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Application of advanced oxidation processes to remove refractory compounds from dye wastewater

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ABSTRACT

The purpose of this study was to investigate the efficacy of ozonation and three AOPs (O_3/H_2O_2, O_3/UV, and O_3/H_2O_2/UV) on synthetic dye-containing wastewater with regard to the removal of chemical oxygen demand (COD) and color and biodegradability (BOD_5/COD). At hydrogen peroxide levels above the optimal value, H_2O_2 tended to accumulate in the reactor, leading to a decrease in COD removal efficiency, because it acted as a radical scavenger. Higher recirculation flow rates increased COD and color removal in the combined UV process. Compared with the O_3/H_2O_2 process, the O_3/UV process enhanced COD removal mildly. Biodegradability increased approximately 12-fold after 150 min of retention time. Although all processes removed color within a short operational time, the O_3/H_2O_2/UV process had the highest removal efficiency of COD and enhancement of biodegradability of the processes that we tested.

Keywords: Advanced oxidation processes (AOPs); Biodegradability; Dye wastewater; Ozonation; Refractory compounds

1. Introduction

The textile industry consumes significant amounts of water, energy, and chemical products due to industrialization, making it one of the primary sources of severe pollution problems worldwide. Textile wastewater is characterized by extreme fluctuations in many parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, color, and salinity [1]. Wastewater composition depends on the organic-based compounds—such as chlorinated organics and carrier organics—chemicals, and dyes that are used in industrial dry and wet processing steps [2–4].

One of the chief problems that are associated with the treatment of textile wastewater is the removal of dyes. Most of the more than 10,000 dyes that are used in the textile processing industry are azo compounds, i.e., molecules that have one or more azo (N=N) bridges that link substituted aromatic structures [5], rendering them more stable and more resistant to biodegradation [6]. Thus, the discharge of azo dyes is undesirable—not only for aesthetic reasons but also because many azo dyes and their metabolites are toxic and mutagenic [7–9].

To remove refractory compounds from textile wastewater, such as azo dyes, integrated processes of combinations of biological, physical, and chemical treatment methods have been developed [10,11]. These methods are efficient but not cost effective. Traditional physicochemi-

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cal technologies, such as membrane filtration (ultrafiltration and reverse osmosis), ion exchange, and adsorption onto various adsorbents, have been used efficiently, but they are commercially unattractive because they are nondestructive (i.e., they merely transfer the pollutant from water to a solid matrix), necessitating consequently expensive operations, such as regeneration and post-treatment of concentrated waste [11–13].

In contrast, ozone has high oxidative potential; therefore, it quickly oxidizes most organic compounds. Advanced oxidation process (AOP) technologies that use ozone for disinfection, water quality improvement, decolorization, odor removal, and degradation of refractory organics are attractive alternatives to conventional treatment methods. AOPs that are based on the generation of reactive and oxidizing free radicals have been used with increasing enthusiasm due to their robust oxidative power. The generation of these radicals is achieved using single oxidants or a combination of ozone, hydrogen peroxide, and UV radiation [14]. Generally, AOPs are characterized by high oxidation rates and easy adaptability to water and wastewater treatment [15].

The purpose of this study is to determine the efficacy of AOPs (ozonation alone, O_3/H_2O_2, O_3/UV, and O_3/H_2O_2/UV) with regard to the removal of refractory organics and especially to investigate the biodegradability improvement of mixed dye wastewater linked in municipal sewage treatment plant is important point of this study.

2. Materials and methods

2.1. Experimental setup

As shown in Fig. 1, the experimental system consisted primarily of a 6-L working volume reactor, with a UV lamp (TUV-15 model, Phillips) as the light source, an ozone monitor, an oxygen generator, an ozone generator, and an ozone off-gas decomposer. All tubes in the reactor were made of NORPRENE® (Cole Parmer®) to withstand oxidation.

The Model Lab-1 ozone generator (Ozonetech, Korea) was used to produce ozone from pure oxygen (99.5%) at 6 g/h. Ozone was supplied from the bottom of the reactor through a diffuser. Two bottles that contained 2%–4% KI (potassium iodide) solution were used to decompose ozone off-gas.

Through a peristaltic pump (Masterflex L/S Easy-Load® II Pump Head and Digital Economy Drive, Cole-Parmer Instrument Co., Vernon Hills, IL), the feed was circulated within the UV lamp enclosed in a quartz sleeve that had an inner diameter of 39 mm and a length of 39 cm. UV lamp was positioned in the center of a 3-L cylindrical stainless steel reactor. The reactor had an inner diameter of 98 mm and a length of 41 cm, based on actinometrical measurements of the length of the radiation that was emitted by the lamp. The light source was a low-pressure mercury UV lamp that emitted 16 W of intensity at 254 nm. pH was adjusted to 9±0.2 by H_2SO_4 and NaOH.

All of the experiments were conducted at 25±1°C, maintained with a warm-water jacket and a temperature sensor that was installed around the reactor. The water was heated with steam, allowing heated water to flow into the water jacket when necessary. For experiments using H_2O_2, a metering pump (FMI Lab Pump, Model QV-PM6014, Fluid Metering, Inc., Syosset, NY) was used to pump H_2O_2, stored in a 4-L chemical feed container, into the AOP loop at a preset flow rate to achieve the desired concentration. The flow rate was adjusted using a

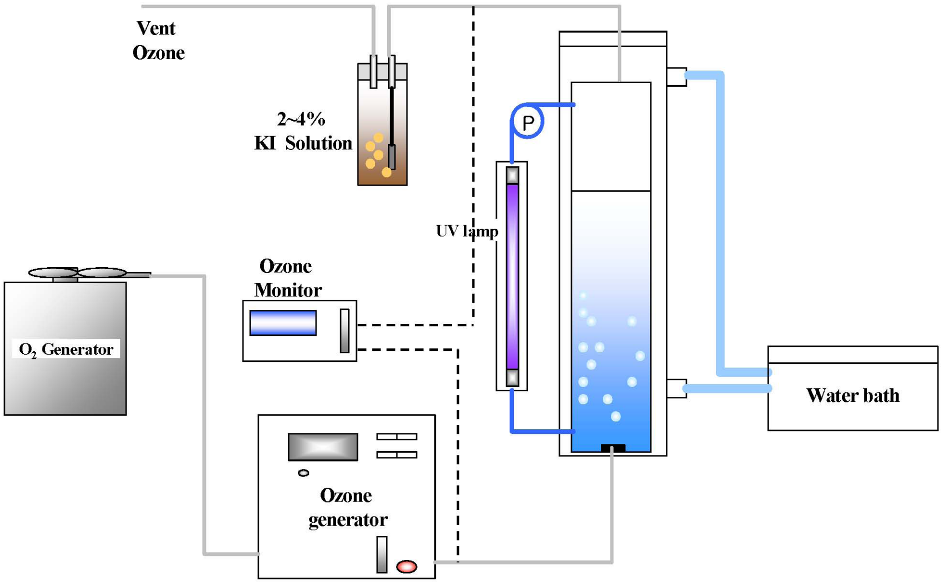

Fig. 1. Schematic of bench-scale AOP system in this study.

controller (FMI Stroke Rate Controller, Model V200, Fluid Metering, Inc., Syosset, NY) to alter feed concentration.

2.2. Preparation of synthetic dye wastewater

The synthetic dye wastewater was prepared to replicate actual dye wastewater. The synthetic dye wastewater was composed primarily of refractory organics, such as reactive black 5, reactive blue 19, reactive red 120, reactive yellow 84, acid black 1, Na_2SO_4, Na_2CO_3, NaCl, and polyvinyl alcohol (PVA). Dye chemicals were provided by RIFA Co., Korea.

One liter of synthetic dye wastewater contained: 0.4 g reactive black 5, 0.4 g reactive blue 19, 0.4 g reactive red 120, 0.4 g reactive yellow 84, 0.2 g acid black 1, 3 g Na_2SO_4, 0.8 g Na_2CO_3, 1 g NaCl, and 0.02 g PVA , and its pH was adjusted with 1 N H_2SO_4 and 1 N NaOH. The COD, BOD_5, color, and chloride ion concentrations of the synthetic dye wastewater were approximately 1,010–1,100 mg/L, 18–20 mg/L, 41,000–43,300 PtCo and 900–1,000 mg/L, respectively.

2.3. Experimental conditions

Experiments were conducted with dechlorinated tap water at a constant temperature of 25±1°C. The AOP system was operated in the flow through mode with recirculation. Three recirculation flow rates were used in this study: 1.2, 1.8, and 2.4 L/min, and ozone concentration and ozone gas flow rate were fixed at 40 g-O_3/m^3 and 2.4 L/min, respectively. On the other hand, in O_3 alone case, experiments were performed at two initial O_3 concentrations of 20 and 40 g-O_3/m^3 and ozone gas flow rates of 4.8 L/min and 2.4 L/min, respectively.

In all of the experiments, concentrated dye wastewater was used to spike the inlet water before it entered the recirculation loop, and the oxidants (O_3 and H_2O_2) were injected into the recirculation loop. The concentrations of O_3 and H_2O_2, injected into the system, were measured separately by shutting off the feed of the other oxidants and the synthetic dye wastewater. Sampling ports were located at the inlet and outlet and within the loop of the AOP system. All experiments were conducted for 3 h to allow the system to stabilize.

2.4. Sampling and analysis

Samples were taken from the continuous reactors at the inlet and outlet at regular intervals in 40-mL borosilicate vials that had caps and disposable Teflon septa. Sampling was performed in accordance with SW-846 EPA Method 5030 [16].

The excess ozone in the sample was quenched by adding 1 g sodium thiosulfate to each 40-mL vial to prevent further reaction of ozone with MTBE and its byproducts [17]. The samples were analyzed in accordance with procedures that are outlined in EPA Method 502.2 [18].

All analyses were performed immediately after sampling. The pH of the samples was measured with a portable pH meter (Model 250A, Orion, USA). The concentration of chloride ion was measured with the 750P pH/ISE meter (Istekco, Korea). After the removal of residual H_2O_2 using sodium sulfite, COD and color measurements were made with a Hach DR/2010 (Hach, USA). TOC was analyzed with a TOC analyzer (TOC-5000, Shimadzu, Japan). BOD_5 was measured according to standard methods [19]. Biodegradability was evaluated by calculating the value of BOD_5/COD. The indigo dye method [20] was used to measure the O_3 concentration, wherein the absorbance of unreacted dye was measured on a spectrophotometer. Hydrogen peroxide concentrations were measured with the HACH test kit (Catalog No: 2291700) [21].

2.5. Calculation of pseudo-first order reaction rate constant (k′)

The oxidation process consists of the direct and indirect reactions which can occur at the same time. A second order rate equation is commonly accepted for both reaction pathways. So that the oxidation of the model compound M can be described as the sum of the two reaction pathways as follows [22]:

$$-d\mathrm{C}(M)/dt = [k_D \mathrm{C}(\mathrm{O_3}) + k_R \mathrm{C}(\mathrm{OH})] \cdot \mathrm{C}(M) \tag{1}$$

M —model compound; k_D — reaction rate constant for the direct reaction; k_R — reaction rate constant for the indirect reaction.

With the assumptions that:

- ozone and hydroxyl radicals are the main oxidants of the pollutant,
- no stripping of the pollutant occurs.

By implying that the ozone concentration in the reaction medium remains constant, Eq. (1) can by rewritten as an apparent pseudo first-order reaction with respect to organic compound M:

$$-d\mathrm{C}(M)/dt = k' \cdot \mathrm{C}(M) \tag{2}$$

where k' is pseudo-first order reaction rate constant, $d\mathrm{C}(M)/dt$ is the rate of change in the concentration of M with time (mg/L·d or h), and $C(M)$ is the concentration of M at any time (mg/L).

The reaction rate constant k' is dependent on the direct and indirect oxidation rate constants as well as ozone and hydroxyl radical concentrations. However, it is assumed be constant with respect to time and reached a steady concentration in a short time.

Rearranging Eq. (2) after integration yields

$$\ln \mathrm{C}(M) = \ln \mathrm{C}(M)_0 - k't \tag{3}$$

This is a linear equation type. If the data plot a straight line, the reaction is pseudo first-order and the slope of the line is equal to *k*. Thus, the pseudo first-order rate constants were calculated from Eq. (3).

3. Results and discussion

3.1. Ozonation alone

The effect of ozone concentration and gas flow rate on color and COD removal was examined at the same total ozone dosage. The experiments were performed at two initial O_3 concentrations of 20 and 40 mg/L (injection flow rates were 4.8 and 2.4 L/min). The influent COD and BOD concentrations were maintained at 1,050 and 20 mg/L. Total ozone dosage can be expressed as follows:

$$\text{Total ozone doze} = \frac{(\text{Ozone conc.} \times \text{Gas flow-rate} \times \text{Reaction time})}{\text{Reactor volume}} \tag{4}$$

As shown in Fig. 2, color and COD removal were robust at high ozone concentrations and low gas flow rates. This result can be attributed to mass transfer theory (the two-film theory), which parses the overall mass transfer mechanism into several steps: (i) diffusion of ozone through the gas phase to the interface between the gas and aqueous phases, (ii) transport across the interface to the aqueous phase boundary, and (iii) transfer into the bulk aqueous phase [23].

Further, many researchers have reported that O_3 decomposes spontaneously during water treatment in a complex mechanism that involves the generation of $OH^\bullet$. O_3 can oxidize refractory organics directly through molecular O_3 ($O_{3(aq)}$) or indirectly through $OH^\bullet$ that is generated during the decomposition of O_3 [24,25] — when ozone gas flow rate increases, the bubbles that are generated become larger. This process leads to a decrease in the total surface area between the bubble and liquid. At low gas flow rates, the bubbles were smaller compared with the high rate. Therefore, at a given dose of ozone, higher ozone gas flow rates favor the removal of organics.

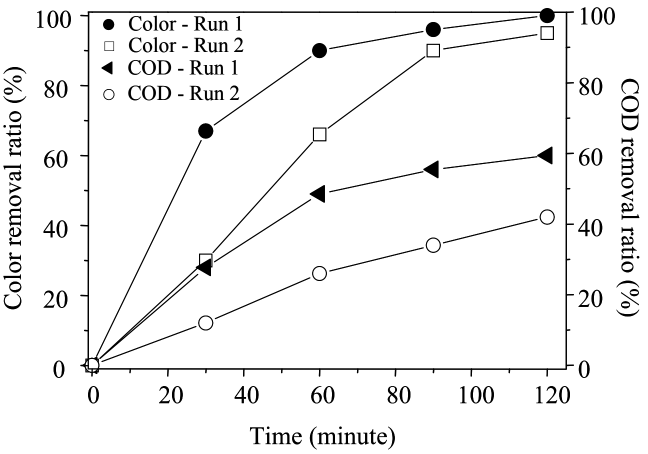

Fig. 2. Effect of ozone concentration and gas flow rate for removal efficiencies of COD and color as a function of time (conditions: Run 1 — ozone concentration 40 g-O_3/m^3, ozone gas flow rate 2.4 L/min, temperature 25°C, initial pH = 9; Run 2 — ozone concentration 20 g-O_3/m^3, ozone gas flow rate 4.8 L/min, temperature 25°C, initial pH = 9).

3.2. O_3/H_2O_2 process (peroxone)

The combination of ozone and hydrogen peroxide to enhance oxidizing ability has been researched extensively and is a promising alternative method of refractory organic removal from dye wastewater. Hydrogen peroxide initiates the decomposition of ozone into hydroxyl radicals more rapidly than hydroxide ion [26].

As discussed, $OH^\bullet$ is generated by the decomposition of O_3 in water, and its production can be increased by accelerating this decomposition. An increase in $OH^\bullet$ production results in higher oxidation rates. One of the most common and effective methods of increasing O_3 decomposition is the addition of H_2O_2 to ozonated water, which results in the net production of 1.0 moles of $OH^\bullet$ per mole of O_3. The dissociation of H_2O_2 in water generates hydroperoxide ion, which reacts with O_3, resulting in the formation of $OH^\bullet$ [27,28]. Subsequently, the $OH^\bullet$ can react with O_3, H_2O_2, hydroperoxide ion, hydroxyl ion, and other species.

Ozonation of synthetic dye wastewater was performed in the presence of up to 150 mg/L H_2O_2. The effect of initial H_2O_2 concentration on the pseudofirst-order rate constant and biodegradability is shown in Figs. 3a and 3b. Similar to ozonation alone, the oxidation of refractory organics in the O_3/H_2O_2 process occurred by direct oxidation by aqueous O_3 and indirect oxidation by $OH^\bullet$ [29]. The dual activity of O_3 molecules and $OH^\bullet$ resulted in significant increases in the rate of degradation of the pollutant.

COD removal rose with increases in H_2O_2 concentration from 0 to 100 mg/L. The highest increases in COD removal and biodegradability were observed at 100 mg/L H_2O_2 (this value indicates that the initial H_2O_2 concentration/total ozone dose was 1/24). This result is attributed to the observation that as hydrogen peroxide levels rose above the optimal value, H_2O_2 tended to accumulate in wastewater and act as a radical scavenger, decreasing removal efficiencies. Therefore, we propose that the ratio of H_2O_2 concentration to total ozone dose is an important operational parameter for improving COD removal efficiency and biodegradability.

3.3. O_3/UV process

Based on the results of the ozonation-alone treatment, additional experiments were performed at the same O_3 concentrations in the presence of UV radiation. Compared with ozonation alone, the O_3/UV combination effected a significant increase in the removal efficiency of refractory organics (37%) Table 1), which is attributed to the

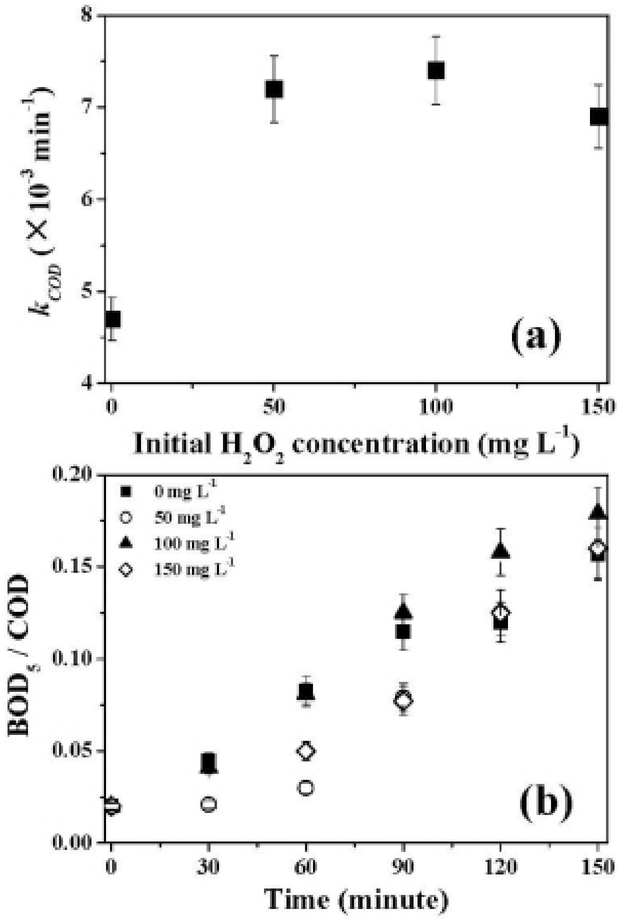

Fig. 3. Effect of initial H_2O_2 concentration on pseudo-first order rate constant (a) and biodegradability (b) in O_3/H_2O_2 process (conditions: ozone concentration 40 g-O_3/m^3, ozone gas flow rate 2.4 L/min, injected time 150 min, temperature 25°C, initial pH = 9).

supplementary generation of $OH^\bullet$ due to UV radiation. On photolysis, O_3 decomposes to form O_2 and the oxygen atoms $O(^1D)$ (excited state) and $O(^3P)$ (ground state) [30–32]. Below 300 nm in the gas phase, the process that predominates is the formation of $O(^1D)$, at a quantum yield of ≈ 0.9.

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{5}$$

$O(^1D)$ is extremely reactive and has a high heat of formation [33]; therefore, it is nonselective and reacts quickly. The $O(^1D)$ reacts primarily by insertion into the C-H or O-H bond [34]. In the liquid phase, $O(^1D)$ reacts with water to form H_2O_2.

$$O(^1D) + H_2O \rightarrow H_2O_2 \tag{6}$$

Because H_2O_2 reacts with O_3 to form $OH^\bullet$, the O_3/UV process is similar to the O_3/H_2O_2 process, in which H_2O_2 is generated in situ, as opposed to being added exogenously in the latter case.

As shown in Fig. 4, the pseudo-first order rate constants of COD rose with increasing recirculation flow rates during the O_3/UV process. This result can be explained by the elevation in recirculation flow rate, resulting in the increase in contact between the organics and ozone. Certain compounds are degraded by direct photolysis, and UV light can excite organic pollutants molecules, rendering them more susceptible to hydroxyl radical attack. Therefore, a higher recirculation flow rate leads to greater COD and color removal.

3.4. O_3/H_2O_2/UV process

The O_3/H_2O_2/UV process is a powerful tool that quickly and completely mineralizes organic compounds

Table 1
Pseudo-first order rate constants and time removal for COD and color removal in each process

COD removal				
Process	k' (× 10^{-2} min^{-1})	t_{50} (min)	t_{90} (min)	R^2
Ozonation	5.64	12	40	0.988
O_3/H_2O_2	6.11	11	37	0.988
O_3/UV	6.73	10	34	0.977
O_3/H_2O_2/UV	6.77	10	34	0.975
Colorlremoval				
Process	k' (× 10^{-3} min^{-1})	t_{50} (min)	t_{90} (min)	R^2
Ozonation	8.63	80	267	0.969
O_3/H_2O_2	10.71	65	215	0.991
O_3/UV	11.83	59	195	0.981
O_3/H_2O_2/UV	15.53	45	148	0.996

*t_{50}, t_{90} : time required for 50 % or 90 % removal.

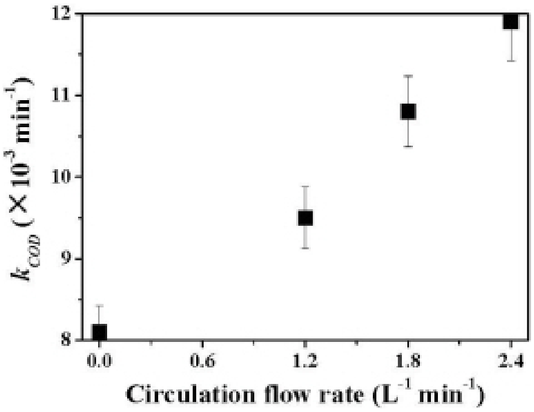

Fig. 4. Variation of pseudo first-order rate constant on COD and color as a function of recirculation flow rate in O_3/UV process (conditions: ozone concentration 40 g-O_3/m^3, ozone gas flow rate 2.4 L/min, injected time 150 min, temperature 25°C, initial pH = 9, UV intensity 16 W).

and is the most effective treatment for high-strength wastewater [35,36]. The reaction pathways that lead to the generation of $OH^{\bullet}$ radicals in this process are the same as in the AOPs that have been discussed. This process has been used infrequently to treat drinking water, because it is an energy-consuming process and is viable only for treating high-concentration effluents.

It is well known that operating with UV light, H_2O_2 is homolytically decomposed into two hydroxyl radicals. This suggests that the hydroxyl radicals formed by homolytic cleavage of the central HO-OH bond enhance the oxidation ability of ozone processes with UV light.

The applicability of this process for the treatment of refractory organics in dye wastewater was evaluated in this study. pH, temperature, ozone flow rate, ozone concentration, and circulation flow rate were set to 9, 2°C, 2.4 L/min, 40 g-O_3/m^3, and 1.8 L/min, respectively. H_2O_2 concentration was varied between 0 and 400 mg/L.

The effects of initial H_2O_2 concentration on pseudo-first order rate constant and biodegradability are shown in Figs. 5a and 5b. The pseudo-first-order rate constant for COD removal increased at 200 mg/L H_2O_2 but decreased in the range above 200 mg/L H_2O_2. Similarly, biodegradability peaked at 200 mg-H_2O_2/L at 150 min of operation (this value indicates that the initial H_2O_2 concentration/total ozone dose was 1/12). Optimal H_2O_2 dosage increased compared with the O_3/H_2O_2 process, which might be due to H_2O_2 decomposition by UV as well as ozone.COD removal, pseudo-first order rate constant, and biodegradability were examined by ozonation and three AOPs. The pseudo-first order rate constant and the times that were required for COD and color removal in each process are presented in Table 1. The change in COD removal and biodegradability after 150 min of operation in each process is shown in Table 2.

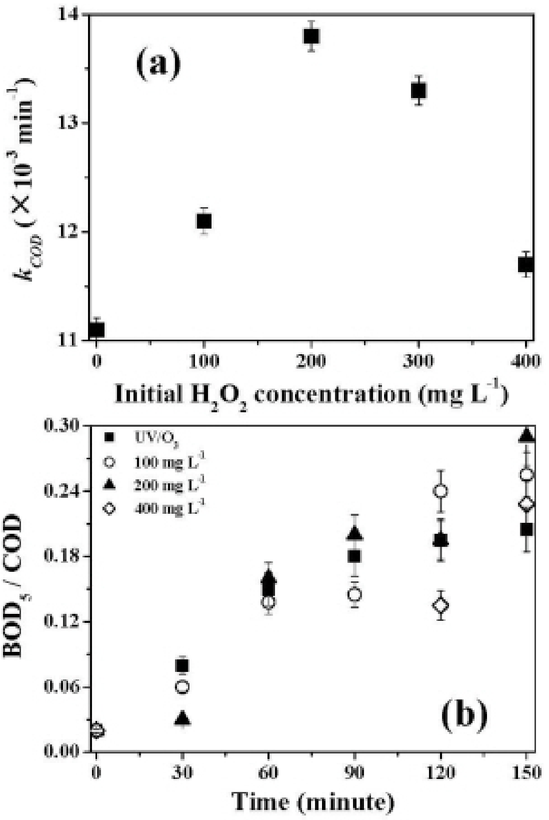

Fig. 5. Effect of initial H_2O_2 concentration on pseudo-first order rate constant (a) and biodegradability (b) in O_3/H_2O_2/UV process (conditions: ozone concentration 40 g-O_3/m^3, ozone gas flow rate 2.4 L/min, injected time 150 min, temperature 25°C, initial pH = 9, UV intensity 16 W).

The O_3/H_2O_2 process had higher COD removal efficiencies than ozonation alone, but biodegradability did not improve. Compared with the O_3/H_2O_2 process, the O_3/UV process failed to enhance COD removal substantially. Biodegradability increased by approximately 12-fold after 150 min of operation. Therefore, O_3/H_2O_2 process is a favorable process for improving the biodegradability of refractory organics in dye wastewater. The O_3/H_2O_2/UV process had the highest COD removal efficiency and BOD_5/COD enhancement of the processes that we tested, as shown in Table 2.

4. Conclusions

Ozonation and three AOPs (O_3/H_2O_2, O_3/UV, and O_3/H_2O_2/UV) were investigated with regard to the treatment of refractory synthetic dye wastewater. The highest efficiency of COD removal and enhancement of biodegradability were observed at 100 mg/L H_2O_2 in the O_3/H_2O_2 process. When H_2O_2 rose above the optimal value, H_2O_2 tended to accumulate in the reactor and act as a radical scavenger, resulting in a decrease in COD removal efficiency. Higher recirculation flow rates led to greater

Table 2
Removal efficiency of COD, TOC and biodegradability after 150 min of reaction time in each process

Process	Removal efficiency of COD and TOC (%)	BOD_5 (mg-O_2/L)	BOD_5/COD	Applied O_3-g COD reduction
Ozonation	67.9 (COD)/58.3 (TOC)	50.2	0.16	19.3
O_3/H_2O_2	80.5/70.1	32.1	0.16	16.3
O_3/UV	81.2/71.4	48.6	0.25	16.1
O_3/H_2O_2/UV	90.4/82.8	42.0	0.42	14.5

Conditions: ozone concentration 40 g-O_3/m^3, ozone gas flow rate 2.4 L/min, injected time 150 min, initial COD concentration 1,100 mg/L.

COD and color removal in the UV combination (O_3/UV, and O_3/H_2O_2/UV) process. Compared with the O_3/H_2O_2 process, the O_3/UV process enhanced COD removal little. Although all processes removed color within a short operational time, the O_3/H_2O_2/UV process effected the greatest COD removal efficiency and improvement in biodegradability.

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