



Journal of Applied Sciences

ISSN 1812-5654

science
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Effect of Bicarbonate on the Mineralization of Methyldiethanolamine by using UV/H₂O₂

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Abstract: The presence of bicarbonate affects the degradation efficiency of effluents containing aqueous methyldiethanolamine (MDEA) solution leaving the CO₂ absorption/regeneration unit of natural gas processing units. In the present study the effect of bicarbonate at three different pH conditions of (acidic, neutral and alkaline) simulated MDEA solution were conducted, by the addition of six different concentration of NaHCO₃ (0.025, 0.05, 0.075, 0.1, 0.125 and 0.15 M). The presence of bicarbonate increased the mineralization of MDEA when the reaction was conducted at neutral initial pH conditions, where as the MDEA mineralization was reduced when the reaction was conducted at alkaline pH condition.

Key words: MDEA, UV/H₂O₂, mineralization, bicarbonate

INTRODUCTION

Methyldiethanolamine (MDEA) is one of the alkanolamines that is commonly used for the removal of acidic gases (such as H₂S and CO₂) from natural gas (Kohl and Nielsen, 1997). Removal of acidic gas from the natural gas is necessary since the acidic gases cause corrosion in pipeline and processing equipment, also reduce the heating value which has an effect on the price of natural gas. MDEA has two ethanol functional groups and one methyl group attached to a nitrogen atom. Due to the existence of nitrogen atom with a pair of free electrons, MDEA forms weak base with water, hence MDEA is often used for scrubbing/sweetening of acidic gases (CO₂ and H₂S) from raw natural gas. Aqueous MDEA solution chemically binds with the acidic gases and when heated it releases the absorbed gases (Kohl and Nielsen, 1997).

During shutdown and maintenance of the processing equipments, high concentrations of residual MDEA will be carried over into the effluent. Conventional biological oxidation process is not effective for the treatment of effluent containing MDEA. Furrhacker *et al.* (2003) reported that MDEA was not biodegradable in the bioreactor for a test period of 28 days. Therefore, an Advanced Oxidation Process (AOP) i.e., UV/H₂O₂ was used to treat the aqueous MDEA solution, by which approximately 86 % of TOC was removed (Harimurti *et al.*, 2012). During the absorption/scrubbing process, the

bicarbonate is also generated and present along with MDEA in the effluent stream. A number of researchers have reported that the presence of bicarbonate during the AOP's reduces the degradation efficiency. Mehrvar *et al.* (2001) reported that the degradation rate of tetrahydrofuran (THF) and 1,4-dioxane (DIOX) were affected/reduced due to the presence of bicarbonate in the system. During the UV/H₂O₂ process, the presence of bicarbonate was reported to be strongly inhibit the degradation of organophosphorus pesticides namely, malathian and diazinon (Fadaei *et al.*, 2012). The addition of inorganic ion such as bicarbonate in the Procion H-ex1 dyes solution gave an adverse effect on the decolorization rate of dye using Fenton's process, as reported by Riga *et al.* (2007). Daneshvar *et al.* (2007) concluded that the presence of bicarbonate during the photooxidative degradation (UV/H₂O₂) reduced the degradation rate of 4-nitrophenol (4-NP) (Daneshvar *et al.*, 2007). Muruganandham and Swaminathan (2004) studied the effect of bicarbonate during the photodecolorization of reactive azo dye (Reactive orange 4) and concluded that only 3.58% of decolorization was achieved (Muruganandham and Swaminathan, 2004). Klamerth *et al.* (2010) reported that bicarbonate competes with the organic contaminant for hydroxyl radical during the degradation of municipal wastewater using photo-Fenton and hence the presence of bicarbonate reduced the degradation efficiency of the

effluent. Degradation of Atrazine by manganese-catalysed ozonation was also inhibited by the presence of bicarbonate (Ma and Graham, 2000). Based on the foregoing observation from the available literature, the present study will focus on the effect of bicarbonate on the mineralization of effluents containing MDEA using UV/H₂O₂ process.

MATERIALS AND METHODS

Methyldiethanolamine (MDEA), potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) were obtained from Merck (Germany). Sodium hydroxide (NaOH) and sodium bicarbonate (NaHCO₃) were obtained from RM Chemicals (Malaysia). Simulated MDEA solution was prepared by dissolving a desired amount of MDEA in distilled water.

All the experiments were conducted in 700 mL cylindrical stirred jacketed glass reactor to monitor the progress of mineralization. The photoreactor was equipped with 8 Watt low pressure Hg vapor lamp GPH295T5L (which produces UV light at 254 nm was made in USA with serial no. EC90277), a current-voltage control unit and an opening at the top for sample collection. Intensity of UV lamp was measured by using UV radiometer (Cole-Parmer model: 97651-10 with sensor UV 254 nm model: 97651-20). The pH value of the solution was measured using pH meter (HACH-senion1) and the adjustment was carried out using NaOH or H₂SO₄ accordingly. The temperature of reaction was adjusted/maintained by circulating cooling water through the jacket. To study the effect of bicarbonate on the degradation of MDEA, NaHCO₃ with known concentrations were added into the mixture and allowed to dissolve before the start of experiments. Liquid samples were withdrawn at specific time intervals and the TOC of the samples were measured using TOC analyzer (Shimadzu TOC-V_{CSH}). H₂O₂ concentration in the solution during the photochemical oxidation process was monitored by titrating the samples using standard KMnO₄ solution (Mendham *et al.*, 2000).

RESULTS AND DISCUSSION

The present research includes the preliminary studies on the individual effect of UV and H₂O₂ as well as the combination of UV/H₂O₂ on the photochemical mineralization of aqueous MDEA solution and later extended to study the effect of the presence of bicarbonate on the photochemical oxidation system. The experiments were conducted using the following optimum conditions: Intensity of UV lamp = 12.06 mW/cm²,

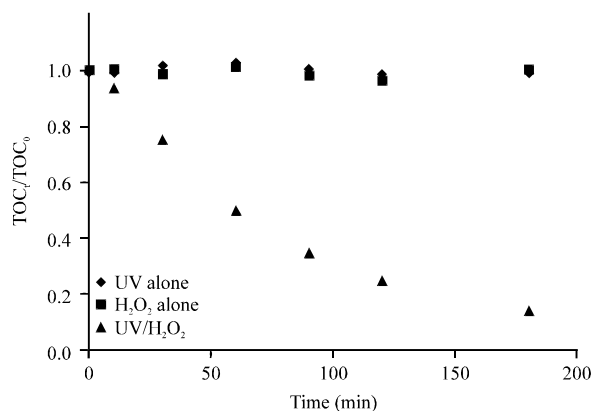


Fig. 1: Individual effect of UV, H₂O₂ and the combination of UV/H₂O₂ on the MDEA mineralization

irradiation time = 3 hours, oxidation temperature = 30°C, [MDEA]₀ = 2000 ppm, [H₂O₂]₀ = 0.22 M (Behnajady *et al.*, 2008). To study the bicarbonate effect, six different concentrations of NaHCO₃ (0.025, 0.05, 0.075, 0.1, 0.125, and 0.15 M) were used. The initial pH of reaction was = 7, since at the acidic conditions, the bicarbonate will be neutralized to form CO₂ and hence for the present work two different initial pH conditions (7 and 10.18) were used.

UV light and H₂O₂ process are well-known for the degradation of many organic compounds in aqueous solution. The capability of UV light to degrade the organic compound follows photolysis mechanism. The organic compound absorbs UV spectrum and then results in an excited (organic) compound which later decomposed to form a product (Massachelein, 2002; Oppenlander, 2003; Lester *et al.*, 2010; Seraghni *et al.*, 2012). Based on the preliminary experiments it was observed that, UV spectrum at 254 nm (used in the present experiments) was not capable to remove the total organic carbon from the system (Fig. 1). The reason could be attributed to the fact that MDEA did not absorb the UV light at 254 nm, since the spectrum absorbed by MDEA was at 200 nm region, therefore, the direct photolysis did not occur (Harimurti *et al.*, 2013). The capability of H₂O₂ to degrade organic compound is mainly due to the high reduction potential of H₂O₂ 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 organic compound and H₂O₂ (Petri *et al.*, 2011). The results of the present experiments showed no degradation when the H₂O₂ alone was used, indicating that H₂O₂ alone was not capable to remove the total organic carbon in the aqueous MDEA solution (Fig. 1). This might be due to the reduction potential of H₂O₂ which is not sufficient for the oxidation process. The photolysis resistance of MDEA

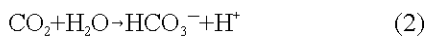
toward UV light and H₂O₂ was in agreement with the observation of (Xu *et al.*, 2009), based on their studies on the photolysis resistance of dimethyl phthalate against UV photolysis and H₂O₂. However, the reduction of total organic carbon was found when the UV and H₂O₂ were applied in combination. The total organic carbon was reduced to a certain level (Fig. 1) which was due to the hydroxyl radical generated from H₂O₂ photolysis. It is well known that H₂O₂ strongly absorbs UV spectrum at 254 nm (Massachelein, 2002). Therefore the probability of H₂O₂ photolysis to generate hydroxyl radicals is very high. In other words, the combination of UV and H₂O₂ will generate hydroxyl radical which plays an important role during the degradation of many recalcitrant organic contaminants (Daneshvar *et al.*, 2007; Lester *et al.*, 2010; Behnajady *et al.*, 2008; Abramovic *et al.*, 2010).

Absorption/scrubbing of CO₂ by aqueous MDEA solution occurs according to the following reactions:

Ionization of water:



Hydrolysis and ionization of dissolve CO₂:



Protonation of MDEA:



Acid-basic reaction with the amine:



During the scheduled shut down of scrubbing unit in the natural gas plant, bicarbonate (HCO₃⁻) is expected to present in the effluents leaving the gas processing unit. Generally, the presence of bicarbonate in the AOP's will act as a scavenger for hydroxyl radical. Bicarbonate (HCO₃⁻) reacts with hydroxyl radical (HO•) to form bicarbonate radical (HCO₃•). This radical is also a well-known oxidant, but much less reactive compared to hydroxyl radical (Riga *et al.*, 2007; Daneshvar *et al.*, 2007; Jones, 1999; Andreozzi *et al.*, 1999; Chiang *et al.*, 2006). Consequently, the degree of oxidation is expected to be less.

In order to study the effect of bicarbonate on the mineralization of aqueous MDEA solution using the combination of UV/H₂O₂ process, experiments were conducted at two different initial pH (7 and 10.18) conditions and six different concentrations of NaHCO₃ in the aqueous MDEA solution. At acidic pH conditions

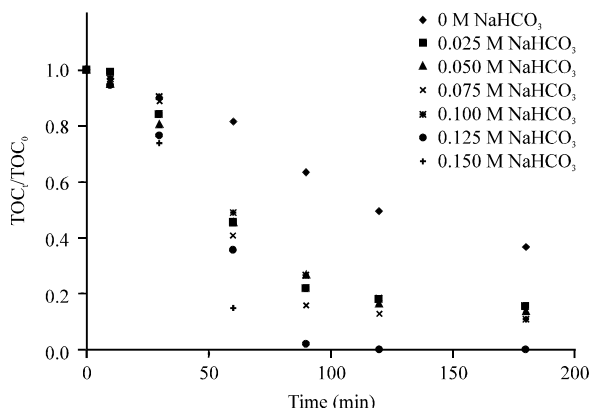


Fig. 2: Total organic carbon profile during the degradation of MDEA in the presence of NaHCO₃ using UV/H₂O₂, Initial pH = 7

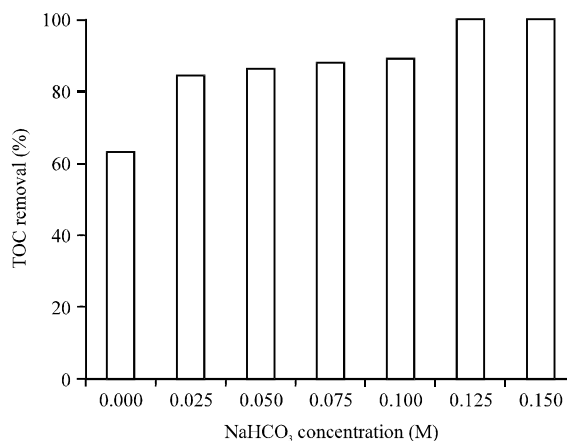
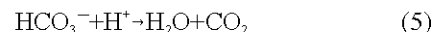


Fig. 3: Percentage TOC removal achieved at initial pH reaction = 7

(pH < 7) the bicarbonate will get neutralized (Eq. 5) and the product i.e., CO₂ will be released from the system, hence there will be no effect on the mineralization process.



When the initial pH of the process was approximately 7, the presence of bicarbonate in the synthetic aq. MDEA solution increased the mineralization of MDEA (Fig. 2). The degree of MDEA mineralization was increased by increasing of NaHCO₃ concentration in the system and complete mineralization was achieved when the concentration of NaHCO₃ was = 0.125 M (Fig. 3). This trend can be explained as: The capability of bicarbonate that can act as a good buffer was found at this condition. The pH during the mineralization process was maintained at 7 (Fig. 4). Bicarbonate is an amphoteric ion that can act

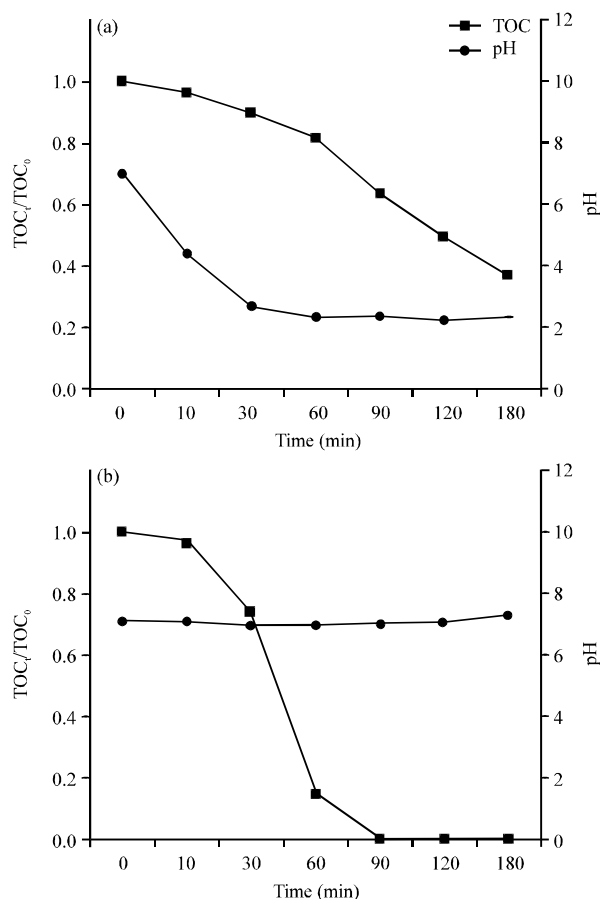
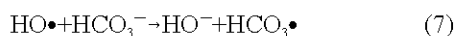


Fig. 4: pH profile during the degradation of MDEA using UV/H₂O₂ at initial pH = 7

either as an acid which can donate its H⁺ to form CO₃²⁻ or as a base which is capable to accept an H⁺ to form H₂CO₃. Formation of organic acid during the degradation process, reduce the pH of the system. At this pH condition (pH = 7), the bicarbonate reacts with the hydroxyl radical (which is available in the system) to form bicarbonate radical, however, the formation rate of bicarbonate radical is less (8.5 × 10⁶ M⁻¹ s⁻¹). Equation 6-7 shows the formation of bicarbonate radical in the system (Oppenlander, 2003; Andreozzi *et al.*, 1999; Tang, 2003).



Klare *et al.*, (2000) reported that free electron pair of nitrogen atom of amine compounds are in un-protonated form for pH = 7 and under these conditions, more active sites for oxidation by hydroxyl radical are available. Thus,

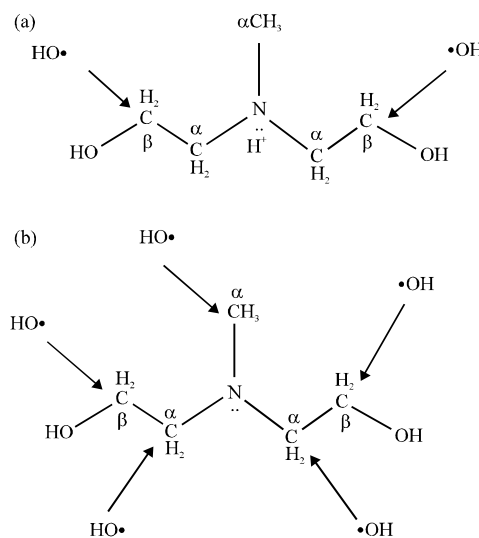


Fig. 5: Active sites of MDEA at (a) Acidic and (b) High pH (pH ≥ 7) for the oxidation by hydroxyl radical

the presence of HCO₃⁻ in the solution maintained the free electron pair of nitrogen atom of MDEA in un-protonated condition and hence more active sites for reaction are always provided (Fig. 5) which in turn leads to higher degradation of MDEA.

The effect of the presence of bicarbonate during mineralization of aq. MDEA solution was also studied at alkaline pH conditions. Based on the preliminary studies, the optimum pH for mineralization process of aqueous MDEA solution was found to be 10.18, hence this pH was chosen for the present study at alkaline pH condition (Harimurti *et al.*, 2012). The presence of bicarbonate (HCO₃⁻) during the UV/H₂O₂ mineralization of simulated aq. MDEA solution at an initial pH of 10.18 was found to reduce the mineralization efficiency (Fig. 6). Approximately 25% of TOC removal was reduced when the concentration of NaHCO₃ was = 0.050 M (Fig. 7). This might be due to the presence of bicarbonate in the system which act as a good buffer and maintain the pH at constant and not allowed to drop to lower pH levels (Fig. 8). At alkaline pH condition, the bicarbonate (HCO₃⁻) was converted into carbonate (CO₃²⁻) and then react with hydroxyl radical to form carbonate radical. Reaction between carbonate and hydroxyl radical is shown below:



Since the reaction rate of carbonate radical formation is high (i.e., 3.9 × 10⁸ M⁻¹ s⁻¹) and the scavenger reaction

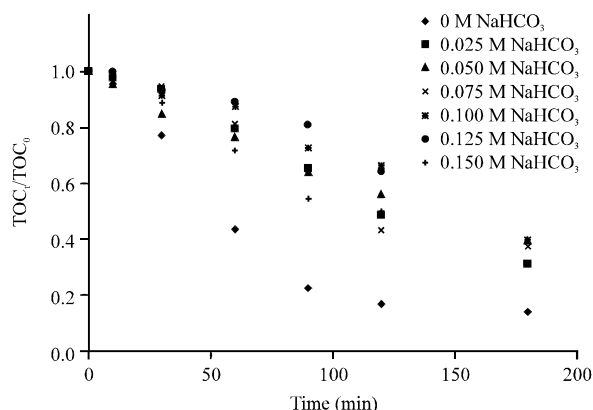


Fig. 6: Total organic carbon profile during the degradation of MDEA in the presence of NaHCO₃ using UV/H₂O₂ at initial pH = 10.18

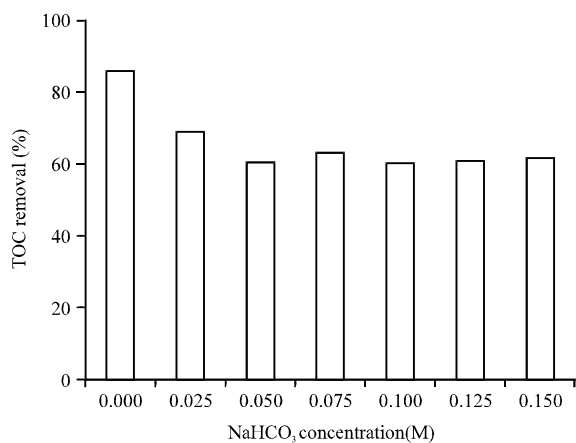
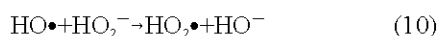
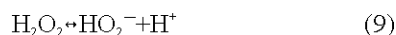


Fig. 7: Percentage TOC removal achieved at initial pH reaction = 10.18

was significant enough to reduce the concentration of hydroxyl radical in the system that act as an important oxidant in the UV/H₂O₂ process, hence the reduction in MDEA mineralization. Moreover, H₂O₂ tend to ionize to form hydroperoxide anion (HO₂⁻) at high pH with pKa equals to 11.6 (Xu *et al.*, 2009; Ren *et al.*, 2010). Hydroperoxide anion is well-known to be a strong scavenger to hydroxyl radical (Eq. 9 and 10).



Reaction between hydroperoxide anion (HO₂⁻) and hydroxyl radical (HO•) generates a less reactive radical species i.e., hydroperoxyl radical (HO₂•) which is very effective to reduce the hydroxyl radical in the system and

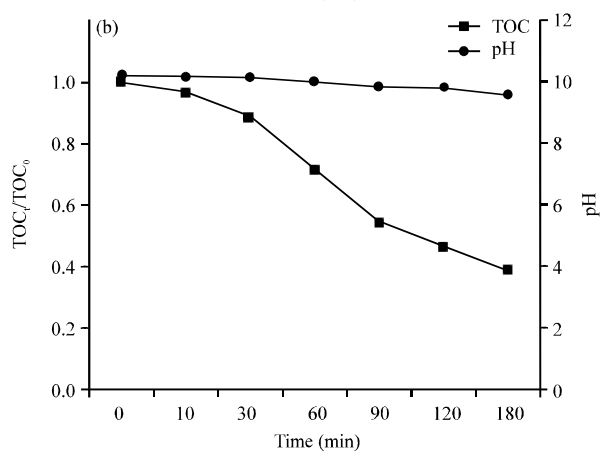
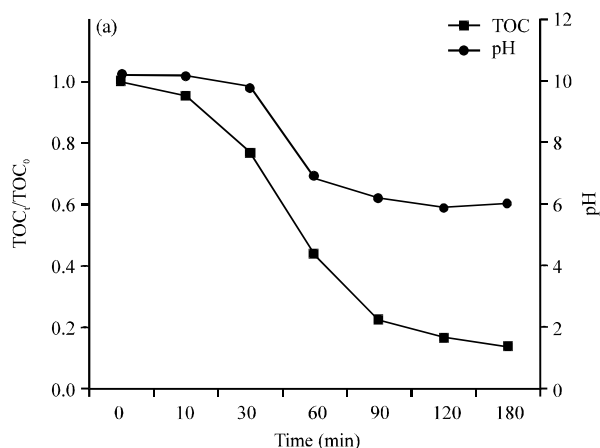


Fig. 8: TOC and pH profile during the degradation of MDEA using UV/H₂O₂ at initial pH = 10.18 at (a) 0 M NaHCO₃ and (b) 0.15 M NaHCO₃

hence, the mineralization efficiency decreased. Even though bicarbonate reacts with the hydroxyl radical to form bicarbonate radical in the neutral pH (initial pH ≈ 7), the presence of bicarbonate radical did not interfere in the photodegradation process, since the reaction rate of bicarbonate and hydroxyl radical was less. Based on these analysis, it can be concluded that at neutral pH, due to the enhancement of active sites of MDEA for oxidation the bicarbonate increases the TOC removal. However, at alkaline pH condition of reaction, the bicarbonate acts as a strong scavenger to hydroxyl radical by converting to carbonate which further reacts with hydroxyl radical and reduce the TOC removal.

CONCLUSION

Based on the present experiments it can be concluded that the presence of bicarbonate increase the mineralization rate of aqueous MDEA solution when the

reaction was conducted at neutral pH conditions (pH = 7) but slows down the mineralization rate of MDEA when the reaction was conducted at pH = 10.18. The enhancement of mineralization efficiency is attributed to the capability of bicarbonate to maintain the pH at 7, during the reaction and hence the active sites for oxidation by hydroxyl radical are always available. This information will be of useful for the design and scale up of the UV/H₂O₂ oxidation process for the photochemical degradation of effluents from CO₂ absorber/scrubbing units which normally contains bicarbonate along with MDEA.

ACKNOWLEDGMENT

The scholarship to Sabtanti Harimurti, under the Graduate Assistant Scheme from Universiti Teknologi PETRONAS, is highly acknowledged.

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