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# NITRITE REMOVAL FROM MARINE AQUACULTURE WASTEWATER USING ELECTROCHEMICAL PROCESS

*M. SALEEM

Karachi Institute of Power Engineering (KINPOE), KNPC, P.O. Box 3183, Karachi, Pakistan

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The hazardous and toxic nature of some of the constituent such as nitrite in the aquaculture wastewater is of major concern. Present study focuses the removal of nitrite from the aquaculture wastewater prior to disposal. Effect of certain operational parameters such as electrode material, current density, initial pH, and electrode spacing on nitrite removal from aquaculture wastewater was elucidated. Better nitrite removal efficiency achieved when nickel used as compared to stainless steel, graphite and aluminum electrodes. Nitrite removal is positively related to the current density however, increase is up to 31.4% when current density increased from 2.5 to 9.3 mA/cm$^2$. Further increase in current density does not improve the process efficiency. Removal efficiency of electrochemical process decreased with the increase in initial pH of test solution. However, with the passage of time this difference is diminishing. This may be attributed to the presence of higher amount of hypochloric acid which does not dissociate at lower pH values. Subsequently faster oxidation of nitrite achieved during first few minutes of test runs. Amount of available hypochloric acid reduced at high pH values and oxidation of nitrite reduced subsequently. Rate of nitrite removal found to be increased as the inter-electrode spacing decreased up to an optimal spacing of 3 cm which showed highest nitrite removal. Further reduction in spacing does not augment the removal efficiency probably due to the formation of scale on cathode surface and passivation of electrode which suppressed further oxidation process.

**Keywords*:*** Electrochemical treatment, Aquaculture wastewater, Nitrite removal efficiency, Operating parameters

## 1. Introduction

During the year 1950 world population was 2.5 billion and exceeded to 6 billion in 2000 and expected to reach 8, 9, or 11 billion by 2050 according to the low, medium and high variant of the UN projection [1]. In addition to other necessities rising population of world required enough food to support the living. Animal farms, agricultural lands and aquaculture ponds are increasing to cope with the demand. Aquaculture industry is increasing in numbers all over the world. Traditionally, large ponds were used for establishing aquaculture systems and water quality maintained with intermittent recycling and cleaning of ponds. In order to overcome rising cost of land and food demand fish densities are increased per unit volume of aquaculture water which ultimately results in highly polluted aquaculture wastewater [2]. Therefore, the increased in fish density has caused deterioration in wastewater quality which would require proper treatment in order to maintain a better aquaculture environment and enhance its economic feasibility. Generally, wastewater produced in aquaculture business is disposed into abundant ground or water bodies. The hazardous and toxic nature of some of the constituents such as nitrite is of major concern. Aquaculture production from an aqueous environment of high nitrite concentration has been correlated with increased risk to human health [3]. Nitrite can interact with substrates such as amine and amide to produce N-nitroso compounds including nitrosamines, many of which may cause cancer in many animal species [4].

Decomposition of fish excretion and unused food results in high nitrite concentration in the wastewater effluents of aquaculture systems. Nitrite is toxic to fish therefore generally its maximum permissible concentration limit (MPCL) is 1 mgl-1 [4, 5]. Various methods have been used for the treatment of nitrite in aquaculture systems such as nitrification/ denitrification using fixed film of fluidized bed biological reactors and suspended solid removal by sedimentation [4-8].

* Corresponding author : i_am_saleem@yahoo.com

Electrochemical treatment of many chemical constituents has been studied by several researchers for possible application in wastewater treatment [6-10]. Different types of electrochemical cells have been developed for industrial wastewater treatment such as flow-through porous electrodes, fluidized beds, rolling tubes, packed beds, and rod electrodes [11, 12]. Several researchers investigated the nitrite removal using electrochemical treatment utilized graphite, titanium dioxide and stainless steel electrodes with various current densities. Jorquera [12] applied the electrochemical treatment method on hatchery aquaculture wastewater treatment. However, scope of the study was disinfection of aquaculture wastewater.

The hazardous and toxic nature of nitrite and its very low tolerable concentration limit in the discharge effluents required a proper nitrite removal method. Method should be simple, robust in nature and economical to afford. This paper presents the results of a detailed electrochemical laboratory scale investigation carried out at King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia. Study focuses the removal of nitrite from the synthetic aquaculture wastewater prior to disposal in order to protect environment and human being. Real aquaculture wastewater was not used in the present study due to the interference of other parameters such as TSS or TOC upon removal of nitrite. A combination of electro-coagulation and flotation was envisaged necessary prior to the denitrification experiments with actual wastewater [13]. The main objective of this study was to investigate the removal efficiency of nitrite using electrochemical treatment method. Effect of certain operational parameters such as electrode material, current density, solution initial pH, and electrode spacing on nitrite removal from synthetic aquaculture wastewater was elucidated.

## 2. Materials and Method

Electrochemical setup made up of Plexiglas reactor, electrodes and other accessories was arranged in the environmental engineering laboratory at KFUPM. Detailed schematic of the setup utilized in the present study is shown in figure 1. Two electrodes, each with a surface area of 32 $cm^2$, were dipped in 1.5 L nitrite solution. The separation between anode and cathode was kept 3 cm during all runs except in the investigation of electrode spacing. The temperature was maintained between 27-30 °C during all runs. Controlled direct current was supplied by a DC power supply (Instek PSP-405). The current was controlled in each test by a rheostat (KEYI-J2354, China) and measured by a multimeter (Bench Top M9803).

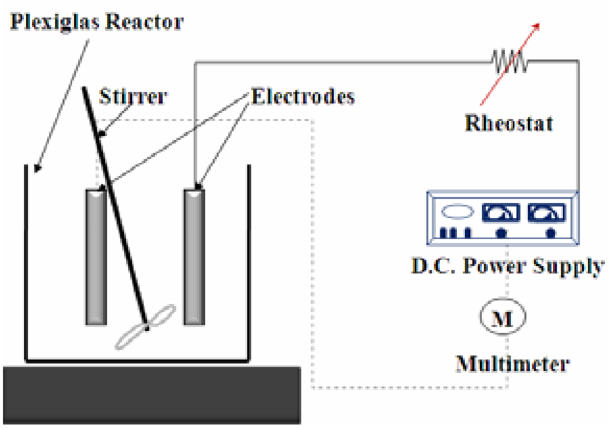


Figure 1. Schematic of electrochemical Set-up for nitrite removal.

Synthetic marine-aquaculture wastewater containing nitrite (10 $mgl^{-1}$) was prepared by dissolving reagent grade sodium nitrite (Fisher, U.K.) in seawater (as most of the aquaculture business in Saudi Arabia is at the sea shore using seawater). Maximum concentration of 10 $mgl^{-1}$ was selected to simulate nitrite contaminated aquaculture wastewater because it is the maximum level of nitrite in aquaculture wastewater reported by many researchers [2, 6, 8, 14]. Characteristics of synthetic marine-aquaculture wastewater was determined in the environmental engineering laboratory at KFUPM and presented in Table 1.

Samples of test solution were taken at predefined time intervals during each run and analyzed for nitrite concentration. Nitrite concentration was measured by photometric method following the procedure outlined in Standard Method [15] using a spectrophotometer (Shimadzu UV-1601PC).

## 3. Results and Discussion

Discussion on the results obtained during the study is given below:

### *3.1. Effect of Electrode Material*

With most of the conventional metal electrodes, electrochemical treatments are useful in only a limited range of potential and are unsuitable

Table 1. Characteristics of synthetic marine-aquaculture wastewater.

| Parameter | Value | Instruments/ Method Used | Reference |
|---|---|---|---|
| pH | 7.65 ±2 | pH meter/Mi-151/Italy | APHA-4500H+ B |
| Conductivity ($dSm^{-1}$) | 43.6±4 | HACH/ 51800-10 | APHA2510 B |
| Nitrite (mg/l) | 10±0.1 | Spectrophotometer | APHA-4500 $NO_3$ B |
| Calcium (mg/l) | 470±6 | Titration | APHA-3500Ca D |
| Magnesium (mg/l) | 1200±14 | Titration | APHA-3500Mg E |
| Sodium (mg/l) | 11,750±9 | Flame Photo Meter | APHA-3500Na D |
| Chloride (mg/l) | 23,000±17 | Titration | APHA-4500Cl G |
| Sulfate (mg/l) | 2800±3 | Spectrophotometer | APHA-4500-$SO_4$ E |
| Total Dissolved Solids (TDS) (mg/l) | 21,300±8 | Gravimetric | APHA-2540 C |
| Total Solids (TS) (mg/l) | 38,200±12 | Gravimetric | APHA-2540 D |

because of the low stability of the anodes and the poor current efficiency. Regarding stability at the required potentials, the selected electrode material must be such that it should not corrode under the application of the needed potentials [7, 10, 16]. As the selection of electrode materials has vital importance in electrochemical process at least from process efficiency and economics point of view a detailed study has been performed to evaluate the removal efficiency of different electrode materials for nitrite removal. Graphite, nickel, 304-stainless steel and aluminum electrodes were tested as possible candidate of electrode material because of their relatively higher electrochemical potential, low fouling tendency and mechanical stability [17].

Temporal concentration of nitrite in the solution was noted while passing current of 150 mA (provided current density of 4.7 $mA/cm^2$). The results of the tested electrodes are shown in figure 2. The relationship between electrode material and nitrite concentration shows that the initial rate of removal is higher as compared to the removal after 5 minutes of experimental run. Among studied electrode materials nickel and graphite gave high nitrite removal. However, removal of nitrite using nickel electrode is highest. The nitrite concentration reached less than 1 $mgl^{-1}$ (MPCL in the effluents) within 5 minutes of experimental run. It is also obvious from figure that complete removal of nitrite could be achieved with above electrode materials within 30 minutes of experimental run. Present study shows much better removal efficiency as compared to study conducted by Abuzaid et al. (1999) in similar experimental conditions [2].

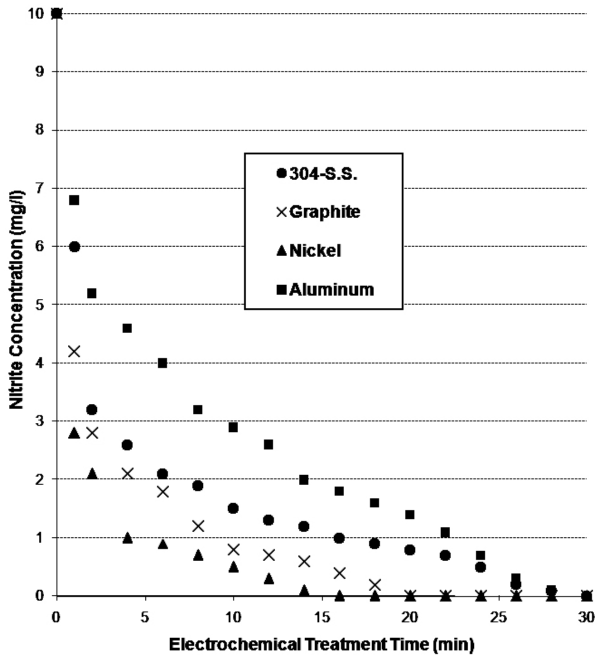


Figure 2. Relation between electrode material and nitrite removal efficiency.

In the case of aluminum electrode, during electrolysis grayish-white color streaks appeared in the solution, which may be attributed to the dissolution of electrode material. In addition to aluminum electrodes color production was also observed in the case of stainless steel and graphite electrodes [18]. Figure 2 suggests nickel as feasible electrodes for the removal of nitrite under studied conditions. As nickel showed maximum removal efficiency for nitrite removal, remaining experiments were performed with nickel electrodes.

### *3.2. Relation Between Current Density and Nitrite Removal Efficiency*

Current density has significant impact on electrochemical process efficiency [2, 19, 20]. Effect of current density on the nitrite removal was investigated using nickel electrodes. In order to apply different current densities supplied DC current from DC power supply was adjusted to obtain current densities ranging from 2.5 mA/cm$^2$ to 18.6 mA/cm$^2$ in four batch experimental runs. The results of the temporal variation of the nitrite removal at various current densities are presented in figure. 3, which depicts that the removal of nitrite from aquaculture wastewater is increasing with run time. It is also depicted in figure 3 that the nitrite removal increases with the increase in current density. Results show that current density of 4.7 mA/cm$^2$ is capable of bringing the nitrite concentration below 1 mgl$^{-1}$ within 6 minutes. Furthermore, study shows that increasing current density from 2.5 mA/cm$^2$ to 9.3 mA/cm$^2$ improves the nitrite removal efficiency about 31.4%. However, further increase up to 18.6 mA/cm$^2$ shows marginal improvement (2.9%). As an increase in current density augment the cost of treatment and lower current density leads to longer treatment time one may use an optimum value of current density for efficient removal and minimum cost. Therefore, current density of 4.7 mA/cm$^2$ is a reasonable value to achieve 91% nitrite removal within 6 minutes of experimental run.

### *3.3. Effect of Initial pH of Wastewater*

It is reported in the literature that value of pH has significant influence on nitrite removal efficiency [2, 9, 21, 22]. Thus effect of the initial pH of test solution on nitrite removal efficiency was investigated. The initial pH of test solution was adjusted by addition of 1 M $H_2SO_4$. Values of pH investigated were 4, 6, 7.6 and 9. The effect of initial pH of test solution on the nitrite removal efficiency is illustrated in figure 4. It can be deduced from figure that initial pH of test solution has significant effect on the rate of nitrite removal. Removal efficiency is decreasing with the increase in initial pH however, with the passage of time this difference is diminishing. This may be attributed to the presence of higher amount of hypochloric acid which does not dissociate at a low pH values. Therefore, at lower pH values oxidation rate of nitrite into nitrate is higher. However, at higher pH values conversion of hypochloric acid into other

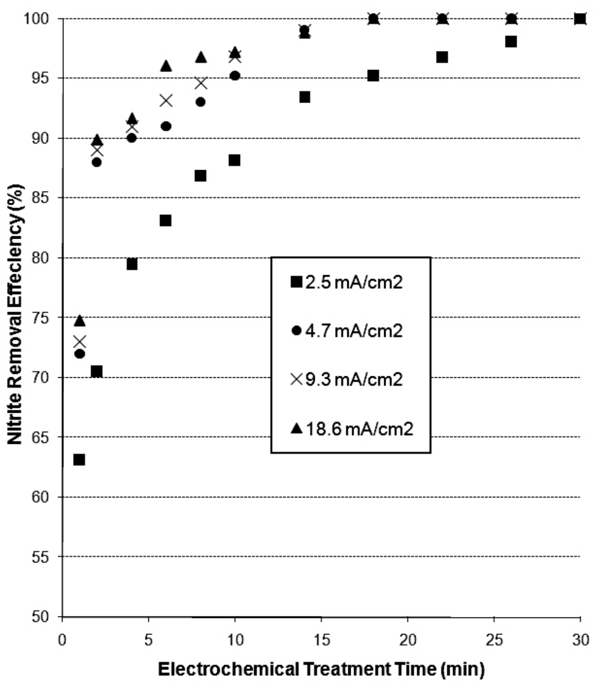


Figure 3. Relation between current density and nitrite removal efficiency using nickel electrodes.

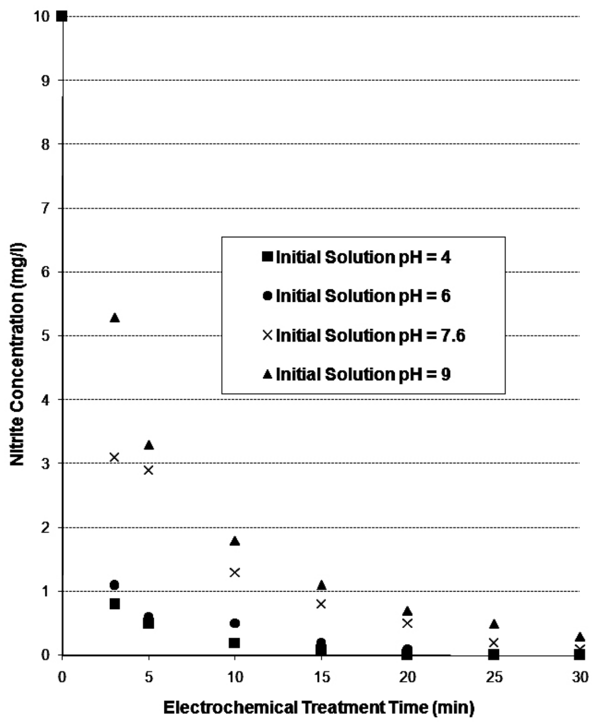


Figure 4. Effect of initial solution pH on nitrite removal efficiency.

compounds is higher and lesser amount is available for oxidation of nitrite [2]. The optimum value of pH for the electrochemical oxidation of nitrite selected as 6 in the present study. This value of pH was selected because below this value no significant improvement in terms of nitrite removal rate was observed. Furthermore, lesser cost is involved in neutralizing the effluent pH value of 6 as compared to lower values before discharging or reuse.

### *3.4. Effect of Inter-Electrodes Spacing*

Inter-electrode spacing is an imperative parameter in electrochemical treatment method. Increasing the electrodes spacing will reduce the capital cost of treatment but may reduce the treatment efficiency. Hence, an optimization of this parameter is critical. Temporal variation of nitrite concentration as a function of inter-electrode spacing is presented in figure 5 which reveals that the rate of nitrite removal increased as the inter-electrode spacing decreased. Its maximum removal was achieved for spacing of 3 cm and beyond a gap of 3 cm, the nitrite removal dropped

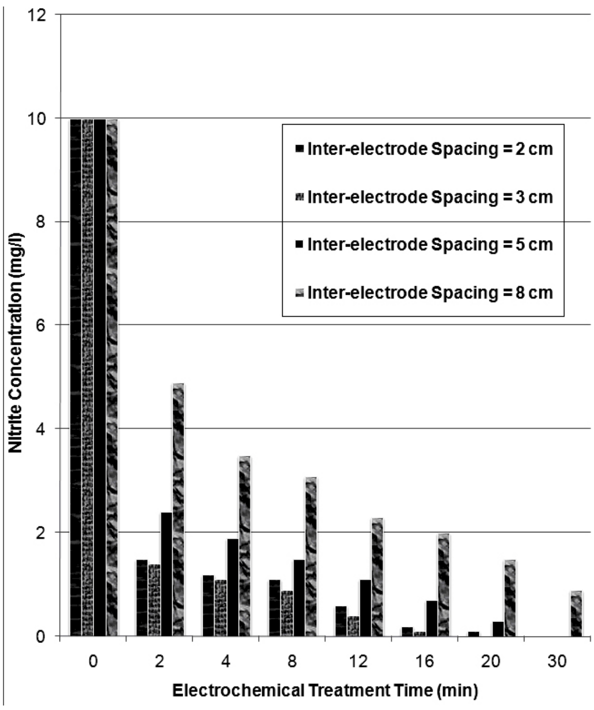


Figure 5. Effect of inter-electrodes spacing on nitrite removal.

and is inauspicious. This observation is in line with the idea that a shorter gap would favor to minimize the potential drop, and lead to higher current density. But after an optimum spacing rate of side reactions tends to increase and suppress the oxidation of nitrite [23]. This phenomenon may be related to the electro-generation of hypochlorite from dissolved salts which reduced the nitrite oxidation. Furthermore, formation of scale on cathode surface may also passivate the electrode [16]. This phenomenon is also pointed out by some other researchers [23-26]. From the present study it may be concluded that an inter electrode spacing of 3 cm is a reasonable spacing to achieve better nitrite removal efficiency.

## 4. Summary and Conclusions

The hazardous nature of nitrite in aquaculture wastewater required proper treatment before discharging into environment. Literature review revealed that electrochemical treatment process to remove nitrite from wastewater is simple, robust and economical to afford [6-10]. Following conclusions are drawn from the results obtained in this study.

- Highest removal of nitrite was achieved with nickel as compared to stainless steel, graphite, and aluminum electrodes.
- The nitrite concentration reduced to less than 1 $mgl^{-1}$ (MPCL in the effluents) within 6 minutes of experimental run. Complete removal of nitrite could be achieved within 30 minutes when using these electrodes.
- Nitrite removal is positively related to the current density. An increase of 31.4% in the removal efficiency noted when current density increased from 2.5 to 9.3 $mA/cm^2$. However further increase does not improve the removal efficiency and was found to be uneconomical.
- The removal efficiency of electrochemical process decreased with the increase in initial pH of test solution. However, with the passage of time this difference diminished. This may be attributed to the presence of higher amount of hypochloric acid which does not dissociates at lower pH values and available for nitrite oxidation. Optimum initial pH of solution for nitrite removal was found to be 6. Further increase of pH reduced the available hypochloric acid and oxidation of nitrite reduced subsequently.
- Rate of nitrite removal increased as the inter-electrode spacing decreased. But after an optimum spacing formation of scale on

cathode surface and electrode passivation suppress the oxidation of nitrite. An optimal spacing of 3 cm was noted which demonstrated highest nitrite removal.

Growing awareness regarding environmental pollution and need for the reuse of treated wastewater necessitate the further exploration in wastewater treatment area. Electrochemical process is focused by many researchers and is found to be a robust, easy to control and economical method for decontamination of wastewater. This study may help to understand the influence of some operational parameters on nitrite removal efficiency. Further study is recommended on real aquaculture wastewater.

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