused by suspended particles. Table 2.1 below show the discharge permits which were outlined by the Department of Environment Malaysia (DOE).

Table 2.1 Parameters for wastewater discharge permits by DOE.

	Parameters	Units	Standards A	Standards B
1	Temperature	^{0}C	< 40.0	< 40.0
2	pH	pH	6.0 – 9.0	5.5 – 9.0
3	BOD_5 at 20 °C	mg/L	< 20.0	< 50.0
4	COD	mg/L	< 50	< 100
5	Suspended Solids	mg/L	< 50	< 100
6	Mercury	mg/L	< 0.005	< 0.05
7	Cadmium	mg/L	< 0.01	< 0.02
8	Chromium, hexavalent	mg/L	< 0.05	< 0.05
9	Arsenic	mg/L	< 0.05	< 0.10
10	Cyanide	mg/L	< 0.05	< 0.10
11	Lead	mg/L	< 0.10	< 0.50
12	Chromium, trivalent	mg/L	< 0.20	< 1.00
13	Copper	mg/L	< 0.20	< 1.00
14	Manganese	mg/L	< 0.20	< 1.00
15	Nickel	mg/L	< 0.20	< 1.00
16	Tin	mg/L	< 0.20	< 1.00
17	Zinc	mg/L	< 2.00	< 2.00
18	Boron	mg/L	< 1.00	< 4.00
19	Iron	mg/L	< 1.00	< 5.00
20	Phenol	mg/L	< 0.001	< 1.000
21	Chlorine, Free	mg/L	< 1.00	< 2.00
22	Sulphide	mg/L	< 0.50	< 0.50
23	Oil & Grease	mg/L	Not Detectable	10.0

Standards A are effluent that is going to be released on the upper stream of the river, which will flow to a Drinking Water Treatment Plant. This sentences means that, the water is safety to drink because the chemical particles in the water is in range of good conditions. Besides, standard B is an effluent that is going to be released on the downstream of the river, which is no Drinking treatment Plant available at the downstream of the river. Which means, the water is dangerous to drink because more chemical particles in the water. Wastewater treatment is a multi-stage process to renovated wastewater before it reenters a body of water, is applied to the land or is reused. The goal is to reduce or remove organic matter, solid, nutrients, disease-causing organism and other pollutants from wastewater. Figure 2.1 shows the process flow of typical wastewater treatment plant.

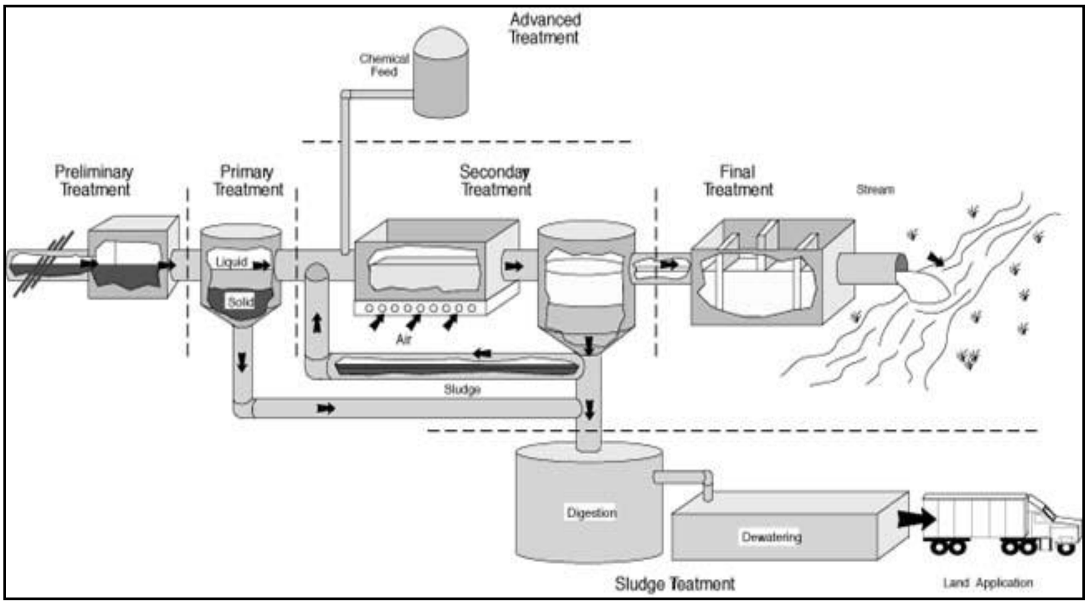

Figure 2.1 Typical wastewater treatment plant.

More information, water and wastewater treatment facilities are usually owned, operated, and managed by the community (the municipality) where they are located. While many of these facilities are privately owned, the majority of Water Treatment Plants (WTPs) and Wastewater Treatment Plants (WWTPs) are Publicly Owned Treatment Works (POTWs). These publicly owned facilities are managed on site by professionals in the field. However, is usually controlled by a board of elected, appointed, or hired directors, who set policy, determine budget, plan for expansion or upgrading, hold decision-making power for large purchases, and in general, control the overall direction of the operation (Drinan, 2001).

2.2 Monoethanolamine (MEA)

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as ETA or MEA). 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., 2004). 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 produced 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 striper due to properties deterioration and thus give difficulties in optimizing the absorption processes and it has been removed as wastewater. Once the MEA wastewater enters the Wastewater Treatment Plant (WTP), it will upset the WTP by increasing the loading and significantly increase the COD, oil concentration and suspended solids which complicate 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 (Razali *et al.*, 2010). The MEA wastewater then has to be stored for disposal and on the other hand, it costs a lot of money for waste disposal handling, to buy fresh MEA and thus, minimizes the profit boundary.

2.2.1 Properties of monoethanolamine

Other research, Ethanolamine is commonly called monoethanolamine or MEA in order to be distinguished from diethanolamine (DEA) and triethanolamine (TEA). Ethanolamine is the second-most-abundant head group for phospholipids, substances found in biological membranes (Calignano et al., 2001). Below are the table properties of monoethanolamine (MEA).

Table 2.2 Properties of Monoethanolamine (MEA)

Molecular formula	C_2H_7NO
Molar mass	61.08 g mol−1
Density	1.012 g/cm3
Melting point	10.3 °C, 283 K, 51 °F
Boiling point	170 °C, 443 K, 338 °F
Solubility in water	Miscible
Vapor pressure	64 Pa
Acidity (pKa)	9.50
Refractive index	1.4539

Otherwise, Monoethanolamine is produced by reacting ethylene oxide with aqueous ammonia. The mechanism shows in figure 2.2 below. The reaction also produces diethanolamine and triethanolamine. The ratio of the products can be controlled by changing the stoichiometry of the reactants (Weissermel et al., 2003).

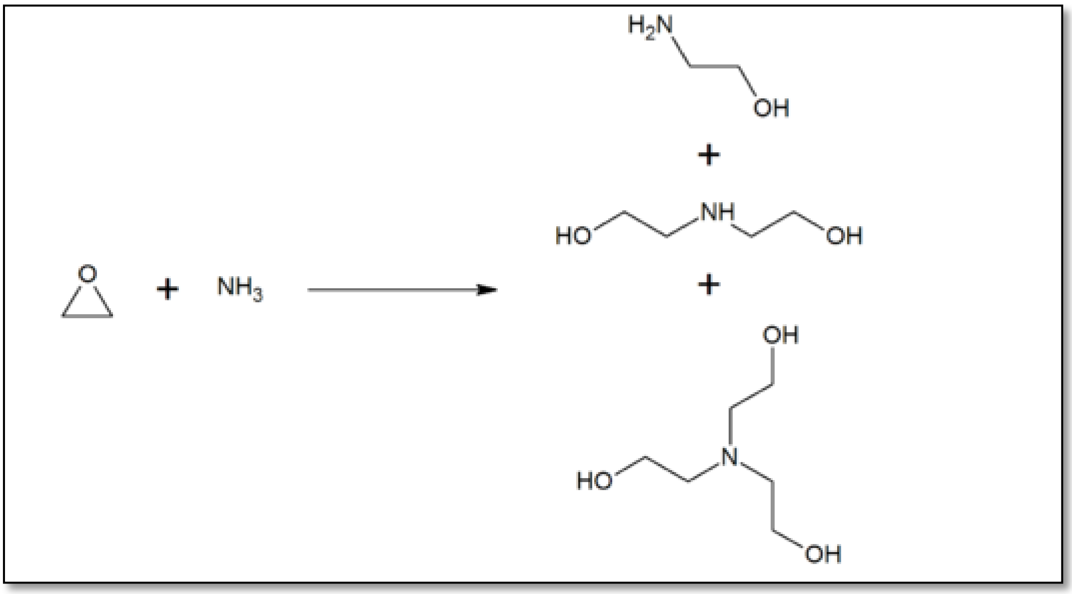

Figure 2.2 Reaction Between Etylene Oxide and Ammonia

Besides, 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 flavorings 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).

2.2.2 Mechanism of monoethanolamine (MEA)

Monoethanolamine (MEA) has been used commercially for many decades to separate CO_2 from natural gas. It is also considered as a prototype for amine-based capture of CO_2 from fossil fuel power plant flue gas. It is typically used as a 30% by weight aqueous mixture in an absorption column, where it reacts to form a carbamate solution, and is then regenerated in a stripping column by heating the solution with low pressure steam to produce a stream of nearly pure CO_2. The MEA process is able to capture 90% of the CO_2 in flue gas (Johnson *et al*., 2010).

Nevertheless, fundamental understanding of the MEA and CO_2 reaction mechanism is needed in order to help design more cost effective amine-based solvents. Despite a number of different experimental and theoretical studies on the reaction mechanism of the MEA and CO_2 system, there is still a controversy regarding the details of the reaction mechanism.

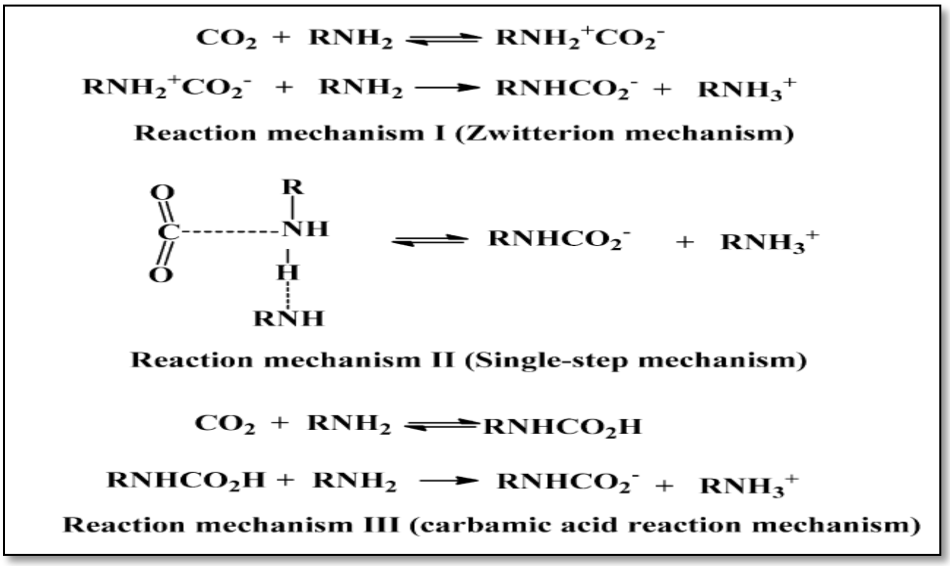

Figure 2.3 Reaction mechanisms for MEA and CO_2 system.

2.3 Adsorption

Adsorption method is chosen due to its direct application, simple, easy and widely used in wastewater treatment plant. 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). Chitosan, activated carbon, alum and zeolite are four types of adsorbents, which have been used in many applications, ranging from food and separation technology to wastewater treatment.