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Degradation of diethanolamine by Fenton's reagent combined with biological post-treatment

Binay K Dutta[1]*, Sabtanti Harimurti[2], , Sampa Chakrabarti[3] and Davide Vione[4]

[1] Chemical Engineering Program, The Petroleum Institute, Abu Dhabi, UAE (bdutta@pi.ac.ae)
[2] Chemical Engineering Program, Universiti Teknologi Petronas, Malaysia
[3] Department of Chemical Engineering, Calcutta University, India
[4] Dipartimento di Chimica Analitica, Università di Torino, Italy

Abstract: Effectiveness of the Fenton's reagent for partial degradation of diethanolamine (DEA) prior to biological treatment is investigated. The effects of the major process parameters on the time evolution of COD, an indicator of the extent of degradation, were measured. The DEA concentration ranged from 800 to 16,000 ppm, in consideration of the COD of real effluents of natural gas processing plants. The initial reaction rate was a strong function of the feed amine concentration. About 70-80% of the ultimate COD removal could be achieved within three minutes. The pH of the medium was varied over 1-4; the best results were obtained at pH 3. The effectiveness of a hybrid scheme of advanced oxidation followed by biodegradation was explored. Activated sludge from a local wastewater treatment pond was used. Fast COD removal of the partially degraded DEA was achieved within a day. Biodegradation of pure DEA was much slower, apparently because of the acclimatization time of the microbes.

Keywords: Diethanolamine; advanced oxidation; Fenton's reagent; biodegradation

INTRODUCTION

Alkanolamines, mainly mono- and di-ethanolamine as well as hindered amines, are extensively used in natural gas sweetening and other processes, involving removal of carbon dioxide. Release of the amines in wastewater occurs during routine cleaning of the absorption and stripping towers as well as during a process upset. In such circumstances, the amine concentration in the wastewater may become too high to be amenable to conventional biological oxidation [1]. Sometimes the wastewater with a high amine loading is disposed of by incineration, which is an expensive option for aqueous solutions [2]. As such, development of an alternative strategy of remediation of amine-loaded wastewater would be greatly useful to the gas processing industry.

Advanced oxidation processes (AOPs) include techniques of degradation of recalcitrant or poorly biodegradable organics by oxidizing species such as hydroxyl ($OH^{\bullet}$) and hydroperoxyl ($^{\bullet}OH_2$) radicals [3-13]. These radicals can be generated by a number of techniques, such as O_3/UV, O_3/H_2O_2, H_2O_2/UV, O_3/H_2O_2/UV, TiO_2/UV, Fe^{2+}/H_2O_2 (Fenton's reaction) and a few more [14]. The Fenton's reaction is used in this work for the remediation of diethanolamine (DEA) in an aqueous solution.

The effectiveness of the Fenton's reagent for the degradation of organic pollutants in wastewater has been reported in a large number of publications. The substrates include aromatic hydrocarbons and other compounds such as amines, phenol and substituted phenols, polycyclic aromatics, chlorinated hydrocarbons and more complex molecules like dyes, pharmaceuticals, alcohols, mineral oils, etc. Lou and Lee [3] used Fenton's reagent to destroy benzene, toluene and xylene (BTX). Almost complete removal was achieved within short time (ten minutes). Degradation of aromatic amines (aniline and a few substituted anilines) was studied by Casero et al. [4], who also identified the transformation intermediates by mass spectrometry. Complete mineralization was achieved within one to three hours. Mineralization of aniline was also studied by Brillas et al. [5] by using a few advanced oxidation techniques – such as anodic oxidation, photo-catalysis, electro-Fenton and photo-Fenton reactions. UV irradiation was found to accelerate the relevant processes. Another study into the degradation of aniline was carried out by Anatoi et al., using Fenton and photo-Fenton techniques [7]. A negative order of aniline removal with respect to the Fe(II) concentration was reported. De et al. [6] studied the degradation of phenol and chlorinated phenols. Interestingly, improvement of the biodegradability of organic pollutants by Fenton's pre-oxidation has been explored by a few researchers. Alaton and Teksoy [8] studied the effectiveness of Fenton's reagent to pre-treat acid dye-bath effluents of a textile industry before conventional biological treatment. Biodegradation of a pharmaceutical wastewater was greatly improved by Fenton's treatment as reported by Tekin et al. [9], because the breakdown of the organics into smaller fragments made the waste amenable to normal biological oxidation. An interesting aspect of coupling Fenton pre-treatment and biological degradation is that the cost of pollutant removal would be significantly lower compared to Fenton degradation alone. Moreover, the preliminary oxidation would enable application of the relatively cheap biological treatment to non-biodegradable or poorly biodegradable wastes. Another advantage of the Fenton process is that Fe(II) can be added as such or produced from the cheaper Fe(III) by photochemical, electrochemical or sonochemical processes [7, 12, 14-16].

To our knowledge, few or no works have studied so far the degradation of DEA with the Fenton's reagent, and *a fortiori* no study has been carried out into the effect of the Fenton pre-treatment on the biodegradation of DEA and its transformation intermediates. The present study focuses on

the partial degradation of DEA, followed by the biological post-treatment. The effects of important process parameters such as reagents dose (H_2O_2 and $FeSO_4$, $7H_2O$), the amine concentration and pH have been investigated in detail. Identification of the main intermediates formed during Fenton's degradation was carried out, and the patterns of COD removal as compared to TOC and total initial nitrogen have been studied. Biological oxidation has been carried out following standard procedures [17].

MATERIALS AND METHODS

The chemicals used in the work were purchased from the following manufacturers: DEA and sodium hydroxide from R & M Chemicals (UK); hydrogen peroxide (30%) and $KMnO_4$ from Merck (Germany); $FeSO_4 \cdot 7H_2O$ from HmbG Chemicals (Germany); H_2SO_4 (analytical grade) from Systerm (Germany).

Experimental set-up and procedure

Experimental runs were carried out in a double-walled glass reactor (1 liter volume), with a ground glass cover that can be fixed by clips. The reactor was provided with pH and temperature probes. Temperature was maintained by circulating water at a controlled value through the glass jacket of the reactor. Mixing of the internal solution was carried out with a stirring bar and a magnetic stirrer placed under the reactor. A solution of the amine at the desired concentration was prepared (synthetic wastewater) and the pH was adjusted by drop-wise addition of sulfuric acid. The requested amount of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was added and the content was mixed well. This was followed by addition of a measured quantity of 30% H_2O_2. The effective reaction volume was about 800 ml. The reaction started immediately and the temperature was maintained by the cooling water circulating through the jacket as stated before. Samples of the liquid were withdrawn from time to time using a syringe and analyzed for the COD, unreacted amine, and residual H_2O_2.

Biodegradability test of partially degraded DEA

Since Fenton's treatment would require a large amount of reagents to achieve complete degradation, coupling of this process with biological oxidation was carried out. Partially degraded DEA was prepared by the Fenton's process. Biodegradation experiments were conducted in a 1 L beaker as an aerobic batch bioreactor following the EPA method (OPPTS

835.3200 Zahn-Wellens/EMPA Test) [17]. Partially degraded DEA solution diluted to about 1000 mg/L COD was mixed with activated sludge having about 1000 mg/L mixed liquor volatile suspended solids (MLVSS, dry matter) from the central wastewater treatment plant of the Petronas University (Malaysia). Samples were withdrawn from the batch bioreactor periodically and the COD, pH, dissolved oxygen (DO), and oxygen uptake rate (OUR) were measured. Observations were made until no further changes in COD were noted. A parallel set of biodegradation experiments was conducted with a pure DEA solution of the same initial COD. Two additional sets of experiments were run in parallel – one using 1000 ppm ethylene glycol (a reference compound, see the EPA method) of the same COD as the partially degraded DEA, and a blank experiment for comparison.

Analytical methods

The course of Fenton oxidation and biological oxidation was determined by COD measurement, using a Hach 5000 instrument and following standard procedure (Method 8000). Removal of H_2O_2 prior to COD analysis was done by warming each sample in a boiling water bath for 10 minutes, after addition of 2 ml of a 1 M NaOH solution to 8 ml of sample. The addition of NaOH was intended to stop the Fenton reaction and to increase the pH above 7. The precipitated hydrated ferric oxide was removed by filtration using a 0.45 μm filter membrane, and the COD of the sample was measured. The change of volume of the sample at different steps was taken into account for COD calculation.

An Agilent series 1100 HPLC (High Performance Liquid Chromatograph) was used to monitor the by-products and unreacted DEA after the Fenton's treatment. YMC-Pack PolymerC18 column was used, with 100mM Na_2HPO_4/100mM NaOH (60/40, pH 12) as eluent, and UV detection (215 nm and 253nm). A Perkin Elmer Spectrum One Fourier Transform Infrared spectrometer was used to obtain the infrared spectra. pH measurement was performed using a pH probe (HACH sens ion 1). Dissolved Oxygen (DO) and Oxygen Uptake Rate (OUR) measurements during the biodegradability test were conducted with HQ30d flexi HACH DO meter with LD0101 DO probe. TOC was determined with a HACH 5000 spectrophotometer and a standard TOC measurement kit.

RESULTS AND DISCUSSION

Treatment studies with Fenton's oxidation

In the acidic pH range, hydrogen peroxide in the presence of ferrous ions undergoes a series of redox reaction, of which the main ones are the following [18]:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^{\bullet} \quad (R1)$$

$$OH^{\bullet} + Fe(II) \rightarrow Fe(III) + OH^- \quad (R2)$$

$$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad (R3)$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (R4)$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H^+ + HO_2^{\bullet} \quad (R5)$$

$$Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + H^+ + O_2 \quad (R6)$$

$$R^{\bullet} + Fe(III) \rightarrow Fe(II) + product \quad (R7)$$

The degradation of organic substrates normally proceeds through hydrogen abstraction (R3) and the reaction rate is controlled by the generation of $OH^{\bullet}$ radicals (R1), which in turn depends upon the concentrations of H_2O_2 and $FeSO_4$. Note that R3 competes with other reactions (R2, R4) that scavenge $OH^{\bullet}$ and may lead to loss of the oxidation power in the system [18].

Interestingly, the production of $OH^{\bullet}$ in the Fenton's reaction takes place via a fast step (R1) that involves Fe(II) and H_2O_2, followed by a considerably slower process that proceeds through the reduction of Fe(III) to Fe(II) (R5-R7) and ends up in R1. The acceleration of Fe(III) reduction, which controls the degradation rates after the very fast initial step, is the main target of the photo-Fenton and electro-Fenton techniques [15, 19]. In some cases the reduction of Fe(III) could be enhanced by quinones, aromatic additives and even humic acids. These compounds, despite their action as $OH^{\bullet}$ scavengers, would be able to enhance degradation by accelerating the slow step of the process [20-22]. Also the transformation intermediates of a given substrate, or the substrate itself, could play a role in the process of Fe(III) reduction.

In this study, rather mild conditions of Fenton treatment were used because the main target was to enhance biodegradability of DEA, rather than achieving complete degradation by the Fenton's reagent alone. The effects of initial concentration of DEA, concentration of H_2O_2, pH and the concentration of ferrous ion were studied independently. The ranges of values of the variables used in the experiments are DEA concentration: 800-16,000 ppm (7.6 mM – 0.15 M); pH: 1 to 4; $FeSO_4,7H_2O$: 0.4 to 16 g in 800 ml solution (1.8 to 72 mM); and H_2O_2 (30% w/w): 50 to 200 ml in 800 ml solution (0.61 to 2.44 M).

Effect of initial DEA concentration

The rate of removal of COD was found to be strongly dependent on the initial DEA concentration. Figure 1 shows that the COD removal was very slow when the DEA concentration was small: it was only 17.9% after 30 minutes for a 800 ppm initial COD solution (7.6 mM DEA). In contrast, about 25-35% COD removal was achieved within 5 minutes when the initial concentration was 16,000 ppm (0.15 M DEA). Note that, while increasing the initial concentration of DEA, the concentrations of both Fe(II) and H_2O_2 where also increased so as to keep constant the concentration ratios Fe(II):H_2O_2:DEA. The adopted pH was 3.

The sharp decrease of COD in a small time (around 1 min), followed by a much slower decrease afterwards, can be ascribed to the combination of a very fast initial reaction (R1 between Fe^{2+} and H_2O_2) and a considerably slower process of Fe(III) reduction. A contribution to slowing down the degradation reactions at longer time could also derive from the transformation intermediates of MEA (*vide infra*). The COD data suggest that the rate of the slower process increases with increasing the concentrations of Fe(II) and H_2O_2. This is reasonable considering that the reduction of Fe(III), which derives from the quantitative initial oxidation of Fe(II), takes place via bimolecular reactions that involve Fe(III) itself and H_2O_2, or H_2O_2–derived radical species.

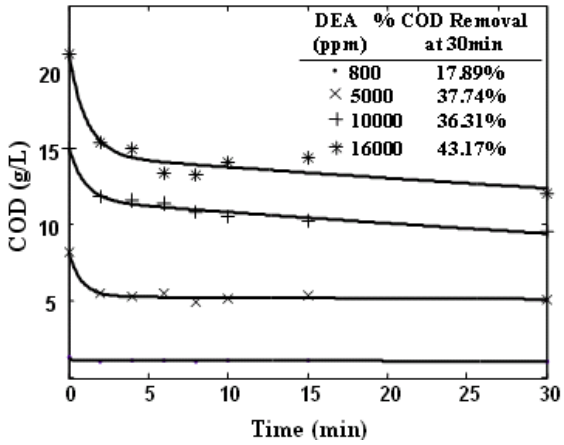

Figure1. Effect of initial DEA concentration on degradation at pH 3 [800 ppm (7.6 mM) DEA, 1.8 mM $FeSO_4$,$7H_2O$, 0.11 M H_2O_2; 5000 ppm (48 mM) DEA, 11 mM $FeSO_4$,$7H_2O$, 0.67 M H_2O_2; 10000 ppm (95 mM) DEA, 22 mM $FeSO_4$,$7H_2O$, 1.3 M H_2O_2; and 16000 ppm (150 mM) DEA, 36 mM $FeSO_4$,7H2O, 2.1 M H_2O_2].

Effect of hydrogen peroxide concentration

By increasing the concentration of H_2O_2 one would expect the reaction R1 to be faster and the production rate of $OH^{\bullet}$ to increase. However, H_2O_2 is also able to scavenge the hydroxyl radicals (R4). It is, therefore, of interest to study the effect of H_2O_2 concentration on the COD removal. The relevant experiments were carried out at pH 3 and at four different H_2O_2 concentrations, while keeping the amine and $FeSO_4,7H_2O$ constant. The maximum COD removal was achieved at 2.1 M H_2O_2, with 16,000 ppm DEA (0.15 M) and 36 mM $FeSO_4,7H_2O$. Above 2.1 M H_2O_2, no further increase of degradation could be observed (see Figure 2). The plateau (or even the slight decrease) of COD removal observed at and above 2.1 M H_2O_2 can be ascribed to the scavenging of $OH^{\bullet}$ by hydrogen peroxide. Indeed, the second-order reaction rate constant between $OH^{\bullet}$ and the diethylammonium ion (the prevailing form of DEA under the adopted pH conditions) is 1.3×10^8 M^{-1} s^{-1}, to be compared with 2.7×10^7 M^{-1} s^{-1} for H_2O_2 [23]. Accordingly, hydrogen peroxide would prevail over DEA as hydroxyl scavenger for $[H_2O_2]/[DEA] > 4.8$ (*i.e.*, for $[H_2O_2] > 0.72$ M in the case of 0.15 M DEA).

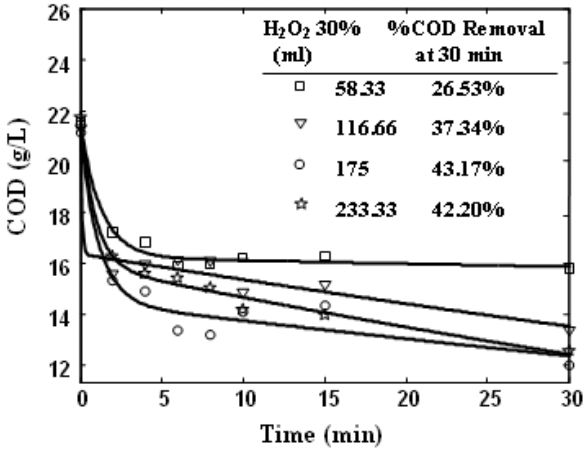

Figure 2. Effect of H_2O_2 on DEA degradation [16000 ppm (0.15 M) DEA, 36 mM $FeSO_4,7H_2O$ at pH 3, at four different H_2O_2 concentrations].

Effect of $FeSO_4 \cdot 7H_2O$ concentration

The effect of $FeSO_4$ dosing on COD removal was measured at an initial DEA concentration of 16,000 ppm (0.15 M) and with constant 2.1 M H_2O_2, at pH 3. The time evolution of COD is shown in Figure 3. The reduction of COD during the first five minutes was highest for 36 mM $FeSO_4$ (8 g in 800 mL), conditions that also afforded the maximum removal of COD after 30 min.

Interestingly, the percentage of COD removal after 30 min would plateau at approximately 40% for $FeSO_4,7H_2O \geq 36$ mM. Note that the second-order reaction rate constant between Fe^{2+} and $OH^{\bullet}$ is 4.3×10^8 M^{-1} s^{-1} [23], thus Fe^{2+} would prevail over DEA as $OH^{\bullet}$ scavenger for $[Fe^{2+}]/[DEA] = 0.3$ (*i.e.*, for $[Fe^{2+}] > 45$ mM at 0.15 M DEA). However, 2.1 M H_2O_2 would still be the most important $OH^{\bullet}$ scavenger in the system at all the adopted concentration values of Fe(II).

The results reported in Figure 3 suggest that the addition of $FeSO_4,7H_2O$ above 36 mM would not help to increase the COD removal in the presence of 0.15 M DEA and 2.1 M H_2O_2.

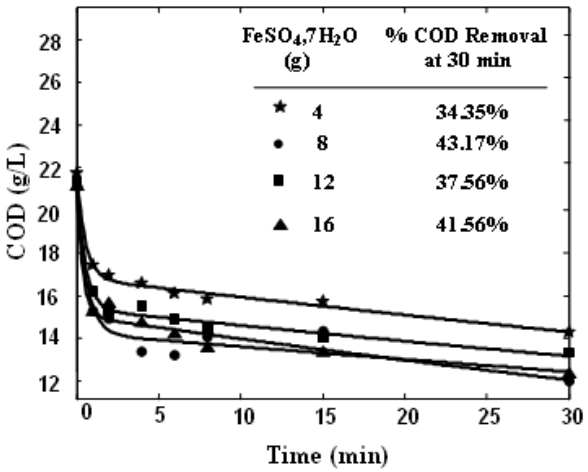

Figure 3. Effect of $FeSO_4;7H_2O$ on DEA degradation (0.15 M DEA and 2.1 M H_2O_2 at pH 3) for different concentrations of $FeSO_4;7H_2O$: 18, 36, 54 and 72 mM, respectively.

Effect of pH

The Fe(II)/Fe(III)-H_2O_2 system has its maximum activity at pH 2.8-3 [24]. A higher or lower pH sharply reduces the effectiveness of the Fenton's reaction. At low pH the complexation of Fe(III) with hydrogen peroxide is inhibited, therefore inhibiting the step of H_2O_2 reduction [18], while at a high pH ferric ions precipitate as ferric hydroxide, which catalyzes the decomposition of hydrogen peroxide.

Zhang et al [25] reported that the optimum pH for the treatment of landfill leachate by Fenton's reagent was 2-3.5. With pH values higher than 3.5, removal efficiency decreased. In this study the best pH was found to be 3, with limited differences in the 2-3 pH range. The effect of pH on DEA

degradation is depicted in Figure 4. Interestingly, in the case of pH 1 the initial decrease of COD was significant, but no further decrease was observed at longer reaction time. This is in agreement with a very slow reduction of Fe(III) to Fe(II) at pH 1, as reported in the literature [18].

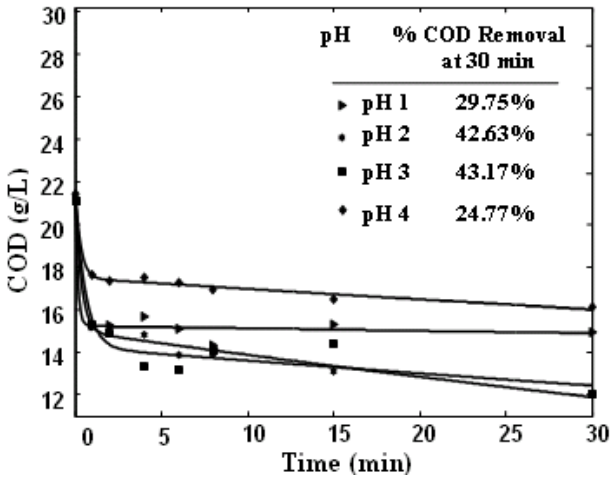

Figure 4. Effect of pH on the degradation DEA [0.15 M DEA, 36 mM $FeSO_4,7H_2O$, 2.1 M H_2O_2 at different pH: 1-4].

Comparison of COD and TOC removal

The patterns of COD and TOC variations in the course of DEA degradation were similar. COD and TOC underwent fast decrease in the initial step, and the decrease slowed down thereafter. Figure 5 shows the corresponding COD and TOC evolution.

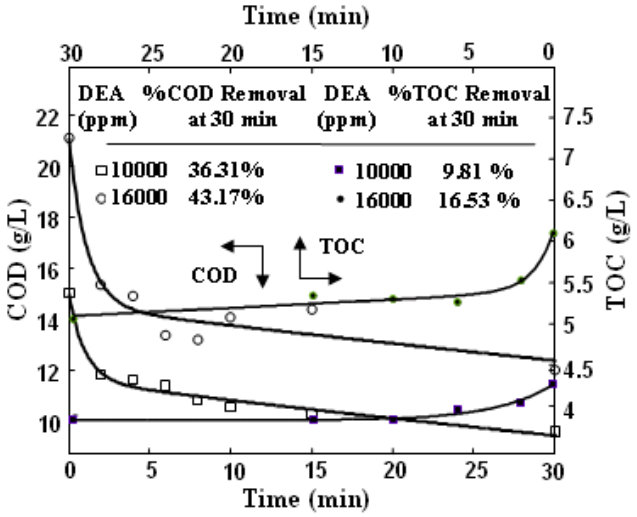

Figure 5. Decrease of COD and TOC by Fenton's reagent. [0.095 and 0.15 M DEA initial concentration (10,000 and 16,000 ppm, respectively)]. Note that COD evolution is plotted vs. the lower *x* axis, TOC vs. the upper one (which has opposite direction)

Figure 5 shows that the decrease of TOC was more limited than that of COD: 9.8 and 16.5% TOC removal was observed for the two adopted initial concentrations of DEA, to be compared with 36.3 and 43.2% for the decrease of COD. Note that the removal of TOC and that of COD can reflect rather different pathways. For the TOC to decrease, it is necessary for the substrate to lose organic carbon atoms and that these atoms are transformed into inorganic carbon (CO_2). In contrast, the decrease of COD can be carried out also by abstraction of hydrogen atoms, a process that is expected to take place upon reaction between DEA and $OH^{\bullet}$, without the need of losing carbon atoms as CO_2. The data reported in Figure 5 suggest that the degradation in the initial 30 minutes could proceed via oxidation of the carbon chains, with limited mineralization. Also note that cleavage of the ethyl groups of DEA to give free, oxidized C_2 organic compounds would decrease the COD but not the TOC. A likely oxidation pathway of the carbon chains would be the production of carboxylic acids, which is partially confirmed by the detection of glycine among the transformation intermediates (*vide infra*). This could also be the preliminary step to mineralization, because the oxidation of the carboxylic group could yield CO_2 [26].

Degradation using stoichiometric amounts of H_2O_2 and $FeSO_4$

An interesting feature of the Fenton's reaction that has already been cited is that, after the fast first step (R1), the process continues more slowly through the reduction of Fe(III) to Fe(II). The occurrence of the second process implies that some residual H_2O_2 is still available for the reactions R5-R7 to take place and, therefore, that H_2O_2 is added in excess with respect to Fe(II). If, on the contrary, stoichiometric amounts of both H_2O_2 and Fe(II) are used, it would be possible to produce $OH^{\bullet}$ very quickly in the first step alone. Figure 6 shows the time trends of COD and H_2O_2 in the presence of 48 mM DEA + 0.55 M H_2O_2 + 0.55 M $FeSO_4$,$7H_2O$. It is noticeable the almost complete disappearance of H_2O_2, as can be expected by a quantitative reaction between Fe(II) and hydrogen peroxide, and a 60% decrease of the COD. Note that after the initial fast decrease, no further disappearance of COD is detected at longer reaction time. This is compatible with the practically complete consumption of hydrogen peroxide, after which the reduction of Fe(III) to Fe(II) and the subsequent generation of $OH^{\bullet}$ would no longer be possible. Also note that the complete mineralization to CO_2 of the carbon chains of a DEA molecule would require 24 electrons and that $OH^{\bullet}$ is a monoelectronic oxidant, whether is reacts by abstraction of electrons or by abstraction of hydrogen atoms [23]. The Fenton's reagent (Fe(II)+H_2O_2) was used in a 11.5:1 molar ratio compared to DEA, and the 60% decrease of the COD is a reasonable result considering that 100% decrease would imply complete oxidation to CO_2. It could even be inferred that some Fe(III), generated in reaction (1), could be involved in the oxidation of DEA or of its transformation intermediates, because from the (Fe(II)+H_2O_2):DEA molar ratio one would foresee a 50% COD decrease if $OH^{\bullet}$ alone was involved in the degradation. However, the addition of Fe(II) in stoichiometric ratio to H_2O_2 in the Fenton's reaction would increase the treatment costs, thus it is also convenient to investigate the use of the Fenton process as a pre-oxidation step before biological treatment.

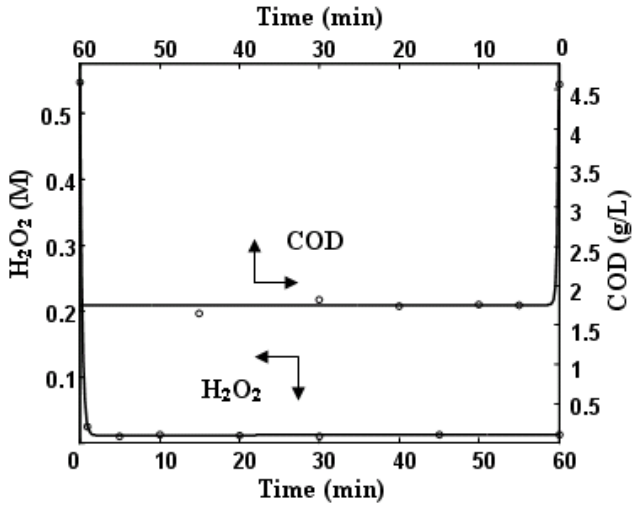

Figure 6. COD profile with 48 mM DEA + 0.55 M H_2O_2 + 0.55 M $FeSO_4$,$7H_2O$ at pH 3. Note that H_2O_2 evolution is plotted vs. the lower *x* axis, COD vs. the upper one (which has opposite direction)

Degradation intermediates

An attempt was made to identify the degradation intermediates by HPLC and FTIR. A sample of liquid after 15 minute Fenton's treatment was run on HPLC. The chromatogram (Figure 7) shows quite a few peaks, one of them being glycine that appears at around 4 minutes. No peak for DEA in the sample was found under the given reaction conditions (retention time around 5.4 minutes); essentially the whole of it had been oxidized. FTIR spectra of the samples (Figure 8) give evidence about functional groups of the degradation intermediates in partially degraded DEA. A carbonyl (C=O) peak appears around 1620 cm^{-1} [(C=O) as carboxylic acid] and bonding between C and N appears on the center of the peak at 1080 cm^{-1} [(C–N) as aliphatic amine]. The sample was in aqueous solution, thus the peak of water (H_2O) is very broad in the region between 3000 – 3700 cm^{-1} and covers many peaks for N–H (amine), O–H (carboxylic acid) and O–H (alcohol) that should be appear in that region. In addition, peaks centered at 2090 cm^{-1} appear as interaction between COO^- from the carboxylic group and N^+ from the ammonium group [27]. Overall, the FTIR results suggest that at least some of the transformation intermediates have retained the C-N bond and that at least some of the lateral carbon chains have been oxidized to carboxylic acids. Both features are compatible with the HPLC detection of glycine as transformation intermediate.

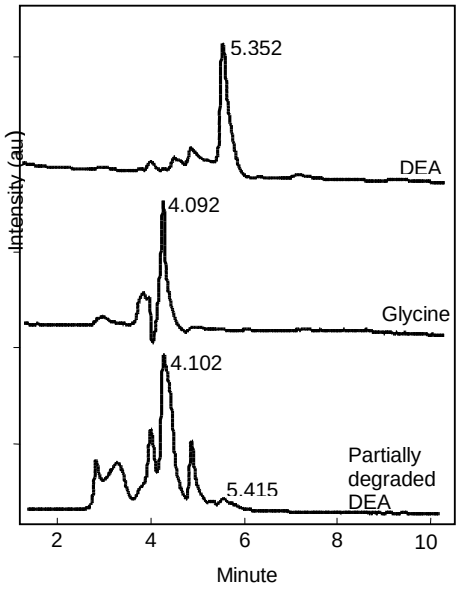

Figure 7. Chromatogram of DEA, glycine and partially degraded DEA.

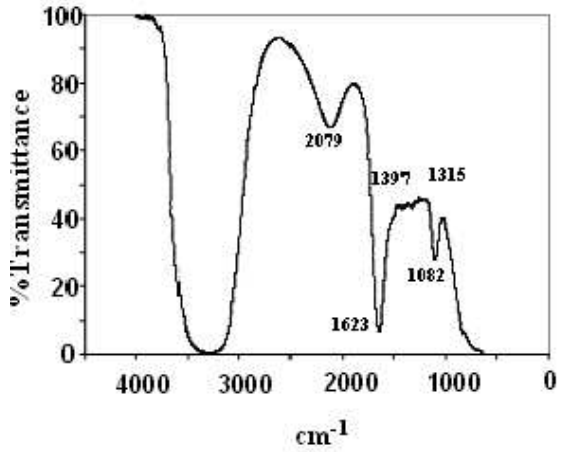

Figure 8. Infrared spectra of partially degraded DEA.

Biodegradation studies of partially degraded DEA

The removal of COD accounted for by DEA and its intermediates would require quite large amounts of Fe(II) and H_2O_2, thus making the treatment rather expensive. However, as stated before, Fenton's reagent is suitable for the partial degradation of organics followed by biological oxidation of the fragments of the original compound. Accordingly, we have carried out biological oxidation of partially degraded DEA using the EPA method OPPTS 835.3200 [17].

A sample of the liquid after about 40% COD removal was subjected to biological oxidation using activated sludge collected from the University wastewater treatment plant. The COD profile of the liquid diluted to an initial COD level of 1000 ppm is plotted in Figure 9. The biological oxidation of 'pure' DEA at the same initial COD level was run in parallel. The results show that the COD of the partially degraded solution is reduced to below 100 ppm within 24 hours. The degradation rate of DEA was much slower, which is probably due to the time required for acclimatization of the bacteria. The oxygen uptake rates (OUR) for both sets of experiments are shown in Figure 10. For 'pure DEA' the growth-phase of the bacteria and the oxygen uptake start after a long time (>50 hours), whereas for the partially degraded solution oxygen uptake starts from the beginning. The OUR trend reflects quite closely that of the COD of the two samples, where further degradation of partially degraded DEA starts at once while 'pure' DEA has a lapse time of over 50 hours (Figure 9).

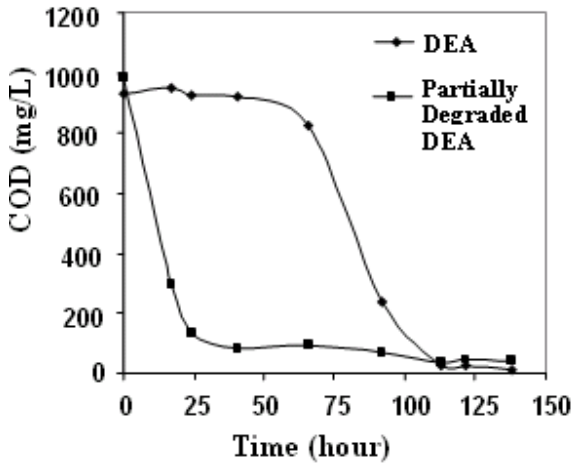

Figure 9. COD profile of degradation of DEA compared with partially degraded DEA by activated sludge.

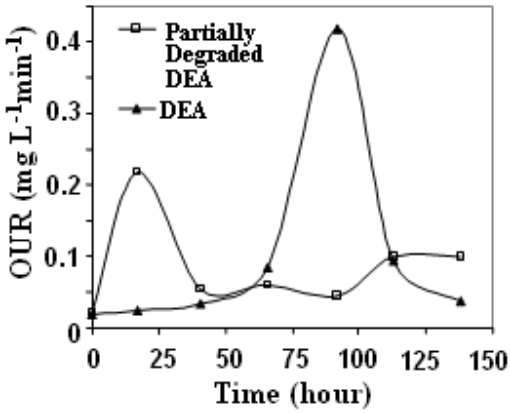

Figure 10. OUR Profile of DEA compared with partially degraded DEA by activated sludge.

CONCLUSIONS

Diethanolamine, a common chemical for acid gas treatment, can be partially degraded by the Fenton's method without excessive consumption of reagents that would, in contrast, be required for complete degradation. The rate of degradation is very fast in the first few minutes because of fast generation of hydroxyl radicals by the reaction between Fe(II) and H_2O_2. The optimum pH was 3, in agreement with literature data concerning the Fenton degradation of most organic substrates. The COD removal after 30 minutes reaction time reached a plateau in the presence of a high dose of either H_2O_2 or $FeSO_4$. Scavenging of $OH^{\bullet}$ could account for this finding, particularly in the case of H_2O_2. Glycine was detected among the transformation intermediates. The partially degraded solution could be effectively degraded by the conventional biological treatment, and the biodegradation of pure DEA was much slower than for the partially degraded material. Accordingly, the combination of Fenton pre-oxidation and biological treatment has potential advantages over the separate techniques, because the Fenton's reaction alone would be quite costly if complete degradation is to be achieved, and the biological treatment alone would be quite slow. The findings of this study will be potentially useful for the treatment of DEA in the wastewater from natural gas processing plants.

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