



Decolorization of Blue CL-BR dye by AOPs using bleach wastewater as source of H₂O₂

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Abstract

This research was focused on the investigation of the efficacy of advanced oxidation processes (Fenton, ozonation and UV/H₂O₂) for decolorization of reactive azo dye (Blue CL-BR) using bleach wastewater as possible source of H₂O₂. All the experiments were performed on the laboratory scale set-up. The results showed that colour removal efficiencies by UV or bleach (H₂O₂) alone were not so efficient. Fenton process with bleach wastewater was found to be the most effective at process conditions such as pH of 3 and H₂O₂/Fe²⁺ ratio of 24:1, resulting in 64% colour removal. Almost complete colour removal, i.e., 99% and 95% were achieved by UV/H₂O₂ and UV/bleach wastewater in 30 and 60 min, respectively. Ozonation proved an efficient method for decolorization of Blue CL-BR dye at alkaline pH. It was possible to achieve 98% colour removal with 30 min of ozonation at pH 9. The colour removal of dye was found to follow first order kinetics.

Key words: azo dye; bleach wastewater; Fenton; hydrogen peroxide; ozone

Introduction

The textile industry being water intensive in nature uses colossal quantity of water during the “wet processes”, such as, dyeing, printing and finishing operations. Hydrogen peroxide is usually used for bleaching of cotton fabrics. The bleaching chemicals have to be removed, generally through a number of rinsing stages or by the addition of a reducing agent to neutralise the bleach. In the both cases, large volume of wastewater is generated. In bleaching wastewater the environmental concerns are associated with the use of strong complexing agents. A strong alkaline effluent is produced if the rinsing water after mercerizing is not recovered or re-used. On the other hand, dyeing effluents are characterized by high levels of colour caused by residual dyes that are not fixed to fibres in the dyeing process with significant quantity of auxiliary chemicals. The presence of dyes in receiving media is easily detectable even when released in small concentrations (Nigam *et al.*, 2000) and causes aesthetic problems. The accumulation of colour hampers sunlight penetration, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem (Kuo, 1992; Georgiou *et al.*, 2003). Furthermore, dyes in effluents are degraded by microorganisms yielding potentially carcinogenic amines that spread in the ecosystem (Chung and Stevens, 1993; Georgiou *et al.*, 2003).

“Azo-reactive” is probably the main class of textile dyes

utilized for cotton fibres while the toxicity of azo dyes is significantly higher as compared to other types of dyes (Grau, 1996). Advanced oxidation processes (AOPs) are widely used for removal of colour from dyeing wastewater (Zhang *et al.*, 2004; Shu and Chang, 2005; Shu, 2006; Yasar *et al.*, 2006). Processes involving H₂O₂ are based on the generation of hydroxyl radicals by the dissociation of hydrogen peroxide. The use of bleaching wastewater as a source of hydrogen peroxide can be a new option that can considerably reduce resource consumption and environmental pollution without incurring expensive investments of a technical and financial nature.

This study was focused on colour removal of reactive dye (Blue CL-BR) by AOPs. The objectives of the study were to investigate the efficiency of bleach wastewater as a source of hydrogen peroxide for various processes (Fenton, ozone, O₃/H₂O₂, and UV/H₂O₂) to reduce colour and to compare it with the results of analytical grade hydrogen peroxide. The effects of the key operating variables such as pH, hydrogen peroxide and ferrous doses on the decolorisation kinetics were also studied.

1 Materials and methods

1.1 Materials

Blue CL-BR dye was obtained from Clariant Pakistan. Aqueous solution of dye was prepared by distilled deionized water (DDW). First the stock solution of 1000

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mg/L was prepared and all the experiments were carried out on 100 mg/L dye solutions. The hydrogen peroxide solution (30%) of analytical grade, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, KIO_3 , and $\text{Na}_2\text{S}_2\text{O}_3$ were obtained from Merck, Germany and extra pure starch of BDH England were used.

Bleach waste water was collected from a finishing mill. Waste water was highly alkaline (10.5); TDS contents were 3809 mg/L with conductivity of 5860 μS . H_2O_2 content of wastewater was determined using standard technique after Gordon *et al.* (1992). H_2O_2 concentration was 1.5 mg/ml of wastewater.

A JQ-6M Puretech model ozone generator was used. The ozonation was carried out in bubble column reactor of 1 L capacity with internal diameter of 3.3 cm. The ozone was supplied at the bottom of the reactor through a diffuser at a rate of 300 mg/h produced by using air. The volume of the dye solution used for analysis was 500 ml.

The optimal UV and UV light assisted experiments were carried out in a cylindrical photo-reactor with an internal diameter of 5 cm and total volume of 1 L. The reactor was wrapped with aluminum foil to enhance the absorbance of UV. A low pressure mercury lamp model PENRAY 3SC9 UPLAND USA with irradiation intensity of 5 mW/cm^2 and wavelength of 254 nm was immersed in 300 ml dye solution in the reactor while ensuring its position at the center. Experiments were performed at ambient temperature and no lamp cooling was provided.

The set-up for H_2O_2 , bleach wastewater and Fenton process was consisted of a graduated Pyrex glass vessel of 250 ml with magnetic stirring facility at a rate of 120 r/min. All the experiments were carried out in batch mode on a sample volume of 100 ml.

1.2 Experimental

Ozone dose was varied from 50 to 300 mg/L of wastewater. The ozonation was performed at various pH (11, 9, 7, and 5) to study the effect of pH on ozonation. In the experiments involving H_2O_2 and bleach wastewater, first the dose of the oxidant was added and then ozonation was carried out at pH 9 at constant ozone dose of 200 mg/L. Ozone treated effluent was sampled at regular intervals for the determination of colour concentrations. UV irradiation time was varied from 5 min to 1 h. For combinations of H_2O_2 /UV, 2.21 mmol/L of H_2O_2 was added to the sample and then UV was applied at pH 7.

Bleach wastewater doses such as 5, 10, 15, 20, 25, 50, 75 and 100 ml/L were used for chemical treatment. The amount of H_2O_2 present in these different doses was 7.5, 15, 22.5, 30, 37.5, 75, 112.5 and 150 mg/L, respectively. These doses were then converted into molar values for convenience in representing molar ratio. Their corresponding molar values were 0.22, 0.44, 0.66, 0.88, 1.1, 2.21, 3.31 and 4.41 mmol/L, respectively. Further experiments involving ferrous sulphate were carried out with varying amount of H_2O_2 and bleach wastewater (1.1, 2.21, 3.31 and 4.41 mmol/L) and ferrous was kept constant at 0.09 mmol/L. In another set various ferrous doses (0.09, 0.18, 0.27, and 0.36 mmol/L) were applied and H_2O_2 content (analytical grade H_2O_2 and in bleach wastewater)

was kept constant at 2.21 mmol/L. These experiments were performed by adjusting pH at 3 ± 0.1 using 0.2 mol/L H_2SO_4 (few drops). After the reaction (40 min) residual iron was removed by raising the pH to 9.0 by adding 1 mol/L NaOH. The precipitates were allowed to settle and the supernatant was taken for analysis. Finally the effect of pH was monitored by varying pH (2, 3, 4, 5 and 6) using optimal ratio (2.21 and 0.18 mmol/L) of bleach wastewater and ferrous sulphate.

2 Results and discussion

2.1 Effect of Fenton's process on colour removal

Several researchers (Bali *et al.*, 2004; Ince and Gonenc, 1997) reported that the rate of decolorization by H_2O_2 alone was very low for many dyes. Similar results were obtained for bleach wastewater (Table 1).

Table 1 Effect of bleach wastewater on colour removal

Bleach wastewater (ml/L)	H_2O_2 contents (mmol/L)	Colour removal (%)		
		1 h	3 h	24 h
5	0.22	0.14	0.37	0.45
10	0.44	0.50	0.74	0.85
15	0.66	0.65	0.96	1.04
20	0.88	0.87	1.19	1.50
25	1.10	1.07	1.41	1.73
50	2.21	1.99	3.48	6.07
75	3.31	1.81	2.49	4.08
100	4.41	1.03	1.42	2.28

Therefore, Fe(II) was used as catalyst to accelerate the production of OH^\cdot radical for colour removal of dye. The selection of an optimum H_2O_2 concentration for the decolorization of the dye by Fenton's process is important from practical point of view (due to the cost of H_2O_2). Several studies (Neamtu *et al.*, 2003; Azbar *et al.*, 2004; Sevimli and Kinaci, 2002) are also available on attempts to find optimal H_2O_2 and Fe^{2+} doses, but still lack consensus on the ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}$ that gives the best results. Thus, first optimization of H_2O_2 content in bleach wastewater was done using various doses of 1.10, 2.21, 3.31 and 4.41 mmol/L while 0.09 mmol/L of Fe^{2+} was kept constant. The results demonstrated that H_2O_2 (analytical grade) dose of 4.4 mmol/L gave 53% colour removal (Table 2). While with H_2O_2 (bleach wastewater) 62% colour removal was achieved at a dose of 2.2 mmol/L and further increase in H_2O_2 doses (3.31 and 4.41 mmol/L) beyond optimal dose results in decline in colour removal to 60% and 59%, respectively (Table 3). Results show higher efficiency of H_2O_2 (bleach wastewater) as compared to H_2O_2 analytical grade even at lower dose. This could be attributed to excessive solids in bleach wastewater which remove colorant by simple adsorption without involving chemical reactions while an iron-based coagulant provides ferrous ions (Fe^{2+}) to further degrade the dye (Wilcock, 1992). During the process, precipitates of Fe(OH)_2 and Fe(OH)_3 were formed and remain in the solution. The gelatinous suspension removes colorants by complexation and electrostatic attraction followed by coagulation with

Table 2 Effect of various doses of hydrogen peroxide on colour removal of Blue dye by Fenton process ($C_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 0.09 \text{ mmol/L}$)

H ₂ O ₂ dose (mmol/L)	Colour removal (%) at various time interval						
	15 min	30 min	45 min	60 min	75 min	90 min	120 min
1.10	7.8	11.6	20.4	21.8	23.9	25.0	27.4
2.21	21.8	28.0	32.0	36.4	38.2	40.0	43.0
3.31	23.5	29.0	34.0	37.0	38.7	41.5	48.3
4.41	28.9	37.0	43.3	45.2	46.7	48.0	53.0

Table 3 Effect of various doses of bleach wastewater on colour removal of Blue dye by Fenton process ($C_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 0.09 \text{ mmol/L}$)

Bleach wastewater (H ₂ O ₂ mmol/L)	Colour removal (%) at various time intervals						
	15 min	30 min	45 min	60 min	75 min	90 min	120 min
1.10	27.6	36.4	42.4	46.1	49.9	52.9	59.6
2.21	29.1	37.6	43.8	48.3	51.3	54.0	62.0
3.31	29.5	39.1	43.1	47.6	50.5	53.0	60.2
4.41	28.3	39.1	42.2	46.7	47.4	49.5	59.4

H₂O₂ (bleach wastewater) in the presence of suspended and colloidal particles. In Fenton process ferrous dose not only accelerate the production of OH radicals but also provided additional benefit of coagulation by iron ions. These radicals led to rapid breaking of conjugated double bond of chromophores (Guivarch *et al.*, 2003).

The selected dose of Fe²⁺ (0.09 mmol/L) was also investigated with higher ferrous doses (0.18, 0.27 and 0.36 mmol/L) at constant H₂O₂ content (2.21 mmol/L) of bleach wastewater. Results demonstrated that Fe²⁺ dose of 0.09 mmol/L gave colour removal of 62% beyond which no appreciable increase in colour removal (63.7%, 64.1% and 64.7%) were obtained (Table 4). Therefore, a molar ratio of 24:1 (H₂O₂/Fe²⁺) was achieved of H₂O₂ and Fe²⁺. In previous studies (Ince and Tezcanli, 1999; Dutta *et al.*, 2001; Perez *et al.*, 2002), H₂O₂/Fe²⁺ ratios recommended for different dyes are from 10:1 to 40:1 for H₂O₂ analytical grade.

The optimization of pH was performed at various pH values from 2 to 6. The results showed that the pH had a significant effect on the colour removal by Fenton's process (Fig.1). The optimum pH for Blue CL-BR was found to be pH 3, where the maximum colour removal of 64% was achieved (Perez *et al.*, 2002; Kang *et al.*, 2002). The hydroxyl radical generation is directly affected by the pH and are formed efficiently under acidic conditions. The low activity detected for high pH has been reported in the literature (Perez *et al.*, 2002; Lee *et al.*, 2003) and can be explained by the formation of Fe(OH)₃. A low pH is also essential to keep ferric ion in solution. At a pH less than 3, Fe(III) is in the solution; at a pH greater than 3 and less than 5, Fe(III) is out of solution in colloidal form; and above pH 5, it precipitates as Fe₂O₃·H₂O.

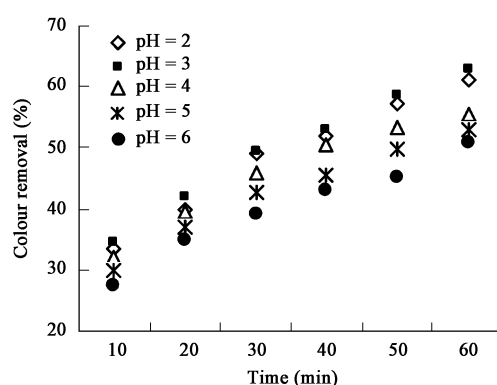


Fig. 1 Dye colour removal by Fenton process at various pH (H₂O₂ = 2.21 mmol/L, Fe²⁺ = 0.18 mmol/L).

2.2 Effect of UV irradiation on colour removal

UV alone did not show appreciable decolorization in case of Blue CL-BR, i.e. 1 h exposure to UV resulted in an unsatisfactory colour removal of 31% (Fig.2). This paucity in colour removal is justified as UV irradiation of

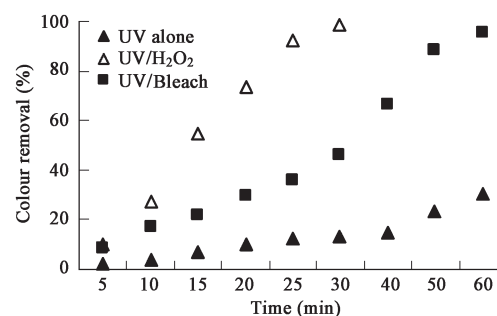


Fig. 2 Colour removal of Blue CL-BR dye by UV alone, UV/H₂O₂ (H₂O₂ = 2.21 mmol/L) and UV/Bleach wastewater (2.21 mmol/L) at pH 7.

Table 4 Effect of various ferrous doses on colour removal of Blue dye by Fenton process (H₂O₂ content (bleach wastewater) = 2.21 mmol/L)

Ferrous dose (mmol/L)	Colour removal (%) at various time intervals						
	10 min	20 min	30 min	40 min	50 min	60 min	120 min
0.09	29.1	37.6	43.8	48.3	51.3	54.0	62.0
0.18	32.0	39.5	45.8	50.5	53.5	55.5	63.7
0.27	34.2	41.8	47.5	51.7	55.0	56.8	64.1
0.36	36.8	43.9	49.8	54.2	56.7	57.6	64.7

organic compounds is of a rather complex nature, it can be speculated that during UV exposure an electronically excited state of the dye was generated where further decomposition of excited molecules to radicals and/or oxidized species did not occur (Arslan and Balcioglu, 2001). From the initial results it could be inferred that Blue CL-BR is photolytically stable and its complete oxidation necessitates the application of H_2O_2 for production of $\text{OH}\cdot$ radicals. Thus a dose of 2.21 mmol/L H_2O_2 was applied prior to UV irradiation, resulting in complete decolorization of Blue CL-BR dye in 30 min exposure (Shu *et al.*, 1994). The introduction of bleach wastewater resulted in 95% colour removal, however, comparatively longer irradiation period (1 h) is required (Fig.2). This extension in UV exposure time is probably by the limited penetrations of photons due to the presence of impurities (total dissolved solids, total suspended solids) in bleach wastewater.

2.3 Effect of pH on colour removal by ozone

The effect of pH was evaluated by varying pH from 5 to 11. The results demonstrated that ozonation was effective in basic medium, i.e. colour removal of 98% was achieved at pH 9 (Fig.3). This observation may be explained by the enhancement of ozone decomposition at higher pH values (Aplin and Waite, 2000). In general ozone oxidation pathway consists of a direct oxidation by ozone or a radical oxidation by $\text{HO}\cdot$ radical (Langlais *et al.*, 1991; Masten and Davies, 1994). The solubility of ozone is readily affected by pH. In fact the influence of pH is a result of the relationship between oxidation potential and decomposition behaviour of ozone. In acidic pH, the ozone is available as molecular O_3 and in alkaline pH it decomposes into secondary oxidants such as $\text{HO}\cdot$, $\text{HO}_2\cdot$ and $\text{HO}_3\cdot$. Among these $\text{HO}\cdot$ is an important one which has rate of attack 10^6 to 10^9 times faster than the corresponding reaction rate for molecular ozone (Chu and Ma, 2000). The oxidation potential of ozone decreases from 2.08 V at acidic pH to 1.4 V in alkaline solutions. This indicates that ozone solubility decreases (O_3 decomposition enhances) with increasing pH resulting in generation of secondary oxidants (Alpin and Waite, 2000; Balcioglu and Arslan, 2001). At higher pH the reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical $\text{O}_2^{\cdot-}$ and hydroperoxyl radical $\text{HO}_2\cdot$ which through various steps yield $\text{HO}\cdot$ radicals (Gottschalk *et al.*, 2000).

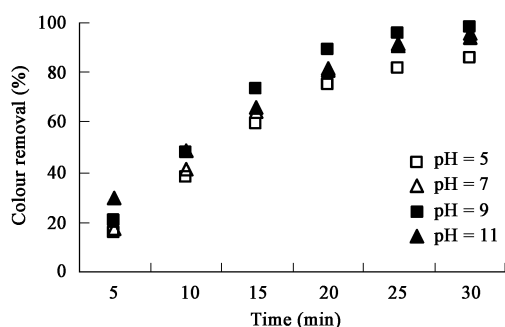


Fig. 3 Colour removal of Blue CL-BR dye by ozone at various pH.

Thus it can be concluded that high initial pH could improve decolorization of dye solutions (Gould and Groff, 1987; Alpin and Waite, 2000).

Following the determination of optimal pH in terms of colour removal the ozone experiments were repeated with O_3 alone, $\text{O}_3/\text{H}_2\text{O}_2$ and O_3 /bleach wastewater. Ozonation alone resulted in colour removal of 98% after 30 min ozonation (Fig.4). Initial 20 min ozonation resulted in colour removal of 90% beyond which colour removal was not appreciable (Azbar *et al.*, 2004). It was reported (Azbar *et al.*, 2004) that ozone in the presence of H_2O_2 can produce more hydroxyl radical and is expected to enhance the decolorization rate. Therefore 2.21 mmol/L of H_2O_2 was added to accelerate the production of $\text{OH}\cdot$ radicals to decolorize dye solution. The results demonstrated that there was no appreciable improvement in colour removal by introduction of H_2O_2 . This discrepancy in result may be explained as H_2O_2 is not only a producer of hydroxyl radical but also a scavenger of hydroxyl radical (Bali *et al.*, 2004). $\text{O}_3/\text{H}_2\text{O}_2$ treatment of synthetic dyes also depends on the pH, $\text{O}_3/\text{H}_2\text{O}_2$ ratio, type of the dye and concentration of H_2O_2 . Some researchers (Beltran *et al.*, 1994; Ledakowicz and Gonera, 1999) have reported that the hydrogen peroxide at higher concentrations act as an inhibitor for the radical reaction mostly by reacting with the hydroxyl radicals, although the exact mechanism is still not clear. They have also indicated that there is an optimum hydrogen peroxide concentration above which the rate of pollutant degradation decreases with an increase in the hydrogen peroxide concentration. It should be noted that along with the consideration of the optimum concentrations of hydrogen peroxide or ozone individually, it is important to consider the ratio of ozone to hydrogen peroxide loading also the optimum dosage has to be in the molar ratio of 0.33 ($\text{O}_3/\text{H}_2\text{O}_2$), beyond which there is not much increase in the rate of degradation (Glaze and Kang, 1989). Another crucial factor in deciding the efficacy of the combination technique is the operating pH. Investigators (Arslan *et al.*, 1999; Nelieu *et al.*, 2000) have studied the effect of pH on the degradation rate and reported that higher pH is favourable for the degradation due to the ease of generation of free radicals at higher pH. The initial concentration and type of the dye also affect the rate of degradation, although the concentrations of ozone and hydrogen peroxide may be suitably adjusted so as to

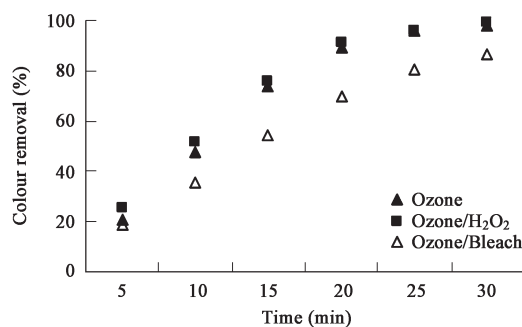


Fig. 4 Colour removal of dye by O_3 alone, $\text{O}_3/\text{H}_2\text{O}_2$ ($\text{H}_2\text{O}_2 = 2.21$ mmol/L) and O_3 /bleach wastewater ($\text{H}_2\text{O}_2 = 2.21$ mmol/L).

treat a particular loading of the pollutant (Echigo *et al.*, 1996; Tanja *et al.*, 2003).

The effect of bleach wastewater on colour removal was also investigated by adding H₂O₂ content of 2.21 mmol/L. The results demonstrated that addition of bleach wastewater showed some reduction (86%) in colour removal efficiency. It is likely that bicarbonate is the principal consumer of the hydroxyl radicals, particularly as relatively high concentrations of bicarbonate are present in bleach water. The scavenging effect of bicarbonate also lies in the fact that it reacts with hydroxyl radicals to generate bicarbonate radicals (HCO₃^{•-}). This acts as a very selective additional oxidation species and which have a lower reaction rate constant than hydroxyl radicals (Oguza *et al.*, 2006).

2.4 Kinetic studies

The decolorization of dissolved dyes in wastewater is a complex process with many reactions which are difficult to distinguished individually. Therefore an approximate kinetic study for the colour removal of dye solution was performed. Several investigations (Bali *et al.*, 2004; Neamtu *et al.*, 2003) reported that most of the colour removal curves obey first-order kinetics. Therefore, all constants were determined based on the first-order kinetics assumption.

$$\ln(C_t/C_0) = -kt \quad (1)$$

where, C₀ is the initial dye concentration, C_t is the concentration of dye at time t, and k is the overall rate constant (time⁻¹).

As illustrated in Fig.5 that a typical plot of linear regression (ln(C_t/C₀)) versus time (t) for the colour removal of Blue CL-BR dye with Fenton, UV/H₂O₂, and O₃/H₂O₂ processes gave straight line. Having this straight-line behaviour, the plot confirms the first order kinetics of these various processes. Their corresponding first-order rate constants (k) calculated from slopes for Blue CL-BR dye are 0.015, 0.052 and 0.093 min⁻¹.

The rates constants determined from graphic method correspond to rate constants (Table 5) measured directly by using equation

$$k = 1/t \ln(C_0/C_t) \quad (2)$$

Decolorization of dyes following first order kinetics was

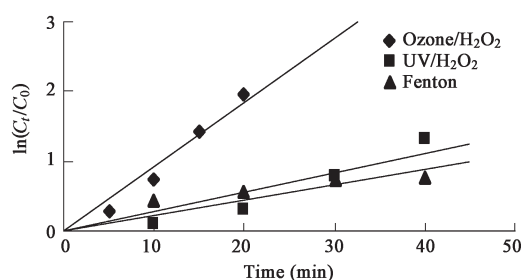


Fig. 5 A typical plot of ln(C_t/C₀) vs. time. UV/H₂O₂ (H₂O₂=2.21 mmol/L) at pH 7; O₃/H₂O₂ (H₂O₂=2.21 mmol/L); Fenton (H₂O₂= 2.21 mmol/L).

Table 5 Determination of rate constant (k) by various methods to show decolorization of dye follow first order reaction kinetics

Process	k (min ⁻¹) (Graphic method)	k (min ⁻¹) (Trial method)	t _{0.5} (min)
Fenton	0.015	0.0206	33.65
UV/H ₂ O ₂	0.052	0.0546	13.33
Ozone/H ₂ O ₂	0.093	0.0958	7.454

also verified by half life time (Table 5), i.e., the time in which initial concentration of dye reduced to its half.

$$t_{0.5} = \ln(2/k) \quad (3)$$

It is evident from Fig.5 that the difference of rates between Fenton and UV/H₂O₂ processes was started in the beginning (initial 10 min duration gave 34% and 27% colour removal respectively), however, soon as reactions proceed Fenton oxidation attain steady state and thus appreciable difference was observed. This might be due to higher colour removal in Fenton process, where at initial stage H₂O₂ doses consumed more rapidly (Azbar *et al.*, 2004). Similarly, initial 10 min process gave 52% and 34% colour removal in O₃/H₂O₂ and Fenton processes, respectively. Higher colour removal in O₃/H₂O₂ may be due to efficient hydroxyl radical generation by ozonation (Azbar *et al.*, 2004). It is evident from comparative study of rate constants of various AOPs for decolorization of Blue CL-BR that O₃/H₂O₂ process is 6.2 times faster than Fenton and 1.8 times from UV/H₂O₂ process.

3 Conclusions

The operating conditions (pH, H₂O₂ (bleach wastewater) and ferrous dose) have an important influence on Fenton oxidation of Blue CL-BR dye. The results indicate that effective system conditions are pH of 3 and H₂O₂/Fe²⁺ molar ratio of 24:1 for bleach wastewater. It also revealed that H₂O₂ (bleach wastewater) was more effective as compared to H₂O₂ analytical grade in Fenton process. It can be concluded that mixing of bleach wastewater and dye effluent in a ratio of 1:2 could be a promising technique for colour removal without addition of any chemical except iron catalyst. Effective decolorization by UV/H₂O₂ and UV/bleach wastewater processes are possible. Complete decolorization of dye is possible by ozonation at optimal pH. The rate constants confirm the colour removal of dye follow first order kinetics.

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