

Degradation of Aqueous Diethanolamine (DEA) solutions using UV/H₂O₂ Process

Nur Madihah Bt Yaser, Fareeda Chemat, Tazien Rashid, Murugesan Thanabalan*

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Perak, Malaysia.
murugesan@petronas.com.my

Aqueous diethanolamine (DEA) solutions are commonly used for the absorption/scrubbing of acidic gases (CO₂ and H₂S) from natural gas apart from its wide applications in the formulations of consumer chemicals namely, soaps, shampoos, emulsifiers etc. During these processes high concentrations of DEA are released into the atmosphere in the form of waste water/effluents causing a severe pollution to the environment. Hence these stable organic compounds need to be treated/degraded/mineralized before being released into the atmosphere. Hence in the present research an attempt was made to employ UV/H₂O₂ based advanced oxidation process for the degradation of DEA. Experiments were conducted using a synthetic solution of DEA with a concentration range of 500 - 2000 ppm. The other variables used for the DEA degradation experiments were, the initial concentrations of H₂O₂, pH and the temperature. Experiments were conducted in a glass reactor, using UV lamp (8W) as radiation source. The DEA removal efficiencies were estimated based on the TOC measurements. Based on the experimental results the optimum conditions for the maximum removal efficiency were obtained by using the Box-Behnken Response Surface Methodology (RSM). A quadratic regression model was developed to represent the present experimental results on the degradation efficiency as a function of the variables. The experiments conducted based on the estimated optimum conditions showed a satisfactory agreement with the predicted values.

1. Introduction

Emission of carbon dioxide (CO₂) which is one of the greenhouse gases lead to serious environmental problem such as global warming and greenhouse effect. The emission of carbon dioxide released to the atmosphere has the largest percentage that cause global warming which is about 84 % compared to the other gases such as nitrous oxide, fluorinated gases and methane which are 5 %, 2 % and 9 % (Mariz, 1998). Other than its contribution towards global warming and greenhouse effect, presence of CO₂ in the gas stream also will cause interference to the process and reduce the quality of the product (Barchas and David, 1992). Releasing untreated flue gas to the atmosphere is becoming an issue because it violates the hazardous air pollutants under the Clean Air Act (Shah et al., 2013). DEA is an organic compound which has primary amine due to the presence of amino group in the molecule. It is a weak base, toxic, flammable, corrosive, colourless and has an odour which similar to ammonia (Razali et al., 2010), which has been used for the scrubbing of acid gases. However, other than being used as CO₂ scrubber, DEA is also widely being used in cutting oils, soaps, shampoos, cleaners, polishers, cosmetics, pharmaceuticals and as an intermediate in the rubber chemical industry. During the processing of the above, high concentrations of DEA in solutions are released in to the atmosphere in the form of wastewater/effluents, particularly during the periodic maintenance and cleaning of the absorber/stripper units. In order to maintain the environmental regulations these effluents containing high concentration of DEA must be treated before their release into atmosphere. Advanced Oxidation Process is one of the common techniques used for the treatment of such stable highly organic compounds (Ghaly et al., 2001). Due to the disadvantages of sludge formation, Fenton's reagents are not preferable, whereas the combination of UV/H₂O₂ is the most preferred AOP's for the treatment of amine solutions (Fauzi, 2010). The main advantages of the UV/H₂O₂ process are: no formation of sludge during the

treatment, high ability to produce hydroxyl radicals and applicability of the process for a wide pH range. The combination of UV/H₂O₂ treatments can create a very fast and efficient for degradation. This is because if UV treatment alone is used, the range of contaminants UV can degrade by itself is very limited, thus slowing degradation and increase the time to degrade (Rinker et al., 1996). For H₂O₂, it is very strong oxidizing agent where it is capable to destroy some halogenated and most non halogenated compounds in aqueous media (Sohrabi and Ghavami, 2008). The combination of UV/H₂O₂ is one of the best known AOP's and their combination will form two free hydroxyl radicals, OH[•] which is potential oxidizing agent. The degradation mechanism of DEA could be explained as follows:



The free hydroxyl radicals are not in the stable state because they are at excited state species since they are characterized by a one-electron deficiency. Therefore, because of its instability, hydroxyl radicals, OH[•] will tend to react with the first chemical that it comes in contact with and tend to completely oxidize dissolved organic contaminants in aqueous media (Peters et al., 2011).



Hence in the present work an attempt has been made to study the effect of UV/H₂O₂ process on the degradation of aqueous solutions of DEA.

2. Materials and Methods

The chemicals used in the present research namely, Diethanolamine (DEA), hydrogen peroxide (H₂O₂), sodium hydroxide (NaOH), concentrated hydrochloric acid (HCl), were purchased from Merck (Germany). All the experiments were conducted in a stirred jacketed glass reactor (700 mL) with a working volume of 400 mL. Provisions were made in the reactor to monitor and also to collect samples for follow the degradation process. NaOH/H₂SO₄ solutions were used to adjust the pH accordingly. The radiation source is a UV lamp (8 W, UV-C manufactured by Philips, Holland) and was protected by a quartz tube. The degradation of the process were followed by measuring the Total Organic Carbon (TOC) of the samples. The TOC were measured using TOC analyzer (Shimadzu TOC-VCSH) and the H₂O₂ concentration was estimated by KMnO₄ titration (Harimurti et al, 2013). Reaction between diethanolamine (DEA) and hydrogen peroxide is as follow:



Degradation percentage of DEA will then be analysed by using TOC analyzer equipment in order to measure the total organic carbon present in the solution. The detailed experimental procedures were discussed elsewhere for oxytetracycline (Rahmah et al., 2014) and MDEA (Harimurti et al, 2013).

3. Results and Discussion

In the present research, preliminary experiments were conducted to study the individual effect of UV, H₂O₂ and the combination of both UV/H₂O₂. The effect of initial concentration of DEA (500 – 2,000 ppm), effect of initial H₂O₂ concentration (500 – 2,000 ppm), effect of pH (3 - 9) and the effect of temperature (30 - 50 °C) on the degradation of DEA were studied. Based on the present results, the optimized conditions for the degradation process were established. The present results are discussed in detail in the following sections.

3.1 Individual effect of UV radiation and H₂O₂

Three experiments were carried out in order to study the TOC removal differences by using UV radiation only, H₂O₂ and the combination both UV radiation plus H₂O₂ and the obtained results are shown in Figure 1. It can be seen that the UV/H₂O₂ combination shows higher TOC removal, which could be attributed to the enhanced production of hydroxyl radicals due the presence of UV in the system. The capacity of H₂O₂ to degrade the stable organic compound is mainly due to its high redox potential i.e., +1.8 V. This reduction potential indicates the high tendency of H₂O₂ to act as an oxidant, which refers to direct electron transfer reaction between the organic compound and H₂O₂. However, a very high reduction of DEA and the total organic carbon was found, when the combination of UV/H₂O₂ were applied. Nearly a complete degradation of DEA was achieved at 240 min of reaction time. Hence it can be concluded that the combination of UV/H₂O₂ will generate more hydroxyl radical, which has a major role to play in the degradation of DEA.

3.2 Effect of initial H₂O₂ concentration

The effect of initial H₂O₂ concentration on the degradation efficiency is investigated by adding different concentration of H₂O₂ ranging from 500 ppm to 2,000 ppm. The degradation efficiency is increasing from 500 ppm to 1,500 ppm of initial H₂O₂ concentration Figure 2. However, as the initial H₂O₂ concentration increases to 2,000 ppm, the degradation efficiency is decreasing. As the initial H₂O₂ concentration increases, the production of hydroxyl radical also increases as well which lead to a faster rate of degradation of DEA. However, when initial H₂O₂ concentration increases to 2,000 ppm, the hydroxyl radicals produced were preferred to react with the excess H₂O₂ rather than reacting with DEA molecule, and hence the reduction in degradation efficiency (Zang and Farnood, 2005). As the H₂O₂ concentration increases, hydroperoxyl radicals which are less reactive compare to hydroxyl radicals also are being produced.

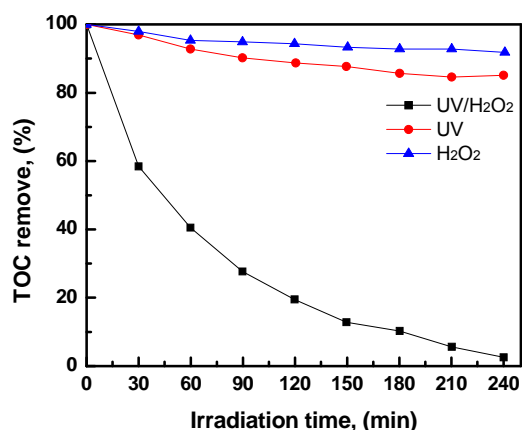


Figure 1: Effect of UV radiation and H₂O₂ on degradation of DEA (DEA = 1000 ppm, H₂O₂ = 1500 ppm, pH = 5)

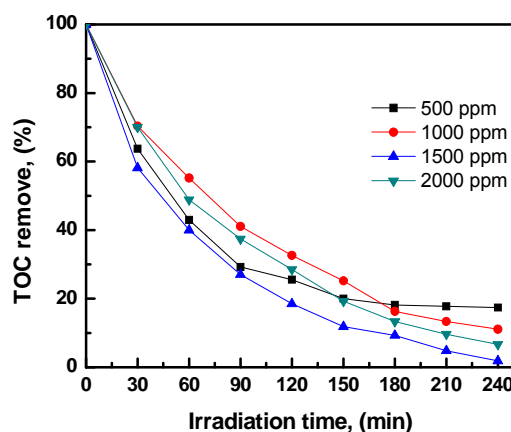


Figure 2: Effect of initial H₂O₂ concentration with irradiation time (DEA = 1000 ppm, pH = 5, Temperature = 30 °C)

3.3 Effect of initial diethanolamine (DEA) concentration

The effect of initial DEA concentration (500 ppm to 2,000 ppm) on the degradation efficiency is shown in Figure 3. As the irradiation time increases, the TOC removes decreases, hence resulting increases in the degradation efficiency for initial DEA concentration from 500 ppm to 1,000 ppm. However, after 1,000 ppm of DEA concentration (1,000 – 2,000 ppm), it shows that the degradation efficiency of DEA is decreasing which is from 97.8 % to 70.2 %. The reason could be that, as the concentration of DEA increases, there is not sufficient hydroxyl radicals available to degrade DEA molecule.

3.4 Effect of initial pH

In order to study the effect of initial pH (3 - 9) on the degradation of DEA four different experiments were conducted. The value of pH were adjusted by adding concentrated hydrochloric acid or sodium hydroxide to the sample solution (Arslan and Balcioglu, 1999). As the pH increases, the TOC removal increases up to pH = 5 within 4 hours of irradiation time, indicating that the degradation of DEA is more effective at acidic condition than at alkaline condition, since at acidic condition more hydroxyl radicals are being produced compared to at alkaline condition (Sohrabi and Ghavami, 2008). Further increase in pH beyond 5, resulted in decrease in percentage TOC removal, which might be due to the decomposition of H₂O₂ itself at higher pH levels. At high pH conditions H₂O₂ tend to ionize to form hydroperoxide anion, which is a well-known strong scavenger to hydroxyl radical. The reaction between hydroperoxide anion and hydroxyl radical generates a less reactive hydroperoxyl radical and hence in the reduction in degradation of DEA/TOC removal

3.5 Effect of temperature

Experiments were conducted at 30 °C to 50 °C, at a pH of 5. The initial concentrations of DEA and H₂O₂ were 1,000 ppm and 1,500 ppm concentration respectively. The percentage degradation increased with increasing temperature. Heating has either increased the generation rate of hydroxyl radicals or directly affected the reaction rate with DEA (Razali et al., 2010). Since the overall rate appears to be limited by the availability of hydroxyl radicals, it is likely that the higher temperature increased the activation energy for the H₂O₂ reaction to hydroxyl radicals. An increase in degradation efficiency with temperature could be attributed to the reason that may be due to an increase in collision frequency between DEA and the hydroxyl radical in the system.

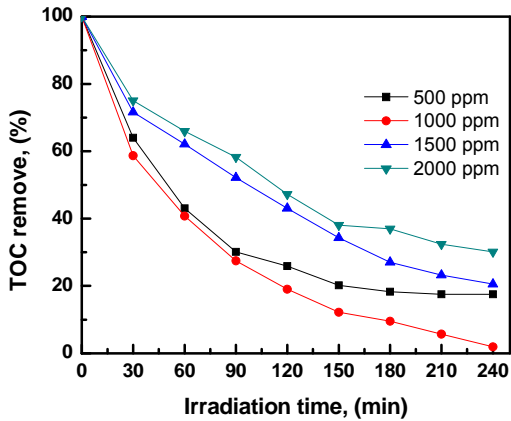


Figure 3: Effect of initial DEA concentrations with irradiation time ($H_2O_2 = 1500 \text{ ppm}$, $pH = 5$, Temperature = $30 \text{ }^\circ\text{C}$)

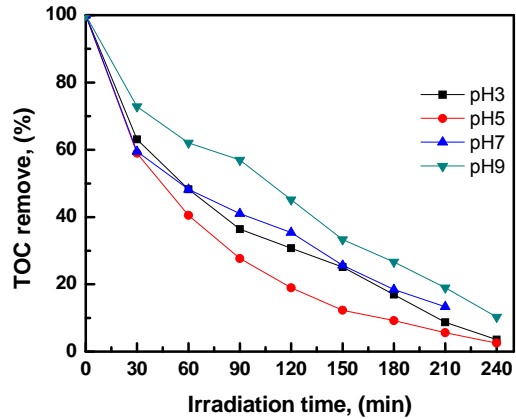


Figure 4: Effect of initial pH with irradiation time (DEA = 1000 ppm , $H_2O_2 = 1500 \text{ ppm}$, Temperature = $30 \text{ }^\circ\text{C}$)

3.6 Optimization studies

Optimization of Diethanolamine (DEA) degradation process was carried out by using Portable Statgraphic Centurion 15.2.11.0 statistical software which then compared with the experimental values. The range and level of the factors (initial concentration of H_2O_2 , initial pH and temperature) were determined based on the initial screening results while the other factors (DEA concentration, UV intensity and irradiation time) were kept constant. Based on the analysis, using the Pareto chart of standardized effect at $p = 0.05$ (Figure 6, which shows that all the three factors namely., initial concentration of H_2O_2 , initial pH and temperature have a significant contribution to the degradation percentage of DEA. The optimum response and relationship between the factors and response were obtained by using Response Surface Methodology (RSM). The quadratic regression model for representing the present experimental data on the percentage degradation on DEA is shown in the following form of equation:

$$Y = 44.9531 + 0.05475 x_1 + 5.90417 x_2 - 0.219167 x_3 - 0.0000187167 x_1^2 - 0.000375 x_1x_2 + 0.00013 x_1x_3 - 0.532292 x_2^2 - 0.0075x_2x_3 + 0.00145833 x_3^2 \quad (5)$$

Where Y is the response , percentage degraded; X_1 is H_2O_2 concentration; X_2 – pH; X_3 is temperature. The proposed empirical correlation represents the present data with an $R^2 = 0.989$. The comparison of the predicted percentage degradation of DEA with those obtained experimentally are shown in Figure 7, which indicates a satisfactory agreement.

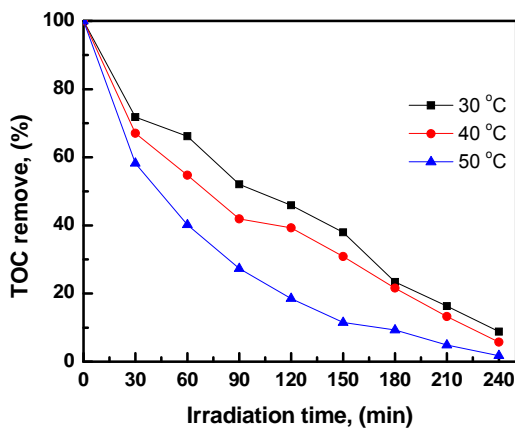


Figure 5: Effect of temperature with irradiation time (DEA = 1000 ppm , $H_2O_2 = 1500 \text{ ppm}$, $pH = 5$)

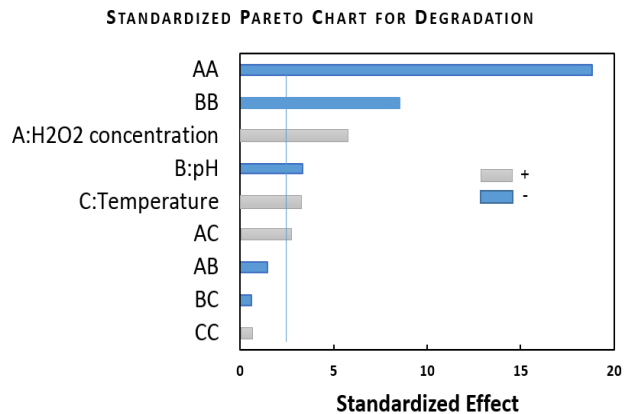


Figure 6: Pareto chart of standardized effect for percentage of degradation

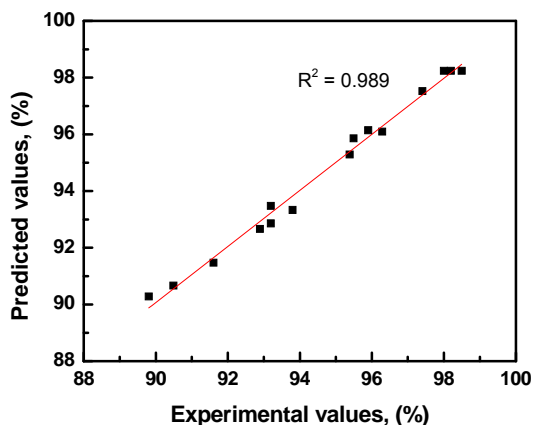


Figure 7: Comparison of the predicted (Eq(5)) and experimental values

4. Conclusions

Based on the present study, it can be concluded that the aqueous DEA solution could be effectively degraded using UV/H₂O₂ process. Initial concentration of H₂O₂, pH and temperature of the system control the degradation efficiency of the process. The optimized parameters for the degradation process are: concentration of H₂O₂ = 1590.13 ppm, pH = 4.63 and temperature = 50 °C. Under these optimized conditions the degradation efficiency was found to be 99.14 %. However, in order to confirm the validity of regression equation, another two experiments were conducted at optimum conditions, and the average degradation was found to be 98.99 %, which satisfactorily agree with the predicted values. All the present experiments were conducted in a batch mode, further experimentation in continuous mode is necessary for establishing the scale up parameters towards its commercial applications.

Acknowledgements

The authors would like to thank Universiti Teknologi PETRONAS for financial support provided for conducting the research.

References

- Arslan, I. Balcioglu, I. A. 1999. Degradation of commercial reactive dyestuffs by heterogenous and homogenous advanced oxidation processes: a comparative study. *Dyes and pigments*, 43, 95-108.
- Barchas, R., Davis, R. 1992. The Kerr-McGee/ABB Lummus Crest technology for the recovery of CO₂ from stack gases. *Energy Conversion and Management*, 33, 333-340.
- Fauzi, I. 2010. Studies on the oxidation of monoethanolamine using UV and H₂O₂ with post-biological treatment. MS Dissertation, Universiti Teknologi PETRONAS, Perak, Malaysia
- Ghaly, M. Y., Härtel, G., Mayer, R., Haseneder, R. 2001. Photochemical oxidation of p-chlorophenol by UV/H₂O₂ and photo-Fenton process. A comparative study. *Waste Management*, 21, 41-47.
- Harimurti, S., Rahmah, A. U., Omar, A. A., Murugesan, T. 2013. Kinetics of Methyl-diethanolamine Mineralization by Using UV/H₂O₂ Process. *CLEAN–Soil, Air, Water*, 41, 1165-1174.
- Mariz, C. L. 1998. Carbon dioxide recovery: Large scale design trends. *Journal of Canadian Petroleum Technology*, 37, 42-47.
- Peters, L., Hussain, A., Follmann, M., Melin, T., Hägg, M. B. 2011. CO₂ removal from natural gas by employing amine absorption and membrane technology-A technical and economical analysis. *Chemical Engineering Journal*, 172, 952-960.
- Rahmah, A. U., Harimurti, S., Omar, A. A., Murugesan, T. 2014. Kinetics and Thermodynamic Studies of Oxytetracycline Mineralization Using UV/H₂O₂. *CLEAN–Soil, Air, Water*.
- Ramli, R. M., Chong, F. K., Omar, A. A., Murugesan, T. 2014. Performance of Surfactant Assisted Synthesis of Fe/TiO₂ on the Photodegradation of Diisopropanolamine. *CLEAN–Soil, Air, Water*.
- Razali, M., Yunus, R., Jemaat, Z., Alias, S. 2010. Monoethanolamine Wastewater Treatment via Adsorption Method: A Study on Comparison of Chitosan, Activated Carbon, Alum and Zeolite. *Journal of Applied Sciences (Faisalabad)*, 10, 2544-2550.
- Rinker, E. B., Ashour, S. S., Sandall, O. C. 1996. Kinetics and modeling of carbon dioxide absorption into aqueous solutions of diethanolamine. *Industrial & Engineering Chemistry Research*, 35, 1107-1114.

- Shah, A. D., Dai, N., Mitch, W. A. 2013. Application of ultraviolet, ozone, and advanced oxidation treatments to washwaters to destroy nitrosamines, nitramines, amines, and aldehydes formed during amine-based carbon capture. *Environmental Science & Technology*, 47, 2799-2808.
- Sohrabi, M., Ghavami, M. 2008. Photocatalytic degradation of Direct Red 23 dye using UV/TiO₂: Effect of operational parameters. *Journal of Hazardous Materials*, 153, 1235-1239.
- Zang, Y., Farnood, R. 2005. Effects of hydrogen peroxide concentration and ultraviolet light intensity on methyl tert-butyl ether degradation kinetics. *Chemical Engineering Science*, 60, 1641-1648.