Full Length Research Paper

Electrochemical removal of nitrite in simulated aquaculture wastewater

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Accepted 3 June, 2011

Electrochemical removal of nitrite at a concentration of 10 mg l⁻¹ from synthetic aquaculture wastewater was investigated in this study using a batch reactor. The effects of important operating parameters such as electrode material and applied current density were studied. The highest nitrite removal is achieved with nickel as compared to stainless steel and other electrode materials. Optimum nitrite removal is achieved at a current density of 3.75 mA cm⁻² and an initial pH of 5. Basic pH tends to inhibit nitrite oxidation, which is consistent with the literature. An optimum anode to cathode surface area ratio of 1 and an inter-electrode spacing of 2 cm gave best results, respectively. Nitrite concentrations are reduced to match USEPA’s discharge limit of 1 mg l⁻¹ within 5 min of experimental runs. This is much better than previously reported results. Nitrate concentrations generated remained within USEPA’s discharge limit of 10 mg l⁻¹. Further experiments are recommended for the conversion of nitrate to nitrogen. Using operating parameters determined here, it was envisaged that real aquaculture wastewater can also be treated efficiently for the removal of nitrite in both batch and continuous scales of operation.

Key words: Electrochemical oxidation, nitrite removal, aquaculture wastewater.

INTRODUCTION

The demand for fish and seafood has directly resulted in the aquaculture industry’s rapid growth and is now regarded as the fastest growing segment of the animal culture industry (Qin et al., 2005). The aquaculture wastewater is characterised by the presence of proteins (Petrilli and Tonukari, 1997) and nitrogenous compounds (ammonia, nitrite and nitrate). Specifically, adverse effects of nitrite toxicity as summarised by Qin et al. (2005), includes the oxidation of blood haemoglobin iron to its ferric state, forming methaemoglobin. The high levels of methaemoglobin in fish cause the blood to turn brown and sometimes result in hypoxia and death of the fish. Although, the toxicity of nitrate ion to fishes is minimal; in the presence of other essential nutrients an excess nitrate concentration causes eutrophication along with its associated algae blooms that can become a serious environmental problem. Treatment of the wastewater generated has become a challenging task for both environmental scientists and engineers throughout the world (Saleem and Essa, 2010; Boggs and Botte, 2009). The concern over the nitrites contamination and discharge of nitrite-containing effluent is coupled with the inadequate and satisfactory adherence to environmental regulation for the treatment and disposal of these wastes (Miao Li et al., 2010). Furthermore, effluents from the aquaculture industry are currently battling with stricter legal regulations (Diaz et al., 2010).

Electrochemical wastewater treatment has been used successfully to remove many priority pollutants from various different industrial wastewaters (Carpenter and Roberts, 1999; Chen, 2004; Martinez-Huitle and Ferro, 2006; Emamjomeh and Sivakumar, 2009). Among these
The hazardous and toxic nature of nitrite is a major concern. Nitrite results in the wastewater effluents of aquaculture systems due to fish excretion and decomposition of unconsumed food (Poxton and Alhoush, 1982). Nitrite is toxic to fish and its maximum permissible concentration limit (MPCL) is usually less than 1 mg l$^{-1}$ (Lin and Wu, 1996) as enforced by the USEPA. Aquaculture production from an aqueous environment of high nitrite concentration has been correlated with increased risk to human health. Nitrite can interact with substrates such as amines and amides to produce N-nitroso compounds including nitrosamines, many of which may cause cancer in several animal species (Liao and Mayo, 1974). Nitrite also can result in the emission of nitrous oxide (N$_2$O) to the atmosphere, which happens to be a greenhouse gas (Foley et al., 2010).

In the case of electrochemical treatment, several researchers reported investigating nitrite removal (Lin and Wu, 1996; Abuzaid et al., 1999; De et al., 2004). They utilized graphite, titanium dioxide, stainless steel and iridium-modified carbon fiber electrodes with various current densities. Specifically, the mechanism of electrochemical nitrite oxidation was reported to involve the generation of chlorine gas from the electrochemical oxidation of chloride at the anode that reacted with water to form hypochlorous acid as shown in Equation 1 (Saleem, 2011).

\[ 2Cl^- (aq.) \rightarrow Cl_2 (g) + 2e^- \]
\[ Cl_2 (g) + H_2O (l) \rightarrow H^+ (aq.) + Cl^- (aq.) + HOCl (l) \]  

Equation 1

Hypochlorous acid produced consequently acted as an oxidizing agent to convert nitrite to nitrate as shown in Equation 2 (Abuzaid et al., 1999; Sun and Chou, 1999).

\[ HOCl (l) + NO_2^- (aq.) \rightarrow NO_3^- (aq.) + H^+ (aq.) + Cl^- (aq.) \]

Equation 2

Electrochemical nitrite removal studies have not been reported much in recent literature after Sun and Chou’s investigation (Sun and Chou, 1999) that yielded a rate equation to predict the effect of [NO$_2^-$] and [Cl$^{-}$] on denitrification of synthetic aquaculture wastewater. This equation was valid when the NaCl concentration was in the range of 0.17 to 0.51 M and the NO$_2^-$ concentration was lower than 20 mg l$^{-1}$ (Sun and Chou, 1999). There are limited literature findings on nitrite removal at lower concentrations than those reported by Sun and Chou (1999) work.

In this study, responses of some specific variables affecting the nitrite electro-oxidation process were investigated using simulated aquaculture wastewater with the aim of reducing the generated nitrate levels below the EPA allowable discharge limit of 10 mg l$^{-1}$ (Ward et al., 2005).

### MATERIALS AND METHODS

A laboratory scale electrochemical setup made up of circular beaker cell, electrodes and other accessories were arranged as shown in Figure 1. Two electrodes (of same material), each with a surface area of 32 cm$^2$, were immersed in 1500 ml of nitrite solution in the undivided cell. Five different types of electrode materials were investigated in this research (stainless steel, graphite, nickel, aluminum and titanium) prior to the selection of the best one suited to efficient oxidation of nitrite to nitrate.

The separation between the anode and cathode was kept at 3 cm following the method of Abuzaid et al. (1999) during all runs except in the investigation of electrode spacing. The temperature was maintained between 25 to 28°C. The solution in the reactor was stirred and sparged with nitrogen until the temperature reached a steady state. Controlled direct current was supplied by a DC power supply (Hitachi Model-17858). The current was kept uniform by an ammeter (ATAGO, Japan). A schematic of the batch electrochemical cell is shown in Figure 1.

Synthetic wastewater containing nitrite (10 mg l$^{-1}$) was prepared by dissolving reagent grade sodium nitrite (Fisher) in 0.17 to 0.51 M NaCl solutions following the literature (Sun and Chou, 1999). To ensure that interference from the water used for solution was nitrite free, ultrapure water purified in an Arium 611 deionised water system (Sartorius Stedim Biotech GmbH) was used. Maximum concentration of 10 mg l$^{-1}$ was selected to simulate nitrite contaminated aquaculture wastewater in order to remain consistent with reported figures in the literature (Abuzaid et al., 1999; Sun and Chou, 1999). The natural pH of the nitrite solution was measured to be 7.65. Electrolysis was carried out initially at 3.1 mA cm$^{-2}$ as per the literature (Abuzaid et al., 1999) except for the cases where an optimum current density was determined for effective nitrite removal. This optimum current density was then employed in all subsequent experiments. This value was determined by investigating the energy consumption during electrolysis at different current densities. The energy consumption in the process can be written as:

\[ \frac{E}{(1000 \times V)} = \frac{(U_i \times I \times t)}{1000 \times V} \]

Equation 3

Where, $U_i$ is the total electrolysis potential (V); $I$ is the total electrolysis current (A); $t$ is the electrolysis time (h) and $V$ is the volume of electrolyte treated (m$^3$).

Electrode potential with respect to each other (by making one electrode as the working and the other as counter and reference) was maintained near or below 1.45 V using the DC power supply unit. Higher potentials than this value tended to increase the chances of chlorine generation and subsequent release into the atmosphere (Sun and Chou, 1999). An optimum initial pH of solution was determined using 1 M H$_2$SO$_4$ (Merck, Reagent grade) to maintain acidic conditions or 1 M NaOH (Merck, Reagent Grade) to maintain basic conditions. This optimum initial pH was used in all subsequent experiments for the determination of electrode surface area and inter-electrode spacing.

Actual aquaculture wastewater was not selected in this study due to the effect of other parameters (such as TSS or TOC) upon nitrite removal. A combination of electro-coagulation and flotation was envisaged necessary prior to the denitrification experiments with actual wastewater (Emamjomeh and Sivakumar, 2009). To keep things simple, the experiments reported in this study can be considered to be the precursor to experiments with real aquaculture wastewater.

Samples of test solution were taken with a pipette from the reactor at different time intervals during each run and analyzed for
Figure 1. Schematic diagram of experimental set up for electrochemical nitrite removal.

nitrite concentration. Each sample volume was 1 ml. Then, the samples were analyzed according to the standard methods established by the American Public Health Association (1998). A color reagent was added to the sample by the NEDA (N-1-naphthyl ethylenediamine dihydrochloride) colorimetric method. The nitrite ion concentration was determined by a UV-vis spectrophotometer (Jasco) at a wavelength of 543 nm following the procedures of Sun and Chou (1999). Nitrate concentrations were also measured by means of UV-vis spectrophotometer (Jasco) at a wavelength of 224 nm following the procedures of Ferree and Shannon (2001).

RESULTS

Five materials were tested to identify a possible candidate for electrode material to be utilized for nitrite removal from synthetic aquaculture wastewater. Electrode materials employed were stainless steel (304 grade), graphite, nickel, aluminum and titanium. Temporal concentrations of nitrite in the solution were noted at a current density of 3.13 mA cm\(^{-2}\). All studied electrodes were tested for nitrite removal and the results are shown in Figure 2. Table 1 shows the comparison of the mass of electrode materials consumed during 20 min run time. The results of the temporal variation of nitrite removal at different current densities are presented in Figure 3a and in Figure 3b the temporal effect of a range of different current densities on electrolyte pH was presented. Rate of nitrite removal was higher at low pH but declined with higher pH (Figure 3c). For the effect of initial pH of the wastewater, the range of initial pH investigated was from 2 to 9 and the effect on the nitrite removal efficiency is illustrated in Figure 3c. The surface area ratio varied by gradually removing the submerged cathode from the solution, while keeping the submerged area of the anode constant. This effect of surface area ratio of anode to cathode is shown in Figure 4. The figure depicts the relation between the remaining nitrite concentration in the solution and the anode to cathode surface area ratio after 5 and 10 min of each run. Temporal variation of nitrite concentration as a function of inter-electrode spacing is presented in Figure 5, this effect of inters electrode spacing had a direct effect on both operating cost as well as nitrite reduction efficiency.

DISCUSSION

Effect of electrode material

Temporal concentrations of nitrite in the solution were noted at a current density of 3.13 mA cm\(^{2}\). Figure 2 shows that the initial rate of nitrite removal was much higher as compared to its removal after 5 min possibly due to the presence of more hypochlorous acid in the early stages. Among all five types of studied electrode materials, nickel, titanium and graphite gave high nitrite removal with nickel giving the best result. The nitrite concentration reached less than 1 mg l\(^{-1}\) (MPCL in the effluents) within 5 min of experimental runs. It was also
obvious from Figure 2 that complete removal of nitrite could be achieved with the earlier mentioned electrode materials within 20 min of the experimental runs. This was better than the results reported by Lin and Wu (1996) and Abuzaid et al. (1999) whose electrochemical cells took almost an hour for complete nitrite removal.
under similar conditions. Other researchers reported similar results using different electrochemical technologies for nitrite removal (Sun and Chou, 1999). Current densities of this study and previous work were comparable and of the same order of magnitude (Ugurlu, 2004).

During electrolysis, grayish-white color streaks appeared in the solution especially using aluminum electrodes, which may be attributed to the dissolution of consumable electrode material (Emamjomeh and Sivakumar, 2009). Color change of electrolyte solutions during experiments was observed in the case of stainless steel and graphite electrodes. As the consumption of electrode was directly related to the economics of the process, the consumption rate was measured using the difference in initial and final masses of the electrodes. The results in Table 1 revealed that the consumption of aluminum electrode was the highest. This attribute was
because of the higher dissolution ability of aluminum, which classified it as a fully consumable material (Ashworth and Booker, 1986). However, titanium was an electrochemically stable material among those tested in this study. Results of Figure 2 (removal efficiency) and Table 1 (material stability) suggested nickel and titanium as feasible electrodes for the removal of nitrite under studied conditions. Variation of supporting electrolyte (NaCl) from 0.17 to 0.51 M also revealed similar results confirming the work of previous researchers (Sun and Chou, 1999). As nickel showed maximum removal efficiency for nitrite oxidation, remaining experiments were performed with nickel electrodes.

**Effect of current density on nitrite removal**

Effect of current density on nitrite removal was investigated using nickel electrodes. In this part of the study, the supply DC current was adjusted in a controlled manner to achieve current densities ranging from 2.2 to 8.5 mA cm$^{-2}$ in seven experimental runs. The results of the temporal variation of nitrite removal at different current densities are presented in Figure 3a. Complete
Figure 3. (a) Effect of current density on the electrolysis of synthetic nitrite solution in the presence of 0.34 M NaCl (aq) at pH 7.65 using nickel electrodes; (b) pH changes during electrolysis of synthetic nitrite solution in the presence of 0.34 M NaCl (aq) at a range of different applied current densities using nickel electrodes; (c) effect of initial pH of test solution on nitrite removal in an electrolyte made up of 0.34 M NaCl (aq) and applied current density of 3.75 mA cm$^{-2}$ using nickel electrodes.
Figure 4. Effect of anode to cathode surface area ratio on nitrite removal efficiency in an electrolyte made up of 0.34 M NaCl (aq), applied current density of 3.75 mA cm\(^{-2}\) and initial solution pH of 5 using nickel electrodes.

Figure 5. Effect of inter electrode spacing on nitrite removal efficiency in an electrolyte made up of 0.34 M NaCl (aq), applied current density of 3.75 mA cm\(^{-2}\), initial solution pH of 5 and nickel anode to cathode surface area of 1.
removal of nitrite took approximately 14 min for each case. Since nitrite removal was found to increase marginally by about 29.1% when current density increased from 2.2 to 8.5 mA cm\(^{-2}\) an optimum value was necessary to be determined. This could be estimated by considering the energy consumption and pH of electrolyte in solution for each case to reduce nitrite concentrations to the desired value of 1 mg l\(^{-1}\). Energy consumption was directly proportional to the cost of the system and took into account the current density applied as well as the time of electrolysis (Table 2). Energy consumption for lower applied current densities was found to be higher due to longer treatment time (Table 2). Higher current densities reduced the time for nitrite removal, but also increased the energy consumption (hence, the cost of the process). The optimum current density to apply for effective nitrite removal was determined to be 3.75 mA cm\(^{-2}\) (Table 2). This value was selected based upon least energy consumption and high nitrite removal rate.

Lin and Wu (1996) reported that current density changes had an effect upon the pH of the electrolyte. In turn, pH had a strong influence on nitrite removal (Lin and Wu, 1996). Thus, this important factor was also investigated in this study. Figure 3b shows the temporal effect of a range of different current densities on electrolyte pH. Same current densities were investigated as in Figure 3a. pH was found to be increasing in proportion to the current density applied. In this case, lines of best fit were not forced through the experimental points as done by Abuzaid et al. (1999) since pH had a non-linear relationship with proton concentration in solution and hence, the current density.

In Figure 3c that the removal efficiency is decreasing with the increase in initial pH. This could be explained based on the fact that at low pH, hypochlorous acid did not dissociate and the whole amount worked in the oxidation process of nitrite (Equation 2). However, the high efficiency of nitrite removal at low pH may be counteracted by the additional cost involved in the pH adjustment process. Furthermore, the pH of the effluent solution had to be neutralized before discharge which caused an extra cost as well (Abuzaid et al., 1999; Ghafari et al., 2009). Hence, an optimum initial pH was determined by evaluating its effect upon nitrite removal rate, time for treatment and energy consumption to achieve nitrite concentration up to 1 mg l\(^{-1}\) in the final solution of electrolysis (Table 3). The best pH value determined for electrochemical nitrite oxidation was 5. This value of pH was selected because below this value no significant improvement in terms of nitrite removal rate was observed. Furthermore, less capital was invested in neutralizing effluent pH value of 5 in comparison to lower values. In addition, an increase of pH from 5 to 7.65 resulted in an increase in energy consumption of more than 500% (compare 0.099 with 0.622 kW-h m\(^{-3}\)) thereby, chemical and photo electrochemical oxidation of nitrite (Sun and Chou, 1999, 2000) also reported similar conclusions. Even bio-electrochemical denitrification of synthetic aquaculture wastewater was found to be inhibited at pH values above 8 (Ghafari et al., 2009) showing that results obtained in this study were consistent with the current literature.

### Table 2. Energy consumption to achieve nitrite concentration of 1 mg l\(^{-1}\) in the final effluent along with solution pH at various current densities.

<table>
<thead>
<tr>
<th>Current density (mA cm(^{-2}))</th>
<th>pH</th>
<th>Time to achieve nitrite concentration 1 mg l(^{-1}) (min)</th>
<th>Energy consumption (kW-h m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20</td>
<td>7.8</td>
<td>10.1</td>
<td>0.193</td>
</tr>
<tr>
<td>3.10</td>
<td>7.9</td>
<td>7.2</td>
<td>0.164</td>
</tr>
<tr>
<td>3.75</td>
<td>8.1</td>
<td>5.1</td>
<td>0.147</td>
</tr>
<tr>
<td>5.60</td>
<td>8.6</td>
<td>4.2</td>
<td>0.236</td>
</tr>
<tr>
<td>6.25</td>
<td>8.7</td>
<td>2.8</td>
<td>0.238</td>
</tr>
<tr>
<td>7.80</td>
<td>9.0</td>
<td>1.9</td>
<td>0.243</td>
</tr>
<tr>
<td>8.50</td>
<td>9.4</td>
<td>1.7</td>
<td>0.263</td>
</tr>
</tbody>
</table>

Effect of initial pH of wastewater

The initial pH of test solution was adjusted by addition of 1 M H\(_2\)SO\(_4\). Range of initial pH investigated was from 2 to 9, which was a higher range than that tested by Lin and Wu (1996) and Abuzaid et al., (1999). The effect of initial pH of test solution on the nitrite removal efficiency was illustrated in Figure 3c. It can be deduced from Figure 3c that initial pH of test solution had a significant effect on the rate of nitrite removal. High removal was achieved within 5 min of experimental runs. It is depicted in Figure 3c that the removal efficiency is decreasing with the increase in initial pH. This could be explained based on the fact that at low pH, hypochlorous acid did not dissociate and the whole amount worked in the oxidation process of nitrite (Equation 2). However, the high efficiency of nitrite removal at low pH may be counteracted by the additional cost involved in the pH adjustment process. Furthermore, the pH of the effluent solution had to be neutralized before discharge which caused an extra cost as well (Abuzaid et al., 1999; Ghafari et al., 2009). Hence, an optimum initial pH was determined by evaluating its effect upon nitrite removal rate, time for treatment and energy consumption to achieve nitrite concentration up to 1 mg l\(^{-1}\) in the final solution of electrolysis (Table 3). The best pH value determined for electrochemical nitrite oxidation was 5. This value of pH was selected because below this value no significant improvement in terms of nitrite removal rate was observed. Furthermore, less capital was invested in neutralizing effluent pH value of 5 in comparison to lower values. In addition, an increase of pH from 5 to 7.65 resulted in an increase in energy consumption of more than 500% (compare 0.099 with 0.622 kW-h m\(^{-3}\)) thereby,
leading to the conclusion that a pH of 5 was optimum for the batch electrochemical oxidation of nitrite.

**Effect of surface area ratio of anode to cathode**

The surface area ratio varied by gradually removing the submerged cathode from the solution while keeping the submerged area of the anode constant. Figure 4 shows the relation between remaining nitrite concentration in the solution and the anode to cathode surface area ratio after 5 and 10 min of each run. It was noted that by increasing the surface area ratio, the nitrite removal rose almost linearly and reached a maximum value of 95% at an optimal ratio of unity. Although, this result agreed with previous work for nitrite removal (Rajeshwar and Inanez, 1997); it was not consistent with that reported by Reyter et al. (2010) for the conversion of nitrate to nitrogen. The cathode to anode surface area ratio was 2.25 for optimum performance in their case. The reason for this may be that the mechanisms of reaction were different for conversion of nitrate to nitrogen (Reyter et al., 2010) in comparison to oxidation of nitrite to nitrate (Sun and Chou, 1999).

**Effect of inter electrode spacing**

This experiment was carried out in order to optimize the electrode spacing as this had a direct effect on both operating cost as well as nitrite reduction efficiency. Analysis of the temporal variation of nitrite concentration as a function of inter-electrode spacing (Figure 5) showed that the maximum rate of nitrite removal was achieved for a spacing of 2 cm. Further reduction in inter electrode spacing did not increase the nitrite removal. It can be seen from Figure 5 that the removal rate of nitrite at a spacing of 1 cm was approximately equal to the spacing of 3 cm. Therefore, beyond a gap of 2 cm, the nitrite removal was not optimal. Although, a shorter gap could normally favor the minimization of potential drop and lead to higher current densities, inter-electrode gaps of less than 2 cm tended to increase the rate of side reactions and cause scale (magnesium or calcium hydroxide) growth on the cathode. These problems were related to the direct electro-generation of hypochlorite from brine and not the consequent oxidation of nitrite to nitrate (Belmont et al., 1998). The accumulation of scale in undivided cells had two effects: on the positive side, it reduced or inhibited hypochlorite reduction at the cathode; but on the negative side, it also increased the energy consumption of the cell and passivated the electrode (Ferrigno et al., 1999). Thus, an inter electrode spacing of 2 cm was feasible for effective nitrite removal in this system considering the fact that resultant nitrate concentration in solution was below 10 mg l\(^{-1}\).

The reduction of nitrate to harmless nitrogen gas is recommended as further work as reported in sufficient detail in the current literature (Reyter et al., 2008, 2009, 2010). Once an optimum procedure is determined for electrochemical nitrate reduction as documented in the literature (Reyter et al., 2006, 2009, 2010), actual aquaculture wastewater may be treated using optimum conditions determined in this study.

**Conclusions**

According to the results obtained, the main conclusions of this study are: highest removal of nitrite is achieved with nickel as compared to stainless steel, graphite, aluminum and titanium electrodes; the nitrite concentration is reduced to less than 1 mg l\(^{-1}\) (MPCL in the effluents) within 10 min of experimental runs at various current densities ranging from 2.2 to 8.5 mA cm\(^{-2}\); optimum current density for nitrite removal is found to be 3.75 mA cm\(^{-2}\); optimum initial pH for nitrite removal is found to be 5; with the increase in anode to cathode surface area ratio, the nitrite removal increases proportionately and reaches up to 95% at an optimal ratio of unity; rate of nitrite removal is found to increase as the inter-electrode spacing decreases. An optimal spacing of 2 cm is determined for the highest nitrite removal. Inter electrode gaps of less than 2 cm results in other problems such as formation of scale on cathode surface; almost complete removal of nitrite is achieved in about 10 min using nickel electrodes and optimum conditions determined earlier; for all optimal values of operating parameters determined in this research, resultant nitrate concentrations in solution are found to be less than 10 mg l\(^{-1}\) (MPCL for nitrate specified by EPA); it is still recommended that experiments are designed for the
reduction of nitrate to harmless nitrogen gas and the use of actual aquaculture wastewater is essential as further study.

In summary, most of the reported researches in open literature failed to achieve removal of more than 95% in 20 min or less due to limitation of operating parameters adopted. Thus, this study has demonstrated the attainment of improved removal efficiencies (above 95%) interestingly, without any elaborate surface modification of electrode and in less time than previously reported work.

ACKNOWLEDGEMENTS

Karachi Institute of Power Engineering and the University of Malaya Institute of Research Management and Monitoring are gratefully acknowledged for providing funding for this research vide research grant number RG096/10AET. The authors are also grateful to the two anonymous reviewers who helped strengthen the quality of the discussion of this paper.

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