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Original Research

Advanced Oxidative Decolorization of Red Cl-5B: Effects of Dye Concentration, Process Optimization and Reaction Kinetics

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Abstract

Process conditions (dye concentration, pH and oxidant dose) were optimized for UV, O_3, H_2O_2/UV, O_3/UV, H_2O_2/O_3, and H_2O_2/O_3/UV to treat Red Cl-5B dye of varying concentrations (100, 300, and 500 mg/L). Ozonation resulted in color removal of more than 90%, whereas H_2O_2/O_3 showed no advantage over the O_3 alone. However, H_2O_2/UV was found to be very suitable as it gave almost 100% decolorization in a relatively short reaction time. Decolorization rate for all processes was reduced to half when the dye concentration was increased from 100 to 300 mg/l. Comparative study of rate constants revealed that H_2O_2/UV is four times faster than that of UV alone. On the other hand O_3/H_2O_2 is three to four times slower than O_3 alone.

Keywords: Red Cl-5B, advanced oxidation processes, color removal, kinetics, dye concentration

Introduction

Among azo dyes, the most abundantly used are the reactive azo dyes because of their high color fastness, wide color spectrum, ease of application and minimal energy consumption. The presence of these dyes in effluent is considered to be very problematic because of the byproducts (such as aromatic amines), which are not only toxic for aquatic life but also carcinogenic to humans [1]. Hence, the toxicity of effluent renders it difficult to be treated through routine chemical methods [2] and biological techniques [3, 4]. This situation accentuates the need to investigate more rigorous, efficient, cost effective and environmentally friendly treatment methods. Advanced oxidation processes could be a viable option because of their ability to completely decolorize and mineralize the textile effluents in short reaction time and almost no sludge production in the end [5-8], and having the ability to break down the aromatic structures [9]. Results presented by several researchers [11-13] demonstrate that ozone decolorize all the textile dyes except non-soluble disperse and vat dyes that react slowly and take longer. During the ozonation process dyes losses their color by the oxidative cleavage of the chromophores. The cleavage of C=C double bonds and other functional groups will shift the absorption spectra of the molecule out of the visible region [14]. Reaction pH is an important operating parameter that significantly influences the performance of ozonation [15-17]. At high pH, ozone reacts indiscriminately with all organic and inorganic compounds present in the reacting medium [18]. Higher pH of wastewater will result in higher removal of color as well as higher reduction of COD. Ozonation at elevated pH is a promising technique for partial oxidation and rapid decolorization of concentrated exhausted textile wastewater [19]. Moreover, color removal of textile effluent by ozonation is dependent on dye concentration and it would cause more ozone to be consumed [20]. Furthermore, as the applied

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ozone is increased, its treatment efficiency is increased because increasing the ozone dosage enhances the mass transfer due to increased ozone concentration in the liquid phase [21]. This augments color removal and consequently increases the rate constants [21-22]. The addition of hydrogen peroxide to ozone (peroxone) can initiate the decomposition cycle of ozone, resulting in the formation of HO· radicals [23]. The role of hydrogen peroxide in ozone oxidation processes is probably to make the pollutant more susceptible to ozone attack and to aid in the overall oxidation (minor effect). Hydrogen peroxide can dissociate into hydroperoxide anions at elevated pH. H_2O_2 is also a source of highly reactive free ·OH radicals. This conversion occurs due to homolytic cleavage via UV-C photolysis [24]. Significant decolorization of reactive dyes (concentrations ranging from 100-300 mg/L) can be achieved at various UV intensities and contact times [25-27], while H_2O_2 alone is extremely inefficient in removing color of synthetic or raw effluent. The addition of UV accelerates the rate of H_2O_2 photolysis with a corresponding increase in the rate of hydroxyl radical formation [28]. Furthermore, organic molecules that absorb UV energy are also turned into the excited state and are more susceptible to attack. Therefore, the rate at which organic compounds are oxidized is significantly higher than that attained by using UV irradiation alone. Factors that affect color removal by the H_2O_2/UV system include initial color intensity, H_2O_2 concentration, UV-irradiation time and intensity, pH and alkalinity [25, 29]. Ozonation effectiveness is enhanced by applying UV. Consequently, the reactant molecules are raised to a higher energy state and react more rapidly. Moreover, free radicals for use in the reaction are readily hydrolyzed by water. Another benefit of combined use of ozone and UV is a substantial reduction in the amount of ozone required as compared to a system using O_3 alone. In this study, an attempt has been made to determine the effectiveness of UV and AOPs (O_3, H_2O_2/UV, O_3/UV, H_2O_2/O_3, and H_2O_2/O_3/UV) in color removal and to optimize the process conditions such as pH, oxidant dose, and initial dye concentration. Reaction kinetics and comparative study of rate constants has also been carried out to understand the reaction mechanism.

Materials and Methods

Chemicals

Hydrogen per oxide (H_2O_2) used in the experimental work was (35% w/w) of analytical grade from Merck, Germany. For pH adjustment of dye solution, H_2SO_4 of 0.1N, 1N and NaOH of 0.1N and 1N were used. Solutions of different normality were prepared using standard laboratory procedures [30]. Decolorization by AOPs was investigated on the aqueous solution of the Red Cl-5B azo dye. The chemical structure is indicated in Fig. 1. Dye was obtained from Clariant Pakistan. The dye stock solution was prepared by dissolving 1 gram of Red Cl-5B dye in one liter distilled water. Measurements of absorption spectra of the dye solutions irradiated by UV light were made using UV WinLab Software of Perkin Elmer in the wavelength range from 190 nm to 1,110 nm, which exhibits a spectrum of Red Cl-5B main band in the visible region with a maximum absorbance at 542 nm. The integrated absorbance unit (IAU) was then used to determine the sample color [31].

A volume of 300 ml dye solution of various concentrations (100, 300 and 500 mg/l) was used in each experiment and samples of the reaction medium were withdrawn at regular intervals of 10, 20, 30, 40, 50 and 60 min. Color analysis was made by UV visible Spectrophotometer at the wavelength of 541 nm. All experiments were carried out at room temperature.

Ozonation Process

Ozonation was carried out in a bubble column reactor made of Plexiglass. The reactor internal diameter was 3.3 cm. An ozone generator (JQ- 6M PURETECH) was employed to produce ozone from air and bubbled at the bottom of the reactor by means of a diffuser at a rate of 300 mg/h (Fig. 2). The ozone dose varied from 50 to 450 mg. In order to investigate the influence of pH, experiments were conducted at initial pH 3, 6, 8, 9 and 10 without further control during reaction.

UV Photo Reactor

Direct UV irradiation experiments were carried out in a reactor wrapped with aluminum foil in order to enhance UV absorbance. The UV irradiation source was a low-pressure mercury vapor lamp (3SC9 PENRAY UPLAND,

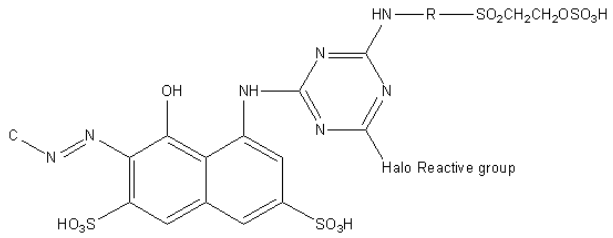

Fig. 1. Molecular Structure of Red Cl-5B. Molecular weight, 1026.41 g/mol; C.I. No. reactive red 241.

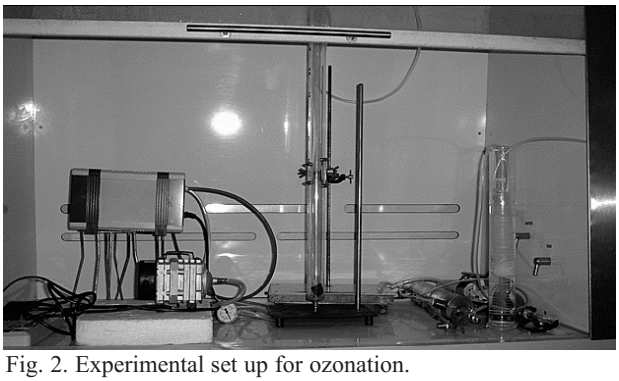

Fig. 2. Experimental set up for ozonation.

USA) with incident light flux of 5 mW/cm^2 and wavelength of 254 nm. The power of the UV lamp was 108.2 watts and positioned in the center of the reactor.

Experimental Set up for H_2O_2/O_3, O_3/UV, H_2O_2/UV, H_2O_2/O_3/UV

For the H_2O_2/O_3 process, H_2O_2 (225 mg) was added in each sample and was ozonated with ozone dose of 75 to 450 mg in bubble column reactor. In O_3/UV process ozonation was carried out for a dose of 50 mg, 100 mg and 150 mg of 100, 300 and 500 mg/l concentrations, respectively. Then dye samples were irradiated by UV 30 to 180W using UV photo reactor. For the H_2O_2/UV process, H_2O_2 (225 mg) was added in each sample and irradiated by UV dose of 30 to 180W with continuous stirring. O_3/H_2O_2/UV was applied only to the 500 mg/l dye concentration. H_2O_2 (225 mg) was added in sample and ozonated for 30 min (150 mg), then ozonated dye solution was irradiated with UV dose of 30 to 180W.

Kinetic Analysis

The color removal of dissolved dyes in wastewater is a complex process involving many reactions that are difficult to differentiate individually. Therefore, approximate kinetics for decolorization of dye solution can be assumed. Several investigators [28, 31-32] have reported that most color removal curves obey the first order kinetic.

The rate equation for a first-order reaction is:

$$\frac{-dC}{dt} = kC \tag{1}$$

...where dC/dt is the rate of change of dye concentration. Negative sign indicates that concentration of dye decreases with time t. k is the rate constant (min^{-1}) and C is the concentration of dye at time t.

If the initial concentration of dye at time $t = 0$ is C_0 and at some later time t, the concentration has fallen to C_t, then the integration of equation (1) between $t = 0$ and $t = t$ gives;

$$\ln\frac{C_t}{C_0} = -kt \tag{2}$$

$$k = \frac{1}{t}\ln\frac{C_0}{C_t} \tag{3}$$

...where:

C_0 = Initial dye concentration at instant $t = 0$.
C_t = Dye concentration at instant t.
k = First order rate constant (min^{-1}).
t = Time of reaction in minutes.

This is known as a kinetic equation for a first-order reaction.

Calculation of Energy Requirement and Cost

Operating costs are directly affected by treatment performances of the applied AOPs. To facilitate comparison of reaction efficiencies, powerful scale-up parameters called EE/O (electrical energy required to remove a pollutant by one order of magnitude in one m^3 of water or wastewater) was employed. EE/O demonstrates a direct link to the electrical efficiency of an advanced oxidation process, independent of the nature of the system and therefore allows for comparison of different AOP technologies. Such figure-of-merit is necessary not only to compare AOP technologies, but also to provide the requisite data for scale-up and economic analysis for comparison with conventional treatment. EE/O values have been calculated by applying the following empirical relationship [33-35].

$$EE/O = \frac{P\,(kW) \times t(\text{min}) \times 1000}{V(L) \times 60\log(C_0/C)}$$

Where:

P = the power input of the UV-lamp or the ozone generator or magnetic stirrer in kW,
t = oxidation time in minutes,
V = the volume of the effluent in liters,
C_0 = initial concentration of contaminant,
C = the final concentration of contaminant.

Results and Discussion

Effect of Ozonation Process

Ozone is considered to be the most feasible decolourization process among the investigated AOPs [36], and a potential alternative for color removal. Fig. 3 represents the effectiveness of ozone alone in the color removal of dye solution of various concentrations. The results demonstrate

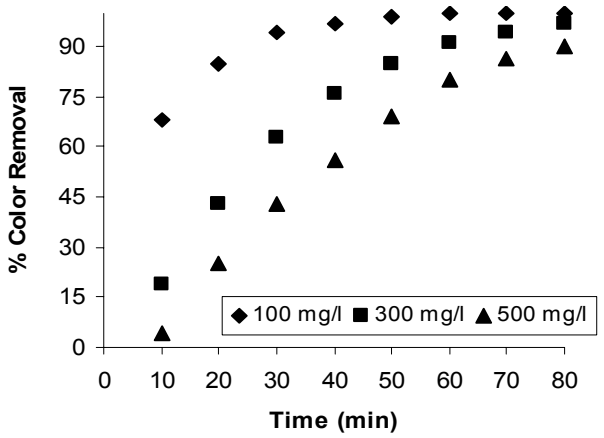

Fig. 3. Influence of ozonation exposure on color removal efficiency of dye solutions of various concentrations.

Table 1. Change in pH during ozonation with time for various dye concentrations.

Ozonztion time	Dye Concentration		
	100 ppm	300 ppm	500 ppm
0.0 min	5.48	4.27	4.11
10 min	5.67	4.82	4.97
20 min	5.81	5.21	5.53
30 min	5.92	5.49	5.97
40 min	ND	6.07	6.21
50 min	ND	6.31	6.43
60 min	ND	6.58	6.71

that decolorization by ozone alone is dependent on the initial dye concentration. Efficiency of ozone decreases with an increase in dye content of the solution. There is more than 92% color removal at 20 minutes ozonation time (100 mg/h ozone dose) when the dye concentration was 100 mg/L. However, effluent of higher initial dye concentration takes much longer to be decolorized [22, 37]. Whereas it requires 70 min. ozonation exposure time (350 mg/h ozone dose) to achieve color removal of 94% and 85% for effluent of dye content of 300 mg/L and 500 mg/L concentrations, respectively [21]. An increase in ozonation time enhances the mass transfer, which results to increased ozone content in liquid phase and enhanced degradation rate constant [31]. However, removal efficiency increases trivially when ozone concentration in the liquid phase approaches its maximum value. This is because the process is controlled by the rate of chemical reaction and any further improvement in ozone mass transfer would have a diminished effect on the observed reaction rate [38]. Another reason may be the change in pH during ozonation that is an increasing trend and approaching 7 (Table 1).

Effect of pH on Ozonation Process

There is an increase in removal efficiency with an increase in the pH of dye solution [22, 35, 39]. Fig. 4 represents the influence of pH on the color removal efficiency of ozone. At constant ozone liquid contact time, the color removal efficiency is a function of pH. At pH 3 and 15 minutes ozonation, the color removal efficiency is 55, 40 and 20% for 100, 300 and 500 mg/L dye concentrations, respectively, which approaches 86, 60 and 30% at pH 9 for the same ozonation time. After an ozonation of 60 min at pH 3, COD removal efficiency is 54, 48 and 36%, and COD removal efficiency increases with an increase in pH of the solution (Table 2). Higher color and COD removal efficiency at pH 9 can best be explained by the fact that in highly alkaline medium, ozone dissociated to hydroperoxide anions. HO· radical is especially important in the decolorization process because of its high oxidation potential of 2.8 eV [37, 40]. Free radicals cleave the conjugated bonds of dye, resulting in decolorization. The color removal efficiency of ozone is reasonably good in slightly acidic environment (pH=6) 80 and 50% for the lower concentrations of 100 and 300 mg/L as well [32]. This points to why molecular ozone cleaves the double bond (-N=N-) of the chromophoric group, and dye structure also reacts readily with molecular ozone via electrophilic insertion or additional reactions, and due to the direct reactivity of ozone molecules toward the chromophoric groups of dyestuffs, decolorization efficiency is achieved at both acidic and neutral pH [41]. Almost complete color removal was achieved for all dye concentrations at an ozonation time of 60, 80 and 90 min for 100, 300 and 500 mg/L dye concentrations, respectively, irrespective of initial pH values. This owes to the increased production of free radicals, which contributed to the change in the acidic environment of the dye solution.

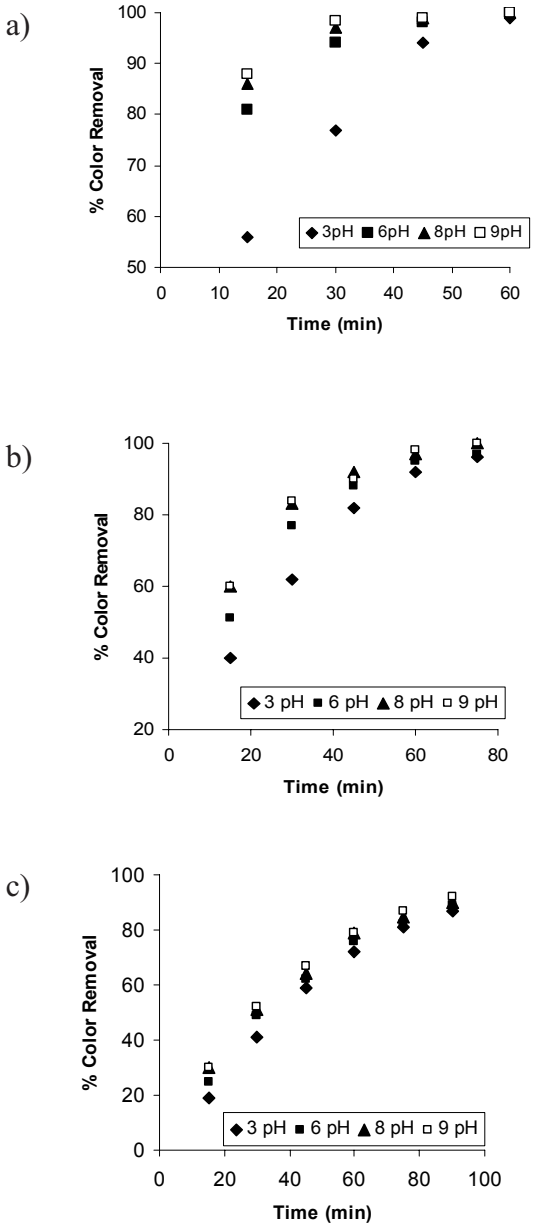

Fig. 4. Effect of initial pH on Ozonation process for removal of color on: (a) 100 mg/L dye, (b) 300 mg/L, (c) 500 mg/L concentrations.

Table 2. Effect of initial pH on Ozonation process on COD removal (%) of Red Cl-5B dye at various concentrations.

pH	100 mg/L			300 mg/L			500 mg/L		
	10 min	30 min	60 min	10 min	30 min	60 min	10 min	30 min	60 min
7	28	43	69	22	40	56	14	38	52
3	14	26	54	11	21	48	11	32	36
6	30	45	72	25	43	71	20	42	72
8	35	49	78	28	47	76	25	48	75
9	39	56	84	31	51	80	28	53	78

Table 3. Effect of UV Irradiation with time on color and COD removal of Red Cl-5B azo dye at various concentrations.

UV Time (min)	Color and COD removal (%) of various dye concentrations								
	100			300			500		
	Color	COD	pH	Color	COD	pH	Color	COD	pH
10	37	43	5.3	10	38	4.1	7	35	3.8
20	54	57	5.1	23	60	3.7	16	50	3.4
30	76	71	4.5	40	66	3.5	27	56	3.2
40	86	79	4.2	49	70	3.4	36	63	3.1
50	94	85	4.1	58	74	3.3	47	69	3.0
60	98	-	4.1	68	76	3.2	57	74	2.9

Effect of UV Irradiation

The performance of UV irradiation in decolorizing the effluent of various concentrations is given in Table 2. UV efficiency appears to be a function of irradiation time and initial dye content. There is an increase in efficiency with increasing UV irradiation time, and the efficiency is substantially decreased by increasing the initial dye concentration of the solution. In the case of effluent with 100 mg/L dye content, about 94% decolorization and 84% COD removal is evident at UV irradiation time of 50 min, whereas the UV efficiency for color and COD removal at the same time was only 58, 74 and 47, 69% in case of effluent with 300 mg/L and 500 mg/L dye concentrations, respectively. It also appeared from the results that UV irradiation time influence pH. Initial pH for 100 mg/L, 300 mg/L and 500 mg/L was 6.3, 4.8 and 3.8, respectively, which was further dropped to 4.1, 3.2 and 2.9 for UV irradiation time of 60 min.

Effect of H_2O_2/O_3, O_3/UV, H_2O_2/UV, H_2O_2/O_3/UV

Fig. 5 represents color removal efficiency of a combined system of ozone and H_2O_2 on the color removal efficiency of dye solutions of various concentrations. Results demonstrate that at 60 min. of ozone exposure there was 90% color removal efficiency for 100 mg/L dye concentration. However, efficiency substantially decreased by increasing the initial dye concentration of the solution and efficiency remain at 70 and 45%, respectively, for 300 and 500 mg/l dye concentration at the same exposure time and H_2O_2 dose. Comparison of these results with color removal efficiency of O_3 alone shows that there was almost 10% decrease in the color removal efficiency of H_2O_2/O_3 at the same ozone exposure time of 60 min. This may be due to

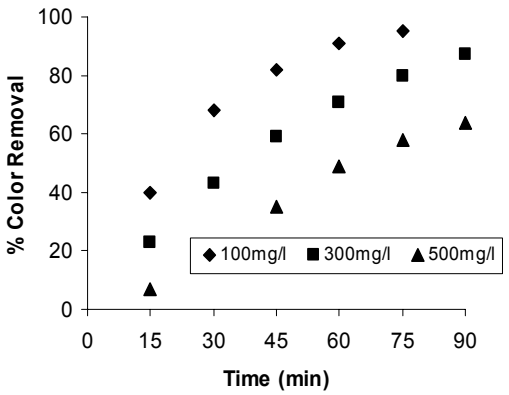

Fig. 5. Effect of H_2O_2/O_3 process on various dye concentrations (H_2O_2 = 2.0 x 10^{-2} mol/l).

the higher initial concentration of H_2O_2 (225 mg), which played the role of scavenger instead of initiator. Fig. 6 represents the effect of combined treatment of O_3/UV. Results demonstrate that O_3/UV combination is dependent on the initial dye concentration; for 100 mg/L concentration of dye solution 70% color removal efficiency was achieved after 10 min ozonation and with the addition of UV irradiation dose of 40 min., color removal efficiency was raised to 96%, while for 300 and 500 mg/L concentration of dye solutions efficiency of the process was 76 and 58%, respectively, after the same irradiation time. Fig. 7 represents the effect of combined treatment of UV with H_2O_2 on color removal efficiency. It appears that the efficiency of the H_2O_2/UV system decreases with an increase in dye content of the solution. There is 100% color removal after 30 min. of UV exposure when the dye concentration was 100 mg/L, whereas an increase in the dye contents of the solution the UV light efficiency for color removal decreases for the same dose which remains at 77 and 37%, respectively, for 300 and 500 mg/L dye concentrations. It is evident that the addition of UV in the system has a significant effect (20% increases for all dye concentrations) on color removal efficiency. Hydrogen peroxide undergoes decomposition, leading to the production of hydroxyl radicals and other species under UV radiation. Therefore, the instantaneous concentration in HO· is higher than expected. Furthermore, the H_2O_2/UV process is more effective in controlling the scavenging effect [42]. Fig. 8 shows the decolorization efficacy of H_2O_2/O_3/UV system for higher (500 mg/L) dye concentrations. It appears that the addition of H_2O_2 in the O_3/UV has accelerated the decomposition of ozone, which resulted in an increased rate of OH· generation. It is evident from the results that O_3/UV was able to furnish only 51% color removal efficiency. But, a significant enhancement (96%) of color removal was achieved by adding 60 min. of UV irradiation. It is obvious from results that a combination of these processes is necessary to achieve the desirable level of treatment [36, 43].

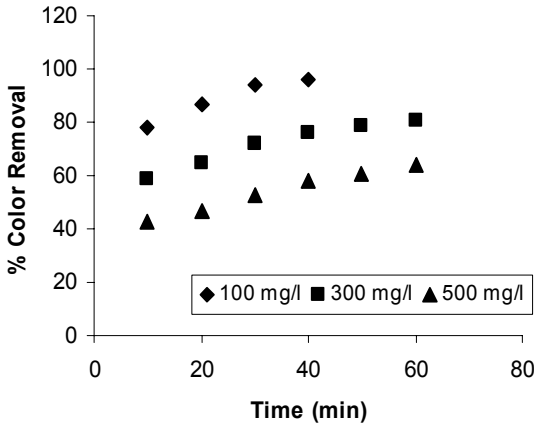

Fig. 6. Effect of O_3/UV process on various dye concentrations (O_3 = 0.3 x 10^{-2} mol/l).

Kinetics

It is apparent from Fig. 9 that the value of reaction rate constant k (min^{-1}) varies significantly for different dye concentrations. In the case of ozonation the value decreases from 0.12 /min to 0.075 and 0.02 for concentrations 100, 300 and 500 mg/L, respectively. A similar trend can be observed for the H_2O_2/UV process, the values for which are 0.16, 0.06 and 0.02/min for the concentrations 100, 300 and 500 mg/L. It is also apparent that H_2O_2/UV is 4 times faster than that of UV alone for all dye concentrations. This implies that the decolorization proceeds much faster by combined processes than UV alone. The reason behind these findings is that Red Cl-5B is photolytically stable under direct UV radiation, as it plays a minor role in the degradation of hydrolyzed Red Cl-5B dye [44], while the addition of H_2O_2 ensures the additional ·OH radicals production that enhances the decolorization reaction rate significantly by rapid destruction of the chromophoric group of dye molecules as through H_2O_2 photolysis. UV light and H_2O_2 are most pronounced for Red Cl-5B in contrast to other aromatic compounds. On the other hand, in the case of O_3 and O_3/H_2O_2, it reveals that there is about four times variation in rate constant k (min^{-1}) values by the O_3 and

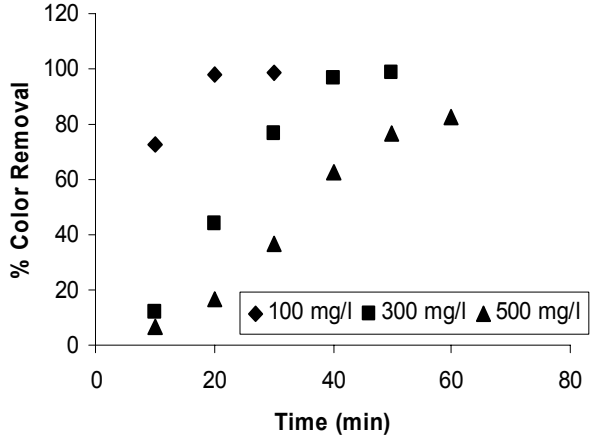

Fig. 7. Effect of H_2O_2/UV on color removal of various dye concentrations (H_2O_2 = 2.0 x 10^{-2} mol/l).

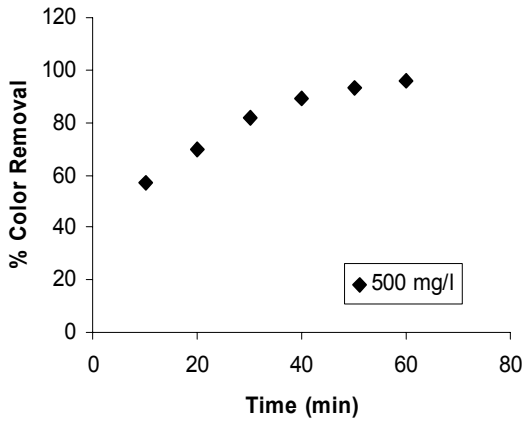

Fig. 8. Effect of H_2O_2/O_3/UV on 500 mg/L dye concentration (H_2O_2 = 2.0 x 10^{-2} mol/l, O_3 = 2.5 x 10^{-2} mol/l).

O_3/H_2O_2 processes. It is clear from the graph that reaction rate constant decline significantly (three to four times) by the addition of H_2O_2. This discrepancy is attributed to the fact that H_2O_2 is not only the producer of hydroxyl radicals but also can act as an ·OH scavenger [25, 28], which is why the expected enhancement in reaction rate by the addition of H_2O_2 did not occur and thus lowers the decolorization rate constant for O_3/H_2O_2.

Several investigators [28, 31-32] have reported that the decolorization process mainly follows first-order kinetics. Kinetics experiments were conducted under optimized reaction conditions for applied AOPs. In all experiments the disappearance of dye is described as first-order reaction kinetics with regard to dye concentration. The corresponding first-order correlation is shown in Fig. 10, as illustrated the typical plot of linear regression (-ln C_t/C_0) verses time for color removal against different advanced oxidation

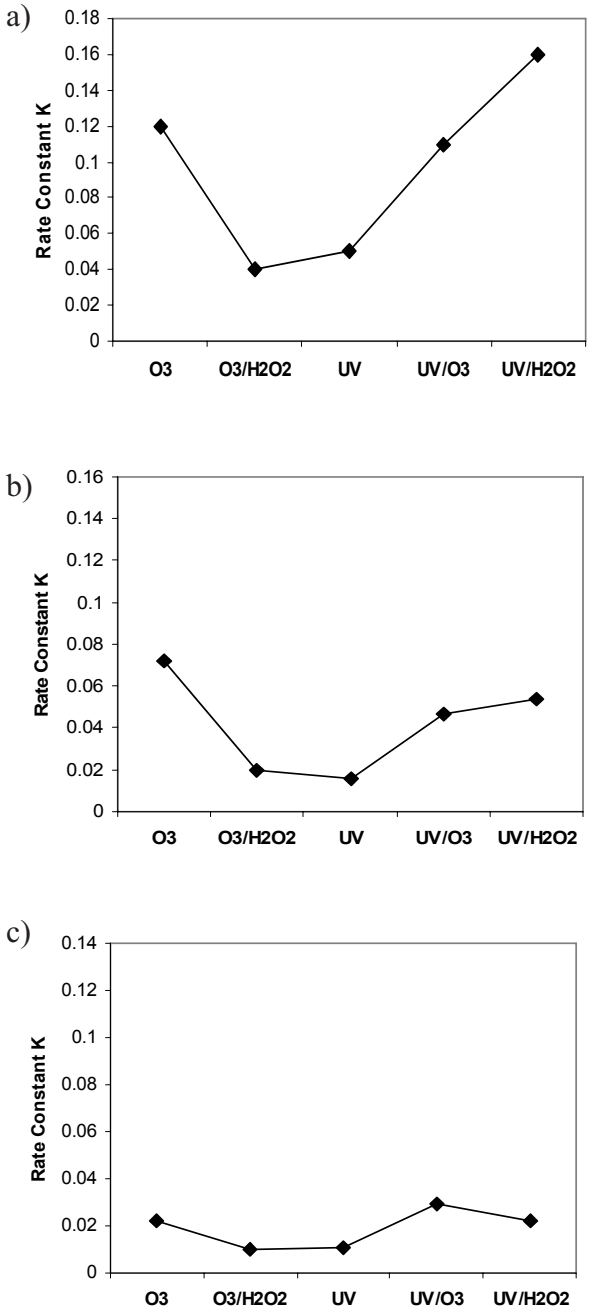

Fig. 9. Comparison of rate constants k (min^{-1}) regarding decolorization of: (a) 100 mg/l, (b) 300mg/l, (c) 500mg/l at optimized process conditions.

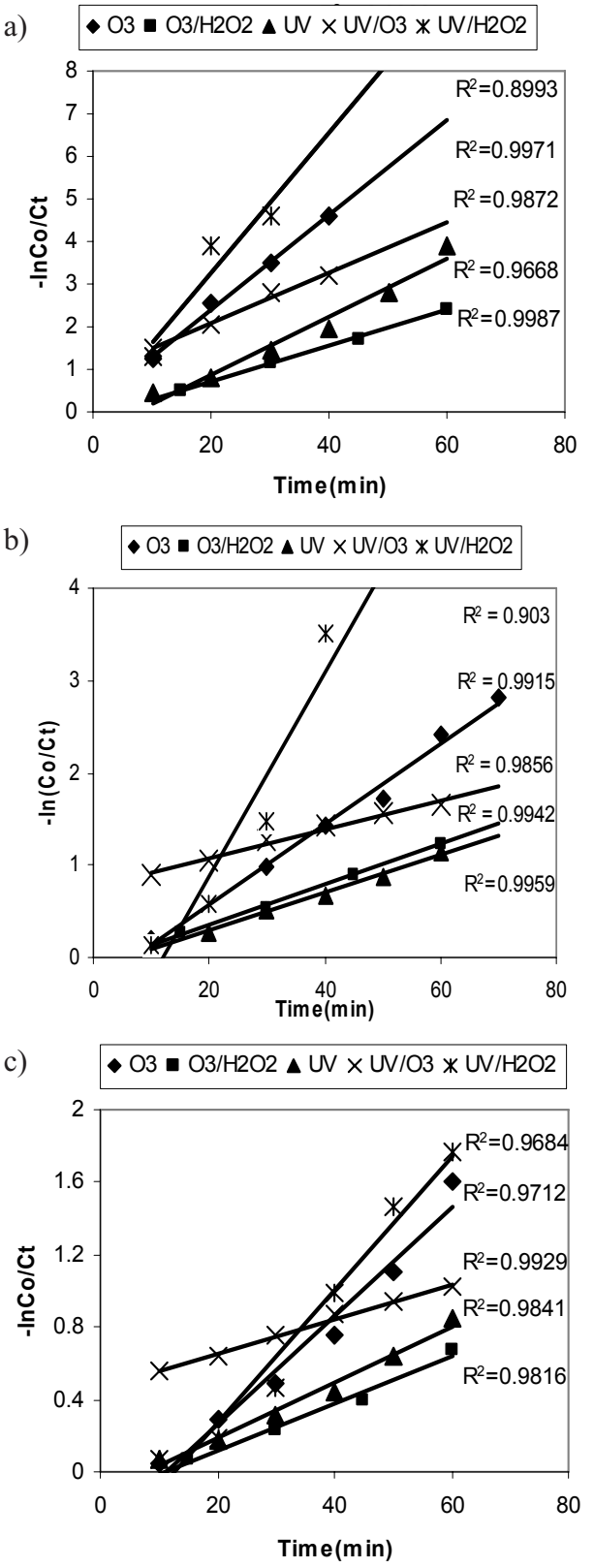

Fig. 10. Rate of decomposition of colour versus time graphs representing 1st order kinetics of various dye concentration (a) 100mg/L (b), 300mg/L, (c) 500mg/L.

Table 4. Comparison of electrical energy requirements by different processes for color removal of various dye concentrations.

Processes	100 mg/L		300 mg/L		500 mg/L	
	Removal %	EE/O (kWh/m^3)	Removal %	EE/O (kWh/m^3)	Removal %	EE/O (kWh/m^3)
O_3	97	20.86	91	48.78	80	65.99
UV	94	21.99	60	753.96	57	982.3
UV/H_2O_2	79	69.5	69	710.9	53	1,103
H_2O_2/O_3	91	46.50	80	53.04	64	146.85
O_3/UV	94	184.7	76	717.52	61	794.81

processes (O_3, O_3/H_2O_2/, UV, O_3/UV and H_2O_2/UV) for different initial dye concentrations in the range 100, 300 and 500 mg/l. It can be observed that the correlation between ln C/C_0 and the irradiation time is linear. This is a typical pseudo first-order reaction plot. The kinetic expression can be presented as follows:

$$\ln C/C_0 = -kt$$

...where: C is the dye concentration at instant t, C_0 the dye concentration at $t = 0$, k the pseudo first-order rate constant (min^{-1}) and t the time of reaction (min).

The correlation coefficient that can explain the fitting extent of the function equation and experimental data is presented by R^2. In all cases the values of these R^2 are almost greater than 0.9, which confirms the goodness of the assumed kinetics for O_3, O_3/H_2O_2, UV, O_3/UV, and H_2O_2/UV decolorization reactions of Red Cl-5B. It is also obvious from the results (Fig. 10) that decolorization rates are initially (for the first ten minutes) slow and then remained steady or on an increasing trend, because initially OH· radicals converted the substrate into the readily decomposable intermediates in the first phase [45]. In the second phase, these intermediates were decomposed to almost stable end products, keeping the rates stable or increasing in the end.

The decolorization rate also depends on Red Cl-5B initial concentration. Increasing the dye concentration logically must enhance the probability of collision between Red Cl-5B molecules and oxidizing species (·OH), leading to an increase in the discoloration rate. However, in our case the decolorization rate for almost all processes reduces to half by increasing the dye concentration. The reason for this might be the parameter that is assumed to remain constant throughout the reaction changes (ozone or hydrogen peroxide concentration) so that the overall rate constant (k') decreases and rises in concentration to induce a rise of the internal optical density. An inert filter effect [46] on the solution becomes more and more impermeable to UV irradiation. Hydrogen peroxide can only then be irradiated by a smaller portion of UV light. As the rate of photolysis of H_2O_2 directly depends on the fraction of incident light absorbed by H_2O_2 molecules, the ·OH formation rate slows down and the rate of decolorization of dye decreases.

Comparison of Energy Requirements for Decolorization of Red Cl-5B Textile Azo Dye Solution with AOPs

In an energy-intense treatment, processes such as ozone and UV-induced photochemical processes (UV, UV/H_2O_2, O_3/UV, O_3/H_2O_2) are key design variables, i.e., exposure to UV radiation and order of magnitude of contaminant concentration removal combined into a single function, the so-called electrical energy per order of pollutant removal (EE/O). The EE/O is a powerful scale-up parameter and a measure of the treatment rates obtained in a fixed volume of contaminated water as a function of the applied specific energy [33, 34]. It is apparent that the ozonation process proved to be the best option in terms of energy consumption and decolorization of dye solution. Energy consumption and cost of the treatment process increase with an increased in initial dye concentrations, and as well as an increase in the applied dose.

Conclusions

From results of this study the following conclusions can be drawn.

- All AOPs used in this study appear to be capable of decolorizing Red Cl-5B to a reasonable level within a feasible reaction time ranging from 10 to 60 min. However, the efficiency of AOPs was gradually decreased with an increase in the initial dye concentration. In the case of UV alone this effect was more pronounced for the higher concentrations as the dye proved to be resistant to direct photolysis of the dye stuff in the effluent, and for higher decolorization a longer process time was required.
- The ozonation process appeared to be promising for decolorization of Red Cl-5B synthetic dye solution and resulted in more than 90% color removal and 80% COD removal for all the selected concentrations. It is also evident from the result that when treatment time and

applied ozone dose is increased, its treatment efficiency is increased and the decolorization time increases with increasing initial dye content of the solution. The ozonation process worked well both in acidic and basic environments. However, overall efficiency of the ozonatin process was slightly better at alkaline pH. The O_3/H_2O_2 combination has no advantage over direct O_3 applications.

- H_2O_2/UV was also found to be a suitable and promising treatment method as compared to other AOPs. It gave complete decolorization of Red Cl-5B in a relatively short reaction time, i.e. 100% in 30 and 50 min for the dye concentrations of 100 and 300 mg/L, respectively.
- In all experiments the disappearance of dye is described as a first-order kinetics reaction for all advanced oxidation processes and for different initial dye concentrations in the range 100, 300 and 500 mg/L. In all cases R^2 values are almost greater than 0.9, which confirms the goodness of the assumed kinetics for O_3, O_3/H_2O_2/, UV, O_3/UV, and H_2O_2/UV decolorization reactions of Red Cl-5B. It is also obvious that decolorization rates are initially (for the first ten minutes) slow and then remained steady or on increasing trend. Reaction rate depends on Red Cl-5B initial concentration. Increasing the dye concentration from 100 to 300 mg/L, the decolorization rate for almost all processes is reduced to half.
- Comparative study of rate constants of various treatment processes for decolorization of Red Cl-5B revealed that H_2O_2/UV is 4 times faster than that of UV alone. On the other hand, O_3/H_2O_2 is three to four times slower than O_3 alone (because of hydrogen peroxide overdosing). It is also apparent that for UV and H_2O_2/UV processes, the increase in dye concentration has a detrimental effect on rate constant k (min^{-1}) values, while O_3/UV is not affected by the dye concentration and it is the fastest process even for the highest concentration (500 mg/L) as compared to other used processes. An increase in dye concentration increases the opacity of the solution, which hinders UV to furnish its efficiency while in O_3/UV process UV followed the O_3; prior application of O_3 decreased the murkiness to deliver UV its maximum efficiency.

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