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Short Communication

Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process

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Abstract

In this study, Reactive Black 5 (RB5) was removed from synthetic wastewater using Fenton's oxidation (FO) process. Experiments were conducted on the samples containing 100 and 200 mgl^{-1} of RB5 to remove the dye toxicity. Seventy-five milligram per litre of RB5 caused 25% toxicity on 24-h born daphnids whereas 100 mgl^{-1} of RB5 displayed 100% toxicity on *Daphnia magna*. The study was performed in a systematic approach searching optimum values of $FeSO_4$ and H_2O_2 concentrations, pH and temperature. Optimum pH and temperature for 100 mgl^{-1} of RB5 were observed as 3.0 and 40 °C, respectively, using 100 mgl^{-1} of $FeSO_4$ and 400 mgl^{-1} of H_2O_2 resulted in 71% chemical oxygen demand (COD) and 99% color removal. For 200 mgl^{-1} of RB5, 84% COD removal was obtained using 225 mgl^{-1} of $FeSO_4$ and 1000 mgl^{-1} of H_2O_2 yielding 0.05 molar ratio at pH 3.0 and 40 °C. Color removal was also more than 99%. The optimum conditions determined in accordance with the literature data. The H_2O_2 requirement seems to be related to initial COD of the sample. $FeSO_4/H_2O_2$ ratios found were not changed for both concentrations. The temperature affected the COD removal significantly at high degrees. Toxicity was completely removed for each concentration of RB5 at optimum removal conditions.
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1. Introduction

Wastewaters originated from textile industry contain various pollutants including a high content of organic matter and color problem depending on forms of dyes, surface active materials and textile additives materials used in the process (Grau, 1991). Textile dyes can be structurally different. Reactive azo dyes are the most commonly applied among more than 10 000 dyes applied in textile processing industries (van der Zee et al., 2001). Discharge of azo dyes is undesirable not only for aesthetic reasons but also because many azo dyes and their intermediate products are toxic to aquatic life (Chung and Stevens, 1993) and mutagenic to humans (Chung et al., 1992).

Azo dyes are resistant to biodegradation under aerobic conditions (Ganesh et al., 1994) although anaerobic color removal was applied by many researchers successfully (O'Neill et al., 2000; Panswad and Luangdilok, 2000; van der Zee et al., 2001). However, the high quantity and the context of wastewater originated from textile industry are not proper to apply anaerobic process because the decolorization takes place by the breakdown of the azo bonds which leads to formation of aromatic amines. The formed intermediates are not biodegradable under aerobic condition, and they are toxic than the dye molecules themselves.

Many chemical treatment processes have been used extensively to treat textile wastewaters. Most of the

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studies, such as chemical precipitation (Tünay et al., 1996), adsorption by activated carbon (Al-Degs et al., 2000) and some natural absorbents (Morais et al., 1999), photocatalytic oxidation (Arslan et al., 1999; So et al., 2002), ozonation (Liokou et al., 1997; Ölmez, 1999; Lin and Lai, 2000) and Fenton's oxidation (Kuo, 1992; Solozhenko et al., 1995; Kang and Chang, 1997; Lin and Lo, 1997; Park et al., 1999; Kang and Hwang, 2000; Arslan and Balcioglu, 2001; Kang et al., 2002) focused on color removal.

Fenton oxidation (FO) process which is one of the oldest advanced oxidation processes is composed at acidic pH yielding hydroxy radicals directly. It is performed in four stages, which are pH adjustment to low acidic values, oxidation reaction, neutralization and coagulation. At pH lower than 3.5, H_2O_2 and ferrous ions are more stable resulting in a better redox system and decolorizing better. However, at pH values higher than 4.0, ferrous ions easily form ferric ions which have a tendency to produce ferric hydroxo complexes. H_2O_2 is unstable and easily decomposes itself in the basic (pH > 10) solutions (Kuo, 1992).

The chemistry of FO process is explained. The reactions are given by Walling and Kato as cited in Lin and Peng (1995). Chemical oxygen demand (COD) and color removal reactions are initiated by the hydroxy radical.

It is mentioned that for decolorization purpose of azo dyes so deep destruction up to obtaining mineralization may not be necessary because the removal of color is associated with break of the conjugated unsaturated bonds in molecules (Solozhenko et al., 1995). In that case the dose of H_2O_2 must be well defined.

FO process was studied by many researchers to remove color and COD from textile wastewaters. Some of these studies have focused on the dyes (Kuo, 1992; Solozhenko et al., 1995; Arslan and Balcioglu, 2001), textile additives (Kang et al., 2002) and textile wastewater (Kang and Chang, 1997; Lin and Lo, 1997; Park et al., 1999). FO process has been suggested to treat recalcitrant/toxic wastewaters (Gulyas, 1997). However, application of FO process is rare in practice. Although organic content of wastewater is oxidized to the end products by the FO process, the sludge produced contains high amount of Fe(III) which needs to be managed by a safe disposal method.

The purpose of this study is to investigate the FO process to remove COD, color and toxicity from Reactive Black 5 (RB5) containing synthetic wastewater. The reason of selecting RB5 is that it has the largest consumption rate among all reactive dyes with an annual consumption of 1000 tonnes in Turkey (Balcioglu et al., 2001). The investigation covered the determination of parameters affecting the process efficiency to find out optimum values and to make comparisons with the literature values. Effect of temperature was also evaluated to assess the advantage of high temperature of spent baths.

2. Materials and methods

2.1. Experimental set-up

The molecular structure of RB5 in non-hydrolyzed form is illustrated in Fig. 1.

Experimental study was designed to obtain maximum COD and color removal at optimum pH, temperature and $FeSO_4$ and H_2O_2 doses.

FO process was performed considering Kuo's (1992) method with a modification of 2 min rapid mixing at 100 rpm and then 20 min slow mixing at 30 rpm and subsequently settling for 30 min (Kaptan, 2002). First, the pH of the sample was lowered up to desired pH value using 1 N H_2SO_4. Later, $FeSO_4$ and H_2O_2 were added to the 500 ml beakers containing 100 and 200 mg l^{-1} of RB5 solutions. These dye concentrations were chosen due to the actual dye mixtures used in the textile industry. After rapid and slow mixing, and settling period, pH of the supernatant was readjusted using 1 N NaOH up to 7.5 and the supernatant was left to settle for 2 h. During mixing, reactors were kept at constant temperature.

Experiments were conducted on the dye solutions at 30, 40, 50 and 60 °C temperature ranges. The temperature range was chosen for representing the actual conditions occurred in the industry as dyehouse effluent alone (60 °C) and when it is mixed with general wastewater (30 °C). $FeSO_4$ and H_2O_2 ratio varied from 0.5 to 0.2. pH was changed between 2.5 and 4.0.

Experimental study was designed in four stages. In the first stage H_2O_2, temperature, pH was kept constant to determine $FeSO_4$ concentration for maximum color and COD removal. For that $FeSO_4$ concentration and the same oxidation conditions, optimum H_2O_2 concentration was investigated in the second stage. By considering the optimum doses of first and second stages, optimum pH and temperature were investigated in the third, fourth stages, respectively. By taking into consideration the optimum values of each parameter, the effect of slow mixing time on COD and color removal was also investigated.

The dye solution of RB5 was hydrolyzed at pH higher than 11.5 and at 80 °C temperature for at least 4 h (Ganesh et al., 1994). COD equivalent of RB5 was determined as 0.75 mg COD (mg RB5)$^{-1}$. Initial maximum absorbance of RB5 solution was measured at 600 nm wavelength.
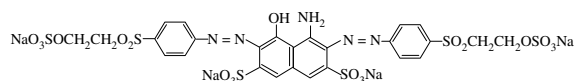

Fig. 1. Molecular formula of RB5 in non-hydrolyzed form.

2.2. Toxicity measurements

Effluent toxicity was tested using 24-h born *Daphnia magna* at 50% dilution rate as described in Standard Methods (1998). Test animals were obtained from Regional Environmental Protection Agency Laboratory in Naples, Italy where *D. magna* is referred for toxicity monitoring in the wastewater discharge limits. After a cloning period in our laboratory the experiments were conducted on. Toxicity tests were repeated four times using five daphnids in test beakers with 100 ml of effective volume at 8.0 pH, providing minimum 6 mg l^{-1} of dissolved oxygen and 20 ± 1 °C constant temperature. Test animals were grown by 16-h light/8-h dark lighting with 1000 lux. A blank was also carried on in parallel. Results were expressed as immobilization percentage of the daphnids after 24 h by dividing immobile animals, which were not able to move, were determined as death to total test number.

2.3. Analytical methods

COD was measured according to Standard Methods (1998). Absorbance measurements were made using Pharmacia LKB-Novaspe II model spectrophotometer. HACH-Dr-B model spectrophotometer was used for the color measurements in APHA Pt–Co (cobalt) unit.

The supernatants were filtered by 0.45 μm Millipore membrane filter for measuring COD, color and absorbance at 436, 525 and 620 nm wavelengths which were referred in German wastewater discharge standards (Gahr et al., 1994). One centimetre crystal beam was used in color measurement. COD and color efficiency for each dye concentration were obtained.

RB5 was obtained from Dyestuff company. FeSO$_4$ solution was prepared daily and all chemicals used were of analytical grade.

Considering the influence of H$_2$O$_2$ on COD measurement that was defined 10% of the initial COD by Talınlı and Anderson (1992) at much more higher H$_2$O$_2$ doses, the residual H$_2$O$_2$ concentration was not measured in this study.

3. Results and discussion

3.1. Toxicity results

Toxicity test results showed that the toxic effect of RB5 is becoming significantly after 75 mg l^{-1} concentration (25% immobilization), however, 100% immobilization was resulted by 100 mg l^{-1} of RB5. That is why 100 and 200 mg l^{-1} concentrations of RB5 were based to our FO process studies to remove its toxicity.
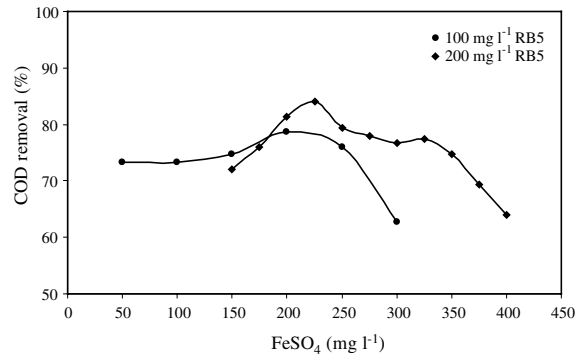

Fig. 2. Effect of FeSO$_4$ concentration on COD removal [(●) 100 mg l^{-1} RB5 using 400 mg l^{-1} H$_2$O$_2$, (◆) 200 mg l^{-1} RB5 using 1000 mg l^{-1} H$_2$O$_2$] at 40 °C and 3.0 pH.

3.2. Decolorization results

3.2.1. Effect of FeSO$_4$ concentration

The effect of FeSO$_4$ concentration on COD removal efficiency for 100 and 200 mg l^{-1} of RB5 is given in Fig. 2. According to Fig. 2, maximum COD removal (79%) for 100 mg l^{-1} of RB5 was obtained in the case of using 200 mg l^{-1} of FeSO$_4$ (1.315 mM) and 400 mg l^{-1} of H$_2$O$_2$ (11.76 mM). pH and temperature were kept at 3.0 and 40 °C, respectively. At the same time, more than 99% of color removal was obtained at all FeSO$_4$ concentration (50–100 mg l^{-1}). The absorbance measurements showed that the limits were provided for each wavelength (0.2/0.1/0.1) m^{-1} even at 50 mg l^{-1} of FeSO$_4$ (data not shown). Although for 50 mg l^{-1} concentration of FeSO$_4$ COD removal was also high as well as using 100 mg l^{-1} of FeSO$_4$, higher hydroxyl radicals produced during FO process resulting in higher COD removal forced us to choose 100 mg l^{-1} of FeSO$_4$ as optimum concentration at which 71% COD removal was obtained. However, as seen from Fig. 2, the COD removal efficiency started to decrease for 250 and 300 mg l^{-1} doses of FeSO$_4$. It may be explained by redox reactions since OH radicals may be scavenged by the reaction with the hydrogen peroxide present or with another Fe^{2+} molecule as below (Benitez et al., 2001).

$$Fe^{2+} + \cdot OH \rightarrow OH^{\cdot} + Fe^{3+} \tag{1}$$

$$H_2O_2 + \cdot OH \rightarrow HO_2^{\cdot} + H_2O^+ \tag{2}$$
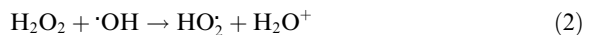
The Fe^{3+} formed can react with H$_2$O$_2$ as well as with hydroperoxy radicals with regeneration of Fe^{2+} in the solution resulting in decrease in COD removal.

For 200 mg l^{-1} of RB5, the concentration of FeSO$_4$ was changed between 150 and 400 mg l^{-1} by keeping H$_2$O$_2$ concentration constant as 1000 mg l^{-1} at pH 3.0 and at 40 °C. Maximum COD removal (84%) was obtained at 225 mg l^{-1} of FeSO$_4$ concentration. However,

Table 1
Color and COD removal results for 100 mg l^{-1} RB5 using 100 mg l^{-1} FeSO$_4$ at 40 °C and 3.0 pH

H$_2$O$_2$ (mg l^{-1})	Absorbance (m^{-1})			Color (Pt–Co)	Color removal (%)
	436 nm	525 nm	620 nm		
100	0.297	0.445	0.459	800	68
200	0.187	0.203	0.164	580	77
300	0.200	0.101	0.003	530	79
400	0.021	0.01	0.006	40	98
500	0.002	0.001	0.001	<10	>99

since the good flocculation phenomenon started even at 200 mg l^{-1} yielding 81% COD removal, that concentration was defined as optimum. Color removal was more than 99% at all FeSO$_4$ concentrations. The same decrease in COD removal after 225 mg l^{-1} of FeSO$_4$ can be explained due to the scavenging effect of over doses of FeSO$_4$ or H$_2$O$_2$ on OH radicals.

3.2.2. Effect of H$_2$O$_2$ concentration

The results of absorbance measurements and the color removal for 100 mg l^{-1} of RB5 for determination of optimum H$_2$O$_2$ concentration are illustrated in Table 1. As shown in Table 1, color removal efficiency increased by increasing H$_2$O$_2$ concentration from 100 mg l^{-1} (68%) to 500 mg l^{-1} (>99%). Four hundred milligram per litre of H$_2$O$_2$ was defined as optimum concentration providing 98% color and 76% COD removals as seen in Fig. 3. The absorbance measurements were in accord with the color measurement (40Pt–Co) at 400 mg l^{-1} of H$_2$O$_2$ dose.

The results of H$_2$O$_2$ optimisation for 200 mg l^{-1} of RB5 are reported in Table 2. These results indicated the optimum conditions yielding 82% COD removal. Increasing the concentration of H$_2$O$_2$ up to 1200 mg l^{-1} did not improve COD removal more in turn it decreased to 80% because of scavenging effect of H$_2$O$_2$ on OH radicals as explained above (Benitez et al., 2001). At 200 mg l^{-1} of
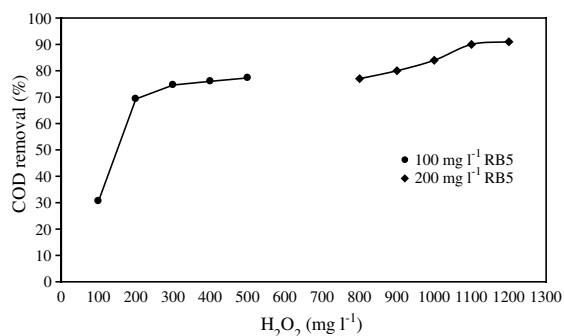
Fig. 3. Effect of H$_2$O$_2$ concentration on COD removal [(●) 100 mg l^{-1} RB5 using 100 mg l^{-1} FeSO$_4$, (◆) 200 mg l^{-1} RB5 using 225 mg l^{-1} FeSO$_4$] at 40 °C and 3.0 pH.

FeSO$_4$ and 1000 mg l^{-1} of H$_2$O$_2$ concentrations, absorbances were met the limits desired (7/5/3) m^{-1}.

Considering this point, H$_2$O$_2$ optimisation experiments were repeated using 225 mg l^{-1} of FeSO$_4$. Although the COD removal increased up to 91% by increasing H$_2$O$_2$ concentration up to 1200 mg l^{-1}, optimum H$_2$O$_2$ concentration was chosen as 1000 mg l^{-1} yielding 84% COD and >99% color removal (Fig. 3). Absorbance measurements were also lowered below the limits as expected for that concentration (1.9/0.9/0.8) m^{-1}.

3.2.3. Effect of pH

To determine the optimum pH, pH was changed between 2.5 and 4.0 as illustrated in Fig. 4. A 78.6% COD removal was obtained at 3.0 pH, but the maximum COD removal (87%) was proved at 3.5 pH for 100 mg l^{-1} of RB5. Color removal was more than 99% at all pH values. Increasing dye concentration upto 200 mg l^{-1}, maximum COD and color removal were obtained as 84% and 99%, respectively, at 3.0 pH. Absorbance measurements were in accord with COD and color results (1.3/0.9/0.8) m^{-1}. Fig. 4 indicates that optimum pH varies in a small scale between 3.0 and 3.5 for doubling the dye concentration.

3.2.4. Effect of temperature

As seen from Fig. 5, optimum temperature is 40 °C at which 71% COD and 99% color removal were obtained for 100 mg l^{-1} of RB5 concentration. The maximum COD removal (84%) for 200 mg l^{-1} of RB5 was also obtained at 40 °C. Highering temperature up to 60 °C affected COD removal negatively at both dye concentrations due to the destabilisation of flocs resulting in increased ferrous ions which scavenged OH radicals during Fenton's reactions (Benitez et al., 2001).

3.2.5. Effect of slow mixing time

Maximum COD removals for both dye concentrations (68% and 84%, respectively) were obtained at 20th min. When mixing time increased up to 30 min COD removal decreased to 55% for 100 mg l^{-1} of RB5 due to floc destabilisation. Color was removed higher than 99% for all mixing times.

Table 2
Color and COD removal results for 200 mg l^{-1} RB5 using 200 mg l^{-1} FeSO$_4$ at 40 °C and 3.0 pH

H$_2$O$_2$ (mg l^{-1})	Absorbance (m^{-1})			Color (Pt–Co)	Color removal (%)	COD (mg l^{-1})	COD removal (%)
	436 nm	525 nm	620 nm				
800	0.012	0.01	0.01	100	96	36	76
900	0.014	0.005	0.005	100	98	35	77
1000	0.007	0.005	0.003	15	>99	28	82
1100	0.009	0.008	0.005	<10	>99	30	80
1200	0.011	0.01	0.01	<10	>99	30	80
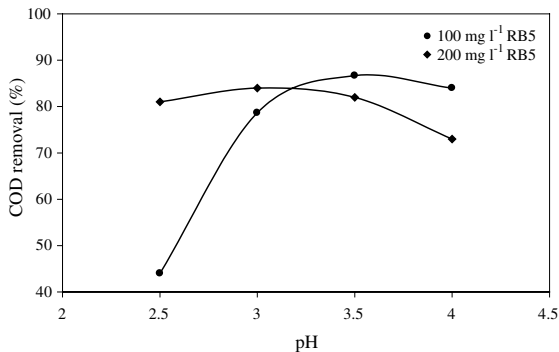
Fig. 4. Effect of pH on COD removal [(●) 100 mg l^{-1} RB5 using 100 mg l^{-1} FeSO$_4$ and 400 mg l^{-1} H$_2$O$_2$, (◆) 200 mg l^{-1} RB5 using 225 mg l^{-1} FeSO$_4$ and 1000 mg l^{-1} H$_2$O$_2$] at 40 °C.
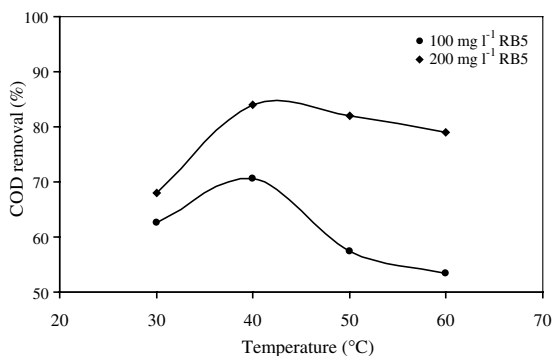
Fig. 5. Effect of temperature on COD removal [(●) 100 mg l^{-1} RB5 using 100 mg l^{-1} FeSO$_4$ and 400 mg l^{-1} H$_2$O$_2$, (◆) 200 mg l^{-1} RB5 using 225 mg l^{-1} FeSO$_4$ and 1000 mg l^{-1} H$_2$O$_2$] at 3.0 pH.

3.3. Evaluation of the systematic used

Toxicity test results showed that optimum conditions of FO process determined in the study removed the initial toxicity (100%) completely at both RB5 concentrations.

Optimum conditions determined for each concentration of RB5 are summarized in Table 3. As shown in

Table 3
Optimum removal conditions for RB5 using FO process

RB5 dye (mg l^{-1})	100	200
COD removal (%)	70.6	84
Color removal (%)	>99	>99
T (°C)	40	40
pH	3	3
FeSO$_4$ (mg l^{-1})	100	225
H$_2$O$_2$ (mg l^{-1})	400	1000
Molar ratio [FeSO$_4$/H$_2$O$_2$]	0.055	0.0503

Table 3, molar ratio between FeSO$_4$/H$_2$O$_2$ was constant, although their concentrations increased 2.25–2.5 fold by increasing the concentration of RB5 to 200 mg l^{-1}. Since color removal was obtained (higher than 99%) at almost all conditions, absorbance measurements were more indicating for defining the optimum process conditions.

The optimum conditions from this study for each concentration of RB5 are in accordance with the literature data. Balcioglu et al. (2001) applied FO process for treatment 75 mg l^{-1} of RB5 (= 55 mg l^{-1} of COD) at 3.0 pH using 5 mM of H$_2$O$_2$ and 0.5 mM of FeSO$_4$. They reported that FO process was capable to decolorize RB5 in 2–5 min resulting in more than 97% COD removal.

Results of this study indicated that the H$_2$O$_2$ requirement seems to be related to initial COD of the sample. The optimum pH determined (3.0) corresponds the range of 2.5–4.0 given for FO process in the previous studies (Kuo, 1992; Balcioglu et al., 2001). FeSO$_4$/H$_2$O$_2$ ratios were found constant for both concentrations and that ratio was determined in accordance with the literature value of 0.42 (Kuo, 1992; Kang and Chang, 1997).

The temperature affected the COD removal negatively at high degrees. With this in mind it can be dedicated that applying FO process directly to the spent baths having high temperatures needs to be evaluated in detail.

The method of FO process application in this study with 2 min rapid mixing before slow mixing served as accelerator for formation and the consuming up the radicals in the oxidation reactions resulting in the

shortened total reaction time and yielding higher color and COD removal.

4. Conclusions

In this study, the removal of color and COD of Reactive Black 5 was studied using FO process. The effectiveness of FO process for removing the RB5 toxicity was investigated by running toxicity test on *D. magna*. A systematic approach was followed for the determination of FeSO$_4$ and H$_2$O$_2$ concentrations, effective pH, temperature values which are the important parameters for FO process. The following results can be summarized of this study.

Optimum pH, temperature were observed as 3.0, 40 °C for 100 mg l^{-1} of RB5 using 100 mg l^{-1} of FeSO$_4$ and 400 mg l^{-1} of H$_2$O$_2$. The pH and temperature values did not change for decolorizing 200 mg l^{-1} of RB5 using 225 mg l^{-1} of FeSO$_4$ and 1000 mg l^{-1} of H$_2$O$_2$. Thus, increasing the concentration of RB5 from 100 to 200 mg l^{-1} did not change the optimum conditions drastically, especially on the basis of the molar ratio between FeSO$_4$ and H$_2$O$_2$.

COD removal efficiency was not affected significantly when the concentration of FeSO$_4$ was increased whereas the change of pH and temperature affected system performance more. Applying FO process to the spent baths at more than 60 °C could not provide the required treatment efficiency. Further study may be done to investigate the effect of temperature on color and COD removal of RB5 by mixing it with the other process wastewater.

The initial toxicity measured by *D. magna* was completely removed at each dye concentration at optimum system conditions determined. Beyond the toxicity removal effectiveness of FO process, running toxicity test in the effluent parallel to treatment application provides further information for using advanced oxidation processes.

TOC measurement is strongly recommended for avoiding the possible interference of H$_2$O$_2$ on COD via scavenging effects on OH radicals produced during FO oxidation which is one of advanced oxidation processes producing hydroxyl radicals.

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