Mechanism and influence of removing algae with chlorine dioxide treatment for ship ballast water

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Abstract. This study aims at examining the performance of the ClO$_2$ on treating ballast water of Dalian new port area foreign trade oil pool in the cases of different experimental parameters, and Cylindrospermopsis raciborskii (CR), Gymnodinium catenatum (GC) and Gymnodinium cf. mikimotoi (GCM) are used for this experiment. The results shows that under certain test condition, the removal rates are in proportion to the dosage of ClO$_2$ and reaction time, and inversely proportion to pH value, humic acid and ammonia nitrogen content. Accordingly, on operating at the optimal dosage of ClO$_2$ and parameters of experiment, this process is proven to be an effective technology to remove these three algae and organic compounds in ballast water. In ballast water, the removal ability of ClO$_2$ for these three algae is less sensitive to pH value, humic acid and ammonia nitrogen content than to ClO$_2$ dosage and reaction time. Removing GC, GCM and CR with ClO$_2$ are attributed to the second order reaction. Investigating the performance of such process, could serve to develop management strategies that enable mitigating the impacts of harmful substance in ballast water and help improving and ensuring quality of ballast water.

1. Introduction

Ballast water is water carried by ships to ensure stability, trim and structural integrity. Every year ten billion tons of ballast water are transported and exchanged through ship all over the world [1]. That results in increasing the worldwide invasion of alien marine species and damaging oceanic ecosystem [2]. Ballast water has been considered as a main vector of initial transport of non-indigenous species (NIS) [3]. The International Convention for the Management and Control of Ballast Water and Sediments has been adopted by the International Maritime Organization (IMO), which set the global standards on ballast water management (BWM) requirements [4]. IMO has also developed regulations to reduce the spread of NIS between ecosystems involving mid-ocean exchange (MOE) protocols which require vessels to replace ballast water collected at the port of origin with open-ocean water.

In ballast water, microorganisms include viruses, algae and animal plankton, etc. Microorganisms have different influences upon human’s health and environment, which could result in incidence of mass epidemic disease causing illness or death, e.g. poliomyelitis, hepatitis, mumps and encephalitis, etc [5]. Special emphasis was given to onboard treatment methods, which can be categorized as physical separation, mechanical and chemical methods. There are a number of techniques that can be used to minimize and prevent the introduction of non-indigenous aquatic nuisance species from ballast water. Unfortunately, there is not a single ballast water technique to remove all invasive species from ballast water tank. Ship owners would not introduce ballast technology that is expensive, unreliable, or time consuming. Therefore, some criteria for choosing a treatment method could be [6]: safety of the crew and passengers; effectiveness in removing target organisms; ease of operating treatment
equipment; amount of interference with normal ship operations and travel time; structural integrity of the ship; size and expense of treatment equipment; amount of potential damage of the environment; ease of port authorities to monitor for compliance with regulation. Oxidants are usually applied in water treatment process to kill algae. The most commonly used oxidants include ozone, potassium, permanganate, chlorine (Cl₂) and chlorine dioxide (ClO₂), etc [7]. ClO₂ is a strong disinfectant produced on site. ClO₂ is toxic to aquatic organisms, but under normal dosing conditions, it will decrease to very low levels before release. Many researchers have reported the inactivation effects and killing effects of ClO₂ on algae and planktons in water including ballast water, lake and reservoir, etc [5]. The theory of killing algae is to destroy the cell wall structure [8]. When ClO₂ performed on the algal cells, ClO₂ reacts with Pyrrole ring in chlorophyll-a, which would destroy the structure of chlorophyll-a and hence remove chlorophyll-a.

In this paper, the disinfection effects of ClO₂ on algae in ballast water of Dalian new port area foreign trade oil pool are investigated. The experimental parameters including dosage of ClO₂, reaction time, pH of reaction, humic acid and ammonia nitrogen content in ballast water are examined to optimize water treatment process. The reaction order for removing Cylindrospermopsis raciborskii, Gymnodinium catenatum and Gymnodinium cf. mikimotoi is also investigated.

2. Experimental

Cylindrospermopsis raciborskii (CR), Gymnodinium catenatum (GC) and Gymnodinium cf. Mikimotoi (GCM) were selected as the main algae investigated in this experiment. CR was the main algae in Dalian new port. GC and GCM were found in Dalian port, as two main toxic algae from foreign ships ballast water. GC and GCM were derived from natural bodies of water and centrifuged, then distilled to obtain algae fluid. This algae fluid was added into water samples from Dalian new port area foreign trade oil pool, and both the densities of GC and GCM in water sample were 1.0×10⁹ cells L⁻¹.

ClO₂ was derived from NaClO₂ and H₂SO₄ as shown in Eq. (1), and dissolved in distilled water as the reserve liquid in brown bottle. ClO₂ with doses of 1 g L⁻¹ was added into water samples prepared in a beaker of 1 L during stirring. Then aged for 15 min, and the efficiency of algae removal in ballast water was determined by the residual chlorophyll-a value. Sampling was carried out in different time by stopping the reaction of chloride dioxide and algae with sodium thiosulfate, and the residual chlorophyll-a value in 1 L water sample was determined.

\[
5\text{NaClO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 4\text{ClO}_2 + 2\text{Na}_2\text{SO}_4 + \text{NaCl} + 2\text{H}_2\text{O}
\]  

(1)

In this study, the removal efficiency of CR, GC and GCM for ClO₂ was studied. The disinfection influence factors including the doses of ClO₂, time and pH of reaction, humic acid and ammonia nitrogen content in ballast water for these three algae were investigated. The number of animal planktons was determined by microscopic count. The algae removal rate (η) was calculated as:

\[
\eta = \frac{C_o - C_f}{C_o} \times 100\%
\]  

(2)

where \(C_o\) was the initial cell density of algae (cells·L⁻¹) and \(C_f\) was the final cell density of algae (cells·L⁻¹) [9]. The ammonia nitrogen content of organic humic acid in water sample was determined by UV⁺⁺⁺⁺.  

3. Results and Discussion

3.1. Removal efficiency of different algae for ClO₂

Under the immobilization conditions including pH (7), reaction temperature (20°C), the same number concentration of GC and GCM (1.0×10⁹ cells·L⁻¹), the effects of 0.5 mg·L⁻¹ ClO₂ on different algae removals was studied. Figure 1 shows the results of CR, GC and GCM removal rates with different reaction time after adding 0.5 mg·L⁻¹ of ClO₂.
3. Removal rates of different algae with different reaction time

It is demonstrated that removal rate of GC rises after reaction for 240 s. The removal rates of GCM and CR stably rise after 360 s and 60 s, respectively. After that, the removal rates of all these three algae increased slowly. During the initial process to 1080 s, the removal rates of GC varied from 15% to 85.94%, which were higher than the removal rates of GCM. During the reaction time from 1140 s to 1800 s, the removal rates of GC, were lower than the removal rates of GCM, of which the removal rates increased from 86.14% to 93.1%. Moreover, the removal rates of CR were higher than the removal rates of GC and GCM in the reaction process. It can be demonstrated that the removal rates of CR increased with the reaction time increasing. When the reaction time exceeds 900 s, the removal rates will not increase significantly with the time. Therefore, the optimal reaction time for removing CR should be around 900 s. After the reaction time reached to 1440 s, the removal rates of GC and GCM were basically unchanged. When the reaction time reached to 900 s, the removal rates of GC, GCM and CR reached to 88.01%, 93.10% and 96.78%. That can be demonstrated that the efficiency of removing CR with ClO$_2$ was higher than the efficiency of removing GC and GCM in water.

3.2. Effect of doses of ClO$_2$

The CR, GC and GCM were used for the experiment, and distilled water was used as basement. According to the experiment in advance and experience, at 20$^\circ$C fixed the reaction time of 15 min in the neutral condition, the experiments of ClO$_2$ with the dosage from 0.1 to 1.1 mg·L$^{-1}$ were carried out. As shown in Figure 2, it can be observed that with the increasing dosage of ClO$_2$, the residual chlorophyll-a content of CR decreased, and the algae removal rates increased. When the dosage of ClO$_2$ researched to 0.9 mg·L$^{-1}$, the residual chlorophyll-a content and algae removal rates would not change any more, while the algae removal rates increased to 98.57%.

![Figure 1. Removal rates of different algae with different reaction time](image1)

In Figure 3, it can be seen that the ability of removing algae with ClO$_2$ was enhanced with the increasing ClO$_2$ dosage. With the ClO$_2$ dosage from 0.1 to 1.1 mg·L$^{-1}$, the removal rates of GCM were higher than that of GC. When the dosage of ClO$_2$ researched to 0.7 mg·L$^{-1}$, the removal rates of GC and GCM increased to 89.98% and 95.18%, and then will only change a little in spite of the dosage increase of ClO$_2$. As shown in Figure 2 and 3, when 1.1 mg·L$^{-1}$ ClO$_2$ added into the water sample, the
removal rates of CR, GC and GCM reached to 98.57%, 90.12%, and 96.54%, respectively.

![Figure 3. The removal effect with different dosage of ClO₂ for GC and GCM](image)

**3.3. Effect of initial chlorophyll-a concentration**

The CR was used for the experiment, the removal efficiency of chlorophyll-a content during 1~13 μg·L⁻¹ after adding 0.5 mg·L⁻¹ ClO₂ in the neutral condition was studied, the results were shown in Figure 4. It was shown that with the increasing initial concentration of chlorophyll-a, the residual chlorophyll-a content increased after algae removing. With the initial concentration of chlorophyll-a increasing from 1 to 14 μg·L⁻¹, the removal rates increased significantly from 60% to 84.62%, and then the removal rates would not increase significantly. It can be concluded once the initial concentration of chlorophyll-a increases, it has a significant effect on algae removal ability.

![Figure 4. The removal effect of CR for different chlorophyll-a content](image)

**3.4. Effect of pH value**

In the experiment, the CR, GC and GCM were used. Under the immobilization conditions at 20°C, ClO₂ concentration (0.5 mg·L⁻¹), reaction time (15 min), the same number concentration of GC and GCM (3×10⁷ A·L⁻¹), the effects on different pH during 4~10 for different algae removals was studied. As shown in Figure 5, with the pH value increasing, the removal rates of CR, GC and GCM were decreased from 97.68%, 89.96%, and 94.32% to 92.85%, 77.21%, and 90.11%, respectively. It can be seen that the removal rates of GC was decreased from 88.01% to 80.73% remarkably when the pH value increased from 7 to 8. Thus the removal algae efficiency of ClO₂ was higher under acidic and nature condition.
According to the electrode reaction of ClO$_2$[10, 11]:

$$\text{ClO}_2 + 4\text{H}^+ + 5e^- = \text{Cl}^- + 2\text{H}_2\text{O}$$

(3)

$$\phi_0 = 1.511 - 0.0473p\text{H} + 0.0118\log[\text{ClO}_2]/[\text{Cl}^-]$$

(4)

where $\phi_0$ represents the redox potential of ClO$_2$, and is related to both the changes of pH value and ClO$_2$ concentration. As the redox potential of ClO$_2$, $\phi_0$ and pH value are assumed to be in a linear relationship. The lower the pH value was, the higher the electrode potential of ClO$_2$ was, and the better the inoxidizability and algae removal ability were[11].

### 3.5. Effect of organic compound

In general, ballast water contains high concentration of humic organic matter, which cannot be ignored in the prevention and control of pollution sources. Since humic acid accounts for 50%-90% of humus, it is considered as the main component of humus, and hence has been the main control object during micro-polluted ballast water[12, 13]. Therefore, the removal efficiency of CR, GC and GCM containing different concentrations of humic acid was studied with the application of 0.5 mg·L$^{-1}$ClO$_2$ in the neutral condition. As shown in Figure 6, it can be seen that the removal rates of these three algae were decreased with the increase of humic acid concentration in water sample. Without humic acid in ballast water, the removal rates of CR, GC and GCM reached to 97.32%, 89.78% and 94.21%, respectively. When the humic acid content in ballast water increased to 21 mg·L$^{-1}$, the removal rate of these three algae decreased to 84.63%, 45.21% and 68.43%, respectively.

![Figure 5](image-url)

Figure 5. The removal effect of three algae for different pH value

The removal efficiency for these three algae decreased with the increase of organic matter concentration in water sample. The reaction of chlorine dioxide and humic acid is attributed to the secondary reaction, and chlorine dioxide has better ability for removing humic acid in water. It would consume a part of chlorine dioxide to react with organic matter in water sample. Thus, the algae removal became less efficient, with actual concentration of chlorine dioxide decreased.

### 3.6. Effect of ammonia nitrogen

Ammonia nitrogen is contained in many common pollutants in ballast water and would lead to
eutrophication, and therefore it is a serious threat to water quality [14]. After adding 0.5 mg·L\(^{-1}\) ClO\(_2\) in the neutral condition, the removal efficiency of CR, GC and GCM with different ammonia nitrogen concentration 0–6 mg·L\(^{-1}\) for 15 min was studied. As shown in Figure 7, it can be seen that the change of ClO\(_2\) removal rates was small with NH\(_3\)·H\(_2\)O added. With the ammonia nitrogen concentration increase in ballast water, the removal rates of ClO\(_2\) for these three algae were decreased from 98.03%, 88.21%, and 93.44% to 97.62%, 87.98%, and 92.95%, respectively. That is because second-order reaction rate constant of ClO\(_2\) and NH\(_3\)·H\(_2\)O was much lower than 10\(^{-2}\) L·mol\(^{-1}\)·s\(^{-1}\) under nature condition. Hence, ClO\(_2\), which exists in the form of free molecules in water sample, has better removal algae ability, since it leads to reaction of hydrolysis and ionization.

Figure 7. The removal effect of three algae for different concentration of ammonia nitrogen

3.7. Removal kinetics mechanism of ClO\(_2\) for algae

According to various types of rate equation’s integral form, the reaction order is called integration method. Usually, the reactant concentration at time \(t\) is called \(C_t\), and can be plotted as \(C_t-t\) according to every order reaction. If a straight line obtained from \(C_t-t\), the corresponding order of this relational expression is the desired order. Table 1 shows the integral relationship between reaction time \(t\) and concentration \(C_t\) for different orders.

| Orders | Type | Integral form | Linear relationship |
|--------|------|--------------|---------------------|
| 0      | A→P | \(k_t=C_t\)  | \((a-C_t)\cdot t\)  |
| 1      | A→P | \(k_t = \ln \frac{a}{a-C_t}\) | \(\ln(a-C_t)\cdot t\) |
| 2      | A+B→P (a=b) | \(k_t = \frac{1}{a-C_t} - \frac{1}{a}\) | \(\frac{1}{a-C_t} - t\) |
| 2      | A+B→P (a≠b) | \(k_t = \frac{1}{a-b} \ln \frac{b(a-C_t)}{a(b-C_T)}\) | \(\ln \frac{b(a-C_t)}{a(b-C_T)} - t\) |
| 3      | A+B+C→P (a=b=c) | \(k_t = \frac{1}{2} \left( \frac{1}{(a-C_t)^2} - \frac{1}{a^2} \right)\) | \(\ln \frac{b(a-C_t)}{a(b-C_T)} - t\) |
| \(n\)  | A→P | \(k_t = \frac{1}{n-1} \left[ \frac{1}{(a-C_t)^{n-1}} - \frac{1}{(a-C_t)^2} \right] - \frac{1}{(a-C_t)^2} - t\) |                      |

where \(a\), \(b\), \(c\) are initial reactant concentrations, respectively, and \(C_t\) is product concentration.

The reaction between algae and ClO\(_2\) is shown as:

Alage + ClO\(_2\) → Product

\(t=0\)
\(C_0\quad C_0\quad 0\)

\(t=t\)
\(C_0-C_t\quad C_0-C_t\quad C_t\)

\(t=t_\infty\)
\(C_0-C_\infty\quad C_0-C_\infty\quad C_\infty\)
Experiments of removing algae were carried out under the condition: the pH values of water samples were 7, water temperature were 20℃, the concentration of ClO₂ was 0.5 mg·L⁻¹, the concentrations of GC and GCM were 1.0×10⁹ cells·L⁻¹, and the concentration of chlorophyll-a from CR was 55.94 μg·L⁻¹, respectively.

Figure 8 has shown the relationship between 1/(C₀−Cₜ) and t for removing GC, GCM and CR, respectively. The fitting results were shown in Table.2.

![Figure 8. Relationships between 1/(C₀−Cₜ) and reaction time for removing alage](image)

Table 2. The fitting results of reaction orders for these three algae

| Parameter | GC | GCM | CR |
|-----------|----|-----|----|
| Fitting results | $y=ax+b$ | $a=1/(C₀−Cₜ)$ |
| Reaction order | 2 | 2 | 2 |
| $a$ | 4.37474 | 0.50394 | 0.15555 |
| $b$ | 0.14259 | 0.43645 | 0.01683 |
| $R^2$ | 0.92156 | 0.9460 | 0.93537 |

As shown in Figure 8(a), the results show that correlation coefficient of $R^2$ is 0.92156, and this reaction order is 2. For removing GCM and CR in Figure 8(b) and Figure 8(c), both of their reaction orders are 2, and the correlation coefficients of $R^2$ are 0.9460 and 0.93537, respectively. It can be concluded that removing GC, GCM and CR for ClO₂ all belong to the second order reaction.

4. Conclusion

In this paper, the removal effects of CR, GC and GCM for ClO₂ on algae in ballast water of Dalian new port area foreign trade oil pool with different experimental parameters was investigated. The results show that with the ClO₂ concentration increased, the removal rates of these three algae were increased. When the ClO₂ content exceeds 0.9 mg·L⁻¹, the removal rates of these three algae are basically unchanged. Increasing concentration of chlorophyll-a can increase concentration of the
residual chlorophyll-a. Once the concentration of chlorophyll-a exceeds 7 μg·L⁻¹, the removal efficiency is less affected by initial concentration. The lower the pH value is, the higher the electrode potential of ClO₂, oxidizing and removal efficiency ability higher will be. With the concentration of humic acid and ammonia nitrogen in ballast water increased, the removal efficiency of ClO₂ for algae decreases. Thus, using ClO₂ as the disinfectant can effectively remove algae through reasonably controlling parameters during reaction.

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