

UV/H₂O₂ Process for Removal of Total Organic Carbon from Refinery Effluent: Screening of Influence Factors using Response Surface Methodology

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Keywords: Refinery effluent; RSM; screening; TOC; UV/H₂O₂.

Abstract. Effluent containing high concentration of alkanolamine from a sweetening process of natural gas plant is commonly generated during maintaining, cleaning and scheduled inspection of the absorption and desorption column. The effluent is not readily biodegradable and cannot be treated in the conventional biological treatment. Advanced oxidation processes (AOP's) is a promising method for the treatment of recalcitrant organic contaminant. Most methods used are Fenton' reagent, UV/Ozone and UV/H₂O₂. Based on the advantages of the UV/H₂O₂ such as no formation of sludge during the treatment, high ability in production of hydroxyl radical and applicable in the wide range of pH, the UV/H₂O₂ has been chosen to treat the effluent from refinery plant, which has high concentration of methyldietnaolamine (MDEA). The factors influencing in the degradation of refinery wastewater that contain MDEA were screened using response surface methodology (RSM). It was found that degradation process of the refinery effluent was highly dependent on oxidant concentration (H₂O₂) and initial pH. Temperature of oxidation process was found oppositely. Since the temperature gave insignificant effect on the TOC removal process, hence the independent factor temperature will be eliminated during the further optimization process condition of degradation. Thus, the optimization process condition of degradation will be more effective and simpler.

Introduction

Natural gas is one of the safest energy sources. Increasing of natural gas demand is affecting the increase of natural gas fabrication. One step of natural gas fabrication named scrubbing/sweetening acidic gas. In this process, alkanolamine is commonly used as the scrubber. The alkanolamines that are frequently used are monoethanolamine (MEA), diethanolamine(DEA), methyldiethanolamine (MDEA) and di-isopropanolamine [1].

During maintaining, cleaning and scheduled inspection of the sweetening process, high concentration of alkanolamine is generated in the effluent. This effluent is toxic to bacteria and can not be treated using biological oxidation in the conventional biological treatment. Advanced oxidation processes (AOP's) is a promising method for the treatment of recalcitrant organic contaminant in the wastewater which is involving a very reactive species named hydroxyl radical (\bullet OH). The most techniques used in the AOP's are Fenton's reagent, UV/Ozone and UV/H₂O₂. As reported by Harimurti *et al.*, Dutta *et al.*, and Omar *et al.*, Fenton's reagent has been used for treatment of wastewater contains alkanolamine (MEA, DEA and DIPA, respectively) [2-4]. However, some problems such as forming sludge during treatment and only applicable in the particular pH i.e. acidic pH was appearing in this treatment. Hence, the other method may be required to figure out the Fenton treatment. Ariff had implemented the UV/H₂O₂ for

monoethanolamine (MEA) degradation [5]. UV/H₂O₂ has several advantages such as no forming sludge during the process, high ability on production of hydroxyl radical, and applicable in wide range of pH. Based on the advantages of UV/H₂O₂ method, the UV/H₂O₂ is used in this research to remove organic carbon from refinery effluent contains MDEA. This UV/H₂O₂ process for refinery effluent may be necessary to conduct since an effluent standard regulation is commonly requires a maximum value of organic contaminant in the effluent in order the effluent will be safely discarded into environment. The admissible maximum values of contaminant in the effluent of different countries are regulated in their own regulation. Malaysian standard for industrial effluent regulates the maximum organic carbon presence in the industrial effluent is 50 mg/L COD for standard A and 100 mg/L COD for standard B [6]. “Standard A is commonly applicable to activities and industries that are sited within, or in the near vicinity of, cachement areas and is more stringent. Standard B is generally applicable to both industrial and development activities throughout the country” (Law of Malaysia, 1999). The Malaysian standard for industrial effluent is presented in Table 1.

Table 1: Permissible level of contaminant in industrial effluent based on Malaysian effluent standard regulation for sewage and industrial effluents (environmental quality act 1974 [Laws of Malaysia; (act 127). 1999 [6]

Parameters	Unit	Standard (A)	Standard (B)
Temperature	[°C]	40	40
pH Value		6.0 - 9.0	5.5 - 9.0
BOD5 at 20°C	[mg/l]	20	50
COD	[mg/l]	50	100
Suspended Solids	[mg/l]	50	100
Mercury	[mg/l]	0.005	0.05
Cadmium	[mg/l]	0.01	0.02
Chromium, Hexavalent	[mg/l]	0.05	0.05
Arsenic	[mg/l]	0.05	0.10
Cyanide	[mg/l]	0.05	0.10
Lead	[mg/l]	0.10	0.5
Chromium, Trivalent	[mg/l]	0.20	1.0
Copper	[mg/l]	0.20	1.0
Manganese	[mg/l]	0.20	1.0
Nickel	[mg/l]	0.20	1.0
Tin	[mg/l]	0.20	1.0
Zinc	[mg/l]	1.0	1.0
Boron	[mg/l]	1.0	4.0
Iron (Fe)	[mg/l]	1.0	5.0
Phenol	[mg/l]	0.001	1.0
Free Chlorine	[mg/l]	1.0	2.0
Sulphide	[mg/l]	0.50	0.50

The treatment of refinery effluent contains MDEA was conducted in the jacketed borosilicate glass reactor. During the treatment, there are many possible factors influencing in the degradation process. Those factors are UV intensity, initial concentration of effluent, initial concentration of oxidant, initial pH and temperature of oxidation. For the effectiveness of screening process of factors influencing in the degradation, statistic software named response surface methodology (RSM) has been used to select the most factors influencing in the degradation. RSM is a software on mathematical and statistical that applicable for designing experiments, building models, evaluating the effects of variable, and searching optimum condition of variables to predict targeted response [7]. RSM had been used by Rauf *et al.* [8] and Rahmah *et al.* [9] to optimize the degradation process condition of Basic Red 2 dye and oxytetracycline in aqueous solution by UV/H₂O₂, respectively. Ismail *et al.* also used the RSM to optimize the Therazil Red Dye wastewater using H₂O₂/pyridine/Cu(II) system [10]. This paper involves the screening of factors influencing in the

degradation of effluent from refinery plant containing MDEA for the fundamental design in the further study of optimization process condition of degradation

Materials and Method

Materials. Refinery effluent was obtained from local refinery plant in Malaysia. Methyldiethanolamine (MDEA), Potassium Permanganate (KMnO_4), Sulfuric Acid (H_2SO_4), and Hydrogen Peroxide (H_2O_2) were obtained from Merck (Germany). Sodium Hydroxide (NaOH) was obtained from RM Chemicals (Malaysia).

Experiment. The degradation process were conducted in 700 ml cylinder stirred jacketed glass reactor (Fig. 1) to monitor the degradation progress. The reaction zone is a cylindrical borosilicate glass tube, 14 inch long with internal diameter of 2 inch. The photo reactor is equipped with a low pressure Hg vapour lamp GPH295T5L (which produces UV light at 254 nm was made in USA with serial no. EC90277), a currents-voltage control unit, and a hole for collecting the sample. Hydrogen sulphate (H_2S), oil, and grease contained in the effluent were removed first before UV/ H_2O_2 treatment. Hydrogen sulphate was removed by oxidation process with H_2O_2 and precipitate produced was separated by filtration. While oil and grease were separated by settling in the reparatory fennel for overnight. A solution with known in concentration was taken in the glass reactor. A required amount of H_2O_2 was added in to the amine solution. Total volume of amine solution and H_2O_2 was 400 ml. The pH adjustment was made using 1 mol L^{-1} of NaOH or 0.5 mol L^{-1} of H_2SO_4 . The temperature was maintained by circulating cooling water through the jacket. During the process, of samples of the liquid were withdrawn from time to time and then diluted for total organic carbon (TOC) and remaining H_2O_2 analysis. The TOC concentration was measured using TOC analyzer (Shimadzu TOC-V_{CSH} - Japan), while the H_2O_2 concentration is measured using KMnO_4 titration [11]. The range of variables conducted in the present studies include: i) initial amine concentration (1000 mg L^{-1} of organic carbon); ii) UV intensity (12.06 mW/cm^2); iii) three initial concentration of H_2O_2 (0.12, 0.18, and 0.24 mol L^{-1}); iv) three initial pH (5, 7, and 9); and v) three different temperatures (30, 40, and $50 \text{ }^\circ\text{C}$).

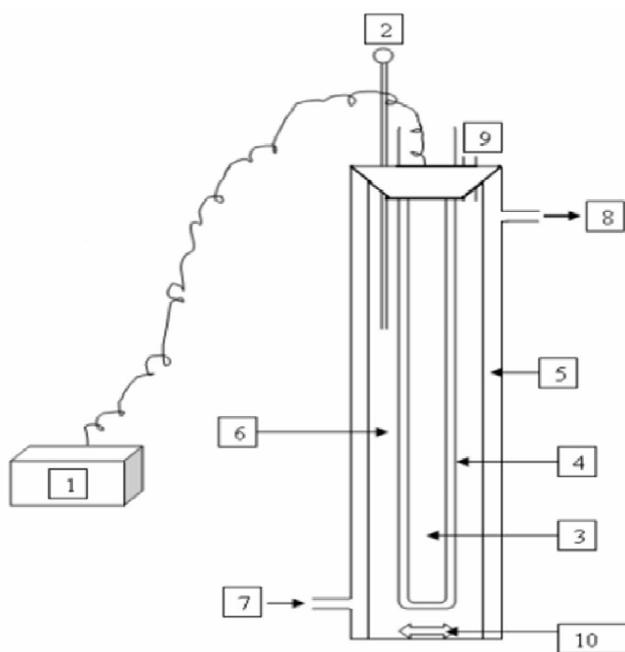


Fig. 1. Scheme of the UV/ H_2O_2 photoreactor. Where: 1). Curent-voltage control unit; 2). Thermometer; 3). UV lamp; 4). Quartz tube; 5). Jacket; 6). Reaction zone; 7). Water in; 8). Water out; 9). Sample port; and 10). Stirrer bar.

Statistical design of Experiment. The screening of factors influencing in the degradation of wastewater from refinery plant was conducted according to Table 2. The experiment was done in two blocks of experiment and one center point. Low level and high level of each factor were determined according to the previous experiment i.e. screening of factors influencing in the synthetic MDEA waste mineralization by UV/H₂O₂ [12]. This was done since the main component of the refinery waste was MDEA. The property of refinery waste is shown in Table 3. During the screening process, three factors i.e. initial concentration of oxidant (H₂O₂), pH, and temperature of oxidation were tested. In the meantime, other factors i.e. UV intensity and initial concentration of waste was kept in constant at 12.06 mW cm⁻² and 1000 mg L⁻¹ of organic carbon, respectively. UV intensity was kept constant regarding to the limitation of UV lamp, which was provided in the laboratory. Meanwhile keeping constant in initial concentration of waste at 1000 mg L⁻¹ of organic carbon was done since in this concentration the degradation was easier to follow up. Portable Statgraphics Centurion 15.2.11.0 was used as mathematical and statistical software for RSM analysis. Quality of analysis was determined by the P-value on the ANOVA test with significance of 0.05 probabilities.

Results

Three factors (i.e. H₂O₂, pH, and temperature of reaction) affecting the TOC removal process of refinery effluent using UV/H₂O₂ were screened. The screening process was conducted in duplicate with 2 block of experiment. Each block contains one center point. Low level and high level of input factors was according to the preliminary study on TOC removal of synthetic MDEA waste using UV/H₂O₂. The input data of screening process are presented in Table 2.

Table 2. The input data of screening factors influencing in the refinery effluent mineralization by UV/H₂O₂ (TOC_i = 1000 ppm; UV intensity = 12.06 mW/cm²).

Block	H ₂ O ₂ (M)	pH	Temp. °C	TOC removal observed (%)	TOC removal fitted (%)
1	0.12	5.0	30.0	26.99	25.87
1	0.12	9.0	30.0	43.75	47.19
1	0.24	5.0	50.0	67.81	66.89
1	0.24	9.0	50.0	63.11	67.29
1	0.12	9.0	50.0	45.75	45.31
1	0.24	5.0	30.0	60.13	63.45
1	0.18	7.0	40.0	68.15	56.86
1	0.12	5.0	50.0	46.18	49.49
1	0.24	9.0	30.0	89.83	89.37
2	0.12	5.0	30.0	26.61	26.15
2	0.12	9.0	30.0	44.01	47.47
2	0.24	5.0	50.0	67.83	67.17
2	0.24	9.0	50.0	64.85	67.57
2	0.12	9.0	50.0	46.73	45.58
2	0.24	5.0	30.0	60.15	63.73
2	0.18	7.0	40.0	67.09	57.14
2	0.12	5.0	50.0	46.19	49.77
2	0.24	9.0	30.0	90.77	89.65
Factors	Levels				
	Low level	High level			
A: H ₂ O ₂	0.12 M	0.24 M			
B: Temp.	30 °C	50 °C			
C: pH	5	9			

Table 3. The property of refinery effluent

Measures	Mark
MDEA	34.00 % w/v
S ₂ ⁻	0.050 % w/v
NH ₄ ⁺	0.416 % w/v
Acetic acid	0.157 % w/v
Oxalic acid	1.385 % w/v
Oil and grease	0.025 % w/v
pH	10

Table 4. The ANOVA analyses for TOC removal of refinery effluent by UV/H₂O₂

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:H ₂ O ₂	3548.35	1	3548.35	107.95	0.0000
B:pH	472.05	1	472.05	14.36	0.0035
C:Temperature	2.41	1	2.41	0.07	0.7920
AB	21.11	1	21.11	0.64	0.4415
AC	407.64	1	407.64	12.40	0.0055
BC	650.85	1	650.85	19.80	0.0012
blocks	0.35	1	0.35	0.01	0.9201
Total error	328.70	10	32.87		
Total (corr.)	5431.46	17			

R-squared = 93.95 %, R-squared (adjusted for d.f.) = 90.65 %

ANOVA results of this model were presented in Table 4. Table 4 shows that P-value of H₂O₂ and pH was 0.0000 and 0.0035, respectively. This P-value indicated that H₂O₂ and pH gave significant effect on TOC removal of refinery waste. Meanwhile, the temperature has opposite result.

Pareto chart of standardize effect at P-value = 0.05 (Fig. 2) shows that the most significant effect on increasing of TOC removal was given by H₂O₂, continued by initial pH. Interaction between H₂O₂/temperature and pH/temperature gave significant effect on decreasing of TOC removal. Fig. 3 shows the response surface of TOC removal against the H₂O₂ and pH. Correlation between fitted model and observed experiment are shown in Fig. 4.

Discussion

Refinery effluent with high concentration of MDEA was diluted to prepare approximately 1000 mg L⁻¹ initial concentration of organic carbon and then placed in the reactor. After adding the oxidant (H₂O₂), the waste was subjected with UV lamp and the degradation started. The degradation was followed up by measuring the total organic carbon (TOC) time to time. The process was conducted in 3 hours then the percentage of TOC removal was calculated accordingly with the Eq. (1):

$$\% \text{TOC removal} = \left[\frac{\Delta \text{TOC}_{i-f}}{\text{TOC}_i} \right] \times 100\% \quad (1)$$

where ΔTOC_{i-f} is the difference between initial total organic carbon and final total organic carbon, while TOC_i is initial total organic carbon.

Two blocks of experiments with one centre point was conducted, see Table 2. By using RSM analysis, the independent factors such as initial concentration of oxidant (H₂O₂), initial pH, and temperature of process were tested to see the effects of the independent factors influencing in the

degradation. ANOVA results of this model are presented in Table 4. Table 4 shows that the H_2O_2 and pH give F-ratio of 107.95 and 14.36, respectively. Whilst the P-value of H_2O_2 and pH were 0.0000 and 0.0035, respectively. These results imply that the independent factors H_2O_2 and pH gave significant effect in the degradation. Meanwhile, the temperature gave opposite result. The P-value less than 0.05 indicate that the model term is significant, while the P-value of above 0.05 indicates insignificant. Based on the Pareto chart of standardize effect at $P = 0.05$ (Fig. 2) can be explained that the factor of temperature gave insignificant contribution in the TOC removal. Meanwhile, initial concentration of H_2O_2 and pH gave significant contribution on the TOC removal. The most significant effect on increasing of TOC removal was given by H_2O_2 , continued by initial pH. Meanwhile, interaction between H_2O_2 /temperature and pH/temperature gave significant effect on decreasing of TOC removal. This was due to the H_2O_2 which tends to accelerate the decomposition in the high temperature and also in the high pH. Hence the source of hydroxyl radical was decreased and then result in decreasing of TOC removal.

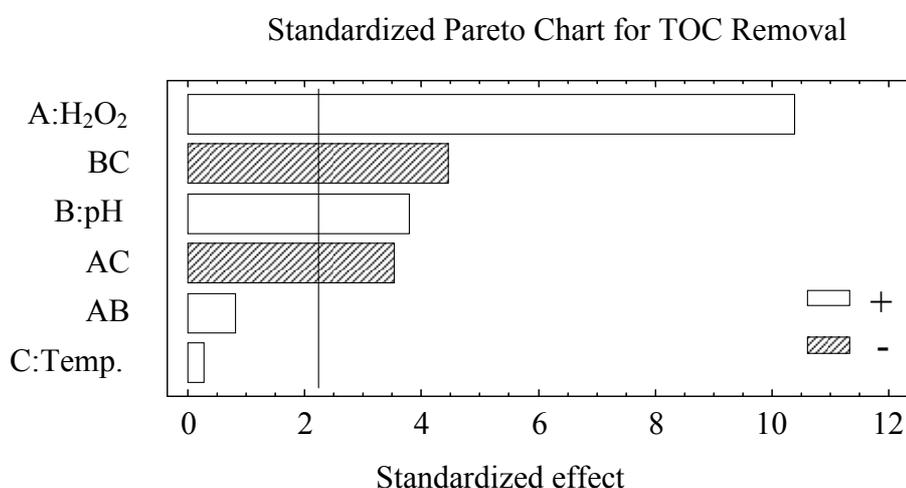


Fig. 2. Pareto chart of the standardized effect for percentage TOC removal

Fig. 3 presents the response surface of TOC removal against the H_2O_2 concentration and pH. The goal of the mineralization process is 100 % of TOC removal. It is shown clearly in Fig. 3 that increasing of H_2O_2 concentration and pH results in increasing of TOC removal. Relation of experimental value and fitted value can be seen in Fig. 4. The relation gave R^2 equals to 0.9395. This high R^2 indicated the fitted model proposed was appropriate to predict the value of organic carbon removal.

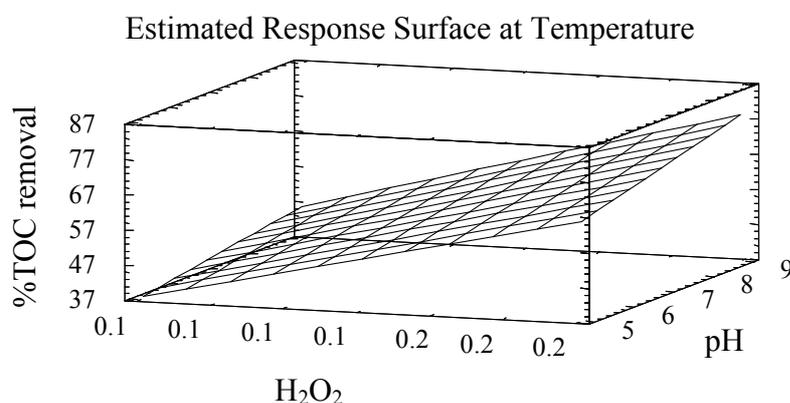


Fig. 3. The plot of percentage TOC removal against H_2O_2 concentration and pH.

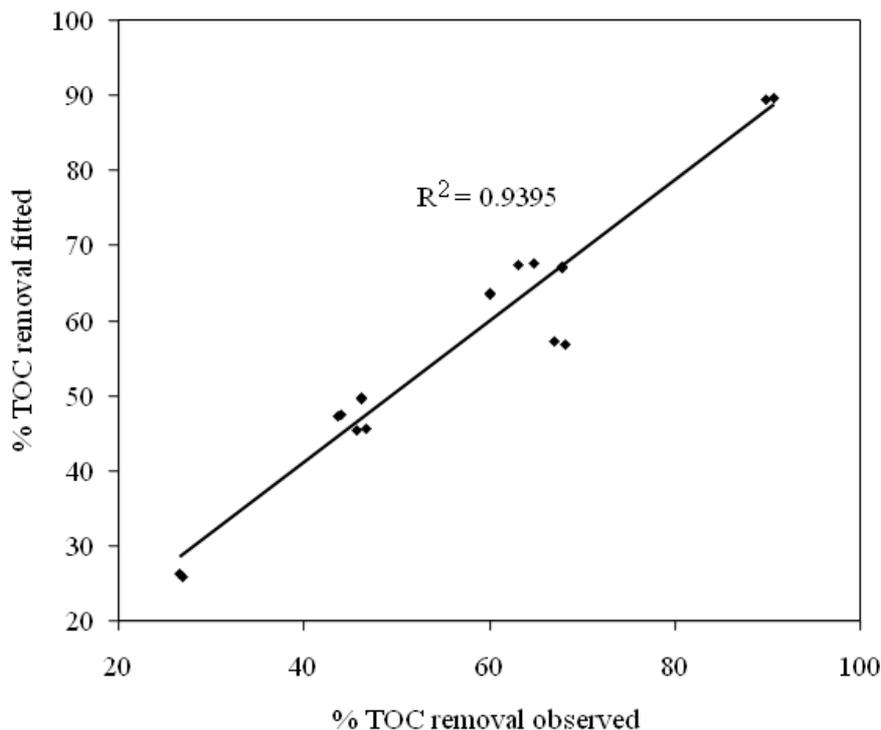


Fig. 4. Relation between experimental value and fitted value of TOC removal

The increase of H_2O_2 concentration leads an increase of hydroxyl radical ($\bullet\text{OH}$) concentration in the system. Increasing of hydroxyl radical concentration in the system leads an increase of TOC removal, since the hydroxyl radical is a well known species that has an important role in the degradation process. Most of researchers agreed that generation of hydroxyl radical in the UV/ H_2O_2 process is following Eq. (2) [13-17]. Two moles of hydroxyl radical will be generated in the irradiation of one mole hydrogen peroxide.



Meanwhile the increase of TOC removal by increasing of pH may be explained by the mechanism reaction of hydroxyl radical towards the main component in the refinery effluent. MDEA is a weak basic that contains two groups of ethanol and one group of methyl. These groups are attached in the nitrogen atom, which has free electron pair. The structure formula of MDEA is depicted in Fig. 5.

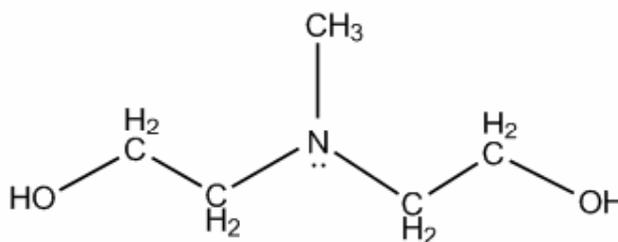


Fig. 5. The structure formula of Methyldiethanolamine (MDEA)

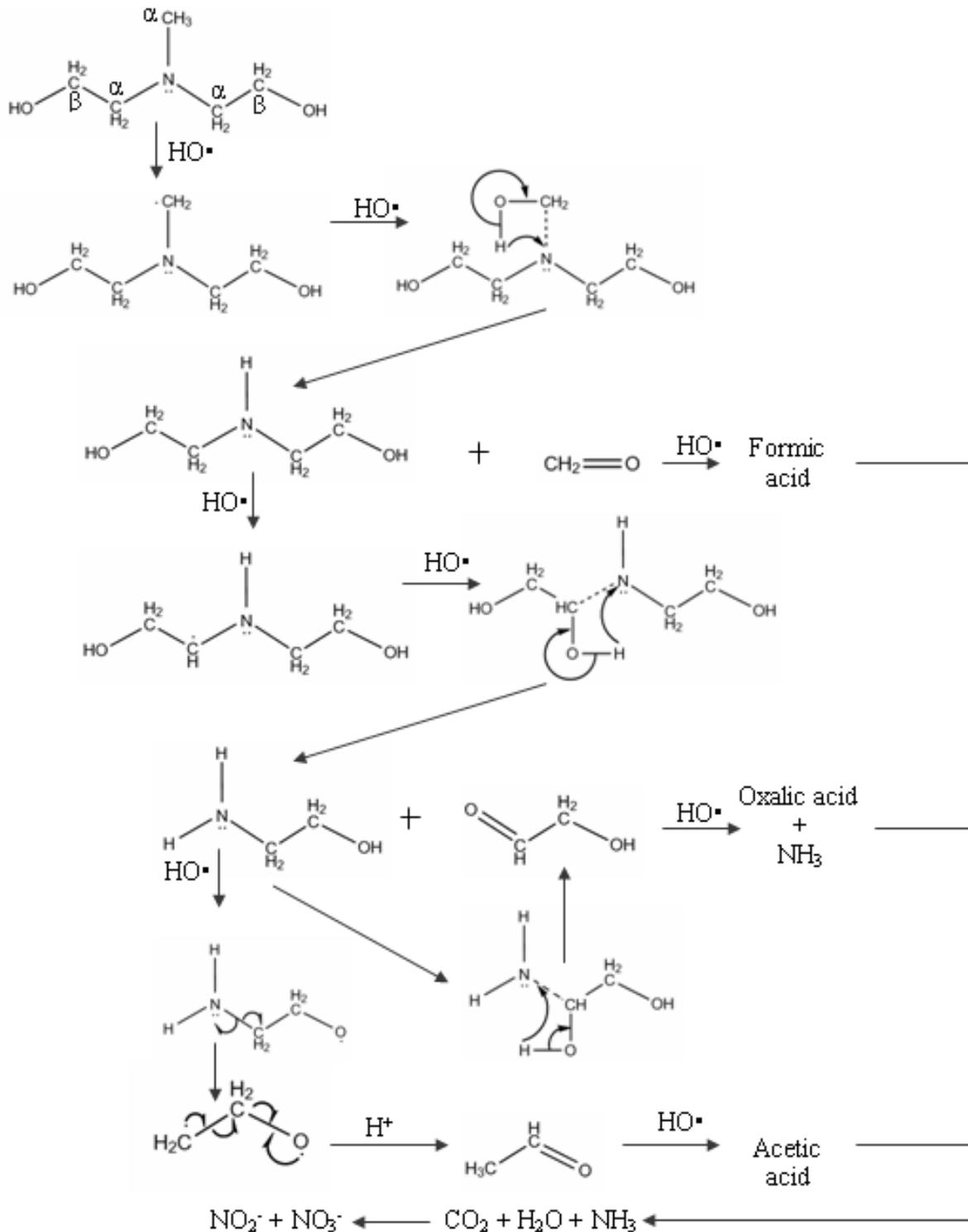


Fig. 6. The proposed of degradation mechanism of MDEA by hydroxyl radical [19].

In the acidic pH, the nitrogen atom of MDEA was protonated and then results in deactivation of amino group and α -CH bond next to the nitrogen atom. The hydroxyl radical will then only attack in the axial β -CH bond. However, in the high pH i.e. $\text{pH} \geq 7$, the nitrogen atom was un-protonated hence the nitrogen atom with free electron pair α -CH bond, and β -CH bond were activated [18-19]. Therefore in the high pH, active side for oxidation was more provided compared in the low pH. Thus, the TOC removal was higher in the high pH. The degradation mechanism of MDEA by hydroxyl radical proposed by Harimurti *et al.* is presented in Fig. 6.

Conclusion

Response surface methodology (RSM) was applicable in the screening of factors influencing in the degradation of refinery effluent from natural sweetening gas plant. Concentration of oxidant (H_2O_2) and pH gave significant effect on increasing of TOC removal, while temperature has opposite effect. Therefore, the temperature factor will be removed for further experiment on optimization of the process conditions of degradation process.

Acknowledgement

The authors are thankful to Universiti Teknologi PETRONAS Malaysia for the financial support and laboratory

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**The Proceedings of the International Conference on Process Engineering and Advanced Materials 2012
(ICPEAM 2012)**

10.4028/www.scientific.net/AMR.917

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10.4028/www.scientific.net/AMR.917.168