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Effects of UV/Ag-TiO_2/O_3 advanced oxidation on unicellular green alga *Dunaliella salina*: Implications for removal of invasive species from ballast water

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Abstract

The UV/Ag-TiO_2/O_3 process was investigated for ballast water treatment using *Dunaliella salina* as an indicator. Inactivation curves were obtained, and the toxicity of effluent was determined. Compared with individual unit processes using ozone or UV/Ag-TiO_2, the inactivation efficiency of *D. salina* by the combined UV/Ag-TiO_2/O_3 process was enhanced. The presence of ozone caused an immediate decrease in chlorophyll *a* (chl-*a*) concentration. Inactivation efficiency and chl-*a* removal efficiency were positively correlated with ozone dose and ultraviolet intensity. The initial total residual oxidant (TRO) concentration of effluent increased with increasing ozone dose, and persistence of TRO resulted in an extended period of toxicity. The results suggest that UV/Ag-TiO_2/O_3 has potential for ballast water treatment.

Key words: ballast water; UV/Ag-TiO_2/O_3 process; *Dunaliella salina*; inactivation; total residual oxidant

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Introduction

Ballast water is used widely to maintain stability and maneuverability of ships during transit (Hua and Liu, 2007; Boldor et al., 2008). It is estimated that about 10 billion tons of ballast water are transferred globally each year (Oemcke and van Leeuwen, 2003). However, the transport of ballast water introduces unwanted organisms and damage to the environment, and is regarded as one of the major risk factors threatening global marine environmental safety (Bax et al., 2003; Lewis et al., 2003). Ballast water management and treatment are essential to prevent invasive species' introduction.

In recent years, many technologies have been studied for ballast water treatment, including ballast water exchange (McCollin et al., 2007), hydrogen peroxide (Smit et al., 2008), filtration (Tang et al., 2009), ultraviolet (Sutherland et al., 2001), ozonation (Oemcke and van Leeuwen, 2005; Perrins et al., 2006), heat treatment (Rigby et al., 1999), and ultrasound (Holm et al., 2008). Each method has its own advantages and disadvantages. According to factors of safety, effectiveness, and cost, when using a single method the requirements of International Maritime Organization are not reached. Thus, the combined treatment of ballast water has become a major research direction.

Ozone is an effective biocide and widely applied in water disinfection. The reaction rate of ozone is rapid, and operation is convenient. Some species of marine microorganisms have shown high resistance to ozonated seawater (Liltved et al., 2006), however, and ozonation alone may not be suitable for ballast water treatment (Oemcke and van Leeuwen, 2005).

TiO_2 photocatalysis has been proposed as one of the best disinfection technologies as it produces no dangerous or malodorous byproducts (Yao et al., 2007). Moreover, evidence has shown that the photoreactivation and dark repair of bacteria can be repressed by TiO_2 modified UV-C disinfection (Shang et al., 2009). Traditional methods using colloidal and particulate TiO_2 catalyst suspensions are not suitable for ballast water treatment, however, due to separation and reuse difficulties and reduced disinfection efficiency caused by light screening of TiO_2 particulates in solution (Benabbou et al., 2007). Therefore, TiO_2 thin film, a relatively new catalyst, has gained much attention (Wu et al., 2008; Zhang et al., 2009).

Compared with individual treatment, a combination of methods results in higher treatment efficiency (Wang et al., 2002; Nakamura et al., 2008). The combination of ozonation and TiO_2 photocatalysis (UV/TiO_2/O_3) enhances oxidative degradation of pollutants by the generation of highly reactive hydroxyl radical (OH·), which eventually

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leads to higher oxidation rates (Agustina et al., 2005). Hence, the UV/TiO_2/O_3 process might be an effective purification method for ballast water treatment.

In this study, we evaluated the effectiveness of UV/Ag-TiO_2/O_3 treatment in preventing the introduction of invasive species during the ballasting/deballasting process. The inactivation of *D. salina* by the UV/Ag-TiO_2/O_3 process was systematically studied. The effects of two important reaction parameters, ozone dose and UV light intensity, were examined in this system, and the toxicity of effluent was investigated.

1 Materials and methods

1.1 Preparation of artificial seawater and test culture

All experiments were conducted in artificial seawater, which was mixed with autoclaved salt and sterilized deionized water. It consisted of the following compositions (g/L): NaCl, 26.73; $MgSO_4 \cdot 7H_2O$, 6.66; $MgCl_2 \cdot 6H_2O$, 4.86; KCl, 0.72; NaBr, 0.084; $CaCl_2$, 1.15; $Na_2SiO_3 \cdot 9H_2O$, 0.0024; H_3BO_3, 0.058; $NaHCO_3$, 0.2; H_3PO_4, 0.001; and $NH_3 \cdot H_2O$, 0.002.

D. salina obtained from Marine Microalgae Research Center, Ocean University of China, was used as an indicator as it is widely distributed and easy to culture. It was cultured in artificial seawater enriched with Guillard's f/2 medium, receiving 2400 lx of white fluorescence light with an automated light/dark cycle of 12 hr/12 hr at 22°C. Growth was monitored daily by cell count using a hemocytometer. Cultures were harvested in the logarithmic growth phase and then diluted in artificial seawater to give a cell concentration of approximately 6.0×10^5 cells/mL for testing.

1.2 Preparation of the catalyst

The Ag-TiO_2 thin film was prepared by anodic oxidation and photodeposition (Wu et al., 2011). Microporous titanium dioxide film was prepared directly on the surface of pure titanium (99.5 wt.%) by anodic oxidation in 1.0 mol/L sulfuric acid solution. Titanium specimen and copper plate were used as the anode and cathode, respectively. The anodizing process was firstly carried out at a constant current of 150 mA/cm^2 until potential reached 140 V, and then the process was carried out at a constant potential until the current decayed to stability (close to zero), and the reaction was completed.

The prepared TiO_2/Ti catalyst was then put into 3 g/L silver nitrate solution (volume ratio of ethanol/deionized water equaled to 1:4), and exposed to UV irradiation (at 254 nm, 3.5 mW/cm^2) for 30 min with continuous stirring under N_2 atmosphere. The Ag-TiO_2 thin film was then obtained.

1.3 UV/Ag-TiO_2/O_3 system design and set-up

The experimental device used in this study is shown in Fig. 1. The pumped raw water firstly passed through a venture injector, where ozonized gas generated from dry oxygen by a laboratory ozone generator (COM-AD-01, Anseros, Germany) was introduced into water. The ozonized water was then introduced into an inactivation reactor (46 mm inner diameter, 540 mm height) with a water distributor at the bottom. The centre of the reactor consisted of a quartz tube (30 mm diameter, 540 mm height), which held a low pressure UV lamp (UV-C light at 253.7 nm). The Ag-TiO_2 thin film was fixed on the inner surface of the reactor. The experiments were carried out at 20°C under pH 8.0. The water flow rate was 100 L/hr, corresponding with hydraulic residence time (HRT) of 2.5–15.0 sec at different sampling ports.

Algal inactivation efficiencies at various reaction times were studied by testing viable algae cells and chlorophyll *a* (chl-*a*) concentrations at different sample ports of the reactor. To determine TRO decay and effluent toxicity, samples were then stored in dark airtight incubators at 20°C and TRO and chl-*a* concentrations were measured periodically. When samples were used for algae counts and chl-*a* analysis, 0.02 mL of 0.1 mol/L $Na_2S_2O_3$ in 1 mL sample was previously added to stop the residual oxidant reaction. The ozone dose was adjusted by changing the input flow rate, and UV light intensity was varied by changing the lamp and quartz tube. When considering UV/Ag-TiO_2 treatment only, the power to the ozone

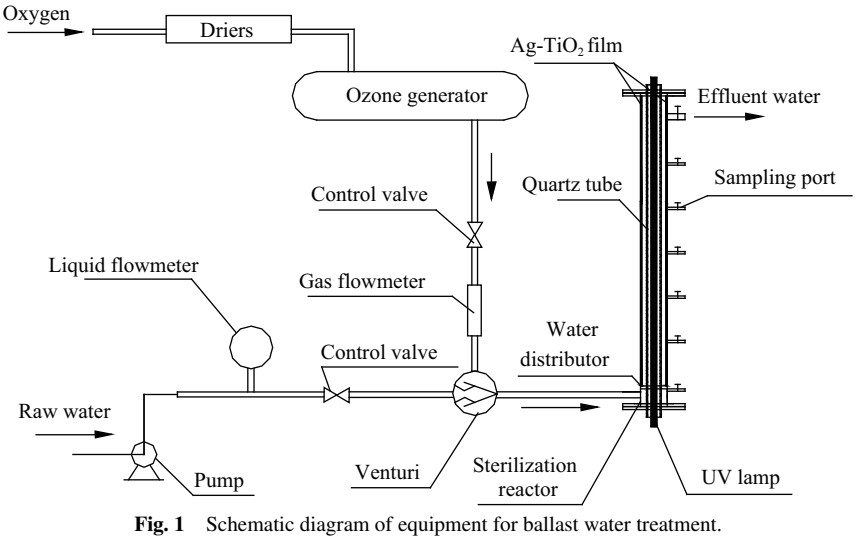

Fig. 1 Schematic diagram of equipment for ballast water treatment.

generator was interrupted. When using ozone treatment only, the UV lamp was removed from the experimental apparatus described above. All inactivation experiments were performed in triplicate, and error bars are the standard deviation of the mean.

1.4 Determination of viability of algal cells

Algal cell viability was determined following previous studies (Amsler et al., 2000; Gavand et al., 2007). Two vital stains, fluorescein diacetate (Sigma) and Evan's Blue (Sigma), were used and cells were incubated with the stain solution for 15 min at 20°C. Live cells were stained green by fluorescein diacetate under blue epi-illumination, while dead cells were stained blue by Evan's blue under bright field illumination. At least 100 algal cells from each sample were counted as live or dead for use in inactivation efficiency calculation. Inactivation efficiency of algal (η) was calculated utilizing the following equation:

$$\eta = -\lg(N_t/N_0) \quad (1)$$

where, N_0 (cells/mL) is the initial *D. salina* population and N_t (cells/mL) is the vital *D. salina* population remaining at time t.

1.5 Chl-*a* analysis

The concentration of chl-*a* was determined by spectroscopy (APHA, 1998). Briefly, algal samples were harvested by filtration and extracted with a 90% acetone solution for 16 hr in the dark at 4°C. After extraction and centrifugation (10 min at 5000 r/min), absorbance spectra were recorded with a spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd., China).

1.6 Photosynthetic activity

Photosynthetic activities of treated and untreated algal cells were measured by oxygen method (APHA, 1998). In brief, effluent samples were withdrawn from the reactor at different reaction conditions, and were charged into 50 mL light and dark airtight bottles, respectively. The two water sample bottles were then incubated at 22°C with 2400 lx white fluorescence light irradiation. At every time interval dissolved oxygen (DO) concentrations of samples were determined using the calculation formula as follows:

$$\text{Gross photosynthesis} = \text{Light bottle DO} - \text{Dark bottle DO} \quad (2)$$

1.7 Chemical analysis

Ozone supply was measured with an ozone monitor (MP, Anseros, Germany). Ultraviolet light intensity on the outer surface of the quartz tube was measured by a UV irradiance meter (UV-B, Photoelectric Instrument Factory of Beijing Normal University, China). The TRO concentration was determined using a standard DPD (N, N-diethyl-*p*-phenylenediamine) colorimetric analysis for total chlorine (APHA, 1998). Both DO and pH values were measured with a Hach sension 378 meter (USA).

2 Results and discussion

2.1 Individual and combined treatments for *D. salina* inactivation

2.1.1 Inactivation efficiency

The inactivation efficiency of *D. salina* measured during algae inactivation by the combined UV/Ag-TiO_2/O_3 process was compared with each individual unit process under identical conditions (Fig. 2a). When exposed to UV/Ag-TiO_2 irradiation alone, the levels of *D. salina* inactivation efficiency were comparable low. Contrarily, when 0.36 g/hr of ozone was initially injected into the reactor during UV/Ag-TiO_2 exposure, a significant enhancement was obtained, especially in the initial phase of the reaction. For inactivation with ozone alone, the inactivation profile was similar to that obtained for the UV/Ag-TiO_2/O_3 process, except that the latter resulted in more inactivated cells. For instance, with a UV intensity of 3.2 mW/cm^2 and HRT of 2.5 sec, the inactivation efficiencies of *D. salina* in UV/Ag-TiO_2, O_3, and UV/Ag-TiO_2/O_3 processes were 0.09, 0.33, and 0.56, respectively. Even when taking the UV/Ag-TiO_2 and O_3 effect into consideration, enhancement in the combined UV/Ag-TiO_2/O_3 process was significant. The inactivation of *D. salina* under the effect of UV/O_3 is also presented in the figure as a reference, and about 0.49–0.98 log inactivation was obtained over a HRT range of 2.5–

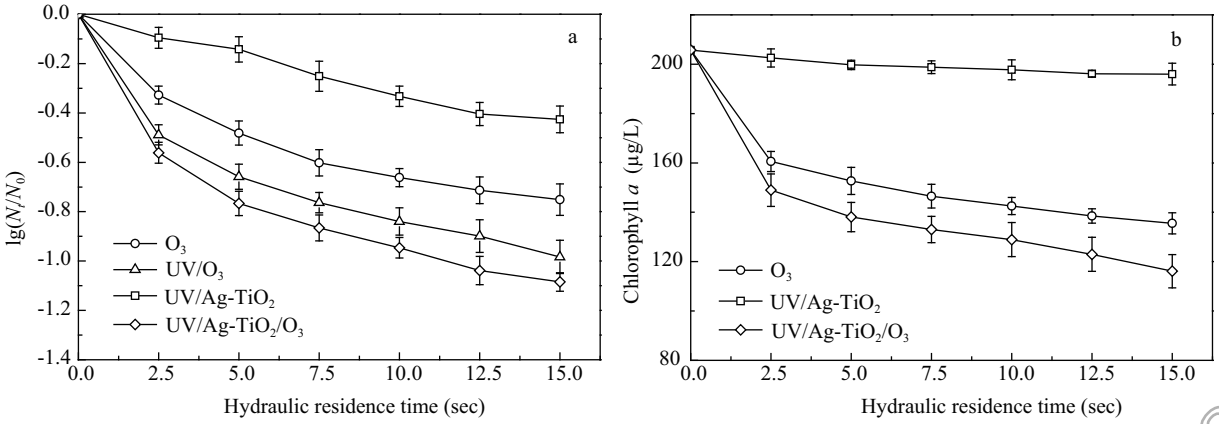

Fig. 2 Comparison of the inactivation of *D. salina* using the combined UV/Ag-TiO_2/O_3 process with that in individual unit processes. (a) inactivation efficiency; (b) chl-*a* removal efficiency (UV intensity = 3.2 mW/cm^2; ozone dose = 0.36 g/hr; temperature = 20°C).

15.0 sec. Compared with the result of UV/Ag-TiO_2/O_3 process, this result indicated that the presence of Ag-TiO_2 thin film during UV/O_3 exposure can expedite the inactivation of *D. salina*.

On the basis of the above investigation, ozone played a critical role in the inactivation mechanism of *D. salina* in the UV/Ag-TiO_2/O_3 system, and the application of UV/Ag-TiO_2 enhanced this effect. This observation can be explained by the established mechanism from previous research. Specifically, a larger number of hydrogen peroxide and hydroxyl radicals were produced during the ozonation under UV irradiation (Mirat and Vatistas, 1987; Peyton and Glaze, 1988). When the photocatalytic and ozonation treatments were carried out simultaneously, the adsorbed ozone reacted with the TiO_2 surface to generate ozonide radicals ($O_3 \cdot^-$) in the adsorption layer by accepting electron transfer from the surface of TiO_2. Consequently, the recombination of electrons and positive holes interfered, and a larger number of radicals were produced, thereby accelerating the photocatalytic ozonation reaction (Agustina et al., 2005; Zou and Zhu, 2008).

2.1.2 Chl-*a* removal

Chl-*a* exists universally in algae, and plays an important role in the photosynthesis of algae (Baker, 2008). In the present work, the reduction of chl-*a* was used to evaluate *D. salina* inactivation efficiency indirectly. As seen from Fig. 2b, in the absence of ozone, no obvious decrease in chl-*a* concentration was observed, suggesting that UV/Ag-TiO_2 exposure is ineffective for chl-*a* removal over the short time. In contrast, however, chl-*a* concentration decreased from 205.75 to 135.51 μg/L within 15 sec when using the ozone treatment alone. A better reduction in chl-*a* concentration was obtained in the UV/Ag-TiO_2/O_3 process compared to ozone process, with only 116.13 μg/L of chl-*a* detected after 15 sec. Maximum chl-*a* removal was always observed in the initial phase of the reaction for experiments with ozone presence, which was consistent with previous studies (Perrins et al., 2006; Miao and Tao, 2009).

Compared with the curves in Fig. 2a, we found that the tendency of *D. salina* and chl-*a* reduction agrees with the results of *D. salina* inactivation in the ozone and UV/Ag-TiO_2/O_3 processes. When treated by UV/Ag-TiO_2 alone, however, there was no obvious reduction in chl-*a* even as evident inactivation of *D. salina* was obtained. It should be pointed out that decomposition of cell structure significantly contributes to algae death in ozonized water, while UV-C induced DNA damage may be the major lethal effect on microorganisms in the UV/Ag-TiO_2 system (Miao and Tao, 2009; Shang et al., 2009). Thus, the combination of ozonation and photocatalysis with Ag-TiO_2 thin film under UV-C irradiation may not only destroy the cell structure, but also induce cell DNA damage and result in the enhancement of inactivation efficiency.

2.2 Effect of operational parameters

2.2.1 Effect of ozone dose

To investigate the effect of ozone dose on *D. salina* inactivation efficiency for the UV/Ag-TiO_2/O_3 process, a series of experiments were carried out varying the ozone dose from 0.36 to 1.36 g/hr with the UV intensity of 3.2 mW/cm^2. As shown in Fig. 3, ozone dose had a significant influence on inactivation efficiency of *D. salina*, and both algae inactivation efficiency and chl-*a* removal efficiency increased with increasing ozone dose, especially at the initial stage of the reaction. When HRT was 15.0 sec, only 1.19 log reduction in vital cells number and 86.17 μg/L of chl-*a* were obtained with ozone dose of 0.62 g/hr, whereas 1.56 log reduction and 20.37 μg/L of chl-*a* were observed for ozone dose of 1.36 g/hr.

Increasing ozone dose improved the chance of direct ozonation by dissolved ozone. Similar results were also obtained by Oemcke and van Leeuwen (2005) for their inactivation experiments with ozone using marine dinoflagellate alga *Amphidinium* sp. As discussed in Section 2.1, another possible reason may be that increasing ozone dose also enhanced the number of reactive oxygen species (ROS), thereby accelerating the photocatalytic ozonation process.

2.2.2 Effect of UV light intensity

To investigate the influence of UV light intensity on the efficiency of *D. salina* inactivation by the combined treatment of photocatalysis and ozonation, different UV intensity inactivation experiments were performed with an ozone dose of 0.36 g/hr. As depicted in Fig. 4, the addition

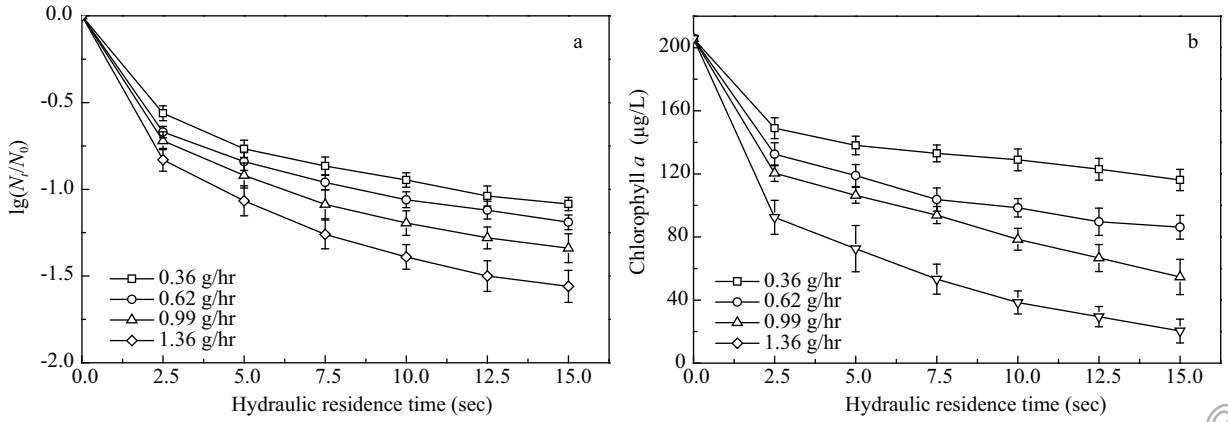

Fig. 3 Effect of ozone dose on *D. salina* inactivation in UV/Ag-TiO_2/O_3 system. (a) inactivation efficiency; (b) chl-*a* removal efficiency (UV intensity = 3.2 mW/cm^2; temperature = 20°C).

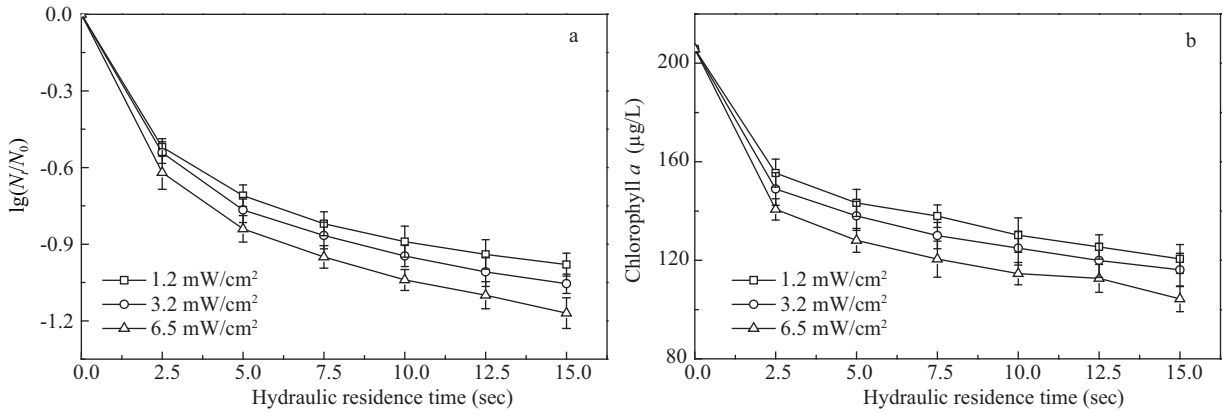

Fig. 4 Effect of UV intensity on *D. salina* inactivation in UV/Ag-TiO_2/O_3 system. (a) inactivation efficiency; (b) chl-*a* removal efficiency (ozone dose = 0.36 g/hr; temperature = 20°C).

of UV intensity improved treatment efficiency, although this was not as significant as ozone dose (Fig. 3). With HRT of 15.0 sec, when UV light intensity increased from 1.2 to 6.5 mW/cm^2, *D. salina* inactivation efficiency improved from 0.98 to 1.17, and the detected chl-*a* decreased from 120.55 to 104.37 μg/L, respectively.

UV irradiation plays an important role in photocatalytic ozonation process. Increasing UV light intensity enhanced the effect of UV-C irradiation and improved the ROS produced in the UV/Ag-TiO_2/O_3 system, resulting in enhanced inactivation efficiency.

2.3 Characteristics of the effluent

Table 1 shows the characteristics of the effluent after treatment by UV/Ag-TiO_2/O_3 process. Compared with raw water (pH 8.0), the pH value of the effluent changed little, which probably had no positive or adverse affects on the organisms in the effluent. Initial TRO concentration was positively correlated with ozone dose, and resulted in faster decay rate for lower initial concentration. All TRO concentrations reduced rapidly at first and attenuated slowly as the duration increased. After 72 hr, the detected TRO concentrations were close to zero in all experiments.

The biggest difference with ozone chemistry in marine ballast water compared to freshwater is the presence of bromide ion in seawater. Bromide can be oxidized by ozone, and the produced bromine, which is quantified as TRO (White, 1999), is a weaker but more stable disinfectant. The rate of TRO decay determines the time that effluent will be toxic to organisms residing within the ballast tank. Our results suggested that effluent with higher initial TRO concentration may be toxic for a longer time.

Table 1 Chemical characterization of effluent after treatment by UV/Ag-TiO_2/O_3 process at 20°C

Ozone dose (g/hr)	Initial pH value	Total residual oxidant (mg/L)				
		Initial	After 24 hr	After 48 hr	After 72 hr	After 96 hr
0.36	8.01	0.42	0.03	0.02	0.01	0.01
0.62	7.98	0.67	0.07	0.04	0.03	0.01
0.99	8.02	0.98	0.11	0.06	0.04	0.02
1.36	8.03	1.24	0.18	0.1	0.06	0.04

2.4 Effluent toxicity testing

After UV/Ag-TiO_2/O_3 treatment, the reduction of chl-*a* and photosynthetic activity of *D. salina* were used to evaluate the toxicity of effluent. Figure 5 shows the variation of chl-*a* concentration with stored time. Chl-*a* concentrations declined rapidly for all TRO levels, especially in the initial 24 hr, consistent with the results of TRO decay (Table 1). There was no significant difference in final chl-*a* concentration between treatments with initial TRO concentrations greater than 0.99 mg/L after 96 hr. Control concentrations (raw water, TRO 0 mg/L) also declined slightly over time, which may be due to the lack of light.

Figure 6 shows the profile of *D. salina* photosynthetic activity as the rate of oxygen evolution. With no treatment, detected gross photosynthesis increased with time, suggesting that *D. salina* cells in raw water have normal photosynthetic activities. In contrast, however, UV/Ag-TiO_2/O_3 exposure resulted in a reduction of *D. salina* photosynthetic activity in effluent, with almost no gross photosynthesis detected in treatment effluents after 96 hr. After UV/Ag-TiO_2/O_3 treatment, most *D. salina* cells had already lost their viability (Fig. 3a), and the resultant

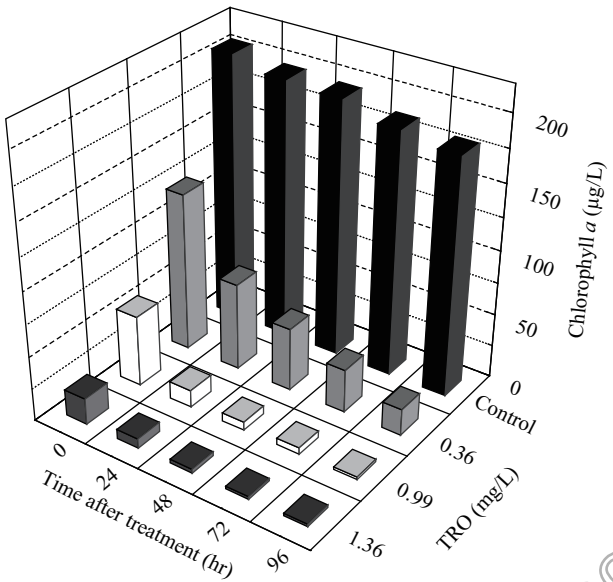

Fig. 5 Decay of *D. salina* and chl-*a* in the effluent of UV/Ag-TiO_2/O_3 process at 20°C.

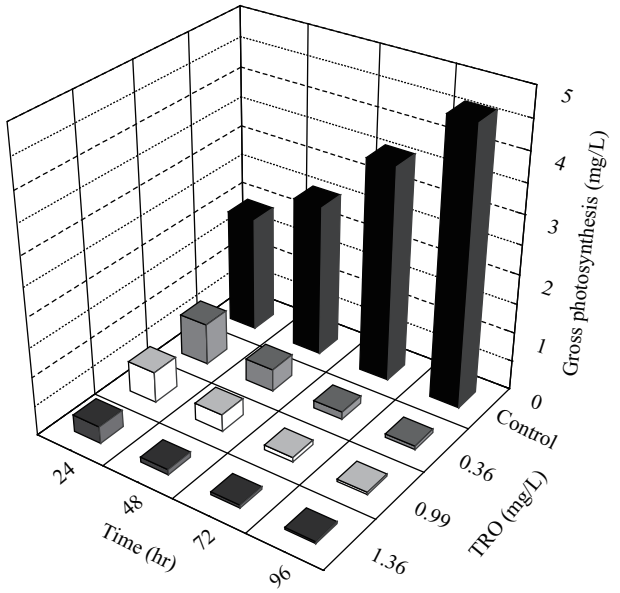

Fig. 6 Reduction in gross photosynthesis of *D. salina* in the effluent of UV/Ag-TiO_2/O_3 process (white fluorescence light intensity = 2400 lx; temperature = 22°C).

decomposition of dead *D. salina* cells caused the levels of dissolved oxygen to decrease rapidly with time in effluent. This may explain the reduction in gross photosynthesis as stored time increased in effluent.

3 Conclusions

The UV/Ag-TiO_2/O_3 process is a novel ballast water treatment method, which was proven to be efficient for *D. salina* inactivation. Compared with individual processes, the combination of ozonation and photocatalysis with Ag-TiO_2 thin film under UV-C irradiation gave higher treatment efficiency. Inactivation efficiency was improved when ultraviolet intensity and ozone dose were increased, and was more obvious in the initial phase of the reaction. In addition, the TRO concentration of effluent was positively correlated with ozone dose, and the persistence of TRO resulted in cumulative mortality. These findings suggest that UV/Ag-TiO_2/O_3 has significant potential for ballast water treatment.

Acknowledgments

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