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# Degradation of Monoethanolamine in Aqueous Solution by Fenton's Reagent with Biological Post-treatment

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**Abstract** Alkanolamines in the wastewater from gas treating plants are not readily biodegradable. In this work, we have investigated the effectiveness of the Fenton's reagent ( $\text{H}_2\text{O}_2\text{-Fe}^{2+}$ ) to treat monoethanolamine (MEA) as a model compound in simulated wastewater. Degradation studies were carried out in a jacketed glass reactor. The effects of concentrations of ferrous sulfate, hydrogen peroxide, and the pH of a solution on the rate of reaction were determined. A pH of 3 was found to be the optimum. The degradation reaction proceeds very fast at the beginning but slows down significantly at a longer time. A

larger fractional degradation of the organics in solution was observed if the initial chemical oxygen demand (COD) of the feed solution was high. Gradual addition of  $\text{H}_2\text{O}_2$  to the reaction mixture increased the COD removal by about 60% compared to one-time addition of the reagent at the beginning of the process. A rate equation for mineralization of the amine was developed on the basis of a simplified mechanistic model, and the lumped value of the rate constant for COD removal was determined. A partially degraded MEA solution as well as "pure" MEA was subjected to biological oxidation by activated sludge. The former substrate degraded much faster. The degradation rate and biomass generation data could be fitted by the Monod kinetic equations.

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## 1 Introduction

Monoethanolamine (MEA) in aqueous solution is widely used for scrubbing acidic molecules such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from natural gas as well as from synthesis gas (Kohl and Nielsen 1997). It is also used in the formulation of surface-active agents, emulsifiers, polishes, pharmaceuticals, corrosion inhibitors, and as a chemical intermediate. A substantial quantity of the amine is released in the wastewater generated in a natural gas processing plant during periodic

cleaning of the absorption and stripping towers for CO<sub>2</sub> separation or during a process upset. Since MEA or other alkanolamines are difficult to biodegrade, this wastewater cannot be cleaned in the conventional activated sludge biological oxidation tank. This is particularly true in case of discharge of the amine during a process upset when the chemical oxygen demand (COD) in the contaminated effluent may exceed 20,000 mg/l (MLNG 2007). In another emerging application of amines for CO<sub>2</sub> capture from flue gasses, degradation of the reagent occurs slowly in the column in presence of oxygen (Goff and Rochelle 2004). A degraded solution must be discarded but properly treated before release.

Advanced oxidation processes (AOPs) have proved to be extremely effective for the degradation of organics which are resistant to conventional biological oxidation. The more common AOPs use either H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> as the source materials for the generation of strongly oxidizing radicals such as hydroxyl ( $\bullet$ OH) and hydroperoxyl ( $\bullet$ O<sub>2</sub>H) in solution. It is well known that these radicals have very high oxidation potentials (Burbano et al. 2005). For example, the  $\bullet$ OH radical has an oxidation potential of 2.8 V (at a pH 3) which is second only to fluorine. Ferrous sulfate and ultraviolet radiation, separately or in combination, is used to initiate the process of generation of the oxidizing radicals. Fenton's reagent (Walling 1975), a mixture of hydrogen peroxide and ferrous sulfate in aqueous solution, has proved to be stronger than UV-H<sub>2</sub>O<sub>2</sub> or UV-O<sub>3</sub> for many of the recalcitrant organics. The major reactions for generation of the oxidizing radicals may be represented as



The reaction rate is normally controlled by the rate of generation of  $\bullet$ OH and  $\bullet$ O<sub>2</sub>H radicals, which in turn depends upon the concentrations of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> as well as the solution pH. Since the oxidizing radicals are highly reactive, their concentrations remain very low in the solution (Haag and Yao 1992).

A fairly large number of experimental investigations on the application of the Fenton's reagent for the degradation of a variety of organic molecules have been reported in the literature, and it will be pertinent to review the relevant ones. These organics include aromatic hydrocarbons and compounds such as amines,

phenol and substituted phenols, polycyclic aromatics, chlorinated hydrocarbons, and more complex molecules like dyes, pharmaceuticals, surfactants, pesticides, and mineral oils. Lou and Lee (1995) used Fenton's reagent to destroy benzene, toluene, and xylene (BTX). Almost complete removal was claimed to have been achieved within a short reaction time of 10 min. Many recent studies reaffirmed the power of Fenton's reagent to degrade a variety of contaminants, including amines and other nitrogenous compounds, in industrial wastewater. Degradation of aromatic amines (aniline and a few substituted anilines) was studied by Casero et al. (1997). They identified the intermediates by mass spectrometry. Complete mineralization was achieved within 1 to 3 h. Mineralization of aniline was also studied by Brillas et al. (1998) by using different alternative advanced oxidation techniques—such as anodic oxidation, photo-catalysis, electro-Fenton, and photo-Fenton techniques. A similar study was reported by Anotai et al. (2006). De et al. (2006) studied degradation of phenol and chlorinated phenols. Quite a few studies were reported on the degradation of residual dyes and dyeing wastewater using the Fenton's reagent. Up to 95% of COD removal from carpet dyeing wastewater was reported by Gulkaya et al. (2006) by suitably adjusting the ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> concentration. The efficiencies of degradation of crystal violet by the competing methods of UV-H<sub>2</sub>O<sub>2</sub> and Fenton's reagent were reported by Alshamsi et al. (2006). The Fenton's technique proved to be more effective than the photochemical route, but pH was reported to have surprisingly little effect on degradation in the range of values of the parameters studied. Alaton and Teksoy (2007) studied the effectiveness of Fenton's reagent to pretreat acid dye-bath effluents of a textile industry prior to conventional biological treatment. Solozhenko et al. (1995) could successfully degrade the contaminants in wastewater from dyeing and finishing industries. Biodegradation of a pharmaceutical wastewater was greatly enhanced by Fenton's pre-treatment as reported by Tekin et al. (2006) since breakdown of the organics into smaller fragments makes it amenable to normal biological oxidation. In fact, wastewater from the drug and pharmaceutical industries are often found to contain a very high COD comparable to that of gas treating wastewater studied in the present work. Since an AOP involves substantial capital and operating costs (Anotai et al. 2006), partial degradation by an AOP followed by conventional

biological oxidation of the residual organic has proved to be a pragmatic strategy (Alanton and Teksoy 2007; Tekin et al. 2006). Oturan et al. (2001) used the Fenton's reagent to degrade pentachlorophenol, which is often found in effluents from pesticide industries. These authors used the electro-Fenton technique of electrochemically generating hydroxyl radicals in situ thereby reducing the consumption of  $\text{H}_2\text{O}_2$ . Successful use of the modified Fenton technique has been reported by a few other workers (Hsiao and Nobe 1993; Pignatello 1992). Nesheiwat and Swanson (2000) discussed application of the Fenton's technique for destruction of contaminated soil washings containing a spectrum of refractory organics.

Since alkanolamines are not readily amenable to biological oxidation, we have used the Fenton's technique for the treatment of simulated wastewater containing MEA. Despite the challenge facing the natural gas industries (Goff and Rochelle 2004) to degrade amines in the effluents, not much has been reported in this direction except photocatalytic degradation of several alkyl and alkanolamines by Klare et al. (2000). However, photocatalytic degradation of an industrial wastewater in presence of a semiconductor catalyst is not yet a proven technology for practical application and is admittedly much more expensive. Since the ultimate goal is complete oxidation of the substrate either using an AOP alone or, alternatively, using an AOP followed by biological oxidation, reduction of COD is a more important indicator than breakdown of the substrate. In this work, the degradation rate was monitored by measuring over time the COD of the reaction mixture. The effects of different process variables on the rate and extent of COD removal have also been studied in order to identify suitable operating conditions. This was followed by biological oxidation of the partially degraded amine in order to assess the enhancement of biodegradability as a result of partial oxidation by the Fenton's reagent. Biodegradation of "pure" MEA was also done alongside for comparison.

## 2 Materials and Methods

### 2.1 Reagents

MEA was obtained from R & M Chemicals, UK;  $\text{H}_2\text{O}_2$  (30% in aqueous solution) and NaOH were obtained

from System, Malaysia;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was obtained from Hamburg Chemicals;  $\text{H}_2\text{SO}_4$  was obtained from Malinckrodt and KI from Merck, Germany. The chemicals and reagents were used as received.

### 2.2 Experimental

Simulated wastewater was prepared by dissolving a suitable quantity of the amine in distilled water. Since amine-contaminated wastewater from an acid gas removal unit has a high COD, we have used in the experiments feed solutions of COD values matching such industrial wastewaters. The experiments were conducted in a 1-L stirred jacketed glass reactor having a ground glass cover. The reactor was provided with feed inlet, temperature and pH sensor ports, as well as sampling points. It was placed on a magnetic stirrer to keep the content well mixed. A solution of the amine in desired concentration was prepared, and the required amount of solid  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added to the amine solution. The pH adjustment was done with 1 M of NaOH and 1 M of  $\text{H}_2\text{SO}_4$  followed by addition of the requisite quantity of  $\text{H}_2\text{O}_2$ . The temperature was maintained at 300 K by circulating cooling water through the jacket. Samples of the liquid were withdrawn from time to time and analyzed in order to monitor the course of degradation of the organics and to determine the residual  $\text{H}_2\text{O}_2$ . The COD of the samples was determined using a Hach DR5000 spectrophotometer following the standard procedure of digesting a sample with the prescribed reagent. Since identification of all the degradation products and their measurement were difficult, COD of the liquid was taken as a measure of concentration of the organics in solution as a whole.

A sample contained unreacted  $\text{H}_2\text{O}_2$  and suspended particles of hydrated ferric oxide besides COD. The presence of  $\text{H}_2\text{O}_2$  in a sample interferes with COD determination, and its prior removal was done. For this purpose, 8 ml of a sample was mixed with 2 ml of 1 M NaOH and heated in a boiling water bath for 10 min (Lou and Lee 1995). The suspended hydrated ferric oxide was removed by centrifugation, and the COD of the clear solution was measured. The change of sample volume due to addition of the alkali was taken into account for COD calculation. The reproducibility of the experimental data was checked at the beginning by repeating the same set of

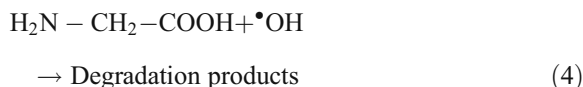
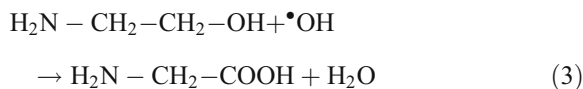
experiment thrice. The average error remained within  $\pm 3\%$ . Calibration of the Hach DR5000 COD spectrophotometer was checked by measuring the COD of a 2.08-mM solution of potassium hydrogen phthalate. The pH measurements were performed using a pH meter, model Mettler Toledo 320. Concentration of  $\text{H}_2\text{O}_2$  was determined by the potassium permanganate method (CEFIC 2003). In an attempt to identify the reaction intermediates, the amine and a partially degraded sample were tested by using Agilent 1100 high-performance liquid chromatography (HPLC) provided with a YMC Pack Polymer C18 reverse phase column, 100 mM  $\text{Na}_2\text{HPO}_4$ /100 mM NaOH (60/40, pH 12, 1 mL/min) as the mobile phase, and UV detector at 253 nm. Fourier transform infrared (FTIR) spectra of liquid samples were taken using a Perkin-Elmer Spectrum One machine.

Biodegradation studies were conducted in an aerobic batch bioreactor according to Section 2 specifications in the Zahn-Wellens/EMPA test according to the US Environmental Protection Agency (EPA) method OPPTS 835.3200 (US EPA 1998). Partially degraded MEA and “pure” MEA were taken in separate reactors at an initial COD of 1,000 mg/L, and seed bacterial sludge collected from the central activated sludge sewage treatment plant of the university was added to the reactors. The initial biomass concentration was 100 mg/L mixed-liquor suspended solids (MLSS). To ensure sufficient micro-nutrients and suitable growth conditions, a mineral medium as suggested in the US EPA method mentioned above was provided, and the pH of the liquid was maintained at 7. Aeration was done by bubbling compressed air through the wastewater using a perforated plastic air disperser. Samples were withdrawn every 6 h and analyzed for COD and MLSS.

### 3 Results and Discussion

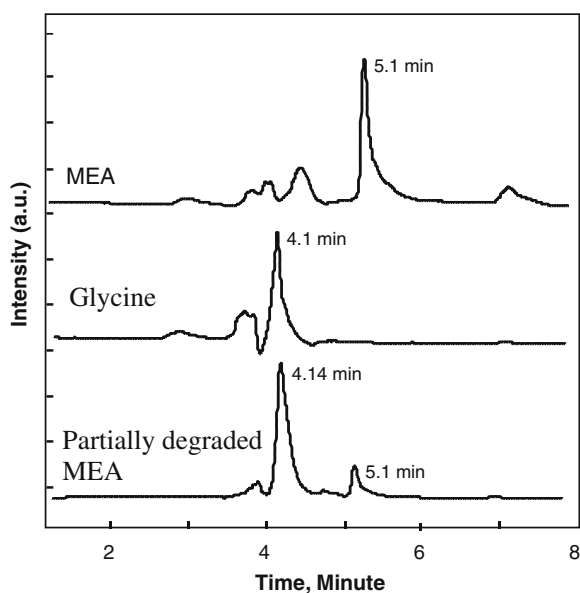
The substrate (MEA) has two functional groups—an alcoholic group and an amino group. Oxidation of a substrate by the hydroxyl radical proceeds through hydrogen abstraction. In MEA, the possible sites of hydrogen abstraction are the nitrogen atom or the  $\alpha$ - or  $\beta$ -carbon atom. It is likely to occur at the  $\beta$ -carbon atom because of its proximity with the electron-rich amino group. Alternatively, the degradation process

may start by oxidation of the alcoholic  $-\text{OH}$  group of the substrate. Turan-Ertas and Gurol (2002) studied the degradation of diethylene glycol by a modified Fenton’s reagent composed of  $\text{H}_2\text{O}_2$  and  $\text{FeCl}_3$  and explained the course of degradation hypothesizing the formation of aldehydes and acids in succession till complete mineralization. McGinnis et al. (2000) studied the degradation of ethylene glycol by the photo-Fenton technique and suggested a reaction pathway involving successive oxidation of the alcohol groups to aldehyde and acid up to complete mineralization. If the alcoholic group in MEA is oxidized as the first step of the degradation process, the product, which is an organic acid—in this case, glycine—should be amenable to further degradation.



In order to check the formation of glycine as an intermediate, a solution of “pure” MEA and a solution of glycine, as well as a few partially reacted samples, were run on the HPLC as mentioned in the previous section. Typical chromatograms of “pure” MEA, “pure” glycine, and partially degraded samples are shown in Fig. 1. The retention times of MEA and glycine are 5.1 and 4.1 min, respectively. The chromatogram of the partially degraded amine showed two peaks—one corresponding to glycine and the other to a small quantity of residual MEA apparently indicating that the degradation process follows the pathways given by Eqs. 3 and 4 above.

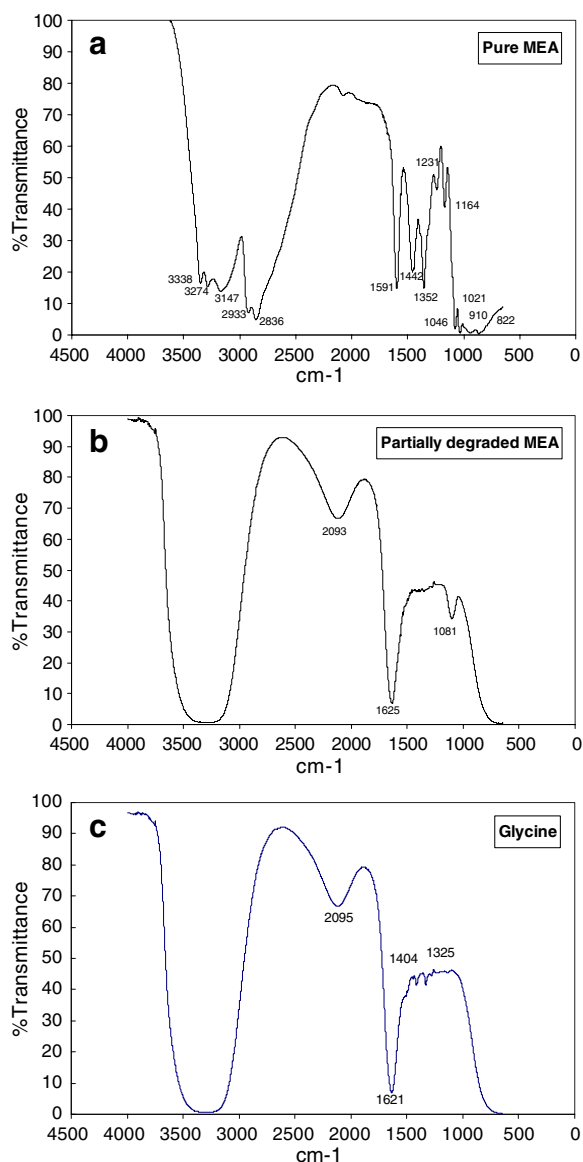
In order to check the above conclusion further, IR spectra of the liquids (pure MEA, glycine solution, and a sample of MEA partially degraded by Fenton’s reaction) were recorded using a Perkin-Elmer Spectrum 1 machine. The results shown in Fig. 2(a), (b), and (c) can be interpreted using the standard database available in the literature (Silverstein et al. 2005; Coates 2000). The spectra of pure MEA (Fig. 2a) consist of peaks indicative of the bonds and hydrogen bonding interactions of the compound. The peaks at 1,352 and 1,442  $\text{cm}^{-1}$  are characteristic of a primary alcohol ( $-\text{OH}$ ) group, and the one at 3,338  $\text{cm}^{-1}$



**Fig. 1** Chromatograms of pure monoethanolamine (1), pure glycine (2), and a sample of partially degraded solution at 30 min run time

refers to O/H hydrogen bonding. The peak at  $3,274\text{ cm}^{-1}$  indicate N–H stretching;  $1,591$  and  $1,046\text{ cm}^{-1}$  indicates aliphatic amine group. The spectra of a sample of partially degraded MEA (Fig. 2b) closely resemble that of glycine (Fig. 2c). The peak around  $2,093\text{ cm}^{-1}$  stands for the interaction of  $\text{COO}^-$  and  $\text{N}^+$  in glycine, which is conspicuous in both Fig. 2(b) and (c); the peak around  $1,625\text{ cm}^{-1}$  indicates C=O in a carboxylic acid. A peak characteristic of C–N bonding appears at  $1,081\text{ cm}^{-1}$  but is not clearly distinguishable in Fig. 2(c). Absorption in the region covering  $3,000\text{--}3,700\text{ cm}^{-1}$  occurs due to the large excess of water present in both the aqueous solutions.

Existence of any other compound in the partially degraded liquid is not discernible in either the chromatogram or the FTIR spectra, but oxidation of glycine to the final products  $\text{CO}_2$  and  $\text{H}_2\text{O}$  must involve intermediate compounds. We carried out Fenton degradation of pure glycine to compare its degradability with that of MEA. Typical results presented in Fig. 3 on the reduction of COD with time show that degradation of glycine is much slower than that of MEA. If mineralization of MEA proceeds through the glycine route only, the COD reduction process would have been much slower than what we experienced in the detailed experiments described

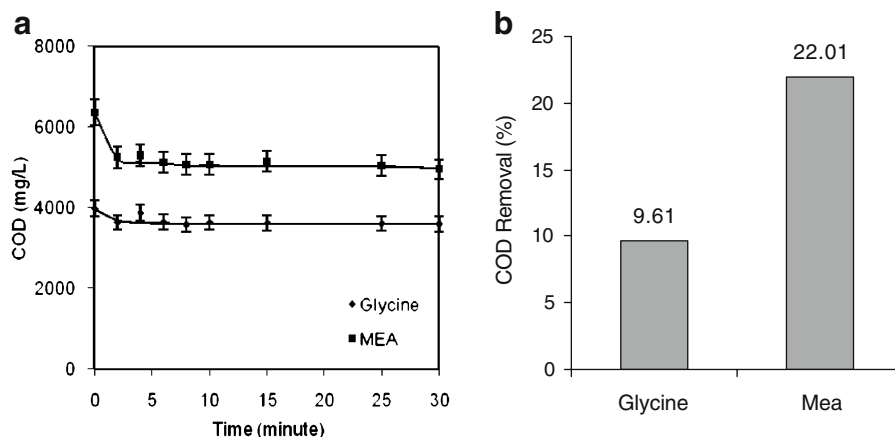


**Fig. 2** a Fourier transform infrared (FTIR) spectra of pure monoethanolamine. b FTIR spectra of partially degraded liquid. c FTIR spectra of pure glycine solution

later. It is therefore likely that the process proceeds through abstraction of hydrogen from the  $\beta$ -carbon atom of the substrate or directly from the electron-rich nitrogen atom simultaneously. However, we could not identify the intermediates to confirm this hypothesis at this stage. Notably, Klare et al. (2000) suggested that electrophilic attack of the hydroxyl radical leads to cleavage of the C–N bond in the degradation of lower alkyl and alkanolamines using the photocatalytic route.



**Fig. 3** Comparison of chemical oxygen demand (COD) reduction of monoethanolamine and glycine solutions ( $0.66 \text{ M H}_2\text{O}_2$  and  $8.99 \times 10^{-3} \text{ M Fe}^{2+}$  at pH 3). **a** Change of COD with time and **(b)** COD reduction after 30 min run time



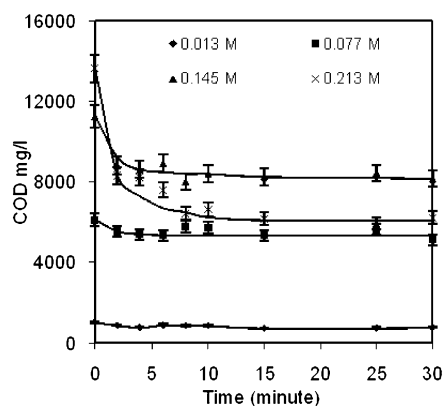
### 3.1 The Effects of System Variables

The more important system variables that influence the degradation or reduction of COD are concentration of the substrate (MEA), concentration of  $\text{H}_2\text{O}_2$ , pH, and concentration of the ferrous ion (Burbano et al. 2005; Lou and Lee 1995; De et al. 2006). All experiments were done at 300 K. Experiments were designed in such a way that the effects of these variables could be studied independently. While investigating the effect of MEA concentration, we maintained the initial concentration ratios  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  and  $[\text{MEA}]/[\text{H}_2\text{O}_2]$  approximately constant. The ranges of values of these variables used in the experiments are MEA concentration: 0.013–0.213 M (after dosing of  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$ ); pH: 2 to 5;  $\text{Fe}^{2+}$ : 0.0144 to 0.0575 M; and  $\text{H}_2\text{O}_2$ : 0.708 to 2.83 M. The higher  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosing was done in consideration of the larger COD in the feed solution. Up to 6 M  $\text{H}_2\text{O}_2$  and 0.6 M  $\text{Fe}^{2+}$  were used by Martinez et al. (2003) for partial degradation of high COD pharmaceutical wastewater. It is to be noted that at a high  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosage, the Fenton reaction becomes vigorous with quick rise in the temperature of the reaction mixture as experienced by us and reported by others (Martinez et al. 2003).

#### 3.1.1 Effect of Initial Concentration of MEA

In most of the investigations on Fenton's degradation, the substrate concentration is maintained low. This conforms to concentrations of organic pollutants found in industrial wastewaters from gas processing industries. However, effluent wastewater generated during cleaning and maintenance of absorption and

stripping towers of  $\text{CO}_2$  separation units, the amine concentration remains significantly high—sometimes nearing 50,000 ppm (MLNG 2007). For this reason, Fenton's degradation has been studied in this work with relatively high-COD feed solutions. The change of COD of the feed solution with time is depicted in Fig. 4 for four initial concentrations of the substrate. The ratio of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  was maintained constant. It was found that the COD value decreased very rapidly at a high initial amine concentration. More than 50% of the COD was removed within a short reaction time of about 5 min. After this, the degradation rate decreased abruptly. Martinez et al. (2003) also reported more than 60% oxidation within the first 2 min and nearly 98% removal of COD from a high-COD wastewater feed within 10 min. Similar observations were made by Burbano et al. (2005) for



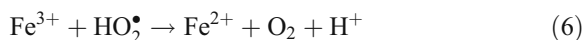
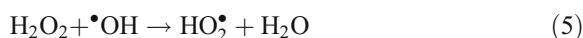
**Fig. 4** Effect of initial monoethanolamine (MEA) concentration on degradation (0.013(M) MEA: 0.00288 M  $\text{Fe}^{2+}$ , 0.227 (M)  $\text{H}_2\text{O}_2$ ; 0.077(M) MEA: 0.009 (M)  $\text{Fe}^{2+}$ , 0.665(M)  $\text{H}_2\text{O}_2$ ; 0.145(M) MEA: 0.018 (M)  $\text{Fe}^{2+}$ , 1.331 M  $\text{H}_2\text{O}_2$ ; and 0.213 M MEA: 0.0288 M  $\text{Fe}^{2+}$ , 2.123 M  $\text{H}_2\text{O}_2$ ). pH=3

MTBE degradation, Tekin et al. (2006), Tang and Huang (1997), and by Kitis et al. (1999) who worked with water containing non-ionic surfactants. They observed a drastic fall in the rate of degradation after 2 min. Although the trends are similar, MEA degradation appears to be slower than other substrates cited here, presumably because of formation of more resistant degradation products including organic acids. This type of two-step kinetics consisting of a fast organic destruction in the first step followed by a slower second step is not uncommon for the Fenton's reaction. It has been observed for instance in the degradation of phenol (Vione et al. 2004) and attributed to the transition from an Fe(II)-driven degradation to an Fe(III)-controlled one. The first step of Fenton's degradation is driven by Eq. 1 between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ . It is rather fast and is completed within a few minutes, when  $\text{Fe}^{2+}$  gets totally consumed if  $\text{H}_2\text{O}_2$  is in excess. After the consumption of  $\text{Fe}^{2+}$ , the rate-determining step of the degradation process becomes the much slower reduction of Fe(III) to  $\text{Fe}^{2+}$  by  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ , followed by the faster Eq. 1 that yields  $\bullet\text{OH}$  (De Laat and Gallard 1999). In the second Fe(III)-controlled step, the concentration of  $\text{Fe}^{2+}$  reaches a very low steady-state value, and the observed degradation rates are considerably lower than for the initial step. Both the rate of degradation and the fractional COD removal were low at a low initial amine concentration. A plausible explanation of the phenomenon may be provided in consideration of the reaction of the OH radicals with the organic substrate(s) and its loss through parallel decomposition reactions catalyzed by the Fe(III) oxides (De Laat and Gallard 1999).

### 3.1.2 Effect of $\text{H}_2\text{O}_2$

The effect of  $\text{H}_2\text{O}_2$  dosing on Fenton's treatment was investigated at a  $\text{H}_2\text{O}_2$  concentration range of 0.708 to 2.831 M, while keeping the initial MEA concentration at 0.213 M in the presence of 0.028 M  $\text{Fe}^{2+}$  at pH 3.0. The pH and  $\text{Fe}^{2+}$  concentration were selected since these are optimum values of the parameters as described later. Figure 5 shows the time evolution of COD when varying amounts of  $\text{H}_2\text{O}_2$  are used. At 0.708 M  $\text{H}_2\text{O}_2$  concentration, COD removal was 37.3%, and it increased to 54.54% when  $\text{H}_2\text{O}_2$  was raised 2.123 M. It is due to the increase in the rate of formation of hydroxyl radical ( $\bullet\text{OH}$ ) that plays the

most important role in MEA degradation. The degradation rate and the fractional COD removal increased with  $\text{H}_2\text{O}_2$  concentration to a certain limit. However, complete removal of COD could not be achieved even with higher than stoichiometric quantity of  $\text{H}_2\text{O}_2$ . Too high a concentration of  $\text{H}_2\text{O}_2$  has a negative effect on degradation (Fig. 5). Such an effect of  $\text{H}_2\text{O}_2$  concentration was reported by other researchers as well (Martinez et al. 2003; Vione et al. 2004). At a high concentration,  $\text{H}_2\text{O}_2$  acts as a scavenger of  $\bullet\text{OH}$  radicals with simultaneous generation of oxygen that does not help in the degradation process. A series of reactions including the following has been suggested.



Equation 5 is expected to be highly detrimental to degradation, whereas Eq. 6 could have a limited influence on the initial degradation rate because Fe (III) is not present in the system from the beginning. Equation 6 could even enhance degradation in the second step of the Fenton's reaction, where the reduction of Fe(III) to  $\text{Fe}^{2+}$  becomes the rate-determining step of the process.

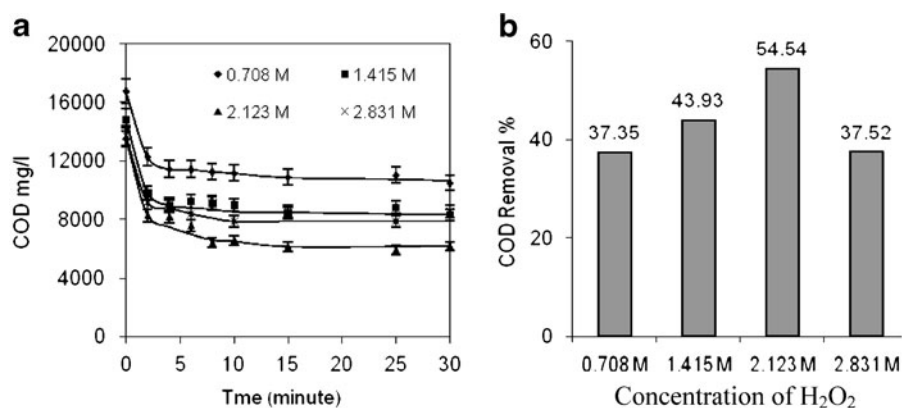
Thus, a high concentration of hydrogen peroxide prevents efficient utilization of the hydroxyl radicals. Casero et al. (1997) also found the concentration of  $\text{H}_2\text{O}_2$  to have an optimum value in their work on degradation of aromatic amines by the Fenton's reagent. However, Zhang et al. (2006) in their work on Fenton degradation of landfill leachate observed that the COD removal remained virtually the same on increasing the  $\text{H}_2\text{O}_2$  concentration above 0.15 mol/l at a constant  $[\text{Fe}^{2+}]$  of 0.05 mol/l. The optimum ratio of  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  depends upon the type of organics in the wastewater.

### 3.1.3 Effect of pH

There are disagreements in the literature about the effect of pH on the rate of Fenton peroxidation. Tekin et al. (2006) observed little effect of pH on degradation of pharmaceutical wastewater in the range of 3–4.5. Kuo (1992) and Hickey et al. (1995) found the best pH to be 3.5 for the degradation of textile wastewater. Zhang et al. (2006) reported a lower

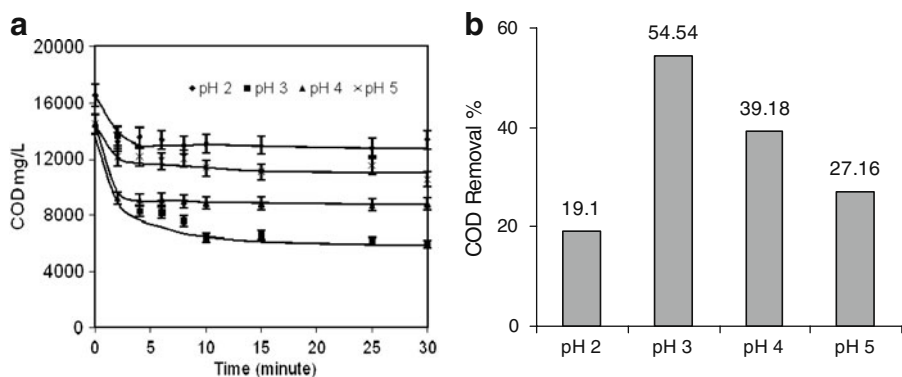


**Fig. 5** Effect of  $\text{H}_2\text{O}_2$  concentration (0.708, 1.415, 2.123, and 2.831 M) on monoethanolamine (MEA) degradation (MEA: 0.213 M);  $\text{Fe}^{2+}$ : 0.0288 (M); pH=3). **a** Change of chemical oxygen demand (COD) with time and **(b)** COD removal after 30 min run time



optimum pH of 2.5. In this study also, we observed that pH has a significant effect on the degradation of MEA. The rate of degradation is low at pH 2. It is due to the formation of complex species between  $\text{Fe(III)}$  and  $\text{H}_2\text{O}_2$ . In addition, the peroxide gets protonated in the presence of high concentration of  $\text{H}^+$  to form the stable oxonium ion  $\text{H}_3\text{O}_2^+$ . Protonation to the oxonium ion increases the electrophilicity and stability of hydrogen peroxide and presumably causes substantial reduction of the reactivity with  $\text{Fe}^{2+}$ . The rate of degradation is also low at a pH higher than 5 because  $\text{H}_2\text{O}_2$  would be decomposed to give  $\text{O}_2$  and  $\text{H}_2\text{O}$ , and would therefore lose its oxidation ability (Gulkaya et al. 2006). The effect of pH in our work is depicted in Fig. 6. The variation of pH during an experimental run generally remained within  $\pm 0.05$ . The optimum pH is found to be 3.0, where all the  $\text{Fe(II)}$  remains as  $\text{Fe}^{2+}$  thus maximizing the generation of  $\cdot\text{OH}$  radicals. Hickey et al. (1995) found the optimum pH of 3.0 in their work on degradation of atrazine using Fenton's reagent. Gulkaya et al. (2006) also reported an optimum pH of 3 in their work on degradation of a high COD carpet dyeing wastewater.

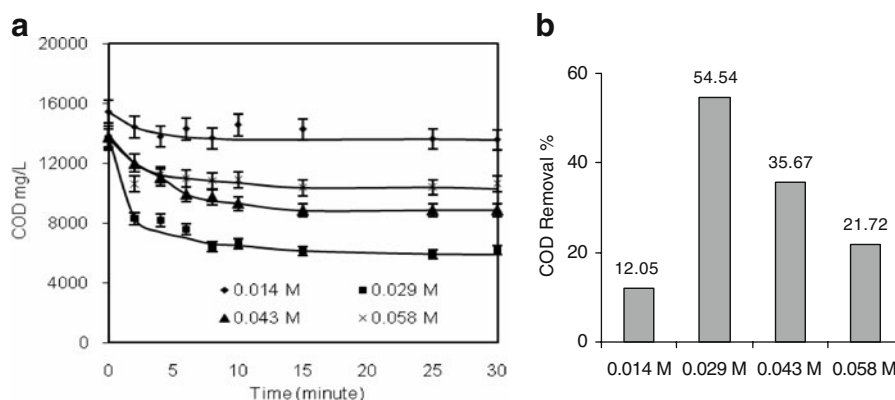
**Fig. 6** Effect of pH on degradation of monoethanolamine (MEA; 0.213 M) MEA: 0.0288 (M)  $\text{Fe}^{2+}$ , 2.123 (M)  $\text{H}_2\text{O}_2$  at different pH values). **a** Change of chemical oxygen demand (COD) with time and **(b)** reduction of COD at 30 min run time



### 3.1.4 Effect of $\text{Fe}^{2+}$

We studied the effect of dosing of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  on the degradation rate by adding different quantities of the salt (0.0144 to 0.0575 M) to 800 ml of 0.213 M MEA solution at pH 3.0. The results are shown in Fig. 7.

The COD removal increases with increasing  $\text{Fe}^{2+}$  concentration. At a lower  $\text{Fe}^{2+}$  concentration, less  $\cdot\text{OH}$  radicals are available for oxidation of MEA. The COD removal reaches the optimum value at 0.0288 M  $\text{Fe}^{2+}$  under the given set of conditions. A higher concentration of  $\text{Fe}^{2+}$  reduces the degradation rate. It has been reported that the hydrated ferric oxide formed during Fenton's reaction catalyzes decomposition of  $\text{H}_2\text{O}_2$ , and therefore a large concentration of  $\text{Fe}^{2+}$  proves detrimental (Tekin et al. 2006). A more important parameter is perhaps the ratio of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . We got the best result for a value of 73.7 of this ratio. However, literature reports on the best value of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  are diverging. Tekin et al. (2006) reported an optimum value of 150, whereas Martinez et al. (2003) and Tang and



**Fig. 7** Effect of  $\text{Fe}^{2+}$  dosing on degradation of monoethanolamine (MEA) and DEA ((0.213 M MEA, 2.123 M  $\text{H}_2\text{O}_2$  at pH 3) in the different  $\text{Fe}^{2+}$  concentration). **a** Chemical oxygen demand (COD)

reading by time and **(b)** COD removal at 30 min run in different  $\text{Fe}^{2+}$  concentration

Tassos (1997), both working with high COD pharmaceutical wastewater, found an optimum value of 10 for the ratio  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ . Martinez et al. (2003) also presented a response surface to show the effect of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio on the degradation. Gulkaya et al. (2006) found a plateau in COD removal beyond 5.5 g/L ferrous sulfate. In a previous work (De et al. 2006), we found an even higher optimum  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ . The effects of high, medium, and low values of this ratio have been comprehensively discussed by Neyens and Baeyens (2003) and by Yoon et al. (2001).

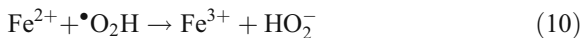
### 3.2 Degradation Model and Rate Constant

There has been considerable debate in the literature concerning the involvement of the hydroxyl radical in the Fenton's reaction. According to some authors (Turan-Ertas and Gurol 2002), the reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  would produce a highly reactive ferrate species instead of  $\bullet\text{OH}$ , in which the nominal oxidation number of Fe would be +4. The reactivity of such a species would be similar to that of  $\bullet\text{OH}$  with certain substrates, but in other cases, significant differences could be highlighted concerning the degradation intermediates and the rate constants as determined in competition kinetics (Kang et al. 2002). However, the relevant debate has not been resolved to date and, for instance, it is not possible to exclude that the ferrate species is a precursor of the  $\bullet\text{OH}$  radical and that either of the species reacts depending on the substrate that undergoes degradation. In the kinetic treatment that follows, the traditional representation

of the Fenton reaction that hypothesizes  $\bullet\text{OH}$  as the reactive species has been adopted. The chosen formalism could easily be adapted to a different reactive species.

The degradation process involves a series of reactions that have been reported in varying degree of details in a number of papers (see, for example, Neyens and Baeyens 2003; Kou 1992; Zhang et al. 2006; Kremer 2003; Bossmann et al. 1998; Lee et al. 2003). Kang et al. (2002) classified the possible reactions of the Fenton's system in three categories: inorganic reactions involving  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ , inorganic-organic reactions leading to mineralization, and Fe-organic reactions that influence the Fe-redox cycle. They listed the reaction rate constants of the various reactions collected from different sources. The major reactions are also outlined by Neyens and Baeyens (2003). Even Eq. 1, which is the principal route of generation of  $\bullet\text{OH}$  radicals, is associated with a series of reactions involving free radicals,  $\text{Fe}^{2+}$ , and  $\text{H}_2\text{O}_2$  in solution (Burbano et al. 2005). Similarly, multiple steps are involved in the process of oxidative degradation of the substrate. Elaborate studies have been done on Eq. 1 and on the degradation of selected organic compounds such as lower aromatic hydrocarbons and phenol. For practical purposes, it is adequate to consider only the major reaction steps in order to develop a rate model and to estimate the rate constants for the oxidation of the substrate and further degradation of the smaller species. It is to be noted that the total organic concentration (MEA and its degradation products) is expressed in terms of COD,

which is a practical measure of concentration of organic pollutants in wastewater.



Since the degradation rate is very fast at the beginning and most of the Fenton mineralization occurs within a few minutes of addition of the reagents, determination of the initial rate constant assumes greater practical importance. Quite a few species involved in the above reaction scheme are not present at the beginning, and  $\bullet\text{OH}$  is assumed to be the primary oxidizing species in the overall process. We consider Eqs. 1, 5, 7, and 8 only in this simplified analysis. Degradation of the substrate through Eq. 9 has been neglected since the rate of formation of  $\bullet\text{O}_2\text{H}$  radicals through Eq. 2 itself is much slower than the rate of formation of  $\bullet\text{OH}$  radicals (De Laat and Gallard 1999). The rate equation developed below is based on a “pseudo-steady-state” balance of the rates of generation and disappearance of the  $\bullet\text{OH}$  radicals.

Rate of formation of  $\bullet\text{OH}$  radicals [Eq.(1)]

$$= k_1 [\text{H}_2\text{O}_2] [\text{Fe}^{2+}] \quad (11a)$$

Rate of consumption of  $\bullet\text{OH}$  radicals (11b)

[Eqs.(5), (7), and (8)]

$$= k_5 [\text{H}_2\text{O}_2] + k_7 [\text{S}] [\text{Fe}^{2+}] + k_8 [\text{OH}] [\text{Fe}^{2+}]$$

Therefore,

$$\begin{aligned} -\frac{d}{dt} [\bullet\text{OH}] &= k_1 [\text{H}_2\text{O}_2] [\text{Fe}^{2+}] - k_5 [\text{H}_2\text{O}_2] [\bullet\text{OH}] - k_7 [\bullet\text{OH}] [\text{S}] \\ &\quad + k_8 [\bullet\text{OH}] [\text{Fe}^{2+}] \\ &= 0 \text{ (at pseudo-steady state)} \end{aligned} \quad (12)$$

$$\Rightarrow [\bullet\text{OH}] = \frac{k_1 [\text{H}_2\text{O}_2] [\text{Fe}^{2+}]}{k_5 [\text{H}_2\text{O}_2] + k_7 [\text{S}] + k_8 [\text{Fe}^{2+}]} \quad (13)$$

where  $k_1$ ,  $k_5$ ,  $k_7$ , and  $k_8$  are the rate constants for Eqs. 1, 5, 7, and 8, respectively, and a quantity in the square

bracket denotes its concentration. The initial rate of mineralization of the substrate can be written as

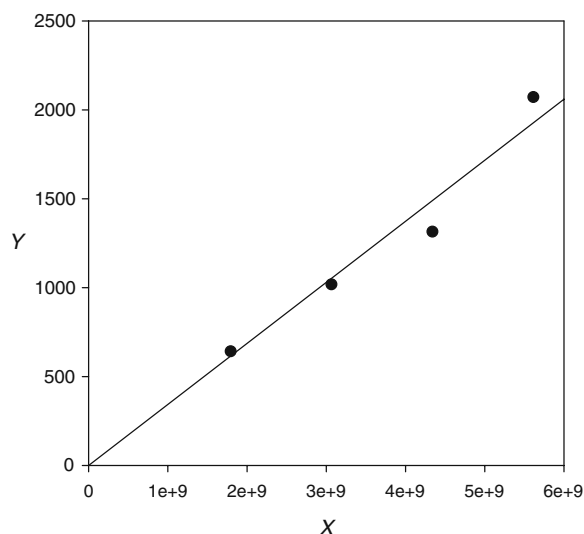
$$\begin{aligned} [r_s]_0 &= k_7 [\text{S}]_0 [\bullet\text{OH}]_0 \\ &= k_7 [\text{S}]_0 \frac{k_1 [\text{H}_2\text{O}_2]_0 [\text{Fe}^{2+}]_0}{k_5 [\text{H}_2\text{O}_2]_0 + k_7 [\text{S}]_0 + k_8 [\text{Fe}^{2+}]_0} \end{aligned} \quad (14)$$

where the subscript 0 denotes zero time. The equation can be rearranged to

$$\begin{aligned} &\left\{ \frac{k_1 [\text{H}_2\text{O}_2]_0 [\text{Fe}^{2+}]_0 [\text{S}]_0}{[r_s]_0} - [\text{S}]_0 \right\} \\ &= \frac{1}{k_7} \left\{ k_5 [\text{H}_2\text{O}_2]_0 + k_8 [\text{Fe}^{2+}]_0 \right\} \end{aligned} \quad (15)$$

$$\Rightarrow Y = \frac{1}{k_7} X \quad (16)$$

The above equation can be used to determine the degradation rate constant  $k_7$  from the experimental data on the initial rate of COD removal when only the concentration of added  $\text{H}_2\text{O}_2$  is varied keeping constant those of the substrate (S) and of  $\text{Fe}^{2+}$ . The rate constants  $k_1$ ,  $k_5$ , and  $k_8$  for Eqs. 1, 5, and 8, respectively, are available in the literature (De Laat and Gallard 1999; Lee et al. 2003). We have taken the following values of the above rate constants:  $k_1 = 70$ ,  $k_5 = 3 \times 10^7$ , and  $k_8 = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. A plot of the quantity  $Y$  against  $X$  (see Eq. 16) should produce a straight line passing through the origin with a slope equal to the inverse of the rate constant,  $k_7$ . In fact, the plot the experimental data in the form of Eq. 16 gives a straight line shown in Fig. 8. From the slope of the line, the rate constant for mineralization is estimated to be  $k_7 = 2.9 \times 10^6 \text{ M}^{-1} \text{ min}^{-1} = 4.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . It is to be noted that we have taken the calculated rate of degradation as the rate of removal of COD or, in other words, the rate of complete oxidation of the substrate. It may be considered to be a lumped representation of the process of degradation of the substrate and the intermediates taken together. As a comparison, consider that the second-order rate constant with  $\bullet\text{OH}$  of the similar compound ethylamine is around  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Buxton et al. 1988), which additionally suggests that the measured  $k_7$  is not the rate constant of the particular reaction between the Fenton's reactive species and MEA.



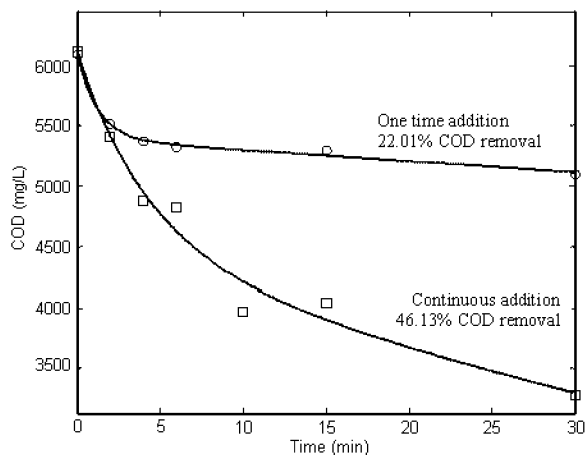
**Fig. 8** Plot of Eq. 14 for monoethanolamine degradation

### 3.3 Effect of the Mode of $H_2O_2$ Addition

One-time addition of  $H_2O_2$  to the reaction mixture was carried in this work. However, we have also compared the effect of  $H_2O_2$  feeding in the continuous mode with that of one-time addition of the reagent. More  $\bullet OH$  radicals would be generated at the beginning in the latter mode of addition, and more scavenging of the radicals would occur as a result. In an experimental run taken in the continuous mode, the same quantity of  $H_2O_2$  was added to the reaction mixture over a 30-min run time at a constant rate using a peristaltic pump. The comparison of the COD reduction is shown in Fig. 9. It appears that the final COD removal is more than double for the continuous feeding mode as compared with the case of one-time dosing under otherwise identical process conditions. The time evolution of  $H_2O_2$  concentration in solution was determined by titration against a standard potassium permanganate solution after separation of the iron oxide particles. For one-time addition, hydrogen peroxide concentration drops down very fast during the first 2–3 min and slows down thereafter. For continuous addition, the  $H_2O_2$  concentration builds up slowly while it is consumed simultaneously. However, the  $H_2O_2$  concentrations at the end of 30 min run converge to nearly equal values.

### 3.4 Efficiency of $H_2O_2$ Utilization

Hydrogen peroxide is the source material for the generation of the  $\bullet OH$  radicals. In the complex



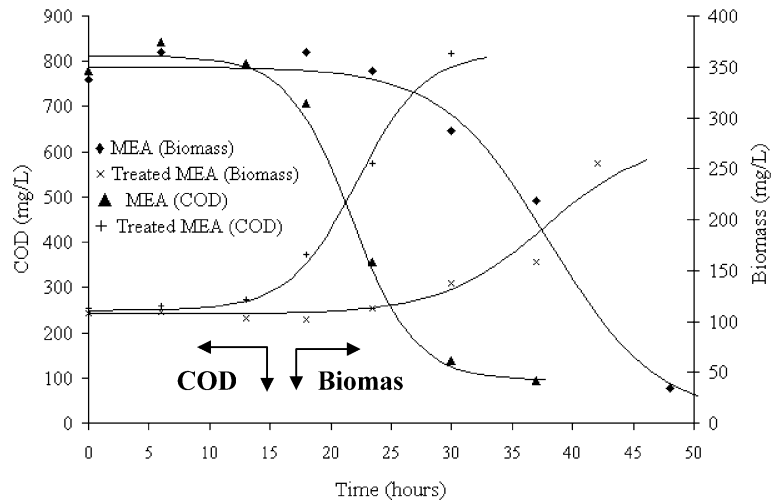
**Fig. 9** Comparison of chemical oxygen demand removal for one-time addition and continuous addition of  $H_2O_2$

sequence of reactions that follow, a part of the reagent is decomposed to gaseous oxygen that does not contribute to the degradation of the substrate. We attempted to make an estimate of the efficiency of  $H_2O_2$  utilization by analyzing a few samples withdrawn at minutes after the reaction started. The samples were analyzed for the COD and the unreacted  $H_2O_2$  remaining in the liquid soon after filtering out the iron. For example, while treating a low COD feed solution (0.013 M amine) with 0.231 M  $H_2O_2$  and 0.00288 M  $Fe^{2+}$ , a sample at 10 min was found to contain 20% of the original  $H_2O_2$ . About 50% of the decrease of  $H_2O_2$  could be accounted for by the loss of COD and the oxidation of the iron(II) to iron(III). The remaining 30% could not be accounted for and was presumably lost. It is to be noted that  $H_2O_2$  undergoes slow catalytic decomposition in presence of ferric oxides, and this explains the loss of the reagent during the process (De Laat and Gallard 1999). However, the efficiency of utilization was better for a higher COD feed solution.

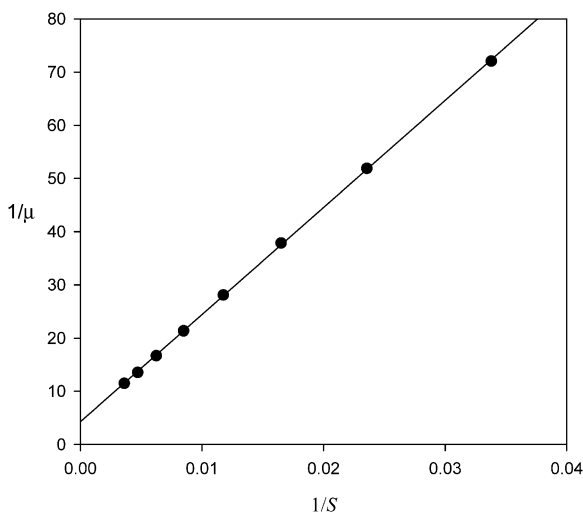
### 3.5 Biological Oxidation of MEA and Partially Degraded MEA

A sample of MEA solution was degraded with Fenton's reagent to remove 40% of the COD, the ferric sludge was separated, and the clear liquid was diluted to adjust the COD to 1,000 mg/L. It was subjected to biological oxidation using activated sludge collected from the central wastewater treatment plant of this university.

**Fig. 10** Chemical oxygen demand degradation and mixed-liquor suspended solids (MLSS) profile for biological oxidation of partially degraded monoethanolamine (MEA) and pure MEA; biomass concentration in 100 mg/L MLSS (US EPA 1998)



The change of biomass and substrate concentration with respect to time for both partially degraded MEA and untreated MEA are shown in Fig. 10. The data clearly indicate that the biomass acclimatization was much faster in partially degraded amine compared to untreated MEA; the “lag phase” for the former was about 50% of that for the latter. Glycine, an amino acid, and other degradation intermediates expectedly promote faster growth of the biomass. The duration for maximum COD removal was about 30 h for the partially degraded MEA as compared to 50 h for MEA. The ultimate COD removal (substrate utilization) does not seem to have been affected by Fenton’s oxidation. Nonetheless, the biomass yield appears to be higher in partially degraded MEA.



**Fig. 11** Monod plot for partially degraded monoethanolamine

In order to quantify biological oxidation of the substrates, we have selected the Monod model that describes the relationship between the biomass growth rate and the substrate concentration and is represented by Eqs. 17 and 18 below:

$$\mu = \mu_{\max} \frac{S}{K_S + S} \quad (17)$$

$$k = k_{\max} \frac{S}{K_S + S} \quad (18)$$

where  $\mu_{\max}$  is the maximum specific growth rate ( $\text{h}^{-1}$ ),  $K_S$  is the half saturation coefficient (mg/l COD), and  $k_{\max}$  is the maximum substrate utilization rate ( $\text{h}^{-1}$ ). The constants  $K_S$  and  $\mu_{\max}$  can be obtained from the slope and intercept of a plot of  $1/\mu$  against  $1/S$ . Such a plot for partially degraded MEA by Fenton’s reagent is shown in Fig. 11. The calculated rate parameters for biological oxidation are presented in Table 1.

**Table 1** Estimated Monod kinetic constants for “pure” monoethanolamine (MEA) and partially degraded MEA

	$\mu_{\max}$ ( $\text{h}^{-1}$ )	$K_S$ (mg/ l COD)	$k_{\max}$ ( $\text{h}^{-1}$ )
Untreated MEA	0.14	691	0.63
Partially degraded MEA (after 40% COD removal)	0.24	475.6	0.67

#### 4 Conclusions

The results of this study shows that the Fenton's reagent could be effectively used for partial degradation of a high COD simulated wastewater containing MEA at concentrations comparable to that found in wastewaters from natural gas treating plants. Very fast removal of COD occurs within the first a few minutes. The degradation rate slows down thereafter even if unreacted  $\text{H}_2\text{O}_2$  remains in the solution. The extent of degradation attains a peak with increase in  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentration. A pH of 3 is found to be the optimum. A fraction of the  $\text{H}_2\text{O}_2$  decomposes by the catalytic action of the Fe(III) oxide particles to release oxygen, and its oxidizing capacity could not be fully exploited. However, continuous dosing of the reagent rather than one-time addition yielded significantly higher degradation and a better utilization of  $\text{H}_2\text{O}_2$  as a result. At a low initial amine concentration, the rate of COD removal is slow because a part of the hydroxyl radicals is wasted by decomposition before reaction with the organic substrates. A rate model was proposed on the basis of a simplified set of reaction steps, and a rate equation for degradation of the substrate was developed with pseudo-steady-state approximation. The lumped degradation rate constant was evaluated from the experimental data using this model. Since COD removal rate becomes slow after partial degradation, the AOP was followed by biodegradation. Activated sludge from a local wastewater treatment facility was used. Biological oxidation of the partially degraded amine was substantially higher with less acclimatization time than the "pure" amine. Almost complete COD removal could be achieved within 24 h. The biodegradation process followed the Monod kinetics. The rate parameters for biological oxidation have been reported.

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