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

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ABSTRACT

Monoethanolamine (MEA) is commonly used for treating synthesis gases stream formed in ammonia, hydrogen, carbon monoxide, and flue gas facilities. Throughout shutdown and maintenance of these facilities, high concentrations of residual alkanolamine may be carried over into the wastewater, as a result of which they can disturb the biological treatment system of the plant. This research was conducted to determine the best adsorbent and process condition in treating MEA wastewater via adsorption method by observing three parameters that are residue oil, COD and at the same time to maintaining the amine concentration level. There were two differents type of adsorbents were used which are untreated rice husk and treated rice husk. The batch adsorption process were used to determine the best adsorbent. The parameters were used in this experiment was the adsorbent dosage, and mixing speed. From the result that collected, treated rice husk has potential as an adsorbent to in removing residue oil with up to 51%, reducing COD up to 66% compared to untreated rice husk which reduce oil up to 47%, and COD up to 54% while the amine concentration were remained same after the treatment for both adsorbents.

KAJIAN TENTANG PROSES PENJERAPAN AIR SISA MONOETHANOLAMINE (MEA) MENGGUNAKAN SEKAM PADI TIDAK TERAWAT DAN SEKAM PADI TERAWAT

ABSTRAK

Monoethanolamine (MEA) biasanya digunakan untuk merawat aliran gas sintesis yang terbentuk dalam ammonia, hidrogen, karbon monoksida, dan fasiliti serombong gas. Sepanjang penutupan dan fasiliti penyelenggaraan ini, baki kepekatan tinggi alkanolamin yang disalur ke air kumbahan, boleh mengganggu sistem rawatan biologi tumbuhan. Kajian ini telah dijalankan untuk menentukan keadaan terbaik adsorben dan proses dalam merawat sisa MEA melalui kaedah penjerapan dengan memerhatikan tiga parameter iaitu sisa minyak, COD dan pada masa yang sama untuk mengekalkan tahap kepekatan amine. Terdapat dua jenis adsorben yang digunakan iaitu sekam padi yang tidak dirawat dan sekam padi yang dirawat. Proses batch penjerapan telah digunakan untuk menentukan adsorben terbaik. Parameter digunakan dalam eksperimen ini adalah dos adsorben, dan kelajuan pencampuran. Daripada hasil yang dikumpul, beras sekam yang dirawat mempunyai potensi sebagai bahan penjerap dalam membuang sisa minyak sehingga 51%, mengurangkan COD sehingga kepada 66% berbanding dengan sekam padi yang tidak dirawat yang mengurangkan minyak sehingga 47%, dan COD sehingga ke 54% manakala kepekatan amine kekal sama selepas rawatan untuk kedua-dua adsorben.

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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

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Monoethanolamine (MEA) is a clear viscous, liquid organic compound with a mild ammonia-like odour, derived from ethylene oxide and ammonia. It is a chemical intermediate used in the production of a wide range of heavy duty detergents and soaps, and in the neat form to purify refinery and natural gases. Monoethanolamine (MEA) is commonly used for treating synthesis gases stream formed in ammonia, hydrogen, carbon monoxide, and flue gas facilities. Most of Monoethanolamine (MEA) are using in preservatives in wood treating industry, as a pH control agent in the formulation of packaging and printing inks, used in Pharmaceuticals industry as antihistamines, antimalarials, antibiotics, local anesthetics, antidepressants and muscle relaxants, and also used 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 (M.N. Razali, et al. 2010).

Nowadays, a lot of industrial has been grown up. Because of this, so many pollutant spread causing so much pollution in the forest, seas, land, and also air. The chemical industry usually leads to water pollution because of their wastewater in not suitable to release to the seas or rivers. The level of COD that contain in the wastewater should be determined before releasing the wastewater that contains high level of COD into the seas or rivers. This will lead to water pollution that endanger to aquatic species. For the natural gas industry, they usually use the MEA to remove the CO_2 refinary stack. As a result, they will produce the MEA wastewater.

The MEA wastewater usually was removed without treating it. Since MEA exist primarily as cations at the pH of site soils, their persistence apparently results from strong binding to soil, as well as inhibition of natural bioremediation in highly contaminated field soils (Hawthorne SB, 2005). Recently, the researcher discovered that this wastewater can be treated to reduce the COD, oil concentration in the MEA wastewater and at the same time maintaining the level of amine concentration at acceptable limit (M.N. Razali, et al. 2010). There were two adsorbents were used to treat this wastewater which are untreated rice husk and treated rice husk. Using the adsorption method is the best way to treat this wastewater due to its application which is binding of molecules or particles to a surface. The Chemical Oxygen Demand (COD), oil and grease, and amine concentration were determined before and after the CO_2 removal.

This study is to compare the performance of untreated rice husk and treated rice husk in treating MEA wastewater and to investigate, which adsorbent projected the highest removal efficiency. The objectives of this study is to determine the best adsorbent and process condition in treating MEA wastewater via adsorption method by observing three parameters that are COD, oil and grease, and amine concentration, to analyze the kinetic of adsorption process and also to determine the concentration of MEA recovered from the adsorption process.

1.2 PROBLEM STATEMENT

Amine based post-combustion capture of carbon dioxide (CO_2) from industrial gas streams, especially from fossil fuel derived power stations, has been demonstrated as a high performance technology to mitigate the emission of CO_2, a major greenhouse gas (T. Supap, 2011). Usually industries just removed this waste amine and this will make the companies spend a cost on buying new amine instead of threatening it that save a lot of cost. Throughout shutdown and maintenance of these facilities, high concentrations of residual alkanolamine may be carried over into the wastewater, as a result of which they can disturb the biological treatment system of the plant (S. Harimurti et. al, 2010).

Nowadays, the researcher found a way how to treat this amine waste as monoethanolamine wastewater by using the adsorption method to reduce the COD, suspended solid and oil concentration in the MEA wastewater and at the same time maintaining the level of amine concentration at acceptable limit. Rice husk were usually disposed as waste in the paddy processing fatory. According to researcher, rice husk can be used as the adsorbent in adsorption for threatening the MEA wastewater. By using rice husk, we believe that this will save a lot of money rather than buying other adsorbent that would costly because rice husk were a waste and people usually disposed them.

According to Occupational Safety and Health Guideline, a small amount of concentration of monoethanolamine did not effects the animal and human but if it come in high concentration, this will lead to irritant of the eyes, skin, and lungs, inhalation causes lung irritation, and the alkalinity of monothanolamine will produce mucosal burns of the mouth and esophagus (Gosselin, 1984). This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200. Because of this, we need to check its COD whether it is suitable to disposed or reuse. According to HUNTSMAN, a high purity monoethanolamine for use in applications where guaranteed low levels of chloride and iron are required. This means that the chloride concentration is need to be determine to make sure that the monoethanolamine can be use for its application.

1.3 RESEARCH OBJECTIVES

The objective is to determine the best adsorbent and process condition in treating MEA wastewater via adsorption method by observing three parameters which are oil residue, amine concentration, and Chemical Oxygen Demand (COD).

1.4 SCOPE OF RESEARCH

1.4.1 To compare the effectiveness of the treatment using the different type of adsorbent which untreated rice husk and treated rice husk in determine the reducing oil residue, Chemical Oxygen Demand (COD), and at the same time maintaining the amine concentration level.

1.4.2 To examine the mechanism of adsorption for each technique in reducing the measured parameter.

1.4.3 To study the influence of variables such as adsorbent dosages and mixing speed for treatment process of MEA wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION PROCESS

An adhesion of atoms, ions, or molecules from any physical properties to a surface is called adsorption. The different between absorption and adsorption is the absorption include whole of the volume and adsorption is surface-based process. Adsorption is present in natural physical stats, biological, and chemical system (Atkins, P. W. 1998). They were used as activated charcoal, capturing heat for cooling process (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons for tunable nanoporous carbon, and water purification. According to IUPAC Compendium of Chemical Terminology 2nd Edition (1997), if the temperature coefficient of the rate of adsorption is substantial, an adsorption process is said to be activated (i.e. to have a significant activatiosn energy). In this case, the sticking coefficient is small. According to Novasep, 2010, there are several mechanisms which cause adsorption: we can list Van der Waals forces, steric interaction, hydrogen bonds, hydrophobicity and polarity. Since the solution to be treated contains a mixture of organics with different properties, the adsorption process is a combination of these mechanisms. Color removal with ion exchange resins is also a combination of ion exchange and adsorption. In fact, the main mechanism is adsorption rather ion exchange.

2.2 ADSORBENT

Adsorbent is a substance, usually porous in nature that has a high surface area that can adsorbs substances onto its surface by intermolecular forces. Only at very low concentrations is the adsorption isotherm linear, at higher concentrations the adsorption isotherm may be Langmuir or Freundlich in nature. Due to the fact that solutes can distribute between the adsorbent surface and a mobile phase, adsorbents are used as a stationary phases in gas-solid and liquid-solid chromatography. Adsorbents are also used for extraction purposes removing traces of organic materials from large volumes of water very efficiently (c_f solid phase extraction devices). Typical adsorbents used in gas-solid chromatography are silica gel, alumina, carbon and bonded phases. These are mostly used in the separation of the permanent gases and the low molecular weight hydrocarbon gasses. Adsorbents used in liquid solid chromatography are mostly silica gel and various types of bonded phases. Adsorbents in liquid-solid chromatography have a very wide variety of application areas.

2.3 INTRODUCTION TO RICE HUSK

Rice is a primary source of food especially in the Asian region. It covers 1% of the earth's surface and ranks second to wheat in term of area and production. Globally, approximately 600 million tonnes of rice paddy are produced each year. Rice husks are by-products of rice paddy milling industries and each ton of dried rice paddy produces about 20% husks (Beagle, E.C.,1978), giving an annual total production of 120 million tonnes. Assuming an ash to husk ratio of 18% (Velupillai, L.,1997), therefore the total ash production could be as high as 22 million tonnes per year.

Rice husk is the outermost layer of paddy. In other hand, it is called rice hull. Rice hulls are the coating for the seeds, or grains, of the rice plant. To protect the seed during the growing season, the hull forms from hard materials, including opaline silica and lignin. The hull is mostly indigestible to humans.

One practice, started in the seventeenth century, to separate the rice from hulls, it to put the whole rice into a pan and throw it into the air while the wind blows. The hulls are blown away while the rice fell back into the pan. This happens because the hull isn't nearly as dense as the rice. These steps are known as winnowing. Later pestles and a simple machine called a rice pounder were developed to remove hulls. In 1885 the modern rice hulling machine was invented in Brazil. During the milling processes, the hulls are removed from the raw grain to reveal whole brown rice, which may then sometimes be milled further to remove the bran layer, resulting in white rice.

The main components of rice husk are cellulose (25% to 35%), hemicellulose (18% to 21%), lignin (26% to 31%), silica (15% to 17%), solubles (2% to 5%), and moisture ca. 7.5% (Leiva et. al, 2007). Some of these ingredients can be recovered for further applications by suitably combining chemical and thermal treatment.

Burning rice husk produced rice husk ash (RHA), if the burning process is incomplete the carbonized rice husk (CRH) is produced. Rice husk contains high silica (SiO_2) which means that it decomposes slowly. Rice husk as the sole carbon source as well as biofilm carrier in the biological denitrification of wastewater in up-flow laboratory reactors (L. Shao, Z. X. Xu, 2008). The rice husk also were used as oil removal as it can be used as absorbent in absorption process. According to Bachelor of Science 1st Semester, Fall 2005, Roskilde University, they were calculated that 73% oil were adsorbed by rice husk.

Figure 2.1 Rice Husk

Overall results of the sorption tests

Sorbents	Operational time (min)	Influent oil concentration ($mg l^{-1}$)	Effluent oil concentration ($mg l^{-1}$)	Total oil input (mg)	Oil sorbed		
		Max; Avg.; Min	Max; Avg.; Min		Total (mg)	Per mass ($mg g^{-1}$)	(%)
Kapok fiber	360	58.5; 40.9; 14.0	15.0; 6.4; 1.8	248 710	206862	827	83
Cattail fiber	360	62.5; 45.3; 33.5	9.6; 5.8; 2.8	320 680	277648	1107	87
Salvinia sp.	300	62.5; 49.3; 39.0	27.8; 7.1; 0.8	288 900	236120	944	82
Polyester fiber	300	54.0; 45.3; 39.0	7.6; 2.6; 0.8	270 850	253 130	1008	94
Wood chip	120	61.5; 49.8; 38.0	27.2; 11.4; 5.8	116 300	86 020	343	74
Rice husk	120	58.0; 42.3; 27.0	15.2; 11.2; 8.2	102 000	74 660	298	73
Coconut husk	60	44.0; 37.6; 32.0	37.4; 24.0; 15.0	45 100	14 480	58	32
Bagasse	30	48.5; 40.7; 36.5	34.2; 32.7; 29.6	24 400	4800	19	20

Figure 2.2 Overall results of the sorption tests

2.3.1 Treated Rice Husk

The rice husk that undergoes pretreatment with mineral acids gives silica with high purity (S. Chandrasekhar et. al, 2005) is called treated rice husk. Amorphous silica with high purity and reactivity is an excellent starting material for the synthesis of advanced materials such as carbides and nitrides of silicon, magnesium silicide, high purity elemental silicon etc. Properties like high surface area and porosity give added advantage to the silica for its use as adsorbents, catalysts and catalyst supports. Treated rice husk usually used in the water treatment process since it can remove phenol, dyes, residue oil, Chemical Oxygen Demand (COD) from wastewater in batch adsorption procedures (Samah B. Daffalla et. al, 2011).

Figure 2.3 Treated Rice Husk

2.3.2 Rice Husk Ash

Rice milling generates a by product know as husk . This surrounds the paddy grain. During milling of paddy about 78 % of weight is received as rice , broken rice and bran .Rest 22 % of the weight of paddy is received as husk . This husk is used as fuel in the rice mills to generate steam for the parboiling process . This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process , is known as rice husk ash (RHA). This RHA in turn contains around 85 % - 90 % amorphous silica.

So for every 1000 kgs of paddy milled , about 220 kgs (22 %) of husk is produced , and when this husk is burnt in the boilers , about 55 kgs (25 %) of RHA is generated.

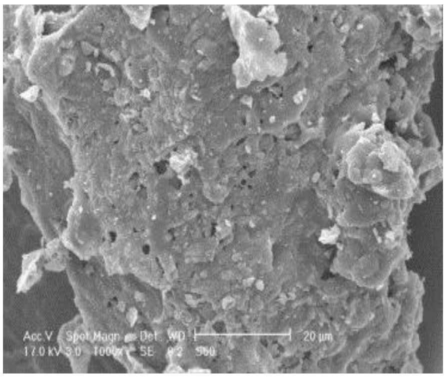

Figure 2.4 Rice Husk Ash **Figure 2.5** Rice Husk Ash at 20μm

India is a major rice producing country , and the husk generated during milling is mostly used as a fuel in the boilers for processing paddy , producing energy through direct combustion and / or by gasification . About 20 million tones of RHA is produced annually. This RHA is a great environment threat causing damage to the land and the surrounding area in which it is dumped. Lots of ways are being thought of for disposing them by making commercial use of this RHA.

Rice husk ash (RHA) is as has the potential to be used as a substitute silica fumes or micro silica as a much lower cost , without compromising on the quality aspect . Adding RHA to the concrete mix even in low replacement will dramatically enhance the workability , strength and impermeability of concrete mixes , while making the concrete durable to chemical attacks , abrasion and reinforcement corrosion , increasing the compressive strength by 10% - 20 % .

Rice husk ash (RHA) also can be use to remove some particle since it has good adsorptive properties and has been used for the removal of various dyes (Mane et al., 2007), heavy metals (Srivastava et al., 2007), and other compounds like chlorinated hydrocarbons (Imagawa et al., 2000), palmytic acid (Adam and Chua, 2004), etc.

2.4 MONOETHANOLAMINE (MEA)

MEA is widely used for removing carbon dioxide (CO_2) from natural gas streams and refinery process streams. It is also used in abatement greenhouse gases and removal CO_2 from combustion gases. MEA is a 2-aminoethanol or monoethanolamine (usually called MEA or ETA). MEA is organic chemical compound that consists of primary alcohol and primary amine (based on a hydroxyl group). MEA has a boiling point, 760 mm Hg, °F/°C=339/171, flash point, PMCC, °F/°C=204/96, melting point, °F/°C=51/11, specific gravity, 20/20°C=1.0179, vapor pressure, mm Hg, 20°C (68°F) P<1, and weight, lb/gal, 20°C (68°F)=8.47 (HUNTSMAN, 2007/2011). The rate of absorption of MEA with CO_2 is fast but it still controlled by reaction kinetic.

MEA degrades in the presence of oxygen and CO_2 resulting in extensive amine loss and equipment corrosion as well as generating environmental impacts. The flue gas stream, which contains 5-10% O_2 and 10% CO_2, there were three types of degradation can occur. A carbamate polymerization requires high temperatures and carbon dioxide, produces high molecular weight degradation products that is expect can occur at high temperature.

Oxidative degradation requires oxygen and is catalyzed by iron, produces oxidized fragments of the solvent such as organic acids and NH3, and is expected to occur in the presence of dissolved O_2 in the liquid hold up at the bottom of the absorber. Lastly, thermal degradation is encountered at temperatures higher than 205°C; therefore, it is the least common. This work focuses on the oxidative degradation of MEA (Susan Chi, 2001). According to International Agency for Research on Cancer (IARC), they havedecided that MEA is not posed cancer to human body in a small concentration.

2.5 INTRODUCTION TO WASTEWATER

Wastewater is the water that has been affected its quality by anthropogenic influence. It is discharged by domestic residences, commercial, industry, and agriculture and can encompass a wide range of potential contaminants and concentrations. This wastewater can affects the human body if it were use as drinking water or any purpose of using this wastewater as daily use. The Malaysia government has proposed a standard Department of Environment Malaysia (DOE) which is it can guide to manage the wastewater as it can be reuse by treating in water treatment plant or release to downstream of a river, which is no water treatment plant.

The standard DOE which is has two categories which is Standard A and Standard B. Standard A is an effluent that is going to be released on the upper stream of a river, which will flow to a Drinking Water Treatment Plant. Standard B however is an effluent that is going to be released on the downstream of a river, which is no Drinking Treatment Plant available at the downstream of the river. Wastewater treatment is a multi-stage process to renovate 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, solids, nutrients, disease-causing organisms and other pollutants from wastewater (Fatima Abdul-Hamid, 2003).

2.6 CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand is a vital test for assessing the quality of effluents and waste waters prior to discharge. The Chemical Oxygen Demand (COD) test predicts the oxygen requirement of the effluent and is used for monitoring and control of discharges, and for assessing treatment plant performance. The impact of an effluent or waste water discharge on the receiving water is predicted by its oxygen demand. This is because the removal of oxygen from the natural water reduces its ability to sustain aquatic life. The COD test is therefore performed as routine in laboratories of water utilities and industrial
companies.