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RESEARCH ARTICLE

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PHOTOCATALYTIC OXIDATION AND HETEROGENEOUS FENTON APPLICATIONS  
WITH PAPER INDUSTRY WASTEWATER

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ABSTRACT

Nowadays, leaving industrial wastewater into receiving environment causes serious environmental problems. In this study, experimental studies on color and chemical oxygen demand (COD) removal of paper industrial wastewater were carried out. In this context, heterogeneous Fenton and photocatalytic oxidation processes were applied and removal efficiencies were compared. The Fe(III)/MnO<sub>2</sub> catalyst containing 8% w/w of iron ion was synthesized to be used in experimental studies. The effects of parameters such as pH, catalyst amount, hydrogen peroxide concentration and reaction time were investigated. At the end of the experimental studies, 90% color and 55% COD removal efficiencies were obtained in heterogeneous Fenton process after 120 minutes reaction time under optimum conditions. After 60 minutes reaction time under the same optimum conditions, 97% color and 91% COD removal efficiencies were achieved in photocatalytic oxidation process.

**Keywords:** Heterogeneous Fenton, Photocatalytic oxidation, Paper

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1. INTRODUCTION

In recent years, the paper industry has been known to be the largest water consumer in the world and as a result produces a large amount of wastewater [1]. The high amount of water used during paper production and the fact that wastewaters contain non-biodegradable pollutants make the wastewater of these industries an environmental problem [2]. Paper wastewater generally contains carbohydrates (glucose, xylose, galactose, mannose, arabinose, etc.), extracts (fatty acids, resin acids, triglycerides) and low molecular weight compounds (formic acid, acetic acid, oxalic acid) [3]. These wastewaters disrupt the ecological balance in the receiving water environments, as well as cause the rapidly decreased dissolved oxygen levels. They cause problems in wastewater treatment due to their non-biodegradability and potential and toxicity on living organisms [4, 5]. In recent years, advanced oxidation processes are preferred, which oxidize non-biodegradable industrial wastewater into more harmless form (carbon dioxide, water and inorganic salts) [6, 7].

Fenton process, which is one of the advanced oxidation processes, consists of four stages: oxidation, neutralization, coagulation/flocculation and precipitation. It is based on catalytic degradation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) by reacting with ferro iron (Fe (II)) under strong acidic conditions. This reaction produces hydroxyl (OH·), which is a strong oxidant radical. Hydroxyl radical is a non-selective radical with high oxidation potential (2.8 eV), capable of oxidizing structures of organic and inorganic origin. With these advantages, Fenton process is an advanced oxidation process that can easily be used in the treatment of industrial wastewater and can provide wastewater discharge limits [8-10].



In the classical Fenton process; There are many limitations such as a large amount of sludge waste, non-recovery of iron ions and the non-discharge of waste water with iron ions. Such problems have

developed heterogeneous Fenton process applications using catalysts in which iron ions are fixed to a catalyst support. In heterogeneous Fenton process, the catalyst can be easily recovered and reused from the solution medium [11, 12].

The processes in which UV rays are used together with the catalyst are called photocatalytic oxidation processes [13]. When UV rays are used together with the catalyst, it increases the efficiency of the catalyst and provides more hydroxyl radical formation. In addition, two moles of hydroxyl radicals are formed as a result of photolysis of H<sub>2</sub>O<sub>2</sub> by UV rays. The radicals formed undergo an oxidation reaction with the organic compounds in the environment and break down the organic compounds [14-16].



Semiconductor metal oxides are used as catalysts in photocatalytic oxidation processes. Semiconductor induced by a light source can be defined as photocatalysis by eliminating photoactive organic and toxic components on the oxidizing surface by converting them to radical, H<sub>2</sub>O and/or CO<sub>2</sub> [17]. When photocatalytic semiconductors interact with UV light, an electron emerges into the conductivity band and an electron-gap pair is formed, and the resulting electron-gap pair can cause a series of reactions to form OH· and break down organics [18].

In recent years, metal oxides such as titanium dioxide (TiO<sub>2</sub>), copper oxide (CuO), zinc oxide (ZnO), tin dioxide (SnO<sub>2</sub>) have been used in many wastewater removal studies [19]. MnO<sub>2</sub> metal oxide has been preferred recently due to its superior physicochemical, mechanical and photocatalytic properties. Its low cost, high redox potential and non-toxic properties have attracted considerable attention [20, 21].

In this study, color and COD removal of paper industry wastewater was investigated by applying heterogeneous Fenton and photocatalytic oxidation processes. In this context, Fe(III)/MnO<sub>2</sub> containing 8% w/w of iron ion was synthesized as catalyst. The effects of parameters such as pH, catalyst amount, hydrogen peroxide concentration and reaction time on color and COD removal were investigated.

## 2. MATERIALS AND METHODS

### 2.1. Materials

In heterogeneous Fenton and photocatalytic oxidation processes experimental studies the wastewater obtained from a paper mill located in Turkey was used. The characteristics of wastewater are given in Table 1. Iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) (Sigma Aldrich), manganese(IV) oxide (MnO<sub>2</sub>) (Merck) and ammonium hydroxide (NH<sub>4</sub>OH) (Sigma Aldrich) were used in catalyst synthesis. 30% w/w hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was supplied from Sigma Aldrich.

**Table1.** The characteristics of wastewater

Characteristic	pH	COD (mg/l)	TSS (mg/l)
Value	6.5	6320	263

### 2.2. Preparation of Catalyst

Fe(III)/MnO<sub>2</sub> catalysts containing 8% w/w Fe(III) were synthesized by co-precipitation procedure. For this purpose, solutions containing the metal salt and salt of a compound are mixed with a base solution and provided to precipitate as hydroxide form. It is then converted to oxides by heating.

According to this method,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{MnO}_2$  salts were dissolved in 100 ml of distilled water. The solution was then heated to  $65^\circ\text{C}$  with stirring in a heated magnetic stirrer.  $\text{NH}_4\text{OH}$  was added to the solution until the pH reached 9. The next step in the process was to agitate the solution at  $65^\circ\text{C}$  for 2 hours at 300 rpm. After the aging process, the precipitate was separated and dried in the oven at  $105^\circ\text{C}$  for 24 hours. Finally, the dried precipitate was left in the ash oven at  $600^\circ\text{C}$  for 2 hours [22, 23].

### **2.3. Methods**

In the heterogeneous Fenton experimental studies, the pH value of the wastewater sample was first adjusted to the desired value. The determined amounts of catalyst were added to the sample and  $\text{H}_2\text{O}_2$  solution was added and shaken in the shaking water bath at constant temperature. At the end of the reaction period, the required color and COD analyzes of the sample were performed.

Photoreactor device was used in experimental studies of photocatalytic oxidation process. There were 18 UV (365nm) lamps each with 8 W intensity in the photoreactor device. All experiments were performed using a quartz glass beaker. In the experimental studies, a predetermined amount of catalyst and  $\text{H}_2\text{O}_2$  solution were added to the pH-adjusted sample and the lamps of the photoreactor were switched on. Then samples were taken periodically and color and COD analyzes were performed.

### **2.4. Analysis**

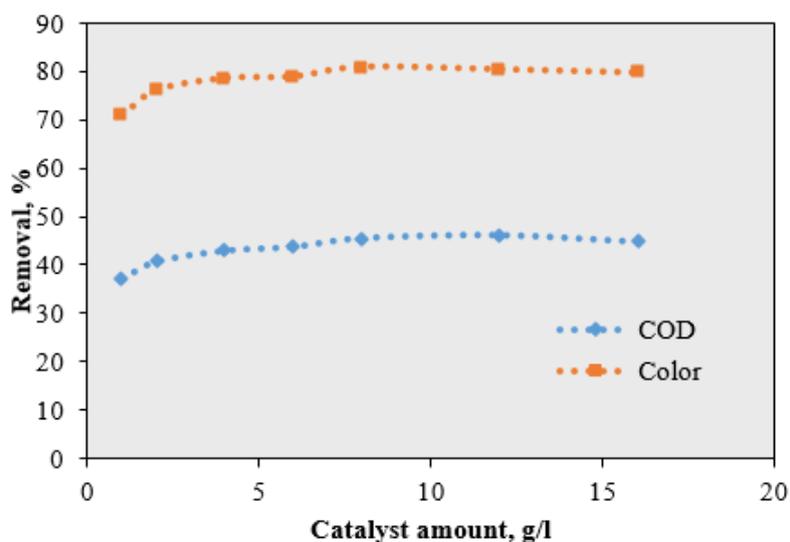
Color and COD analyzes were performed on a spectrophotometer (Hach Lange DR 3900). For the COD analysis, Hach Lange LCK 514 13 mm diameter COD test kits were used. The color analyzes were realized at 365.6 nm ( $\lambda_{\text{max}}$ ).

Surface area and pore size analyzes of the synthesized  $\text{Fe}(\text{III})/\text{MnO}_2$  catalyst were determined by Brunauer, Emmet and Teller (BET) method. According to the results of the analysis, the surface area was  $30.91 \text{ m}^2/\text{g}$  and the pore size was 2.01 nm. Since the pore sizes of the catalysts are between 2-50 nm, they are classified as mesoporous catalysts. The mass transport in most heterogeneous catalysts take place primarily mesopores [24].

## **3. RESULTS AND DISCUSSION**

### **3.1. Effect of Catalyst Amount on Heterogeneous Fenton**

In heterogeneous Fenton processes, it is important to use reagents at appropriate concentrations. Excess or deficiency of a reagent can significantly affect process efficiency. Iron is stabilized in the catalyst in heterogeneous Fenton processes and reacts with hydrogen peroxide to produce hydroxyl radicals [25]. Therefore, the determination of the amount of catalyst in oxidation processes is one of the important parameters. For this purpose, experimental studies were carried out in different amounts of  $\text{Fe}(\text{III})/\text{MnO}_2$  (1.0, 2.0, 4.0, 6.0, 8.0, 12.0 and 16.0 g/l) and their effects on color and COD removal efficiencies were investigated. The results were given in Figure 1.

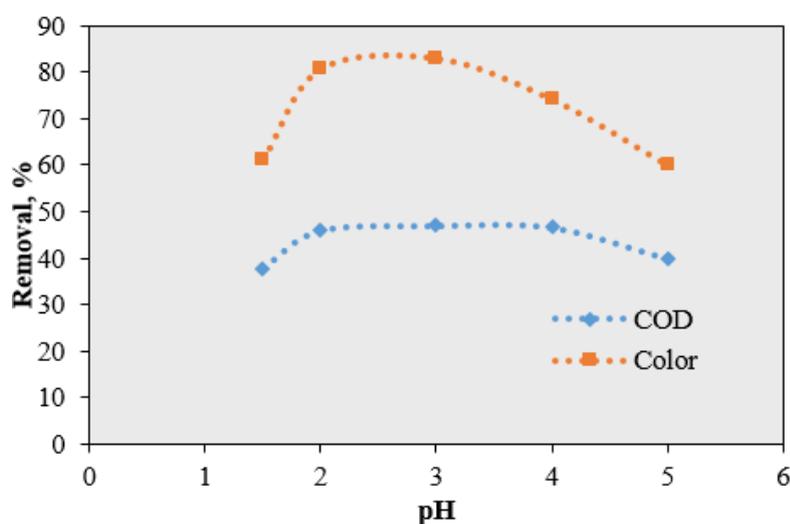


**Figure 1.** Effect of catalyst amount (pH=2, H<sub>2</sub>O<sub>2</sub>=250 ppm, T=30°C, reaction time 120 minutes).

When the effect of catalyst amount on paper industrial wastewater treatment was examined, color and COD removal efficiencies increased with increasing amount of catalyst and remained constant after 8.0 g/l. As shown in Figure 1, color removal efficiency was obtained higher than COD removal efficiency. The color removal efficiency as 80.9% and the COD removal efficiency as 45.5% were obtained in the catalyst amount of 8.0 g/l which was determined as optimum value. As the amount of Fe(III)/MnO<sub>2</sub> catalyst increases, the active sites catalyzing the formation of hydroxyl radicals by H<sub>2</sub>O<sub>2</sub> on the catalyst surface are increased. This situation increases the color and COD removal efficiencies of the wastewater [26, 27].

### 3.2. Effect of pH on Heterogeneous Fenton

The activity of iron is greatly influenced by the pH in heterogeneous Fenton processes. The precipitation of iron ion at high pH values causes it to lose its activity. Therefore, oxidation process is more efficient under acidic conditions [28, 29]. However, at very low pH values, hydrogen ions react with hydroxyl radicals and create a scavenging effect [30]. Therefore, to determine the effect of pH on color and COD removal, the experimental studies were carried out by changing the pH values between 1.5-5.

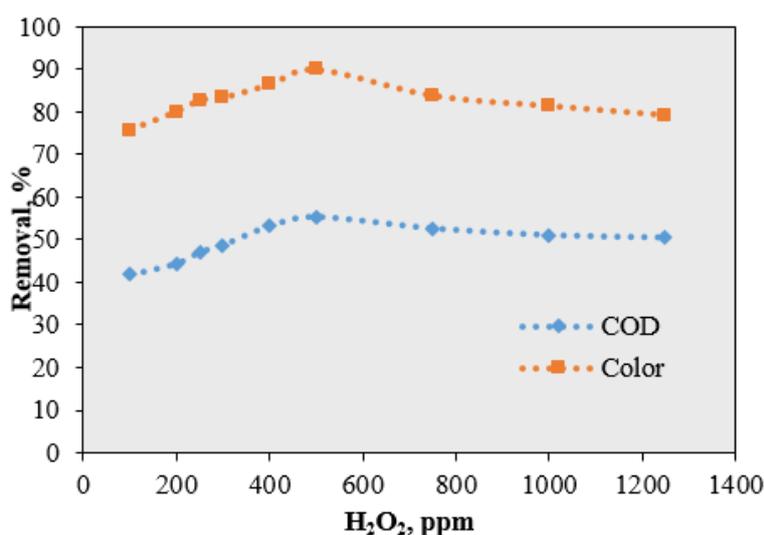


**Figure 2.** Effect of pH (m=8.0 g/l, H<sub>2</sub>O<sub>2</sub>=250 ppm, T=30°C, reaction time 120 minutes).

Considering by the results given in Figure 2, the optimum pH value for heterogeneous Fenton process was determined as 3. As pH increased, color and COD removal efficiencies decreased due to the loss of iron ion activity. At high pH values, the formation of ferric hydroxide complexes and the presence of passive iron oxohydroxides reduces the activity of Fenton reagents. Since the ferric hydroxide formed decomposes hydrogen peroxide to oxygen and water, the oxidation potential of hydroxyl radicals decreases as the pH increases [31, 32]. The color and COD removal efficiencies at optimum pH were obtained as 83.0% and 47.0%, respectively.

### 3.3. Effect of H<sub>2</sub>O<sub>2</sub> concentration on Heterogeneous Fenton

Since hydrogen peroxide is a source of hydroxyl radical is an important parameter in the studies. It is important to determine the optimum concentration as the excess hydrogen peroxide remaining in the environment as a result of its reaction with iron ion will cause pollution [33]. The hydrogen peroxide concentration was changed between 100 ppm and 1250 ppm values and the effects on color and COD removal efficiencies were investigated.

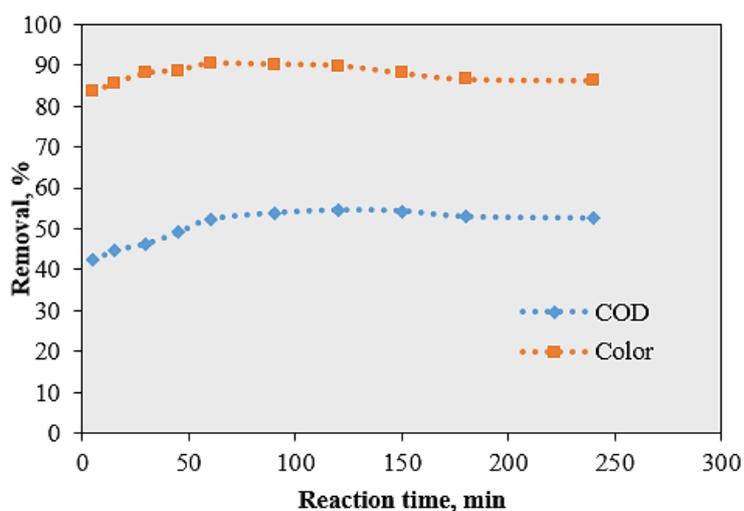


**Figure 3.** Effect of H<sub>2</sub>O<sub>2</sub> concentration (m=8.0 g/l, pH=3, T=30°C, reaction time 120 minutes).

According to Figure 3, increasing hydrogen peroxide concentration increased color and COD removal efficiencies. Increasing the concentration of hydrogen peroxide increases the removal efficiency to since it will provide more hydroxyl radicals to the environment. However, at higher hydrogen peroxide concentrations, the removal efficiency decreases due to the scavenging effect of hydrogen peroxide. This can be explained by the reaction of hydrogen peroxide and hydroxyl radicals to produce hydroperoxyl radicals (HO<sub>2</sub><sup>•</sup>). Hydroperoxyl radicals are less reactive than hydroxyl radicals and therefore do not contribute to degradation of the compounds [34, 35]. The maximum color and COD removal efficiencies were obtained at 500 ppm hydrogen peroxide concentration. Since the color and COD removal efficiencies started to decrease at higher concentrations than 500 ppm, the optimum value was determined as 500 ppm.

### 3.4. Effect of Reaction Time on Heterogeneous Fenton

In order to examine the effect of reaction time on color and COD removal efficiencies, 5, 15, 30, 45, 60, 90, 120, 150, 180, 240 minutes values were studied. The obtained results were given in Figure 4.

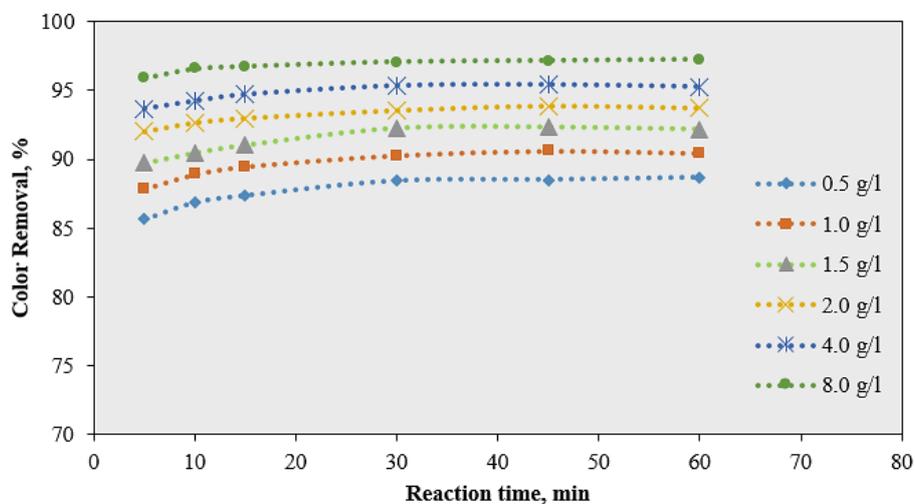


**Figure 4.** Effect of reaction time (m=8.0 g/l, pH=3, H<sub>2</sub>O<sub>2</sub>=500 ppm, T=30°C).

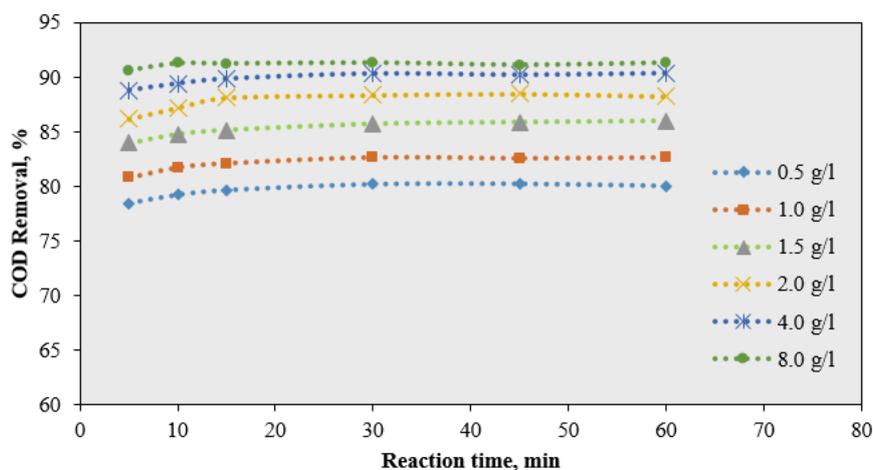
When Figure 4 was examined, it was concluded that effective color and COD removal efficiencies were achieved at low reaction times in heterogeneous Fenton process for paper industrial wastewater treatment. According to the results, color and COD removal efficiencies rates increased in the first 60 minutes. Then, the rate of increase of removal efficiencies decreased and remained constant after 120 minutes. Since no significant increase was observed after 120 minutes, optimum reaction time was determined as 120 minutes in the experimental study. In the determined optimum reaction time, the color removal efficiency was 90.1% and the COD efficiency was 55.2%.

### 3.5. Photocatalytic Oxidation Results

To investigate the effect of UV light on color and COD removal efficiencies, photocatalytic oxidation process experimental studies were conducted. In the experimental studies, a photoreactor device having 18 UV (365 nm) lamps was used. The studies were carried out at optimum pH (3) and optimum hydrogen peroxide concentration (500 ppm) determined in heterogeneous Fenton process. The amount of catalyst was changed at 0.5, 1.0, 1.5, 2.0, 4.0 and 8.0 g/l to investigate the effect on color and COD removal efficiencies. The experimental results obtained were reported in Figure 5 and Figure 6.



**Figure 5.** Effect of catalyst amount on color removal ( pH=3, H<sub>2</sub>O<sub>2</sub>=500 ppm, T=30°C).



**Figure 6.** Effect of catalyst amount on COD removal ( pH=3, H<sub>2</sub>O<sub>2</sub>=500 ppm, T=30°C).

In photocatalytic oxidation processes, due to UV light effect, it was observed that color and COD removal efficiencies were higher than heterogeneous Fenton process with low catalyst amount and short reaction times. When the amount of catalyst was 0.5 g/l, 88.7% color and 80.0% COD removal efficiencies were achieved in the first 60 minutes. At the amount of catalyst 4.0 g/l, color and COD removal efficiencies increased to 95.3% and 90.3%, respectively, within the first 60 minutes. These amount of catalyst and reaction time were half of the optimum amount of catalyst (8.0 g/l) and optimum reaction time (120 min) determined in the heterogeneous Fenton process. However, the achieved color and COD removal efficiency increases considerably compared to the heterogeneous Fenton process. When the amount of catalyst was 8.0 g/l and the reaction time was 60 minutes, the color removal efficiency was 97.2% and the COD removal efficiency was 91.3%. The use of UV rays increases the efficiency of the oxidation process. In addition to their oxidation activity, UV rays increase the efficiency and conversion of the catalyst, resulting in more radical formation. As a result, the rate of decomposition of organic pollutants in the reaction with hydroxyl radicals is greater than the heterogeneous Fenton reaction and the reaction time is low [15, 36, 37].

#### 4. CONCLUSION

In this study, color and COD removal from paper industry wastewater was investigated comparatively with heterogeneous Fenton and photocatalytic Fenton processes. In this study, the effects of pH, catalyst amount, hydrogen peroxide concentration and reaction time which were the main parameters of heterogeneous Fenton process were investigated and optimum experimental conditions were determined. As a result of the experimental study, optimum conditions such as pH 3, the amount of catalyst 8.0 g/l, hydrogen peroxide concentration 500 ppm and reaction time 120 minutes were determined for heterogeneous Fenton process.

Under these optimum conditions, 90% color and 55% COD removal efficiencies were obtained by heterogeneous Fenton process. In the photocatalytic oxidation process under the same optimum conditions, higher color (97%) and COD (91%) removal efficiencies were obtained at lower reaction time. It has been found that, with the use of catalyst and UV radiation together, it increases the production of hydroxyl radicals, thus increasing the color and COD removal efficiencies by better decomposition of organic pollutants. As a result, heterogeneous Fenton process and photocatalytic oxidation processes have been identified as efficient processes for the treatment of such industrial wastewater.

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