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# DEGRADATION OF MONOETHANOLAMINE IN AQUEOUS SOLUTION BY FENTON'S REAGENT

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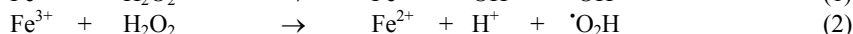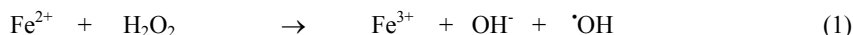31750 Tronoh, Perak Darul Ridzuan, Malaysia
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## *ABSTRACT*

*Alkanolamines such as mono- and diethanol-amine are routinely used for the removal of carbon dioxide and hydrogen sulfide from natural gas in a packed or tray tower. Periodic cleaning of the tower is done by high speed water jet and the wastewater generated contains a significantly high concentration of the amine. This wastewater is toxic to bacteria and cannot be treated in a conventional treatment unit by biological oxidation. An alternative technique of treatment is advanced oxidation such as UV-$H_2O_2$ or Fenton's reaction. In the present work, Fenton's reagent – a combination of ferrous sulfate and hydrogen peroxide – has been used to study the degradation of monoethnolamine in wastewater. Simulated wastewater was prepared by dissolving the amine in distilled water. Degradation studies were carried out in a jacketed glass reactor. Samples were drawn from time to time and the COD was determined to follow the course of degradation. The rate of degradation declines above a pH of 4 because of decomposition of hydrogen peroxide. The concentration of ferrous sulfate, the amount of hydrogen peroxide and the pH are the important parameters that determine the rate of reaction. The effects of all these parameters have been studied. The reaction proceeds very fast at the beginning but the rate of degradation slows down at larger time. The samples drawn at different times have been run on the HPLC to find out the degradation products. Over sixty percent degradation could be achieved by using nearly stoichiomentric quantity of hydrogen peroxide. A simple pathway of the oxidation process through is proposed.*

## INTRODUCTION

Removal of carbon dioxide and other acid gases such as hydrogen sulfide is an important step of natural gas processing to meet pipeline requirement. The most common solvent for carbon dioxide removal is an aqueous solution of an alkanolamine. Mono- and di-ethanolamine are more commonly used. During shutdown and maintenance, the $CO_2$-absorber in a natural gas processing plant is washed with a high speed water jet or using a similar technique when the residual amine appears in the wastewater. Since these alkanolamines are difficult to biodegrade, this wastewater cannot be cleaned in the usual effluent treatment tank.

Advanced Oxidation Processes (AOP's) have proved to be extremely effective in the degradation of organics which are resistant to conventional biological oxidation. The more common AOP's use either $H_2O_2$ or $O_3$ as the source materials for the generation of strongly oxidizing radicals such as hydroxyl ($HO^•$) and hydroperoxyl ($HO_2^•$) in solution. These radicals have very high oxidation potentials. For example, the $HO^•$ radical has an oxidation potential of 2.06 volts (relative to chlorine = 1.0) which is second only to fluorine. Ultraviolet radiation or ferrous sulfate, separately or in combination, is used to initiate the process of generation of the oxidizing radicals. Fenton's reagent [1], a mixture of hydrogen peroxide and ferrous sulfate in aqueous solution, has proved to be stronger than UV-$H_2O_2$ or UV-$O_3$ for most of the recalcitrant organics. The reactions may be represented as

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^•OH \quad\quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + {}^•O_2H \quad\quad (2)$$

The reaction rate is normally controlled by the rate of generation of $^•OH$ radicals which in turn depends upon the concentrations of $H_2O_2$ and $FeSO_4$. The concentration of the oxidizing radicals remain very low in the medium.

A large number of experimental work on the application of the Fenton's reagent for the degradation of a variety of organic molecules have been reported in the literature.  These include aromatic hydrocarbons and other compounds such as amines, phenol and substituted phenols, polycyclic aromatics, chlorinated hydrocarbons and more complex molecules like dyes, pharmaceuticals, amines, alcohols, mineral oils, etc.  Lou and Lee [2] used Fenton's reagent to destroy benzene, toluene and xylene (BTX).  Almost complete removal was claimed to have achieved within a short time of ten minutes.  Degradation of aromatic amines (aniline and a few substituted anilines) was studied by Casero et et al [3].  They identified the  intermediates by mass spectrometry.  Complete mineralization was achieved within one to three hours.  Mineralization of aniline was also studied by Brillas et al [4] by using a few advanced oxidation techniques – such as anodic oxidation, photo-catalysis, electro-Fenton and photo-Fenton techniques.  UV irradiation was found to accelerate each off the process.  De et al. [5] studied degradation of phenol and chlorinated phenols.  Quite a few studies were reported on degradation of residual dyes or dyeing wastewater using the Fenton's reagent.  Up to 95% of COD removal from carpet dyring wastewater was reported by Gulkaya et al [6] by suitably adjusting the ratio of $H_2O_2/Fe^{2+}$ concentration.  The efficiencies of degradation of Crystal Violet by the competing methods of UV-$H_2O_2$ and Fenton's reagent was reported by Alshamsi et al. [7].  Fenton's reagent proved to be more effective than the photo-chemical route but pH was found to have little effect in the range of parameters studied.  Alaton and Teksoy [8] studied the effectiveness of Fenton's reagent to pretreat acid dye-bath effluents of a textile industry before conventional biological treatment.  Solozhenko et al. [9] could successfully degrade the contaminants in wastewater from dyeing and finishing industries. Biodegradation of a pharmaceutical wastewater was greatly improved by Fenton's treatment as reported by Tekin et al. [10] since of breakdown of the organics into smaller fragments makes it amenable to normal biological oxidation.  The optimum pH was found to be 3.5.  Oturan et al. [11] used the Fenton's reagent to degrade pentachlorophenol which isoften found to be present in effluents from pesticide industries.  These authors used a novel technique of electrochemically generating hydroxyl radicals in situ thereby reducing the consumption of $H_2O_2$.  The technique is called electro-Fenton process.  There are quite a few work reported on this technique [12, 13].  Nesheiwat[14] discussed application of the Fenton's technique for destruction of contaminated soil washings that contained a spectrum of refractory organics.

Since alkanolamines are not amenable to biological oxidation, we have used the advanced oxidation techniques for treatment of simulated wastewater containing monoethanolamine using the Fenton's reagent.  The degradation rate was monitored by measuring the chemical oxidation demand (COD) of the reaction mixture from time to time.  The effect of different process variables have also been .studied.

## MATERIALS AND METHODS

Mono-ethanolamine and starch wrer obtained from R & M Chemicals;  $H_2O_2$ and NaOH wrer obtained from Systerm; $FeSO_4,7H_2O$ was obtained from Hamburg Chemicals;  $H_2SO_4$ was obtained from Malinckrodt and KI from Merck.  COD was measured by Hach 5000.
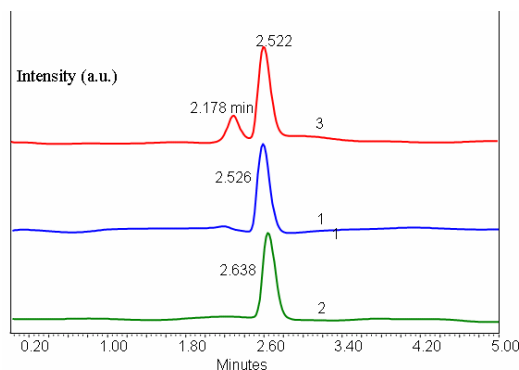


*Figure 1. Chromatogram of pure MEA (1), pure glycin (2), and sample of 30 minute run (3)   using Fenton's regent.*

A stirred jacketed glass reactor was used to monitor the progress of Fenton's degradation reaction of the alkanolamine. A solution of the amine in desired concentration was prepared and (M) $H_2SO_4$ was added to it to adjust the pH to the desired value. The ferrous sulfate catalyst was added and the content was mixed well. This was followed by addition of requisite quantity of 35% $H_2O_2$. The reaction starts immediately and the temperature is maintained by circulating cooling water through the jacket. Samples of
the liquid were withdrawn from time to time and the COD of the samples were measured following standard procedure. Calibration of the Hach 5000 COD instrument was checked by measuring the COD of a 2.08mM potassium hydrogen phthalate.

Unreacted $H_2O_2$ present in a sample seriously interferes with COD measurement. Removal of the $H_2O_2$ was done by warming a sample in a boiling water bath for 10 minutes [2] after addition of 2 ml of 1(M) NaOH solution to 8 ml sample. The precipitated hydrated ferric oxide was removed by centrifugation and the COD of the sample was measured. The change of volume of a sample at different steps was taken into account for COD calculation.

We could not identify the degradation products of the Fenton's reaction. However, neutralized samples were run on HPLC (Waters, column 4.6×250 mm; 60% methanol, 40% water mobile phase; RI detector) to find out the number of degradation products in partially oxidized amine samples. In all the samples two compounds were found to be present – the unconverted amine itself and one degradation product. A typical chromatogram is shown in Figure 1.

## RESULTS AND DISCUSSION

The substrate (MEA) has two functional groups – an alcoholic group and an amino group. An alcoholic group is more susceptible to oxidation than the latter. This is particularly true in the present case since at an acidic pH an amino group becomes further stabilized due to salt formation. On being oxidized by the hydroxyl radical, the –OH group should be converted to an organic acid – in this case, glycin. This amino acid will undergo further degradation losing the carbon atoms in succession and ultimately being completely destroyed.
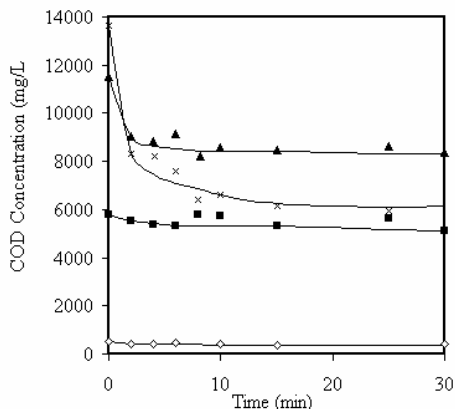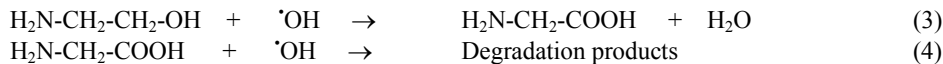
$$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH \quad + \quad {}^{\bullet}OH \quad \rightarrow \quad H_2N\text{-}CH_2\text{-}COOH \quad + \quad H_2O \tag{3}$$
$$H_2N\text{-}CH_2\text{-}COOH \quad + \quad {}^{\bullet}OH \quad \rightarrow \quad \text{Degradation products} \tag{4}$$



Figure 2. Effect of Initial MEA concentration on degradation [◊ 800ppmMEA (16ml $H_2O_2$ in 800ml, 1g FeSO₄ in 1L), 5000ppm MEA (47ml $H_2O_2$, 3.12g FeSO₄), ▲ 10000ppm MEA (94ml $H_2O_2$, 6.25g FeSO₄), × 16000ppm MEA (150ml $H_2O_2$, 10g FeSO₄)] at pH 3.
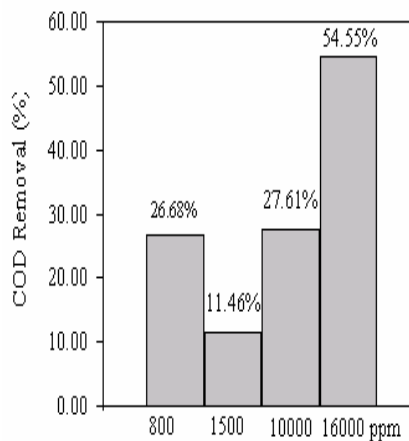


Figure 3. Effect of initial MEA concentration on degradation (pH = 3; constant ratio of H2O2/FeSO4

We attempted to follow the course of the reaction by running 'pure' MEA as well as a few samples withdrawn from time to time on HPLC. Typical chromatograms are shown in Figure 1. The sample containing pure amine shows only one peak at a retention time of 2. 52 minutes. All other samples display two peaks – one at 2.52 min, and another at 2.23 min. The former one obviously corresponds to the unreacted amine. The other peak appears

to be due to the first degradation product, glycine.   It is intriguing to note that no other peak appears even for samples withdrawn at a reaction time as high as 30 minutes.  This leads us to conclude that the first oxidation product (glycine) reacts rather slowly to generate products that disappear fast in the presence of the  $^\cdot$OH radicals.  According to our hypothesis, which remains to be proved by direct measurements, reaction (4) should be slow but the degradation products of this reaction reacts fast and cannot be detected by the HPLC.  It is to be noted, however, that the retention times of the degradation product and pure glycine injected separately are a little different (Figure 1).

The more important system variables that influence the rate of degradation are:  concentration of MEA, concentration of $H_2O_2$, pH and the concentration of ferrous ion.   Experiments were designed in such a way that the effects of these variables could be studied independently.  The ranges of values of these variables used in the experiments are -  MEA concentration: 800-16,000 ppm;  pH:  2 to 5;  $FeSO_4,7H_2O$:  5 to 20   g in 800 ml solution; and $H_2O_2$:  50  to 200  (35%) ml in 800 ml solution.

## Effect of MEA Concentration

At the beginning of this study, we tried with a low concentration solution of MEA of 800 ppm and UV-$H_2O_2$ to generate the $^\cdot$OH  radicals.   Surprisingly the reaction was very slow and only about 10% degradation was achieved  at the end of  30 minutes reaction time.   A higher dosing of $H_2O_2$ did not help.    Next we applied Fenton's reagent which is widely used for advanced oxidation of refractory organics.  The rate of degradation, howver, remained very slow at a low amine concentration of 800 ppm.  This prompted us to use a higher amine concentration.  The change of COD values of the feed amine solution with time is depicted in Figure 2 for four initial concentrations of the substrate.  The ratio of $H_2O_2$ and $FeSO_4,7H_2O$  was maintained approximately constant.  It was found that the COD value decreased vary rapidly at a high initial amine concentration.  More than 50% of the COD was removed within a short reaction time of about 5 minutes.  After this the degradation rate decreased abruptly.  Also both the rate of degradation and the fractional COD removal were low at a low initial amine concentration.  The degradation achieved over a 30 minute reaction time is shown in Figure 3.
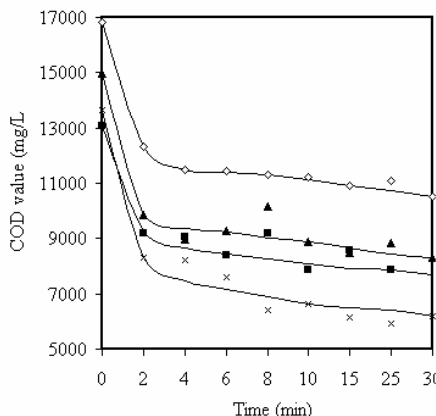


Figure 4. Effect of  $H_2O_2$ concentration  on degradation [◊ 50 $H_2O_2$, ▲ 100ml $H_2O_2$, × 150ml $H_2O_2$, ■ MEA 200ml $H_2O_2$ (16000ppm MEA, 10g in 1L, at pH 3)].
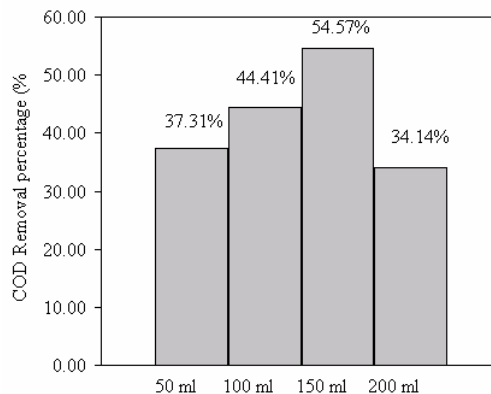


Figure 5. Effect  of amount of H2O2 added, Initial MEA = 16000 ppm, pH = 3, FeSO4 = 10 g

## Effect of H$_2$O$_2$ concentration

Since the hydroxyl radicals are generated from $H_2O_2$, its concentration should have a major influence on the rate of degradation.  Figure 4 shows the history of COD change when varying amounts of $H_2O_2$ were added, keeping the pH constant at 3.0 and in the presence of 10g $FeSO_4,7H_2O$ per liter of the solution.   The degradation rate and the fraction of COD removal increases with increase in the amount of $H_2O_2$ added up to certain limit.  A still higher concentration of $H_2O_2$ has a retrograde effect on degradation (Figures 4 and 5).  Such an effect of $H_2O_2$ concentration was reported by other researchers as well.  At a high concentration, $H_2O_2$ acts as a scavenger of $^\cdot$OH radicals with simultaneous generation of oxygen that does not help in the degradation process.  Thus a high concentration of hydrogen peroxide prevents efficient utilization of the hydroxyl radicals.
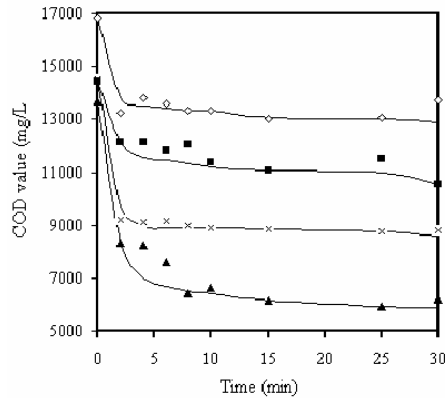
Fig. 6. Effect of pH on degradation [◊ pH 2, ▲ pH 3, ×
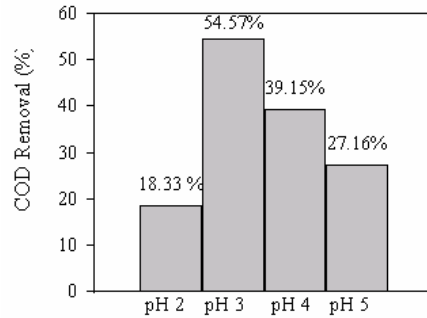pH 4, ■ pH5 (16000ppm MEA, 10g in 1L, 150ml



Figure 7. Effect of pH on degradation of MEA
(16000 ppm MEA, 150 ml H2O2, 10 g FeSO4)

## Effect of pH

There are disagreements in the literature on the effect of pH on the rate of Fenton peroxidation. Tekin [10] observed little effect of pH on degradation of pharmaceutical wastewater. In the range 3-4.5. Kuo [15] found the best pH to be 3.5 for the degradation of textile wastewater. In this study we observed that pH has a significant effect on the degradation of MEA. The rate of degradation is low at a pH as low as 2. It is also low at a pH higher than 5 because of the degradation of pH. The effect of pH in our work is depicted in Figure 6 and 7. The optimum pH is found to be 3.0. Hickey et al. [16] found the optimum pH of 3.0 in their work on degradation of atrazine using Fenton's reagent.
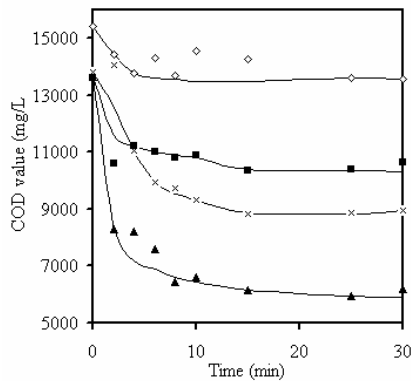


Fig. 8. Effect of FeSO₄ concentration on
degradation [◊ 5g FeSO₄, ▲ 10g FeSO₄, ×
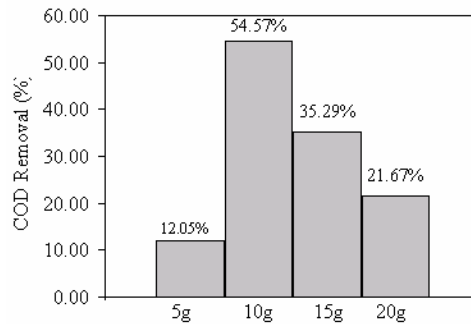15g FeSO₄, ■ 20g FeSO₄ (16000ppm



Figure 9. Effect of addition of dosing of FeSO4 on
degradation (16000ppm amine; 150 ml H2O2, pH 3)

## Effect of FeSO₄ dosing

We studied the effect of dosing of $FeSO_4,7H_2O$ on the degradation rate by adding different quantities of the salt (5g, 10g, 15g and 20g) to one liter solution of 16000 ppm MEA solution at a pH of 3.0. The results are shown in Figures 8 and 9. It is found that a dosage of 10g of the salt per liter solution is the optimum under the given set of conditions. A higher dosage reduces degradation rate. It has been reported that the hydrated ferric oxide formed during Fenton's reaction producing hydroxyl radicals catalyze decomposition of $H_2O_2$ and therefore a large dosing of the salt proves detrimental.

## CONCLUSION

Monoethanolamine undergoes degradation by reaction with hydroxyl radicals in the Fenton's hydroperoxidation process. The reaction appears to be very slow at a low concentration of the amine. But at a higher concentration of the substrate, it proceeds very fast. More than 50% of the COD is removed within about two minutes from an amine solution of initial concentration of 16,000 ppm. The degradation rate is the highest at a pH of 3.0. The dosing of both ferrous sulfate and hydrogen peroxide has similar effects – the degradation rate increases, reaches a peak and then decreases. This is because the precipitated iron compound acts as a catalyst for decomposition of $H_2O_2$, and $H_2O_2$ scavenges hydroxyl radicals. By proper selection of the concentrations and pH it is possible to achieve a high degradation of the amine.

## ACKNOWLEDGEMENT

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