R&D NOTE

Decolorization of RR-120 Dye Using Ozone and Ozone/UV in a Semi-Batch Reactor

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Treatability of RR-120 aqueous dye solutions using O_3 and O_3/UV was studied in a bench scale set-up. Reduction in colour and chemical oxygen demand (COD) under various pH and initial dye concentrations were investigated. Pseudo first order reaction rate was satisfactorily used for kinetic interpretations in destruction of the dye. The results showed that decolorization with O_3 was faster at neutral pH values. While use of UV had a small effect on ozonation at low pH values, UV radiation had a considerable effect at pH values of 7 and above. It was found that ozone utilization efficiency of higher than 95% could be attained in the experimental set up.

On a étudié la possibilité de traitement de solutions aqueuses de colorant RR-120 à l'aide d'O_3 et O_3/UV dans un banc d'essai. La réduction de la demande chimique en oxygène (DCO) et en colorant a été étudiée pour différentes concentrations initiales de colorant. La vitesse de réaction du pseudo-premier ordre a été utilisée avec succès pour les interprétations cinétiques de la destruction du colorant. Les résultats montrent que la décoloration avec l'O_3 est plus rapide à des valeurs de pH neutres. Alors que le recours aux UV a un faible effet sur l'ozonation à de faibles valeurs de pH, la radiation par UV a un effet considérable à des valeurs de pH de 7 et au-dessus. On a trouvé qu'une efficacité d'utilisation de l'ozone supérieure à 95% pouvait être atteinte dans l'installation expérimentale.

Keywords: ozone, UV, RR-120, decolorization, ozone utalization efficiency.

Dye manufacturing, textile dyeing and finishing processes generate a large amount of wastewater. Dyes, some mordants, sizing agents and dyeing aids are deep in colour and highly pollutant (Hsu et al., 2001). Treatment of wastewater from textile dyeing is an environmental problem that has received considerable attention. Effluent from textile processing is often discharged into municipal sewage treatment plants or waterways (Aplin and Waite, 2000). Textile dyes are not easily biodegradable, and consequently sewage treatment removes only a small amount of certain types of dyes by adsorption and settling but it fails to remove reactive dyes (Aplin and Waite, 2000). Reactive dyes are one of the most widely used classes of dyes, accounting for almost 32% by quantity and about 43% by value of world consumption of dyes by cellulosic fibres in 1993 (Holme, 1997). They also have lower fixation compared to other classes of dyes. Reactive dye that remains in the effluent has been hydrolyzed during the dyeing process and therefore cannot be reused (Cooper, 1993). The reactive dyeing process produces two different waste streams. The initial concentrated dye bath effluent with a temperature of above 50°C, has a pH of at least 11 (Grovers et al., 1998) and contains up to 0.6 g/L unfixed dye and about 40–80 g/L of salt (NaCl or Na_2SO_4) and small quantities of other additives.

In most countries national standards place strict restrictions on the colour of wastewater. There are several possible methods for treating wastewater from textile dyeing (Hazel, 1995). Some methods such as coagulation, adsorption and nanofiltration remove dyes from wastewater and produce a secondary waste stream that requires further treatment or disposal. On the other hand, other methods like sequential anaerobic/aerobic treatment or aerobic treatment using fungi and advanced oxidation processes can degrade dyes in the effluent with a good efficiency.

Advanced oxidation processes (AOPs) are a group of processes that are based on the generation of hydroxyl radicals, which are highly reactive oxidants. AOPs can oxidize a wide range of compounds that are otherwise difficult to degrade. The five AOPs that have been most widely studied are based on reaction with ozone, O_3/UV, H_2O_2/UV, Fenton's reagent (Fe^{2+}/H_2O_2) and catalytic (e.g. TiO_2) UV radiation.

Ozone processing is a promising alternative. Ozone is an extremely strong oxidant. It can undergo self-decomposition in an aqueous medium to form hydroxyl free radicals that have a stronger oxidation capacity (Staehelin and Hoigene, 1985; Sotelo et al., 1987). Therefore, ozone has found many applications. In some industrial applications, it has been widely accepted as an effective disinfectant and a chemical oxidant (Gould and Weber, 1976; Beltran et al., 1993; Perkins et al., 1995). Studies that have been reported on the reaction between ozone and dye (Saunders et al., 1983; Benitez et al., 1993; Gahr et al., 1994) indicate that ozone has an excellent decolorizing capability. In studies of the ozonation of dye solutions, Gahr et al. (1994) found that dye degradation was faster at lower initial concentrations, and that pH decreased

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**Author to whom correspondence may be addressed. E-mail address: soltan@sut.ac.ir* during the reaction time. However, industrial applications have been limited due to low utilization efficiency of ozone and its high production cost (Hsu et al., 2001). The low utilization efficiency of ozone can be improved by increasing the retention time of ozone gas in an aqueous solution (Hsu et al., 2001) or by using an effective contacting scheme. To increase ozone utilization efficiency, an effective venturi injection system has been utilized in this work. As an effective ozone injection method, this system has ozone utilization efficiency (OUE) of above 95%. An improvement in ozone utilization efficiency without any additional utilities can be a major advantage in cost reduction. In this work, decolorization of a reactive red dye solution has been studied using an efficient O_3 oxidation system. The effect of UV radiation on performance of ozone oxidation system in decolorization has also been investigated. Experimental results showed that, at various pH values and initial dye concentrations, the ozone utilization efficiency remains above 95%. This can reduce cost of application of ozone effectively.

Experimental

C.I. Reactive Red 120 (RR-120) was provided by Chinas chemicals company. Its maximum absorbance occurs at 284.6 nm. The synthetic wastewater was prepared by dissolving the required amounts (200 to 500 ± 30 mg/L) of RR-120 in distilled water. The pH was adjusted to 3.0, 6.0, 8.0 and 11.0 (±0.2), by using buffer solutions.

Schematic diagram of the experimental apparatus is shown in Figure 1. Pure oxygen was fed to ozone generator (Ozomatic Lab 802, Wedeco, Germany) with 4 g/h capacity. Ozone concentration (measured by BMT, Press version) and volumetric flow rate were monitored. UV radiation was supplied with one 30-watt low-pressure mercury lamp with radiation wavelength of 253.7 nm.

For all experiments, the ozone generator was adjusted at 2 g/h ozone generation capacity. At the beginning of each run, 5.5 L of dye solution with the desired concentration and pH was transferred into the reactor. All experiments were conducted at room temperature in a water- jacketed reactor. Ozone was injected into the dye solution through a standard ozone injector (Lab 802) using a stainless steel circulation pump (CRN2-30). The flow rate and concentration of the ozone gas were 50 NL/h and 40 g/m^3, respectively.

To measure excess ozone in outlet gas stream, a KI trap was used. Excess ozone reacted with KI which was then titrated with Na_2SO_4 solution. Each experiment was repeated twice and samples were collected at an approximate 5-min based intervals. Each sample was divided into three sub-samples that were analyzed separately. As soon as the samples were taken from the reactor, their colour values were determined using a UV/Vis spectrophotometer (Lambda 2- Perkin Elmer) at 284.6 nm. An Eco8 COD thermal reactor (VELP Scientifica, Italy) was employed to digest oxidizable organic compounds at 150°C for chemical oxygen demand (COD) analyses.

Ozone utilization efficiency is defined by Equation (1), as suggested by Hsu and Hung (2001).

$$OUE\% = \frac{O_{3_{in}} - O_{3_{out}}}{O_{3_{in}}} \times 100 \qquad (1)$$

OUE values are based on 90% decolorization of the dye solution in which a light colour can be observed. O_{3in} and O_{3out} are the total input and output ozone measured in gas phase.

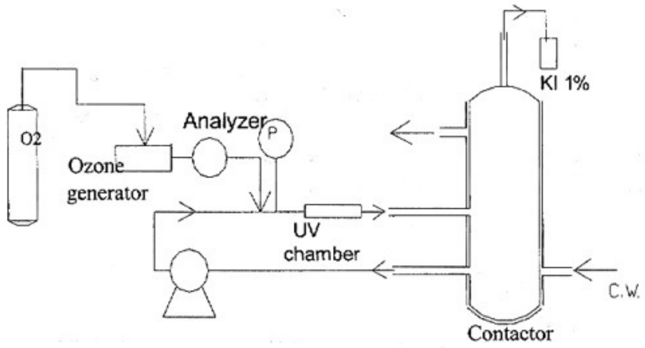

Figure 1. Schematic diagram of the experimental apparatus.

Results and Discussion

Kinetic Analysis for Decolorization

Reaction between dye and ozone is a relatively fast reaction, and ozone is consumed almost completely in the liquid film (Perkins et al., 1995; Hsu et al., 2001). The kinetic model of decolorization reaction can be assumed as a pseudo first order reaction (Perkins et al., 1995). In this work, decolorization reaction of RR-120 is studied in semi-batch reactor (batch with respect to the dye solution). The pseudo first order expression is assumed to describe the heterogeneous ozonation of the dye solution. Furthermore, the ozone input concentration is constant and no residual ozone remains in the bulk liquid (Perkins et al., 1995; Hsu et al., 2001). In addition, ozone utilization efficiency is high in this pilot system (above 90%). Hence, an almost constant ozone influence, which can be incorporated into the overall reaction rate constant (*k*) can be considered. The rate constant of the pseudo first order reaction can be calculated by Equation (2).

$$-Ln\left(\frac{C}{C_0}\right) = kt \qquad (2)$$

in which *C* and C_0 are concentration and initial concentration of dye in mg/L, *k* is the reaction rate constant (min^{-1}) and t is ozonation time (min).

Figure 2 shows a plot of $-Ln\,(C/C_0)$ vs. reaction time for a typical reaction condition of initial dye concentration of 500 mg/L and different pH values in O_3 oxidation system. It can be observed that the data points fall on a reasonably straight line. Based on examination of all reaction data, it was assumed that oxidation of RR-120 reaction rate follows a pseudo first order kinetics. Experimental data also revealed that for reaction of oxidation with O_3/UV, assumption of pseudo first order kinetics was valid.

Comparison of Oxidation with O_3 and O_3/UV

In Figure 3, profile of concentration of RR-120 dye with time is shown for oxidation with O_3 and O_3/UV at pH of 3. The figure shows that adding UV radiation to O_3 does not have any detectable effect on the rate of destruction of the dye. At higher pH values, ozone decomposition and production of free hydroxyl radical is encouraged. Therefore, application of UV radiation along with ozone increases rate of oxidation reaction compared to oxidation with O_3 alone at pH values of

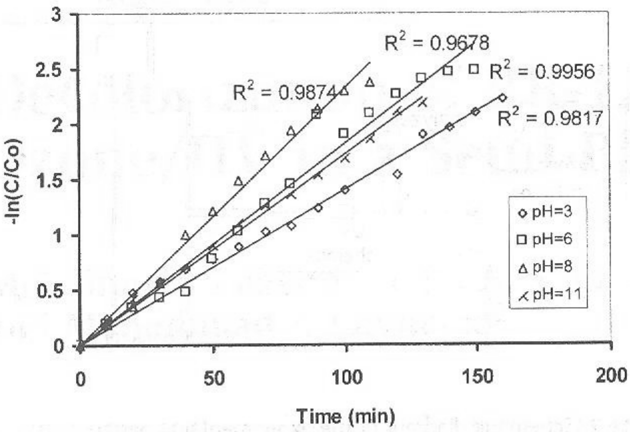

Figure 2. Plot of - *Ln* (C/C_0) vs. reaction time, O_3 oxidation system, C_0 = 500 mg/L.

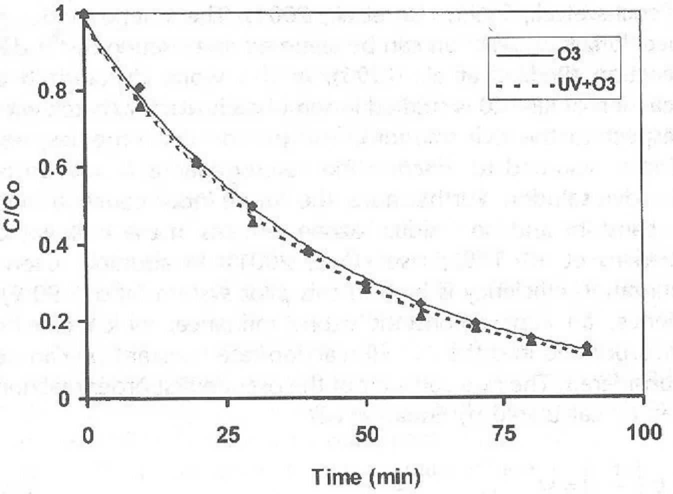

Figure 3. Effect of adding UV radiation to ozone oxidation, pH = 3, C_0 = 200 mg/L.

7 and above. Figure 4 shows that for solution with the initial dye concentration of 200 mg/L and pH of 11, the time for 50% destruction of dye with O_3 is 26 min, whereas combined O_3 and UV bring about 50% destruction in 18 min. That is, addition of UV to ozone reduces the 50% destruction time by about 30% at pH of 11.

Decolorization Time of Dye

Figures 5 and 6 depict the decolorization of RR-120 with the initial dye concentration of 200 mg/L at various pH values for O_3 and O_3/UV oxidation systems, respectively. The figures indicate that during oxidation by both O_3 and O_3/UV, the colour value of RR-120 is reduced exponentially. The decolorization profiles of RR-120 were approximately the same in other initial dye concentrations. At all pH values, the dye molecules are destroyed by direct ozone and/or hydroxyl free radicals mechanisms. As the decolorization process continues various intermediate products are generated and accumulated to such an extent that the difference in reaction rate becomes significant at different pH values. After that, the decolorization rates are slower than the initial rate for all pH values. This is because most

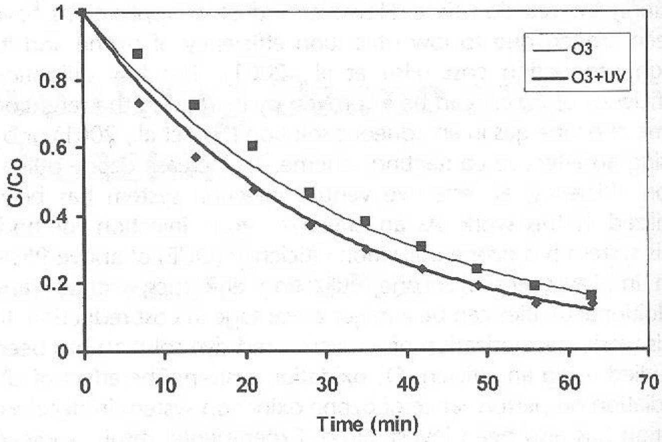

Figure 4. Effect of adding UV radiation to ozone oxidation, C_0 = 300 mg/L, pH = 11.

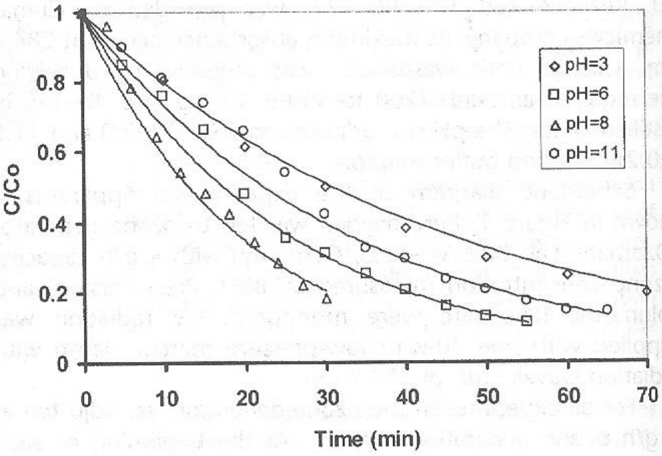

Figure 5. Effect of pH on decolorization of RR-120, O_3 oxidation system, C_0 = 200 mg/L.

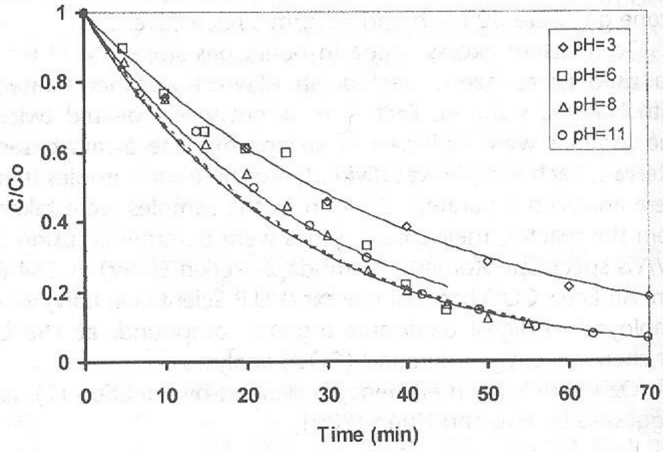

Figure 6. Effect of pH on decolorization of RR-120, O_3/UV oxidation system, C_0 = 200 mg/L.

Table 1. Experimental results for oxidation of RR-120 with O_3 and O_3/UV.

pH	C_0 (mg/L)	OUE% O_3	OUE% O_3/UV	k (min^{-1}) O_3	k (min^{-1}) O_3/UV
3	200 ± 30	97.01	97.03	0.0230	0.0245
6	200 ± 30	97.10	96.85	0.0344	0.0363
8	200 ± 30	97.30	97.22	0.0390	0.0410
11	200 ± 30	97.17	97.05	0.0312	0.0399
8	300 ± 30	98.03	98.41	0.0314	0.0330
8	400 ± 30	98.10	98.77	0.026	0.0274
8	500 ± 30	98.71	99.2	0.0207	0.0232

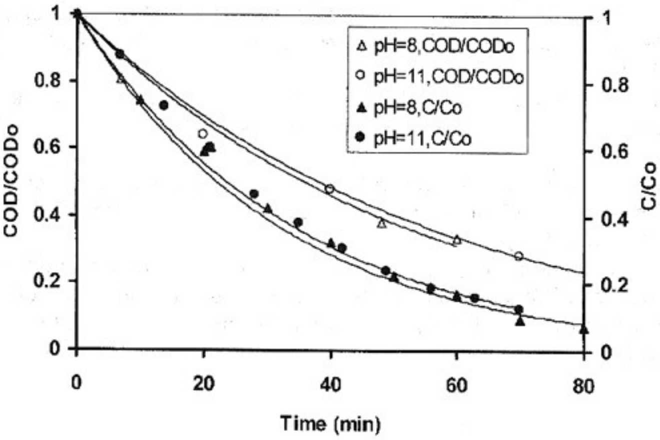

Figure 7. Comparison of the rate of decolorization and mineralization in O_3 oxidation system, C_0 = 300 mg/L.

dye molecules are destroyed and the persistent intermediate products become the primary substrates for ozone molecules and hydroxyl free radicals. The figures also indicate that decolorization at range of low pH value (e.g. pH of 3) has the lowest rate. At low pH, decolorization is favored by a more direct ozone attack (molecular mechanism) whereas at higher pH values ozone decomposition is accelerated primarily by hydroxyl free radicals, thus a less selective hydroxyl attack on dye molecules occurs. At near neutral pH (pH of 6 and 8), the combined effect of free radical and molecular reaction of oxidant agents with dye greatly enhances the rate of decolorizatioin. Figures 5 shows that reaction rate increases from acidic conditions, reaching maximum at neutral pH values and then a slight decrease at higher pH values is observed. This trend is observed for other initial concentrations. The maximum decolorization rate is observed at neutral pH values for O_3 oxidation system. It is also interesting to note that the rate of decolorization for pH values of 6 and 11 have a little difference in the initial dye concentrations.

The colour destruction rate at pH values of 7 and higher increases with adding UV to ozone oxidation system. Also, it was observed that there was a considerable enhancement in dye destruction at pH value of 11 owing to higher production of free hydroxyl radicals. The rate of decolorization for pH values of 8 and 11 are almost identical because of higher production of hydroxyl free radicals at pH of 11.

Table 1 summarizes the results of the decolorization of the RR-120 dye with O_3 and O_3/UV at different initial dye concentrations and pH values. Table 1 shows that for all pH values and initial dye concentrations, OUE is higher than 95%, i.e. the amount of escaped ozone in outlet gas stream is negligible.

According to Table 1, the decoloration rates are higher at lower initial dye concentrations during both O_3 and O_3/UV oxidation. This confirms the results of the previous reports (Gahr et al., 1994). This is due to production of less intermediates at lower initial dye concentrations. Moreover, the table shows that the rate constants for O_3/UV oxidation are higher than O_3 oxidation system. At high pH values the UV radiation has stronger encouraging effect on O_3 oxidation system.

COD Elimination

Figure 7 shows the normalized profiles of COD and dye concentration of RR-120 with time at pH values of 8 and 11 (O_3 oxidation system and C_0 = 300 mg/L). Comparison of variations of normalized COD and concentration with time reveals that despite an almost identical trend for reduction of both colour and COD in O_3 oxidation system, the time required for mineralization is approximately 1.5 times more than that of decoloration. Figure 7 shows that mineralization process is slower than decolorization due to presence of intermediate products.

Ozone Utilization Efficiency

Ozone utilization efficiency for decolorization of RR-120 at various pH values and different initial dye concentrations is presented in Table 1. As Table 1 shows ozone utilization efficiencies are above 95% and more or less constant at various pH values. From the data shown in Table 1, it can be concluded that OUE increases with increasing initial dye concentration. OUE for oxidation with O_3/UV is also above 95%. The OUE in O_3/UV process is slightly higher than that for oxidation with O_3. This increase in OUE is most likely due to the increase in production of hydroxyl free radicals in O_3/UV system compared to O_3 system.

Conclusions

This work showed that both decolorization and mineralization processes of RR-120 dye occur during oxidation by O_3 and O_3/UV systems. The pseudo first order reaction rate constant were determined for R-1209 destruction in O_3 and O_3/UV systems at different initial dye concentrations and pH values. Because of production of intermediates, the decolorization rate was about 1.5 times the mineralization rate. The results also showed that at low pH values (pH of 3) the decolorization rate constant had the lowest value and adding UV had no detectable effect on RR-120 decolorization rate. At near neutral pH values (pH of 8) decolorization was fastest in both oxidation systems and a considerable increase in decolorization at higher pH values (pH of 11) in O_3/UV system was observed. Approximately 65 to 115 min contact time was required for a 90% decolorization at concentrations of between 200 to 500 ± 30 mg/L, 2 g/h ozone, at different pH values and room temperature in the experimental set up. The ozone utilization efficiency was above 95% at all pH values and initial dye concentrations (in the range of 200 to 500 mg/L). Adding UV could also accelerate decolorization and mineralization especially at pH values of 7 and above. Hence, ozone treatment of various dye solutions can be faster, more efficient and economical by adding UV and an effective ozone injection system.

Nomenclature

C_0	initial dye concentration, (mg/L)
C	dye concentration, (mg/L)
COD	chemical oxygen demand, (mg/L)
k	first order reaction rate constant, (min^{-1})
OUE	ozone utilization efficiency
t	time, (min)

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