

Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study

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Abstract

Pulp mill effluent containing toxic chemicals was treated by different advanced oxidation processes (AOPs) consisting of treatments by hydrogen peroxide, Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), UV, UV/ H_2O_2 , photo-Fenton (UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$), ozonation and peroxone (ozone/ H_2O_2) in laboratory-scale reactors for color, total organic carbon (TOC) and adsorbable organic halogens (AOX) removals from the pulp mill effluent. Effects of some operating parameters such as the initial pH, oxidant and catalyst concentrations on TOC, color, AOX removals were investigated. Almost every method used resulted in some degree of color removal from the pulp mill effluent. However, the Fenton's reagent utilizing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ resulted in the highest color, TOC and AOX removals under acidic conditions when compared with the other AOPs tested. Approximately, 88% TOC, 85% color and 89% AOX removals were obtained by the Fenton's reagent at pH 5 within 30 min. Photo-Fenton process yielded comparable TOC (85%), color (82%) and AOX (93%) removals within 5 min due to oxidations by UV light in addition to the Fenton's reagent. Fast oxidation reactions by the photo-Fenton treatment makes this approach more favorable as compared to the others used.

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1. Introduction

Effluents of the pulp and paper industry contain a number of toxic compounds and may cause deleterious environmental impacts upon direct discharge to receiving waters. Pulping processes utilize large amounts of water, which reappear in form of an effluent. The most significant sources of pollution in pulp and paper industry are wood preparation, pulping, pulp washing, screening, bleaching and coating operations. Among the various processing steps, pulping generates a high-strength wastewater containing toxic chemicals such as phenolics.

Three main groups of organic compounds present in paper industry are: (a) starch degradation products, such as saccharides or carboxylic acids; (b) phenolic compounds arising from lignin; (c) other pollutants that may be present in the fresh waters such as surfactants [1]. Major pollutants present in the effluents of paper industry are suspended solids, chemical oxygen demand (COD), toxicity, color, adsorbable organic halogens (AOX) and high

concentration of nutrients that cause eutrophication in receiving water [2,3]. Since some of the contaminants in pulp and paper industry effluents are non-biodegradable, conventional biological treatment processes are not sufficient for treatment. The extent of toxicity and color removal by conventional biological treatment vary depending on the pulping process used. In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt technologically advanced treatment systems. Organic compounds such as chlorophenols are not fully degraded by biological processes which require advanced oxidation after biological treatment to reduce refractory organics and color of the pulp mill wastewater [4,5,7–10,13–19].

Advanced oxidation processes (AOPs) were developed and used as potentially powerful methods capable of transforming the pollutants into harmless substances [4]. AOPs are based on the generation of very reactive non-selective transient oxidizing species such as the hydroxyl radicals (OH^\bullet), which were identified as the dominant oxidizing species [5]. For effective oxidations of refractory organic compounds, the hydroxyl radicals must be generated continuously in situ through chemical or photochemical reactions due to their instability. Generation of OH^\bullet is commonly accelerated by combining some oxidizing

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agents such as ozone (O_3), hydrogen peroxide (H_2O_2), UV radiation, ferrous and ferric salts (Fe^{2+} and Fe^{3+}). Of these, UV plus hydrogen peroxide (UV/ H_2O_2), Fenton's reagent (H_2O_2/Fe^{2+}), photo-Fenton (UV/ H_2O_2/Fe^{2+}), O_3/H_2O_2 and O_3/UV hold the greatest promise for detoxification of wastewaters.

The major objective of this study is to investigate the performance of different oxidation methods and their combinations for color and TOC removal from paper mill effluents. Different oxidation methods such as hydrogen peroxide, Fenton's reagent, direct photolysis with UV, hydrogen peroxide/UV, Photo-Fenton, ozonation and peroxone treatments were used. Effect of operating conditions such as pH (3–11), H_2O_2 (5–100 mM), Fe^{2+} (1–5 mM) and ozone doses (4.7–11.9 g/h) on color, TOC and AOX removals were investigated for each oxidation method tested.

2. Materials and methods

2.1. Materials

Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$, Merck) was used as source of Fe(II) in the Fenton and photo-Fenton treatment. Fe(II) stock solution (1000 mg l^{-1}) was used for preparation of Fe(II) solutions of desired concentrations by dilution. Hydrogen peroxide solution (35%, w/w, Merck) was diluted with deionized water before treatment. The pH of aqueous solutions was adjusted using dilute (1%) sodium hydroxide or sulfuric acid solutions. All solutions were prepared by using distilled water.

2.2. Reactor configurations

A schematic diagram of the laboratory-scale ozone reactor is depicted in Fig. 1. The reactor was made of pyrex-glass with a total reactor volume of 3 l. Ozone was produced by a corona discharge of OZO 3VTT model ozone generator with a maximum ozone production capacity of 15 g h^{-1} . The ozone produced from pure oxygen with a purity of 99.5% was bubbled through the reactor with different rates using a diffuser of diameter 15 mm. The actual ozone production rate was controlled by the current input and the air flow rate. The flow rate of

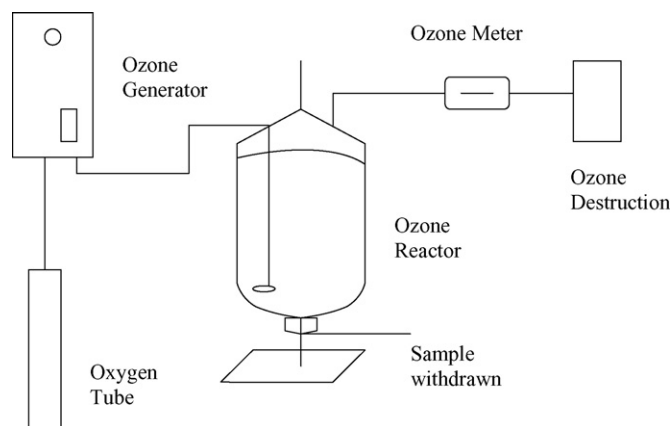


Fig. 1. A schematic diagram of experimental set-up for the ozone reactor.

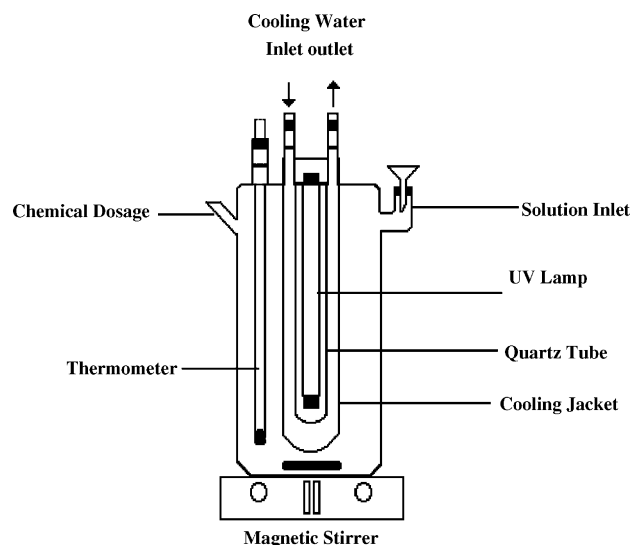


Fig. 2. A schematic diagram of experimental set-up for the UV reactor.

($O_2 + O_3$) was continuously monitored with a rotameter incorporated into the ozone generator. The ozone-feeding rate was measured by the standard potassium iodide absorption method [6]. The concentration of ozone in the effluent of the ozone reactor was measured by an ozone monitor (Eco sensors). Excess ozone leaving the reactor was destroyed by a catalytic ozone-destruction unit.

Fig. 2 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations. All photo-oxidation experiments were performed in the completely mixed, batch, cylindrical photo-reactor made of pyrex-glass with a total volume of 2.2 l. The reactor was covered with an aluminum foil to avoid any light leakage to the outside. The reactor was placed on a magnetic stirrer and contained inlets for feeding the reactants, and ports for sample removal and temperature measurements. The UV irradiation source was a 16 W low-pressure mercury vapor lamp (maximum emission at 254 nm) placed in a quartz tube. The intensity of the UV radiation was measured using the ferrioxalate actinometry method and estimated to be 4.98×10^{-6} einstein/s (mole of photons/s). The lamp was surrounded with a water-cooling jacket to remove the heat produced by the lamp and to maintain a constant temperature. The lamp tube was immersed in the aqueous solution to be treated.

2.3. Experimental procedure

Chemical oxidation with H_2O_2 was carried out by using 50 mM H_2O_2 at a pH of 11. The conventional jar tests were started by adding varying amounts of H_2O_2 to pH-adjusted wastewater samples. After pH adjustment and oxidant addition, wastewater was mixed rapidly for 30 min at 200 rpm. Samples were withdrawn for analysis at the end of the mixing period.

Fenton's reagent experiments were carried out at room temperature using different hydrogen peroxide and ferrous ion concentrations at different pH values in order to determine the optimum conditions for the highest TOC and color removals. Desired amounts of hydrogen peroxide and Fe(II) were added

to pH-adjusted wastewater samples. After fast mixing for 5 min at 200 rpm and slow mixing for 30 min at 25 rpm, 1 h sedimentation was applied. The supernatant was removed and pH was adjusted to 10 with the addition of 10% Ca(OH)₂ solution. The samples from the supernatant were analyzed for TOC, color and AOX contents after 4 h of standing period. The products of oxidation were CO₂, water and unoxidized organics present in the wastewater.

In advanced oxidation treatments with UV and ozone, the pH was manually adjusted to desired level using dilute sulfuric acid or sodium hydroxide, then pre-determined amounts of oxidants (H₂O₂ or/and Fe²⁺) were injected to the reactor at the beginning of each experiment. For experiments using UV/H₂O₂ and peroxone treatment, desired amounts of hydrogen peroxide was injected into the reactor at the beginning of each experiment. In photo-Fenton treatment, the pH of the solution was adjusted to acidic conditions by the addition of dilute H₂SO₄ solution before start-up, and then a desired amount of iron salt was added. The iron salt was mixed well with wastewater before the addition of hydrogen peroxide solution. The experiments were started by turning the UV lamp and the ozone generator on and when the oxidant added. All experiments were carried out in batch mode.

2.4. Analytical methods

Samples were removed from the UV and ozone reactors at pre-determined time intervals for immediate analysis of color, TOC and AOX. The temperature of the solution was kept constant at 25 ± 2 °C throughout all experiments. In order to decompose residual H₂O₂ to avoid interference with the color measurement, the samples containing H₂O₂ were treated with MnO₂ powder (50 mg MnO₂/25 ml sample) and were centrifuged and filtered through 0.45 μm millipore membranes to remove MnO₂. A spectrophotometer (Novaspec II, Pharmacia Biotech) was used for color measurements at 450 nm at which the absorbance was maximum. A bench scale pH meter (NEL pH meter 890) was used for pH measurements. TOC analyzes were done using a DOHRMAN DC 190 TOC Analyzer. AOX contents were determined by an AOX MT 20 TOX analyzer after enrichment by activated carbon. In advanced oxidation processes with ozone, feed and effluent flow rates were determined by the standard potassium iodide absorption method [6]. Soluble COD and other wastewater parameters presented in Table 1 were determined using the standard methods of analysis [6]. A conductivity meter (YSI 33) was used for conductivity measurements.

3. Results and discussion

3.1. Characterization of the pulp mill effluent

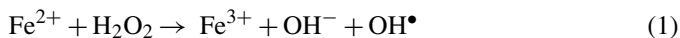
Wastewater used in this study was obtained from biological wastewater treatment plant of a pulp and paper manufacturing company located in Dalaman, Turkey. Composition of the pulp mill wastewater used in this study is presented in Table 1. Low BOD/COD ratio of 0.6 indicated low biodegradability of the organic compounds present in the wastewater.

Table 1
Characterization of pulp mill effluent used in this study

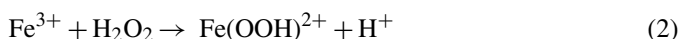
Parameters	
pH	7.08
COD (mg l ⁻¹)	400
BOD (mg l ⁻¹)	240
TOC (mg l ⁻¹)	110
AOX (mg l ⁻¹)	1.94
Suspended solids (mg l ⁻¹)	50
Oil and grease (mg l ⁻¹)	50
Phenol (mg l ⁻¹)	3.2
Color (abs) (m ⁻¹)	0.78
Conductivity (μmhos/cm)	2300
Chloride (mg l ⁻¹)	1.6
Total P (mg l ⁻¹)	0.9
Total N (mg l ⁻¹)	12
Detergents (mg l ⁻¹)	1

3.2. Treatment by Fenton reagent

The Fenton reaction is a widely used catalytic oxidation method based on electron transfer between H₂O₂ and metal ions (Fe²⁺) serving as homogeneous catalyst. The efficiency of the Fenton's reagent is based on the hydroxyl radical generation by a mixture of H₂O₂ and Fe(II) ions as shown in the following reaction [7].



The Fe³⁺ produced in this reaction reacts with H₂O₂ to regenerate Fe²⁺ as shown in the following equations:



A number of experiments were carried out with the Fenton's reagent to determine the effects of initial hydrogen peroxide and Fe(II) concentrations, and pH on color, TOC and AOX removals from the pulp mill effluent.

3.2.1. Effects of initial pH

pH of the treatment solution is an important factor for effective oxidation by the Fenton's reagent [8]. Batch oxidation experiments with the Fenton's reagent were carried out under acidic pH levels (pH 3–5), since higher pH values were reported to be unsatisfactory for oxidations of organic compounds by the Fenton's reagent [9–12]. Fe(II) and H₂O₂ concentrations were constant at 5 and 50 mM, respectively and the reaction time was 30 min throughout the variable pH experiments. Table 2 shows variation of percent color and TOC removals from the

Table 2
Effects of initial pH on percent color and TOC removals from the pulp mill effluent by Fenton treatment

pH	Color removal (%)	TOC removal (%)
3	66.6	63.4
4	71.1	78.8
5	88.1	84.6

H₂O₂ 50 mM, Fe(II) 5 mM, reaction time 30 min.

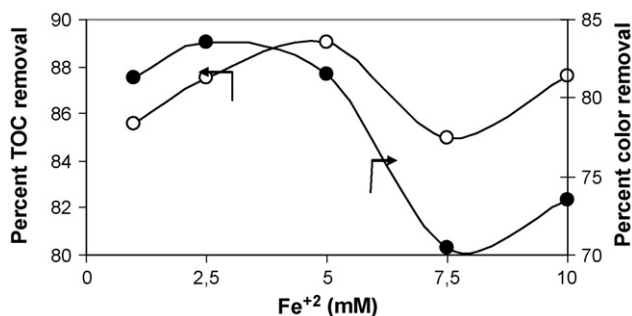


Fig. 3. Variations of percent color and TOC removals with the Fe^{2+} concentration in Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, H_2O_2 50 mM, reaction time 30 min).

wastewater with pH of the solution. Percent color and TOC removals increased with pH yielding 88.1% color and 84.6% TOC removals at pH 5, which was selected as the most suitable pH closer to the neutral conditions.

3.2.2. Effects of initial Fe(II) concentration

Both the color and TOC removals from the wastewater were significantly improved with the addition of ferrous salt to H_2O_2 in our preliminary studies even at very low Fe(II) concentrations. Percent color and TOC removals increased to 81.3% and 85.6%, respectively when 1 mM Fe(II) was added to the H_2O_2 solution, while the color and TOC removals were around 24% and 5.1%, respectively with oxidation by H_2O_2 solution alone. Fig. 3 depicts variations of percent color and TOC removals with the Fe(II) concentration at a constant initial pH of 5 and H_2O_2 concentration of 50 mM for the reaction time of 30 min. Percent TOC removals varied between 85% and 89% depending on Fe(II) concentrations with a maximum at 5 mM Fe(II) concentration. However, percent color removal decreased from 83% to 73% when Fe(II) concentration increased from 2.5 to 10 mM due to inhibition effect of iron [13,14]. Therefore, an initial ferrous concentration of 2.5 mM was selected as the most suitable Fe(II) concentration yielding 83% color and 87% TOC removal and used in further experiments.

3.2.3. Effects of initial H_2O_2 concentration

H_2O_2 concentration was varied between 5 and 100 mM in this set of experiments while the Fe(II) concentration was constant at 2.5 mM. Variations of percent color and TOC removals from the pulp mill effluent with H_2O_2 concentrations are depicted in Fig. 4. Percent TOC removals increased up to H_2O_2 concentration of 50 mM and then decreased with further increases. The highest percent color, TOC and AOX removals were 84.7%, 87.5% and 89%, respectively after 30 min of oxidation with a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 20. In other studies, optimum molar ratio in Fenton oxidation was found as 20–40 [15,16]. Percent color and TOC removals decreased to 84.7% and 75.6%, respectively at a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 40. Therefore, the optimal molar ratio for $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ yielding the highest color and TOC removals was found to be 20 corresponding to 2.5 mM Fe^{2+} and 50 mM H_2O_2 concentrations.

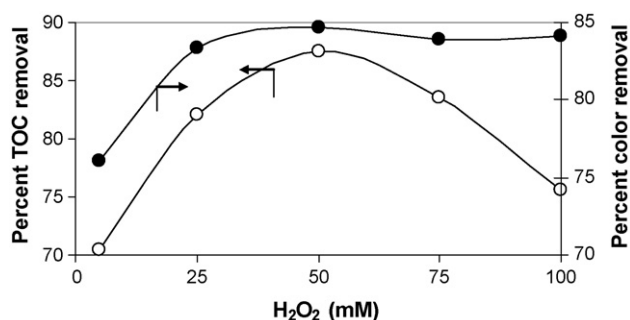


Fig. 4. Variations of percent color and TOC removals with initial H_2O_2 concentration in Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, Fe(II) 2.5 mM, reaction time 30 min).

3.3. Photolysis by UV irradiation

A number of experiments were carried out with the direct UV photolysis of pulp mill effluent to determine the effects of pH on color and TOC removals. These experiments were used as the reference for UV radiation combinations with hydrogen peroxide or Fenton's reagent used to improve the oxidation performance.

3.3.1. Effects of initial pH

Acidic (pH 3), neutral (pH 7) and alkaline (pH 11) pH levels were used in order to determine the most suitable pH for direct UV photolysis in terms of percent color and TOC removals from the pulp mill effluent. Percent color removal from the wastewater decreased with increasing pH yielding 6.6% removal at initial pH of 3 and 0.8% at pH values of 7 and 11. TOC and AOX removals also decreased with increasing pH. Maximum TOC (4.1%) and AOX (17%) removals were also obtained at pH 3. Apparently, direct UV photolysis alone was not effective and suitable for color and TOC removals from the pulp mill effluent. Direct UV photolysis alone is known to decompose some organic molecules with very slow rates. However, UV radiation may be more effective when combined with H_2O_2 , salts of particular metals (Fe^{2+}), or ozone. Therefore, a number of experiments with UV/ H_2O_2 and UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ were carried out to investigate effects of hydrogen peroxide and Fe(II) on color and TOC removals from the pulp mill effluent.

3.4. UV/ H_2O_2 treatment

Ultraviolet photolysis combined with hydrogen peroxide (UV/ H_2O_2) is one of the most appropriate AOP technologies for degradation of toxic organics since this process may occur in nature itself. The OH^\bullet produced through UV/ H_2O_2 system as shown below activate organic compounds for oxidations by subtracting hydrogen atoms or by adding to double bonds [17,18]:



3.4.1. Effects of initial pH

Experiments were carried out at acidic (pH 3), neutral (pH 7) and basic (pH 11) pH levels at a constant initial a hydrogen peroxide concentration of 50 mM. Table 3 shows variation

Table 3

Effects of initial pH on percent color and TOC removals from the pulp mill effluent by UV/H₂O₂ treatment

pH	Color removal (%)	TOC removal (%)
3	12.3	8
7	22.3	10
11	41	11.1

H₂O₂ 50 mM, reaction time 30 min.

of percent color and TOC removals with the initial pH at constant hydrogen peroxide concentration of 50 mM and reaction time of 30 min. Percent color removal increased with pH resulting in 41% color removal at pH 11. However, percent TOC removals were not affected from pH changes yielding 8–11% TOC removals. Since the maximum color and TOC removals were obtained at pH 11, further experiments with UV/H₂O₂ were carried out at this pH. In another UV/H₂O₂ oxidation study, pH 11 was also found to be the optimum pH for the treatment of phenol containing wastewater [19].

3.4.2. Effects of initial H₂O₂ concentration

A set of experiments with UV/H₂O₂ were carried out with variable H₂O₂ concentration at pH of 11. Fig. 5 depicts variation of percent color and TOC removals with the H₂O₂ concentration at constant initial pH of 11, reaction time of 30 min and hydrogen peroxide doses of between 5 and 100 mM. Addition of H₂O₂ to the UV system improved both color and TOC removals considerably as compared to UV treatment alone even at low H₂O₂ concentrations. Percent color removal increased with increasing H₂O₂ concentration. Percent TOC removal slightly increased with H₂O₂ concentration up to 50 mM and then decreased with further increases in H₂O₂. The optimal H₂O₂ concentration was found to be 50 mM yielding 41% color and nearly 11% TOC removals. At high concentrations, hydrogen peroxide probably served as a free-radical scavenger according to the following reaction causing decreases in the hydroxyl radical concentration [7,20,21]:

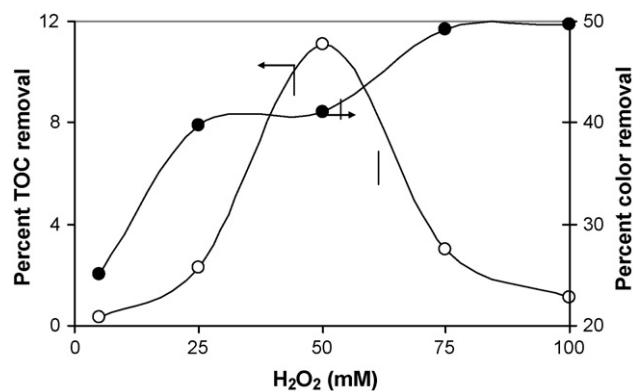
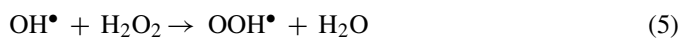


Fig. 5. Variations of percent color and TOC removals with initial H₂O₂ concentration in UV/H₂O₂ treatment. (●) percent color removal and (○) percent TOC removal (pH 11, reaction time 30 min).

Table 4

Effects of initial pH on percent color and TOC removals from the pulp mill effluent by the photo-Fenton treatment

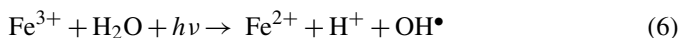
pH	Color removal (%)	TOC removal (%)
3	66	56.8
4	67.4	77.7
5	66.8	79.2

H₂O₂ 50 mM, Fe(II) 5 mM, reaction time 30 min.

3.5. Photo-Fenton treatment

The recently developed photo-Fenton treatment was shown to be an effective AOP for oxidation of recalcitrant organic compounds [22]. The mechanism of the photo-Fenton treatment is based on the hydroxyl radical generation by a mixture of H₂O₂ and Fe(II) ions (Fenton reaction) as explained in Section 3.2.

In the presence of UV radiation, in addition to reactions (1)–(3), photo-Fenton reaction producing additional hydroxyl radicals and Fe(II) ions takes place as depicted in the following reaction [23]:



Consequently, higher concentrations of OH[•] and Fe(II) can be attained with the UV/H₂O₂/Fe²⁺ treatment as compared to the conventional Fenton's reagent treatment. The reaction time needed for the photo-Fenton process is extremely low and depends on the operating pH and the concentrations of H₂O₂ and Fe(II). In UV/H₂O₂ treatment, maximum color removal was 41% at the optimal hydrogen peroxide concentration (50 mM) at the end of 30 min oxidation period. Besides, the maximum TOC and AOX removal efficiencies were only around 11 and 18.5%, respectively. Therefore, in order to shorten the required irradiation time and enhance the TOC and AOX removals, a number of experiments were carried out using the photo-Fenton treatment.

3.5.1. Effects of initial pH

Experiments were carried out at three different pH levels of 3–5 at a constant initial hydrogen peroxide and Fe(II) concentrations of 50 and 5 mM, respectively for 30 min since higher pH levels were proven to be ineffective for the Fenton treatment [9–11]. Table 4 summarizes the experimental results. Color removal was not affected by pH changes (66–67%). However, percent TOC removals increased with pH yielding 79% TOC removal at pH 5. Therefore, pH 5 was considered to be the optimal and further photo-Fenton experiments were carried out at pH 5.

3.5.2. Effects of initial Fe(II) concentration

In order to investigate the effect of ferrous ions on the performance of the photo-Fenton treatment, experiments were carried out at a constant H₂O₂ concentration of 50 mM, pH of 5, reaction time of 30 min and temperature of 25 ± 2 °C at different Fe(II) concentrations between 1 and 10 mM.

Variations of color and TOC removals with the Fe(II) concentration in the photo-Fenton treatment are depicted in Fig. 6.

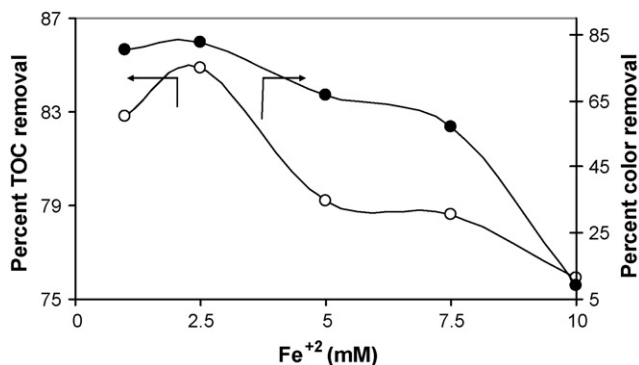


Fig. 6. Variations of percent color and TOC removals with initial Fe²⁺ concentration in the photo-Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, H₂O₂ 50 mM, reaction time 30 min).

Addition of Fe(II) to UV/H₂O₂ considerably enhanced color and TOC removals even at very low Fe(II) concentrations. Percent color and TOC removals after 30 min of UV irradiation was around 41% and 11%, respectively with UV/H₂O₂ treatment which increased up to 80.6% and 82.8% when 1 mM Fe(II) was added to the reaction medium. When Fe(II) concentration was increased to the optimum concentration of 2.5 mM, 85% TOC removal was achieved even after 5 min of irradiation. Therefore, photo-Fenton method improved both the extent and the rate of TOC and color removals as compared to the UV/H₂O₂ treatment and provided much faster oxidations. Both percent TOC and color removals were maximum at Fe(II) concentration of 2.5 mM and decreased with increasing Fe(II) at higher concentrations. At high Fe(II) concentrations such as 10 mM, the initial hydroxyl radicals were probably originated from the decomposition of H₂O₂, which were consumed by the side reactions yielding low TOC removals from the wastewater [13,14].

3.5.3. Effects of initial H₂O₂ concentration

Fig. 7 depicts variation of percent color and TOC removals with the H₂O₂ concentration at a constant Fe(II) concentration of 2.5 mM, pH 5 and reaction time of 30 min while hydrogen peroxide concentration was varied between 5 and 100 mM.

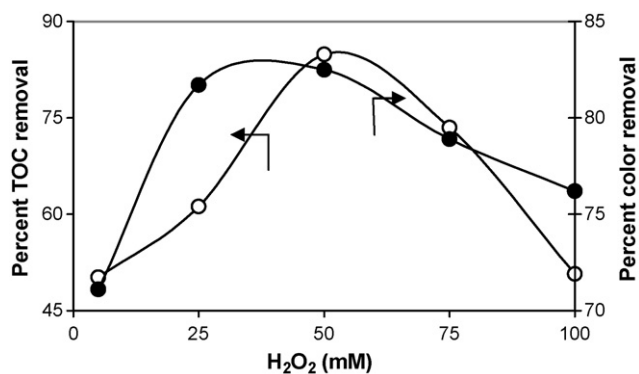


Fig. 7. Variations of percent color and TOC removals with initial H₂O₂ concentration in the photo-Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, Fe(II) 2.5 mM, reaction time 30 min).

The highest percent color and TOC removals were obtained at H₂O₂ concentration of 50 mM, which decreased with further increases in H₂O₂ dose. Percent color and TOC removals with UV/H₂O₂ treatment were around 41% and 11% after 30 min of irradiation which increased up to 82.3% and 85%, respectively at 50 mM H₂O₂ and 2.5 mM Fe(II) or at a H₂O₂/Fe²⁺ molar ratio of 20 after 5 min of irradiation. At a H₂O₂ dose of 100 mM or H₂O₂/Fe²⁺ molar ratio of 40, hydrogen peroxide adversely affected the UV treatment because of high rates of free-radical production. Color and TOC removals obtained at a H₂O₂/Fe²⁺ ratio of 40 after 30 min of irradiation was approximately 76.2% and 50.7%, which were much less than those obtained at a ratio of 20. The highest color, TOC and AOX removals of 82.3%, 85% and 93.5% were obtained at H₂O₂ concentration of 50 mM and Fe(II) concentration of 2.5 mM or at a H₂O₂/Fe²⁺ ratio of 20.

3.6. Ozone treatment

Ozone is a strong oxidizing agent with oxidation mechanism either by direct reaction with dissolved compounds or by the generated radicals depending on the pH of the solution [24]. The ozone dosage to be applied to the pulp mill effluent depends on total color and TOC content [25] and also on the presence of toxic metabolites [26]. For effective ozone treatment, continuous ozonation is required due to short half-life (20 min) of ozone. For this reason, the cost of continuous ozone production is one of the major drawbacks in ozone treatment. Stability of ozone is also affected by the presence of salts, pH and temperature. Alkaline solutions accelerate ozone decomposition [27]. Ozone treatment was proven to be rather inefficient for the reduction of chemical oxygen demand (COD) or total organic carbon (TOC), usually not exceeding 50% and 40% removals, respectively [28]. Therefore, ozone treatment alone can only be used for partial oxidation of organic compounds, while it is expected to be effective for color removal.

3.6.1. Effects of initial pH

To investigate the effects of pH on color and TOC removals, the pH of the pulp mill effluent was adjusted to 3, 7 and 11 with an ozone-feeding rate of 4.7 g h⁻¹. Variations of percent color, TOC removals with time by ozone treatment are depicted in Fig. 8 for different initial pH values. Almost complete color removals were observed for all pH values. Percent TOC removal at pH 7 was much higher than those obtained at pH 3 and 11. Percent color removal at pH 11 was 81% which increased to 91% at pH 7, while color removal at pH 3 was 95% at the end of 30 min. The highest percent TOC and color removals were 29 and 91%, respectively at pH 7. Percent AOX removal (62.4%) at pH 7 was also higher than those obtained at pH 3 and 11. These observations indicated that COD removal could be simply achieved via both reaction pathways of ozone whereas the reaction pH had to be at least 7 to enhance decomposition by ozone for higher TOC, color and AOX reduction. For this reason, further ozonation experiments were carried out at pH 7. In another ozonation study, optimum pH value was also found to be 7 for the treatment of pharmaceutical wastewater [29].

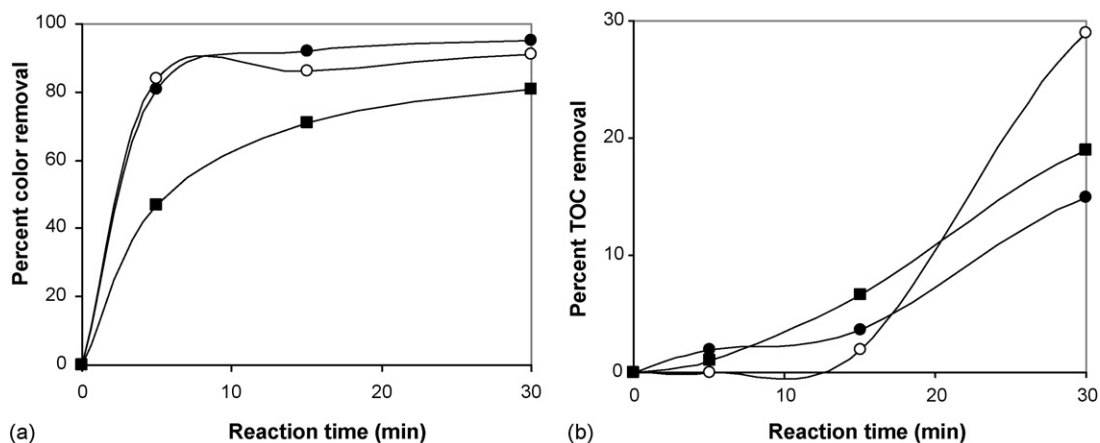


Fig. 8. Variations of: (a) percent color and (b) percent TOC removals with time at different initial pH levels in ozone treatment. pH: (●) 3; (○) 7; (■) 11 (ozone 4.7 g h^{-1} , reaction time 30 min).

3.6.2. Effects of ozone-feeding rate

Ozone concentration and therefore ozone-feeding rate to the reactor is an important variable affecting the rate and the extent of oxidation. Ozone was fed to the reactor with a rate of $4.7\text{--}11.9 \text{ g h}^{-1}$ while the pH of the wastewater was kept at pH 7 for a reaction period of 30 min. Fig. 9 depicts variations of percent color and TOC removals by ozonation at three different ozone-feeding rates. Percent color and TOC removals were not significantly affected by the increases in ozone-feeding rate. Percent color removals were nearly 93% at the end of 30 min of reaction time independent from the ozone dose. The highest TOC removal of 29% was obtained with the lowest ozone-feeding rate of 4.7 g h^{-1} which was slightly higher than that obtained with the highest ozone-feeding rate of 11.9 g h^{-1} . However, final percent AOX removal increased from 62.4% to 80.2% when ozonation rate was increased from 4.7 to 11.9 g h^{-1} . Therefore, the lowest ozonation rate (4.7 g h^{-1}) was found to be satisfactory for color and TOC removals, although AOX removals required much higher rates of ozonation. In another experimental study for the treatment of pulp mill effluent, 12% TOC removal was obtained by ozonation [30]. Zhou and Smith showed that the ozonation of biologically pretreated pulp mill effluents resulted

in up to 80% reduction in color and 60% reduction in adsorbable organic halogens (AOX) [31]. In addition, color, COD and AOX removals of 95%, 50% and 67% were reported for the treatment of pulp mill effluent by Mobius and Cordus-Talle [32]. Percent AOX removal was reported as 80% by Hostacy et al. [33] using ozone treatment.

As compared with the photo-Fenton treatment, which yielded 82.5% color removal, ozonation has improved the color removal to 91% while the TOC removal decreased from 82.8% to 29% by ozonation. Therefore, ozonation was found to be relatively inefficient for the removal of total organic carbon (TOC) as compared to the photo-Fenton treatment. This may be incomplete oxidation of organic compounds by ozone under the experimental conditions.

3.7. Peroxone treatment ($\text{O}_3/\text{H}_2\text{O}_2$)

Combination of ozone with hydrogen peroxide is considered to be a promising alternative for refractory organics removal from wastewater [5]. The conjugate base of H_2O_2 at millimolar concentrations could initiate the decomposition of ozone much more rapidly into hydroxyl radicals than with the hydroxide ion

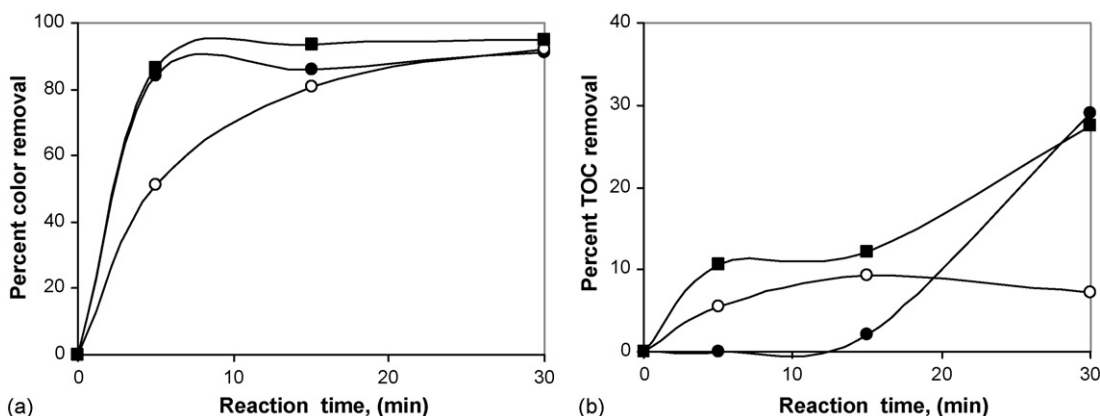


Fig. 9. Variations of: (a) percent color and (b) percent TOC removals with time for different ozone-feeding rates. Ozone (g h^{-1}): (●) 4.7; (○) 5.1; (■) 11.9 (pH 7, reaction time 30 min).

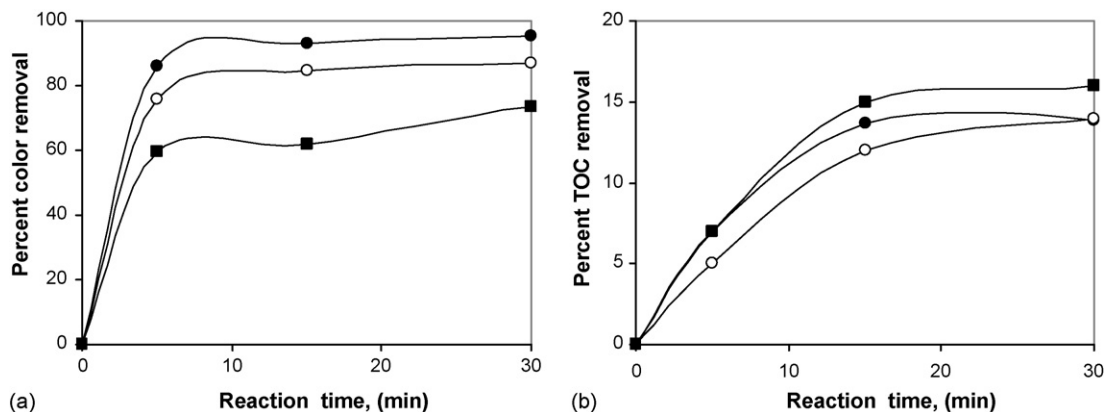
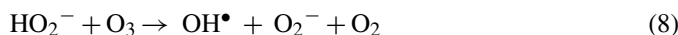
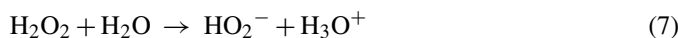


Fig. 10. Variations of: (a) percent color and (b) percent TOC removal with time at different initial pH levels in the peroxone treatment. pH: (●) 3; (○) 7; (■) 11 (ozone 4.7 g h^{-1} , reaction time 30 min).

as shown in following reaction [34]:



In order to improve the percent color and TOC removals, ozone was supplied to the pulp mill effluent in the presence of H_2O_2 up to 100 mM concentration.

3.7.1. Effects of initial pH

Peroxone treatment of the pulp mill effluent was realized at three different pH levels of 3, 7 and 11 with an ozone-feeding rate of 4.7 g h^{-1} . Fig. 10 depicts variations of percent color and TOC removals with time by the peroxone treatment at three different pH levels. Color removals at the end of 30 min varied between 73.4% and 95% depending on the pH. Percent TOC removals increased from 14% to 14.3% and further to 16% when pH was increased from 3 to 7 and further to 11. The ozone decomposition rate was increased with increasing pH, because H_2O_2 was dissociated into HO_2^- ions. For this reason pH 11 was considered to be the most suitable pH for the peroxone treatment.

In hydrogen peroxide treatment alone, percent color and TOC removals were 24% and 5%, respectively at the end of 30 min at pH 11 with a H_2O_2 dose of 50 mM. Color and TOC removals increased to 73.4% and 16% by the peroxone treatment at pH 11 with a H_2O_2 dose of 50 mM at the end of 30 min indicating the significant advantage of using ozone along with H_2O_2 in the peroxone treatment.

3.7.2. Effects of initial H_2O_2 concentration

Hydrogen peroxide concentrations were varied between 5 and 100 mM in the peroxone treatment of the paper mill effluent while the ozone-feeding rate was 4.7 g h^{-1} at pH of 11 for a reaction period of 30 min. Variations of percent color and TOC removals with time are depicted in Fig. 11 for different H_2O_2 concentrations. Percent color removal varied between 69% and 81.2% with the highest percent removal at 5 mM H_2O_2 concentration at the end of 30 min. Percent TOC removal showed fluctuations with time and the highest (34.7%) percent removal was obtained at 100 mM H_2O_2 dose while TOC removal (30.9%) at 5 mM H_2O_2 was comparable with that. The fluctuations in TOC concentrations with peroxone treatment (Fig. 11) is probably due to release of soluble compounds by ozone from suspended solids as stated by Fontanier [35]. On the basis of those results

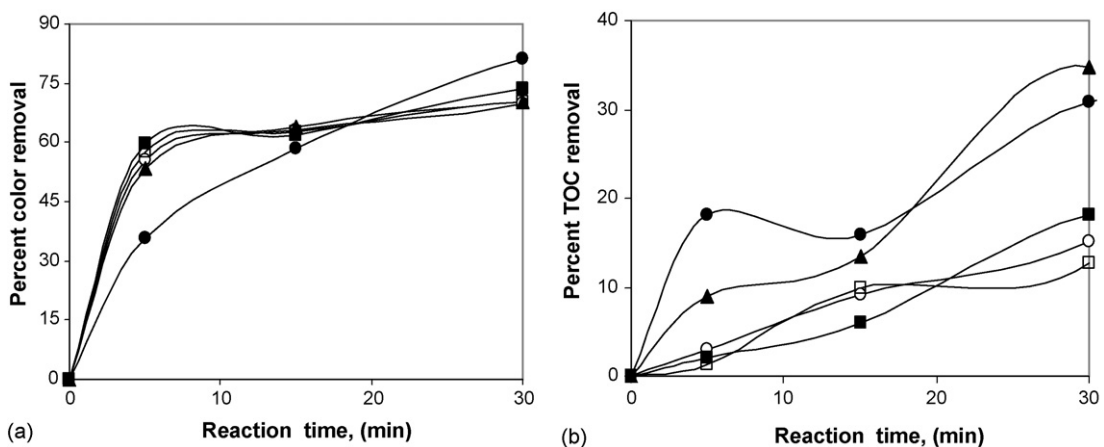


Fig. 11. Variations of: (a) percent color and (b) percent TOC removals with time at different initial H_2O_2 concentrations in the peroxone treatment. H_2O_2 (mM): (●) 5 (○) 25 (■) 50 (□) 75 and (▲) 100. (pH 11, ozone 4.7 g h^{-1} , reaction time 30 min).

Table 5
Comparison of the maximum removal efficiencies obtained by the advanced oxidation processes at the end of 30 min of treatment

Post-treatment method	pH	H ₂ O ₂ (mM)	Fe(II) (mM)	O ₃ (g/h)	Color removal (%)	TOC removal (%)	AOX removal (%)
H ₂ O ₂	11	50	–	–	24	5.1	34
H ₂ O ₂ /Fe(II)	5	50	2.5	–	84.6	88	89
UV	3	–	–	–	6.6	4.1	17
UV/H ₂ O ₂	11	50	–	–	41	11.1	18.5
UV/H ₂ O ₂ /Fe(II)	5	50	2.5	–	82.5	82.8	94
UV/H ₂ O ₂ /Fe(II) ^a	5	50	2.5	–	82	85	93
O ₃	7	–	–	4.7	91	29	62.4
O ₃ /H ₂ O ₂	11	5	–	4.7	81.2	30.9	95

^a Percent removals at the end of 5 min reaction time.

the most suitable H₂O₂ dose was found to be 5 mM with an optimum peroxide/ozone dose of 1.06 maximizing the reaction rate of 1.06. Maximum percent color, TOC and AOX removals of 81.2%, 30.9% and 95% were obtained with 5 mM H₂O₂, 4.7 g h⁻¹ ozone-feeding rate at pH 11 at the end of 30 min. Murphy et al. [36] studied the removal of color from three effluent streams from a pulp and paper mill and reported that the O₃/H₂O₂ process could achieve color removal up to 85% from the caustic extract stream, up to 90% from the acidic stream, and up to 50% from the final effluent.

Peroxone treatment did not significantly improve percent color and TOC removals even at the highest hydrogen peroxide dose as compared to the ozone treatment. Color and TOC removals were around 81% and 19%, respectively after 30 min of ozonation at pH 11 while only 81.2% color and 30.9% TOC removals were obtained with the peroxone treatment in the presence of 5 mM H₂O₂ at pH 11. Therefore, ozone treatment alone was more effective than the peroxone treatment.

4. Conclusions

Color, TOC and AOX removals from a pulp mill effluent were investigated by using different advanced oxidation methods (AOPs) and comparing their peak performances. Effects of pH and concentrations of the reagents were investigated for each treatment method. Table 5 summarizes the conditions and the performances of the AOPs used for treatment of the paper mill wastewater. Hydrogen peroxide treatment alone resulted in very low TOC (5.1%), AOX (34%) and color (24%) removals at an extreme pH of 11, which were not satisfactory. Fenton's reagent (H₂O₂/Fe²⁺) yielded very high color (85%), TOC (88%) and AOX (89%) removals within 30 min at a pH of 5, which makes this treatment more favorable among the others tested. UV treatment alone is an ineffective treatment method yielding unacceptably low color, TOC and AOX removals. Performance of the UV/H₂O₂ treatment was also unsatisfactory yielding low percent removals of color, TOC and AOX. Percent removals obtained with the photo-Fenton treatment were comparable with those obtained with the Fenton's reagent. Photo-Fenton treatment yielded high TOC (85%), color (82%) and AOX (93%) removals within 5 min indicating the effectiveness of this treatment. Oxidation rates increased considerably due to contribution of UV radiation to the Fenton treatment. Ozone treatment alone was not as effective as the treatment by the Fenton's

reagent yielding low TOC and AOX removals. Peroxone treatment improved the AOX removal, however reduced the color and TOC removals as compared to the ozone treatment alone. On the basis of the experimental results summarized in Table 5, either Fenton or photo-Fenton treatment can be used for effective removal of color, TOC or AOX from the paper mill wastewater. However, photo-Fenton treatment seems to be more advantageous requiring much less reaction times and therefore smaller reactor volumes as compared to the Fenton treatment.

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