Electrochemical removal of ammonia, chemical oxygen demand and energy consumption from aquaculture waters containing different marine algal species

RG Saman Wijesekara, Nakao Nomura and Masatoshi Matsumura∗
Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennodai 1-1-1 Tsukuba City, Japan

Abstract: Phytoplankton over-blooming and consequent die-off is one of the major contributory factors for ammonia and chemical oxygen demand (COD) loadings. In this work, electrolysis technology was applied to determine its ability to remove ammonia and total chemical oxygen demand (TCOD) in both laboratory-scale batch and continuous systems. Under an initially set voltage of 5 V, a constant current of 0.1 A was applied and different retention times were used for ammonia-removal experiments. Results showed that these conditions are not satisfactory in removing TCOD loadings contributed by algal cells. However, a retention time of 35.7 min was sufficient to remove 100% ammonia from algal-uncontaminated waters. Ammonia removals in waters containing Chlorella spp and Isochrysis spp were 87 and 68%, respectively, after 140 min of electrolysis. Energy consumption for ammonia removal in algal-free water was 50 W mg⁻¹ of ammonia. For waters containing Chlorella spp and Isochrysis spp energy consumptions were 67 and 85 W mg⁻¹ of ammonia, respectively. Interestingly, the applied mild electrolysis condition was just sufficient to control excess algal blooming and ammonia without increasing the dissolved COD and chlorine in shrimp grow-out ponds. This minimizes operating costs due the process requiring less energy. Furthermore, it was also found that electrolysis does not lower alkalinity.

Keywords: ammonia removal; total chemical oxygen demand (TCOD) removal; electrolysis; marine algae; energy consumption

INTRODUCTION

Intensive shrimp aquaculture leads to the accumulation of large amounts of uneaten feed, feces, and metabolic wastes in pond waters and pond soils. These wastes are degraded through microbial processes to produce ammonia and other unfavorable compounds, creating an unfavorable aquatic environment for aquatic organisms.1 Shrimp pond effluents are often high in suspended and dissolved organic matter.2 This increases the chemical oxygen demand (COD) and ammonia in the pond, thus rapidly deteriorating the water quality in intensive shrimp grow-out systems. These processes then accelerate the over-blooming of phytoplankton in the presence of sunlight and oxygen. Algal over-blooming and consequent algal die-off not only cause the water quality to deteriorate but also lead to the proliferation of pathogenic bacteria in shrimp cultivation systems.3

In our previous report we described an electrolytic process to selectively control algal over-blooming to allow for the dominance of beneficial algae. In this paper we describe the ammonia and total COD (TCOD) removal in seawater by electrolysis. Some of the innovations that have been explored to help clean up aquaculture effluents include re-circulating systems,4 and application of zeolites, plant extracts and formalin to remove ammonia from shrimp culture systems.5 However, each of these treatments has specific disadvantages such as high cost, a need for sophisticated equipment and the production of toxic residues for the cultured organisms. At the same time the efficiencies of ammonia and COD removal are lower. It may also take longer to treat intensive aquaculture systems by these methods. Among the advanced oxidation processes available, ozonation in shrimp grow-out ponds has been applied successfully for the removal of ammonia in shrimp grow-out systems.6 Specifically, Tanaka and Matsumura have also reported ammonia removal by ozone treatment in brine containing high concentrations of ammonia.7 However, removal efficiency depends on the input of dry air to the ozone generator. Therefore, the
application of ozone may be much more expensive. Alkalinity is a very important water quality parameter as it governs the buffering activity which stabilizes the pH in aquaculture systems. However, it has been found that ozone application in ammonia removal from shrimp grow-out ponds reduces the alkalinity, thus affecting the pH-buffering capacity of the system.\(^8\) This loss of alkalinity has to be corrected by application of suitable liming materials, which is an additional cost to the process.

Electro-oxidation is one of the emerging technologies available for removal of ammonia and COD from marine shrimp culture systems. Electrochemical oxidation at a high current dosage of 15 A dm\(^{-2}\) has been applied to remove COD and ammonia from landfill leachates.\(^9\) Electrolysis at 26 A dm\(^{-2}\) has also been reported to remove ammonia, COD and other toxic materials from tannery wastes and close to 100% ammonia and 83% COD removals have been achieved.\(^10\) In the present work, the electrochemical removal of total ammonia and TCOD in algal-containing seawater was studied.

### MATERIAL AND METHODS

#### Preparation of algal cultures

Pure algal cultures were isolated from shrimp culture ponds in Thailand, through Kasetsart University Bangkok. The algal species used in this study belong to three different classes: *Chlorella* spp and *Tetraselmis* spp (Chlorophyceae), *Isochrysis* spp (Prymnesiophyceae) and *Chaetoceros* spp (Bacillariophyceae). These species include chlorophytes and chrysophytes of different size categories.\(^11\) The *Chlorella* spp is the smallest (2.8 \(\mu\)m) and the *Tetraselmis* spp is the largest (10–15 \(\mu\)m) among the four species. The size of *Chaetoceros* spp and *Isochrysis* spp range from 4 to 6 and 3 to 5 \(\mu\)m, respectively. These selected algae are common species in shrimp grow-out ponds.

Seawater of 30 ppt salinity was prepared with artificial seawater powder (Marine Art, Tokushima, Japan). Prepared seawater was filtered through Whatman 47 mm glass micro fiber filter papers. It was sterilized at 121 \(^\circ\)C for 15 min and cooled to room temperature before inoculation of micro-algae. Sterilized seawater was enriched with Daigo’s IMK medium (Wako Pure Chemical Industries, Osaka, Japan) according to the manufacturer’s instructions. Seawater enrichment and algal inoculation procedures were conducted on a clean bench to avoid contamination. Glass test tubes of 50 mL were used to maintain stock algal cultures and 1000 mL conical flasks were used for the first multiplication stage. These cultures were incubated in a growth cabinet, MLR 350-T (Sanyo Company, Japan) (controlled environment), at 25 \(^\circ\)C, pH 8.0–8.2 and light intensity of 2500 (Lux).\(^10\) Glass tanks of 20 L capacity were used during the second algal multiplication stage. Algal cultures were sufficiently aerated with aquarium air pumps (New CALM Five Plan Taiwan) and 0.20 \(\mu\)m Advantec cellulose acetate air filters (Advantec, Toyo Roshi Kaisha Ltd, Japan) were fitted to the gas line.

#### Batch electrolysis system

In batch experiments with algal cells, the total volume (electrolysis medium) was subjected to electrolysis at the same time. The medium was not renewed during the electrolysis process. The reaction in the batch system was fast due to the rapid accumulation of chlorine compounds and Total Residual Oxidant (TRO). Batch experiments were conducted in 1000 mL glass beakers. The beakers were filled with 1000 mL of stock algal suspension that was pre-cultured in the laboratory. The stock algal suspension in 30 ppt artificial seawater has a cell concentration of 5 \(\times\) 10\(^{5}\) algal cells mL\(^{-1}\). The anode (15 \(\times\) 5 \(\times\) 0.1cm\(^3\)) used in this work was made from titanium base metal sintered with Pt, Ru and Pd Mode 2 (Ishifuku Metal Industry Co, Ltd, Japan). The cathode (10 \(\times\) 5 \(\times\) 0.1 cm\(^3\)) was of stainless steel (Model SUS 304, Nilaco Corporation, Japan). Both electrodes were fixed in the reactor vessel to utilize an area of 15 cm\(^2\) for electrolysis. A minimum electrode spacing of 5 mm was maintained to allow for a faster reaction. Stirring (Iuchi model 70-24-20 HS-3E) at 500 rpm was maintained for proper mixing of both algal cells and oxidants generated, thus allowing for uniform reactions. A DC unit Model EX-750L2 (Takasago Ltd, Japan) was used to supply power (Fig 1). Since the production of oxidant depends mainly on the electric current, the supply of a constant current during electrolysis is very important. In this work however, only a minimum constant current supply of 0.1A was applied. To achieve this condition, the voltage was adjusted automatically from 2.5 to 2.6 V. Electrolysis was conducted continuously for 7 min and samples for analysis were collected before electrolysis and after every minute. Samples were taken using a syringe at a point approximately 2–3 cm below the medium’s surface.

#### Continuous electrolysis system

The continuous electrolysis system consists of a reactor vessel and reservoir. Electrolysis medium was pumped continuously from the reservoir to the reactor vessel by a standard pump. The volume of medium in the reactor was kept constant by an overflow tube to remove excess medium. Different retention times were...
attained by changing the flow rate of the pump. The retention time is generally expressed by the equation:

\[
\text{Retention time (min)} = \frac{\text{Volume of the reactor vessel (mL)}}{\text{Flow rate (mL min}^{-1})}
\]

Figure 2 is a schematic diagram of the continuous electrolysis system. The plastic reactor has a 2 L capacity. The electrode composition and connection as well as the power supply unit are exactly the same as that of the batch system. Continuous electrolysis with ammonia was conducted at a continuous constant current of 0.1 A. Similarly, the voltage was adjusted automatically between 2.6 and 2.9 V to achieve this current flow. Two magnetic stirrers were used to mix the reactor medium as well as the algal reservoir. A Master Flex Standard Drive rotary pump model 7024-20 (Cole-Parmer Instrument Company, Illinois, USA) was used to supply algal solution from the reservoir tank to the reactor vessel. Continuous electrolysis experiments were conducted for 45, 55, 60, 80, 90 and 140 min. The total electrolysis time generally depends on the retention time and the expected final ammonia concentration of the electrolysis medium. In practice, it is nearly four times that of the retention time. Samples (50 mL) were collected from the reactor overflow for analysis every 5 min for the experiments of 45, 55, 60 and 90 min. However, samples were collected at 10 min intervals for the experiments of 80 and 140 min. Sample preservation and parameter analyses were similar to the batch culture system.

Two algal species, *Chlorella* spp and *Isochrysis* spp, were selected for continuous electrolysis. Selection of these two algal species was based on our previous research on their sensitivity during electrolysis. *Chlorella* spp was the most sensitive and *Isochrysis* spp was the most resistant species among the four species previously evaluated. Furthermore *Isochrysis* spp is considered beneficial while *Chlorella* spp is non-beneficial for shrimp culture. Continuous electrolysis experiments with ammonia were conducted at retention times of 13.5, 19.5, 25.6 and 35.7 min and these were attained by changing the flow rate from the reservoir to the reactor vessel. A separate continuous experiment was conducted with ammonia and the algal species *Chlorella* spp and *Isochrysis* spp for 140 min at a retention time of 35.7 min. An algal concentration of $5 \times 10^5$ cells mL$^{-1}$ applied in the batch system was used. An initial total ammonia concentration of 4–6.3 mg L$^{-1}$ was maintained in all runs.

**Parameter analysis**

Total and free chlorine were measured just after sampling before and after electrolysis using a chlorine tester H1 93711 (Hanna Instruments Company, Japan). Salinity and pH and temperature were measured by a hand refractometer S/Mill (Atago, Japan) and TOKO pH meter (TPX 90), respectively. The pH and water temperature were recorded every sampling time. The TRO was determined according to the method of Sugita$^{13}$ by a U-2000 spectrophotometer (Hitachi Company, Japan) at a wavelength of 352 nm. TCOD was evaluated by a mercuric sulfate method following potassium dichromate and sulfuric acid digestion in solutions of high chloride concentration.$^{14}$ Total ammonia was analyzed by an ammonia test kit (Wako, Japan) using a U-2000 spectrophotometer at a wavelength of 630 nm. All samples were centrifuged (M 200 IVD, Sakuma, Japan) and the ammonia analysis was conducted according to the manufacturer's instructions. Alkalinity was determined by a Hach (HA-DT) test kit and a digital titrator 16 900 (Hach Company, USA). All parameter analyses were replicated.

**RESULTS AND DISCUSSION**

**COD removal**

The TCOD values of batch culture experiments are shown in Fig 3. These TCOD values were mainly attributed to the solid COD (SCOD). The lowest TCOD value was observed in *Chlorella* spp. *Chlorella* spp has the smallest size (2.8 µm) and may have the lowest biomass among the four species, hence it registered a low cell content. The largest cell among the four species, *Tetraselmis* spp (three to five times larger than *Chlorella* spp), showed the highest TCOD.

According to previous researchers,$^{10}$ (Table 1), there is a direct relationship between the dry matter content, chlorophyll-a, protein and carbohydrate content and the SCOD. This may explain the higher TCOD values of *Tetraselmis* spp. Between the two algal species, *Chaetoceros* spp whose cell size is greater than
that of *Isochrysis* spp showed a higher TCOD value. Boyd has reported that the SCOD of phytoplankton is five times greater than that of other wastes.15 Therefore, careful attention must be made to maintaining a healthy algal bloom and removal of COD in shrimp culture ponds. TCOD results of the batch experiment showed no significant reduction of TCOD after culture ponds. TCOD values of all other species did not show any significant reduction. However, the TCOD of *Chlorella* spp where a decrease to 15 mg L\(^{-1}\) from its initial value of 39 mg L\(^{-1}\) was observed. TCOD values of all other species did not show any significant reduction. However, the TCOD of *Chlorella* spp in the continuous experiment increased slightly with electrolysis time due possibly to cell mortality and lyses (Fig 4). Lower cell mortality was observed in *Isochrysis* spp as compared with *Chlorella* spp, therefore, the accumulation of cell content in the medium was minimal. This may have decreased the TCOD only slightly. Analysis showed a dissolved COD (DCOD) in artificial seawater of 3.5 mg L\(^{-1}\). Comparing the above results with current work on electrolysis for wastewater treatment, TCOD removal of 83% has been attained with basic tannery waste liquors (pH 9) at current density 26 A dm\(^{-2}\) in 3.5h.16 The current density applied was approximately 40 times higher than that in the present work.

Furthermore, based on the results of Chiang *et al* on TCOD removal from landfill leachates, 30% COD removal in 4 h at 7.5 A dm\(^{-2}\) current density has been attained.9 Our results of low TCOD removal indicated that breakdown of TCOD by applying low current density of 0.66 A dm\(^{-2}\) was not achieved. This suggests that a mild electrolysis condition is not sufficient to remove the TCOD of marine algae. However, it is expected that application of a high current density such as 7.5 and 26 A dm\(^{-2}\) may also increase the production of free and total chlorine and the TRO in the medium, giving an adverse effect on aquatic organisms. Furthermore, the energy consumption at these conditions is expected to be very much higher. (The mild electrolysis condition applied in this work does not increase the dissolved DCOD in the medium as the algal cells are not completely destroyed, therefore we concentrated only on TCOD analysis.)

### Ammonia removal at mild electrolysis conditions

#### Mechanism for ammonia removal

The mechanism for ammonia removal by electrolysis has been well established. Chlorine (Cl\(_2\)) is produced at the anode in the presence of chloride ions (Cl\(^-\)) and it forms hypochlorous acid (HOCl). Seawater contains Br\(^-\) ions, which react with hypochlorite ions (OCl\(^-\)) and hydrogen ions (H\(^+\)) to form hypobromous acid (HOB). Hypochlorous acid and hypobromous acids are the main oxidants formed during electrolysis of seawater. These two oxidants are involved in the formation of chloramines and bromamines, which react with the ammonia present in the solution according to the equations below:17

#### Ammonia reactions with hypochlorous acid

\[
\text{NH}_3 + \text{HOCI} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}
\]

\[
\text{NH}_2\text{Cl} + \text{HOCI} \rightarrow \text{NCl}_2 + \text{H}_2\text{O}
\]

### Ammonia reactions with hypobromous acid

\[
\text{NH}_3 + \text{HOB} \rightarrow \text{NH}_2\text{Br} + \text{H}_2\text{O}
\]

\[
\text{NH}_2\text{Br} + \text{HOB} \rightarrow \text{NBr}_2 + \text{H}_2\text{O}
\]

### Nitrogen gas and nitrous oxide formation

\[
\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{N}_2 + 3\text{HCl}
\]

\[
\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} + \text{HOCI} \rightarrow \text{N}_2\text{O} + 4\text{HCl}
\]
Nitrogen gas formation with hypobromous acid

\[2\text{NH}_3 + 3\text{HOBr} \rightarrow \text{N}_2 + 3\text{Br}^- + 3\text{H}^+ + 3\text{H}_2\text{O}\]
\[\text{NH}_2\text{Br} + \text{NBr}_3 + 2\text{H}_2\text{O} \rightarrow \text{N}_2 + 3\text{Br}^- + 3\text{H}^+ + 2\text{HOBr}\]

Ammonia removal at different retention times

Retention time is one of the most important factors affecting ammonia removal in field conditions. The present work was conducted at four different retention times to determine the best condition. Complete ammonia removal, as well as maintaining minimum ammonia levels in aquatic environment, would be ideal for the aquatic organisms. Generally, the tolerance of aquatic organisms to ammonia varies with species, physiological condition, and environmental factors. However, the recommended unionized ammonia (NH\text{\text{3}}) concentration is said to be less than 0.03 ppm (Table 2). The short-term (48–96 h) LC\text{50} values for unionized ammonia range from about 0.2 to 3 mg L\text{\text{\textsuperscript{-1}}} , suggesting that its safe levels in aquaculture ponds should be lower than this range. The first electrolysis experiment was conducted for 50 min with a retention time of 13.5 min. The initial total ammonia concentration was around 4.4 mg L\text{\text{\textsuperscript{-1}}}. Figure 5 shows that ammonia degraded gradually with electrolysis time to the value of around 2 mg L\text{\text{\textsuperscript{-1}}} at steady state after about 30 min. This corresponds to an unionized ammonia concentration of 0.082 mg L\text{\text{\textsuperscript{-1}}} (based on pH and temperature). This concentration exceeds the recommended level of unionized ammonia by 0.052 mg L\text{\text{\textsuperscript{-1}}}.

Since ammonia concentration did not decrease below the recommended levels, the experiment was conducted at a higher retention time (19.5 min) for 55 min. Still, no significant ammonia removal was observed at this condition. At a much higher retention time of 26.5 for 60 min, ammonia concentration decreased further to 1.5 mg L\text{\text{\textsuperscript{-1}}} at the end of the experiment (Fig 6). To possibly remove total ammonia completely, the retention time and electrolysis time were increased to 35.7 min and 140 min, respectively. At this retention time, no detectable ammonia was present even after only 80 min of electrolysis (Fig 7), suggesting that complete ammonia removal can be achieved by the process. It is also important to mention

![Figure 5](image-url)  
Figure 5. Ammonia removal with 13.5 min retention time and TRO and chlorine production and pH during electrolysis process.

![Figure 6](image-url)  
Figure 6. Ammonia removal (mg L\text{\text{\textsuperscript{-1}}}) with retention times of 19.5 min and 26.5 min.

![Figure 7](image-url)  
Figure 7. Ammonia removal (mg L\text{\text{\textsuperscript{-1}}}), TRO (mg L\text{\text{\textsuperscript{-1}}}), chlorine production (mg L\text{\text{\textsuperscript{-1}}}), and pH values during electrolysis process of retention time 35.7 min.

Table 2. Recommended water quality parameters for marine shrimp culture

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>Recommended range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>28–32 °C</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>5.0–9.0 ppm</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>20 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>7.0–8.3</td>
</tr>
<tr>
<td>Salinity</td>
<td>0.5–35 ppt</td>
</tr>
<tr>
<td>Chloride</td>
<td>≥300 ppm</td>
</tr>
<tr>
<td>Sodium</td>
<td>≥200 ppm</td>
</tr>
<tr>
<td>Total hardness (as CaCO\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≥150 ppm</td>
</tr>
<tr>
<td>Calcium hardness (as CaCO\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≥100 ppm</td>
</tr>
<tr>
<td>Magnesium hardness (as CaCO\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≥50 ppm</td>
</tr>
<tr>
<td>Total alkalinity (as CaCO\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≥100 ppm</td>
</tr>
<tr>
<td>Unionized ammonia (NH\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≤0.03 ppm</td>
</tr>
<tr>
<td>Nitrite (NO\text{\text{\textsuperscript{2}}}\text{\textsuperscript{-1}})</td>
<td>≤1 ppm</td>
</tr>
<tr>
<td>Nitrate (NO\text{\text{\textsuperscript{3}}}\text{\textsuperscript{-1}})</td>
<td>≤60 ppm</td>
</tr>
<tr>
<td>Total iron</td>
<td>≤1 ppm</td>
</tr>
<tr>
<td>Hydrogen sulfide (H\text{\text{\textsuperscript{2}}}S)</td>
<td>≤2 ppb</td>
</tr>
<tr>
<td>Chlorine</td>
<td>≤10 ppb</td>
</tr>
<tr>
<td>Cadmium</td>
<td>≤10 ppb</td>
</tr>
<tr>
<td>Chromium</td>
<td>≤100 ppb</td>
</tr>
<tr>
<td>Copper</td>
<td>≤25 ppb</td>
</tr>
<tr>
<td>Lead</td>
<td>≤100 ppb</td>
</tr>
<tr>
<td>Mercury</td>
<td>≤0.1 ppb</td>
</tr>
<tr>
<td>Zinc</td>
<td>≤100 ppb</td>
</tr>
</tbody>
</table>

that at this retention time the TRO and free chlorine levels were also at their minimum value, indicating that TRO was consumed for ammonia oxidation during electrolysis.

Comparing electrolysis with other methods for ammonia removal, Burgess et al have reported the use of zeolite and aeration to remove ammonia from marine sediment; however, the removal efficiency was very low. Biological treatment by immobilized nitrifiers has been reported to effectively remove ammonia in marine fish aquaria but it takes around 40 days for this method. Ammonia removal by electrolysis experiment at 35.7 min retention time for 140 min (Fig 8). Ammonia removal at 80 min of electrolysis addition of algal species was 100%. The present section at 35.7 min retention time without this corresponds to an increase of 26 mg L\(^{-1}\) as CaCO\(_3\). This value decreased to 131 mg L\(^{-1}\) during the first 20 min of electrolysis. However, the alkalinity then increased gradually with electrolysis time. Alkalinity was 166 mg L\(^{-1}\) at the last min of electrolysis and this corresponds to an increase of 26 mg L\(^{-1}\) during the entire electrolysis process. This result reveals that the application of continuous electrolysis does reduce with 35.7 min retention time was 77% for Chlorella spp and 55% for Isochrysis spp. Ammonia removal at steady state after 140 min was 88% and 62% for Chlorella spp and Isochrysis spp, respectively.

The lower ammonia removal was mainly due to the competing reaction of oxidant with algal cells. The oxidants HOBr and HOCl react with organic matter present in the medium. Alternatively this can be explained by the chlorine demand. If water contains any organic matter, eventually the chlorine demand increases. Chlorine compounds are consumed for the oxidation of organic matter, resulting in the formation of combined chlorinated compounds. As shown in Fig 9 the reaction of free chlorine with ammonia and organic matter decreased free chlorine levels to form combined chlorine, resulting in an increase in the total chlorine content. Similar results were observed in the two algal species.

Free chlorine levels recorded at the end of the electrolysis experiment were below the lethal concentration for marine shrimp, which ranges from 8 to 23 g. Generally, the toxicity of free chlorine depends on the chlorine demand.

The pH of the system only slightly decreased during electrolysis and this could be due to the generation of TRO. Initially, in the absence of TRO, the initial pH was around 8.5. However, pH dropped with increasing TRO (HOCl and HOBr are acidic) as electrolysis progressed. Consequently, there was no significant accumulation of TRO as it was consumed for ammonia and algal degradation. As a result, the pH in the system did not decrease further, instead it stabilized at around pH 8.3 (Fig 10).

Figure 11 shows the time course of alkalinity during electrolysis. Initially, the total alkalinity in seawater at 30 ppt salinity was 140 mg L\(^{-1}\) as CaCO\(_3\). This value decreased to 131 mg L\(^{-1}\) during the first 20 min of electrolysis. However, the alkalinity then increased gradually with electrolysis time. Alkalinity was 166 mg L\(^{-1}\) at the last min of electrolysis and this corresponds to an increase of 26 mg L\(^{-1}\) during the entire electrolysis process. This result reveals that the application of continuous electrolysis does reduce

Ammonia removal in marine algal-containing waters

The ammonia removal efficiency in water containing marine algal species is expected to be different from pure water containing ammonia. In the presence of organic matter the oxidants (HOBr and HOCl) produced during electrolysis process will also be consumed by organic matter during oxidation (reaction of organic matter with HOBr is more efficient than HOCl). The ammonia removal described in the previous section at 35.7 min retention time showed 100% removal. The present results indicated that the ammonia removal efficiency slightly decreased in the presence of micro-algae (Fig 8). Ammonia removal at 80 min of electrolysis was 88% and 62% for Chlorella spp and Isochrysis spp, respectively.

Figure 8. Ammonia removal efficiency of Chlorella spp in continuous electrolysis experiment at 35.7 min retention time for 140 min electrolysis time.

Figure 9. Free chlorine reaction with ammonia and formation of combined chlorine. Continuous electrolysis at 35.7 min retention time.
alkalinity. It maintains pond alkalinity due to the production of an array of hydroxides at the cathode. As seawater contains calcium and magnesium ions, it can generate calcium and magnesium hydroxides.\(^{24,25}\) In contrast, the application of ozonation in shrimp grow-out ponds has been reported to significantly decrease alkalinity and this has to be corrected by the supplementation of liming materials.\(^8\) This recarbonation to improve alkalinity loss by ozonation may not be practical in large-scale shrimp grow-out ponds.

### Power and energy consumption of ammonia removal

Table 3 summarizes the power, current density, electrodosage and energy consumption during ammonia removal for the two algal species. Values of power (0.25 W), current density (0.67 A dm\(^{-2}\)) and electrodosage (268 W L\(^{-1}\)) were the same for both species.

<table>
<thead>
<tr>
<th></th>
<th>Chlorella spp</th>
<th>Isochrysis spp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (W)</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Current density (A dm(^{-2}))</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Electrodosage (W L(^{-1}))</td>
<td>268</td>
<td>268</td>
</tr>
<tr>
<td>Energy consumption to remove 1 mg of ammonia (W mg(^{-1}))</td>
<td>67</td>
<td>85</td>
</tr>
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</table>

The results show that the energy consumption patterns for both algal species are almost the same. The total energy consumption for both algal species was 2100 W. However, the ammonia removal efficiencies were slightly different. The energy consumptions for ammonia removal in *Chlorella* spp and *Isochrysis* spp were 67 and 85 W mg\(^{-1}\) respectively. Since the energy requirement to remove 1 mg of total ammonia in waters without cells was 50 W mg\(^{-1}\), clearly excess power (around 17–35 W in the evaluated systems) is necessary to remove total ammonia in waters containing algal cells. It must be emphasized however that the energy consumption for ammonia removal in waters containing different marine algal species may vary with respect to cell size and cell content.

In conclusion, electrolysis conditions suitable for ammonia removal without affecting TCOD in marine algal-containing waters have been established in this research. The total ammonia in algal-free water can be removed completely in 80 min with the retention time of 35.7 min. The mild electrolysis conditions (0.1 A current, 5 V initial set voltage, and 35.7 min retention time) was however insufficient for the removal of TCOD. Though complete TCOD removal could be achieved by increasing current, voltage and retention time, this will eventually increase the energy consumption as well as TRO and chlorine compounds in the water. This could create adverse environmental conditions for shrimps. By our approach, COD in seawater remains in the form of SCOD. Unless algal cell walls are damaged, the SCOD has no significant effect on water quality. The application of strong electrolysis conditions in shrimp grow-out ponds may damage algal cell walls completely, thus increasing the DCOD. This condition is enough to remove ammonia as well as control algal over-blooming without destroying the algal cell walls completely. Therefore the proposed electrolysis conditions could be applied directly in shrimp grow-out systems. In the case of higher dosage of electrolysis to remove TCOD, this could be used only in treatment ponds. The treated water in such instances has to pass through biological treatment systems. As the cost of electricity is very high, complete removal of TCOD will increase the cost of production in aquaculture systems. As an additional benefit, as compared with other advanced oxidation methods such as ozonation, electrolysis does not destroy total alkalinity in shrimp grow-out ponds. Similar electrolysis experiments using real shrimp grow-out pond water is worth evaluating for future research activities.

### REFERENCES


Removal of ammonia and COD and energy consumption from aquaculture waters


