



Assessment of Fenton's reagent and ozonation as pre-treatments for increasing the biodegradability of aqueous diethanolamine solutions from an oil refinery gas sweetening process

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ARTICLE INFO

Article history:

Received 1 June 2010

Received in revised form 1 December 2010

Accepted 10 December 2010

Available online 21 December 2010

Keywords:

Spent amine

Fenton's reagent

Ozone

Advanced oxidation

Biodegradability test

ABSTRACT

The aim of this work was to evaluate the efficiency of three chemical oxidation processes for increasing the biodegradability of aqueous diethanolamine solutions (aqueous DEA solutions), to be used as pre-treatments before a biological process. The raw aqueous DEA solution, sourced from a sour gas sweetening plant at a Mexican oil refinery, was first characterized by standardized physico-chemical methods. Then experiments were conducted on diluted aqueous DEA solutions to test the effects of Fenton's reagent, ozone and ozone–hydrogen peroxide on the removal of some physicochemical parameters of these solutions. Lastly, biodegradability tests based on Dissolved Organic Carbon Die Away OECD301-A, were carried out on a dilution of the raw aqueous DEA solution and on the treated aqueous DEA solutions, produced by applying the best experimental conditions determined during the aforementioned oxidation tests. Experimental results showed that for aqueous DEA solutions treated with Fenton's reagent, the best degradation rate (70%) was obtained at pH 2.8, with Fe^{2+} and H_2O_2 at doses of 1000 and 10 000 mg/L respectively. In the ozone process, the best degradation (60%) was observed in aqueous DEA solution (100 mg COD/L), using 100 mg O_3 /L at pH 5. In the ozone–hydrogen peroxide process, no COD or DOC removals were observed. The diluted spent diethanolamine solution showed its greatest increase in biodegradability after a reaction period of 28 days when treated with Fenton's reagent, but after only 15 days in the case of ozonation.

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1. Introduction

Alkanolamines act to purify sour gas streams by a process of chemical absorption. As there are many amines capable of ridding sour gas streams of pollutants such as CO_2 and H_2S compounds, selection of the most suitable for a given application will depend on the following key factors: temperature, pressure, composition of the sour gas, and purity requirements for the treated gas [1–3]. For example, alkanolamines absorb CO_2 and H_2S at lower temperatures (35 °C) but release them at higher temperatures (80–130 °C), thereby allowing separation of these acid gases from sour gas streams [3].

The amines most commonly employed are: methanolamine (MEA), diethanolamine (DEA) and methyl-diethanolamine (MDEA). MEA is effective at low pressure, whereas DEA requires higher pressure [1,3,4]. The advantage of MDEA is that, in addition to the absorption and stripping of hydrogen sulfide (H_2S) and carbon dioxide (CO_2), it can also be used to remove carbonyl sulfide (COS). Other amines used include diglycolamine (DGA), diisopropanolamine (DIPA) and triethanolamine (TEA).

During absorption and desorption in the gas sweetening process, non-reclaimable contaminants called “spent amines” tend to accumulate in the closed loop structure of the system, causing reduced efficiency and other operational problems [1,5]. The situation can be improved by: (i) partially purging the contaminated solution and replacing it with fresh amine; (ii) replacing the entire volume of contaminated solution; (iii) injecting caustic solution to free the amines bound up as heat stable salts and various CO_2 -induced degradation products; or (iv) reclaiming the solutions [3].

Spent amines cannot be ignored because diethanolamine (DEA) has been classified as a substance that is “reasonably anticipated to be a human carcinogen” (National Toxicology Program, Research

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Triangle Park, North Carolina). Although the relationship between exposure to DEA and human cancer has not been specifically documented, experimental studies on B6C3F1 mice (dermal application of DEA) have induced increased incidences of liver neoplasms in the males (hepatocellular adenoma, hepatocellular carcinoma, hepatoblastoma) and females (hepatocellular adenoma, hepatocellular carcinoma), plus renal tubule adenoma in males [6]. The extreme toxicity of spent diethanolamine (DEA) is due to its high content of nitrogen and dissolved organic compounds (chemical oxygen demand (COD) concentrations higher than 300 000 mg/L), thus any wastewater containing DEA will be a hazardous waste. Fürhacker and Allabashi [3] showed COD removal efficiencies of 96% when applying a concentration of 4 g/L of MDEA (10 mL MDEA-solution 40%), but as high concentrations of MDEA inhibited biomass increase, it was impossible to achieve complete degradation of organic matter. An alternative approach was, therefore, to seek ways of increasing the biodegradability of spent diethanolamine prior to treatment, in other words by applying an advanced oxidation process as a pre-treatment.

An AOP is defined as “oxidation process involving the generation of hydroxyl radicals in sufficient quantity to interact with the organic compounds in a given solution” [7]. Since the early 1970s, advanced oxidation processes (AOPs) have been used considerably to remove both low and high concentrations of organic compounds from diverse sources such as groundwater, municipal and industrial wastewater, sludge destruction, and volatile organic compound (VOC) control. These processes, although often having high capital and operating costs, are the only viable pre-treatment methods for effluents containing refractory, toxic, and non-biodegradable materials present in high concentrations. In the AOP, the organic compounds can be completely mineralized to carbon dioxide and water mostly by hydroxyl radicals ([8]). The hydroxyl (the second most powerful oxidizing agent generated *in situ*), some strong oxidants such as ozone and other radicals produced in these technologies, oxidize recalcitrant, toxic and non-biodegradable compounds into different by-products and eventually into inert end-products. This suggests that AOPs are worth considered as pre-treatment methods of biological processes for the treatment and disposal of spent amines solutions. The efficiency of the biological oxidation techniques is often hampered by the presence of bio-refractory materials, though these are most conventionally used and economical treatment strategies. On the other hand, though AOPs promise degradation of almost all the contaminants, their use is hampered by the fact that the knowledge required for the design and efficient operation of the large-scale reactors is perhaps lacking. Moreover, considering the economical aspects, the use of advanced oxidation processes alone as treatment procedure may not look lucrative. Thus, a hybrid method consisting of using advanced oxidation processes to reduce the toxicity of

the effluent up to a desired level followed by biological oxidation is perhaps needed for the future [9]. The O₃-H₂O₂ system and the Fenton's reagent could be ones of the most feasible AOP's due to their relatively high availability and relatively low cost. The principle of Fenton's reagent [10] is the production of hydroxyl radicals (HO[•]) and other organic radicals (RHO[•]), as a result of the reaction at low pH (ranging from 2.5 to 5) between reducing transition metals (Fe⁺², Cu⁺, Co⁺², Mn⁺³) with the hydrogen peroxide in order to facilitate the oxidation of organic substances. The first application of this method was the removal of organic pollutants in municipal wastewater [11,12] and after that many applications have been found for this AOP [9]. However, none report has been identified for the application of Fenton's reagent as pre-treatment of alkanolamines solutions for biological treatment, and for ozone only two specific reports have been found [13,14], one of them combining this oxidant with TiO₂. Thus it is important to develop research projects for evaluating such oxidation processes as a pre-treatment step for biological treatment of the alkanolamines most commonly employed in refinery plants.

This project therefore sets out to assess the efficacy of Fenton's reagent, ozone alone and ozone-hydrogen peroxide, with a view to using them as possible pre-treatments prior to biological processing of wastewaters polluted with DEA issued from a Mexican refinery plant.

2. Materials and methods

2.1. Characterization of spent amines

A single raw spent aqueous DEA sample was sourced from a sour gas sweetening plant at an oil refinery in Mexico. A total volume of 80 L of sample was collected in a high-density polyethylene (HDPE) vessel from the main storage tank in the refinery plant. Sample was stored at 4 °C until characterization (COD, DOC, TKN, sulfides and pH) or its use in oxidation experiments. Table 1 shows the parameters, and the analysis techniques employed.

2.2. Oxidation tests

Oxidation with Fenton's reagent used the traditional Jar Test Methodology (Phipps and Bird equipment model PB-700), all the experiments started with two litres of diluted raw spent DEA solution. The pH varied from 2.05 to 5.70, the ferrous iron concentration was fixed at 1000 mg/L, and the hydrogen peroxide dose was varied from 600 to 12 000 mg/L (doses were selected on the basis of information reported in literature [13,14,19,20] and from preliminary experiments not discussed in this paper). To stop the reaction in each sample, a solution of sodium hydroxide was added for causing a sudden change in pH after addition of NaOH (pH 10) and to inac-

Table 1
Parameters and methods employed in the characterization tests of aqueous DEA solutions.

Parameter	Analytical technique/measuring device	Standard deviation	Method by APHA et al. [11]
Chemical oxygen demand ×	Closed reflux, colorimetric method – Spectrophotometer Merck Nova 60	±17 mg/L	5220 D
Sulfides	Methylene blue method – Spectrophotometric/Merck Nova 60	±0.04 mg/L	4500-S ² -D
Nitrates	Spectrophotometric/Merck Nova 60	±0.15 mg/L	4500-NO ₃ ⁻ B
Ammoniacal nitrogen	Distillation and titration/Semi-micro Kjeldahl Rapid Still I Labconco	±0.043 mg/L	4500-NH ₄ B
Organic nitrogen	Acid digestion distillation and titration Semi-micro Kjeldahl Micro Digestor and Rapid Still I Labconco	±0.01 mg/L	4500-NH ₄ C 4500-Norg B
Total Kjeldahl nitrogen	Sum of organic and ammoniacal nitrogen	–	–
pH	Electrometric method/Thermo Scientific Orion Multi-Parametric, Model 210	±0.02 pH unit	4500-H ⁺ B
Dissolved organic carbon	High-temperature combustion and NDIR detector/Shimadzu TOC-V analyzer	±0.05 mg/L	5310 B

tivate the residual content of hydrogen peroxide [9]. The resulting mixture was left for 30 min for sludge settling. Total reaction time in all the experiments was 5 h.

Oxidation tests with ozone and ozone–hydrogen peroxide were carried out as semi-continuous processes, employing a bubbling column with an AKAL 1000-L ozone lab generator, maximum ozone production being 700 mg/h. The experimental system consisted of a 1.5-L Pyrex glass column (100 cm in height) packed up to a height of 75 cm with Pyrex glass Rashing rings 0.5 cm and 1 cm in diameter. Gas produced by the ozone generator was fed in at the bottom of the column through a porous diffuser. At the top, the column was provided with a gas exit for quantification of the residual ozone in the gas phase (Iodometric method).

2.3. Biodegradability tests

All biodegradability tests followed the OECD 301-A protocol, which is the method established by the Organization for Economic Co-Operation and Development [15], it consists on measures of dissolved organic carbon (DOC) removal over a period of 28 days. The inoculum was obtained from a wastewater treatment plant located on the UNAM campus (Universidad Nacional Autónoma de México). Before use, the inoculum was passed through a 149 µm sieve and washed out several times with mineral solutions to rid the samples of any unwanted external contribution of DOC. In the biomass, Total and volatile suspended solids were measured (TSS 3004 mg/L and VSS 2240 mg/L) using analytical techniques 2540 D and E taken from APHA et al. [16]. DOC was quantified using a TOC-V CSN Shimadzu analyzer, after previous filtration through a 0.45 µm polytetrafluoroethylene syringe membrane.

Five control solutions were set up for the application of the OECD 301-A test: an experimental control, an inoculum control, a toxicity control, an adsorption control, and an abiotic degradation control. The initial COD concentration for the raw and wastewaters treated by ozone and Fenton's reagent was of 51.90 mg/L, 32.54 mg/L and 36.81 mg/L respectively.

2.4. Experimental design

A central composite experimental design, with two replicates at the central point, was selected for the oxidation experiments. Experimental factors considered in the tests were: dose of ozone and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ mass ratio (for ozonation and Fenton's reagent respectively), initial concentration of raw spent aqueous DEA solu-

Table 2

Average values of characteristics of the raw spent aqueous DEA solution collected in the refinery plant.

Parameter	Units	Value (n = 3)
COD	mg/L	313 597 ± 13
Sulfides	mg S ⁻² /L	5450 ± 0.5
Nitrates	mg N-NO ₃ ⁻ /L	4.4 ± 0.5
Ammoniacal nitrogen	mg N-NH ₃ /L	117 ± 0.43
Organic nitrogen	mg N-Org/L	33 373 ± 3.27
Total Kjeldahl nitrogen	mg N-TKN/L	33 491
pH	–	12 ± 0.12
Total organic carbon	mg/L	236 000 ± 2.0

tions and pH. These parameters were defined as $X_1 = \text{Fe}^{2+}/\text{H}_2\text{O}_2$ mass ratio or O₃ dose, $X_2 = \text{Co}$ (initial concentration of aqueous DEA solution), and $X_3 = \text{pH}$. [17]. As mentioned in Section 2.2 of this work, the values of these parameters were set up according to information reported by Mare et al. [13], Langlais et al. [14] for ozonation as well San Sebastián Martínez et al. [18] and Duesterberg et al. [19] for Fenton's reagent and also from preliminary experiments not discussed in this paper. The response factor was the removal of COD in the treated solutions. The results were analyzed with the Statgraphics statistical software using the response surface methodology (RSM) [20,21].

3. Results and discussion

3.1. Characterization of raw spent aqueous DEA solution

Table 2 gives the average values of the physico-chemical parameters measured by triplicate in the raw spent aqueous DEA solution. Readings showed as expected an extremely basic pH and very high concentrations of organic compounds (DOC and TKN (sum of ammoniacal and organic nitrogen)) and COD, which made impossible a direct application of the selected oxidation processes. Hence the samples were diluted to concentrations that would allow carry out the tests; these dilutions are given in Tables 3 and 4. Measures of nitrates, one of the main inorganic ions resulting from OH radical oxidation of alkanolamines [22], showed low initial contents. Also, sulfides (producers of sulfate ions) were slower than data (75 000 ppm) reported for raw spent amines aqueous solutions [1]. Nitrate and sulfate ions can inhibit •OH radical production that may contribute to the oxidation of organic compounds. The inhibitory effects of sulfate ions have been attributed to a decrease

Table 3

Experimental design of Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) tests.

Sample	Codified levels			Natural levels			Response factor		
	Co amine	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Ratio	pH	Co amine (±17 mg COD/L)	Mass ratio $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (mg/mg)	pH ±0.02	% COD removal		
							t = 1 h	t = 2 h	t = 5 h
1	–1	–1	–1	1000	$\text{Fe}^{2+}/3\text{H}_2\text{O}_2$	2.80	51.12	64.64	70.34
2	1	–1	–1	10000	$\text{Fe}^{2+}/3\text{H}_2\text{O}_2$	2.80	27.31	37.61	41.73
3	–1	1	–1	1000	$\text{Fe}^{2+}/10\text{H}_2\text{O}_2$	2.80	65.13	78.15	78.15
4	1	1	–1	10000	$\text{Fe}^{2+}/10\text{H}_2\text{O}_2$	2.80	38.34	48.06	58.54
5	–1	–1	1	1000	$\text{Fe}^{2+}/3\text{H}_2\text{O}_2$	5.00	45.26	61.54	63.33
6	1	–1	1	10000	$\text{Fe}^{2+}/3\text{H}_2\text{O}_2$	5.00	9.34	30.83	37.37
7	–1	1	1	1000	$\text{Fe}^{2+}/10\text{H}_2\text{O}_2$	5.00	63.66	72.94	75.87
8	1	1	1	10000	$\text{Fe}^{2+}/10\text{H}_2\text{O}_2$	5.00	38.59	47.49	48.81
9	–1.32	0	0	0	$\text{Fe}^{2+}/6.5\text{H}_2\text{O}_2$	3.90	0.00	0.00	0.00
10	+1.32	0	0	13 068	$\text{Fe}^{2+}/6.5\text{H}_2\text{O}_2$	3.90	5.16	16.12	18.20
11	0	–1.32	0	5500	$\text{Fe}^{2+}/0.006\text{H}_2\text{O}_2$	3.90	0.50	1.00	2.00
12	0	+1.32	0	5500	$\text{Fe}^{2+}/12.386\text{H}_2\text{O}_2$	3.90	7.20	16.12	19.00
13	0	0	–1.32	5500	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.05	21.30	37.30	43.13
14	0	0	+1.32	5500	$\text{Fe}^{2+}/6.5\text{H}_2\text{O}_2$	5.70	17.76	17.76	18.47
15	0	0	0	5500	$\text{Fe}^{2+}/6.5\text{H}_2\text{O}_2$	3.90	26.49	35.21	44.27
16	0	0	0	5500	$\text{Fe}^{2+}/6.5\text{H}_2\text{O}_2$	3.90	29.79	38.76	44.20

Table 4
Experimental design of the ozone tests.

Sample	Codified levels			Natural levels			Response factor
	Co amine	O ₃ doses	pH	Co amine ± 17 (mg COD/L)	Doses (mgO ₃ /L ± 0.02 mg/L)	pH ± 0.02	% COD removal
1	-1	-1	-1	100	100	2.80	20.96
2	1	-1	-1	1000	100	2.80	10.07
3	-1	1	-1	100	1000	2.80	23.95
4	1	1	-1	1000	1000	2.80	4.69
5	-1	-1	1	100	100	5.00	61.88
6	1	-1	1	1000	100	5.00	2.92
7	-1	1	1	100	1000	5.00	60.92
8	1	1	1	1000	1000	5.00	8.25
9	-1.32	0	0	550	550	3.90	0.00
10	+1.32	0	0	1306	550	3.90	4.51
11	0	-1.32	0	550	0	3.90	0.00
12	0	+1.32	0	550	1306	3.90	10.52
13	0	0	-1.32	550	550	2.05	12.23
14	0	0	+1.32	550	550	5.70	20.47
15	0	0	0	550	550	3.90	9.47
16	0	0	0	550	550	3.90	9.45

of the rate generation of hydroxyl radicals resulting from the formation of Fe(III) complexes and the formation of less reactive ($\text{SO}_4^{\bullet-}$) inorganic radicals [23].

3.2. Oxidation tests with Fenton's reagent

It is important to mention that sulfides content decreased lesser than the detection limit value (0.002 mg/L) when pH was adjusted to 2.8 and 5.0 since these ions are transformed to hydrogen sulfide which is removed by degasification from water [24]. Thus the inhibitory effect of sulfate ions should not be observed in these experiments. When applying Fenton's reagent (Table 3), after 5 h of reaction time, results for the two different concentrations of COD evaluated (1000 and 10 000 mg/L), showed that the removal rate increased slightly when decreasing the mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and increasing the pH value. For example, with an initial amine or DEA concentration of 1000 mg COD/L, a mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ of 1/3 and a pH value of 2.80, the percentage of COD removal was 70.34% (experiment 1). In experiment 7, using the same concentration of amine but with a different mass ratio $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (1/10) and pH 5.00, the removal percentage was 75.87%.

By the same token, when maintaining constant $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and pH values but varying the initial concentrations of aqueous DEA solutions, results showed that as the value of this parameter increased, the percentage of COD removal decreased. For example, when applying 1 mg $\text{Fe}^{2+}/3$ mg H_2O_2 at a pH of 2.80 to a spent aqueous DEA solution with concentration of 1000 mg COD/L, there was 70.34% COD removal; but when concentration was increased to 10 000 mg COD/L, the percentage of COD removal fell to 41.73% (Table 3). These results demonstrate that the percentage of COD removal depends on the pH values and dose of hydrogen peroxide, and that the best COD removals were obtained when the dilution of aqueous DEA solution and the hydrogen peroxide dose increased. The influence of amine concentration and H_2O_2 dose can be observed more clearly in the response surface graph produced by statistical analysis of data. The example given in Fig. 1 is the response surface graph for a constant pH of 2.80.

For one of the two best experimental conditions (1000 mg COD/L, 1000 mg/L $\text{Fe}^{2+}/10$ 000 mg/L H_2O_2 and pH 2.80) obtained in this work for removing any organic material present in the aqueous DEA solution, the behaviour of COD removal was analyzed using a maximum reaction time of 5 h. Fig. 2 demonstrates that the percentage of COD removal as a function of time shows an exponential behaviour. A significant increase was only observed during the first hour of reaction. After the first hour up to the time the reaction was

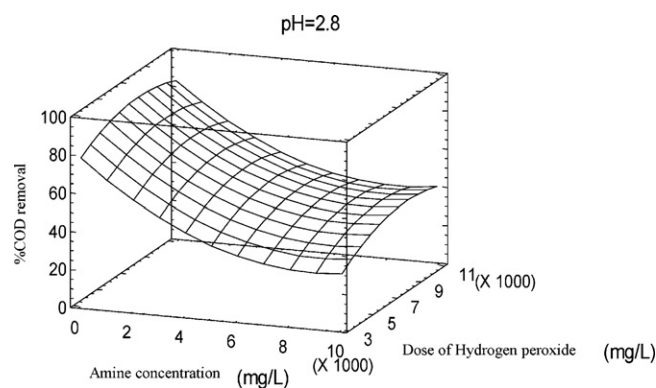


Fig. 1. Surface response obtained from statistical analysis of oxidation with Fenton's reagent.

halted (300 min), the percentage of COD removal remained almost constant. This pattern may be due to the formation of intermediates during the reaction that are only oxidized very slowly. Previous studies have shown that complete mineralization of the organic compounds cannot be achieved using Fenton's reagent, because the

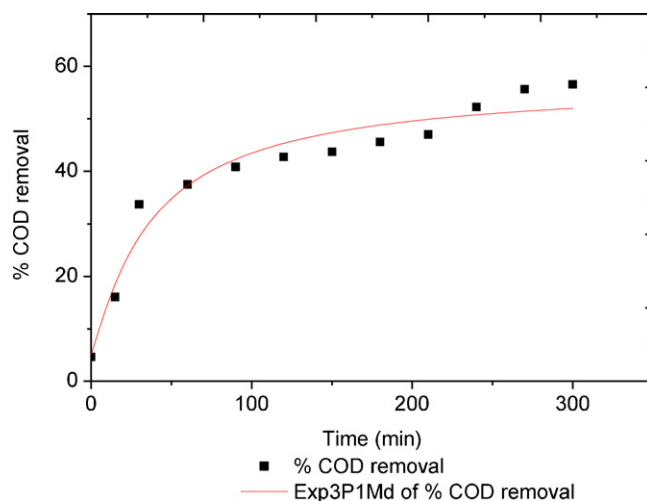


Fig. 2. COD removal in oxidation tests of an aqueous DEA solution treated with Fenton's reagent (1000 mg/L $\text{Fe}^{2+}/10$ 000 mg/L, H_2O_2 and pH 2.80).

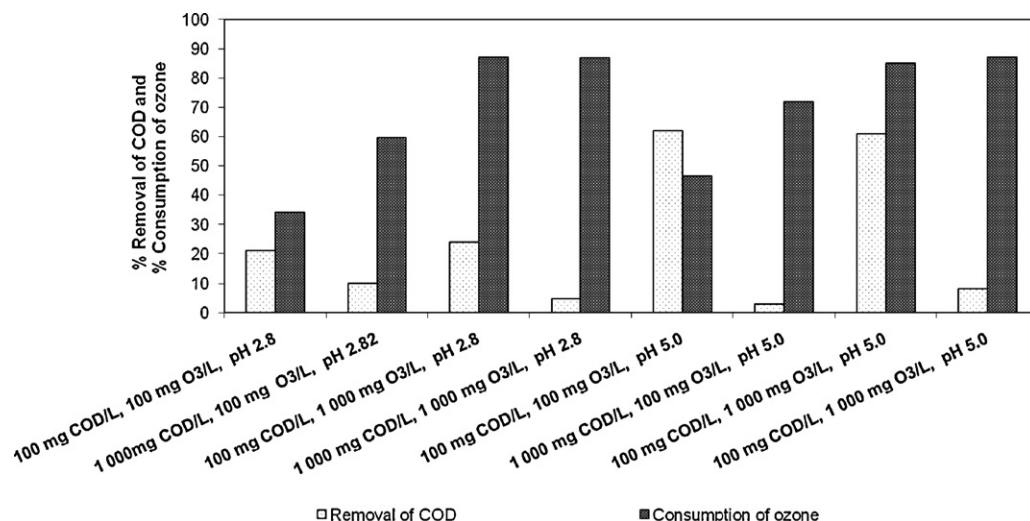


Fig. 3. Ozone consumption and COD removal during oxidation of aqueous DEA solutions.

reaction produces some intermediates (carboxylic acids) which are resistant to treatment and therefore extremely slow to react with the $\bullet\text{OH}$ radical [14,25].

3.3. Oxidation tests with ozone

Table 4 shows the results obtained during oxidation with ozone. Comparing the results obtained at a fixed pH value but using different amine and ozone concentrations, it was observed that the initial concentration of amine could be the main factor influencing better COD removals. This is verified in Section 3.5 for the regression models. For example, at a pH value of 2.80, 100 mg COD/L concentration of spent amine and 100 mg O₃/L of ozone, the percentage of COD removal was 20.96%, whereas at the same pH value and ozone dose, but with ten times more DEA (1000 mg COD/L), removal of COD fell to 10.07%. Conducting the same analysis but keeping the initial concentration of amine fixed and varying the initial pH and ozone doses, it was observed that the amine concentration had a more significant effect than the ozone dose on the percentages of COD removal. In this case, the best results were obtained at a pH value of 5.0.

Fig. 3 shows ozone consumptions in the first 8 experiments of the experimental design. The amount of ozone consumed during oxidation of the diluted aqueous DEA solutions indicated that organic matter was transformed into different by-products but not mineralized. Indeed, the maximum COD removal obtained was only 60%, and that was only possible when the initial DEA solution was diluted to 100 mg COD/L. Some studies have shown that ethanolamines [25] (DEA, MEA and TEA) and aliphatic amines [26] (octadecylamine (ODA) and hexadecylamine (HAD)) can react with ozone and the $\bullet\text{OH}$ radical. However, the reaction between ozone and the by-products generated is very slow, thereby making it impossible to achieve complete degradation of the organic material [14,25].

Thus, under the best ozonation conditions (pH 5.0, initial spent amine concentration 100 mg/L, and 100 mg/L O₃), the highest percentage of COD removal achieved was 61.88%.

3.4. Oxidation tests with ozone and hydrogen peroxide

These tests were conducted using a fixed initial concentration of aqueous DEA solution (500 mg/L), and doses of hydrogen peroxide varying from 125 mg/L to 750 mg/L. At the end of each experiment the pH was fixed at 9. The quantity of oxidant at the beginning of the

experiment was the same as at the end. Removal of COD and DOC was not achieved using the ozone–peroxide process. These could be due to the formation of intermediates in the reaction that are slowly oxidized.

3.5. Regression models, statistical testing and optimization of responses

After running the 16 trials of the central composite experimental design, the data produced from the statistical experiment were treated using the coded design matrix. The significant effects having *p*-values less than 0.05, indicating that they are significantly different from zero at the 95% confidence level, were used for further analysis, while the rest of them were excluded from the models. Thus, the following reduced second order regression models fitted to the data for the coded values of factors after having excluded the insignificant effects for both, the ozone treatment, and the 1 h, 2 h, and 5 h duration Fenton treatment:

$$Y_1 = [\text{Fenton 1 h, COD removal}] = 17.34 - 9.12 \times Co + 14.75 \times \text{pH}^2 \quad (1)$$

$$Y_2 = [\text{Fenton 2 h, COD removal}] = 24.91 - 8.01 \times Co + 17.84 \times \text{pH}^2 \quad (2)$$

$$Y_3 = [\text{Fenton 5 h, COD removal}] = 18.68 - 6.72 \times Co + 6.18 \times \text{ratio} - 4.87 \times \text{pH} + 6.15 \times Co^2 + 0.98 \times Co \times \text{ratio} - 0.6 \times Co \times \text{pH} + 6.96 \times \text{ratio}^2 + 18.61 \times \text{pH}^2 \quad (3)$$

$$Y_4 = [\text{ozone, COD removal}] = 8.41 - 11.82 \times Co + 7.41 \times \text{pH} - 10.18 \times Co \times \text{pH} + 10.94 \times \text{pH}^2 \quad (4)$$

The reduced models (those including only the significant factors) were tested with the statistics: model significance, lack-of-fit and adequate precision (Table 5).

The model significance test checks whether the model *F* value occurs due to noise. To do this, the probability of sensing the observed *F* value ($\text{prob} > F$, or *p*-value) is used to test, if the null hypothesis is true. The *p*-value is the proportion of the area under the curve of the *F*-distribution that lies beyond the observed *F* value.

Table 5

Model significance and adequate precision used to test the adequacy of the reduced (only significant effects) models.

Response	Model significance (p -value < 0.05)	Lack of fit (p -value > 0.05)	Adequate precision (ratio > 4)	Number of statistics fulfilled
Y_1	0.726	0.0942	4.300	2
Y_2	0.0948	0.0880	4.503	2
Y_3	0.7679	0.0013	2.290	0
Y_4	0.0067	0.0009	8.223	2

Table 6Natural values of the design factors for the optima of responses for models Y_1 , Y_2 and Y_3 .

Optima (removal)	Y_1	Y_2	Y_3
	41.22%	50.77%	66.61%
X_1 (Co amine, mg COD/L)	1000	1000	1000
X_2 (mass ratio, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$)	1/5.43	1/5.43	1/10
X_3 (pH)	5	5	2.80

Small p -values dictate rejection of the null hypothesis, meaning that if a p -value is less than 0.05 the model is significant at the 95% confidence level.

The lack-of-fit test is designed to determine whether the selected model is adequate to describe the observed data, or whether a more complicated model should be used. The test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the factors. A model is considered adequate (significant) at the 95% confidence level, if the p -value of the lack-of-fit test is higher than 0.05.

The adequate precision test measures the signal to noise ratio. It compares the range of the predicted values at the design points to the average prediction error. A ratio greater than 4 indicates adequate model discrimination and then the model can be used to navigate the design space.

The results shown in Table 5 indicate that all models, except the model for response Y_3 (Fenton 5 h, COD removal), comply with at least two of the desired values of the statistics considered (model significance, lack-of-fit test and adequate precision).

The optimal values of the responses were calculated from their reduced models and are shown together with the corresponding natural values of factors in Tables 6 and 7. Much higher optima are estimated when the maximal axial coded distances (+1.32 and -1.32) are used in calculations, but these values are not sufficiently reliable because they are located at the extreme regions of the space of factors considered in this study, where the estimation errors are usually high. The higher standard error of design is clearly demonstrated in Fig. 4 for Y_4 (ozone, COD removal).

3.6. Biodegradability tests on treated aqueous DEA solutions resulting from chemical oxidation with Fenton's reagent and ozone

After the oxidation experiments, biodegradability tests were conducted on a dilution of the raw spent DEA aqueous solution and on the effluents issued from the application of Fenton's reagent and ozone under the best oxidation conditions selected in this research. The initial COD concentration for the raw and wastewaters treated by ozone and Fenton's reagent was of 51.90 mg/L, 32.54 mg/L and

Table 7Natural values of the design factors for the optimum of model Y_4 .

Optimum	Y_4
	48.78%
X_1 (Co amine, mg COD/L)	100
X_2 (ozone dose, mg/L)	100
X_3 (pH)	5

DESIGN-EXPERT Plot

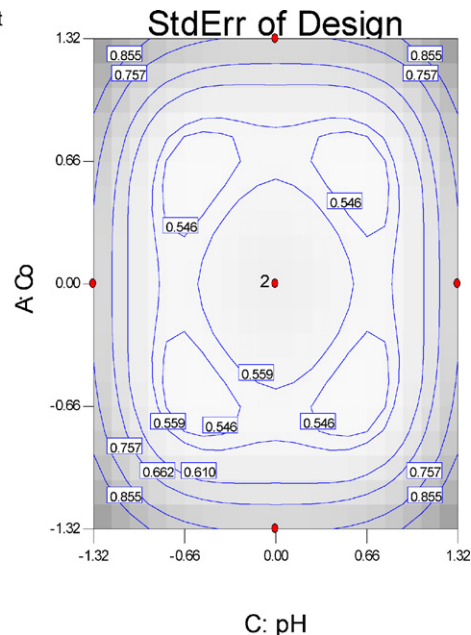
StdErr of Design
● Design PointsX = C: pH
Y = A: CoActual Factor
B: O3 Dose = 0.00

Fig. 4. Standard error of design for Y_4 (COD removal by ozone) for the factors A (Co amine) and C (pH) with the.

36.81 mg/L respectively. The objective was to show the influence of these oxidation treatments on the biodegradability of spent DEA aqueous solutions, in order to decide on a viable method that could be used as a pre-treatment for degradation prior to a biological process.

For the tests on the raw spent aqueous DEA sample, removal of DOC in the abiotic degradation control was 16% (Table 8), and 6% in the adsorption control. As the percentage of DOC removal had raised to 88.9% after a period of 28 days, this suggests degradation occurred mainly as a result of action by microbial activity.

Tables 9 and 10 give the results of DOC removal in tests on the aqueous DEA solutions after both pre-treatments, Fenton's reagent and the ozonation process.

In the ozonated sample, removal of DOC in the abiotic degradation control was 19.7%, and 12.8% in the adsorption control. Again at the end of 28 days the percentage of DOC removal had increased, this time to 81.8%, and therefore these results also show that degradation took place mainly as a result of action by microbial activity.

Table 8

Removal percentage of dissolved organic carbon in samples of raw spent aqueous DEA solution (DOC initial = 51.90 mg/L).

Time	% DOC removal				
	Day 0	Day 7	Day 14	Day 21	Day 28
Experimental control	0.0	11.3	26.1	82.9	82.9
Inoculum control (for verifying an eventual DOC increase)	1.4	1.5	1.5	1.5	1.5
Toxicity control	0.0	43.5	75.9	95.4	95.8
Adsorption control	0.0	0.0	3.8	4.2	6.6
Abiotic degradation control	0.0	11.7	11.6	11.4	16.5

Table 9

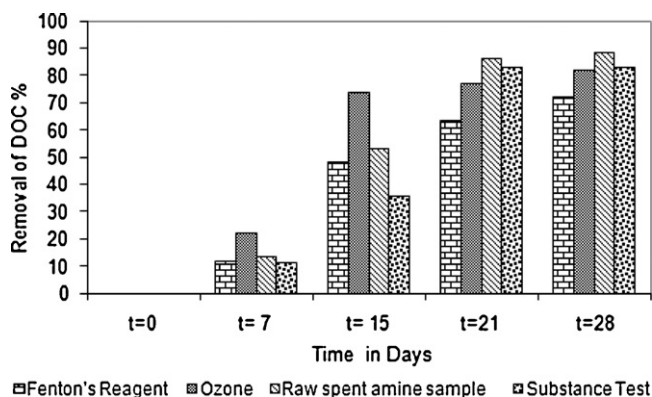
Removal percentage of dissolved organic carbon in aqueous DEA solutions treated with ozone (DOC initial = 32.54 mg/L).

Time	% DOC removal				
	Day 0	Day 7	Day 14	Day 21	Day 28
Experimental control	0.0	11.3	26.1	82.9	82.9
Inoculum control (for verifying an eventual DOC increase)	2.3	2.3	2.3	2.4	2.4
Toxicity control	0.0	14.3	52.0	89.8	89.6
Adsorption control	0.0	11.9	12.7	9.9	12.8
Abiotic degradation control	0.0	8.6	15.4	16.4	19.7

Table 10

Removal percentage of dissolved organic carbon in aqueous DEA solutions treated with Fenton's reagent solution (DOC initial = 36.81 mg/L).

Controls/time	% DOC removal				
	Day 0	Day 7	Day 14	Day 21	Day 28
Experimental control	0.0	11.3	26.1	82.9	82.9
Inoculum control (for verifying an eventual DOC increase)	2.0	2.1	2.1	2.1	2.1
Toxicity control	0.0	0.7	35.2	68.9	87.7
Adsorption control	0.0	8.4	33.8	35.7	37.9
Abiotic degradation control	0.0	4.6	31.4	39.3	39.6

**Fig. 5.** Removal of COD in the biodegradability tests second factor B (dose of ozone) set at its basic level with the aid of DesignExpert software.

Abiotic degradation in the samples treated with Fenton's reagent was better than in either the diluted raw spent aqueous DEA solution or the samples oxidized with ozone. Indeed, as no micro-organisms were found, the conclusion can be drawn that Fenton's reagent generated by-products that can be hydrolyzed more easily than those generated by ozonation. Since all tests were conducted in a dark stage and also considering that abiotic and adsorption controls showed results very similar, thus only hydrolysis contributed to organic compounds degradation.

The percentages of COD removal were different for each test (Fig. 5). In the ozone tests, COD removal (achieved in the first 15 days) was 70%, but after this time the rate for having the breakdown of the pollutants by micro-organisms was slower. The same pattern behaviour was observed in all the analyzed samples.

When ozone was used for the pre-oxidation of DEA samples, the best degradation efficiency was observed after 15 days. However, in oxidation processes using Fenton's reagent, the by-products formed are more hydrolyzable, and this could be an advantage in situations where follow-up biological treatment of the wastewater is not an option.

4. Conclusions

For the best experimental conditions obtained in this work, both Fenton's reagent (FR) and ozonation (O_3) showed acceptable COD removal values (up to 70% and 60%, respectively) in the pre-oxidation tests of diluted aqueous DEA solutions with starting COD

concentrations of 1000 mg COD/L and 100 mg COD/L respectively. When comparing the influence of these processes on the biodegradability of aqueous DEA solutions, only effluent treated by ozone showed the advantage of time, because the best removal of COD (up to 70% for considered as biologically treatable for the OECD301-A method) occurred after only 15 days of degradation versus 28 days for Fenton's reagent. However, the advantage of Fenton's reagent is that the greater hydrolyzability of the by-products generated means a subsequent biological treatment would not always be essential.

Acknowledgments

The authors are grateful to Universidad Nacional Autónoma de México for the financial support received under grant number UNAM DGAPA-PAPIIT IN109005.

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