Fenton’s reagent application in the domestic sewers disinfection

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ABSTRACT

This paper investigated the application of advanced oxidative processes – Fenton’s reagent - in wastewater disinfection. The treatments included the variation of the hydrogen peroxide and ferrous ions concentrations (Fe²⁺/H₂O₂) and pH values. The sewage samples were collected at Ilha do Governador Wastewater Treatment Plant (ETIG) in Rio de Janeiro, Brazil, before the biological treatment with activated sludge. The average pH fluctuated from 6.5 to 7.2 and the most common value was 6.7. The reactions with the Fenton’s reagents, as well as the beginning of the analysis occurred within 24 hours after the sewage sample’s collection. The oxidative process, its behavior and the treatment effectiveness have been monitored by microorganism counting, COD, BOD, ammoniacal nitrogen and others. The results have shown a total elimination of the fecal coliforms in the wastewater samples when treated with H₂O₂ and Fe²⁺ in concentrations of 200 mg/L of 50 mg/L, respectively.

Keywords: Pollution control; water disinfection; oxidative process; Fenton’s reagent.

Aplicação do reagente de Fenton na desinfecção de esgotos domésticos

RESUMO

Neste trabalho estudou-se a aplicação de processos oxidativos avançados - reagente de Fenton - para desinfecção de esgotos domésticos. Os experimentos para o tratamento foram realizados variando-se as concentrações de peróxido de hidrogênio e ions ferrosos (Fe²⁺/H₂O₂) e valores de pH. As amostras de esgoto foram coletadas na Estação de Tratamento de Esgotos da Ilha do Governador (ETIG) na cidade do Rio de Janeiro, Brasil, com as amostras recolhidas anteriormente ao tratamento biológico por lodos ativados. O pH médio oscilou entre 6,5-7,2 e o valor mais comum foi igual a 6,7. As reações com reagentes de Fenton e início das análises foram realizadas após 24 horas após coleta das amostras. O processo oxidativo, seu comportamento e a eficácia do tratamento foram monitorados por meio da contagem de microorganismos, DQO, DBO, nitrogênio amoniacal entre outros parâmetros. Os resultados obtidos mostraram a eliminação total dos coliformes fecais presentes nas amostras de esgoto bruto quando tratadas com H₂O₂ e Fe²⁺ em concentrações iguais a, respectivamente, 200 e 50 mg/L.

Palavras-chave: Controle da poluição; desinfecção; processo oxidativo; Reagente Fenton.
1. INTRODUCTION

Advanced oxidation processes (AOP) are chemical processes that can be applied to wastewater treatment in order to oxidize pollutants, especially hazardous compounds found in industrial wastewater (Will et al., 2004).

AOP are based on the production of free radicals, hydroxyl radicals (•OH) that have a high potential electrochemical oxidation. The generation of hydroxyl radicals involves the combination of classical oxidants such as H₂O₂ and O₃ with ultraviolet light (UV) or a catalyst. The radicals that are formed react with organic matter eliminating it gradually.

In advanced oxidative processes, Fenton’s reagent has been efficiently used as a chemical process in order to undergo not only the pretreatment, but also the treatment of residual waters. It was discovered more than 100 years ago, but its application as an oxidative process for the destruction of toxic organic composites occurred in the 1960’s (Lin and Jlang, 2002). Fenton’s reagent is a mixture of hydrogen peroxide (H₂O₂) and iron ions (Fe²⁺) generating hydroxyl radical, which is a strong oxidant and reacts rapidly with the most organic compounds present in solution (Amiri et al., 1997). It is recognized not only for its efficiency in the removal of many hazardous organic pollutants in water, but also for the important advantage of mineralizing the organic compounds completely, converting it into carbon dioxide and water or less harmful compounds (Martinez et al., 2003).

Many authors work on the identification of hydroxyl radical as an intermediate in Fenton’s reagent, such as Haber and Weiss (1934) and Lloyd et al. (1997). Until the combination of H₂O₂ and UV radiation with Fe²⁺ ions, known as Photo-fenton process, produces more hydroxyl radicals compared to the conventional Fenton method. In this case, the main advantage of this process is the direct photolysis of H₂O₂ molecules in aqueous solutions by UV radiation of wavelength shorter than 600 nm.

Several applications of Fenton and Photo-fenton processes have been reported, such as treatment of textile wastewaters (Pérez et al., 2002), reduction of Polynuclear Aromatic Hydrocarbons (PAH) in water (Beltran et al., 1998), removal of Adsorbable Organic Halogens (AOX) from pharmaceutical wastewater (Holff et al., 1997), treatment of paper pulp manufacturing effluents (Pérez et al., 2002), and others.

Considering that this study focus on the use of Fenton as a bacteriological disinfectant, some results obtained in laboratory experiments and presented by Diao et al. (2004) are also worth mentioning. Those experiments were carried out in order to investigate the mechanisms of electrochemical (EC) disinfection of artificial wastewater contaminated by *Escherichia coli* culture. Comparative disinfection tests with chlorine, ozone, and hydroxyl (•OH) radicals produced by the Fenton reaction were conducted. The results were performed based on Fe²⁺ and H₂O₂ in concentrations equal to 8.5 mg/L and 0.85 mg/L, respectively; when reaction occurred at pH 4, lasting from 10 to 30 minutes.

As a result, the authors found that Fenton reaction was not the most powerful type of effluent disinfection of E. coli contamination, probably due to the low dosage of Fenton reagent used in the experimental tests compared to most of the conditions of Fenton reaction. However, the Fenton’s reagents were efficient in disinfecting at least 99.4% as shown in Table 1 (Dial et al., 2004).

### Table 1. Laboratory results and bactericidal efficiency of different disinfection methods.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Test Conditions</th>
<th>Bactericidal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton reaction</td>
<td>8.5 mg/L H₂O₂, 0.85 mg/L Fe²⁺, pH 4, 10 min</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>8.5 mg/L H₂O₂, 0.85 mg/L Fe²⁺, pH 4, 30 min</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>10 mg/L, 2.5 min</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>10 mg/L, 5 min</td>
<td>100</td>
</tr>
<tr>
<td>Chlorine</td>
<td>5 mg/L, 30 min</td>
<td>99.94</td>
</tr>
<tr>
<td></td>
<td>5 mg/L, 60 min</td>
<td>99.98</td>
</tr>
</tbody>
</table>
Touati (2000), in *Escherichia coli* culture experiments, has also concluded that the soluble iron in the presence of hydrogen peroxide, due to the Fenton reaction, prevented the aerobic life of cultivated crops. The same occurs with groundwater wells that contain large amounts of ferrous ions (up to 500 μM) and quickly eliminate immersed bacteria such as *E. coli*, resulting in highly pure water wells.

In this context, the aim of this paper is not only to present the results obtained through the implementation of the AOP for wastewater disinfection, but also verify its effectiveness in reducing coliform levels. The efficiency of this process in wastewater treatment in pH similar to the original samples was also observed. In this case, the acidification was dispensed, thereby lowering the operating costs of the process.

Next section presents a brief description of the experimental research divided into three stages.

2. MATERIAL AND METHODS

2.1. Stage 1

The preliminary investigation was based on the concentration rate of Fe$^{+2}$ and H$_2$O$_2$ and the reaction time, which are most commonly used in other researches. The inferior and superior limits of Fe$^{+2}$ and H$_2$O$_2$ and the reaction time were fixed. For H$_2$O$_2$, 25 and 500 mg/L were applied as minimum and maximum limits, respectively. The relation between the concentrations of H$_2$O$_2$ and Fe$^{2+}$ was 5:1 to 10:1 ([H$_2$O$_2$]:[Fe$^{2+}$]) and the inferior limit and superior limit of Fe$^{2+}$ were equal to 5 and 50 mg/L, respectively. The reaction times considered were 15, 30, and 60 minutes. The treatment effectiveness was monitored through dissolved organic carbon (DOC) and fecal coliforms. A previous analysis was performed on each concentration of Fenton’s reagent using only H$_2$O$_2$, named “peroxide blank” or H$_2$O$_2$-blank. This stage was performed using pH 3.0, which is considered the optimum pH level in terms of Fenton’s reagent (Lipczynska-Kochany, 1991) but also the original pH value of the wastewater.

2.2. Stage 2

Once the rate of reagents and reaction time were established, the second stage focused not only on determining the amount of material used, but also on pointing out the optimum concentrations of Fenton’s reagent concerning Fe$^{2+}$ and H$_2$O$_2$ solutions, which should be employed in wastewater treatment without any reaction acidification. All the others experimental conditions were kept the same as the ones described in stage 1.

2.3. Stage 3

The last stage aimed to evaluate the efficiency of Fenton’s reagent applied to the wastewater treatment. The qualifications of the H$_2$O$_2$-blank and the analysis of acid pH were put aside; only the reaction behavior concerning pH level in the wastewater sample was studied. No coagulant compounds were added. After the end of the reaction, it was possible to notice that the pH level had increased to 8.5 and remained at this value for 60 minutes. The sewage samples were collected at Ilha do Governador Wastewater Treatment Plant (ETIG), Rio de Janeiro, Brazil, after physical treatment and before biological treatment with activated sludge. The average pH fluctuated from 6.5 to 7.2, and the most common value was 6.7. The analyses were conducted within 24 hours after sample collection in order to prevent microbial degradation.
3. RESULTS AND DISCUSSION

3.1. Stage 1

Figure 1 shows the results of Dissolved Organic Carbon (DOC) removal using Fenton reaction for the condition \([\text{H}_2\text{O}_2] = 50 \text{ mg/L} \) and \([\text{Fe}^{2+}] = 5 \text{ mg/L}\). The same result was obtained for conditions \((\text{[H}_2\text{O}_2] = 25, 50, 250 \text{ and } 500 \text{ mg/L}; \text{[Fe}^{2+}] = 5 \text{ and } 50 \text{ mg/L})\) and fixed ratio between \text{H}_2\text{O}_2 and \text{Fe}^{2+} concentrations of 5:1 and 10:1. These results indicate that the organic matter removal in effluent was not significant even when the reaction time variation was applied. At pH 3.0 (optimum pH level in terms of Fenton’s reagent) a slight reduction of organic carbon was observed, although in an insignificant portion of the samples. However, at pH 7.1, originated from the same wastewater sample, the DOC rate was slightly higher for all reaction times. In this case, it is likely that some of the DOC removal may be associated with the mature domestic wastewater.

![Figure 1. DOC results for the condition \([\text{H}_2\text{O}_2] = 50 \text{ mg/L} \) and \([\text{Fe}^{2+}] = 5 \text{ mg/L}\).](image1)

In terms of fecal coliforms, the effect of Fenton reaction on the degradability was studied considering only the hydrogen peroxide action (\text{H}_2\text{O}_2-blank) in a concentration equal to 25 mg/L and using both pH values. Figure 2 shows that at pH 6.6, the most probable number of fecal coliforms (MPN) remaining per 100 mL, maintains a rate of \(10^5\) to \(10^7\) for all reaction times. At pH 3.0 this value ranges from \(10^3\) and \(10^4\) fecal coliforms per 100 mL of treated wastewater.

![Figure 2. Result of the effluent's treatment (fecal coliform results) using only \text{H}_2\text{O}_2 in a concentration equals to 25 mg/L.](image2)
Figure 3 shows the results of the wastewater treatment with Fenton’s reagent with $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio equals to 5:1. The results show that at pH 3.0 the quantity of coliforms is less than 10 NMP/100mL and that it also decreases with time. This can be associated with the oxidative degradation capacity and average acidity. At pH 6.8 of the wastewater samples and $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ equal to 25 e 5 mg/L, respectively, the Fenton’s reagent did not enable wastewater disinfection.

The next reaction condition was to analyze the results using $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ ratio equals to 10:1. It was observed that also in this case the peroxide blank results allowed to evaluate the contribution of the Fenton’s reagent applied to sewage treatment compared to applying a simple treatment that uses only a common oxidant compound. The $\text{H}_2\text{O}_2$ concentration of this test was 50 mg/L. Figure 4 shows the results obtained under this condition.
In this case, taking into consideration normal pH from wastewater sample and all reaction times adopted, the disinfection occurs in two orders of magnitude leading to an amount of remaining fecal coliforms in the order of $10^6$ NMP/100 mL.

At pH 3.0 the amount of coliforms was less than 10 per 100 milliliters. Once again, that can be associated not only with the oxidative process degradation capacity but also to the average acidity, as a result of the peroxide action.

Figure 5 shows the results of the wastewater treatment with Fenton’s reagent with $H_2O_2:Fe^{2+}$ ratio equals to 10:1.

![Figure 5](image.png)

**Figure 5.** Fecal coliform results for the condition $[H_2O_2] = 50$ mg/L $H_2O_2$ and $[Fe^{2+}] = 5$ mg/L and $H_2O_2:Fe^{2+}$ ratio equals to 10:1.

In this case, the effluent showed a slight increase of pH value when compared to the value normally found. The oxidative process, at the original pH value of 7.1, did not show any substantial reduction. The degradable capacity can be associated with the pH value of the wastewater, which demonstrated a slight increase tending to neutrality.

At pH 3.0, once again, the remaining amount of coliforms was kept less than 10 NMP/100 mL. The same conditions - concentrations and pH variation - lead to the conclusion that the Fenton’s reagent oxidation capacity is not largely responsible for the elimination of the microorganisms. For both pH values the results are extremely different indicating that, under the condition of low reagent concentrations, the sulfuric acid should probably be the most responsible for the disinfection.

Figure 6 presents the analysis of $H_2O_2$-blank with a 250 mg/L concentration. At pH 3.0 the disinfection is complete as a result of the hydrogen peroxide oxidation capacity combined with the harmful capacity of the acid medium. At pH 6.6 (sewage sample) and $[H_2O_2] = 250$ mg/L, the peroxide showed significant disinfection capacity with values less than 100 NMP/100 mL undergoing a 30-minute reaction.
Similar results can be observed using $\text{H}_2\text{O}_2$:Fe$^{2+}$ ratio equals to 5:1 (Figure 7). In concentrations of $\text{H}_2\text{O}_2$ and Fe$^{2+}$ equal to 250 and 50 mg/L, respectively, under both pH values, the elimination of fecal coliforms is quite satisfactory leaving less than 10 fecal coliforms per 100 mL of treated wastewater.

In order to complete the analysis proposed for stage 1, the fecal coliform analysis was performed using only $\text{H}_2\text{O}_2$-blank with 500 mg/L concentration (Figure 8a) and Fenton’s reagent at the same $\text{H}_2\text{O}_2$-blank concentration, [Fe$^{2+}$] = 50 mg/L (Figure 8b), and $\text{H}_2\text{O}_2$:Fe$^{2+}$ ratio equals to 10:1.
Figure 8. Fecal coliform results: a) for the condition $[\text{H}_2\text{O}_2] = 500 \text{ mg/L}$ $\text{H}_2\text{O}_2$; b) for the condition $[\text{H}_2\text{O}_2] = 500 \text{ mg/L}$ $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+} = 50 \text{ mg/L}$.

It can be observed that, except for a possible contamination in the analysis of the $\text{H}_2\text{O}_2$-blank, the results are similar for both tests, for all pH values and reaction times.

3.2. Stage 2

Based on the previous results, the second stage focused on pointing out the optimum configuration of Fenton’s reagents ($\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ solutions) that could be applied to wastewater treatment without any reaction acidification. In this study, a $\text{Fe}^{2+}$ concentration of 50 mg/L was used. Through the use of Jar-Test, it was possible to analyze 6 values of hydrogen peroxide concentration simultaneously: 50, 100, 200, 300, 400, and 500 mg/L. Figure 9 shows the fecal coliform analysis of $\text{H}_2\text{O}_2$-blank in the two pH conditions.

Figure 9. Fecal coliform results in the condition of 50 to 500 mg/L $\text{Fe}^{2+}$.

Figure 10 shows the results obtained considering the number of coliforms remaining after the treatment with Fenton’s reagent with both pH values.
In order to understand the results obtained in this stage, Figure 11 shows the results of H2O2-blank and Fenton’s reagent reactions with wastewater pH original value.

In this case, except for a possible bacteriological contamination, Fenton’s reagent was used with the highest concentrations of H2O2 and Fe2+ that is 200 mg/L and 50 mg/L, respectively.

3.3. Stage 3

The goal of this stage was to evaluate the practical effectiveness of wastewater treatment using a laboratory-scale system. The coagulation was initiated after the end of the oxidation reaction, in H2O2 and Fe2+ concentrations of 200 and 50 mg/L, respectively.

The volume of treated effluent remained under coagulation effect for 60 minutes at 100 rpm rotation. The pH value was monitored and kept at 8.5 by increasing NaOH concentration, which was equal to 1.0 mol/L. Table 2 shows the comparison of obtained values for raw and treated wastewater.
Table 2. Results for raw and treated wastewater analysis at 200 mg/L H₂O₂ and 50 mg/L Fe²⁺ conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw wastewater</th>
<th>Methodology of wastewater treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fenton’s reagent</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Fecal Coliforms (NMP/100 mL)</td>
<td>4.6x10⁵</td>
<td>0</td>
</tr>
<tr>
<td>Total Alkalinity (mg CaCO₃/L)</td>
<td>126</td>
<td>44</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>0.87</td>
<td>0.91</td>
</tr>
<tr>
<td>Chloride (mg Cl/L)</td>
<td>112</td>
<td>121</td>
</tr>
<tr>
<td>DOC (mg O₂/L)</td>
<td>373</td>
<td>333</td>
</tr>
<tr>
<td>BOD (mg O₂/L)</td>
<td>176</td>
<td>66</td>
</tr>
<tr>
<td>Total suspended solids (mg/L)</td>
<td>120</td>
<td>134</td>
</tr>
<tr>
<td>Volatile suspended solids (mg/L)</td>
<td>112</td>
<td>86</td>
</tr>
<tr>
<td>Ammoniacal nitrogen (mg N-NH₃/L)</td>
<td>29</td>
<td>25</td>
</tr>
</tbody>
</table>

In order to provide comparable scenarios, result analysis are presented in comparison to Brazilian water quality standards established by the National Council for the Environment in its Resolution CONAMA¹ 357/05, as presented in Table 3.

Table 3. Parameters established by CONAMA in its Resolution 357/05.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Water Classification - Maximum Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1*</td>
</tr>
<tr>
<td>pH</td>
<td>6.0 – 9.0</td>
</tr>
<tr>
<td>Fecal Coliforms (NMP/100 mL)</td>
<td>200</td>
</tr>
<tr>
<td>Chloride (mg Cl/L)</td>
<td>250</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>3.0</td>
</tr>
<tr>
<td>Ammoniacal nitrogen (mg N-NH₃/L)</td>
<td>0.5 – 3.7</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Class 1*: freshwater used for: a) water supply after simplified treatment, b) protection of aquatic communities, c) primary contact recreation; d) irrigation of vegetables that are consumed raw and fruits which grew close to the ground and are eaten raw without peel removal; e) protection of aquatic communities on Indigenous Lands.

**Class 2**: freshwater used for: a) water supply after conventional treatment, b) protection of aquatic communities, c) primary contact recreation; d) irrigation of vegetables, fruit trees and plants in parks, gardens, sports fields, and recreation with which the public might have direct contact; e) aquaculture and fishing activity.

***Class 3**: freshwater used for: a) water supply after conventional or advanced treatment, b) irrigation of trees, crops, cereals and fodder; c) recreational fishing; d) secondary contact recreation; e) watering livestock.

Through the result analysis (Tables 2 and 3) it is possible to affirm that applying BOD and ammoniacal nitrogen indicators, Fenton’s reagent and its variation, combined with coagulation effect, were not only able to treat the effluent, but also to reduce some of the parameters to acceptable concentration levels. Some of them were even considered to have high quality water body characteristics by reaching CONAMA 357/05 Resolution Class 1 maximum limits.

The elimination of fecal coliforms was satisfactory with both processes (Fenton’s reagent and Fenton’s reagent + coagulation), that was expected considering the concentrations of

¹ CONAMA - National Council for the Environment – Conselho Nacional do Meio Ambiente - Provides for the classification of water bodies and establishes the conditions and discharge standards for effluents, and other measures.
H₂O₂ and Fe²⁺ used. For Fenton’s reagent + coagulation the value of 4 NMP/100 mL may have occurred due to contamination caused by a long air contact.

4. CONCLUSIONS

Several researchers have already investigated the Fenton and photo-Fenton reactions as an alternative and promising wastewater treatment process. However, it is recognized that a major disadvantage of AOP for wastewater treatment is the high investment costs (plant complexity) and operation (high consumption of reagents and energy). This fact implies that AOP for wastewater treatment are usually more appropriate when biological treatments are not totally effective.

In this work, the effectiveness of the Fenton’s reaction in wastewater disinfection was studied and it was possible to conclude that the efficiency of chlorination was highly recognized in the disinfection process. The results have shown a total elimination of the fecal coliforms in the wastewater samples when treated with H₂O₂ and Fe²⁺ in concentrations of 200 mg/L of 50 mg/L, respectively.

Non-relevant result was verified on the reduction of organic matter and nitrogen by the analysis of total organic carbon, BOD, and ammoniacal nitrogen. Such fact may not be a concern if the intended use is, for instance, crop irrigation. In addition, it may provide an extra supply of nutrients to the soil.

5. REFERENCES


