

The synergistic effect of ozonation and photocatalysis on color removal from reused water

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Abstract

In this study, the treatment efficiency of different AOPs (UV/O₃, UV/TiO₂ and UV/TiO₂/O₃) was compared for the reduction of color and trace organics remained in the actual-treated wastewater using a laboratory scale recirculating ozonation photocatalytic system. Color, A₂₅₄ (the organics absorption at the wavelength of 254 nm), and total organic carbon (TOC) were characterized to assess the process efficiency. The effects of ozone dose, circulation flow rate, UV intensity, ozone input flow rate, ozonation procedure, as well as UV light source on the process efficiency were also investigated. The results showed that the combined ozonation and photocatalytic process (UV/TiO₂/O₃) is more efficient than ozonation (UV/O₃) or photocatalysis (UV/TiO₂) alone, particularly in total mineralization of TOCs. It was evident that a synergistic effect occurred in the combined ozonation and photocatalytic process. The ozone dose and ozonation procedure were found to have a significant impact on the process efficiency whereas circulation flow rate, UV intensity, ozone input flow rate, and UV light source had relatively less effect. The color removal rate was significantly increased with the increase of O₃ dose. The co-treatment of ozonation and photocatalytic oxidation increased TOC removal rate by nearly 50% compared to the process when ozonation was used as a pre-treatment for photocatalysis. This was due to the synergistic effect between photocatalysis and ozonation.

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1. Introduction

The available water resources in Australia are decreasing whereas the wastewater volume is constantly increasing. After the bulk of organic material (measured as BOD or COD) and other contaminants are removed by biological treatment from a sewage treatment plant (STP), the treated wastewater is usually discharged to the ocean. There are significant opportunities to reuse a larger amount of this treated wastewater. Many uses of water do not require treatment to drinking water standard, and the use of recycled water for non-drinking purposes is not only an effective means of coping with the water shortage in Australia, but also a minimization of detrimental discharges to the environment. New residential, commercial and industrial developments provide the greatest opportunities for the distribution of recycled water via dual pipe systems (one pipe for potable

water supply and a second pipe for recycled water supply). The recycled water in the dual pipe system can be used for the toilet flushing, garden watering and open space irrigation.

Barriers to the reuse of the treated wastewater, however, do exist, particularly if the treated wastewater contains contaminants, which may adversely affect human or environment health, or because it is aesthetically unappealing (i.e. odorous or visually unattractive). Color and non-biodegradable trace organics present in the treated wastewater from STPs can affect the options for disposal or recycling water. Color is sometimes a concern because its aesthetics impacts on public acceptance of recycling. As more stringent water quality standards for color and total organic matter are introduced, improved public acceptance of water recycling will be essential.

Since trace recalcitrant organic compounds in wastewaters, such as organo-halogens, organic pesticides, surfactants, and coloring matters, are resistant to the conventional chemical and biological treatments, advanced oxidation processes (AOPs) are being studied as an alternative to traditional methods and will probably constitute the best option in the near future. In general,

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a combination of several methods gives high-treatment efficiency compared with individual treatment [1]. AOPs are based on the generation of very reactive species such as hydroxyl radicals (OH^\bullet) that oxidize a broad range of organic pollutants quickly and non-selectively. Consequently, a combination of two or more AOPs enhances free radical generation, which eventually leads to higher oxidation rates [2].

Among AOPs, photocatalysis has a great potential for the removal of organic pollutants from wastewaters [3–5], although it is not yet in full-scale application because of its low-oxidation rate. In photocatalysis, the hydroxyl radical is generally considered to be mainly responsible for the degradation of organic matters. The mechanism is usually proposed as follows [6–10]:

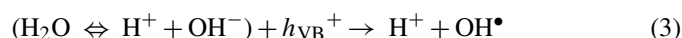
Absorption of efficient photons ($h\nu \geq \text{EG} = 3.02 \text{ eV}$) by TiO_2 :



Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to $-1/2$):



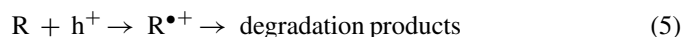
Neutralization of OH^- groups by photoholes which produces OH^\bullet radicals:



Oxidation of the organic reactant via successive attacks by OH^\bullet radicals:



Direct oxidation by reaction with holes:



Ozone is a strong oxidizer having high reactivity with organic compounds and has been used for various aspects of water treatments. However, it has been reported that in conventional ozonation process, most of the organic compounds are not completely degraded by ozone alone and sometimes toxic intermediates are produced [11]. It is known that at acidic or neutral conditions, ozone can degrade organic pollutants (R) by direct electrophilic attack [2]. Direct attack by molecular ozone (commonly known as ozonolysis) is a selective reaction which results in the formation of carboxylic acids as end products. These oxidized organic products (ROX) cannot be further oxidized by molecular ozone:



Therefore, a combination of photocatalyst with ozone is a reasonable choice for the treatment of hardly degradable organic compounds since the organic compounds are expected to decompose more quickly and achieve complete mineralization to carbon dioxide, water, or inorganic ions.

The combined ozonation and photocatalysis method has been successfully used for the degradation of organic substances in aqueous solutions, such as formic acids [1], aniline [12], monochloroacetic acid and pyridine [13], humic acids [14], and dibutyl phthalate [15]. A synergetic effect of these two oxidation methods was observed from the greatly enhanced mineralization

rate of organic substances. For example, Sanchez et al. [12] combined these two methods for the removal of aniline from water and found that the combined process was more efficient for the decomposition of aniline than ozone or photocatalyst alone. A mechanism involving the formation of an ozonide anion radical, previous to the generation of OH radicals, was suggested to explain the synergetic effect between ozone and TiO_2 under illumination. Wang et al. [1] examined the kinetic parameters for the decomposition of formic acid by photocatalysis, ozonation and their combination, and found that a synergetic effect occurred when photocatalysis and ozonation were conducted simultaneously. A synergetic effect was also observed by Li et al. [15] in their study of the degradation of dibutyl phthalate over TiO_2 film. The TOC removal was considerably improved by the addition of ozone compared to photocatalysis alone and ozonolysis with UV (O_3/UV). Agustina et al. [2] have summarized the compounds degraded by various researchers using photocatalytic ozonation and the results showed that the combination of two methods gave the minimum total degradation time and produced the highest removal of the organics in effluent. The combined advantage of photocatalytic oxidation, giving better reduction in TOC, and the ozonation giving no increase to high-intermediate concentrations, was effectively utilized.

Photocatalysis and ozonation appear to be the most promising technology for developing real applications in water treatment compared with other AOPs, as shown in the literature [2]. However, nearly all the studies have been conducted in artificial systems using only one organic compound as model molecule [16]. Investigations in actual wastewater containing both natural organic matter (NOM) and residuals from biological treatment process, therefore, are very important for developing processes for real applications.

In the present work, the actual wastewater from STP as feed water was treated by a combined ozonation and photocatalytic process to reduce color and trace organics, and therefore improve the clarity of water for reuse. The objective of this study is to target the end of treatment color at an acceptable level of 30–40 Pt–Co units. This makes the color in the treated water almost invisible, so that it is fit-for-purpose as non-potable recycled water. The effects of the operating parameters, such as ozone dosage, flow rate, UV intensity, as well as light source on the efficiency of the process were investigated.

2. Experimental and methods

2.1. Materials

The water sample (Table 1) used for this study was non-chlorinated effluent sampled from Melbourne's STP by the authorized operator. The high performance size exclusion chromatography (HPSEC) profiles [5] showed that the molecular weights of the color-causing organic compounds in the effluent sample were in the range of 400–10,000. The origins of these organic compounds included natural organic matter and residuals from biological treatment process. TiO_2 pellets (Degussa, Germany) were used as a photocatalyst. They contain pure TiO_2 (83.2% anatase and 16.8% rutile), with a S-content of <20 ppm

Table 1
Characterization of STP non-chlorinated effluent sample

Parameter	Value
pH	6.7
TSS (total suspended solids) (mg/L)	22
True color, Pt–Co units	116
A_{254} (UV absorption) (cm^{-1})	0.385
TOC (total organic carbon) (mg/L)	17.5

and a Cl-content of the order of 0.1 wt.%. No further elements are present in contents above 0.05 wt.%. The pellets are in a small pillar shape having the size ranging from 2.5–5.3 mm long and with a diameter of 3.7 mm. The BET surface area of the pellets was measured to be $48 \text{ m}^2/\text{g}$, using a TriStar 3000 porosity analyzer (Micromeritics, USA).

2.2. Apparatus

The photocatalytic oxidation and ozonation experiments were carried out on a laboratory scale recirculating photocatalytic ozonation system (Fig. 1a), which comprised five parts namely the photocatalytic labyrinth flow reactor, the UV panel, the ozone generator, the circulating pump and the storage tank. The photocatalytic reactor was made of stainless steel with baffle plates (Fig. 1b). The UV panel consisted of six 18 W UV-A (NEC Blacklight Lamp) or UV-C lamps (NEC Germicide lamp); UV light intensity can be varied by changing the vertical distance between the UV light and the reactor and the number of lamp tubes. UV-A intensity was measured by a UV irradiance meter with a range of 320–400 nm (UV-A, Photoelectric Instrument Factory of Beijing Normal University, China). Ozone was generated from pure oxygen by an ozone generator (SOZ-6G, A2Z

Ozone Systems Inc., USA) with an ozone production capacity of 6 g/h. The production of ozone used for this study was setup at 4.8 g/h with an oxygen flow rate of 4 L/min. The ozone input flow rate for the treatments of effluent samples was controlled by a Y-piece and a needle valve, which could be adjusted by a flow meter (0–1.0 L/min). The effluent sample stored in the storage tank was circulated by a peristaltic pump (Masterflex 7592-45, Cole-Parmer, USA) during each treatment.

2.3. Experimental procedures

For each photocatalytic treatment (with or without ozonation), 240 g TiO_2 pellets were used to just cover the bottom area of the reactor. The effluent (1.5 L), to be treated, was pumped from the tank into the reactor at a certain circulation flow rate that was irradiated by UV for a certain time. Different UV sources and intensities were trialed. During the ozonation, ozone containing pure oxygen was continuously bubbled into the water sample in the storage tank through a porous diffuser. The ozone dose can be adjusted by changing the input flow rate or the ozonation time. For the co-treatments of photocatalysis and ozonation, ozonation started at the beginning of the photocatalytic oxidation process under circulation and UV irradiating conditions. For those experiments that ozonation was used as pre-treatment, the ozone was bubbled in the effluent tank at an ozone input flow rate of 0.4 L/min for 6 min without circulating and then, photocatalytic treatment was followed for a certain time. In the case of ozonation alone, the effluent was treated by ozone for 6 min at an ozone input flow rate of 0.4 L/min under circulation and UV irradiating conditions with a UV treatment time of 40 min. All the experiments were carried out at room temperature. Effluent samples were withdrawn from the outlet of the reactor for analysis.

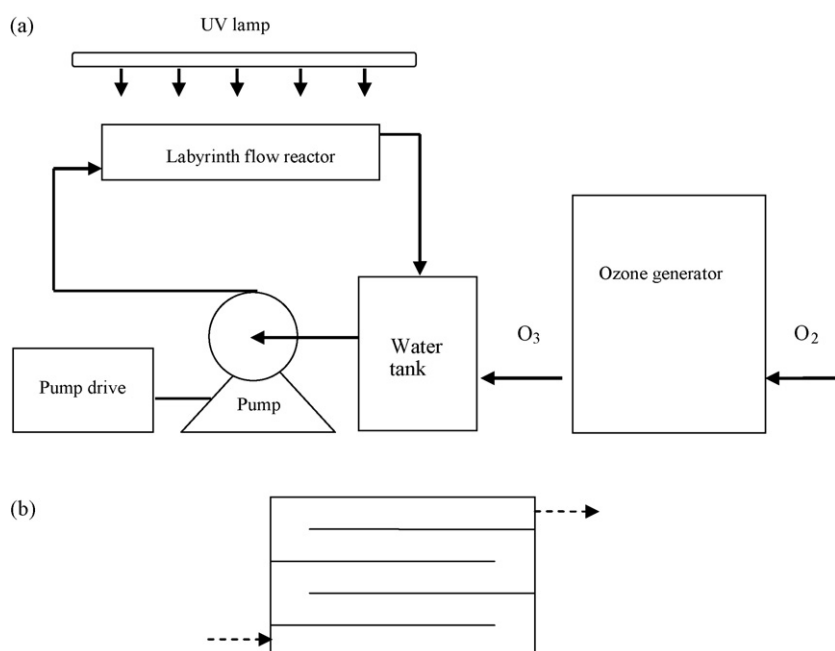


Fig. 1. (a) Schematic diagram of the installation setup for photocatalytic oxidation and ozonation and (b) top view of the labyrinth reactor.

2.4. Analyses

Measurements of true color and A_{254} were carried out with a spectrophotometer (HACH DR5000, USA) using the methods provided by HACH Company. Color is a useful index of dissolved humic substances in water. Platinum–cobalt standard method (Method 8025, HACH) was used in the current work for true color measurement. All samples were firstly filtered using 0.45 μm membrane filters and the filtered samples were measured at 455 nm and reported as true color (Pt–Co units). The presence of organic constituents in the water sample is indicated by measuring the absorption of the filtered sample at a wavelength of 254 nm against organic-free water as blank (A_{254} -UV absorbing, Method 10054, HACH). Results are reported in absorbance per centimeter (cm^{-1}). The TOC was determined by an Aurora 1030W wet chemical oxidation TOC analyzer (O.I. Analytical, USA) calibrated with potassium hydrogen phthalate.

3. Results and discussion

3.1. Comparison of different oxidation processes for color, A_{254} and TOC removal

The effect of different oxidation processes (UV-A/ O_3 , UV-A/ TiO_2 and UV-A/ TiO_2/O_3) on the efficiencies of color, A_{254} and TOC removal was investigated. The rates of color removal and A_{254} reduction for different processes are depicted in Figs. 2 and 3, respectively, as a function of treatment time. For each treatment, the effluent sample was continuously bubbled with ozone (produced from pure oxygen) for 6 min at an ozone input flow rate of 0.4 L/min, and was irradiated for 40 min using three 18 W UV-A lamps with the mean intensity measured at around 11.1 W/m^2 . The circulation flow rate of the water sample between the storage tank and reactor was 0.6 L/min. As shown in Fig. 2, for TiO_2 /UV-A process without ozone, the removal rate of color was the lowest, with only 33.0% color removal after 40-min treatment. For the other processes, in the presence of ozone, the color removal rate was greater than 50%, with a significant removal within the first 10 min. These results show

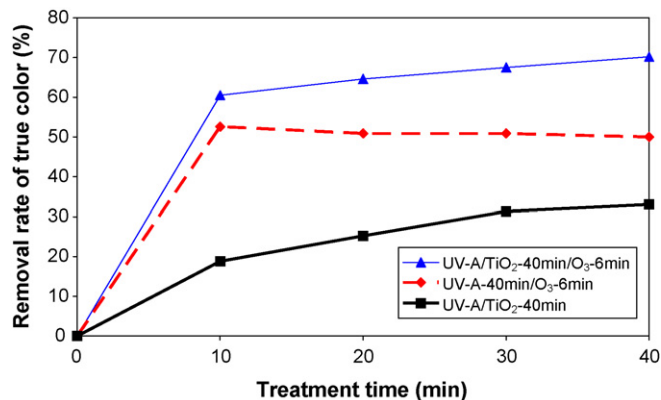


Fig. 2. Color removal rate for the different processes. UV-A intensity = 11.1 W/m^2 , O_3 input flow rate = 0.4 L/min, ozonation time = 6 min, UV irradiation time = 40 min, TiO_2 treatment time = 40 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO_2 = 240 g.

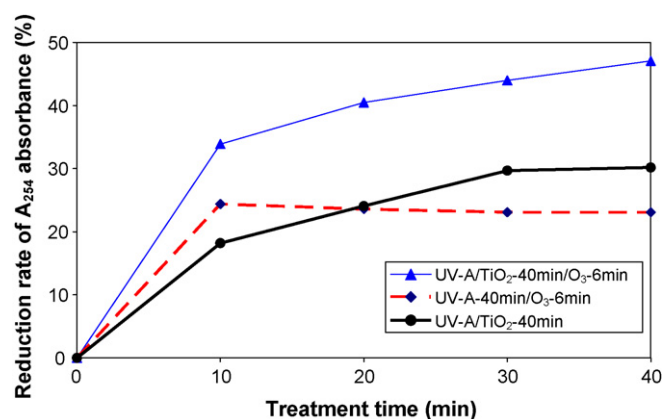


Fig. 3. Reduction rate of A_{254} absorbance for the different processes. UV-A intensity = 11.1 W/m^2 , O_3 input flow rate = 0.4 L/min, ozonation time = 6 min, UV irradiation time = 40 min, TiO_2 treatment time = 40 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO_2 = 240 g.

that the ozonation did have positive effect on the color removal. The highest color removal rate (70.2%) was achieved by the combined treatment of photocatalysis and ozonation. It can also be seen from the figure that in the presence of TiO_2 , the color removal rate still increased continuously with the increase of treatment time after the first 10-min reaction. This was contrasted with no further color reduction occurred for the same experiments performed in the absence of TiO_2 .

It was proposed by Goel et al. [17] that the specific ultraviolet light absorption (SUVA) was a parameter indicating the quantity of unsaturated bonds contained in organic matters; that is, higher the quantity of unsaturated bonds higher the A_{254} absorbance. The A_{254} measurement that indicates the quantity of unsaturated bonds in the treated effluent is an effective parameter to indicate the efficiency of oxidative degradation of organic matters. Similar to the results of color removal (Fig. 2), the time-dependent variation of A_{254} absorbance for the processes with photocatalysis (Fig. 3) implies that, with TiO_2 catalyst, those unsaturated bonds in the effluent are continuously decomposed with extending reaction time. Without TiO_2 catalyst, no further reduction of A_{254} absorbance was observed after the first 10-min treatment by O_3 /UV-A. The combined treatment of photocatalysis and ozonation also showed the best performance with 47.1% A_{254} reduction after 40-min reaction.

The reductions of both color and A_{254} absorbance values within 40 min indicated the progress of the TOC during the reaction. This progress was confirmed by the TOC analysis with the results shown in Fig. 4. It can be seen that there were significant differences in the efficiency of TOC removal between different processes, which is corresponding to the reductions of A_{254} absorbance. As mentioned earlier, many organic compounds cannot be completely degraded by ozonation alone. This was confirmed by our experiments. The TOC reduction was the lowest by using ozonation alone, with only 2.6% TOC removal after 40-min treatment under UV irradiation. This indicates that the intermediate compounds produced during the ozonation process are not easily mineralized. However, the TOC removal rate was significantly increased in the presence of TiO_2 , i.e. 15.7%

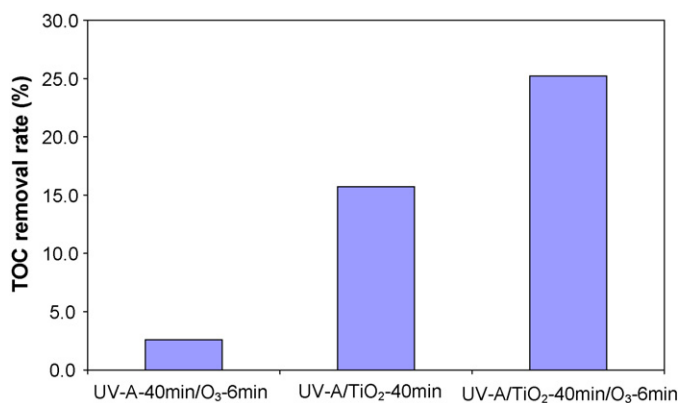


Fig. 4. TOC removal rate after 40 min of treatment for the different processes. UV-A intensity = 11.1 W/m², O₃ input flow rate = 0.4 L/min, ozonation time = 6 min, UV irradiation time = 40 min, TiO₂ treatment time = 40 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO₂ = 240 g.

and 25.2% of TOC removal were obtained over the same reaction period by using TiO₂ alone, and combined photocatalysis and ozonation, respectively, corresponding to the total mineralization of organic matters. This indicates that the removal efficiency of TOC can be significantly improved by the photocatalytic process. It is also found from Fig. 4 that the TOC removal rate for the combination of photocatalysis and ozonation was considerably higher than the sum of that using TiO₂ and ozone alone, which implies a synergistic effect between photocatalysis and ozonation [1,12,13].

This synergistic effect can be explained by the established mechanism from several researchers [1,12,13,18,19] in their studies on the degradation of different organic substances. Most of them have suggested that the great enhancement in mineralization rate of organic substances by using photocatalysis in combination with ozone is due to the fact that ozone is able to generate OH radicals on the TiO₂ surface through the formation of an ozonide anion radical (O₃^{•-}). Hernández-Alonso et al. [18,19] conducted EPR studies either in the dark or under UV irradiation to determine the role of ozone in the photooxidation of cyanide. Their results indicate that ozone strongly interact with TiO₂, resulting in the formation of ozonide radicals (O₃^{•-}). They found that several parallel routes are contributing to the overall reaction. The synergistic effect between photocatalysis and ozonation observed in the current study may be attributed to the following combined reaction routes proposed by Hernández-Alonso et al. [18,19]:

- The homogeneous reaction: In the presence of ozone, oxidation of organic compounds remained in the effluent samples (pH ~ 6.7) occur through a homogeneous reaction of direct ozonation of dissolved ozone as described in Eq. (7).
- The heterogeneous catalytic one: In addition to the homogeneous one (Eq. (7)), heterogeneous catalytic reactions will take place when ozone is present in photocatalyst TiO₂. In the presence of TiO₂, adsorption of ozone molecules on the TiO₂ surface occurs [20]. The adsorbed ozone can react with the TiO₂ surface to generate ozonide radicals (O₃^{•-}) in the adsorption layer by accepting electrons transfer from the

surface of TiO₂ [18]:



The O₃^{•-} species rapidly reacts with H⁺ in the solution to generate HO₃[•] radical, which evolves to give O₂ and OH[•] as shown below:



- The heterogeneous photocatalytic one with oxygen: It is known that oxygen is used as an oxidant compound for conventional photocatalytic processes. Investigation by Kopf et al. [13] indicated that oxygen should have an impact on the photocatalytic ozonation. In this work, ozone containing pure oxygen was bubbled into the effluent samples during the photocatalytic ozonation processes. Apart from ozone, dissolved oxygen itself can act as electron trap to capture TiO₂ conduction band electron and generate superoxide species (O₂^{•-}). The O₂^{•-} radicals are very active and may evolve in several ways to produce OH radicals according to [21]:



In contrast with HO₃[•] (Eq. (9)), HO₂[•] species formed in Eq. (11) cannot produce OH radicals in a single step. A total of three electrons are required for the generation of a single OH radical in this mechanism. This is a less-favoured situation compared to the O₃^{•-} reaction pathways (Eqs. (7)–(9)) that only one electron is needed or the generation of a hydroxyl radical (OH[•]).

- The heterogeneous photocatalytic one with ozone: In the presence of TiO₂ under UV illumination, adsorbed ozone can obviously act as a very strong electrophilic agent to generate OH radicals through O₃^{•-} reaction pathways (Eqs. (7)–(9)) by trapping photoproducted electrons [12,22].

The contributions of the homogeneous and heterogeneous catalytic reactions ((a) and (b)) to the degradation of organic substances are relatively small when compared to the photocatalytic ones with oxygen or ozone–oxygen mixture ((c) and (d)), but are not negligible [18]. OH radicals are generated in both photocatalytic reaction routes ((c) and (d)). A greater number of OH radicals, however, are produced when TiO₂ is irradiated in the presence of ozone due to the higher ability of ozone to capture electrons photogenerated on the surface of TiO₂ [1,18]. Therefore, the color and TOC removal efficiencies of the heterogeneous photocatalytic reactions are reasonably higher with ozone (d) than with oxygen (c).

Using the ozone in combination with a photocatalyst TiO₂ and UV radiation to remove color from actual wastewater from treatment plants, the color removal efficiency has been greatly

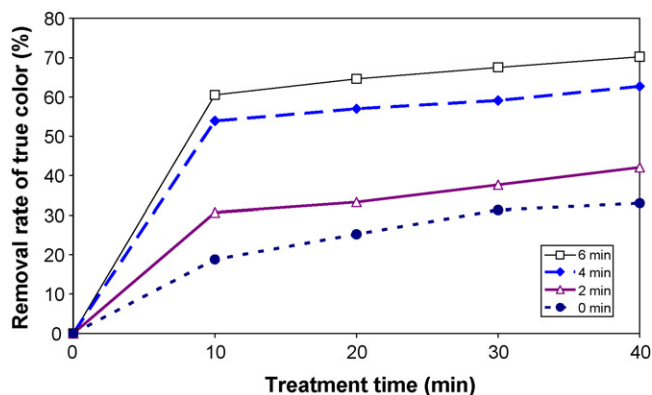


Fig. 5. Variation of color removal rate with ozone dose. UV-A intensity = 11.1 W/m², UV irradiation time = 40 min, TiO₂ treatment time = 40 min, O₃ input flow rate = 0.4 L/min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO₂ = 240 g.

enhanced by the synergistic effect compared to individual ozonation and photocatalysis. This finding confirmed the previous studies of treating synthetic water [1,12,13].

3.2. Effect of ozone dose on color removal

To determine the effect of the ozone dose on the color removal efficiency of the combined treatment of photocatalysis and ozonation, a series of experiments were carried out by varying the ozonation time from 0 to 6 min at an ozone input flow rate of 0.4 L/min. The rates of color removal for various ozone doses are shown in Fig. 5, as a function of treatment time. Water samples were circulated at a flow rate of 0.6 L/min for 40 min under the irradiation of UV-A with the mean intensity of 11.1 W/m². It is found from Fig. 5 that the ozone dose significantly affects the efficiency of the photocatalytic ozonation for color removal. The results show that in the presence of ozone, the removal of color was very quick at the first 10 min in the oxidation process, but the action gradually slowed down with the increase of oxidation time. The removal rate of color increased with an increase in the ozonation time, with a great increase by increasing the ozonation time from 2 to 4 min.

Similar results have been obtained by other researchers [14,15,23] for the effect of ozone dosage on the efficiency of the photocatalytic ozonation process. Li et al. [15] accounted the effect of ozone dosage on the photocatalytic ozonation in their study of the degradation of dibutyl phthalate over TiO₂ film. The TOC removal was considerably improved by the addition of ozone dose. Effect of ozone dosage was also investigated by Li et al. [23] in their research on removing organic pollutants in secondary effluents using photocatalysis ozonation and subsequent biological activated carbon. Their results showed that dissolved organic carbon (DOC) removal efficiency increased with ozone dosage. The total DOC removal efficiency increased from about 52% to 59% in the process when ozone dosage increased from 3 to 9 mg/L. Kerc et al. [14] examined the effect of ozone dosage on the degradation of humic acids by photocatalysis and ozonation and found that the maximum reduction achieved was 80% for organic matter degradation and 90% for color reduction at

higher ozone application rates. The synergistic effect between photocatalysis and ozonation was also evident in those studies.

As discussed in Section 3.1, four parallel routes were found to be contributing to the overall reaction of the photocatalytic ozonation. Increasing of ozone dose by varying the bubbling time of the mixture of ozone and oxygen increase not only the chances of direct ozonation by dissolved ozone (reaction route (a)), but also the number of OH radicals through the generated ozonide anion radicals (O₃^{•-}) and superoxide species (O₂^{•-}) (reactions (b)–(d)), thereby accelerating the photocatalytic ozonation process.

3.3. Effect of UV light intensity on color removal

UV light intensity is an important factor in photocatalytic reaction. The influence of UV light intensity on the efficiency of color removal by the combined treatment of photocatalysis and ozonation was examined at a constant circulation flow rate of 0.6 L/min under UV irradiation for 40 min. The ozone dosage was at input flow rate of 0.4 L/min for 6 min. UV-A lamps were used to supply irradiation. The UV light intensity was simply altered by varying the vertical distance between the UV light and the reactor and the number of lamp tubes. The mean intensities used for this study were measured at 11.1, 21.1 and 32.3 W/m². As seen in Fig. 6, no significant differences were found in the color removal within the tested reaction period of 40 min with the use of different UV intensities; the efficiency of color removal only increased slightly with the increase of UV light intensity. This is reasonable because the stronger the UV light intensity, the more the UV light reaches the catalyst and therefore the production of hydroxyl radicals (OH[•]) is enhanced.

3.4. Effect of circulation flow rate on color removal

The effect of circulation flow rate of the reactor on color removal of the photocatalytic ozonation was investigated by varying the circulation flow rate from 0.3 to 1.2 L/min (Fig. 7). At the beginning of each photocatalytic process, the effluent sample was continuously bubbled with ozone (produced from

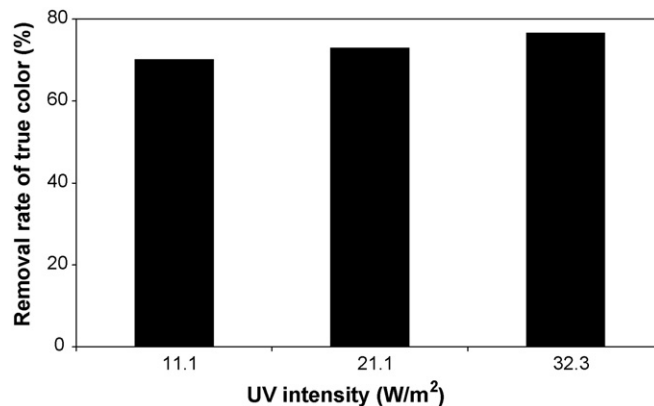


Fig. 6. Effect of UV intensity on color removal rate. UV-A irradiation time = 40 min, TiO₂ treatment time = 40 min, O₃ input flow rate = 0.4 L/min, ozonation time = 6 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO₂ = 240 g.

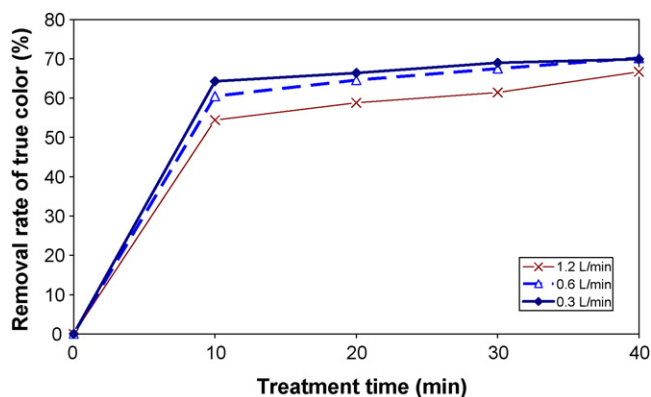


Fig. 7. Effect of circulation flow rate on color removal rate. UV-A intensity = 11.1 W/m², UV-A irradiation time = 40 min, TiO₂ treatment time = 40 min, O₃ input flow rate = 0.4 L/min, ozonation time = 6 min, effluent = 1.5 L, TiO₂ = 240 g.

pure oxygen) at an ozone input flow rate of 0.4 L/min for 6 min. The entire treatment process lasted 40 min under UV-A irradiation with the mean intensity of around 11.1 W/m². Three 18 W UV-A lamps were used as UV source. It is found that the circulation flow rate of the reactor did affect the efficiencies of the photocatalytic ozonation for the color removal, to some extent. The efficiency for color removal achieved at lower circulation flow rates (0.3 and 0.6 L/min) was better than that obtained at a higher circulation flow rate (1.2 L/min).

This effect was caused by several reasons. When increasing the circulation flow rate, the thickness of the liquid film increases, less photons reach the photocatalyst surface, resulting in slower production of hydroxyl radicals (OH•), and consequently lower photocatalytic reaction rates. Details of this effect have been discussed in our previous work [5]. On the other hand, as the circulation flow rate is increased, the residence time of the effluent on the photocatalyst and contact time of the effluent with ozone is decreased, which results in slowing down the reaction of organic molecules with photo-generated holes or OH• radicals because of the lack of direct contact between them. Similar results were obtained by Roselin et al. [24] from their study on photocatalytic degradation of reactive red 22. Their results demonstrated that the percentage removal of dye decreases with increasing flow rate from 15 to 35 mL/min, and the decrease slowed down after a flow rate of about 30 mL/min.

3.5. Effect of ozone input flow rate on color removal

Two photocatalytic ozonation processes were carried out using different ozonation input flow rates and time to determine the effect of ozone input flow rate on the efficiency of the process for color removal. One ozonation treatment was conducted at an ozone input flow rate of 0.4 L/min for 2 min. A lower ozone input flow rate (0.1 L/min) was used for longer time (8 min) in another ozonation experiment. The input quantities of ozone were theoretically the same for both processes. All the other experimental procedures and conditions were the same as those used in Section 3.1. The plots of color removal against

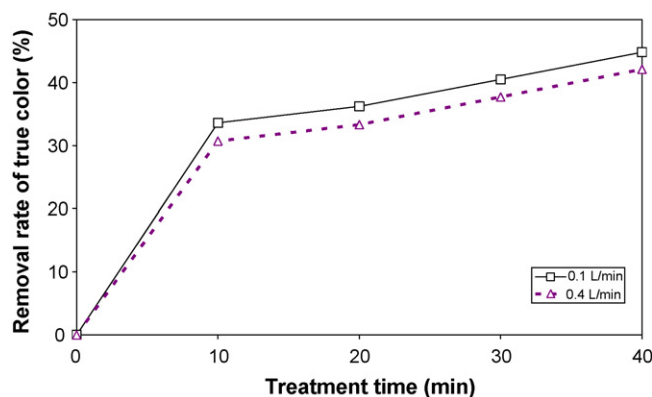


Fig. 8. Effect of ozone input flow rate on color removal. 8 min of ozonation time was used for an ozone input flow rate of 0.1 L/min. 2 min of ozonation time was used for an ozone input flow rate of 0.4 L/min. UV-A intensity = 11.1 W/m², UV-A irradiation time = 40 min, TiO₂ treatment time = 40 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO₂ = 240 g.

treatment time (Fig. 8) show that both processes achieved the similar efficiency for color removal within the oxidation reaction period of 40 min. Longer ozonation treatments at a lower ozone input flow rate, therefore, are not recommended for the combined ozonation and photocatalytic process for economic reasons.

3.6. Effect of ozonation as pre-treatment versus as co-treatment

In two separate experiments, ozone was used as pre-treatment followed by photocatalysis and as co-treatment together with photocatalysis (Fig. 9). In the first experiment, the effluent sample was continuously bubbled with ozone at an ozone input flow rate of 0.4 L/min for 6 min. This was followed by a 40 min of photocatalytic reaction under UV-A irradiation with a mean intensity of around 11.1 W/m². In the second experiment, ozonation was conducted together with the photocatalysis for the first 6 min of the treatment. All the operating conditions for the co-

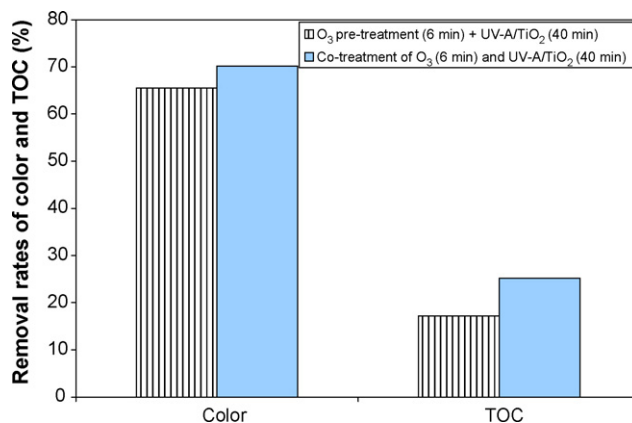


Fig. 9. Effect of ozonation procedures on removal of color and TOC. UV-A intensity = 11.1 W/m², UV-A irradiation time = 40 min, TiO₂ treatment time = 40 min, O₃ input flow rate = 0.4 L/min, ozonation time = 6 min, reactor flow rate = 0.6 L/min, effluent = 1.5 L, TiO₂ = 240 g.

Table 2
Differences in color and TOC removal between UV-A and UV-C

Treatment time (min)	Color removal rate (%)		TOC removal rate (%)	
	UV-A	UV-C	UV-A	UV-C
40	65.5	69.0	17.2	18.2
120	84.3	87.2	34.3	37.3

treatment procedure were the same as those used for the above pre-treatment experiments. Fig. 9 shows significant differences in the efficiencies of color and TOC removal between two treatments. For the color removal, the co-treatment method was slightly better than the pre-treatment procedure. But significant differences were found for TOC reduction. The efficiency of the co-treatment method for TOC removal (25.2%), however, was nearly 50% higher than that of pre-treatment procedure (17.2%). This indicates that the co-treatment of photocatalysis and ozonation is more efficient for the mineralization of organic matter in the effluent sample compared to the pre-treatment procedure, which is again attributed to the synergistic effect between photocatalysis and ozonation, as discussed in the earlier sections.

3.7. Effect of UV source on color and TOC removal

UV light source is another factor in photocatalytic reaction. To evaluate the influence of UV light source on the efficiency of photocatalytic process, the 2 h of TiO₂ photocatalytic oxidation reactions with UV-A or UV-C irradiation were compared. Three 18 W UV-A lamps were used to emit UV-A source (peaked at 365 nm). UV-C light (peaked at 254 nm) was supplied by another three 18 W UV-C lamps. The catalyst amount, volume of effluent and circulation flow rate were the same as those used in Section 3.6. Samples were withdrawn at a reaction time of 40 min and the end of 2 h reaction period for color and TOC analyses. In general, the UV-C light is considerably more beneficial to the photocatalytic process than the UV-A light as it provides high-photon energy. However, the results (Table 2) show that there were no significant differences in the process efficiency between UV-A and UV-C light within the reaction period of 2 h. The efficiencies for both color and TOC removal under UV-C light were only slightly higher than those of UV-A light. It is confirmed that the process efficiency is not necessarily enhanced by using more powerful, shorter wavelength light [5,25]. It has been proposed by Herrmann [26] that threshold wavelength corresponds to the band gap energy for the semiconductor catalyst, e.g. for the TiO₂ catalyst having a band gap energy of 3.02 eV, the ideal wavelength is at 400 nm. Therefore, it is evident that UV-A can provide sufficient energy required for color reduction, and the energy intensive UV-C source is not necessary for this application.

4. Conclusions

This study presents the results of treating actual STP effluent using a combined ozonation and TiO₂ photocatalytic process

with UV irradiation under a range of operating conditions. The results indicated that the method has been efficient in the reduction of the most important parameters that account for the environmental impact such as color, A₂₅₄ absorbance and TOC. Ozone did significantly improve the process efficiency in reducing color of the effluent, and the color removal rate increased with an increase in ozone dose. However, only very low percentage of organic matters in the effluent sample was totally mineralized by using ozone alone. The overall process efficiency in TOC removal was significantly improved by combining the ozonation with photocatalytic process because of the synergistic effect between two methods. Stronger UV intensity, lower circulation flow rate gave higher efficiency in reducing color but not significant in the range studied. UV light source had very little impact on the efficiency of color and TOC removal within 2 h of reaction for this reused water application.

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