

# DYNAMIC FLOW TREATMENT OF MONOETHANOLAMINE(MEA) WASTEWATER USING ACTIVATED CARBON, CHITOSAN AND RICE HUSK

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## ABSTRACT

*This paper presents the performance of activated carbon, chitosan and rice husk in treating monoethanolamine (MEA) wastewater in order to evaluate the feasible method to recycle and reuse the MEA in the carbon dioxide (CO<sub>2</sub>) removal unit and at the same time maintaining the amine concentration. The adsorption performance of activated carbon was compared to the chitosan and rice husk. Adsorbent dosage and circulation time were varied in this experiment. MEA wastewater before and after the treatment were analyzed for residue oil and amine concentration. Amine contaminated wastewater contains about 2057 mg/L of residue oil and 65 % of amine concentration. The results showed that application of activated carbon managed to reduce the residue oil by up to 95 % and maintained the amine concentration with loss of 6 % at the defined optimum experimental condition (weight of adsorbent: 6 wt% , contact time: 8.5 h). For chitosan and rice husk, the results showed reduction of residue oil by up to 90 % and 71 % respectively. Meanwhile for amine concentration, both showed the same result as activated carbon which is 6 % loss at the same experiment conditions. In conclusion, activated carbon showed the best adsorption performance followed by chitosan and rice husk. Activated carbon showed the best performance as it has the highest surface area compared to chitosan and rice husk.*

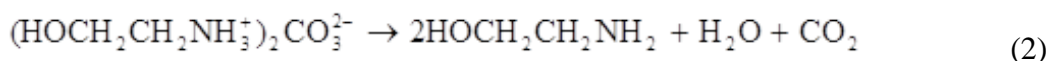
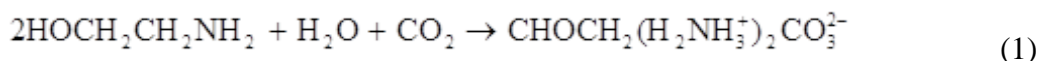
**Keywords:** monoethanolamine; adsorption; activated carbon; rice husk; chitosan; residue oil; amine concentration.

## 1. INTRODUCTION

Environmental issues due to emissions of pollutant from combustion of fossil fuels have become global problems, including air toxics and greenhouse gases (GHG). Increasing GHG level in atmosphere is believed to cause global warming. Among these GHG, carbon dioxide (CO<sub>2</sub>) is the largest contributor in regard of its amount present in the atmosphere contributing to 55 % of global warming effects (Mondal et. al., 2012). The petrochemical plant had

generated the largest amount of CO<sub>2</sub> emission for about 33-40 % of the total. CO<sub>2</sub> emission from combustion flue gases needs to be captured and removed as this CO<sub>2</sub> is posing as interference in the processing activities and would thwart the product quality. Therefore, the stability, safety and environment acceptability of CO<sub>2</sub> capture and storage (CCS) technologies have been paid worldwide attention. These technologies include the chemical absorption and adsorption methods (Xia et al, 1999), membrane separation (Mohamed et. al., 2011) and chemical looping combustion (Matissson et. al., 2001). Removing CO<sub>2</sub> from combustion flue gases by chemical method usually uses amine, ammonia and alkaline solution as absorbents. In recent years, some domestic and foreign researches have deeply researched amine solution, ammonia and alkaline solution as absorbents to absorb CO<sub>2</sub> from aspects of the mechanism, mass transfer coefficient and absorption efficiency. The leading option for CO<sub>2</sub> capture is an absorption process in which the solvent can be a chemical such as monoethanolamine (MEA) absorption process. This technique has been widely used in chemical process industry for over 60 years (Yang et al., 2008). This chemical method has been used due to its advantages of high absorption efficiency, it can produce a relatively pure CO<sub>2</sub> stream, low energy consumption and can be used for dilute systems and low CO<sub>2</sub> concentration (Razali et. al., 2010). Currently, aqueous MEA is widely used for removing CO<sub>2</sub> and hydrogen sulfide, (H<sub>2</sub>S) from flue gas streams. MEA has the advantages of absorbing low concentration CO<sub>2</sub> from combustion flue gases for its small molecular weight and large ability to absorb acid gases such as CO<sub>2</sub> (Kuntz & Aroonwilas, 2009). The absorption efficiency of amine is between 61 %-90 % (Peng et. al., 2012).

Figure 1 shows the basic flow scheme for the MEA process of which principal reactions of MEA with CO<sub>2</sub> are represented as follows:



There are two major units in this process, namely absorber and stripper. Absorber is the place where CO<sub>2</sub> absorption process takes place. Flue gas stream containing CO<sub>2</sub> is introduced at the bottom of the absorber. Absorbent is introduced from the top of the column that leads counter current contact between flue gas and solvent and a selective absorption of CO<sub>2</sub> take place. The reaction in the absorber as shown in equation (1) is occurred at 38-49 °C (Ohtaguchi & Yokoyama, 2007). Then, CO<sub>2</sub> rich stream is fed to the regenerator/ stripper, where desorption of CO<sub>2</sub> occurs and regenerated solvent is recycled for further use, desorbed CO<sub>2</sub> is compressed and sent to storage (Mondal et al, 2012). The chemical solvent is regenerated in the stripper at elevated temperature of 93-127 °C in equation (2). Heat is supplied to the reboiler using low pressure steam to maintain regeneration conditions. This leads to a thermal energy penalty because the solvent has to be heated to provide the required desorption heat for the removal of the chemically bound CO<sub>2</sub> and for the production of steam, which acts as a stripping gas (Razali et al., 2010). Steam is recovered in the condenser and feed back to the stripper, after which the produced CO<sub>2</sub> gas leaves the condenser. The lean MEA is then recycled back to the absorber. Process illustration of CO<sub>2</sub> capture by alkaline amine based solution is shown in figure 1.

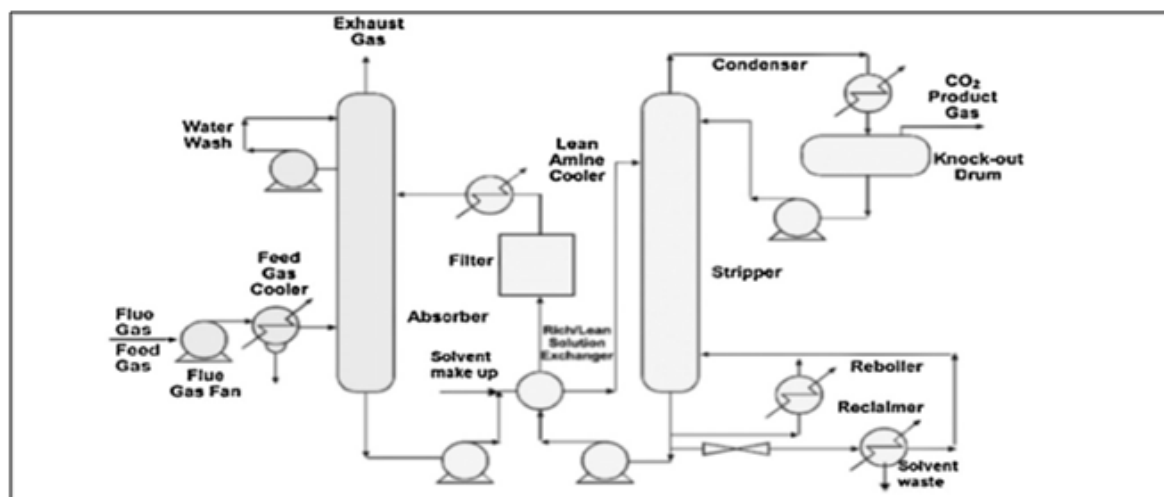


Figure 1: Typical process diagram of CO<sub>2</sub> capture using solvent absorption in industry.

From the literature point of view, it is found that there is 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<sub>2</sub> and MEA also contributed to the foaming problems because the reaction will produce some salt and increased the amount of suspended solids in absorber. This phenomenon will lead to a number of different problems. Foaming impacts integrity of plant operation, causing excessive loss of absorption solvents, premature flooding, reduction in plant throughput, off-specification of products, decreased absorption efficiency, increased amine losses, reduced quality of product gas and MEA somehow is not appropriate to feed back into the stripper due to properties deterioration and thus give difficulties in optimizing the absorption processes and it has been removed as a wastewater (Thitakamol et. al., 2009). These problems have led to the removing of wastewater from the plant. However, it is found that there is an increasing in the oil concentration which complicates the effective treatment of such wastewater in Wastewater Treatment Plant (WTP). On the other hand, the concentration of amine in the wastewater triggers the Chemical Oxygen Demand (COD) to exceed 200, 000 ppm level and not possible to be sent to the WTP. The MEA wastewater then has to be stored for disposal and it needs high costs for waste disposal handling, to buy fresh MEA and thus, minimizes the profit margin (Razali et al., 2010).

In this study, three types of adsorbents which are activated carbon, chitosan and rice husk based adsorption method were employed in order to study its ability in reducing oil concentration in the wastewater and at the same time maintaining the level of amine concentration. Adsorption process has become an importance in industry and environmental protection especially in treating wastewater. With the help of a solid surface, adsorption can be defined as a process of removal of one or more components of a mixture. In addition, adsorption is a method which are high reliability, energy efficiency, design flexibility and low in cost when use waste product as an adsorbent. Adsorption processes are an attractive approach for water treatment, particularly if the adsorbent is cheap and does not require a pre-treatment step before its application (Wang et. al., 2005). Adsorption method is selected, employed and explored in order to study the adsorption performance of residue oil and amine

concentration in this research. These parameters evaluation were very crucial in determining the treated MEA could be recycled or else.

## **2. MATERIALS AND METHODS**

### ***2.1 Sample preparation***

MEA is made at the laboratory of chemical engineering, Universiti Malaysia Pahang. 8 L of amine is diluted with 12 L of water to obtain solution of 40 wt%. Then, diluted amine is mixing with 50 mL of crude oil and 50 mL petrol to produce synthetic wastewater. A portion of the samples are analyse for its characteristics. MEA wastewater is black in colour and oily with obnoxious odour.

### ***2.2 Experimental materials***

Chitosan is in off-white flakes with viscosities and DDA about 30-3000 mPa.S (at 25°C) and 85-89 %, respectively are used for the amine contaminated wastewater treatment. Activated carbon in a porous form with absolute density 2.1 g/cm<sup>3</sup> was used as one of the adsorbent. It is in black powder form. Rice husk were collected from the factory of Ong Chang Hin Rice Mill Sdn. Bhd at Kedah. The density of the rice husk is 0.35 g/cm<sup>3</sup>. The size of these three adsorbents were 650 µm. N-hexane was used as the solvent for oil extraction in the residue oil analysis.

### ***2.3 Experimental procedure***

A series of columns was set up in the experiments to treat MEA wastewater with the adsorbents. It was carried out as a continuous test, accommodating a series of 3 columns. The samples were mix homogeneously before placed into the feed tank. Prior to the test, the samples were measured for residue oil and amine concentration. After the desired amount of adsorbents was added to the column, the valve was opened to allow the MEA wastewater flow through the adsorbents. 500 mL of the treated wastewater was withdrawn from the last column for analysis, representing the final concentration. The pH of samples was also determined.

### ***2.4 Analysis***

The residue oil content was measured by using the oil and grease method recommended by APHA method (APHA, 1992), with n-hexane being used as the oil-extraction solvent. The residue oil content in the treated MEA wastewater was determined both before and after each experiment. 350 mL of the sample was transferred into the separating funnel. Then, 4 mL of 1:1 hydrochloric acid solution to the separating funnel to hydrolyze oils and grease and prevent a sodium sulfate interference. 20 mL of n-hexane were added into the separating funnel to collect the oil content. The contents were shaken vigorously for 2 minutes. The samples were allowed to separate into layers for 10 minutes and the aqueous layer was drip drained into second separating funnel. Extraction was repeated twice with two portions of 20 mL n-hexane. Then, all the surface layers were collected and 2 scoops of anhydrous sodium sulphate were added to expel the water in the layers. The samples of extracted residual oil

with n-hexane transferred into round bottom flask and the samples were heated to remove n-hexane. The initial weight was measured and the drying and cooling were repeated until the weight becomes constant in every 1 h.

The amine concentration was measured by using titration method recommended by APHA method which Tashiro indicator used as amine indicator. The residue oil and amine concentration were determined for each sample of MEA wastewater both before and after experiment. Three replicates of each test were undertaken with the mean value obtained being calculated from the replicates. All tests were performed at an ambient temperature in the range of 26-30 °C.

### 3. RESULTS AND DISCUSSION

The finding and data gathered from the experimental works were discussed thoroughly and the discussion was encapsulated on the removal efficiency of the adsorbents in term of residue oil and amine concentration. These parameters evaluation were very important in determining the teated MEA could be recycled.

#### 3.1 Effect on removal of residue oil

The effects of adsorbent dosage (wt%) on the removal of residue oil from MEA wastewater was carried out by varying the weight percentage of adsorbents at 4 L/hr of flow rate and 1 hour of circulation time at temperature of 30°C with 2 L of MEA wastewater. The pH of MEA wastewater is maintained throughout the experiment which is 12. It is important to make sure the pH is there in order to synchronize it with the operating condition of removing CO<sub>2</sub> in absorber (Mores et. al, 2011). Figure 2 showed that the removal of residue oil from MEA wastewater using activated carbon, chitosan and rice husk. It clearly shown that at all the adsorbents was capable to remove the oil upon increasing the dosage of adsorbents. At the highest adsorbent dosage (6 wt%), activated carbon showed the highest removal of residue oil compared to other adsorbents which is 51 %. It was followed by chitosan by 46 % and rice husk 33 %. Based on the results, activated carbon proved to be the best adsorbent in removing residue oil from MEA wastewater compared to chitosan and rice husk.

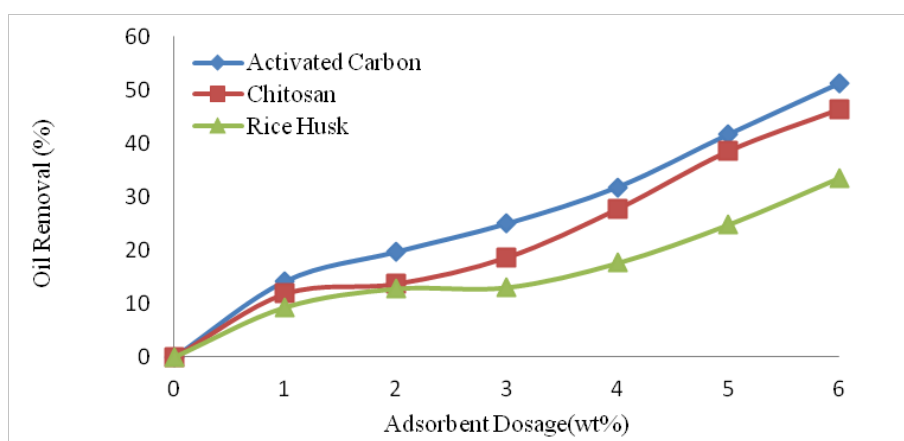


Figure 2: Percentage of residue oil removed versus dosage of adsorbents.



The effect of circulation time (h) for different adsorbents was compared to activated carbon on the removing residue oil of MEA was analyzed by varying the contact time with 6 wt% of adsorbent dosage at 25-30 °C of temperature. The tests were carried out at original pH of the sample which is 12. The pH level was maintained as required in the CO<sub>2</sub> removal unit system. Figure 3 shows that removal percentage of residue oil from MEA wastewater using activated carbon, chitosan and rice husk. From figure 3, it was observed that at the highest adsorbent dosage (6 wt%) and at seven hours of contact time, activated carbon show the highest removal rate of residue oil compared to others. Activated carbon managed to remove 95 % of residue oil while chitosan was 90 % and rice husk was 71 %. Besides that, activated carbon shows the highest maximum capacity where it can maintain adsorbed the oil by up to 8.5 hours before desorption occurs. Desorption occurs once the adsorbent cannot adsorb the oil anymore otherwise desorbed the oil. That is why figure 3 shows the decreasing in the trend at a certain time. It was followed by chitosan and rice husk which are 8 and 7 hours respectively. It can be concluded that activated carbon was the best adsorbents to remove the residue oil.

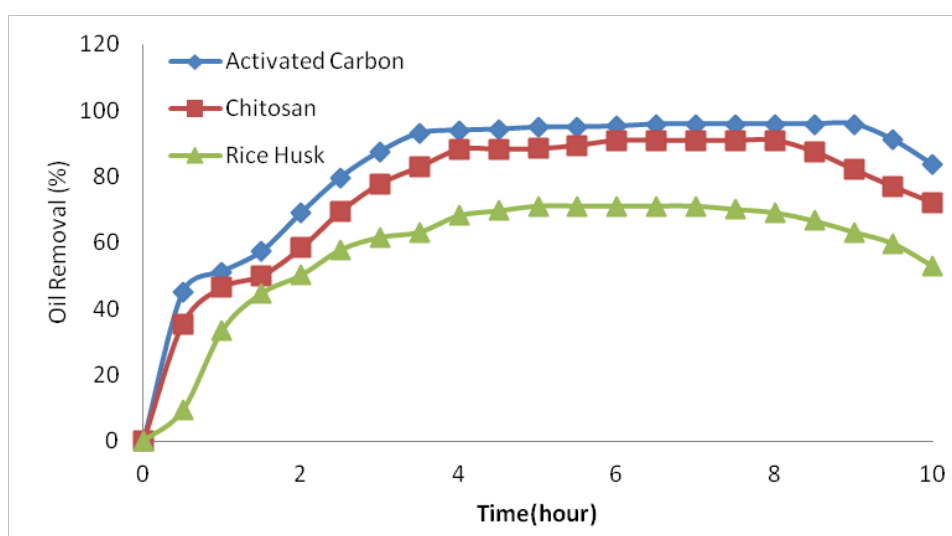


Figure 3: Percentage of residue oil removed versus circulation time.

Activated carbon proved to be the best adsorbent in removing residue oil in MEA wastewater compared to chitosan and rice husk. This phenomenon may be explained by the high surface area of activated carbon. Activated carbon can be considered as a material of phenomena surface area made up millions of pores-rather like a 'molecular sponge'. It consists of highest volume of adsorbing porosity of any material known. Activated carbon is produced specifically so as to achieve a very big internal surface (between 500-1500 m<sup>2</sup>/g). Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. Activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1000 m<sup>2</sup>. This high surface area permits the accumulation of a large number of contaminant molecules. Therefore, as the mass increase, the adsorption of residue oil into activated carbon increase. Activated carbon is the most effective adsorbents in treating drinking water and industrial wastewater (Yi et al., 2013). Moreover, activated carbon has a great capacity to adsorb a wide range of pollutants, fast kinetics, high quality in treating the

effluents (Mohan & Pittman, 2006) and activated carbon are generally adsorb the organics (Geankoplis, 2003). This is why it is applicable for adsorption process and its performance is better than chitosan and rice husk.

It was followed by chitosan which reducing 90 % residue oil. Although chitosan has a smaller surface area compared to activated carbon, chitosan shows the good performance in treating the wastewater due to the accessibility of hydroxyl groups in chitosan. The deprotonation of the hydroxyl group occurred under alkaline conditions (Sakkayawang et. al., 2005). The hydroxyl group of the chitosan polymer could adsorb residue oil by covalent bonding. The negative charge from MEA wastewater might attach to the chitosan surface. The strong alkaline condition aggravates MEA wastewater to break oil droplets. Chitosan provokes physio-chemical effect, apparently serving to demulsify, increase the droplets size and enhance the adsorption of residue oil. More ions particles will be available to form a bond with hydroxyl groups at chitosan surface. Therefore, the electrostatic attraction between residue oils molecules and adsorption site increase and indirectly increase the adsorption of residue oil onto chitosan surface. Rice husk showed the lowest performance with 71 % of residue oil reduction. It is due to it character which is very hydrophilic.

### 3.2 Effect on MEA concentration

Figure 4 and 5 shows that application of activated carbon, chitosan and rice husk did not significantly affect the level of MEA concentration. From figure 5, at 6 wt% of activated carbon, the MEA concentration is reducing from 65 to 61 % for 10 hours contact time. Chitosan was reducing the residue oil from 65 to 59 %. At the same experimental condition, rice husk shows the same results as activated carbon where the amine loss was from 65 to 61 %.

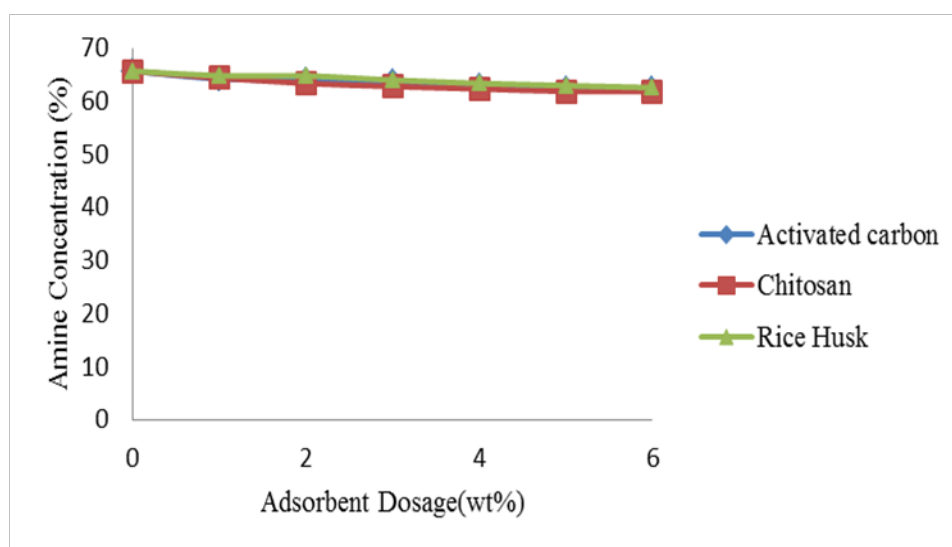


Figure 4: MEA concentration versus dosage of adsorbents.

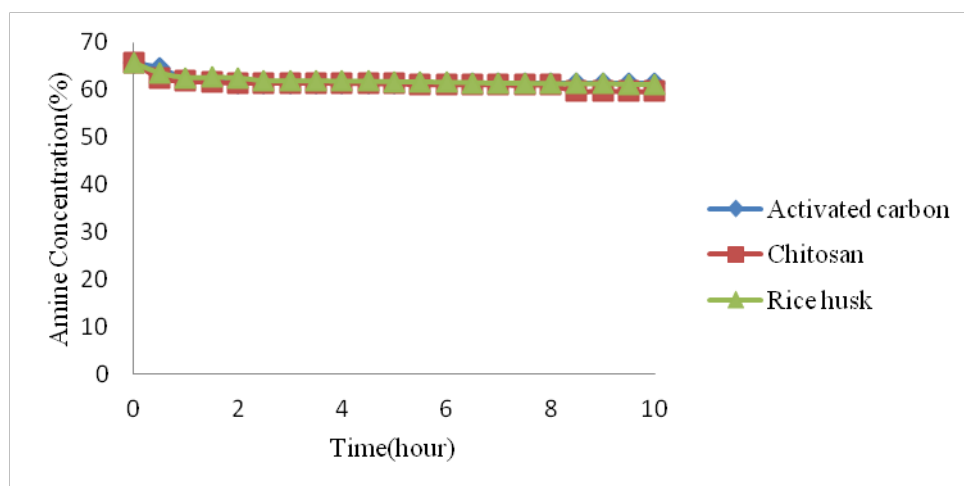


Figure 5: MEA concentration versus dosage of circulation time

This phenomenon may be explained by the amino groups in these three adsorbents (France Chitine, n.d; Thomas, 2013; Gidde et. al., 2009). The amino groups in the adsorbents are not affected by amino molecules in MEA due to same groups. Amine in the MEA functioned well in absorbing  $\text{CO}_2$  in the absorber during  $\text{CO}_2$  removal process (Dugas & Rochelle, 2011). However, there were no chemical reactions or electron transfer between MEA wastewater and adsorbents during the treatment. It clearly shows that amine group is function as absorber. Thus, adsorbents would not be able to adsorb amine during adsorption treatment of the MEA. This phenomenon may be explained by the amino groups in these three adsorbents. Based on the results, it can be concluded that there were no chemical reactions or electron transfer between MEA wastewater and adsorbents.

#### 4. CONCLUSION

Activated carbon showed the best performance as an adsorbent to remove residue oil and at the same time maintaining the level of MEA concentration in the MEA wastewater. The preliminary result shows that treated MEA wastewater potentially can be recycled and reused in  $\text{CO}_2$  removal unit. The results showed that application of activated carbon managed to reduce the residue oil by up to 95% and maintained the amine concentration with loss of 6% at the defined optimum experimental condition (weight of adsorbent: 6%, contact time: 8.5 h). For chitosan and rice husk, the results showed reduction of residue oil by up to 90% and 71% respectively. Meanwhile for amine concentration, both showed the same result as activated carbon which is 6% loss at the same experiment conditions. Activated carbon lead the performance as it has the highest surface area that contribute to the accumulation of a large number of contaminant molecules. Further investigation need to be carried out to evaluate the potential of treated MEA wastewater employs in  $\text{CO}_2$  removal.

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