Treatment of Industrial Wastewater Using Advanced Oxidation Processes

Abdel-Aal, E.A.1*; Farghaly, F.E.1; Abdel-Wahed, R.T.1; El-Shahat, M.F.2

1Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87 Helwan, Egypt
2Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt
*Corresponding Author: Email: eabde2@gmail.com

Abstract. Nowadays, water pollution and its scarcity are the main problems that humankind is facing. In this regards, great attention is being given to the removal of organic pollutants from wastewater by advanced oxidation processes (AOPs) that are based on generation of highly reactive species, especially hydroxyl radicals. Among them, Fenton and photo-Fenton’s oxidation processes. In this work, a comparison between fenton process and photo-fenton oxidation process as advanced oxidation processes for treatment of tannery wastewater was made. Firstly, the physicochemical characteristics of the filtered effluent were determined. The chemical oxygen demand (COD) is 554 ppm, total organic carbon (TOC) is 170.8 ppm, total dissolved solids is 50 gj-1 and the pH is 3.5. The maximum COD removal is (82.7%) for fenton’s oxidation process and for photo-Fenton process giving maximum COD removal (90.1%) at pH 3, Fe2+ 0.5 gj-1, H2O2 30 gj-1 and time 2h. All experiments were performed at ambient temperature followed by precipitation of chromium with NaOH at pH 8.5, stirring 0.5 h, settling 2h. The low cost iron sulfate and high COD removal make photo-fenton process superior method for degradation of organic pollutants from tannery wastewater. This study was made with the help of UV-Vis/NIR spectrophotometer and FT-IR analyses.

Keywords: photodegradation, Tannery wastewater, Photo-fenton

1. INTRODUCTION

Nowadays, tanning industry is the backbone of the Egyptian economy. The tanning process includes chemical operations that use different chemicals which after use are discharged as wastewater. These chemical pollutants include fats, proteins, chromium-complexed collagen, surfactants, tannins, sulfide, chromium, chlorides and salts. Thus the tannery wastewater is a mixture of biogenic materials of hides and a wide variety of organic and inorganic chemicals. Many of these materials are recalcitrant and not easily biodegradable. About 40 m3 of water and 700 kg of various chemicals are used to convert one tone of hides or skins into leather generating about 32 m3 wastewater.

Various physicochemical processes are used for tannery wastewater treatment such as ozonation (Houshyar et al., 2012), reverse osmosis (Hafez and El-Manharawy, 2004); Ranganathan and Kabadgi, 2011), activated carbon adsorption (Ayoub et al., 2011), ion exchange (Deep et al., 2006), coagulation (Song et al., 2004), electrodialysis (Rodrigues et al., 2008), flocculation (Ranganathan and Kabadgi, 2011) and biological (Lofrano et al., 2013) processes. The presence of these organic pollutants represents obstacles for conventional chemical and biological wastewater technologies (Schrank et al., 2005). For this reason, other advanced and hybrid processes should be studied for heavily polluted tannery wastewater treatment (Mandal et al., 2010) and converting the inert COD to biodegradable forms and increasing of the rates of biodegradation of organics in tannery wastewater (Iaconi, 2012; Dogruel et al., 2006; Iaconi et al., 2010).

Advanced oxidation processes (AOPs) are promising methods for generation of hydroxyl radical which is a powerful and non selective oxidant for mineralization or degradation of these recalcitrant organic pollutants present in tannery effluent (Schrank et al., 2005). One of these processes is Fenton’s oxidation process in which organic pollutants react with hydrogen peroxide in the presence of inexpensive ferrous sulfate to reduce toxicity and organic load (COD). This oxidation may occur via one of three general pathways: hydrogen abstraction, electron transfer and radical addition (Alnaizy and Akgerman, 2000) (Eqs. (1)-(4)) (Kang and Hwang, 2000).

Many of commercial AOPs including photo-fenton process use the UV photolysis of H2O2 to generate hydroxyl radical, Eq. (5) (Amiri, 1997). Other reactions can also take place depending on the conditions (Eqs. (6)-(8)) (Crittenden et al., 1999).
The mechanism of photo-fenton process includes photolysis of H$_2$O$_2$ for generation of hydroxyl radical (Eq.(5)). The reactions of hydrogen abstraction and Fe$^{2+}$ regeneration can take place (Eqs.(2), (3)).

Previous studies focused on AOPs applications on tannery wastewater treatment such as Schrank et al and Porkrywiecki Sauer who observed an increase of toxicity to Daphnia magna and Artemia salina after UV/TiO$_2$ treatment respectively (Schrank et al., 2004; Sauer et al., 2006). Bauer et al used UV/TiO$_2$ and photo-fenton (Fe$^{2+}$/H$_2$O$_2$/UV-Vis) processes for degradation of 4-Chlorophenol (Bauer et al., 1999). Other researchers reported the use of mesoporous activated carbon with fenton method to reduce organic load in tannery wastewater (Sekaran et al., 2013; Karthikeyan et al., 2012). S. Karthikeyan suggested heterogenous and homogenous fenton oxidation process (Karthikeyan et al., 2011). The conditions of fenton and photo-fenton experiments depend on the type of wastewater and organic load. Richard G. Zepp, et al mentioned the principle of formation of hydroxyl radical in the pH range (3-8) in aqueous photo-fenton reaction (Zepp et al., 1992). A typical AOPs includes O$_3$/UV, TiO$_2$/UV, O$_3$/H$_2$O$_2$, H$_2$O$_2$/UV (Vijayalakshmi et al., 2011, Estrada et al., 2007) and UV/O$_3$/H$_2$O$_2$ oxidation methods were reported for photodegradation of organic pollutants (Popiel et al., 2008).

The aim of this work is the study of advanced oxidation of organic pollutants present in tannery wastewater applying Fe$^{2+}$/H$_2$O$_2$, H$_2$O$_2$/UV, Fe$^{2+}$/H$_2$O$_2$/UV oxidation processes. The efficiencies of these AOPs for the treatment of such wastewater were judged by the percentage of removal of chemical oxygen demand. Post-treatment proceeds with chemical precipitation for chromium and residual iron using sodium hydroxide at pH 8.5, stirring time 0.5h, settling time 3h at ambient temperature.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Tannery wastewater

The wastewater used in this study was supplied by a commercial tannery in the region of Ain El-Sira, Misr El-kadima, and Cairo, Egypt. Their main characteristics are given in table. 1. The elemental analysis of tannery wastewater conducted with the help of inductive couple plasma anlysis is given in table 2.

2.1.2. Chemicals

For fenton and photo-fenton processes, the chemicals used in this study are ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O), hydrogen peroxide solution (30% w/v), deionized water, sulfuric acid 98%, sodium sulfite, sodium hydroxide, potassium dichromate, 1,5 diphenyl carbazide, silver sulfate 99% and acetone. All chemicals are of analytical grade.
2.2. Methods

2.2.1. Fenton's oxidation process

All homogenous fenton experiments were carried out in 500 ml flask with constant magnetic stirring at ambient temperature. Different concentrations of ferrous sulfate heptahydrate were mixed with untreated tannery wastewater and the pH value was adjusted using pH meter model 211, USA. The reaction started when $\text{H}_2\text{O}_2$ was added to the tannery solution.

![Graph showing COD removal percentage versus Fe$^{2+}$ concentration]

**Fig. 1:** The effect of Fe$^{2+}$ concentration on COD removal from tannery wastewater by (A) fenton process (pH 3.5 and $\text{H}_2\text{O}_2$ 35 g/l, time 2h) and (B) photo-fenton process ($\text{H}_2\text{O}_2$ (30 g/l), pH 3, time 2h)

2.2.2. Photo-fenton's oxidation process

Photo-fenton experiments were carried out in 500 ml Pyrex photo reactor surrounded by a quartz jacket for cooling. Inside the reactor a medium pressure mercury lamp (150W, Heraeus (noblelight-TQ150), Germany) having a continuous emission at wave length 254 nm was placed. The solution was bubbled with air generator and magnetically stirred during irradiation. Different concentrations of Fe(II) were mixed with 200 ml of tannery wastewater and the pH value was adjusted using pH meter. The reaction starts when irradiation starts. All experiments were carried out at ambient temperature. Samples were taken from the photoreactor at certain times for measurement of COD value using open reflux method as a standard method for measuring of COD in water and wastewater (Lenor et al., 1999).

3. RESULTS AND DISCUSSIONS

3.1. Fenton process

The study of different parameters affecting the COD removal percentage such as $\text{H}_2\text{O}_2$ concentration, FeSO$_4$.7H$_2$O concentration, pH value and reaction time was performed at ambient temperature since high temperature is determinial for COD removal beyond 300K. Maximum COD removal (82.7%) was obtained at reaction time of 2h.

3.1.1. Effect of $\text{H}_2\text{O}_2$ concentration on COD removal by fenton process

Because hydrogen peroxide is a source for 'OH radical as oxidant for organic pollutants' degradation, addition of high $\text{H}_2\text{O}_2$ concentration beyond the optimum concentration acts as scavenger of 'OH radical. (Figure 1.A) shows the effect of $\text{H}_2\text{O}_2$ concentration on COD removal percentage from tannery wastewater at pH 3.5 and Fe$^{2+}$ 0.8g/l. The COD removal % increased up to 82.7% then decreased to 75.7% at a concentration of $\text{H}_2\text{O}_2$ 35 g/l and 40g/l respectively. It can be observed from the results that the COD removal increases with increase in $\text{H}_2\text{O}_2$ concentration up to the optimum concentration (35g/l) beyond which it decreases again. This is due to the degradation of organic pollutants present in tannery wastewater which is increased with increase of $\text{H}_2\text{O}_2$ concentration. Beyond the optimum concentration, generation of less reactive HO$^-$ radical and scavenging of hydroxyl radical inhibit the degradation rates of organic pollutants (Popiel et al., 2008). Thus the percentage of COD removal decreased.
3.1.2. Effect of Fe$^{2+}$ concentration on COD removal by fenton process

Generation of OH radicals from H$_2$O$_2$ is catalyzed by Fe$^{2+}$ and thus mineralization of organic pollutants depends on the concentration of the catalyst and optimization of Fe$^{2+}$ concentration was investigated. (Figure 2.A) shows the effect of Fe$^{2+}$ concentration on COD removal from tannery wastewater. Fe$^{2+}$ concentration varies from 0.2 g/l to 1 g/l at pH 3.5 and H$_2$O$_2$ concentration of 35 g/l. The optimum Fe$^{2+}$ concentration achieved was 0.8 g/l for COD removal of (82.6%) after a time of 2h. This indicate that excess of Fe$^{2+}$ acts as a scavenger for OH radical, as shown in equation (4).
Fig. 4: Effect of reaction time on COD removal by (A) fenton process (pH 3.5 Fe$^{2+}$ 0.8g/l$^{-1}$ and H$_2$O$_2$ 35g/l$^{-1}$) and (B) photo-fenton process (Fe$^{2+}$ (0.5g/l$^{-1}$), H$_2$O$_2$ (30g/l$^{-1}$), pH 3)

Fig. 5: Effect of UV irradiation alone on COD removal

Table 1: Characterization of filtered tannery wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.5</td>
</tr>
<tr>
<td>Conductivity</td>
<td>74.6 ms/cm</td>
</tr>
<tr>
<td>TOC</td>
<td>170.8 ppm</td>
</tr>
<tr>
<td>COD</td>
<td>554.56 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>50 g/l$^{-1}$</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>34.28 ppm</td>
</tr>
</tbody>
</table>

3.1.3. Effect of initial pH on COD removal by fenton process

In this set of experiments as shown in (figure.3.A) the effect of initial pH on COD removal % from tannery wastewater was investigated. In all experiments, Fe$^{2+}$ concentration was 0.8 g/l and H$_2$O$_2$ concentration was 35g/l. The initial pH values of wastewater were adjusted at 2.5, 3, 3.5, 4, 5 by addition of 6N H$_2$SO$_4$ and 1M NaOH. At pH 3.5 maximum COD removal 82.7% was obtained but lower COD removal was obtained at pH 2.5 due to hydroxyl radical scavenging at very low pH values, also iron complex species [Fe(H$_2$O)$_6$]$^{2+}$ exists, which reacts more slowly with
hydrogen peroxide than other species (Xu et al., 2009). This phenomenon was influenced by the concentration of ferrous ion present. In addition, the peroxide gets solvated in the presence of high concentration of H\(^+\) ions to form stable oxonium ion \([\text{H}_3\text{O}_2]^+\). Oxonium ions make hydrogen peroxide more stable and reduce its reactivity with ferrous ions (Kavitha and Palanivelu, 2005; Kwon et al., 1999). Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. Thus an adequate control of pH would increase process efficiency since ferric hydroxide was formed and no regeneration of Fe\(^{2+}\) from Fe\(^{3+}\) and H\(_2\)O\(_2\) occurs so that the efficiency of degradation of organic pollutants decreased.

![Figure 6](image1.png)

**Fig. 6:** Effect of H\(_2\)O\(_2\) concentration COD removal by H\(_2\)O\(_2\)/UV oxidation process

![Figure 7](image2.png)

**Fig. 7:** Effect of pH on COD removal by H\(_2\)O\(_2\)/UV oxidation process

### 3.1.4. Effect of reaction time on COD removal by fenton process

At optimum conditions of Fe\(^{2+}\) 0.8g/l, H\(_2\)O\(_2\) 35g/l and pH 3.5, the effect of time on COD removal percentage was investigated as shown in (figure 4A). The optimum reaction time for obtaining a high COD removal with little amount of sludge at a time 2h. Therefore the amount of sludge increased as time increases more than two hours.

### 3.2. UV degradation process

UV degradation processes is applied for wastewater treatment to investigate the efficiency of UV irradiation alone on removal of COD. From (figure 5)
it is seen that the UV radiation alone is poor efficient for removal of COD (10%). Because of the poor direct photolysis of organic pollutants (Lofrano et al., 2007), the oxidation requires the use of an oxidant such as H$_2$O$_2$ for photodegradation or mineralization of organic pollutant.

3.3. H$_2$O$_2$/UV oxidation process

The study of different parameters affecting the COD removal percentage such as H$_2$O$_2$ concentration, pH value and reaction time was performed at ambient temperature. Maximum COD removal (85%) was obtained at reaction time of 2h.

3.3.1. Effect of H$_2$O$_2$ concentration on COD removal by H$_2$O$_2$/UV oxidation process

Because hydrogen peroxide is a source for 'OH radical as oxidant for organic pollutants’ degradation, addition of high H$_2$O$_2$ concentration beyond the optimum concentration acts as scavenger of 'OH radical. Figure 6 shows the effect of H$_2$O$_2$ concentration on COD removal percentage from tannery wastewater at pH 3.5 and UV irradiation. The COD removal percentage increased up to 85% then decreased to 81.7% at a concentration of H$_2$O$_2$ 20 g/l and 25g/l respectively. It can be observed from the results that the COD removal increases with increase in H$_2$O$_2$ concentration up to the optimum concentration (20g/l) beyond which it decreases again. This is due to the degradation of organic pollutants present in tannery wastewater which is increased with increase of H$_2$O$_2$. 

![Fig. 8: Effect of time on COD removal by H$_2$O$_2$/UV oxidation process](image)

![Fig. 9: UV–visible spectra of the tannery effluent (a) filtered tannery wastewater (b) after Fenton oxidation (c) after photofenton oxidation, (d) after fenton oxidation and chemical precipitation with NaOH and (e) after photo-fenton oxidation and chemical precipitation with NaOH](image)
concentration. Beyond the optimum concentration, generation of less reactive \( \text{HO}_2 \) radical and scavenging of hydroxyl radical inhibit the degradation rates of organic pollutants (Popiel et al., 2008 and Alnaizy and Akgerman, 2000). Thus the percentage of COD removal decreased.

![Fig. 10: FT-IR analysis of filtered tannery wastewater (a) before any treatment (b) after Fenton oxidation (c) after photo-fenton oxidation, (d) after photo-fenton oxidation and chemical precipitation with NaOH](image)

3.3.2. Effect of initial pH on COD removal by \( \text{H}_2\text{O}_2/\text{UV} \) oxidation process

In this set of experiments as shown in (figure 7). The effect of initial pH on COD removal % from tannery wastewater was investigated. In all experiments, \( \text{H}_2\text{O}_2 \) concentration was 20g/l. The initial pH values of wastewater were adjusted at 2.5, 3, 3.5, 4, 5 and 7 by addition of 6N \( \text{H}_2\text{SO}_4 \) and 1M NaOH. At pH 3 maximum COD removal 85% was obtained but lower COD removal was obtained at pH 2.5 due to hydroxyl radical scavenging at very low pH values. In addition, the peroxide gets solvated in the presence of high concentration of \( \text{H}^+ \) ions to form stable oxonium ion \( [\text{H}_3\text{O}_2]^+ \). Oxonium ions make hydrogen peroxide more stable (Kavitha and Palanivelu, 2005 and Kwon et al., 1999). Therefore, the efficiency of the by \( \text{H}_2\text{O}_2/\text{UV} \) oxidation process to degrade organic compounds is reduced both at high and low pH. Thus an adequate control of pH would increase the efficiency of degradation of organic pollutants decreased using \( \text{H}_2\text{O}_2/\text{UV} \) oxidation process. Also \( \text{H}_2\text{O}_2 \) is unstable and decomposing in basic solutions (Kuo, 1992).

3.3.3. Effect of reaction time on COD removal by \( \text{H}_2\text{O}_2/\text{UV} \) oxidation process

At optimum conditions of \( \text{H}_2\text{O}_2 \) 20g/l and pH 3, the effect of time on COD removal percentage was investigated as shown in (figure 8). The optimum
reaction time for obtaining a high COD removal is at a time 2h. Then COD removal remains constant with increasing of time over 2h.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>560.33</td>
</tr>
<tr>
<td>Mg</td>
<td>1416</td>
</tr>
<tr>
<td>Ca</td>
<td>683.25</td>
</tr>
<tr>
<td>K</td>
<td>181.25</td>
</tr>
<tr>
<td>Na</td>
<td>26,000</td>
</tr>
<tr>
<td>Ni</td>
<td>1.25</td>
</tr>
<tr>
<td>Fe</td>
<td>1.08</td>
</tr>
<tr>
<td>Mn</td>
<td>17.83</td>
</tr>
</tbody>
</table>

### 3.4. Photo-fenton (Fe$^{2+}$/H$_2$O$_2$/UV) processes

Photo-fenton (Fe$^{2+}$/H$_2$O$_2$/UV) process as AOPs most often is applied for wastewater treatment because of no sludge formation and more efficient removal of COD.

#### 3.4.1. Effect of H$_2$O$_2$ dosage on COD removal by photo-fenton process

There is no certain molar ratio of H$_2$O$_2$/Fe$^{2+}$ in photo-fenton process which can achieve high degradation rates for organic contaminants (Figure 1B). shows the effect of H$_2$O$_2$ dosage on COD removal percentage using Fe$^{2+}$ (0.5 gl$^{-1}$), pH 3, time 2h. Experiments with hydrogen peroxide dosage (10-22 gl$^{-1}$) were carried out. It was observed that the optimum H$_2$O$_2$ dosage was 30 gl$^{-1}$ to obtain a maximum COD removal (90.1%). This can be explained by the effect of additionally generated OH radicals by increase of H$_2$O$_2$ dosage to give high degradation rates. On the other hand, higher initial H$_2$O$_2$ dosages beyond the optimum dosage did not give satisfactory results. This is possibly due to hydroxyl radical scavenging by recombination.

#### 3.4.2. Effect of Fe$^{2+}$ concentration on COD removal by photo-fenton process

Ferrous sulfate acts as photocatalyst for organic pollutants degradation from tannery wastewater using hydrogen peroxide. Effect of different Fe$^{2+}$ dosage (0.2-0.6 gl/l) on COD removal by photo-fenton oxidation process was investigated. Almost complete COD removal (90.1%) occurred at Fe$^{2+}$ concentration 0.5 gl$^{-1}$ as seen in (figure 2B). All experiments were performed at H$_2$O$_2$ concentration 30 gl$^{-1}$, pH 3 and time 2h. This clearly demonstrates the advantage of photo-fenton oxidation process over fenton oxidation process. Excess of ferrous ion led to decrease in COD removal since Fe$^{2+}$ recombines with hydroxyl radical and precipitates as ferric hydroxide.

#### 3.4.3. Effect of initial pH on COD removal by photo-fenton process

Photo-fenton process strongly depends on initial pH value in tanning solution as shown in (figure 3B). The COD removal decreased at pH 2.5 this is attributed to scavenging of hydroxyl radical with H$^+$ ion as the decrease in COD removal at pH (3.5-5) is due to decomposition of H$_2$O$_2$ (Ramírez et al., 2010).

#### 3.4.4. Effect of reaction time on COD removal by photo-fenton process

A set of experiments was carried out under the optimum conditions of Fe$^{2+}$ concentration (0.5 gl$^{-1}$), H$_2$O$_2$ concentration (30 gl$^{-1}$) and pH 3 to study the effect of reaction time on COD removal. The results shown in (figure 4.A) indicate that the optimum time for higher COD removal was 2h beyond which more amount of ferric hydroxide was formed as sludge (Ramírez et al., 2010; Oller et al., 2011).

### 3.5. UV-Visible spectra studies

Typical UV-Visible spectra for untreated and treated tannery effluent have been done and the changes in absorbance of tannery effluent were recorded (Figure 9). The initial spectra of tannery effluent show that the wavelength of maximum absorbance (λmax) was at 420 nm and 580 nm in the visible region and corresponds to the presence of chromophores (colour producing) groups and chromium. In order to differentiate between intermediates and initial tannery effluent absorbance was monitored during fenton and photo-fenton processes. The maximum discoloration of effluent was observed after photo-fenton process followed by chemical precipitation for chromium (figure. 9e). During fenton and photofenton processes the cleavage of chromophoric groups present in the tannery wastewater has taken place, which results in the decrease of optical density of the effluent. Also the absorption band has been shifted from visible to UV region, which indicates the degradation of organic pollutants (present in the effluent) into smaller fragments.

### 3.6. FT-IR spectra studies

Figure 10a shows the FT-IR spectrum of the initial tannery effluent sample. A broad peak at 3400 cm$^{-1}$ may be attributed to the presence of –NH$_2$ and O-H bonded hydroxyl groups. Another peak at 2,047 cm$^{-1}$
4. CONCLUSION

The target from this study is the comparison between different advanced oxidation process of tannery wastewater treatment. In this experimental work, The COD removal percentage by fenton (Fe$^{2+}$/H$_2$O$_2$) and photo-fenton followed by coagulation with NaOH was investigated. The optimum COD removal under these AOPs indicated that the efficiency for degradation of organic pollutants present in tannery wastewater was in the case of photo-fenton (90.1%) > H$_2$O$_2$/UV oxidation (85%) > fenton (82.7%). The use of high concentration of hydrogen peroxide for tannery wastewater treatment by AOPs results in mineralization of the recalcitrant organic pollutants. Reduction of COD percentage by hybrid technology of AOPs and chemical precipitation of chromium is a cost-effective method for tannery wastewater treatment.

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