Synergistic degradation of hospital wastewater by solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process

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ABSTRACT

Combined heterogeneous and homogenous photo-catalytic degradation of hospital wastewater was investigated. Three processes – solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2}, solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} and solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} – were evaluated. The solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process displayed increased efficiency due to the synergetic effect of homogeneous and heterogeneous photo-catalytic reaction. The combination increased the photo process efficiency by decreasing the reaction time of the separate operations and decreased the cost of treatment. The optimal conditions enabling over 99% reduction of chemical oxygen demand (COD) were pH 7, 0.5 g/L Fe\textsuperscript{2+}, 0.2 g/L TiO\textsubscript{2} and 1.35 g/L H\textsubscript{2}O\textsubscript{2}. The effluent COD and total suspended solids concentrations were 20 and 30 mg/L, respectively, which met the discharge standard requirements.

Key words | biodegradability, hospital wastewater, photo-catalysis, photo-Fenton, solar energy, synergetic effect

INTRODUCTION

Hospital wastewater can contain human waste, similar to domestic wastewater, but is additionally replete with pathogenic microorganisms, partially metabolized pharmaceutical substances, radioactive elements, hazardous chemical compounds and disinfectants. Hospitals in general nominally generate 400–1,200 L of wastewater per bed each day, with an average of approximately 750 L/bed/day (Chong & Jin 2012). The chemical oxygen demand (COD) and biological oxygen demand (BOD\textsubscript{5}) of hospital wastewater is in the range of 500–1,900 and 400–700 mg/L, respectively. Furthermore, hospital wastewater can be appreciably toxic, due to the presence of highly complex organohalogen compounds generated during disinfection (Gautam et al. 2007).

Disinfection is not the norm – most hospital wastewater is discharged directly to the public sewer system, which increases the load in municipal wastewater treatment plants. These pollutants may not be removed even after treatment and can be discharged into the environment, with consequences for the biological balance of natural environments (Sun et al. 2006). Since some components of hospital wastewater, such as antibiotics, can be environmentally problematic even at low concentrations, on-site wastewater treatment is best (Badejo et al. 2011).

Advanced oxidation processes (AOPs) are defined as processes that generate hydroxyl radicals (OH\textsuperscript{•}) in quantities sufficient to oxidize most complex chemicals of concern. The ultimate aim of AOPs is the mineralization of pollutants (Gogate & Aniruddha 2004). AOPs have emerged as viable technologies for the treatment and removal of pollutants present in wastewater that are refractory to conventional treatments. These processes can be used before or after conventional treatment or even as the principal stage, depending on the characteristics of the wastewater and the quality requirements of the treated effluent. Sometimes the combination use of AOPs can synergistically elevate OH\textsuperscript{•} production beyond the sum of the yields of OH\textsuperscript{•} from the individual AOP. An example is the combination of titanium oxide (TiO\textsubscript{2}) photocatalysis (the solar/TiO\textsubscript{2} system) with the Fenton (Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}) system.

Dual roles of iron in the solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} system synergistically boosts OH\textsuperscript{•} production at neutral pH. First,
Fe(III) adsorbed on the TiO₂ surface is reductively converted to ferrous ion (Fe(II)) via the conduction band (CB) electron, preventing the recombination of electron-hole pairs. The charge separation makes valence band (VB) holes more available for oxidation of adsorbed organic compounds, and for oxidation of surface-bound hydroxyl groups and adsorbed water molecules into OH⁻. In particular, in combination with reoxidation of Fe(II) by hydrogen peroxide (H₂O₂), the CB electron-mediated reduction enables the Fe(II)/Fe(III) catalytic cycle, which maintains a considerable concentration of Fe(III) as an electron acceptor. Second, Fe(II) bound to the photo-excited TiO₂ surface transforms H₂O₂ into a reactive oxidant (i.e. OH⁻) capable of oxidizing organic compounds at neutral pH (Kitsiou et al. 2009).

The present study demonstrates that the synergistic combination of TiO₂ photocatalysis and Fenton reaction (Fe²⁺/H₂O₂) produces a marked kinetic enhancement of the oxidation of pollutants at neutral pH conditions, which is detrimental to Fenton oxidation.

**MATERIALS AND METHODS**

**Wastewater source and characterization**

Hospital wastewater was obtained from a hospital near Karakonam, Kerala, India. The treatment system, consisting of a plain sedimentation tank as primary treatment, extended activated sludge process as secondary treatment, sand filter beds and carbon filter as tertiary treatment has a capacity of 500 m³/day. The primary treated, secondary treated and tertiary treated samples were collected continuously for 5 days at regular times due to large variations in concentration. The sample was collected in plastic cans that were transported to the laboratory and stored at 4°C. The physicochemical characteristics of the wastewater (Table 1) were determined using standard methods. After the primary treatment, the ratio of 3-day BOD to COD ratio was 0.18, indicating the non-biodegradable character of the wastewater and the possible presence of minimally biodegradable chemical substances, which undermine biological treatment. Hence, the experiments were performed with primary treated wastewater (collected at the outlet of the plain sedimentation tank). Even after complete treatment; the treated wastewater did not satisfy the Minimum National Standards for discharge (MINAS). Upgrade of the hospital’s existing hospital wastewater treatment system is needed.

**Chemicals**

All reagents were of analytical grade and were used as received without further purification. H₂O₂ (30% w/w), ferrous sulphate, sulphuric acid, potassium dichromate, sodium hydroxide, mercuric sulphate, ferrous ammonium sulphate and sodium thio-sulphate were purchased from Merk (India). The photocatalyst employed was commercial TiO₂ (P25) and was supplied by Degussa (Germany). According to the manufacturer’s specifications, P25 has an elementary particle size of 30 nm, Brunauer, Emmett and Teller specific surface area of 50 m²/g and crystalline mode comprising 80% anatase and 20% rutile.

**Experimental methods**

All photocatalytic experiments were carried out at Anna University Campus, Tirunelveli, India (8 44’N 77 44’E). The tests were performed with primary treated wastewater (collected at the outlet of the plain sedimentation tank). Open borosilicate glass trays of 2 L capacity were used as the reaction vessels. The size of the reactor was 0.3 × 0.2 ×
0.04 m. The irradiation surface area was 0.06 m². Suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between pollutants and TiO₂. Irradiation was carried out in the open air with continuously aerated by a pump to provide oxygen and for the complete mixing of the reaction mixture. In all cases, 1 L of reaction mixture was irradiated. The reactor was exposed to strong solar irradiation from January to April. The solar ultraviolet radiation was measured by a global UV radiometer which provided data in terms of incident energy per surface area (ultraviolet intensity 32 ± 2 W/m²). The tests began at 12.00 noon and stopped at 1.00 p.m. Initially, the pH of the wastewater was adjusted using sulphuric acid or sodium hydroxide. Then the required amount of ferrous sulphate and/or TiO₂ was added to the wastewater and stirred well to enhance the homogeneity of wastewater during the reaction. H₂O₂ was added (considered the beginning of the experiment) and the mixture was solar irradiated. Samples were withdrawn from the reactor every 15 minutes for COD analysis. Immediately after collecting each sample, sodium sulphite solution (approximately 0.5 mL per 10 mL wastewater sample) was added to quench the oxidation reaction for H₂O₂ decomposition and the pH was raised by adding sodium hydroxide to precipitate iron salt. All experiments were performed in triplicates and averages were reported. The COD and BOD₃ of the samples were carried out as per Standard Methods (APHA 2005).

RESULTS AND DISCUSSION

Solar/TiO₂/H₂O₂ process

Effect of pH

To determine the effect of pH, the degradation of hospital wastewater was investigated at pH values ranging from 5 to 8. After 1 hour of solar irradiation, the maximum COD removal was 72% at pH 7 and 8 (Figure 1). In this study pH 7 was found to be optimum pH under the given experimental conditions, because the first-order rate constant decreased at pH 8. Since the charge of the organic molecules and the surface of the TiO₂ catalyst are both pH dependent, pH changes influence the adsorption of organic molecules to the catalyst surface, which is an important step for photo-catalytic oxidation. As indicated in reaction (1), OH⁻ can be formed by the reaction between hydroxide ion and the positive hole. An alkaline condition would thus favor OH⁻ formation and enhance degradation. TiO₂ particles tend to agglomerate under an acidic condition, reducing the surface area available for organic adsorption and photon absorption (Chong et al. 2010)

\[
\text{HO}_2^+ + h_{\text{VB}}^+ \rightarrow \text{OH}^– + \text{H}^+ \tag{1}
\]

Effect of TiO₂ dosage

To determine the effect of TiO₂ dosage, the degradation of hospital wastewater was investigated by varying TiO₂ dosage from 0 to 2 g/L. Maximum COD removal of 70% was obtained at 1.5 g/L TiO₂ (Figure 2). As the TiO₂ dosage increased from 0.5 to 1.5 g/L, the number of photons absorbed and the number of organic molecules adsorbed also increased because of the increased number of catalytic particles. The density of particles in the area of illumination also increased, enhancing degradation, likely due to an increased number of available adsorption and catalytic sites on TiO₂. A further increase beyond this optimum catalyst loading, however, may cause light scattering and a screening effect, reducing the specific activity of the catalyst (Ghaly et al. 2007). In addition, at high TiO₂ concentrations,
aggregation of particles will reduce the interfacial area between the reaction solution and the photo catalyst, decreasing the number of active sites on the catalyst surface. Agglomeration and sedimentation of the TiO\textsubscript{2} particles were observed when more than 1.5 g/L of TiO\textsubscript{2} was added. In such a condition, part of the catalyst surface probably became unavailable for photon absorption and organic adsorption, providing little stimulation to the catalytic reaction. This may have been the reason for the decrease in the degradation rate (Oller et al. 2006; Bulskaya et al. 2009).

**Effect of H\textsubscript{2}O\textsubscript{2} concentration**

To maintain efficiency, it is necessary to choose the optimum concentration of H\textsubscript{2}O\textsubscript{2}. The effect of the addition of 0–1.8 g/L H\textsubscript{2}O\textsubscript{2} on the COD removal is shown in Figure 3. Increasing the concentration of H\textsubscript{2}O\textsubscript{2} correspondingly increased COD removal up to a H\textsubscript{2}O\textsubscript{2} concentration of 1.35 g/L. The enhancement of degradation by addition of H\textsubscript{2}O\textsubscript{2} is due to increase in the hydroxyl radical concentration. H\textsubscript{2}O\textsubscript{2} can compensate for the lack of O\textsubscript{2} and can function as an external electron scavenger (Barakat et al. 2005), trapping the photo-generated CB electron, inhibiting the electron-hole recombination and producing hydroxyl radicals (Equations (2)–(4))

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH} + \text{OH}^- \quad (2) \\
\text{H}_2\text{O}_2 + 2h^+ \rightarrow \text{O}_2 + 2\text{H}^+ \quad (3) \\
\text{OH}^- + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} \quad (4)
\]

Mahmoudi et al. (2005) reported that an optimal concentration of H\textsubscript{2}O\textsubscript{2} increases the formation rate of hydroxyl radicals due to reduction of H\textsubscript{2}O\textsubscript{2} at the CB and because of self-decomposition occurring during solar illumination. Increased H\textsubscript{2}O\textsubscript{2} concentration may promote an inhibitory effect due to the hydroxyl radical scavenging and the formation of another radical (HO\textsuperscript{2}_\textsubscript{-}), having an oxidation potential considerably smaller than HO\textsuperscript{-} (Equations (5) and (6))

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2\text{H}_2\text{O} \quad (5) \\
\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (6)
\]

**Effect of contact time and biodegradability**

To determine the effect of contact time and biodegradability, the degradation of hospital wastewater was investigated at the optimum condition of pH 7, TiO\textsubscript{2} dosage of 1.5 g/L and H\textsubscript{2}O\textsubscript{2} dosage of 1.35 g/L. The wastewater COD decreased with increase in contact time to solar irradiation (Figure 4). With increasing contact time, more solar energy can be trapped by TiO\textsubscript{2}, increasing the efficiency. Within 4
hours, COD removal was 85%. The biodegradability of hospital wastewater was evaluated by determining the BOD₃/COD ratio. For untreated wastewater, BOD₃/COD ratio was 0.21, indicating the presence of compounds that were slowly biodegradable. A 4-hour solar/TiO₂/H₂O₂ treatment enhanced the biodegradability value to 0.6, indicating the capability of the solar photo-catalytic process to degrade or rearrange molecular structures of organic material, and convert non-biodegradable organics to more biodegradable forms. Similar results were observed for degradation of phenolic wastewater (Adishkumar & Kanmani 2010).

**Solar/Fe²⁺/H₂O₂ process**

**Effect of pH**

To determine the effect of pH, the degradation of hospital wastewater was investigated at pH values ranging from 2 to 5. After 1 hour of solar irradiation, the maximum COD removal was 78% at pH 2 and 3 (Figure 5). In this study pH 3 was found to be optimum pH under the given experimental conditions, because the first-order rate constant decreased at pH 2. Generally, high pH decreases the concentration of soluble Fe³⁺ and obstructs the regeneration of Fe³⁺-Fe²⁺. In addition, H₂O₂ is unstable and readily decomposes, leading to a reduction of OH⁻ radicals. On the other hand, when the pH was <3, complex iron species including [Fe(H₂O)₆]²⁺ [Fe(H₂O)₆]³⁺, and [Fe(OH)(H₂O)₅]²⁺ were formed. The oxidation process declined because the formed complex species reacted relatively slowly with H₂O₂.

Moreover, high H⁺ concentration provides more scavengers for OH⁻, which hinders oxidation (Feng et al. 2013). The optimum pH for the treatment of landfill leachate by Fenton’s reagent was reported as 2–3.5 (Deng 2007).

**Effect of Fe²⁺ dosage**

To determine the effect of Fe²⁺ dosage, the degradation of hospital wastewater was investigated by varying Fe²⁺ dosage from 0.3 to 1.7 g/L. Maximum COD removal of 79% was observed for 1.4 g/L Fe²⁺ (Figure 6). The relatively low treatment efficiency of hospital wastewater at a low dosage of Fe²⁺ likely reflected an insufficient number of Fe²⁺ ions, leading to the low production of hydroxyl radicals.

Figure 4 | COD and BOD removal during the treatment of the wastewater by solar/TiO₂/H₂O₂ process against reaction time (pH = 7, TiO₂ = 1.5 g/L, H₂O₂ = 1.35 g/L).

Figure 5 | COD removal during the treatment of the wastewater by solar/Fe²⁺/H₂O₂ process against reaction time at different pH (Fe²⁺ = 1.4 g/L, H₂O₂ = 1.35 g/L).

Figure 6 | COD removal during the treatment of the wastewater by solar/Fe²⁺/H₂O₂ process against reaction time at different doses of Fe²⁺ (pH = 3, H₂O₂ = 1.35 g/L).
available for the Fenton reaction. Treatment efficiency increased with Fe$^{2+}$ dosage, because as the amount of Fe$^{2+}$ and Fe$^{3+}$ ions increased, the catalytic effect on H$_2$O$_2$ also increased. As the dosage of Fe$^{2+}$ exceeded 1.4 g/L, copious leaching of Fe$^{2+}$ in the form of Fe(OH)$_2$ would occur, restricting the decrease in COD. Fe$^{2+}$ may also tend to scavenge ·OH, decreasing treatment efficiency (Equation (7)). Liou et al. (2005) reported that OH$^-$ inhibition occurs in the photo-Fenton reaction with high ferrous concentrations

$$\text{OH}^- + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+}$$  \hspace{1cm} (7)

Moreover, high iron concentrations are not desirable since they are likely to increase iron precipitation (Deng 2007; Adishkumar et al. 2012).

**Effect of H$_2$O$_2$ concentration**

The amount of H$_2$O$_2$ is another parameter that influences the Fenton process. At the range tested, the degradation of hospital wastewater was slightly enhanced when H$_2$O$_2$ was increased from 0.45 to 1.35 g/L (Figure 7). For higher H$_2$O$_2$ concentrations, the performance of the reaction oxidation remained practically unchanged (Figure 7), as has been previously described (Anastasiou et al. 2009; Ginni et al. 2013). Increased H$_2$O$_2$ concentration may promote an inhibitory effect due to the hydroxyl radical scavenging (Equation (8)) and the formation of another radical (HO$_2$), having an oxidation potential considerably smaller than HO$^-$

$$\text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (8)

**Effect of contact time and biodegradability**

To determine the effect of contact time and biodegradability, the degradation of hospital wastewater was investigated at optimum conditions of pH 3, 1.4 g/L Fe$^{2+}$ and 1.35 g/L H$_2$O$_2$. The maximum COD removal efficiency of 95% was observed at 4 hours (Figure 8). By increasing the contact time, the exposure of the reaction mixture to solar light allowed the utilization of more energy to produce more hydroxyl radicals (Adishkumar et al. 2012). Fenton process involves the use of Fe$^{2+}$ and H$_2$O$_2$ thus resulting in the production of one hydroxyl radical per molecule of hydrogen peroxide (Equation (9)). In the presence of UV-Vis light (photo-Fenton process), Fe(II) species can be regenerated through the equation and Fe(II) can be considered as true catalytic species (Equation (10))

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{O}_2\text{H}^-$$  \hspace{1cm} (9)

$$\text{Fe}^{2+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{OH}^- + \text{Fe}^{2+} + \text{H}$$  \hspace{1cm} (10)

After 4 hours of the solar/Fe$^{2+}$/H$_2$O$_2$ treatment process, the biodegradability increased from 0.21 to 0.63. The solar photo-Fenton process is capable of degrading non-biodegradable organics to more biodegradable forms, suggesting that further degradation could be achieved by coupling solar
photo-Fenton and biological treatment processes, thereby reducing the cost of treatment (Ahmadi et al. 2008).

**Solar/ TiO₂/Fe²⁺/H₂O₂ process**

**Effect of pH**

To determine the effect of pH, the degradation of hospital wastewater was investigated at pH values of 2–7. After 1 hour of solar irradiation, the maximum COD removal was 88% at pH 5 and 7 (Figure 9). In this study pH 7 was found to be optimum pH under the given experimental conditions, because the first-order rate constant decreased at pH 5. In the solar/Fe²⁺/H₂O₂ process, degradation occurs only at acidic pH. The effluent after treatment will also be acidic, which is the main disadvantage (Kitsiou et al. 2009). In the solar/TiO₂/Fe²⁺/H₂O₂ process, at an acidic pH, the surface of TiO₂ is occupied with H⁺ ions, which retards the generation of OH⁻. When the pH increases, the active hydroxyl groups on the TiO₂ surface also increase. Consequently, the faster generation of OH⁻ radicals accelerates COD removal efficiency (Kashif & Ouyang 2009).

**Effect of TiO₂ dosage**

To determine the effect of TiO₂ dosage, the degradation of hospital wastewater was investigated by varying TiO₂ dosage from 0 to 0.25 g/L. Maximum COD removal of 87% was observed for the TiO₂ dosage of 0.2 g/L (Figure 10). The increase in TiO₂ dosage increased the degradation rate because of the adsorption of many photons on the active site of TiO₂. The excess amount of TiO₂ above the optimum dosage leads to increased opacity and sedimentation of TiO₂ (Chong & Jin 2012). The maximum COD removal in the solar/TiO₂/H₂O₂ process was 70% for 1.5 g/L TiO₂, whereas in the solar/TiO₂/Fe²⁺/H₂O₂ process, COD removal increased to 87% at 0.2 g/L TiO₂. Addition of small amounts of Fe²⁺ can significantly increase the generation rate of hydroxyl radicals, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO₂ (Parilti & Akten 2011). The positive effect of coupling photo-Fenton-like reactions with semiconductor photo-catalysis can be attributed to the increased production of active radicals through decomposition of oxidants by both heterogeneous and homogeneous catalysts (Kuriechen et al. 2013).

**Effect of Fe²⁺ dosage**

To determine the effect of Fe²⁺ dosage, the degradation of hospital wastewater was investigated by varying Fe²⁺ from 0 to 1 g/L. Maximum COD removal of 88% was observed for 0.5 g/L Fe²⁺ (Figure 11). TiO₂ is more effective due to the formation of electron-hole pairs under UV illumination. Nevertheless, recombination of electrons and holes inhibits the photo-catalytic reaction process. Some oxidants improve
the performance of UV/TiO₂ treatment by capturing the electrons ejected from TiO₂, reducing the probability of recombination of e⁻ and h⁺, and yielding higher available numbers and the survival time of h⁺. The addition of small amounts of Fe²⁺ can significantly increase the generation rate of OH⁻, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO₂. To improve the performance of UV/TiO₂ treatment, Fe²⁺ was added using the most suitable operating conditions (TiO₂ = 188 mg/L and Fe(III) = 0.5 mM) determined. COD from the wastewater was significantly degraded with the addition of Fe²⁺ to TiO₂ even at very low Fe²⁺ concentrations. In the presence of solar radiation, photo-catalytic reaction producing additional OH⁻ radicals and Fe(II) takes place as depicted in Equation (11) (Parilti & Akten 2014):

\[
\text{Fe}^{3+} + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH}^- \quad (11)
\]

Consequently, higher concentrations of OH⁻ radicals and Fe(II) can be attained with the solar UV/TiO₂/Fe(III) treatment as compared to the conventional TiO₂ treatment process (Parilti & Akten 2011). Kitsiou et al. (2009) reported that separate coupling of TiO₂ with Fe²⁺ or H₂O₂ has little effect on degradation efficiency, while the simultaneous use of TiO₂, Fe²⁺ and H₂O₂ leads to significantly increased rates, presumably due to combined effect of homogenous and heterogeneous photo-catalytic reactions.

Effect of H₂O₂ concentration

To maintain efficiency, it is necessary to choose the optimum concentration of H₂O₂. The effect of addition of 0–1.8 g/L H₂O₂ on COD is as shown in Figure 12. At 1.35 g/L H₂O₂, the maximum COD removal efficiency of 88% was obtained. Addition of H₂O₂ enhances photocatalytic reactions due to inhibition of electron-hole recombination and production of additional OH⁻ radicals (Quici et al. 2007) through reaction with CB electrons or with superoxide radicals, especially at high H₂O₂ concentrations (Equations (12) and (13))

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{HO}^- \quad (12)
\]

\[
\text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{OH}^- + \text{HO}^- \quad (13)
\]

However, an excess of H₂O₂ can be detrimental because it is a hole scavenger and the produced hydroperoxyl radical has a less oxidizing power than OH⁻ (Equation (14))

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (14)
\]

The combination of Fe²⁺, H₂O₂, TiO₂ and irradiation, i.e. photo-Fenton and photo-catalysis, improves the destruction of some resistant pollutants (Quici et al. 2005; Augugliaro et al. 2006).

![Figure 11](https://iwaponline.com/wqrj/article-pdf/49/3/223/379411/223.pdf)  
COD removal during the treatment of the wastewater by solar/TiO₂/Fe²⁺/H₂O₂ process against reaction time at different doses of Fe²⁺ (pH 7, TiO₂ = 0.2 g/L).

![Figure 12](https://iwaponline.com/wqrj/article-pdf/49/3/223/379411/223.pdf)  
COD removal during the treatment of the wastewater by solar/TiO₂/Fe²⁺/H₂O₂ process against reaction time at different doses of H₂O₂ (pH = 7, Fe²⁺ = 0.5 g/L, TiO₂ = 0.2 g/L).
Effect of contact time and biodegradability

In this study, the efficiency of solar/TiO₂/Fe²⁺/H₂O₂ process was carried out under optimum conditions. Nearly all (99%) of COD was depleted at 4 hours (Figure 13). By increasing the contact time, the exposure of the reaction mixture to solar light allowed the utilization of more energy to produce more hydroxyl radicals from H₂O₂, TiO₂ and Fe²⁺. The BOD and COD of hospital wastewater after treatment were both reduced to 20 mg/L. Treatment of hospital wastewater by the solar/TiO₂/Fe²⁺/H₂O₂ process increased biodegradability from 0.25 to 0.7 in 1 hour.

Kinetics of hospital wastewater degradation

The kinetics of degradation of hospital wastewater for the solar/TiO₂/H₂O₂, solar/Fe²⁺/H₂O₂ and solar/TiO₂/Fe²⁺/H₂O₂ AOP processes are discussed below. Table 2 shows the treated characteristics of the hospital wastewater. First-order kinetic model was utilized as follows (Equation (15)):

\[ \ln \frac{C_0}{C} = kt \]  

where \( C_0 \), \( C \), \( t \) and \( k \) are the initial COD, final COD, degradation time (h) and the global reaction apparent rate constant (h⁻¹), respectively. The order of rate constants was solar/TiO₂/Fe²⁺/H₂O₂ (0.771 h⁻¹) > solar/Fe²⁺/H₂O₂ (0.274 h⁻¹) > solar/TiO₂/H₂O₂ (0.253 h⁻¹).

Synergetic effect

The advantage of AOPs is enhanced by the fact that there are different OH radical production possibilities, so they can be adapted to specific treatment requirements. On the other hand, the relatively high operating cost of these processes compared to biological treatment is the main disadvantage. To tackle this problem and to increase the efficiency of AOPs, a combined or integrated process can be used. Using a combined process (solar/TiO₂/Fe²⁺/H₂O₂) as a pretreatment process reduces organic loading and cost of post treatment. The main parameter in the combined process to evaluate the effectiveness of the system is the synergetic effect, a parameter of the enhancement of the degradation of organic compounds using the combined method relative to the linear combination method. The synergetic effect could be estimated as follows in Equation (16):

\[ \text{Synergetic effect} = \frac{k_{\text{solar/TiO}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2}}{k_{\text{solar/TiO}_2/\text{H}_2\text{O}_2} + k_{\text{solar/Fe}^{2+}/\text{H}_2\text{O}_2}} \]  

Factors such as design, construction, operation and maintenance of combined (simultaneous) AOPs are more difficult than those of the individual methods. However, by the various combining technologies (solar/TiO₂/Fe²⁺/H₂O₂, ultrasound/Fe(II), ultrasound/H₂O₂, electro-Fenton, solar photo electro-Fenton), lower capital and operating costs are achievable. The purpose of combination of AOPs is to enhance the degradation rate that is not achievable by a single process alone under the same condition (Mohajerani et al. 2009). Based on the reaction rate constant, the synergetic effect of solar/TiO₂/Fe²⁺/H₂O₂ process was
1.5. The use of combined system in the AOP part will enhance the oxidation and biodegradability in less time. Behavior of the integration of combined AOPs and biological treatment processes is defined (Equation (17)) by a new parameter to depict the biodegradability enhancement.

\[
\text{Synergetic biodegradability enhancement} = \frac{\text{Biodegradable enhancement by solar/} \text{TiO}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2 \text{ process}}{\text{Total biodegradability enhancement by solar TiO}_2/\text{H}_2\text{O}_2 \text{ process and solar/Fe}^{2+}/\text{H}_2\text{O}_2 \text{ process}} \quad (17)
\]

This equation shows the amount of additional BOD produced by combined process. The synergetic biodegradability enhancement effect of this combined homogeneous and heterogeneous advanced oxidation process is based on the BOD/COD ratio. Under the optimum condition, a 1-hour treatment enhanced the biodegradability value to 0.45, 0.33 and 0.70 for solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} process, solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process and solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process, respectively. Based on the BOD\textsubscript{2}/COD ratio, the synergetic biodegradability enhancement effect of the combined process was 0.90. When compared to rate of degradation, the combined homogeneous and heterogeneous process is more effective than the individual processes.

**Cost estimation**

The cost of treatment includes direct cost, indirect cost and annual cost. The direct cost includes reactor civil works, piping and tanks and auxiliary equipment. The indirect cost includes contingences and spare parts. The annual cost includes consumables, operation and maintenance. The treatment cost was estimated to be Can$ 41.73/m\textsuperscript{3}, Can$ 22.27/m\textsuperscript{3}, Can$ 15.81/m\textsuperscript{3} for solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2}, solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} and solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} processes, respectively.

**CONCLUSIONS**

COD removal efficiency for the solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} process at the optimum conditions of pH 7, TiO\textsubscript{2} 1.5 g/L, H\textsubscript{2}O\textsubscript{2} 1.35 g/L was 85% after 4 hours of treatment. The COD removal efficiency for solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process at pH 3, Fe\textsuperscript{2+} -1.4 g/L, H\textsubscript{2}O\textsubscript{2} -1.35 g/L was 94% after 4 hours treatment. While these two processes were combined, the COD removal efficiency was 99% at pH 7, TiO\textsubscript{2} 0.2 g/L, Fe\textsuperscript{2+} 0.5 g/L, H\textsubscript{2}O\textsubscript{2} 1.35 g/L after 4 hours of treatment. Under the optimum condition, a 4-hour solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} treatment enhanced the biodegradability value to 0.6, solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} treatment of 4 hours enhanced the biodegradability value to 0.6, and solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} treatment of 1 hour enhanced the biodegradability value to 0.7. The order of rate constants was solar/TiO\textsubscript{2}/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} (0.771 h\textsuperscript{-1}) > solar/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} (0.274 h\textsuperscript{-1}) > solar/TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} (0.253 h\textsuperscript{-1}). The synergetic effect for the combined process was 1.5 times more efficient than the individual processes. This process can be adopted for neutral pH and reduces the amount of chemicals by increasing the water quality. Economically, the employment of a natural resource, such as solar light, could be an interesting option due to zero input energy cost as an environmentally harmless photo-catalytic treatment of industrial wastewater.

**REFERENCES**

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First received 20 July 2013; accepted in revised form 9 January 2014. Available online 29 January 2014