Comparison of advanced oxidation methods of Fenton, UV/Fenton, and O₃/Fenton in treatment of municipal wastewater

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Abstract

The present study aimed to evaluate the efficiency of advanced oxidation methods: Fenton, UV/Fenton, and O₃/Fenton in the treatment of municipal wastewater. The effect of H₂O₂:Fe²⁺ ratio, pH, and reaction time on chemical and biological parameters: chemical oxygen demand (COD), biological oxygen demand (BOD₅), total coliform (TC), and Fecal coliform (FC) were evaluated in different advanced oxidation processes (AOPs) methods (Fenton, UV/Fenton, and O₃/Fenton). All parameters were measured according to the standards methods. The results obtained from the present study showed that the highest removal of pollutants was achieved in H₂O₂:Fe²⁺ mole ratio of 0.7:1. Furthermore, the removal of COD, BOD₅ were increased when pH increased from 4 to 7. Moreover, reaction time influenced COD, BOD₅, TC, and FC until equilibrium time, however, its influence was not significant after equilibrium value. A comparative study on different AOP systems showed the order of highest to lowest removal efficiency of all parameters is as follows: O₃/H₂O₂/Fe²⁺ > UV/H₂O₂/Fe²⁺ > H₂O₂/Fe²⁺. It can be concluded that Fenton and its modified methods have the promising potential for advanced municipal wastewater treatment.

Keywords: Fenton; UV/Fenton; O₃/Fenton; Advanced treatment; Wastewater

1. Introduction

The World Health Organization (WHO) estimates that half of people worldwide have limited access to water resources. Water restriction has forced authorities and scientists to reuse effluent as the main surrogate source of irrigation [1]. The proximity to agricultural fields is posed as one of the important benefits of effluent reuses [2]. Iran is an arid and semi-arid country; approximately 46 million (59%) of its population live in areas with less than the per capita water consumption (200 L/d per capita) [3,4]. Biological processes as conventional treatment methods are not efficient in the removal of recalcitrant and emerging pollutants, therefore, they are not able to meet the standards required for reusing wastewater [5,6]. Over recent years, significant attention has been devoted to effective non-biodegradable treatment methods for the elimination of biological pathogens found in wastewater [7]. The advanced oxidation processes (AOPs) are the method based on the generation of non-selective and strongly oxidizing radicals [8]. Hydroxyl radical (•OH) is well-known to strongly mineralize most organic waste [9]. Many different AOP methods have been developed for the generation of reactive radicals such as oxidation agents (O₃ and H₂O₂), radiation (ultraviolet or ultrasonic), and catalysts (such as Fe²⁺). The Fenton and its modification have been widely used due to highly efficient, easy
to purify, high react with organic matters, and producing less toxic compounds during the oxidation process [10–12].

The Fenton process is based on the following mechanism (Eqs. (1)–(5)) (Fig. 1) [13]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (1) \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (2) \\
\text{Fe}^{2+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (3) \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (4) \\
\cdot\text{OH} + \cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (5)
\end{align*}
\]

Previous studies revealed that Fenton and pseudo-Fenton processes in alone state and in combination with other oxidants are efficient for pretreatment of wastewaters and landfill leachate [14–17]. As wastewater contains recalcitrant pollutants and some pollutants cannot be degraded by the Fenton process alone, therefore combined Fenton and ultraviolet can improve degradation efficiency; increased hydroxyl radicals are generated. In addition, regeneration of ferrous ions leads to more radical generation (Eqs. (6)–(9)) (Fig. 1) [18].

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{FeOH}^{2+} + \text{H}^+ \quad (6) \\
\text{FeOH}^{2+} + \text{hv} & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} \quad (7) \\
\text{H}_2\text{O}_2 + \text{UV} & \rightarrow 2\cdot\text{OH} \quad (8) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{UV} & \rightarrow \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+ \quad (9)
\end{align*}
\]

Ozone (O$_3$) is classified as a promising advanced oxidation process and grabbed much attention by researchers due to its inherent strong oxidation. The incorporation of O$_3$ alone has some drawbacks: (a) less selectivity to degradation the contaminants, (b) low reactivity with certain organic matters such as inactivated aromatics or saturated carboxylic acids, and (c) in many cases, it does not completely mineralize the organic compounds [19,20]. Therefore, it is suggested to employ with other AOPs such as Fenton. The incorporation of combined O$_3$/Fenton can lower iron consumption in the Fenton process and less O$_3$ dosage. On the other hand, H$_2$O$_2$, iron, and hydroxyl ion can facilitate hydroxyl radical generation through the decomposition of ozone (Eqs. (10)–(12)) (Fig. 1) [21–23].

\[
\begin{align*}
\text{Fe}^{3+} + \text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{FeO}_2^+ + \cdot\text{OH} + \text{O}_2 + \text{H}^+ \quad (10) \\
\text{O}_3 + \text{OH}^- & \rightarrow \text{HO}_2^- + \cdot\text{OH} \quad (11) \\
\text{O}_3 + \text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + \cdot\text{OH} + \text{HO}_2^- \quad (12)
\end{align*}
\]

Since municipal effluents contain a wide range of pollutants including organic and inorganic matters, a comparison study on investigation of the removal efficiency of different AOP methods can help to choose the most effective treatment method [24,25]. Therefore, in the present work, the performance of Fenton (Fe$^{3+}$/H$_2$O$_2$), photo Fenton (UV/Fe$^{3+}$/H$_2$O$_2$), and ozone/Fenton (O$_3$/Fe$^{3+}$/H$_2$O$_2$) methods was compared in order to treat municipal wastewater after the biological process of the aerated lagoon in laboratory scale.

2. Materials and methods

2.1. Features of the effluent studied

Ilam city with 194,030 people is located at a latitude of 33.6350°N and longitude of 46.4153°E in western Iran. The wastewater per capita in this city was estimated to be 148.81 capi$^{-1}$ d$^{-1}$. This large volume of domestic wastewater is treated by two parallel series of aeration lagoons after collecting and passing through a coarse and fine screen. The treated wastewater is discharged to the river after settling and chlorine process [26]. The samples were withdrawn from
the effluent every three days before entering into the river and immediately transferred to the laboratory at 4°C. The chemical and microbial characteristics of the effluent were measured according to the standard methods for the examination of water and wastewater [27,28]. The effluent characteristics of the treatment plant are summarized in Table 1.

2.2. Procedures

2.2.1. Fenton (H₂O₂/Fe²⁺), photo/Fenton (UV/H₂O₂/Fe²⁺), and ozone/Fenton (O₃/H₂O₂/Fe²⁺) oxidation processes

The Fenton process was conducted in different molar ratios of H₂O₂/Fe²⁺ (0.35:1, 0.7:1, 1.06:1, 1.42:1, 1.78:1, and 2:1) using 0.003, 0.006, 0.009, 0.011, 0.015, and 0.017 mol/L H₂O₂ and 0.009 mol/L of FeSO₄·7H₂O. The pH was adjusted using 0.1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) after adding H₂O₂ [29]. The optimal molar ratio of the Fenton process was determined at the initial pH of effluent (7.65) and contact time of 180 min in a beaker with an effective volume of 0.5 L (height: 0.220 mm and internal diameter: 120 mm). A magnetic stirrer (IKA® RH Basic2, Germany) at medium speed was used to create a uniform environment. The effect of contact time (30, 60, 90, 120, 150, and 180 min) and pH (7) were evaluated at optimal H₂O₂/Fe²⁺ molar ratio. The residual H₂O₂ was neutralized using manganese dioxide in order to prevent the interferences due to quenching the hydroxyl radicals by peroxide concentration was increased at a constant concentration of ferrous due to quenching the hydroxyl radicals by humic acid is landfill leachate was decreased when hydrogen peroxide which leads to reduced removal efficiency of organic matters [33]. This phenomenon was confirmed by Kobs of BOD and COD removal (Fig. 2b).

Besides, according to the Eq. (16), the recombination of hydroxyl radicals could occur at a high concentration of hydrogen peroxide which leads to reduced removal efficiency of organic matters [33]. This phenomenon was confirmed by Kobs of BOD and COD removal (Fig. 2b).

On the other hand, at the high H₂O₂/Fe²⁺ molar ratio, there are no adequate iron ions to decompose H₂O₂ and generate ·OH radicals [34]. Wu et al. [35] reported that the removal efficiency of humic acid is landfill leachate was decreased when hydrogen peroxide concentration was increased at a constant concentration of ferrous due to quenching the hydroxyl radicals by H₂O₂. The study of Murray and Parsons [36] revealed that the removal of natural organic matter from drinking water

The combined photo/Fenton process was performed in a similar procedure to Fenton process with except of the presence of four low-pressure UV lights (Philips, 6 W, UV-C, 254 nm) placed vertically in the inner and outer part of the beaker and inside the transparent quartz glass. The beaker was covered with aluminum foil in order to prevent the harmful effects of UV. Similar to the Fenton process, Ozone/Fenton was conducted using two Impinger containers (Schott Duran, Germany) with an effective volume of 0.5 L in a series mode [31]. Ozone generator (model MOG-5G/H, Arda, France) and dry air source fed was used to transfer ozone to the reactor with a flow rate of 1.6 g/h. The amount of ozone was measured using standard method No. 2350E [27].

3. Results and discussion

3.1. Effect of molar ratio (H₂O₂/Fe²⁺)

The molar ratio of Fenton reagent (H₂O₂/Fe²⁺) is one of the most important parameters influencing the Fenton, UV/Fenton, and O₃/Fenton processes [32]. Fig. 2a shows the effect of H₂O₂/Fe²⁺ molar ratio in the removal of COD, BOD₅, total coliform (TC), and fecal coliform (FC) in different processes. Results indicated that increasing the ratio of H₂O₂/Fe²⁺ from 0.7:1 to 1.8:1, decreased the removal efficiency of COD and BOD by 32.15% and 34.56%, respectively. While TC and FC removal were constant in all H₂O₂/Fe²⁺ ratio. Results indicated that maximum removal efficiency for all parameters was observed at 0.7:1 ratio (H₂O₂/Fe²⁺). The decrease of COD and BOD removal at the high H₂O₂/Fe²⁺ ratio is due to the scavenging effect of hydroxyl radicals by excess hydrogen peroxide (Eqs. (15) and (16)):

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (15)
\]
\[
\text{HO}_2^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{O}_2 \quad (16)
\]

Besides, according to the Eq. (16), the recombination of hydroxyl radicals could occur at a high concentration of hydrogen peroxide which leads to reduced removal efficiency of organic matters [33]. This phenomenon was confirmed by Kobs of BOD and COD removal (Fig. 2b).

Wu et al. [35] reported that the removal efficiency of humic acid is landfill leachate was decreased when hydrogen peroxide concentration was increased at a constant concentration of ferrous due to quenching the hydroxyl radicals by H₂O₂. The study of Murray and Parsons [36] revealed that the removal of natural organic matter from drinking water

### Table 1

<table>
<thead>
<tr>
<th>Characteristic of the effluent of the treatment plant</th>
<th>Range value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC (μS cm⁻¹)</td>
<td>240–265</td>
</tr>
<tr>
<td>TDS (mg L⁻¹)</td>
<td>156–172</td>
</tr>
<tr>
<td>pH</td>
<td>6.62–7.85</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
<td>112–336</td>
</tr>
<tr>
<td>BOD₅ (mg L⁻¹)</td>
<td>70–197</td>
</tr>
<tr>
<td>TSS (mg L⁻¹)</td>
<td>60–327</td>
</tr>
<tr>
<td>Total coliform (MPN/100 mL)</td>
<td>1.10E+06–6.30E+06</td>
</tr>
<tr>
<td>Fecal coliform (MPN/100 mL)</td>
<td>1.12E+06–3.60E+06</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>59–150</td>
</tr>
<tr>
<td>Color (TCU)</td>
<td>40–200</td>
</tr>
<tr>
<td>DO (mg L⁻¹)</td>
<td>2.7–5.7</td>
</tr>
</tbody>
</table>
was decreased at H\textsubscript{2}O\textsubscript{2} concentrations higher than 20:1 ratio. Chen et al. [37] demonstrated that excess hydrogen peroxide prevents the decomposition of organic materials.

### 3.2. Effect of pH

pH is the main influencing parameter in the chemical reactions. Fig. 3 shows the removal efficiency of COD, BOD, TC, and FC in Fenton, UV/Fenton, and O\textsubscript{3}/Fenton processes at pH 4–9. Results showed that the removal efficiency of all parameters excepted (TC and FC) was raised for all processes when pH was increased from 4 to 7 (Fig. 3 and Fig. S1). According to Fig. 3, the highest removal efficiency of COD (92.37%, 95.44%, and 98.37%) and BOD (94.12%, 96.64%, and 99.12%) were observed in Fenton, UV/Fenton, and O\textsubscript{3}/Fenton oxidation processes, respectively.

The high efficiency of TC and FC at acidic condition is contributed to the effect of acidic conditions on the microorganism. Because TC and FC bacteria will survive only in a limited pH near the neutral.

However, increasing pH > 8 had no significant effect on the removal of the parameters (COD, BOD, TC, and FC). Therefore, pH = 7 seems to be well-suited for the removal and oxidation. Many studies have proven that the most oxidation occurred at pH 3–5, while, conversely this study showed that maximum oxidation was obtained at pH = 7 [38]. Yang et al. [39] confirmed the hydroxylated form of Fe(OH)	extsuperscript{+} could be formed in the presence of organic...
compounds which has much faster than other species reaction with H$_2$O$_2$ at pH = 7.

Moreover, Chen et al. [37] reported that the effect of pH on the oxidation process is restricted to the first few minutes of reaction. Therefore, the COD and color removal was increased by increasing the pH from 3 to 7 (Eqs. (4) and (17)). The reaction of Eqs. (4) and (17) are important due to the regeneration of ferrous ions at natural pH and hydroxyl radical generation by ferric ion and hydrogen peroxide at pH higher than 5 (Fig. 1).

\[
\text{H}_2\text{O}_2 + \text{Fe(OH)}^+ \rightarrow \text{FeOH}_2^+ + \cdot\text{OH} \quad (17)
\]

On the other hand, decreased removal efficiency in the Fenton process at low pH range is due to the creation of foam in the acidic aqueous which accordingly prevents UV light penetration to the wastewater [40]. Also, there are some limitations (e.g., sulfides or cyanides gases emission, increase of sludge, saltiness, and coasts) to utilize Fenton and its modified process in acidic pH [41].

3.3. Effect of reaction time on H$_2$O$_2$/Fe$^{2+}$, UV/H$_2$O$_2$/Fe$^{2+}$, and O$_3$/H$_2$O$_2$/Fe$^{2+}$

Fig. 4 and Fig. S2 illustrated the effect of reaction time on COD, BOD, TC, and FC removal in Fenton, UV/Fenton, and O$_3$/Fenton processes. Reaction time is one of the most important influencing factors in Fenton process which has been reported to be between 30 and 180 min [42–44] and also the optimum reaction time was reported to be between 60 and 120 min in UV/H$_2$O$_2$/Fe$^{2+}$ and O$_3$/H$_2$O$_2$/Fe$^{2+}$ processes [17,45]. Reaction time can be very helpful in saving energy and chemicals usage in the oxidation processes and the entrance of materials into aquatic environments and ecosystems [46,47]. The results showed that COD, BOD, TC, and FC removal were increased as the time preceded. Equilibrium time for removal of COD and BOD, in H$_2$O$_2$/Fe$^{2+}$ process was found to be 60 min, however, this value in UV/H$_2$O$_2$/Fe$^{2+}$ and O$_3$/H$_2$O$_2$/Fe$^{2+}$ processes were obtained 90–120 min. The removal efficiency of COD, BOD, TC, and FC rates were not significant after equilibrium time due to the resistance of refractory materials against the •OH radical, which is not degraded after this time and the yield remains stable [48]. On the other hand, the amount of H$_2$O$_2$, Fe$^{3+}$, and O$_3$ will be decreased with increasing the reaction time. Therefore, there is no oxidant agent for radical production. Ferreira et al. [49] observed the removal > 90% of the dye in the olive mill wastewater using the UV/Fenton method at H$_2$O$_2$/Fe$^{2+}$ molar ratio of 0.2 and pH = 4.2 within 90 min. Amr and Aziz [50] also reported that removal efficiency over 98% was achieved for removal of dye from leachate using the O$_3$/H$_2$O$_2$/Fe$^{2+}$ method at 90 min, pH = 7, and molar ratio of H$_2$O$_2$/Fe$^{2+}$ = 1 (0.05 mol/L H$_2$O$_2$ and 0.05 mol/L Fe$^{2+}$).

3.4. Comparison of different processes

Results clearly illustrated the differences between the removal efficiency of three methods. The highest removal efficiency for all parameters was obtained as follows: O$_3$/H$_2$O$_2$/Fe$^{2+}$ > UV/H$_2$O$_2$/Fe$^{2+}$ > H$_2$O$_2$/Fe$^{2+}$. As shown, the efficiency of the O$_3$/Fenton process is more than other processes. The explanation for higher corresponding removal efficiency to O$_3$/Fenton process is a combination of two oxidants that have a synergic effect on each other. Although previous studies reported that the O$_3$ alone has low efficiency in removing COD, ozone combined with Fenton leads to more generation of reactive radicals that influence the organic matter degradation. Hagman et al. [51] reported only 22% of COD through O$_3$ process alone. While the conjunction of Fenton oxidation and ozonation are famed as effective oxidation processes in wastewater treatment.

H$_2$O$_2$ in water creates the hydroperoxide ion (HO$_2^-$) which quickly reacts with O$_3$ to initiate a radical chain mechanism (Eqs. (18) and (19)) [52,53].

\[
\text{H}_2\text{O} + \text{O}_3 \rightarrow \cdot\text{OH} + 3\text{O}_2 \quad (18)
\]

Fig. 4. Effect of reaction time on COD and BOD removal in different processes (Fenton, UV/Fenton, and O$_3$/Fenton).
Moreover, as illustrated in Eq. (10), the ferric ions which are predominant in natural pH react with O₃ and generate hydroxyl radicals. Besides, the oxidation ability of O₃ is effective at high pH values [54]. Results indicated that the UV/Fenton process is more effective than Fenton process. The use of H₂O₂/Fe²⁺ in conjunction with the UV light leads to more degradation of organic matters [55]. The major benefits of UV are associated with the regeneration of ferrous ions and direct decomposition of H₂O₂ through the photolysis process (Eqs. (7) and (8)). Therefore, these mechanisms causes an increase in the amount of *OHs in UV/Fenton process [56]. Many studies [17,50,57] revealed that the use of O₃ and UV combined with the H₂O₂/Fe²⁺ method are more effective in the removal of pollutants from wastewater and leachate compared with the use of the H₂O₂/Fe²⁺ method alone.

4. Conclusions

Fenton, photo/Fenton, and ozone/Fenton are the AOP methods that are based on *OH generation facilitates the mineralization of most organic compounds. Maximum removal efficiency for all parameters were obtained at 0.7:1 ratio of H₂O₂:Fe²⁺, while the removal efficiency of COD and BOD were decreased with increasing the ratio of H₂O₂/Fe²⁺ (TC and FC removal were constant). The removal efficiency of all parameters were raised with as pH increased from 4 to 7 (excepted TC and FC). Also, COD, BOD, TC, and FC removal increased with increasing reaction time. Equilibrium time for degradation of COD and BOD in H₂O₂/Fe²⁺ process was found to be 60 min and in UV/H₂O₂/Fe²⁺ and O₃/H₂O₂/Fe²⁺ was 90 to 120 min. A comparison of different processes showed that the highest removal efficiency of all parameters are as follows: O₃/H₂O₂/Fe²⁺ > UV/H₂O₂/Fe²⁺ > H₂O₂/Fe²⁺. The highest removal efficiency of COD (92.57%, 95.44%, and 98.57%) and BOD (94.12%, 96.64%, and 99.12%) were obtained for Fenton, UV/Fenton, and O₃/Fenton processes respectively. Since the effluent of biological wastewater treatment methods cannot be mainly incorporated directly for agricultural purposes, therefore, advanced municipal wastewater treatment using Fenton, UV/Fenton, and O₃/Fenton methods can meet the required standards for limited and unlimited application in different parts of the urban environment, the irrigation of plants with food and non-food consumption, the agricultural irrigation, fish farming, and injecting into the ground or in water bodies. Moreover, these efficient methods can be considered as a promising approach to alleviate the water shortage crisis in Iran and most areas of the world.

References


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Supplementary information

Fig. S1. Effect of pH on TC and FC removal in different processes (Fenton, UV/Fenton, and O3/Fenton).

Fig. S2. Effect of reaction time on TC and FC removal in different processes (Fenton, UV/Fenton, and O3/Fenton).

