Combined homogeneous and heterogeneous advanced oxidation process for the treatment of tannery wastewaters

G. Selvabharathi, S. Adishkumar, S. Jenefa, G. Ginni, J. Rajesh Banu and Ick Tae Yeom

ABSTRACT

This study investigated the practical application of combined advanced oxidation processes (AOPs), such as homogeneous TiO₂ photocatalysis and heterogeneous photo-Fenton, for the treatment of tannery wastewaters. An optimization study was conducted on the photocatalytic degradation of tannery wastewaters, in order to understand the effects of different operating parameters on the degradation kinetics. The chemical oxygen demand of tannery wastewater decreased from an initial level of 3,400 mg/L in raw wastewater to 140 mg/L (96% removal) in wastewater treated by the combined advanced oxidation process at optimum pH 7, TiO₂ dosage of 0.2 g/L, Fe²⁺ dosage of 0.5 g/L, H₂O₂ dosage of 1.8 g/L and a treatment time of 4 hours. The biodegradability of wastewater increased from an initial level of 0.4 to 0.7 after treatment under optimum experimental conditions at a treatment time of 60 min. An annual treatment cost of US$21.34/m³ of treated water was obtained. The combined advanced oxidation process proved to be an efficient and appropriate technique for the effective removal of complex organic compounds in industrial wastewater.

Key words | biodegradability, combined advanced oxidation process, photocatalysis, solar photo-Fenton, synergetic effect, tannery wastewaters

INTRODUCTION

Tanneries are typically characterized as pollution-intensive industrial complexes that generate widely varying, high-strength wastewaters (Chowdhury et al. 2013). The variability of tannery wastewaters arises not only from the fill and draw-type operation associated with tanning processes, but also from the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product. The tanning industry also has a very high toxic intensity per unit of output. During the tanning process at least about 0.3 kg of chemicals are added per kilogram of skin/hides (Durai & Rajasimman 2011). Tanneries generate wastewater in the range of 30–35 litre per kilogram of skin/hide processed with variable pH (6–10.5), total suspended solids (TSS) (526–2,865 mg/L), biochemical oxygen demand (BOD) (100–2,906 mg/L), chemical oxygen demand (COD) (2,102–11,153 mg/L) (Lofrano et al. 2013). One of the refractory groups of chemicals in tannery wastewater derives mainly from tannins. Tannins are characterized by complex chemical structures, because they are composed of an extended set of chemicals such as phenol, naphthalene, formaldehyde and melanime-based syntans, and acrylic resins. The BOD₅/COD ratio of tannins is also lower than other compounds. However, it is worth noting that no one of these compounds showed a BOD₅/COD ratio higher than 0.4, indicating a very low biodegradability for each of them (Lofrano et al. 2013).

The main treatment processes used at tannery plants are primary clarification (sedimentation), secondary treatment (activated sludge process) and/or tertiary processes...
(membrane processes as ultrafiltration). The activated sludge process has been the most common wastewater treatment process for the removal of organics in our country; however, it is inefficient for the removal of recalcitrant organics and micro-pollutants in tannery wastewater. The mixture of compounds used in the tannery process can be released into the environment because the compounds remain even after conventional treatment (activated sludge process, aerobic sequencing batch reactor, anaerobic filters, upflow anaerobic sludge blanket and membrane bioreactor) and negatively affect organisms and the environment. The wastewater of tanneries has also been associated with a huge foaming problem on surface waters (Durai & Rajasimman 2011). The high concentrations of pollutants with low biodegradability in tannery wastewater represent a serious and actual technological and environmental challenge. Therefore, many researchers have attempted to develop new technologies for complementing or even replacing some of these treatments (Khansorthong & Hunsom 2009).

Advanced oxidation processes (AOPs) can be considered an effective alternative and have become the most widely used treatment technologies for organic pollutants not treatable by conventional technologies due to their high chemical stability and/or low biodegradability. AOPs involve the generation of highly reactive radical species, mainly the hydroxyl radical (OH·) to oxidize the organic matter to the end products of water and carbon dioxide (Trabelsi-Souissi et al. 2015). The use of sunlight as the source of irradiation to perform AOPs reduces the processing costs and makes them more affordable for commercial use as a water treatment technology (Babupon-nusami & Muthukumar 2012). 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 wastewater (Zgajnar et al. 2011).

Among various AOPs, Fenton reagent (Fe2+/H2O2) and photocatalysis (TiO2 + UV) have been intensively investigated for environmental applications during the last decades. They have both been recognized as ‘green technologies’. Above all, the Fenton reaction can be initiated in conditions of normal temperature and pressure with no external energy, thus it can hopefully be utilized in water

in situ remediation areas (Eskelinen et al. 2010). In the photocatalytic research field, some catalysts, for example, TiO2, CdS and GaP have proved to possess high activity with solar light irradiation, thus endless clean solar energy is a powerful support for this technology (Sauer et al. 2006; Rauf et al. 2011). However, the classic Fe2+/based Fenton system requires operation at pH < 3.0 to prevent the precipitation of Fe2+ and Fe3+. Usually, a large excess of Fe salts in traditional Fenton systems cannot be recycled, producing large amounts of chemical sludge (Su et al. 2012; Hermosilla et al. 2012). The major drawback of TiO2/UV photocatalysis was that its high efficiency occurred only under UV irradiation, which can use only 3–4% of the solar energy reaching the earth (Portjanskaja et al. 2009).

Thus, in order to extend the practical applications of industrial and environmental interest, some efforts have been made to develop a synergistic reaction to enhance the Fenton reaction and TiO2 photocatalysis. For instance, when Fenton is combined with the TiO2 photocatalysis reaction, the efficacies of both the systems for the production of radicals are enhanced (Chen et al. 2013). The conduction band (CB) electrons and photoenergy can accelerate the ferric and ferrous iron cycles (Fe2+/Fe3+); at the same time, Fenton reagent (Fe2+/H2O2) inhibits the electron-hole recombination by scavenging CB electrons of photoexcited TiO2 to increase the lifetime of the valence band hole and subsequently generate more radicals. Moreover, electrons from TiO2 decompose more oxidants to radicals, which can promote the Fenton reaction efficiency drastically (Kim et al. 2012).

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

MATERIALS AND METHODS

Wastewater source and characterization

Tannery wastewaters were obtained from a tannery near Erode, Tamil Nadu, India. The tests were performed
with primary treated wastewater (collected at the outlet of the plain sedimentation tank). The sample was collected in plastic cans that were transported to a laboratory and stored at 4°C. The physicochemical characteristics of the wastewater, determined using standard methods, are listed in Table 1. After the primary treatment, the BOD$_5$ to COD ratio was 0.40, indicating the non-biodegradable character of the wastewater and the possible presence of minimally biodegradable chemical substances, which undermine biological treatment (Lofrano et al. 2013). Even after complete treatment, the treated wastewater did not satisfy the minimum national standards for discharge (MINAS 2007). Upgrade of the tannery’s existing tannery wastewater treatment system is needed.

Chemicals

All reagents used in this experiment were of analytical grade and used as received without further purification. The chemicals used in this study are ferrous sulphate heptahydrate (FeSO$_4$·7H$_2$O), hydrogen peroxide (H$_2$O$_2$ 30% w/w), sodium thiosulphate (Na$_2$O$_3$S$_2$), sulphuric acid (H$_2$SO$_4$), potassium dichromate (Cr$_2$K$_2$O$_7$), mercuric sulphate (HgSO$_4$), ferrous ammonium sulphate (Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O), sodium hydroxide (NaOH), and sodium sulphite (Na$_2$SO$_3$), and were purchased from Merck (India). The photocatalyst employed was commercial TiO$_2$ (P25), and was supplied by Degussa (Germany). According to the manufacturer’s specifications, P25 has an elementary particle size of 30 nm, a Brunauer–Emmett–Teller (BET) specific surface area of 50 m$^2$/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 experiments were conducted using a laboratory-scale reactor system made from borosilicate glass having a size of 0.3 m (length) × 0.2 m (width) × 0.04 m (depth) operated in the batch mode. The irradiation surface area was 0.06 m$^2$. Irradiation was carried out in the open air with continuous aeration 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 between 11 a.m. and 3 p.m. 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/m$^2$). Initially, the pH of the wastewater was adjusted to a predetermined value (2–8) by adding sulphuric acid or sodium hydroxide. Then the required amount of ferrous sulphate (0–1 g/L) and TiO$_2$ (0–0.25 g/L) was added to the wastewater and stirred well to enhance the homogeneity of wastewater during the reaction. H$_2$O$_2$ (0–2.2 g/L) was added (considered the beginning of the experiment) and the mixture was solar irradiated. The required amount of sample was withdrawn from the reactor at selected time intervals. 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 H$_2$O$_2$ decomposition, and the pH was raised by adding sodium hydroxide to precipitate iron salt and TiO$_2$ particles. All experiments were performed in triplicate and averages were reported. The COD and BOD$_3$ of the samples were carried out as per Standard Methods (APHA 2005).

### Box–Behnken experimental design

The Box–Behnken design (BBD) statistical experiment had been used on the advanced oxidation of pollutants. BBD is the optimization of analytical methods. Hence, BBD was used to investigate the effects of important operating parameters in the degradation of tannery wastewaters and to optimize the system. This is a type of response surface method (RSM) which is based on three level incomplete
factorial designs. It requires fewer runs when compared to other RSM designs, making its application more economical (Masomboon et al. 2010). Basically, this optimization process involves three major steps: (1) performing the statistically designed experiments, (2) estimating the coefficients in a mathematical model and (3) predicting the response and checking the adequacy of the model. The Box–Behnken experimental design is used for evaluation of a dependent variable as functions of independent variables. The pH, TiO₂, Fe²⁺ and H₂O₂ concentrations were considered as independent variables. The COD removal efficiency was considered as a dependent variable in the Box–Behnken statistical design method. The pH was varied between 6 and 8, the TiO₂ concentration was varied between 0.10 g/L and 0.30 g/L, the Fe²⁺ concentration was varied between 0.25 g/L and 0.75 g/L and the H₂O₂ concentration was varied between 1.60 g/L and 2.00 g/L. A total of 29 experiments were employed in this analysis, using Design Expert Version 9.0.2 software (Stat-Ease, Inc., Minneapolis, USA). To simplify the recording of the conditions of each experiment and the processing of the experimental data, the factor levels were selected taking the high level as +1 and the lower level as −1.

RESULTS AND DISCUSSION

Model fitting and statistical analysis

The experimental data for COD removal by combined advanced oxidation process are given in Table 2. From the results obtained in the trials performed with the BBD, the following quadratic model equation was established to correlate the dependent and independent variables:

\[
\text{COD removal (\%)} = 72.06 + 1.33A + 3.54B + 1.46C - 1.83D - 5.75AB + 2.50AC + 2.00AD - 2.25BD - 8.50CD
\]  

(1)

The regression coefficients of the model describing the COD removal are summarized in Table 3. Analysis of variance (ANOVA) was applied in order to evaluate the significance of the fit of the developed model. \( P < 0.05 \) indicates that the model terms are significant at 95% confidence level or more. For the model predicted by Equation (1), \( P \) was less than 0.0001, indicating that it was significant for describing the COD removal efficiency. The lack of fit value 5.77 is not significant at the \( P \) value > 0.05. For a model to be successfully used for prediction, the lack of fit should be insignificant and the response surfaces sufficiently explained by the regression equation. A positive effect of a
factor means that the response is improved when the factor level increases and a negative effect of the factor means that the response is not improved when the factor level increases. The factors that had relatively less effect on COD removal efficiency were the TiO$_2$ concentration ($P = 0.0131$) and the interactions between Fe$^{2+}$ concentration and TiO$_2$ concentration ($P = 0.1445$) and between pH and TiO$_2$ concentration ($P = 0.0139$). As can be seen in Equation (1), the positive effects were the individual factors of TiO$_2$ concentration, pH and Fe$^{2+}$ concentration, in this order. The negative effects were the double interaction between Fe$^{2+}$ concentration and H$_2$O$_2$ concentration, the double interaction between pH and TiO$_2$ concentration and the factor of H$_2$O$_2$ concentration, as well as the double interaction between TiO$_2$ concentration and H$_2$O$_2$ concentration. The high correlation between actual experimental data and the model for COD removal ($R^2 = 0.9785$) showed that 97.85% of the variability observed in data can be explained by the model built for COD removal efficiency, leaving only 2.15% of variability owing to random error. Consequently, the quadratic model given by Equation (1) can be used to predict the COD removal efficiency, create and explore the response surface and find the optimal conditions of the process.

### Effect of pH

To determine the effect of pH, the degradation of tannery wastewater was investigated at pH values of 2 to 8. At an optimal pH of 7, the decrease in COD was greatest (75%) (Figure 1). In the solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process, at an acidic pH, the surface of TiO$_2$ is occupied with H$^+$ ions, which retards the generation of OH$^-$.

![Figure 1](https://iwaponline.com/jwrd/article-pdf/6/1/59/377258/jwrd0060059.pdf)

**Figure 1** COD removal during the treatment of the wastewater by solar/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ process against reaction time at different pH (TiO$_2$ = 0.2 g/L, Fe$^{2+}$ = 0.5 g/L, H$_2$O$_2$ = 1.5 g/L).
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). The Fenton reaction, which occurred on the photo-excited TiO₂ surface, appeared to produce a more reactive oxidant (e.g., OH⁻) than the Fe(IV) species, which was usually formed by the Fenton reaction at neutral pH. As a result, the integrated solar/TiO₂/Fe²⁺/H₂O₂ system can enhance the rate of contaminant oxidation by increased production of reactive oxidants.

Three-dimensional (3D) response surface and contour plot are presented in Figure 2. Such a plot presents the function of two variables, maintaining all others at the fixed levels. According to the literature, 3D surface and corresponding contour plots provide a clear and straightforward evaluation of the effects of the investigated experimental variables. In Figure 2, the influence of initial pH and TiO₂ concentration on the COD removal of tannery wastewater by solar/TiO₂/Fe²⁺/H₂O₂ process is presented. According to the shape of the 3D surface, larger amplitudes of COD removal were obtained by varying the initial pH than by varying TiO₂, so it can be concluded that initial pH is a more influential parameter than TiO₂.

Effect of TiO₂

To determine the effect of TiO₂ dosage, the degradation of tannery wastewater was investigated by varying TiO₂ dosage from 0 to 0.25 g/L. Maximum COD removal of 71% was obtained at 0.2 g/L TiO₂ (Figure 3). As the TiO₂ dosage increased from 0.1 to 0.2 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 the 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; Adishkumar et al. 2014). In addition, at high TiO₂ concentrations, aggregation of particles will reduce the interfacial area between the reaction solution and the photocatalyst, decreasing the number of active sites on the catalyst surface. Agglomeration and sedimentation of the TiO₂ particles were observed when more than 0.2 g/L of TiO₂ 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). The 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 (Baycan Parilti & Atken 2011). The positive effect of coupling photo-Fenton-like reactions with semiconductor
photocatalysis can be attributed to the increased production of active radicals through decomposition of oxidants by both heterogeneous and homogeneous catalysts (Zhang et al. 2011).

**Effect of ferrous dosage**

To determine the effect of Fe$^{2+}$ dosage, the degradation of tannery wastewater was investigated by varying Fe$^{2+}$ dosage from 0 to 1 g/L. Maximum COD removal of 70% was observed for 0.5 g/L Fe$^{2+}$ (Figure 4). The relatively low treatment efficiency of tannery wastewater at a low dosage of Fe$^{2+}$ likely reflected an insufficient number of Fe$^{2+}$ ions, leading to the low production of hydroxyl radicals 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 0.5 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. Liou et al. (2005) reported that OH$^-$ inhibition occurs in the photo-Fenton reaction with high ferrous concentrations. Moreover, high iron concentrations are not desirable since they are likely to increase iron precipitation (Deng 2007; Adishkumar et al. 2012). TiO$_2$ is more effective due to the formation of electron–hole pairs under UV illumination. Nevertheless, recombination of electrons and holes inhibits the photocatalytic reaction process. Some oxidants improve the performance of UV/TiO$_2$ treatment by capturing the electrons ejected from TiO$_2$, reducing the probability of recombination of e$^-$ and h$^+$/B, and yielding higher available numbers and the survival time of h$^+$/B. Baycan Parilti & Atken (2011) reported that for the removal of organic contaminants in pulp mill effluents (COD concentrations = 1,500 mg/L), the addition of small amounts of Fe$^{2+}$ can significantly increase the generation rate of OH$,^-$ thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO$_2$. Consequently, higher concentrations of OH$,^-$ radicals and Fe(III) can be attained in the solar UV/TiO$_2$/Fe(III) treatment compared to the conventional TiO$_2$ treatment process. Kitsiou et al. (2009) reported that separate coupling of TiO$_2$ with Fe$^{2+}$ or H$_2$O$_2$ has little effect on the degradation efficiency of imidacloprid, a systemic chloronicotinoid insecticide (20 mg/L initial concentration), while the simultaneous use of TiO$_2$, Fe$^{2+}$, and H$_2$O$_2$ leads to significantly increased rates, presumably due to the combined effect of homogenous and heterogeneous photocatalytic reactions.

In Figure 5, the influence of Fe$^{2+}$ and TiO$_2$ concentration on the COD removal of tannery wastewater by the solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process is presented. According to the shape of the 3D surface, larger amplitudes of COD removal were obtained by varying the Fe$^{2+}$ than by varying TiO$_2$, and it can be concluded that Fe$^{2+}$ is a more influential parameter than TiO$_2$. Figure 6 presents the influence of
H$_2$O$_2$ concentration and Fe$^{2+}$ concentration. In Figure 6, a much higher influence of Fe$^{2+}$ concentration can be observed than H$_2$O$_2$ concentration.

**Effect of H$_2$O$_2$ dosage**

To maintain efficiency, it is necessary to choose the optimum concentration of H$_2$O$_2$. The effect of the addition of 0–2.2 g/L H$_2$O$_2$ on the COD removal is shown in Figure 7. Increasing the concentration of H$_2$O$_2$ correspondingly increased COD removal up to an H$_2$O$_2$ concentration of 1.8 g/L. The enhancement of degradation by the addition of H$_2$O$_2$ is due to an increase in the hydroxyl radical concentration. H$_2$O$_2$ can compensate for the lack of O$_2$ 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 (Ginni et al. 2014). Figure 8 presents the influence of H$_2$O$_2$ concentration and TiO$_2$ concentration. In Figure 8, a much higher influence of H$_2$O$_2$ concentration can be observed than TiO$_2$ concentration. Mahmoudi et al. (2005) reported that an optimal concentration of H$_2$O$_2$ increases the formation rate of hydroxyl radicals due to reduction of H$_2$O$_2$ at the CB and because of self-decomposition occurring during solar illumination. Increased H$_2$O$_2$ concentration may promote an inhibitory effect, due to the hydroxyl radical scavenging and the formation of another radical (HO$_2$), having an oxidation potential considerably smaller than HO$. The combination of Fe$^{2+}$, H$_2$O$_2$, TiO$_2$ and irradiation, i.e., photo-Fenton and photocatalysis, improves the destruction of some resistant pollutants (Vincenzo et al. 2006).

**Kinetics of tannery wastewater degradation**

In order to achieve the proper design of a solar photo reactor, it is very important to determine the kinetic coefficients involved in a reaction. Treatment efficiency of tannery wastewater by the solar, solar/Fe$^{2+}$, solar/TiO$_2$, solar/H$_2$O$_2$, and solar/TiO$_2$/H$_2$O$_2$ process against reaction time at different H$_2$O$_2$ [pH = 7, TiO$_2$ = 0.2 g/L, Fe$^{2+}$ = 0.5 g/L] is shown in Figure 7.
solar/TiO$_2$/H$_2$O$_2$, solar/Fe$^{2+}$/H$_2$O$_2$ and solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ processes are shown in Figure 9. The kinetics of degradation of tannery wastewater for the solar/TiO$_2$/H$_2$O$_2$, solar/Fe$^{2+}$/H$_2$O$_2$ and solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ processes are discussed below. First-order kinetic model was utilized as follows:

$$\ln \frac{C_0}{C} = kt$$

(2)

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/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ $0.80$ h$^{-1}$ ($R^2 = 0.93$) > solar/Fe$^{2+}$/H$_2$O$_2$ $0.30$ h$^{-1}$ ($R^2 = 0.94$) > solar/TiO$_2$/H$_2$O$_2$ $0.20$ h$^{-1}$ ($R^2 = 0.97$).

**Effect of hydraulic retention time**

In this study, the efficiency of solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process was carried out under optimum conditions. Nearly all (96%) COD was depleted at 4 hours (Figure 10). 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 H$_2$O$_2$, TiO$_2$ and Fe$^{2+}$. Table 4

**Figure 9** | Treatment of tannery wastewater under different systems [pH = 7, TiO$_2$ = 0.2 g/L, Fe$^{2+}$ = 0.5 g/L, H$_2$O$_2$ = 1.8 g/L, contact time = 4 h].

**Figure 10** | Effect of hydraulic retention time during the treatment of the wastewater by solar/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ process [pH = 7, TiO$_2$ = 0.2 g/L, Fe$^{2+}$ = 0.5 g/L, H$_2$O$_2$ = 1.8 g/L].

**Table 4** | Characteristics of solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ treated tannery wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$</th>
<th>Minimal National Standards (MINAS) for disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7</td>
<td>6.5–9.0</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>BOD$_5$ (mg/L)</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>140</td>
<td>250</td>
</tr>
</tbody>
</table>
shows the treated characteristics of the tannery wastewater. The COD and BOD₅ of tannery wastewater after treatment were reduced to 140 mg/L and 90 mg/L. Treatment of tannery wastewater by the solar/TiO₂/Fe²⁺/H₂O₂ process increased biodegradability from 0.4 to 0.7 in 1 hour (Figure 10). The increase of BOD₅/COD ratio to 0.70 upon treatment of the wastewater in the combined advanced oxidation process for 1 hour clearly indicates the breakdown of organic compounds into biodegradable forms, and the improvement in biodegradability of the wastewater. Therefore, wastewaters of combined AOPs can be efficiently post-treated in a biological process for the elimination of residual organic compounds of wastewaters.

**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 as a pretreatment process reduces organic loading and the cost of post-treatment. The main parameter in the combined process used 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:

\[
\text{Synergetic effect} = \frac{k_{(\text{solar/TiO}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2)}}{k_{(\text{solar/TiO}_2/\text{H}_2\text{O}_2)} + k_{(\text{solar/Fe}^{2+}/\text{H}_2\text{O}_2)}} = 1.6
\]  

(3)

Factors such as design, construction, operation and maintenance of combined advanced oxidation processes are more difficult than those of the individual methods. However, by combining the various technologies, lower capital and operating costs are achievable. The purpose of combining AOPs is to enhance the degradation rate that is not achievable by a single process alone under the same condition (Mohejerani et al. 2009). Based on the reaction rate constant, the synergetic effect of solar/TiO₂/Fe²⁺/H₂O₂ process was 1.6. The use of the combined system in the AOP part will enhance the oxidation and biodegradability in less time. Behaviour of the integration of combined AOPs and biological treatment processes is defined in Equation (4) by a new parameter to depict the biodegradability enhancement:

\[
\text{Synergetic biodegradability enhancement} = \frac{\text{Biodegradable enhancement by solar/TiO}_2/\text{H}_2\text{O}_2 \text{ process}}{\text{Total biodegradability enhancement by solar/TiO}_2/\text{H}_2\text{O}_2 \text{ process and solar/Fe}^{2+}/\text{H}_2\text{O}_2 \text{ process}} = 0.70
\]  

(4)

This equation shows the amount of additional BOD produced by the combined process. The synergetic biodegradability enhancement effect of this combined homogeneous and heterogeneous advanced oxidation process is based on the BOD₅/COD ratio. At 1 hour treatment the BOD₅/COD ratio was 0.50, 0.50 and 0.70 for solar/TiO₂/H₂O₂ process, solar/Fe²⁺/H₂O₂ process and solar/TiO₂/Fe²⁺/H₂O₂ process, respectively. Based on the BOD₅/COD ratio, the synergetic biodegradability enhancement effect of the combined process was 0.70. When compared to rate of degradation, the combined homogeneous and heterogeneous process is more effective than the individual processes.

**Design of the field-scale reactor**

The field-scale reactor was designed to treat the tannery wastewater with a flow rate of 96 m³/d. The reactor was designed for 96% COD removal. The average yearly solar UV light intensity for the study location was calculated as 23 ± 2 W/m², and the average daily useful solar hours were found to be 6 hours. Sagawe et al. (2003) suggested the equation for the kinetic model, which accounts for the effect of pollutant concentration, volumetric flow rate, light intensity and solar irradiation area; these were used to arrive at a lump parameter (K₃) (Equation (5)):

\[
K_3 = \ln \left( \frac{C_0}{C} \right) \times \frac{Q}{(q_{UV} \times A)}
\]  

(5)
where $K_3$ = a lump kinetic parameter representing the efficiency of the photocatalyst (m$^3$/W·min); $C_0$ = inlet concentration of COD (mg/L); $C$ = outlet concentration of COD (mg/L); $Q$ = volumetric flow rate (m$^3$/min); $q_{UV}$ = time averaged radiation density (W/m$^2$); and $A$ = effective area of solar irradiation (m$^2$).

$$K_3 = \ln \left( \frac{3400}{140} \right) \times 1.388 \times 10^{-6} / (23 \times 0.043)$$
$$= 4.4766 \times 10^{-6} \text{ m}^3 / \text{W.min}.$$ 

The scaling up of the field-scale reactor can be given by the following equations (Equations (6) and (7)):

$$(K_3)_\text{bench-scale reactor} = (K_3)_\text{field-scale reactor}$$

Area of field-scale reactor
$$= \ln \left( \frac{C_0}{C} \right) \times Q_{\text{field-scale reactor}} / (q_{UV}) \times (K_3)_\text{bench-scale reactor}$$
$$= \ln \left( \frac{3400}{140} \right) \times 0.066 / 23 \times 4.4766 \times 10^{-6}$$
$$= 2045 \text{ m}^2$$

(7)

The depth of the reactor, based on detention time, included free board = 0.1 m.

Cost analysis

Cost analysis was carried out by analysing the degradation process under optimal conditions. The operating cost for treating tannery wastewater by solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process has been evaluated. Table 5 presents the solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process operating and annual treatment costs per m$^3$ of treated water necessary to remove 96% of COD. An annual treatment cost of US$21.34/m$^3$ of treated water was obtained.

CONCLUSIONS

The degradation of tannery wastewater has been studied by means of the combined homogeneous and heterogeneous AOP. Box–Behnken design results confirmed that the TiO$_2$ concentration, pH and Fe$^{2+}$ concentration positively affected COD removal efficiency in the solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process. Based on experimental results, an empirical relationship between the COD removal efficiency and independent variables was obtained and expressed by the quadratic model Equation (1). The effect of experimental parameters on the COD removal efficiency of tannery wastewater was established by the response surfaces of the developed model. The optimal operation parameters for the solar/TiO$_2$/Fe$^{2+}$/H$_2$O$_2$ process for degradation of tannery wastewater were pH = 7, TiO$_2$ = 0.2 g/L, Fe$^{2+}$ = 0.5 g/L and H$_2$O$_2$ = 1.8 g/L. Under this condition, 96% COD removal efficiency was achieved after 4 hours of treatment. The kinetic study indicated that the degradation kinetics of tannery wastewater followed the first-order kinetic. When compared to the rate of degradation, the combined homogeneous and heterogeneous process is more effective than the individual processes. The combined process is a useful tool for enhancing the biodegradability of tannery wastewater in biodegradation of wastewater which enters into a biological wastewater treatment process. The obtained results showed the feasibility of combined advanced

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Estimated operating cost and annual treatment cost (US$) of solar/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ process for treatment of tannery wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Facility cost</td>
<td>2,045 m$^2$ of solar collector system</td>
</tr>
<tr>
<td>B Project contingency</td>
<td>12% of the facility cost is estimated</td>
</tr>
<tr>
<td>C Engineering and setup</td>
<td>50% of A + B (total facility cost)</td>
</tr>
<tr>
<td>D Spare parts</td>
<td>0.5% of A + B (total facility cost)</td>
</tr>
<tr>
<td>E Total installed cost</td>
<td>A + B + C + D</td>
</tr>
<tr>
<td>F Personnel cost</td>
<td>0.20 person/year @ 576/person/year</td>
</tr>
<tr>
<td>G Maintenance material cost</td>
<td>2% of A + B (total facility cost)</td>
</tr>
<tr>
<td>H Electricity</td>
<td>4 kW/hour average consumption, 1,752 operation hours/year</td>
</tr>
<tr>
<td>I Chemical consumption</td>
<td>(FeSO$_4$.7H$_2$O), (H$_2$O$_2$ 30% w/w), TiO$_2$, etc.</td>
</tr>
<tr>
<td>J Total operating cost</td>
<td>F + G + H + I</td>
</tr>
<tr>
<td>K Annual levelized cost</td>
<td>E × fixed charge rate (FCR) + J</td>
</tr>
<tr>
<td>L Annual treatment cost</td>
<td>K is divided by 35,040 (yearly treated volume)</td>
</tr>
</tbody>
</table>
oxidation processes to achieve suitable water qualities for internal reuse.

REFERENCES


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