

Degradation of Reactive Red 198 (RR198) from aqueous solutions by advanced oxidation processes (AOPS): O₃, H₂O₂/O₃ and H₂O₂/ultrasonic

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Received March 24, 2016; Accepted August 8, 2016

The aim of this study was to investigate the degradation of an azo dye, reactive red 198 (RR198), by ozone, H₂O₂/O₃, H₂O₂/ultrasonic and combination of O₃/H₂O₂/ultrasonic from aqueous solutions. The effects of ozone, hydrogen peroxide doses, initial dye concentration, ultrasonic power and solution pH were studied on the degradation of RR198. The concentration of RR 198 was determined by UV–visible spectrophotometer (DR 5000 Hach) at its maximum absorption wavelength of 518 nm. The measurement of chemical oxygen demand (COD) carried out with a standard potassium dichromate oxidation method. The results showed that the degradation rate was increased by increasing H₂O₂ concentration. The optimum H₂O₂ concentration was obtained in the range of 0.03 mM at dye concentration of 200 mg/L. Alkaline pH, and 125 W ultrasonic power were favored in the color and COD removal. Moreover, compared with ozone and peroxone, the O₃/H₂O₂/ultrasonic process could achieve a higher color and COD removal at the same reaction time. Pseudo-first order kinetics with respect to dyestuffs concentrations was found to fit all the experimental data. H₂O₂/ultrasonic process has negligible effect on removal of COD compare to other process (>5%). Ultrasonic was ineffective in activation of H₂O₂ for degradation of RR198. These findings show that oxidation by O₃/H₂O₂/ultrasonic is a promising alternative for the treatment of RR198 containing solution as a recalcitrant pollutant.

Keywords: Reactive red 198, COD, Ultrasonic, Dye removal

INTRODUCTION

Synthetic dyes comprise an important part of industrial waste waters, as they are discharged in abundance by many industries [1]. Due to toxicity on aquatic organisms, disruption of conventional wastewater treatment system performance [2, 3] and the impact on the environment these dyes are in a great concern [1]. Depending on forms of dyes and auxiliary chemicals, Textile wastewaters are strongly colored and contain high amounts of organic matter [4] Among the organic dyes, azo dyes due to complex structure are resistant to biodegradation and are often toxic, carcinogenic and mutagenic [2, 5-7]. Thus, it is important to treat these dyes with appropriate methods before discharging it

in to the environment [3, 8]. Dye removal from industrial wastewater using various methods such as coagulation, flocculation, biological treatment [9], electro chemical oxidation [10] and adsorption [11, 12] have been proved to be technically feasible. Therefore, treatment of textile wastewaters by conventional methods such as biological [13], physical and chemical processes or a combination of each is inefficient for dye removal [14]. Because these methods produced sludge [8] and only changes phase from wastewater to biomass or sludge [9] which are subsequently followed by other environmental problems.

Advanced oxidation processes (AOPs) are another effective treatment method in treating persistent compounds [15]. High efficacy, low cost and simplicity are characteristics that AOPs have

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high acceptance as a new technique for treating the dye-containing wastewater [16]. Furthermore, AOPs can completely mineralized the dye compounds [17]. This methodology is based on the generation of highly reactive radicals such as $\bullet\text{OH}$ produced *in situ*. These molecules are non-selective oxidants and afterward causes a sequence of reactions to destroy the organic compounds into inorganic final products and/or, in most of the cases, to less harmful substances [1,9,18]. Ultrasonic irradiation, ultraviolet (UV) irradiation/ H_2O_2 , Fenton oxidation, $\text{O}_3/\text{H}_2\text{O}_2$ and ozonation can be mentioned as the hydroxyl radical-based advanced oxidation processes (HR-AOPs) [19]. Ozone is a strong oxidant ($E_0 = 2.07 \text{ V}$) and used as a principal component in Most of AOPs [9, 20].

Some of the AOPs such as Fenton's reagent and UV/ H_2O_2 are H_2O_2 based. H_2O_2 has non-selective reactivity for most recalcitrant organic compound and high oxidation potential ($E_0 = 1.78 \text{ V}$) [21]. Activation of H_2O_2 can be performed by application of iron or UV to yield the radical $\bullet\text{OH}$ [22]. Also, sonication of hydrogen peroxide can generate hydroxyl radicals in aqueous solutions [23]. Some research's showed the feasibility of the ultrasonic (US) assisted hydrogen peroxide oxidation process for decolonization of malachite green (24) and Rhodamine B [23] from aqueous solutions. Nonetheless, the literature on application of sonication of hydrogen peroxide for Reactive Red

198 dyes degradation in textile wastewater is limited.

Therefore, in the present work, the application of several AOP including single ozonation, $\text{O}_3/\text{H}_2\text{O}_2$, ultrasonic/ H_2O_2 and combination of $\text{O}_3/\text{H}_2\text{O}_2$ /ultrasonic for degradation of Reactive Red 198 was investigated. Furthermore activation of hydrogen peroxide by Ultrasonic irradiation for removal of Reactive Red 198 dyes was evaluated. The main operational variables of the AOP including the pH, the doses of H_2O_2 , and O_3 , ultrasonic frequency and temperature for the degradation of Reactive Red 198 was studied. Also, kinetics study for each methods were conducted.

2. MATERIALS AND METHODS

Chemicals

Reactive Red 198 (RR198) was purchased from Alvan Sabet Co (Iran). The chemical structure and characteristics of the dye are presented in Fig 1 and Table 1, respectively. NaOH and H_2SO_4 (analytical grade), hydrogen peroxide (H_2O_2 , 30%), potassium iodide (KI, 99.0%), manganese dioxide (MnO_2), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, 99.0%), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 99.0%), HgSO_4 and AgSO_4 were purchased from Merck Co (Germany). The stock dye solution (1000 mg/L) was prepared by dissolving 1 g of RR198 in 1 L of distilled water. The desired dye concentration was provided with dilution of stock solution by distilled water.

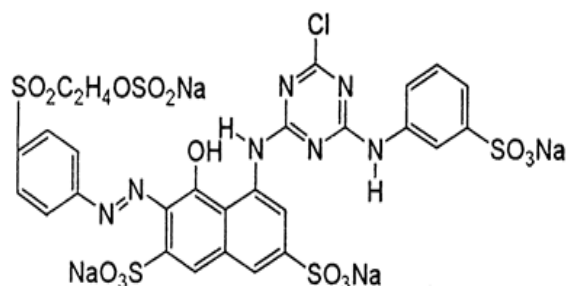


Fig 1. The chemical structure of reactive red 198.

Table 1. General characteristics of Reactive Red 198.

| Characteristics | RR 198 |
|-----------------------------|--|
| Type | Reactive dye |
| Commercial | Remazol Red 133 |
| Chemical | $\text{C}_{27}\text{H}_{18}\text{ClN}_7\text{Na}_4\text{O}_{16}\text{S}$ |
| Molecular | 984.21 |
| λ_{max} (nm) | 518 |
| Appearance | Red powder |

Analytical methods

In order to evaluate the performance of mentioned processes for degradation of reactive red 198, sampling was performed from each

experimental run at the beginning of the experiment and at intervals during the reaction. The samples were analyzed for the desired tests. The concentration of RR 198 was determined by UV-visible spectrophotometer (DR 5000 Hach) at its maximum absorption wavelength of 518 nm. The measurement of chemical oxygen demand (COD) carried out with a standard potassium dichromate oxidation method [25] and the pH was determined using an electrode (Sense Ion 378, Hack). Since hydrogen peroxide interfere with accuracy of COD test, the excess of hydrogen peroxide is removed by adding MnO_2 [26].

Experiments

Ozonation experiment. Ozonation process was conducted with 200 mL of dye solution (200 mg/L) into a plexiglass cylindrical container with total volume of 500 mL. The solution pH was firstly regulated by 0.1 M NaOH and 0.1 M H₂SO₄ to the desired values (6 to 10). The ozonation was then performed by ozone dose of 0.25 g/hr (Ozone generator, OWA 1000 Japan) for 40 min at 25 °C. The unused ozone was taken out of the reactor and bubbled into 2% KI solution in the washing bottles. Samples were finally taken during the process in time intervals of 10 min and were analyzed.

O₃/H₂O₂ experiment. The O₃/H₂O₂ process, such as the above experiments, was carried out by 200 mL of dye solution (200 mg/L) at 25 °C. First, after the adjustment of the solution pH to the above mentioned values, various dosages of H₂O₂ (0.01, 0.02, 0.03, 0.04 and 0.05 mM) were then added to the solution. Afterward, the ozonation was performed with dose of 0.25 g/hr for 40 min and the sampling was finally taken during the process in time intervals of 10 min.

H₂O₂/ultrasonic experiment. The reactor used for the experiments involving the sonication is consisted of a glass cylindrical batch reactor with the cooling jacket and the maximum working volume of 0.5L and an immersed ultrasonic probe placed vertically in the middle of the reactor (ultrasonic homogenizer SONOPLUS HD, 3200, Bandelin, Germany) operating at 20 kHz. Sonication was carried out at 20 kHz and powers range from 100 to 150W. Temperature was kept constant at 25±1 °C through the experiments. For investigation of hydrogen peroxide activation with ultrasonic radiation for

removal of RR 198, various dosages of H₂O₂ (0.01, 0.02, 0.03 and 0.04 mM) were then added to the solution.

3. RESULT AND DISCUSSION

Comparison between efficiency of different processes on the removal of Reactive Red 198 and effect of pH

In order to evaluate the reactive red 198 removal, several treatment processes were performed with a different pH range. Since pH of solution is an important factor in degradation of dyes, effect of pH in dye removal was evaluated. Table 2 shows the results of these experiments, carried out under the following experimental conditions in terms of initial dye concentration (200 mg/L), pH range (6–10) and reaction time of 40 min. The ozone dose was kept constant at 0.20 g/h throughout the experiment.

As shown in Table 2, the percentage of COD removal in ozonation process decreased from 48 to 39 % when pH was increased from 6 to 7 and then increased to 57 % when the pH was 8. At pH above 8 the percentage of COD removal remained almost unchanged. The degradation of dye and then removal of COD at pH of 6 is related to the direct oxidation of ozone with dye molecules which is predominant pathway reaction in acidic condition [16]. As Table 2 shows by increasing pH, the removal of COD was increased. Higher rate of COD removal in alkaline pH can be due to acceleration of ozone decomposition which resulted in production of more reactive radicals. Result of previous study [27] showed that in alkaline conditions, production of reactive radicals increases due to accelerating the rate of ozone decomposition.

Table 2. Performance of different processes in degradation of reactive red 198 as a function of pH in term of COD removal.

| Process | pH | | | | |
|---|-----------------|----|----|----|----|
| | 6 | 7 | 8 | 9 | 10 |
| O ₃ | 48 ^a | 39 | 57 | 56 | 53 |
| Ultrasonic/H ₂ O ₂ | 4 | 1 | 5 | 5 | 4 |
| O ₃ / H ₂ O ₂ | 50 | 51 | 60 | 58 | 58 |
| O ₃ / H ₂ O ₂ / Ultrasonic | 52 | 48 | 69 | 67 | 68 |

^aThe COD removal percentage.

The characteristics of the solution to be treated (i.e. pH, promoters and scavengers in the reacting medium) determined the ozonation reaction pathway [16, 28]. Turhan and Turgut [29] showed that decolorization of direct dyestuff wastewaters were remarkable under the basic condition of pH 12. This result imply the formation of hydroxyl radicals at higher pH values. This is in agreement with the result of present study. It can be further shown in Table 2 that in ozonation process at pH above 8, the

COD percentage removal was decreased. This can be attributed to the compounds that consumed hydroxyl radicals and compensated the acceleration of ozone decomposition to OH· at alkaline pH. Results obtained by Wang et al. [30] and Zhou et al.[31] showed that scavengers such as CO₃²⁻, SO₄²⁻ may exist in the solution and led to reduction of OH· Concentration.

As can be seen in Table 2, COD percentage removal in Ultrasonic/H₂O₂ process compare to

other process was lowest. This can be due to the fact that ultrasonic waves hinder the formation of hydroxyl radicals [32]. Furthermore, this study carried out with low frequency sonication (20 kHz) that yield low concentration of OH radicals. Since the optimum sonication frequency is around 500-600 kHz for maximum production of OH radicals [33]. In addition, low COD removal efficiency related to relative shortness of the contact period. This result is consisted with the result of Ince et al. [34], who reported that minimum contact for maximum removal of RBB color was at last 2 hours.

Also Table 2 shows that COD removal in peroxone (O_3/H_2O_2) was enhanced as pH increased. This can be attributed to the fact that increasing the pH accelerate formation of $OH\cdot$ radicals. Indeed, at pH above 8 the percentage of COD removal was decreased. This can be due to the fact that in higher pH some radicals, such as CO_3^{2-} , SO_4^{2-} and $HO_2\cdot$ can act as a radical scavenger and compensated the formation of OH radical at alkaline pH. The results obtained by others confirmed our results [35].

Table 2 shows that performance of O_3/H_2O_2 /ultrasonic affected by pH solution. Also, higher COD removal percentage obtain in alkaline

pH. Compare to other process, the O_3/H_2O_2 /ultrasonic one has a higher efficiency in mineralization of RR198 due to synergistic effect of ultrasonic waves that led to the increase of hydroxyl radical concentration. Factors, such as enhanced efficiency of ozone dissolution by sonication, higher ozone decomposition in solution by additional pathways such as chain reactions and enhanced O_3 transfer in bulk solution involved in induced synergistic effect [36]. Ince and Tezcanlı [36] reported that degradation of C.I. Reactive Black 5 by combined sonolysis (520 kHz) and ozonation was increased. They attributed this to the fact that during ultrasonic irradiation, hydroxyl radical increased due to synergistic effect.

The effect of initial RR 198 concentration

The effect of dye concentrations of 100–500 mg/L on dye and COD removal in US/ H_2O_2/O_3 process was investigated at pH of 8.0 at 25 °C and 100 W in 40 min with the addition of 0.03 mM H_2O_2 . The results are shown in Fig 1. As it can be seen in Fig. 1, initial concentration has an important effect on the decolorization.

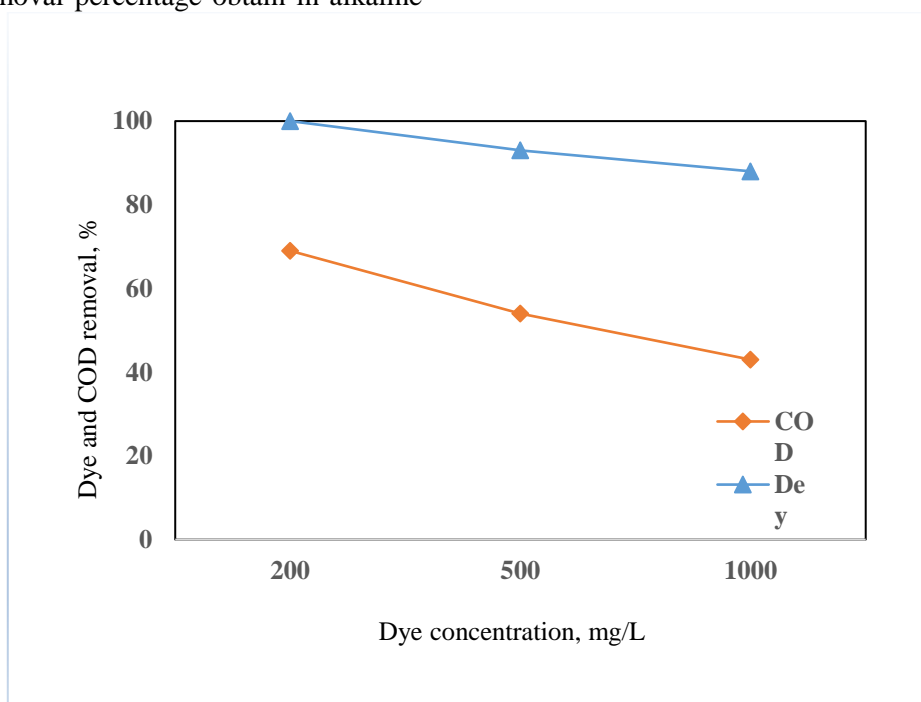


Fig.1- Effect of initial dye concentration on dye and COD removal from RR198 Solution in the US/ O_3/H_2O_2 process (initial pH 8, reaction time = 40 min, H_2O_2 dosage = 0.03Mm, US 100 W).

The efficiency of dye and COD removal were inversely proportional to the dye concentration used in the experiment. The removal efficiencies of COD and dye showing a similar reduction trend. The increase of RR 198 dye concentration from 200 to 1000 mg L⁻¹ decreased the COD removal from 69% to 43% and decolorization from 100% to 88%. This

is in agreement with the results of other researchers, who showed that at considerable concentrations dye degradation and COD removal slowed down [16, 37]. The decrease of color and COD removal with increasing initial dye concentration can be attributed to the fact that higher concentration of dye increases the number of dye molecules and perhaps inorganic

anions which may compete for the reaction with OH radicals. In a study conducted by Siddique et al.[37], it was found that decomposition decreased with the increase of initial dye concentration. Furthermore, with increasing initial dye concentration the cavities

approaches saturation in the US process [32]. Indeed, Fig.1 shows that the rate of COD removal was lower than that for color removal. Thus, for significant COD removal longer time and higher ozonation dose would be required.

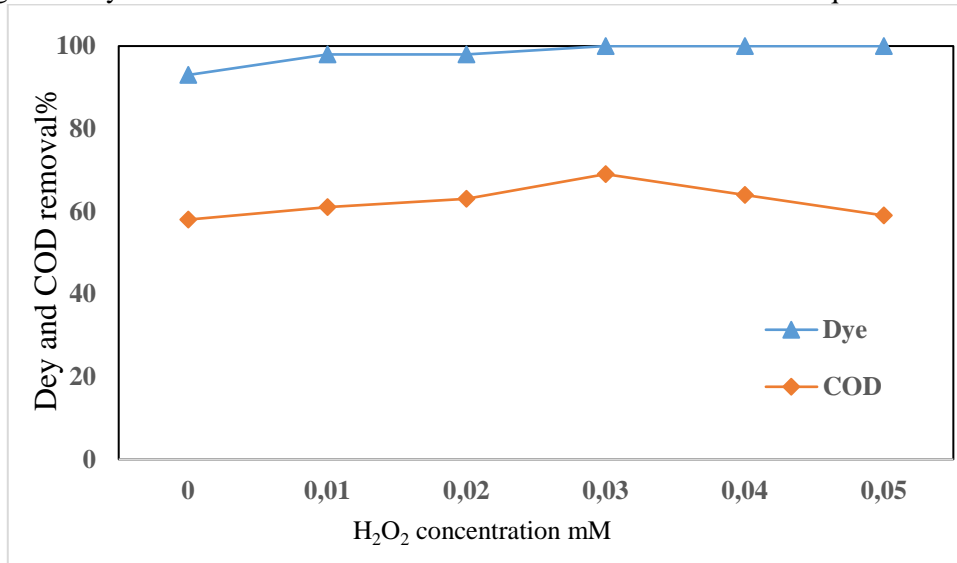


Fig.2- Effect of H₂O₂ concentration (mM) on dye and COD removal from RR198 Solution in the US/O₃/H₂O₂ process (initial pH 8, reaction time = 40 min, dye concentration= 200 mg/L, US 100 W).

The effect of initial H₂O₂ concentration

Fig.2 shows the efficiency of O₃/H₂O₂/US process on color and COD removal at different dosages of hydrogen peroxide reagent under pH 8.0 at 25 °C and 100 W in 40 min. As is apparent from Fig.2, the color and COD removals were enhanced with increasing H₂O₂ dosage until reaching the optimum dosage. In this study the optimum concentration of H₂O₂ was found to be 0.03 M in O₃/H₂O₂/ US experiments. The higher removal rate can be explained as the production of more oxidizing radicals in the presence of a higher dosage of H₂O₂, an essential element of the reaction.

Furthermore, addition of H₂O₂ leads to a decrease in performance efficiency. This phenomena can be due to the reduction of hydroxyl radical's concentration. Consumption of hydroxyl radicals via a number of approaches, including the scavenging effects of H₂O₂ and recombination of OH' radicals(38) or the generation of radicals less reactive than hydroxyl, such as hydroperoxyle(18). Furthermore, overdose of H₂O₂ in the effluent causes an increase in COD [39]. It is very important to optimize the applied H₂O₂ concentration to maximize the treatment performance of the AOP since the presence of excess H₂O₂ can lower the treatment efficiency of AOPs [28].

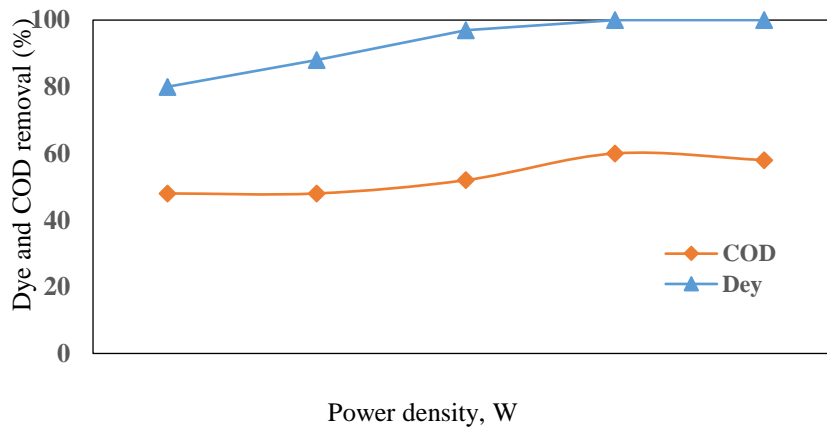


Fig.3- Effect of power density (W) on dye and COD removal from RR198 Solution in the US/O₃/H₂O₂ process (initial pH 8, reaction time = 40 min, dye concentration= 200 mg/L, H₂O₂dosage = 0.03M).

The effect of power density

Color and COD removal of RR198 in the US/O₃/H₂O₂ system was investigated at different ultrasonic powers when the dye concentration was 200 mg/L, ozone concentration was 0.25 g/h, and the initial pH was 8. Experiments were conducted at pH 8 with different ultrasonic power density ranged from 0 to 150 W (Fig.3). The results showed that increase in ultrasonic frequencies has increased dye decomposition. The maximum decrease in color and COD was observed at 125 w after 40 min of reaction time (100 and 69% respectively).

As shown in Fig. 3, the increase in ultrasonic power led to increase in color and COD removal before the ultrasound power reached 150 W. Subsequently, the removal efficiency decreased as the ultrasound power continued to increase. These results are in agreement with other studies [30]. Application of ultrasonic waves led to the sonolysis

of solution and is usually based on the formation of short-lived radical species generated in violent cavitation events. Sonochemical effects of ultrasound produced by the formation of cavitation bubbles (37). As ultrasonic power increased, higher energy was delivered to the reaction system to accelerate the cavitation effect. The intensification in acoustic power increased the number of active cavitation bubbles, as well as the size of the individual bubbles. Results of other studies showed the positive effect of Ultrasonic-assisted ozone oxidation process [24]. However, at power density higher than the optimal value, a large number of gas bubbles appeared in the solution. This bubbles can act as a barrier for further transfer of acoustic [30, 37]. The decrease in COD removal can be attributed to the formation of bubble gas in power of 150 W. Thus, 125 W was selected as the optimum power of ultrasonic for the subsequent experiments.

Table 3 Pseudo first order kinetic and half-life for the dyes degradation processes

| Type of process | K _{app} (min ⁻¹) | T _{1/2} (min) | R ² |
|---|---------------------------------------|------------------------|----------------|
| O ₃ | 0.022 | 30 | 0.995 |
| Ultrasonic/H ₂ O ₂ | 0.0013 | 519 | 0.99 |
| O ₃ / H ₂ O ₂ | 0.025 | 28 | 0.97 |
| O ₃ / H ₂ O ₂ / Ultrasonic | 0.031 | 24 | 0.96 |

Kinetic studies

To describe the degradation of the RR 198 in different AOPs pseudo-first-order model was applied.

Because of the high decolorization ability of ozone, it has been extensively used in dye wastewater treatment. Ozone has a high selectivity in attacking conjugated double bonds (e.g., N=N, C=N, and C=C) that are often the chromophores of dye molecules, and can thus decolorize dye wastewater rapidly. To enhanced pollutant mineralization efficiency, ozone is often used in combination with other technologies such as H₂O₂, UV, and TiO₂ in dye wastewater treatment [35]. Mainly, application of O₃ and H₂O₂ together has a substantial synergistic effect on organic mineralization. This synergy can be due to the reaction of O₃ with H₂O₂ to form hydroxyl radicals (OH·). As mentioned earlier it is a very powerful oxidant and can oxidize most organic solutes at very high rates [27]. As shown in Table 3, the apparent rate constant in O₃/H₂O₂ process was higher than that for ozonation process. This can be due to the synergistic effect of O₃ and H₂O₂ that resulted in higher concentration of hydroxyl radicals. However efficiency of O₃/H₂O₂ can be improved by application of ultrasonic irradiation that accelerated the rate of hydroxyl radical's generation. As Table 3

shows, apparent rate constant in O₃/H₂O₂/ultrasonic process was higher than other AOPs. This can be attributed to the fact that ultrasound waves increases turbulence which reduces the liquid film thickness and therefore increases the mass transfer rate of ozone in aqueous phase. Also, Table 3 showed that ultrasonic/H₂O₂ process was ineffective in degradation of RR198. Since this process was ineffective in removal of color and COD, it can be concluded that less hydroxyl radicals was generated and activation of H₂O₂ was not performed.

CONCLUSION

In this study, degradation of Reactive Red 198 (RR198) by using several advanced oxidation processes including O₃, O₃/H₂O₂, ultrasonic/H₂O₂ and O₃/H₂O₂/Ultrasonic was studied. The effects of various parameters such as hydrogen peroxide dose, ultrasonic power, initial dye concentration and solution pH were studied on the degradation of RR198. The degradation of dye was influenced by the initial solution pH, initial dye concentration, H₂O₂ concentration and ultrasonic power. Increasing initial solution pH, H₂O₂ concentration and ultrasonic power led to enhance the dye degradation, while increasing initial dye concentration led to a decrease the dye degradation. It was observed that, in comparison with other processes, O₃/H₂O₂/ultrasonic caused higher COD removal of

RR198 at reaction time. Since O₃/H₂O₂/ultrasonic as higher efficiency compare to other process, usage of this process is recommended for removal of this type of dye.

Acknowledgements. The authors acknowledge all non-financial supports provided by Isfahan University of Medical Sciences. The authors declare that there is no conflict of interest.

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