

Ballast water treatment by sequential filtration and advanced oxidation process

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ABSTRACT: The ability of a 2-stage (filtration + UV/Ag-TiO₂/O₃) ballast water treatment process to control non-indigenous species introduction has been assessed. The removal efficiencies of turbidity and phytoplankton were monitored during the filtration pretreatment phase, and the degradation of phytoplankton (*Dunaliella salina* and *Phacodactylum tricorntutum*) chlorophyll *a* (chl-*a*) by UV/Ag-TiO₂/O₃ were investigated. Results showed that 50 µm screen filtration could remove a small part of phytoplankton, and reduce the turbidity. Compared to individual unit processes with ozone or UV/Ag-TiO₂, the removal of chl-*a* by the combined UV/Ag-TiO₂/O₃ process was enhanced, and the effluent exhibited a persistence toxicity within 24 h. The results indicate that a combination of filtration and UV/Ag-TiO₂/O₃ advanced oxidation maybe a promising method for ballast water treatment.

INTRODUCTION

Ballast water is essential for ships without sufficient weight of cargo to ensure their balance and structural integrity during voyage. Nevertheless, ships transporting ballast water has been recognized as a major pathway for the spread of aquatic organisms into new habitats (Stehouwer et al. 2015). It is estimated that annually about 10 billion tons of ballast water are transferred globally, and more than 3000 species are transported by ships each day (Banerji et al. 2012). To prevent the introduction of potentially invasive species, regulations for the control and management of ballast water was drafted and ratified by the International Maritime Organization (IMO) in February 2004. According to the Regulation D-2 ballast water discharge standard, the organism concentrations in the discharge of ballast water should be below specified limits (Gollasch et al. 2007): less than 10 viable organisms/m³ for minimum dimension greater than 50 µm; less than 10 viable organisms/mL for the minimum dimension between 10 and 50 µm; *Escherichia coli* less than 250 cfu/100 mL, *intestinal Enterococci* less than 100 cfu/100 mL and Toxicogenic *Vibrio cholerae* (O1 and O139) less than 1 cfu/100 mL or less than 1 cfu/gram wet wt. zooplankton samples.

Various technologies for ballast water treatment have been developed (Boldor et al. 2008), including filtration separation, ballast water heating, ultraviolet (UV) irradiation, electrochemical treatment, and chemical biocides. However, a single technique is not suitable for ballast water treatment when considering the efficiency and safety. Combinations of several methods, which can be more effective than one method standing alone, have been the focus of current researches for ballast water treatment. Recently, primary separation combined with secondary inactivation is emerging as a promising ballast water treatment technology, and filtration is proposed for separation of sediments and organisms from ballast water. Filtration is effective for removing zooplankton, while for bacteria and viruses it cannot reduce them. The removal efficiency of phytoplankton by filtration is complexly as the organisms size are various (Tsolaki & Diamadopoulos 2010).

Ozonation and UV irradiation are the most frequently used methods for water disinfection. However, using these two methods separately, relatively high ozone doses and long UV treatment durations

are required to eliminate the vast majority of species in ballast water. Photocatalytic ozonation (UV/TiO₂/O₃) has been reported as a promising disinfection technology that does not produce halogenated compounds. The application of ozone in combination with titanium dioxide photocatalysis (UV/TiO₂/O₃) brings about enhanced oxidative degradation of pollutants by the generation of highly reactive hydroxyl radical (•OH), which eventually leads to higher oxidation rates (Agustina et al. 2005).

The primary goals of this study was to examine the potential of filtration pretreatment combined UV/Ag-TiO₂/O₃ oxidation to treat ballast water. The removal of turbidity and phytoplankton by filtration was investigated, and the inactivation efficiency of UV/Ag-TiO₂/O₃ on phytoplankton were studied.

MATERIALS AND METHODS

Preparation of artificial seawater and test culture

All experiments were conducted in artificial seawater prepared using procedures reported previously (Wu et al. 2011). Pure culture *Dunaliella salina* (*D. salina*), and *Phacodactylum tricornerutum* (*P. tricornerutum*) were used as the indicator organisms in this study. The cultures were enriched in Guillard's f/2 medium, according to the procedures described elsewhere (Wu et al. 2011). Cells for further tests were harvested in their logarithmic growth phase, which was diluted with artificial seawater for testing.

Ballast water treatment experiments

Experiments were carried out in a laboratory ballast water treatment system, which consisted of a 120 L capacity feed tank, centrifugal pump, flowmeter, 50µm screen filter, venture injector, and the sterilization reactor (46 mm inner diameter, 540 mm height) with a water distributor at the bottom. The pumped raw water from the feed tank firstly went through the filter, and then passed through the venture injector, where ozonized gas that was generated from dry oxygen by a laboratory ozone generator was fed into water. Thereafter, the water went into the inactivation reactor. A quartz tube (30 mm diameter, 540 mm height) holding a low pressure UV-C lamp was placed at the center of the reactor. The Ag-TiO₂ thin film was coated on the inner surface of the reactor. The water flow rate was 500 L/h, corresponding with hydraulic residence time (HRT) of 0.5 - 3.0 s at different sampling ports. 0.02 mL of 0.1 mol/L Na₂S₂O₃ in 1 mL sample was previously added into the sampling pipe to stop the inactivation reaction by residual oxidant. To determine the toxicity of effluent, the samples were then stored in a dark airtight incubator, and chl-*a* concentration was periodically measured.

Analytical method

The chl-*a* concentration was determined using the spectroscopic method (APHA, 1998). Photosynthetic activities of algal cells were measured by oxygen method (APHA, 1998). Absorbance at 254 nm (A₂₅₄) was recorded with a spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd., China). UV-C intensity on the outer surface of the quartz tube was measured by a UV irradiance meter (Photoelectric Instrument Factory of Beijing Normal University, China). Ozone supply was measured with an ozone monitor (MP, Anseros, Germany).

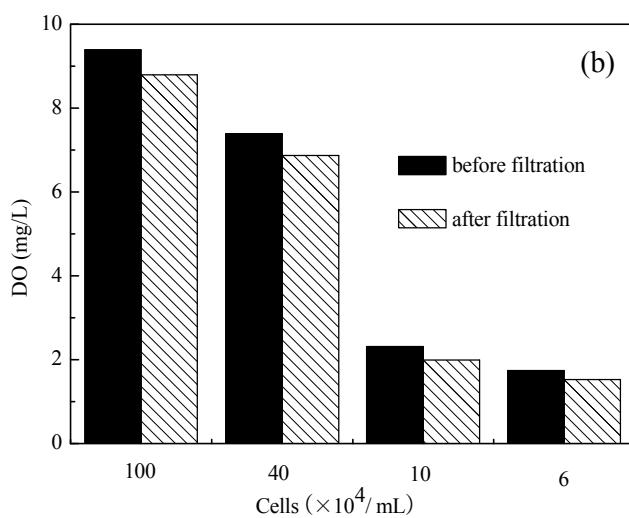
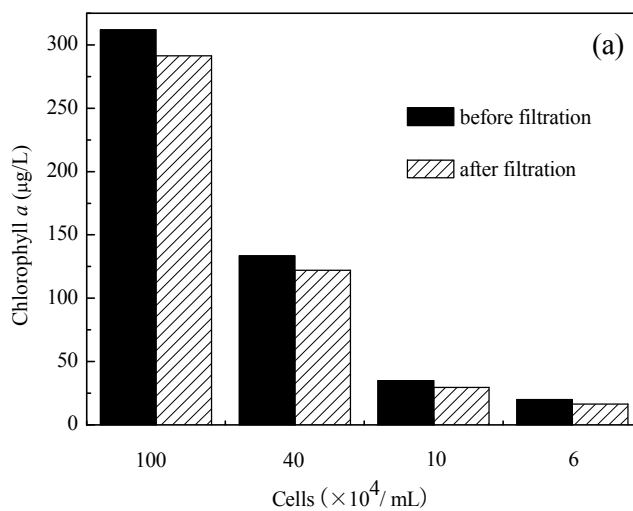
RESULTS AND DISCUSSION

Effectiveness of filtration

Chl-*a*, photosynthetic activity, A₂₅₄, and turbidity of the simulated ballast water contained various *D. salina* cells were characterized to assess the filtration efficiency (Fig. 1). Approximately 12% of the chl-*a* was removed (Fig. 1a), indicating that 50µm screen filtration could remove a small part of *D. salina* cells. The obtained photosynthetic activity reducing was about 10% (Fig. 1b), which is corresponding to the reductions of chl-*a*, and implied that *D. salina* cells would not be injured by filtration. On the other hand, about 20% turbidity removal was detected (Fig. 1c), suggesting that filtration pretreatment could improve water clarity of incoming ballast water. Turbidity can signifi-

cantly influence the photo-induced disinfection efficiency. The above observation showed that filtration pretreatment has the potential for improving the efficiency of followed UV/Ag-TiO₂/O₃ inactivation.

It is noted that when organic materials presence in ballast water, the treatment efficiency will be reduced. In this work, some organic materials that contained in the cultures could be introduced into the testing water, and the change of A₂₅₄ was monitored. However, only about 5% removal was obtained (Fig. 1d), suggesting that dissolved organic matter (DOM) could not be removed by filtration.



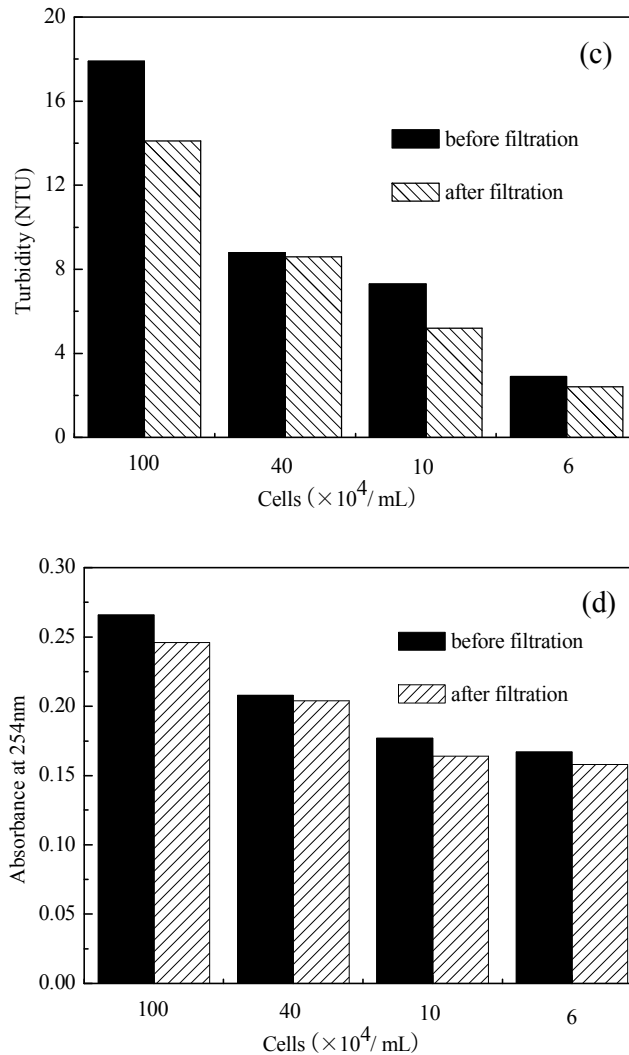


Figure 1. Effects of filtration on the treatment of *D. salina* containing ballast water: (a) chlorophyll *a* concentration, (b) gross photosynthesis, (c) turbidity, (d) absorbance at 254 nm

Inactivation tests

One important aspect of a prospective ballast water treatment is that it should be effective against a wide range of organisms. In an effort to optimize a practical and environmentally acceptable method of treating ballast water, the present study tests the efficacies of UV/Ag-TiO₂/O₃ treatment on the inactivation of *D. salina* and *P. tricornutum*. In experiments, 4.9 g/h of ozone was initially injected into the reactor and UV intensity was fixed at 6.5 mW/cm². As shown in Figure 2, the UV/Ag-TiO₂ process was not effective in algae chl-a degradation. With HRT of 3.0 s, only about 5.9% and 13.9% chl-a removal were detected for *D. salina* and *P. tricornutum*, respectively. In contrast, ozonation treatment rapidly removed chl-a, and combination of UV/Ag-TiO₂ together with ozone further improved treatment efficiency. These observations were agreement with our previous studies (Wu et al. 2011), which suggested that the excess production of •OH in the combined UV/Ag-TiO₂/O₃ process maybe a possible explanation for the enhanced biological efficiency.

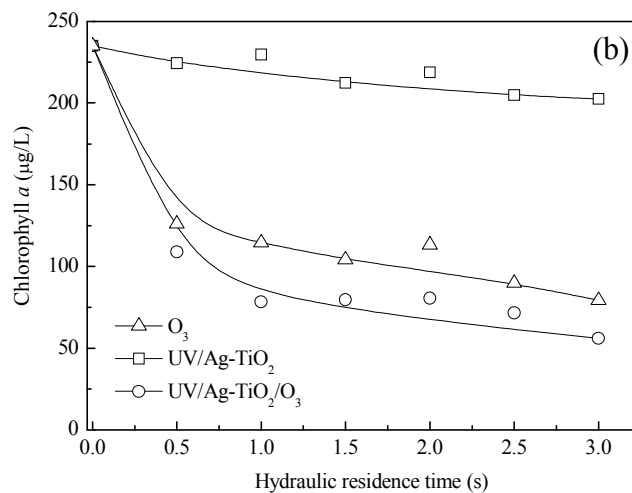
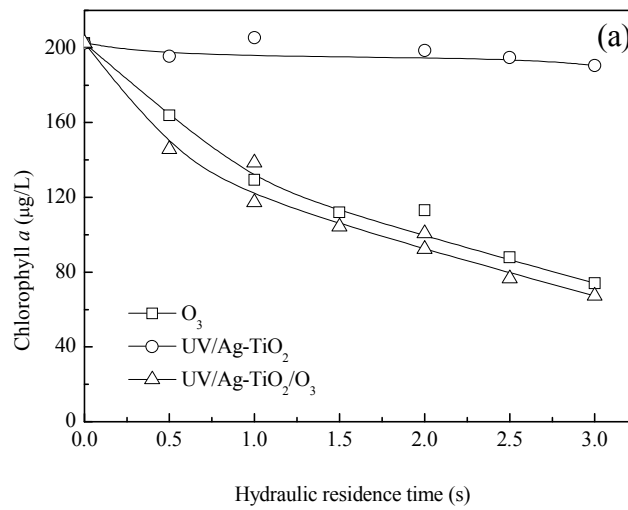


Figure 2. Degradation profiles of phytoplankton chlorophyll a for the different processes: (a) *D. salina*; (b) *P. tricornutum*

Toxicity of effluent

After treatment by sequential filtration and UV/Ag-TiO₂/O₃ process, the toxicity of the effluent was investigated. As shown in Figure 3, the algae chl-a concentration decreased with stored time, especially in the initial 4 h. After 24 h, the chl-a concentrations of *D. salina* and *P. tricornutum* decreased from 67.3 and 56.0 µg/L to 21.2 and 28.1 µg/L, respectively.

UV radiation is a clean technology that exhibits high efficiency for bacteria inactivation. However, ballast water treatment by UV radiation or photocatalysis alone during ballasting maybe requested to be secondary treated during deballasting, owing to the reactivation and multiplication of microorganisms in ballast tank (Martinez et al. 2013). The results in Figure 3 implied that application of UV/Ag-TiO₂ and ozonation simultaneously could overcome the drawbacks of sole UV radiation.

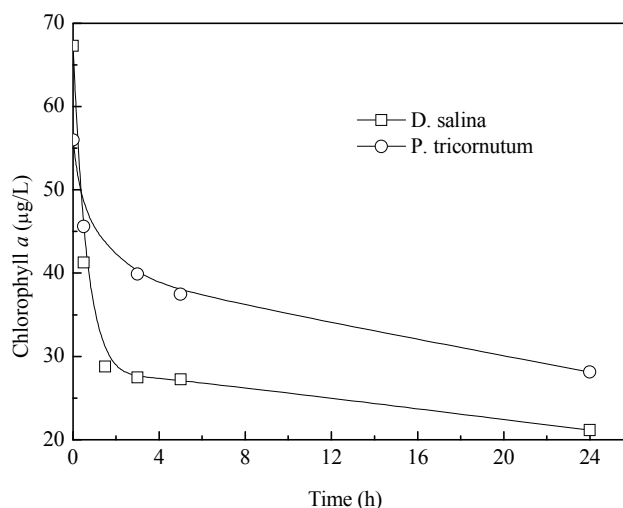


Figure 3. Decay of remaining phytoplankton chl-a in effluent with time

CONCLUSIONS

This study revealed that sequential filtration and UV/Ag-TiO₂/O₃ oxidation process was efficient for ballast water treatment. Screen filtration (50 µm) pretreatment could improve the clarity of incoming ballast water, which may enhance the efficiency of the followed inactivation process. Combination of ozonation and UV/Ag-TiO₂ yield higher chl-a removal efficiency than sole ozonation and UV/Ag-TiO₂, and the effluent exhibited a persistence toxicity within 24 h. It is concluded that sequential filtration and UV/Ag-TiO₂/O₃ process has the potential for ballast water treatment.

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