A comparative treatment of bleaching wastewater by physicochemical processes

Ninad Oke, Swati Singh and Anurag Garg

ABSTRACT

The bleaching effluent discharged from a pulp and paper mill contains chlorinated organic compounds which are toxic to living matter. Physicochemical treatments such as coagulation and different advanced oxidation processes (AOPs) were employed for combined bleaching effluent generated from the first two stages (i.e. chlorination and alkali extraction) (pH = 3.5, chemical oxygen demand (COD) = 1,920 mg/L, and total organic carbon (TOC) = 663 mg/L). At optimum conditions (pH = 7.5, polyaluminium chloride (PAC) dose = 3.84 g/L and slow mixing time = 25 min), ~68% removal in UV254 and ~23% TOC removal was obtained during coagulation. Among various AOPs, UV/Fe²⁺/TiO₂/H₂O₂ system showed the highest TOC and COD removals (~78%) after 2 h duration (Fe²⁺:H₂O₂ molar ratio = 1:100). After the AOP process, chloride ion concentration and biodegradability of the treated wastewater was increased to 2,762 mg/L and 0.46 from an initial value of 2,131 mg/L and 0.29, respectively. The wastewater and sludge analysis showed oxidation and adsorption as the major mechanisms for organics removal. Upon reuse of the regenerated catalysts, TOC removal was reduced significantly. It was found that three times more sludge per unit TOC removal was generated after coagulation in comparison to that produced after UV/Fe²⁺/TiO₂/H₂O₂ treatment.

Key words | advanced oxidation processes, bleaching effluent, coagulation, response surface methodology (RSM), sludge quantification

INTRODUCTION

Pulp and paper mills are water intensive industries and generate highly polluting wastewater requiring proper treatment before discharge into natural water bodies. In India, around 25–35% of total pulp and paper mill effluent is released from bleaching section (Tewari et al. 2009) which contains toxic and persistent chlorinated organics along with residual lignin (Lucas et al. 2012). Therefore, the conventional biological treatment processes are not effective for its treatment (Pérez et al. 2002; Wang et al. 2011a; Qadir & Chhipa 2015). Usually, the bleaching effluent is mixed with less polluted wastewater streams from other unit operations to dilute the combined effluent, though it still remains non-biodegradable in nature. Such a practice also restricts the recycling potential of wastewater. Hence, the present research work was undertaken to treat the real bleaching wastewater generated from initial bleaching stages (i.e. chlorination and alkali extraction only) due to high pollution load.

Physicochemical processes such dissolved air floatation, coagulation, reverse osmosis, flocculation, adsorption and filtration can be used as pre-treatment to enhance biodegradability of such effluents (Wang et al. 2011b; Qadir & Chhipa 2015). However, these processes only transfer the pollutants from one phase to another. Hence, advanced oxidation processes (AOPs) are gaining attention as they destroy the recalcitrant compounds due to generation of highly reactive hydroxyl radicals (Pérez et al. 2002; Torrades et al. 2005; Lucas et al. 2012). The examples of AOPs include conventional Fenton (Fe²⁺/H₂O₂), photo-Fenton (UV/Fe²⁺/H₂O₂), photo-catalysis (UV/TiO₂/H₂O₂) and ozonation (O₃, UV/O₃, UV/O₃/H₂O₂) (Kumar et al. 2011; Qadir & Chhipa 2015).

Nevertheless, coagulation is a simple and widely accepted wastewater treatment method. Hence, the detailed study on this treatment process for bleaching effluent was planned. Moreover, the performance of various AOPs was
also investigated for the same effluent stream. Coagulation–flocculation is capable of removing colour and chemical oxygen demand (COD) from an effluent by forming bigger size flocs (comprising of colloidal impurities) which are settled out. Coagulants like aluminium sulphate, calcium sulphate, aluminium chloride, polyaluminium chloride (PAC), and chitosan have been found effective for the treatment of paper mill effluents (Qadir & Chhipa 2015). The process controlling parameters for coagulation are effluent pH, coagulant dose and slow mixing time. In a study, the addition of PAC reduced around 68% of the initial COD (1,270 mg/L) of a pulp and paper mill wastewater within 90 min at an optimum pH of 8.0 (coagulant dose = 1.5 g/L) (Choudhary et al. 2015). Kim (2016) used coagulation–flocculation process with PAC as coagulant in combination with a flocculent, namely, cationic polyacrylamide (c-PAM) for the treatment of paper industry wastewater. Under optimum conditions (i.e. PAC dose = 3.7 g/L, c-PAM dose = 39.9 mg/L and pH = 5.4), a COD removal of ~35% was observed (initial COD = 3,260 mg/L).

From the existing literature, it was found that the performance of PAC has not been consistent even for wastewater generated from same industry primarily due to the changed concentration of pollutants. Therefore, it is important to optimize the treatment conditions for a waste stream generating from a specific industrial unit.

Among various AOPs, Fenton, and photo-oxidation processes have been reported for the treatment of bleaching effluent (Yeber et al. 1999; Wang et al. 2011a; Lucas et al. 2012). Wang et al. (2011a) reported 88.7% of COD removal (initial COD = 1,830 mg/L) during Fenton’s oxidation of bleaching effluent performed under optimum reaction conditions ([H2O2]/[Fe2+] = 20 and pH = 3) in 120 min. The performance of photo-Fenton and UV/H2O2 was compared for the treatment of pulp bleaching effluent (Silva et al. 2010). Photo-Fenton resulted in higher COD and total organic carbon (TOC) reductions (78% and 91%, respectively) with H2O2/Fe2+ mass ratio of 185:1 (molar ratio = 330:1) compared to UV/H2O2 combination (COD and TOC reductions = 61% and 86%, respectively).

Fenton’s process involves the catalytic reaction of ferrous with H2O2 generating hydroxyl radicals having high oxidation potential (Hubbe et al. 2016). Photocatalytic process generally involves the activation of semiconductor by irradiation of light of equal or higher energy band gap (Rodrigues et al. 2008). Treatment with only UV is not effective, however, its efficiency is increased when UV is combined with ozone, H2O2 or semiconductors (Hubbe et al. 2016). Conversely, H2O2 can absorb light and form hydroxyl radicals directly even without semiconductor (Rodrigues et al. 2008). It has been reported that the integration of two AOPs (TiO2 photo-catalysis and Fenton-like reaction) can lead to synergistic production of hydroxyl radicals resulting in enhanced oxidation of organics (Kim et al. 2012). The enhanced performance is due to the electron accepting nature of iron to facilitate charge separation in TiO2 photo-catalyst, as well as to generate hydroxyl radicals from H2O2.

For planning detailed experimental study, a statistical technique for designing experiments known as response surface methodology (RSM), is employed. The approach determines the optimum operating conditions with minimum number of experimental runs (Trinh & Kang 2011; Wang et al. 2011a; Teh et al. 2014; Zahrim et al. 2015; Kim 2016).

Up to the best of our knowledge, no study has been reported so far on the decontamination of bleaching effluent produced from first two stages (i.e. chlorination and alkali extraction phase). It has been mentioned earlier that the conditions for coagulation process needs to be optimized for a real effluent. Apart from this, scanty information is available on the comparison of AOPs for real bleaching effluent.

Therefore, the aim of the current study was to evaluate the performance of physicochemical treatment processes for pulp bleaching effluent (generated from first two stages) with the following objectives: (i) optimization of the coagulation (using industrial grade PAC) process parameters using RSM technique considering reaction pH, PAC dose and slow mixing time as influencing parameters while UV254 and TOC removals as the response parameters, (ii) study the efficacy of various AOPs, such as Fenton, photo-Fenton and photo-catalytic (at optimum conditions from literature) for the same effluent, and (iii) determination of reuse potential of the recovered catalyst from best performing AOP.

MATERIALS AND METHODS

Effluent

The bleaching effluents from chlorination (D0) and alkali extraction (EOP) stages were obtained from a large scale pulp and paper mill located in western India employing D0EOPD1P bleaching sequence. The effluents were stored at 4 °C temperature in the cold room. For the study, combined effluent, prepared by mixing D0 and EOP stage effluents in 1:1 ratio (by volume), was used.
Coagulants and other chemicals

Industrial grade PAC obtained from the same pulp and paper industry was used in the solution form (Al^{3+} content = 0.14 g/ml, PAC density = 1.305 g/ml) for coagulation studies. The chemicals such as ferrous sulphate (FeSO_4·7H_2O), hydrogen peroxide (H_2O_2, 30% w/w), TiO_2 (anatase grade), H_2SO_4 and NaOH were purchased from Merck Chemicals, Mumbai, India. All these chemicals were of analytical grade.

Experimental methods

Coagulation studies

The coagulation experiments were carried out in a jar-test apparatus (Cintex Floculator, Cintex Industrial Corporation, Mumbai) with working volume of 200 mL. pH of the combined effluent was adjusted to the desired level using NaOH or H_2SO_4 solution before addition of coagulant. The solution was mixed rapidly at 150 rpm for 2 min duration to ensure complete mixing; subsequently slow mixing at 40 rpm was performed for variable durations (18–52 min). Later, the sludge was allowed to settle for 30 min. The supernatant was decanted and analysed for UV absorbance at 254 nm wavelength and TOC. The sludge obtained after coagulation was quantified and characterized using Fourier transform infrared (FTIR) spectroscopy for obtaining information on functional groups. Various steps adopted for coagulation studies are shown in Figure S1 (supplementary information, available with the online version of this paper).

Photo-oxidation studies

Batch photo-catalytic reactions (i.e. UV/Fe^{2+}/H_2O_2 and UV/TiO_2/H_2O_2) were carried out in a photo-chemical reactor (capacity = 500 mL) which was purchased from Lelesil Innovative Systems, Mumbai, India (supplementary information; Figure S2, available online). The reactions were initiated by adding pre-determined amount of H_2O_2 to 200 mL of wastewater containing catalyst. At the same time, UV irradiation (spectral range = 200–390 nm) was also started. The liquid samples were withdrawn periodically and quenched immediately with 1 M NaOH. The quenched samples were filtered using 0.2 μm filter paper and analysed for TOC and COD. All experiments were performed in duplicate while the samples were analysed for COD in triplicate.

The photo-catalytic runs were carried out for 120–180 min duration. Effect of pH on the efficacy of UV/TiO_2/H_2O_2 system was studied. In these studies, TiO_2 and H_2O_2 concentrations were taken as 0.5 g/L and 50 mM. Fenton (Fe^{2+/H_2O_2}) and photo-Fenton process (i.e. UV/Fe^{2+}/H_2O_2) were carried out at a pH of 3, H_2O_2 concentration of 200 mM and [Fe^{2+}] to [H_2O_2] molar ratio of 1:100. Combined photo-catalytic reaction (i.e. UV/Fe^{2+}/TiO_2/H_2O_2 system) was also performed on bleaching effluent. For the run, initial wastewater pH was 3 while H_2O_2, Fe^{2+} and TiO_2 concentrations were 200 mM (stoichiometric), 2 mM and 0.5 g/L, respectively.

Catalyst reusability study was carried for the UV/Fe^{2+}/TiO_2/H_2O_2 system. The run was carried out for 120 min without periodic sampling. After the reaction, pH of treated wastewater was adjusted to 8.5, following which the supernatant was filtered by vacuum filtration (filter pore size =0.45 μm) and analysed for soluble TOC, COD and metal concentration, whereas recovered solids were subjected to oven drying at 103 °C temperature for 24 h. The oven-dried solids were termed as catalyst 1 and analysed for CHONS analysis and FTIR imaging. The oven-dried solids (i.e. catalyst 1) was further calcined at 550 °C temperature for 3 h in a muffle furnace and the residual solids were denoted by catalyst 2.

Analytical methods

pH of the liquid samples was measured with a glass electrode attached to Microprocessor pH Stat/Analyser (Polman, Model: LP-1398). COD of the wastewater samples was measured according to the prescribed closed reflux dichromate titrimetric method (American Public Health Association (APHA) 2005) in which the wastewater samples were digested in a block digestor (HACH, DRB 200), pre-heated to 150 °C temperature before refluxing for 2 h. Five-day biochemical oxygen demand (BOD_5) of the wastewater was determined by modified Winkler’s method as described in APHA (2005). Dissolved oxygen was measured using a Hach HQ30d meter with a LDO10103 probe. Total dissolved solids (TDS) and total suspended solids (TSS) were determined by the respective standard methods outlined in APHA (2002). Absorbance of wastewater samples was measured at 254 nm wavelength (UV254) using a UV-Visible spectrometer (UV-Vis Shimadzu 260, Japan). The parameter can surrogate aromaticity of the wastewater (Weishaar et al. 2005; Gernjak et al. 2006; Song & Li 2014). TOC of wastewater samples was measured on a TOC analyser (TOC-VCSH, Shimadzu, Kyoto, Japan). The dissolved chloride in aqueous medium was determined by argentometric method (APHA 2005). Inorganic metals in treated wastewater were quantified using inductively
coupled plasma-atomic emission spectroscopy (ICP-AES, ACROS from Spectro, Germany).

Elemental analysis of the oven-dried sludge samples (at 103 °C for 24 h) was performed on CHONS analyser (Thermo Finnigan, Italy, FLASH EA 1112 series) while FTIR analysis of sludge samples was performed on 3000 Hyperion microscope with vertex 80 FTIR system (Bruker, Germany).

**Experiment design for coagulation runs**

In the present study, the coagulation process was optimized for three parameters, namely, pH, PAC dose, and slow mixing time, using RSM technique to get insight into the interaction and non-linear dependencies among experimental variables. Central composite design (CCD) approach was selected for this purpose. The value of alpha was selected as 1.414 for assured rotation of CCD (Subramonian et al. 2015). The central point close to the probable optimum region was first chosen from literature and then the levels of different parameters used in the experimental runs, were calculated. The coded, as well as actual, values of the above three parameters are presented in supporting information (Table S1, available with the online version of this paper).

The Design-Expert Software (version 9.0.6.1, Stat-Ease, Inc., Minneapolis, MN, USA) was used for the estimation of coefficient in a second order model. The quadratic model describing the relationship of responses (i.e. UV245 and TOC removals) and different variables can be represented as Equation (1):

$$ Y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot X_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} \cdot X_i \cdot X_j + e $$  \hspace{1cm} (1)

where $i =$ linear coefficient, $j =$ quadratic coefficient, $\beta =$ regression coefficient, $k =$ number of factors for optimization and $e =$ random error. In the experimental design, four runs were carried out at the central point to detect experimental error.

**RESULTS AND DISCUSSION**

**Wastewater characteristics**

The combined effluent characteristics are presented in Table 1. pH of the combined wastewater was in acidic range (≈3.5). BOD$_3$ and COD were found to be 570 and 1,920 mg/L, respectively. Low BOD$_3$/COD ratio (≈0.29) indicates non-biodegradable nature of the effluent for aerobic microbial degradation. The initial background iron concentration in the combined effluent was 78 μg/L.

**Coagulation process**

To optimize the operating conditions for coagulation process, a total 18 experiments were performed, including four at the central point (Table 2). Under the conditions used for the present study, UV254 and TOC removals were in the range of 39.6–66.8% and 13.3–22.3%, respectively, while at the central point the corresponding mean removals in above parameters were ~61% and 20.4%.

The model quadratic equations for two response parameters were as follows:

**UV254 removal (%)**

$$ UV254 \text{ removal} \% = 61.35 + 0.82 \cdot A + 10.92 \cdot B + 0.5 \cdot C + 0.72 \cdot A \cdot B - 1.5 \cdot B \cdot C - 2.33 \cdot A^2 - 4.89 \cdot B^2 - 0.57 \cdot C^2 $$ \hspace{1cm} (2)

**TOC removal (%)**

$$ TOC \text{ removal} \% = 20.44 + 0.25 \cdot A + 3.65 \cdot B + 0.18 \cdot C + 0.23 \cdot A \cdot B - 0.49 \cdot B \cdot C - 0.8 \cdot A^2 - 1.6 \cdot B^2 - 0.16 \cdot C^2 $$ \hspace{1cm} (3)

where the coded values of parameters pH, TOC dose and slow mixing time are represented by A, B and C, respectively.

It can be observed from Equations (2) and (3) that PAC dose exhibited much higher impact on organics
removal compared to the other two parameters. However, the analysis of variance (ANOVA) suggested that pH (A) and PAC dose (B) had significant impact on the organics removal as p-values were below 0.05 (Table 3).

Table 2 | TOC and UV254 reduction for various experimental runs carried out for coagulation of bleaching effluent

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Initial pH</th>
<th>PAC dose (g/L)</th>
<th>Slow mixing time (min)</th>
<th>Percentage UV254 removal</th>
<th>Percentage TOC removal</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
<td>Predicted</td>
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<tr>
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<tr>
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<td>7</td>
<td>2.5</td>
<td>35</td>
<td>61.8</td>
<td>61.35</td>
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<tr>
<td>6</td>
<td>8.5</td>
<td>1.5</td>
<td>25</td>
<td>39.6</td>
<td>40.74</td>
</tr>
<tr>
<td>7</td>
<td>8.5</td>
<td>1.5</td>
<td>45</td>
<td>43.9</td>
<td>44.74</td>
</tr>
<tr>
<td>8</td>
<td>5.5</td>
<td>1.5</td>
<td>45</td>
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<td>44.54</td>
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<td>2.5</td>
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<td>10</td>
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<td>3.5</td>
<td>25</td>
<td>65.2</td>
<td>63.94</td>
</tr>
<tr>
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<tr>
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<td>51.1</td>
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<tr>
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<td>25</td>
<td>66.8</td>
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<td>3.5</td>
<td>45</td>
<td>65.2</td>
<td>65.02</td>
</tr>
</tbody>
</table>

Hence, individual A and B, as well as their interaction were included while determining the optimum conditions for coagulation.

The contour plot and response surface for factors A and B were generated using Design Expert software. The

Table 3 | ANOVA for percentage change in UV254 and TOC during coagulation of bleaching effluent

<table>
<thead>
<tr>
<th>Source</th>
<th>Percent change in UV 254</th>
<th>Percent change in TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sum of squares</td>
<td>DoF</td>
</tr>
<tr>
<td>Model</td>
<td>1,768.88</td>
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</tr>
<tr>
<td>A</td>
<td>7.48</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>1,333.14</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>2.79</td>
<td>1</td>
</tr>
<tr>
<td>AB</td>
<td>3.05</td>
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</tr>
<tr>
<td>AC</td>
<td>0.40</td>
<td>1</td>
</tr>
<tr>
<td>BC</td>
<td>12.98</td>
<td>1</td>
</tr>
<tr>
<td>A^2</td>
<td>67.07</td>
<td>1</td>
</tr>
<tr>
<td>B^2</td>
<td>294.12</td>
<td>1</td>
</tr>
<tr>
<td>C^2</td>
<td>3.98</td>
<td>1</td>
</tr>
<tr>
<td>Residual</td>
<td>13.86</td>
<td>7</td>
</tr>
</tbody>
</table>

A- pH, B- PAC dose, C- Slow mixing time; DoF is degree of freedom.
interaction curves for both the response parameters were plotted by varying two independent variables while keeping third variable constant (Figure 1). It can be observed that slow mixing time does not have a significant effect on UV254 and TOC removals (Figure 1(a), 1(b), 1(d) and 1(e)). It can be seen from Figure 1(b) and 1(e) that pH has no significant effect on UV254 and TOC removals. However, the initial pH range of 6.5–8.5 promoted higher

**Figure 1** | Contours for UV254 reduction at various: (a) PAC dose and slow mixing time (pH = 7.0), (b) pH and slow mixing time (PAC dose = 3.5 g/L) and (c) pH and PAC dose (slow mixing time = 25 min), Contours for TOC reduction at various: (d) PAC dose and slow mixing time (pH = 7.0), (e) pH and slow mixing time (PAC dose = 3.5 g/L) and (f) pH and PAC dose (slow mixing time = 25 min).
UV254 removal. The effect of PAC dose and pH on UV254 and TOC is shown Figure 1(c) and 1(f). It can be observed that an increase in PAC dose enhanced UV254 and TOC removals.

The optimum values for the three parameters, namely, pH, PAC dose and slow mixing time, were found to be 7.5, 3.84 g/L and 25 min, respectively. The UV254 and TOC reductions of 67% and 22% were calculated at these optimum conditions from the above equations. The final pH was found to be ∼4.0 at the end of reaction. The probable aluminium species that may be present at this wastewater pH include Al\(^{3+}\), Al(OH)\(^{2+}\), Al(OH)\(^{3+}\) and tetrahedral AlO\(_4\) units (Exall & vanLoon 2003).

A comparison of predicted vs. actual responses at optimum conditions is tabulated in Table S2 (available with the online version of this paper). The UV254 and TOC removal efficiencies obtained from experiment were found to be ∼68% and ∼22% similar to the predicted values. The final TOC and COD of treated wastewater under the optimized condition were ∼512 mg/L and ∼1,460 mg/L. The optimum pH was found to be similar to that reported in literature (Choudhary et al. 2015), though the optimum PAC dose was higher in this study due to higher organic loading in the effluent. The supernatant (after filtration) was analysed for aluminium concentration in the solution. Only ∼2% of the total Al, i.e. 8 mg/L, was present in the supernatant and the remaining was probably settled down.

**Sludge quantification and characterization**

Around 6.6 g/L of sludge was generated after coagulation of combined bleaching effluent at the following optimum conditions: PAC dose = 3.84 g/L, pH = 7.5, slow mixing time = 25 min. Under these conditions, ∼44 mg of sludge was generated per mg of TOC removal from the wastewater. The sludge settling test was carried out in a 1 L measuring cylinder. The sludge was settled from an initial volume of 500 mL to 75 mL in 2 h duration after which insignificant volume change was observed (supplementary information; Figure S3, available online).

The functional groups present in the sludge were determined using FTIR imaging obtained after scanning through the wave number ranging from 400 to 4,000 cm\(^{-1}\) (Figure 2). The peaks at 1,151 cm\(^{-1}\) and 603 cm\(^{-1}\) wave numbers indicate Al–OH\(_2\) and Al–O bonds, respectively, which exist in PAC (Pinkert et al. 2011; Choudhary et al. 2015).

The C = C and C–H stretching peaks could be observed at wave number ranges of 1,680–1,640 cm\(^{-1}\) and 3,000–2,850 cm\(^{-1}\), respectively. A broad peak at 3,500–3,200 cm\(^{-1}\) corresponds to aliphatic and phenolic
OH groups. In summary, the spectrum suggests the presence of aluminium species, as well as organics in the sludge sample.

Comparison of the performance of various AOPs for bleaching effluent

Fenton’s and photo-catalytic runs were carried out on the combined bleaching effluent. Moreover, the following control runs were also performed: only UV and only Fe²⁺ (both at pH 3), as well as with only TiO₂ at pH 7 in dark.

Insignificant TOC removals were observed during the control runs, indicating that appropriate operating conditions would be required to achieve considerable organic degradation. AOPs like Fe²⁺/H₂O₂, UV/Fe²⁺/H₂O₂, UV/TiO₂, UV/TiO₂/H₂O₂, and UV/Fe²⁺/TiO₂/H₂O₂ were performed under optimized conditions reported in literature (Table 4). It is well reported that Fenton’s process is most effective in acidic pH range of 2–4 (Pérez et al. 2002; Wang et al. 2011b). Pérez et al. (2002) have reported 40% TOC reduction during Fenton’s process and 60% TOC reduction during Fenton’s

Table 4 | Summary of literature used to select reaction conditions for various AOPs

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Wastewater characteristics</th>
<th>AOP</th>
<th>Reaction conditions and major result</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C-stage bleeding effluent (bleaching sequence - DCEod₁D₂) TOC = 441 ± 8 mg/L; COD = 1,584 ± 24 mg/L</td>
<td>Fe²⁺/H₂O₂ and UV/Fe²⁺/H₂O₂</td>
<td>pH = 3; Fe²⁺ dose = 100 mg/L; H₂O₂ dose = 10,000 mg/L; [Fe²⁺][H₂O₂] = 1:100 (mg/L); TOC removal = 60% for UV/Fe²⁺/H₂O₂ at 25 °C in 300 min</td>
<td>Pérez et al. (2002)</td>
</tr>
<tr>
<td>2.</td>
<td>Cellulose bleeding effluent; pH = 1.7; COD = 1,250 mg/L; TOC = 540 mg/L</td>
<td>Fe²⁺/H₂O₂</td>
<td>pH = 3; Fe²⁺ dose = 556 mg/L; H₂O₂ dose = 6,800 mg/L; TOC removal = 64%</td>
<td>Torrades et al. (2003)</td>
</tr>
<tr>
<td>3.</td>
<td>Pretreated bleeding effluent from cellulose and paper industry; COD = 516 mg/L</td>
<td>UV/H₂O₂; UV/TiO₂; UV/TiO₂/H₂O₂</td>
<td>pH = 3; TiO₂ dose = 0.50 g/L; H₂O₂ dose = 10 mM, COD removal = 55% for UV/TiO₂/H₂O₂</td>
<td>Rodrigues et al. (2008)</td>
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<td>4.</td>
<td>Bleached kraft pulp effluent, COD = 403 ± 5 mg/L; TOC = 126 ± 6 mg/L; pH = 8.3</td>
<td>UV/Fe²⁺/H₂O₂ and UV/TiO₂/H₂O₂</td>
<td>[Fe²⁺][H₂O₂] = 1:330; TiO₂ dose = 359 mg/L or more; H₂O₂ dose = 863 mg/L or more, TOC removal = 91%</td>
<td>Silva et al. (2010)</td>
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<td>5.</td>
<td>D- and E-stage effluent (bleaching sequence-OD₁ED₂), pH = 11.4; COD = 340 mg/L</td>
<td>UV/TiO₂</td>
<td>pH = 7; TiO₂ dose = 0.5 g/L; reaction time = 4 h; COD removal = 64% (D₁-stage) and 66% (E-stage)</td>
<td>Kumar et al. (2011)</td>
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<td>6.</td>
<td>Pretreated DEP bleaching sequence effluent, COD = 300 mg/L</td>
<td>Fe²⁺/H₂O₂</td>
<td>pH = 3; [H₂O₂] = 4COD (mM) = 37.5 mg/L; [Fe²⁺][H₂O₂] = 1:20; reaction time = 120 min; temperature = 90 °C; COD removal = 89%</td>
<td>Wang et al. (2011a)</td>
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<td>7.</td>
<td>Pretreated elemental chlorine free bleaching effluent (bleaching sequence-DEP), COD = 560 mg/L</td>
<td>Solar Fenton as post treatment</td>
<td>pH = 3.5; [H₂O₂] dose = 30 mM, [Fe²⁺]/[H₂O₂] = 1:100; reaction time = 120 min, COD removal = 92.8%</td>
<td>Wang et al. (2011b)</td>
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<td>8.</td>
<td>Combined (D₁ + Eop) bleaching effluent: pH = 3.5; COD = 1,920 ± 30 mg/L; TOC = 663 ± 12 mg/L; BOD₂ = 568 ± 40 mg/L; chloride = 2,171 mg/L</td>
<td>(a) Fe²⁺/H₂O₂</td>
<td>(a) pH = 3; H₂O₂ dose = 200 mM; [Fe²⁺]/[H₂O₂] = 1:100; reaction time = 120 min, TOC removal = 56%</td>
<td>Current study</td>
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<td>(b) UV/Fe²⁺/H₂O₂</td>
<td>(b) pH = 3; H₂O₂ dose = 200 mM; [Fe²⁺]/[H₂O₂] = 1:100; reaction time = 120 min, TOC removal = 67%</td>
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<td>(c) UV/TiO₂</td>
<td>(c) pH = 7; TiO₂ dose = 0.5 g/L, TOC removal = 14%</td>
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<td>(d) UV/TiO₂/H₂O₂</td>
<td>(d) pH = 3.7, unadjusted (pH = 3.5); H₂O₂ dose = 50 mM; TiO₂ dose = 0.5 g/L; reaction time = 180 min, TOC removal = 16% at pH = 7</td>
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<td>(e) UV/Fe²⁺/TiO₂/ H₂O₂</td>
<td>(e) pH = 3; H₂O₂ dose = 200 mM; [Fe²⁺]/[H₂O₂] = 1:100 and 1:20; TiO₂ dose = 0.5 g/L, reaction time = 120 min, TOC removal = 78% for [Fe²⁺]/[H₂O₂] = 1:100</td>
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and photo-Fenton process of cellulose bleaching effluent with initial TOC of 440 mg/L. Wang et al. (201b) have reported the optimum [Fe$^{2+}$]/[H$_2$O$_2$] molar ratio of 1:20 and 1:100 for Fenton and solar Fenton processes for the treatment of bleaching effluent. However, the iron sludge will be higher with the molar ratio of 1:20. Hence, Fenton and photo-Fenton processes were conducted at pH 3 with [Fe$^{2+}$]/[H$_2$O$_2$] molar ratio of 1:100. Only for UV/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ system, [Fe$^{2+}$]/[H$_2$O$_2$] molar ratio of 1:20 was considered for the purpose of comparison. For other photo-catalytic runs, TiO$_2$ was used as photo-catalyst due to high activity, photo-stability over a wide pH range, commercial availability, low cost and non-toxic nature (Thiruvengatachari et al. 2008; Ghaly et al. 2011). TiO$_2$ dose of 0.5 g/L was used for photocatalytic process of bleaching effluent (Rodrigues et al. 2008; Kumar et al. 2011). Silva et al. (2010) have reported that TiO$_2$ dose more than 0.36 g/L is effective for photo-oxidation of bleaching effluent.

The results from AOPs carried out under different conditions are presented in Figure 3. All the runs were carried out in duplicates. Amongst all the photo-catalytic systems (UV/TiO$_2$ and UV/TiO$_2$/H$_2$O$_2$), the maximum TOC reduction of 16.5% was observed in case of UV/TiO$_2$/H$_2$O$_2$ performed at pH 7. The final pH of treated wastewater after 3 h UV/TiO$_2$/H$_2$O$_2$ treatment was found to be 5.6. Photo-Fenton showed higher COD and TOC reduction of 65% and 67%, respectively, as compared to Fenton’s oxidation (56% TOC and 55% COD reductions) with stoichiometric H$_2$O$_2$ concentration of 200 mM and Fe$^{2+}$ to H$_2$O$_2$ molar ratio of 1:100. The final pH of treated wastewater by Fenton’s oxidation was found in highly acidic region (i.e. 2) compared to that of photo-Fenton treated wastewater (final pH = 2.55). This observation may be attributed to the following two reasons. (i) The oxidative degradation of organics may occur via the formation of low molecular weight carboxylic acids. Relatively lesser degradation of such compounds during Fenton’s oxidation process would lead to the lower pH of the finally treated wastewater compared to that obtained after photo-Fenton process. (ii) Fe$^{2+}$ regeneration reactions during Fenton’s oxidation process may also reduce wastewater pH as these reactions utilize hydrogen peroxide or free radicals and generate H$^+$ ions as by-product (Pérez et al. 2002). During photo-Fenton process, the Fe$^{2+}$ regeneration takes place via Fe$^{3+}$ hydroxocomplexes (a complex formed at pH 2–3) and no H$^+$ ions are produced during this reaction.

The combined system (i.e. UV/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$) showed the maximum TOC and COD reduction of 78.5% and 76.8% respectively for [Fe$^{2+}$] to [H$_2$O$_2$] ratio of 1:100. The dissolved chloride concentration was found

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**Figure 3** | TOC removals during AOPs applied on real bleaching effluent.
to increase from an initial value of 2,131 mg/L to 2,762 mg/L, which suggests the degradation of chlorinated organic compounds present in bleaching effluent. The treated wastewater pH was reduced to 2.2 from an initial value of 3.0. With higher [Fe²⁺]/[H₂O₂] ratio of 1:20 (H₂O₂ concentration = 200 mM, Fe²⁺ concentration = 10 mM), low organic degradation (i.e. 60% TOC and 61% COD reductions) was observed after the combined catalytic run. The treated wastewater pH was dropped to 2.4 from an initial value of 3.0.

The biodegradability of treated wastewater samples was determined in terms of BOD₅/COD ratio. The ratio in treated wastewater was found to be increased to 0.46 from an initial value of 0.29 after treatment by UV/Fe²⁺/TiO₂/H₂O₂ ([Fe²⁺]/[H₂O₂] ratio = 1:100) which can be considered very close to that for biodegradable wastewater. For photo-Fenton system, the biodegradability ratio was increased to 0.43 while for other AOPs, final BOD₅/COD ratio was in the range of 0.33–0.39. The bar chart showing change in biodegradability is shown as Figure 4.

Catalyst reusability study

The solids recovered after the treatment by UV/Fe²⁺/TiO₂/H₂O₂ system (i.e. catalyst 1 and catalyst 2) were reused. The calcined catalyst (catalyst 2) showed higher TOC and COD reduction (~41%) as compared to oven-dried catalyst (TOC and COD reductions = 18% and 16%, respectively) (Figure 5) though it was much lower than that obtained after run with fresh catalyst system.

It should be noted that only stoichiometric H₂O₂ dose (i.e. 200 mM) was added to the reactor and no additional Fe and TiO₂ was supplemented. Iron leaching in the treated wastewater was very low (~4.4 mg/L, i.e. only ~4% of total iron) while Ti content was below detection limit. So it can be assumed that the majority of metals were present in sludge.
The significant drop in COD and TOC removals may be attributed to the following reasons: conversion of Fe$^{2+}$ into Fe$^{3+}$, organics deposition from first run (which was confirmed by CHNS analysis discussed in next section) and structural change in TiO$_2$. Therefore, detailed study needs to be conducted to understand the overall process. The biodegradability ratio of wastewater after treatment by catalyst 1 and catalyst 2 was increased to 0.30 and 0.35, respectively (Figure 4).

**Characterization of solids obtained after UV/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ process**

The sludge obtained after UV/Fe$^{2+}$/TiO$_2$/H$_2$O$_2$ treatment system was oven-dried and characterized using CHNS and FTIR techniques. Around $7.923 \pm 0.02$ g/L of dried sludge was recovered after the oxidation reaction. CHNS result suggested that the mass of carbon was 3.22% of the total sludge (i.e. 255 mg/L). It could be estimated that oxidation and adsorption both were equally responsible for TOC removal (total TOC removal = 521 mg/L). For the system, ~15 mg of sludge was produced per mg of TOC removal.

The FTIR patterns of TiO$_2$ catalyst and the oven-dried sludge are shown in Figure 6. The wide peak from 410 to 1,000 cm$^{-1}$ was assigned to Ti–O–Ti stretching observed in TiO$_2$ (Figure 6(a)) (Ghaly et al. 2014). The peak in range of 2,850 to 3,000 cm$^{-1}$ corresponds to alkane C–H stretch indicating mineralization of adsorbed organics on the TiO$_2$ catalyst surface (Figure 6(b)). A weak peak in the range of

![Figure 6](https://iwaponline.com/wst/article-pdf/76/9/2367/208825/wst076092367.pdf)
3,200 to 3,500 cm\(^{-1}\) was also observed, indicating presence of aliphatic and phenolic OH groups in settled solids. Another peak at 1,628 cm\(^{-1}\) corresponds to the C-C stretch was also observed (Pinkert et al. 2011).

**CONCLUSIONS**

In the current study, the combined bleaching effluent (from chlorination and alkaline extraction stages) was treated using coagulation and various AOPs. After coagulation process at the optimum operating conditions (i.e. pH = 7.5, PAC dose = 3.84 g/L and slow mixing time = 25 min), ~68% UV254 removal and ~23% TOC removal was achieved. FTIR analysis of the settled sludge showed the presence of organics confirming the removal of TOC and UV254 from wastewater. Among different AOPs, UV/Fe\(^{2+}\)/TiO\(_2\)/H\(_2\)O\(_2\) system exhibited the maximum TOC and COD removals (~78%) from the effluent (initial pH = 3, H\(_2\)O\(_2\) concentration = 200 mM, TiO\(_2\) = 0.5 g/L, [Fe\(^{2+}\)]/[H\(_2\)O\(_2\)] = 1:100). The elemental analysis showed that around 50% of TOC during the oxidation process was removed by adsorption. The increased chloride ions and biodegradability ratio in the treated bleeding effluent confirmed the partial decomposition of chlorinated compounds and other recalcitrant pollutants into biodegradable compounds. The sludge generation on treatment by UV/Fe\(^{2+}\)/TiO\(_2\)/H\(_2\)O\(_2\) system was 1.2 times the sludge produced during coagulation process at the optimum conditions though sludge generation per unit TOC removal after coagulation was ~3 times the UV/Fe\(^{2+}\)/TiO\(_2\)/H\(_2\)O\(_2\) system. Reusing the recovered sludge (mainly supposed to contain Ti and Fe) even after thermal treatment showed significant drop in TOC removal from bleeding effluent. Toxicity evaluation and cost analysis should be performed in future studies.

**ACKNOWLEDGEMENTS**

The authors are thankful to Sophisticated Analytical Instrumentation Facility (SAIF) and IIT Bombay for providing necessary support to carry out FTIR and CHNS analyses.

**REFERENCES**


First received 7 December 2016; accepted in revised form 2 June 2017. Available online 10 July 2017.