Dissolved Organic Carbon Determination Using FIA and Photo-Fenton Reaction

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ABSTRACT

The FIA-photo-Fenton system is based on the flow oxidation of the organic matter. A small amount of the sample containing $\text{H}_2\text{O}_2$ is injected into the acidic flow solution of $\text{Fe}^{2+}$, which passes through a tubular PTFE reactor irradiated with UV light. The generated $\text{CO}_2$ is quantified by a conductometric detector and is directly proportional to the dissolved organic carbon concentration in the sample. The optimization studies were performed using EDTA solutions. The average recovery of organic carbon was 83% with a relative standard deviation of 3.7% using a 1:5 molar ratio of $\text{Fe}^{2+}$:H$_2$O$_2$, pH 2.0, 100 $\mu$L of sample injection and a liquid flow of 1 mL min$^{-1}$. After optimization, the DOC concentration was quantified using 13 different organic compounds, where the average recovery was 90%. The rate of the analysis was in average 50 samples hour$^{-1}$.

Key words: Photo-Fenton reaction, dissolved organic carbon, FIA

INTRODUCTION

Total organic carbon (TOC) is an important parameter used as a tool to assess, for instance, the quality of a purified water. The determination and quantification of organic compounds in aqueous solution is not always an easy process which often, includes an specific analytical method. In this regard, the total organic carbon analysis can be used as an indirect method to quantify the concentration of a solution containing a single organic compound. When a more complex system is involved, TOC analysis shows the results of the sum of all organic compounds (Matthews et al., 1990).

These analyses are performed, usually, by two techniques, combustion at very high temperature, typically at 990°C using cobalt oxide as an oxidative catalyst, and photo-oxidation employing persulfate-ultraviolet irradiation. In both the methods, the organic carbon is converted to carbon dioxide ($\text{CO}_2$) which can be analyzed by infrared analyzer or flame ionization detector (APHA-AAWWA-WPCF, 1995).

Recently, there has been numerous investigations (Huang et al., 1993; Venkatadri & Peters, 1993; Lunar et al., 2000) using alternative processes to oxidize organic compounds, called advanced oxidation processes (AOP). The active species generated are the highly reactive free radicals (Huang et al., 1993; Jardim et al., 1997), mainly hydroxyl radicals ($\text{OH}^-$), which are the initiator of a chain of reactions that leads to the total...
mineralization of the organic compounds to CO₂, H₂O and other inorganic.

The Fenton reaction is, among the AOPs, one of the most investigated. The reagent is a mixture of hydrogen peroxide and ferrous ion which produces OH⁻ according to the equation [1] (Huston & Pignatello, 1999; Pignatello, 1992; Engwall et al., 1999):

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \text{OH}^- \quad [1]
\]

The literature shows that Fenton’s reagent is capable of efficiently degrade several organic compounds (Huang et al., 1993; Venkatadri & Peters, 1993; Lunar et al., 2000). In addition, Fenton reaction efficiency can be enhanced in the presence of UV irradiation (Pignatello, 1992). The iron product in equation [1] can be photoreduced regenerating Fe(II) and producing more OH⁻, as shown in equation [2]:

\[
\text{Fe(OH)}^{2+} \xrightarrow{\text{hv}} \text{Fe}^{2+} + \text{OH}^- \quad [2]
\]

The combination of Fenton reaction and UV irradiation is known as photo-assisted Fenton or photo-Fenton reaction. Bauer and Fallmann (1997) compared the wastewater treatment efficiency in a pilot scale employing AOP systems that can combine sunlight. The studied systems were TiO₂/UV, Fe²⁺/H₂O₂/UV, Fe²⁺/O₃/UV and Fe²⁺/O₃/UV. The authors observed that among the studied system, the one using photo-Fenton reaction was the most effective and also pointed out that the estimated cost is cheaper than other AOP systems.

Several researchers have investigated the photo-Fenton reaction as an alternative and very promising wastewater treatment process. Doong and Chang (1998) investigated the degradation of organophosphorous pesticides, such as malathion, diazoin and phorate, and observed that the degradation efficiency was more effective in a system using Fe²⁺/UV/H₂O₂ than in H₂O₂/UV system. The degradation of several pesticides was also investigated by Huston and Pignatello (1999). The authors showed that the pesticides were removed in less than 30 min and that the complete mineralization of this compounds was achieved in an average of 120 min. Compounds such as 4 chlorobiphenyl, 4,4’-dichlorobiphenyl (Kuo & Lo, 1999), 2,4-chlorophenol, 2,4,6-trichlorophenol (Kuo et al., 1998), and colored compounds (Liao et al., 1999; Kang et al., 1999; Wu et al., 1999) were also employed as target ones for the organic degradation study using photo-Fenton reaction.

Matthews and co-workers (1990) described a new method for the determination of organic carbon using TiO₂/UV, another powerful AOP system. The carbon dioxide produced was monitored by conductivity detection. Sample of 1 to 40 mL containing 0.1 to 30 µg mL⁻¹ of organic carbon was recirculated through a spiral borosilicate glass tube coated with TiO₂. A 20 W black light fluorescent lamp was used as UV source. The authors reported that 99% oxidation was achieved in less than 10 minutes of irradiation. They also mentioned that the main advantages of the apparatus are the low cost and ease operation.

In the present work we investigated the possibility of using Fenton and photo-Fenton reaction as an alternative method to quantify the dissolved organic carbon concentration. As mentioned before, one of the final products of the organic compounds degradation process, in both systems, is CO₂. The constructed apparatus consisted of mineralizing the organics by photo-Fenton reaction using flow injection analysis (FIA) system. The CO₂ generated due to the organic compounds mineralization was quantified by monitoring the increase of the conductivity. This arrangement is similar to the one used by Fadini (1995), where the author used a FIA-condutometric system and persulfate-ultraviolet irradiation to convert organic compounds to CO₂. Under these conditions, Fadini obtained an average of 88% of dissolved organic carbon recovery and the equipment was able to process 14 samples per hour.

**MATERIALS AND METHODS**

**Reagents**

*Inorganic carbon standard solution (1200 mg of C L⁻¹), Na₂CO₃ (Vetec) was dried at 270°C for 1 hour and 10.6 g was dissolved with 1 L to purified water, obtained from Milli-Q Academic.*

*Hydrogen peroxide, 30% (Alfa Caesar) was standardized by permanganate titration with a concentration of 9.7 mol L⁻¹.*

*Fe²⁺ solution (0.10 mol L⁻¹) was prepared dissolving 27.80 g of FeSO₄.7H₂O (Reagen) in 1 L*
of an acidic solution containing 500 mmol L\(^{-1}\) of H\(_2\)SO\(_4\) (Reagen).

Organic carbon standard solutions were prepared containing 1200 mg of C L\(^{-1}\). Organic compounds used in this work were EDTA (Reagen); methanol (Vetec); ethanol (Vetec); isopropanol (Nuclear); acetone (Vetec); phenol (Reagen); ascorbic acid (Reagen); hydroquinone (Vetec); pyridine (Vetec); glucose (Vetec); resorcinol (Vetec); caffeine (Nuclear), and 1,4-dioxane (Nuclear).

**Equipment and Analysis**

Samples containing a pre-determined amount of H\(_2\)O\(_2\) were injected into a carrying flow of 10\(^{-3}\) mol L\(^{-1}\) Fe\(^{2+}\) acidic solution. This solution was allowed to pass through a 1.50 m length PTFE tube which was winded around the UV lamp (6 W, \(\lambda = 254\) nm). Using this tube the UV light can penetrate and irradiate the sample. During this course the organic compounds were oxidized to CO\(_2\) and H\(_2\)O. The CO\(_2\) passed through a PTFE membrane to a purified water flow, in a diffusion cell, increasing the water conductivity, measured with a conductometer (CPH -100). The peak intensity was recorded (Instrumentos Científicos, C.G.). Figure 1 shows a schematic representation of the FIA-photo-Fenton system.

**Organic carbon recovery study**

Several organic compounds were investigated. For each one of them, solutions containing 6, 12, 24, 36 and 60 mg L\(^{-1}\) of organic carbon were prepared. To quantify the percent of organic carbon recovery, the results obtained for these samples were compared to a calibration curve, using the same carbon concentrations, prepared from a stock inorganic carbon (Na\(_2\)CO\(_3\)) standard solution.

**RESULTS AND DISCUSSION**

**Fenton’s Reagent in FIA**

A preliminary investigation was performed to determine the optimum configuration, and to know how the Fenton’s reagents (Fe\(^{2+}\) and H\(_2\)O\(_2\)) should be employed in FIA. Injections of samples to an acidic Fe\(^{2+}\)/H\(_2\)O\(_2\) flow resulted in a severe instability, caused by the formation of, probably, oxygen gas bubbles. Oxygen can be formed due to the decomposition of hydrogen peroxide (Huang et al., 1993; Crittenden et al., 1999).

To avoid this problem, H\(_2\)O\(_2\) was first introduced to the sample and then injected to the carrying flow of the Fe\(^{2+}\) solution. Using this condition, no bubbles were observed and the base line was kept stabilized during the analysis.

**Fenton x Photo-Fenton**

For this comparison study, EDTA was employed as the testing organic compound, and the FIA conditions used were 100 \(\mu\)L of sample volume, 1 mL min\(^{-1}\) of flow rate and 5 mmol L\(^{-1}\) H\(_2\)O\(_2\). As mentioned before, Fenton’s reagent is a strong oxidant that is capable to mineralize many organic compounds. The reaction time for the organic compounds mineralization depends on many parameters, such as the Fe\(^{2+}\)/H\(_2\)O\(_2\) concentration ratio, the chemical structure of testing compound, and pH, among others. The literature shows that this time could vary from 10 to over 120 min (Bandara et al., 1996; Blanco et al., 1999; Kitis et al., 1999). However, due to the short period of reaction allowed in this FIA settings (less than 2 minutes), the present oxidation efficiency was low. The performance was enhanced combining Fenton’s reagent and sample irradiation. Figure 2 shows the comparison of the oxidation results using Fenton and photo-Fenton reactions. Increase in the conductivity of the solution, indicated as peak height, was 9 times higher for the photo-Fenton system than for the Fenton system.

As already mentioned (Pignatello, 1992), the OH\(^{-}\) concentrations is higher in a photo-Fenton system compared to Fenton reaction, due to the photoreduction of Fe(OH)\(^{3+}\) to Fe\(^{2+}\), where more OH\(^{-}\) is generated. Moreover, under UV radiation, the H\(_2\)O\(_2\) undergoes direct photolysis generating two hydroxyl radicals per each peroxide molecule (Topodurti et al., 1993; Legrini et al., 1993). The H\(_2\)O\(_2\) has a maximum absorbance in the range of
210-240 nm, and even though one of the dominant emission wavelength of the mercury UV lamp is at 254 nm, it is possible to generate OH• by direct photolysis of H₂O₂.

The results suggested that the Fenton reaction alone could not generate enough amounts of OH• that would be capable to mineralize the organic compounds in the short time period of the FIA analysis. Under UV assisted Fenton reaction, more OH• are produced and the oxidation of the organics to CO₂ can be enhanced in the same period.

B. pH.

According to Huang et al. (1993), the hydrogen peroxide decomposition rate for Fenton reaction reached the maximum at a pH of 3.5. They attributed this phenomenon to the large catalytically active surface for H₂O₂ contact due to the progressive hydrolysis of the ferric iron. As a consequence, more free hydroxyl radicals were formed. For the photo-Fenton reaction, however, the optimum pH is at 2.8, where both Fe(III) species, present as Fe³⁺ and Fe(OH)²⁺, have approximately the same concentration. At lower pH values, the Fe(OH)²⁺ concentration decreases and at higher pH values, Fe(III) hydroxide precipitates (Pignatello, 1992). Nogueira and Guimarães (2000) also verified that the optimum pH range for photo-Fenton process was at range of 2.5-2.8, studying the degradation of dichloroacetic acid and 2,4-dichlorophenol.

System Optimization

A. Fe²⁺/H₂O₂ Concentration Ratio. The literature shows that apparently there is not an unique ratio between H₂O₂ and Fe²⁺ concentration that could be used to oxidize organic compounds.Degradation studies using 2-chlorophenol and ionic surfactants were reported employing Fe²⁺:H₂O₂ molar ratio of 1:100 and 1:1, respectively (Huang et al., 1993; Kitis et al., 1999). Therefore, in this work, different Fe²⁺:H₂O₂ molar concentration ratios were investigated. The experiments were performed using 1.0 mL min⁻¹ flow rate and 100 µL of sampling volume. Figure 3 shows the average percentage recovery as organic carbon in EDTA solutions. The results showed a higher organic carbon recovery at a Fe²⁺:H₂O₂ molar ratio of 1:3; 1:4 and 1:5. At these ratios the average recovery was 70, 73 and 74%, respectively. Due to the slightly higher recovery obtained using 1:5 of Fe²⁺·H₂O₂ molar concentration ratio, this one was chosen to be used for further studies.

Studies using FIA and conductometric detection (Jardim et al., 1990) to monitor the microorganism CO₂ production in a liquid medium containing Escherichia coli cultures showed better results using 10⁻² mol L⁻¹ of H₂SO₄. The pH of this
solution was theoretically 1.7. Due to the fact that the present apparatus was a combination of photo-Fenton reaction in a FIA system, different pH values for the Fe$^{2+}$ solution were studied. The optimum organic carbon recovery results were obtained using 5 mmol L$^{-1}$ H$_2$SO$_4$ which resulted in pH value of 2.0. At higher pH values, the system presented an increase in instability.

C. Sampling Volume
The sample volume to be injected into FIA system was the other parameter optimized. Figure 4 shows the average organic carbon recovery obtained using four different sampling volumes. Results showed a higher dispersion in recovery tests when 50 or 200 µL of samples were injected. The optimum results were observed using 100 µL of injection volume, with an average organic carbon recovery of 81% and a 5.5% of variation coefficient among results.

D. Flow Rate
Several flow rates were employed. It was observed that the highest organic carbon recovery results were obtained using either 0.8 or 1.0 mL min$^{-1}$. Statistically, using the T test at 95% confidence, there was no difference in the results among them. Lower values of flow rates resulted in system instability. At higher ones, the reagent diffusion into the sample cannot be totally accomplished and consequently, the oxidation of the organic could not be complete.

The following studies were performed using the flow rate of 0.8 mL min$^{-1}$. The reason was that different organic compounds undergo oxidation at the different rates (Huston & Pignatello, 1999; Maletzky & Bauer, 1998; Krutzler & Bauer, 1999), therefore, the reaction time could be slightly higher at 0.8 mL min$^{-1}$ than at 1.0 mL min$^{-1}$. As a consequence, the oxidation percentage should also be higher.

Figure 4 – Organic carbon recovery as a function of sample volume, using different concentration of EDTA (mg.L$^{-1}$) as a testing compound, Fe$^{2+}$:H$_2$O$_2$ molar ratio of 1:5, pH value of 2.0 and 1 mL.min$^{-1}$ of flow rate.

**Organic Carbon Recovery Study.** Although the experimental parameters were optimized using EDTA as a test compound, for practical purpose, they were not modified for this study. Glucose, caffeine, pyridine, methanol, ethanol, isopropanol, resorcinol, phenol, acetone, hydroquinone, ascorbic acid and 1,4-dioxane were used, each one at the same concentration of organic carbon. Table 1 shows the average organic carbon recovery obtained for all the compounds studied. For most of the compounds investigated 100% recovery could be reached. Ascorbic acid recovery was in the range of 90%, EDTA and caffeine at 80% and isopropanol and acetone at 75%. It is known that the degradation rate is different for each compound (Jardim et al., 1997). Therefore, modifications of some of the system parameters, could probably enhance the percentage recovery of the organics that did not reach 100%.

Matthews and co-workers (1990) used TiO$_2$/UV, another powerful AOP system, to oxidize organic compounds to CO$_2$ and consequently determine the total organic carbon concentration. The authors investigated 11 compounds and reported that 99% oxidation was achieved in less than 10 minutes. They reported that the method was suitable for samples containing 0.1 to 30 µg mL$^{-1}$ of organic carbon and sample volumes of 1 to 40 mL.
Table 1 - Average recovery (%) of organic carbon obtained using FIA-photo-Fenton system with several organic compounds:

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Average Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dioxane</td>
<td>100</td>
</tr>
<tr>
<td>Acetone</td>
<td>72</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>91</td>
</tr>
<tr>
<td>Caffeine</td>
<td>83</td>
</tr>
<tr>
<td>EDTA</td>
<td>80</td>
</tr>
<tr>
<td>Ethanol</td>
<td>100</td>
</tr>
<tr>
<td>Glucose</td>
<td>98</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>100</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>74</td>
</tr>
<tr>
<td>Methanol</td>
<td>100</td>
</tr>
<tr>
<td>Phenol</td>
<td>100</td>
</tr>
<tr>
<td>Pyridine</td>
<td>100</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>100</td>
</tr>
</tbody>
</table>

Determination of DOC in real samples. Aqueous samples of four different sources were used to verify the efficiency of the FIA-photo-Fenton system in quantifying the DOC concentration. These results were compared to the ones obtained using a commercial TOC equipment (Shimadzu, TOC 5000). The comparison is presented in table 2. In general, it could be seen that there was not a significant difference among the values obtained using either methods.

Using a similar FIA apparatus, but employing persulfate/UV as the oxidant agent, Fadini (1995) compared the dissolved organic carbon results with the ones using the same commercial TOC equipment. The values obtained from Shimadzu TOC 5000 were on average 12% higher than the FIA system using persulfate/UV.

Table 2 - Comparison of organic carbon results obtained using FIA-photo-Fenton system and a commercially available TOC equipment:

<table>
<thead>
<tr>
<th>Sample</th>
<th>FIA-photo-Fenton org. C (mg L⁻¹)</th>
<th>commercial TOC org. C (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Although further studies have to be done in order to cover a wider range of dissolved organic carbon analysis, it is important to emphasize that the present system has some advantages. The rate of the analysis was on average 50 samples hour⁻¹, using a sample volume of 100 µL. Moreover, using the present apparatus, there was no need for a special carrying gas neither for high temperatures to oxidize the organics, therefore, it could be used during field analysis.

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