

The Degradation Mechanism of Wastewater Containing MDEA using UV/H₂O₂ Advanced Oxidation Process

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Abstract—Alkanolamines such as MEA, DEA, MDEA and DIPA in aqueous solutions is frequently used for scrubbing carbon dioxide from natural gas. High quantity of alkanolamine appears in the wastewater during cleaning and maintenance as well as shutdown of the absorption and desorption columns. The alkanolamines waste is toxic to the environment and this wastewater cannot be treated in the conventional wastewater treatment. Advanced Oxidation Process (AOP) named UV/H₂O₂ is introduced to solve this problem. A laboratory set up of degradation MDEA waste using UV/H₂O₂ was conducted and the degradation mechanism has been studied. Glycine, oxalic acid, acetic acid, nitrate ion, nitrite ion and ammonium ion are identified as degradation intermediate product.

Keywords- MDEA; AOP's; UV/H₂O₂; TOC

I. INTRODUCTION

Natural gas is a major energy source in the world. It is one of the cleanest, safe, and most useful of all energy sources. World natural gas consumption rose by 2.5% from 2938.0 billion cubic meters in 2007 to 3018.7 billion cubic meters in 2008 [1]. Consequently, the production of natural gas is in rise. Natural gas has a wide range of acid gas concentrations, from parts per million to 50 volume percent and higher, depending on the nature of the rock formation from which it comes. Because of the corrosiveness of H₂S and CO₂ in the presence of water and because of the toxicity of H₂S and the lack of heating value of CO₂, sales gas is required to be sweetened.

Alkanolamine in water solution are extensively used for scrubbing certain acidic gases in the natural gas production. The most utilized alkanolamines for scrubbing acidic gases are

monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA) and di-isopropanolamine (DIPA) [11]. The alkanolamines are regenerated in stripping tower for recycling back to the absorber. During shutdown and maintenance of these facilities, huge concentrations of residual alkanolamine may be carried over into the wastewater. As a result, they able disturb the biological treatment system of the plant.

In the recent two decade, advanced oxidation processes (AOP's) have proved to be very important in the degradation of high concentrations of organics which may be difficult to treat in a conventional biological oxidation unit. This process is involving a very reactive species named hydroxyl radical ($\bullet\text{OH}$). Fenton's treatment, UV/O₃ and UV/H₂O₂ are the popular technique for generation of hydroxyl radical. In this paper will be explained concerning the MDEA degradation mechanism by hydroxyl radical in the water solution. The UV/H₂O₂ process in evaluation to other methods of water treatment has additional advantages such as no formation of sludge during the treatment, high ability on producing of hydroxyl radical and applicable in the wide range of pH. In UV/H₂O₂ process oxidation, Equation (1) is generally accepted to generate the hydroxyl radical $\bullet\text{OH}$ [6, 8, 16, and 23]:



The reaction rate of organic contaminant degradation is usually controlled by the rate of generation of $\bullet\text{OH}$ radicals, which depend upon the concentrations of H₂O₂ and UV dose.

A large number of experimental works on the application of advanced oxidation processes (AOP's) to treat high-strength of waste have been reported in the literature. The use of Fenton's reagent in the AOP's was conducted to degrade MEA (monoethanolamine) waste [20, 21, and 22]. Putri et al. [17] also used the Fenton's reagent to study the degradation of sulfolen. In addition, Raihan et al. [18] studied the effect of continuous addition mode of Fenton's reagent on mineralization of di-isopropanolamine (DIPA). The continuous addition mode of Fenton's reagent was better than the one time addition mode. Meanwhile, the used of UV/H₂O₂ in the advance oxidation process had been also examined. Idhizam et al. [5] conducted the degradation of MEA. Malik and Sanyal [12] and Muruganandham and Swamithan [15] studied the effectiveness of UV/H₂O₂ to decolorize azo-dye. The degradation of 4-nitrophenol using UV/H₂O₂ was reported by Daneshvar et al. [3]. Lopez et al. [10] successfully degraded the 4-chloro-3,5-dinitrobenzoic acid (CDNBA) in aqueous solution. Degradation and detoxification of formaline wastewater using UV/H₂O₂ was greatly achieved as reported by Kajitvichyanukul et al. [7]. Mamane H et al. [13] studied inactivation of microbiocidal (*E. coli* and *B. subtilis* spores) and virucidal (MS2, T4, and T7 phage) using UV/H₂O₂. The effect of presence of inorganic salt on advanced oxidation was investigated by Riga et al. [19]. However, Fürhaker et al. [4] reported that MDEA is non-biodegradable in the batch bioreactor during the test period of 28 days. There is a well recognized suggestion to treat the MDEA to become biodegradable. It is suggested that advance oxidation processes (AOP's) are effective to degrade or reduce the toxicity of organic contaminant. Further, the UV/H₂O₂ process in evaluation to other methods of water treatment has additional advantages such as no formation of sludge during the treatment and high removal rate of organic contaminant. Consequently, a study on the degradation process of MDEA using UV/H₂O₂ that may possible as pre-treatment of the MDEA waste before biological oxidation was conducted in this research.

II. EASE MATERIAL AND METHOD

A. Reagent

MDEA, KMnO₄, H₂SO₄ and Hydrogen Peroxide (H₂O₂) were obtained from Merk (German) and NaOH was obtained from RM Chemicals (Malaysia).

B. Experiment

The experiment is conducted in 400 ml stirred jacketed glass reactor to monitor the progress mineralization. The photoreactor is equipped with the low pressure Hg vapor lamp, a currents-voltage control unit and hole for collect the sample. A solution of the amine in desired concentration is prepared and required amount of H₂O₂ is added in the amine solution. The pH adjustment is carried out with NaOH and H₂SO₄. The Process starts immediately and than the temperature is maintained by circulating cooling water through the jacket. Samples of the liquid are withdrawn from time to time and the

TOC of the samples are measured using TOC analyzer from Shimadzu, while the H₂O₂ concentration is measured using KMnO₄ titration [14]. Furthermore, the nitrate ion is determined using a Metrohm of 761 Compact Ion Chromatography with Metrosep A supp 5-150 column and 3.2 mM Na₂CO₃/1.0 mM NaHCO₃ as eluent. NH₄ ion is determined using Ammonia Nessler Method (Method 8038 Standard Methods for Examination of Water and wastewater 4500-NH₃ B&C). After the UV/H₂O₂ process, the monitoring of degradation product and un-reacted MDEA was determined using high performance liquid chromatography (HPLC-Model Agilent series 1100). YMC-Pack PolymerC18 reverse phase column was used. Elucidation was using a mixture between 100mM Na₂HPO₄ and 100mM NaOH with ratio 60% of Na₂HPO₄ and 40% of NaOH at pH of 12. UV light at 215 nm was used as detector. Another column special for organic acid determination was also used. The column was obtained from Transgenomic (Model ORH801) and 0.01 N H₂SO₄ was used as mobile phase. Refractive index was used as detector. Degradation product determination was performed by comparison of the sample with the standard compound.

III. RESULT AND DISCUSSION

Degradation of MDEA in water solution by using UV/H₂O₂ has been studied. MDEA containing the elements C, H, O and N, alkanolamines oxidation by hydroxyl radical HO • is expected to be CO₂, H₂O, NH₄⁺, NO₂⁻ and NO₃⁻. Klare et al. [2] presenting a possible mechanism of secondary amine degradation by hydroxyl radical. NH₃/NH₄⁺ was identified as intermediate product in partially degraded secondary amine. Low et al. [24] found ammonium ion (NH₄⁺) and nitrate ion (NO₃⁻) in the degradation of organic containing nitrogen atom using TiO₂ mediated photo-catalytic.

In this study, the nitrate ion (NO₃⁻), nitrite ion (NO₂⁻) and ammonia nitrogen (NH₃-N) is generated during the oxidation process of MDEA by using UV/H₂O₂. The profile of the nitrate (NO₃⁻) and nitrite (NO₂⁻) was evaluated by using ion chromatography (Metrohm-761 Compact IC) which was equipped with Metrosep A Supp 5-150 column. The ammonia nitrogen (NH₃-N) was evaluated according to Ammonia Nessler (Method 8038 Nitrogen). Figure 1 shows the profile of inorganic by products during UV/H₂O₂ oxidation process.

Identification of the organic intermediate products after UV/H₂O₂ process was made. HPLC was used to characterize the intermediates. An Agilent series 1100 brand of HPLC was used to monitor the degradation products and un-reacted MDEA after UV/H₂O₂. YMC-Pack PolymerC18 reverse phase column was used with 100mM Na₂HPO₄/100mM NaOH (60/40, pH 12) as eluent and UV at 215 nm as detector. Flow rate of the eluent was 1 ml/minute. Another specific column for organic acid determination was also used. The column was obtained from Transgenomic (Model ORH801) and 0.01 N H₂SO₄ was used as mobile phase. Refractive index was used as detector. Degradation product determination was performed by comparison of the sample with the standard.

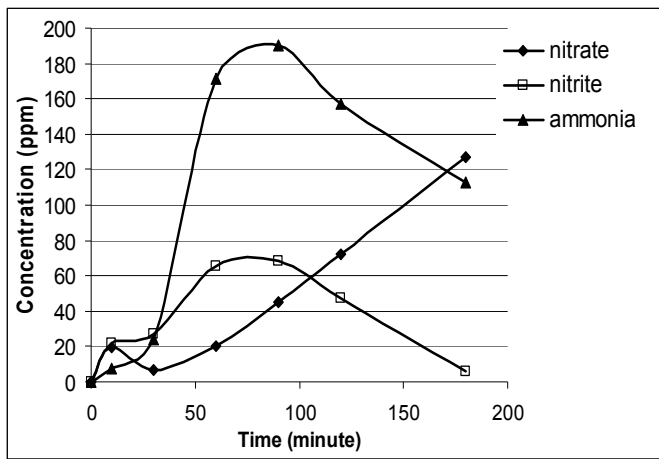


Figure 1. Inorganic by product profile during the UV/H₂O₂ process. MDEA = 2000 ppm (≈1000 ppm TOC), [H₂O₂]₀ concentration = 0.22 M, initial pH = 10.17, temperature = 30°C and with intensity UV was 12.06 mW/cm² for radiation time = 180 minute.

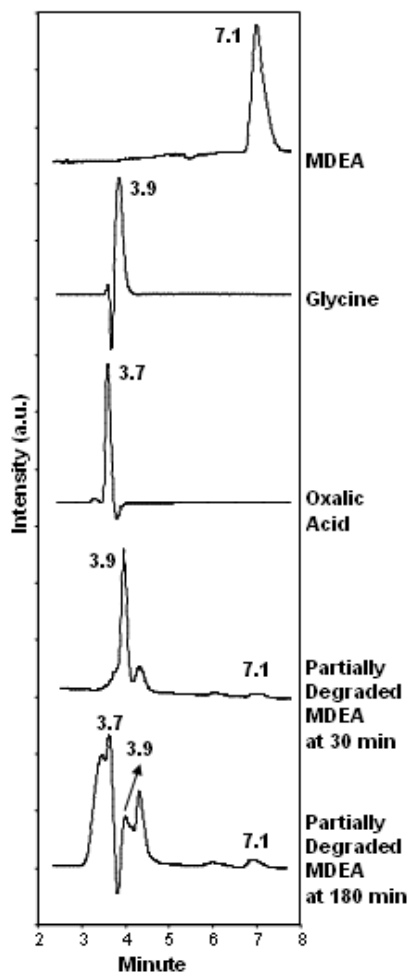


Figure 2. Chromatogram from YMC-PolymerC18 column of MDEA, partially degraded MDEA, Glycine and Oxalic Acid. MDEA = 2000 ppm (≈1000 ppm TOC), [H₂O₂]₀ concentration = 0.09 M, initial pH = 7.2, temperature = 30°C and with intensity UV was 12.06 mW/cm² for radiation time = 180 minute.

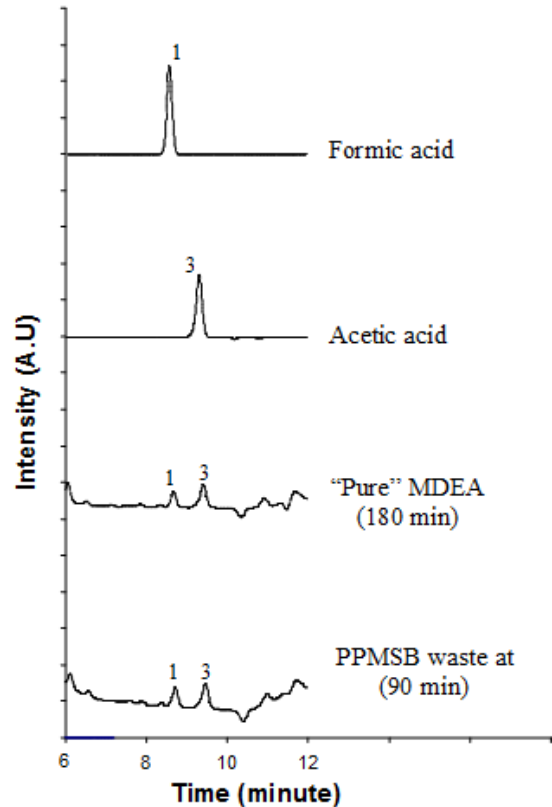


Figure 3. Chromatogram from Transgenomic column of formic acid and acetic acid during UV/H₂O₂ process. MDEA = 2000 ppm (≈1000 ppm TOC), [H₂O₂]₀ concentration = 0.22 M, initial pH = 10.17, temperature = 30°C and with intensity UV was 12.06 mW/cm² for radiation time = 180 minute.

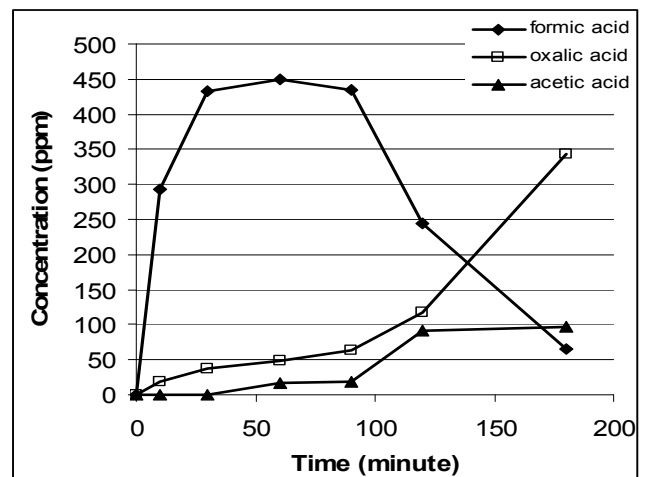


Figure 4. Organic by product profile during the UV/H₂O₂ process. MDEA = 2000 ppm (≈1000 ppm TOC), [H₂O₂]₀ concentration = 0.22 M, initial pH = 10.17, temperature = 30°C and with intensity UV was 12.06 mW/cm² for radiation time = 180 minute.

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