

NITRIFICATION OF AQUACULTURAL WATER BY OZONATION IN A PACKED BED REACTOR*

S. H. LIN

C. M. HUANG

Yuan Ze Institute of Technology, Taiwan

ABSTRACT

Nitrite removal of aquacultural water by ozonation in a packed bed reactor was investigated. The rate of nitrite removal was determined in terms of the liquid and gas flow rates, pH, and ozone and nitrite concentrations. It was also found that an optimum pH around 7 exists for maximum nitrite removal. The experimental results also indicated that the nitrite removal increases with an increase in the inlet ozone concentration and with a decrease in both the nitrite concentration and liquid flow rate. In all circumstances, ozonation was found capable of efficiently reducing and maintaining the nitrite concentrations below 0.25 mg/L, a concentration level required generally for aquacultural activity. These results can be applied in the design of aquaculture systems with high fish density.

INTRODUCTION

Aquaculture is an important business in many countries around the world. Traditional aquacultural activities were conducted in large ponds with low fish density. Such activities required considerable amount of land and water resources. Therefore, they are becoming relatively uneconomic due to increasing cost and decreasing availability of these resources. A recent trend has been to employ high density aquaculture which requires significantly less amount of land and water resources [1, 2]. The economic advantages of this trend are quite strong. However, the high density aquaculture incurs a new problem. Increase in fish density in a limited

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aquatic space would lead to more rapid degradation of the water quality. Hence, treatment of aquacultural water to maintain high water quality required for such activity becomes highly crucial [1, 2]. It is important that such a problem be resolved efficiently before high density aquaculture can yield much real benefit.

A major problem of the aquacultural water is the high nitrite concentration which arises from fish excretion. Nitrite is toxic to marine fishes and the acceptable nitrite concentration for aquacultural activity is quite low, being no more than 0.25 mg/L [1-3]. The water quality of a high density and untreated aquacultural pond can deteriorate fairly rapidly and fall below this level. External pollution abatement units are needed if the water quality is to be sufficiently maintained for a normal aquacultural activity [4, 5]. Treatment methods proposed by the previous investigators included nitrification using fixed film or fluidized bed biological reactors and/or activated carbon columns and suspended solids removal by sedimentation [1-6]. In recent years, nitrification by ozonation has received increasing attention [2, 6, 8]. Ozonation of the aquacultural water is capable of efficiently converting toxic nitrite to non-toxic nitrate, reducing excess algae, disinfecting the water and increasing the dissolved oxygen (DO) concentration. In comparison, no other biological or physical methods can accomplish the same objective in a single treatment. However, the previous investigations [2, 6, 8] provided only qualitative information about the ozonation process of aquacultural water. The purpose of this work is to investigate nitrification by ozonation in a packed bed reactor in a more systematic fashion. Ozonation in such a reactor is significantly more efficient than other ozonation systems because of better gas/liquid contact. Experiments were conducted to examine the operating characteristics and performances of such an ozonation system.

EXPERIMENTAL STUDIES

The experimental schematic is shown in Figure 1. The packed bed reactor was a Pyrex glass column of 5.5 cm in diameter and 70 cm long. The column was randomly packed with ceramic Raschig rings of 5.2 mm \times 7.5 mm in size which yielded a porosity of approximately 55 percent. The specific surface area of the packing was 9.6 cm²/cm³ and the packing height was 60 cm. A similar Pyrex reactor without ceramic Raschig rings was set up in parallel to the packed bed reactor as a bubble column for comparison studies.

The ozone generator employed was a Welsbach Model T816 (Polymetrics Corp., San Jose, California, USA), rated as 8 g/hr of ozone generation capacity using oxygen gas. The generator was connected to an ion exchange system which purifies and dries the incoming oxygen. The purified oxygen was fed to the ozone generator. The ozonated oxygen then went to the bottom distributor of the packed bed reactor or to the spargers of the bubble column. The oxygen flow rate was held at 1.8 L/min throughout all experimental runs. The unadsorbed ozone from the reactor passed through a KI trap to remove the residue ozone before being

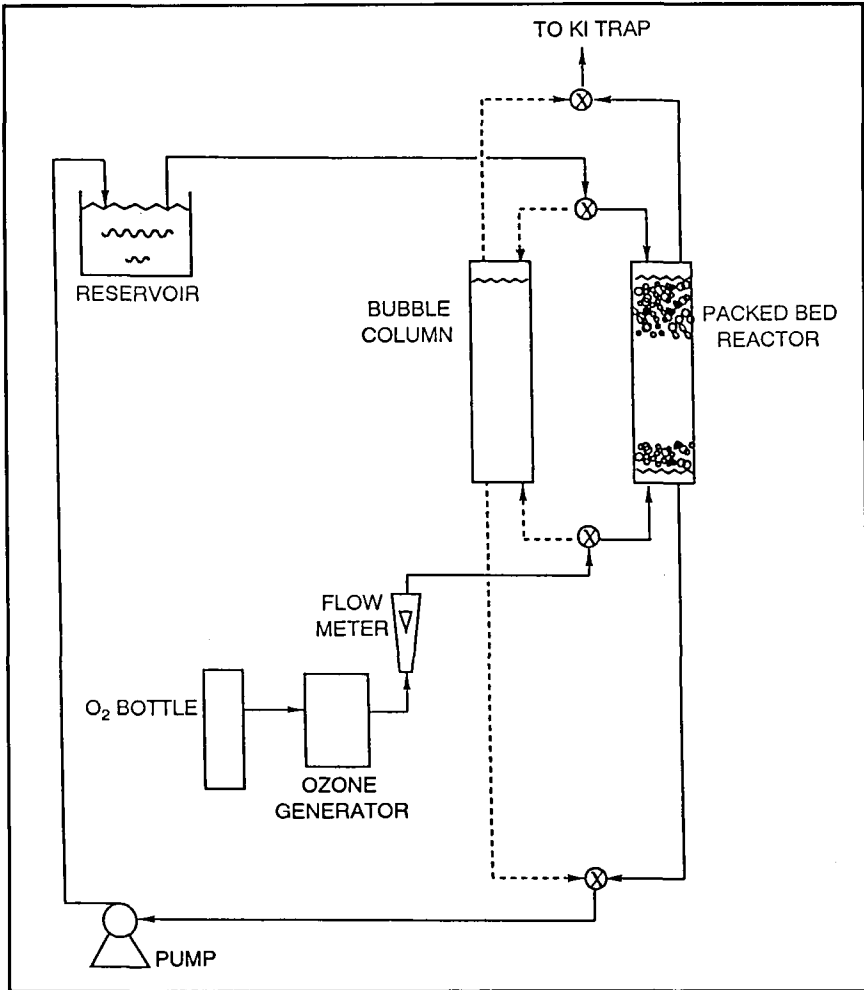


Figure 1. Experimental schematic.

vented to the atmosphere. The ozone concentration in the inlet and outlet gases was measured by the standard KI adsorption method [9] and the data was employed for determining the ozone utilization and nitrite removal efficiencies of the reactor system.

The water used in the experiments was collected from an aquacultural pond. The suspended solids (SS) concentration was rather low, being less than 30 mg/L. The water in the reservoir tank which held 500 liters was adjusted using NaNO_2 to an initial NO_2^- concentration of 300 mg/L for all experimental runs. This

initial NO_2^- concentration was much higher than the usual level found in an aquacultural pond and was artificially selected for the purpose of studying the performance characteristics of the ozonation system. The pH of the water was adjusted to the desired value by using HCl or NaOH. The water was pumped at a flow rate between 0.3 and 0.6 L/min to the top of the reactor countercurrent to the ozonated gas entering at the bottom. Samples were taken from the treated water exiting the reactor bottom every five minutes from the beginning for each run. The NO_2^- concentration was determined by the standard method [9]. The treated water from the bottom of the reactor was recycled back to the reservoir.

MASS TRANSFER COEFFICIENT AND NITRITE REMOVAL

Absorption of ozone from the gas phase by the countercurrent liquid stream was accompanied by a chemical reaction which is sufficiently fast to keep the equilibrium ozone concentration in the liquid phase very low. This was confirmed by the measured ozone concentration in the exit liquid stream, being less than 0.01 mg/L. Hence the equilibrium ozone concentration in the liquid phase (Y^*) could be practically ignored. The number of gas phase transfer unit then can be represented by [10].

$$N_y = \int_{Y_a}^{Y_b} \frac{dY}{(1-Y)(Y-Y^*)} \quad (1)$$

where Y_a and Y_b are, respectively, the ozone concentrations of inlet and outlet gases. Due to relatively low ozone concentration in the gas phase, it is reasonable to approximate $1-Y$ by 1. By letting $1-Y=1$ and $Y^*=0$, the above equation was integrated to yield

$$N_y = \ln \left(\frac{Y_b}{Y_a} \right) \quad (2)$$

The height of gas phase transfer unit is represented by [10]

$$H_y = \frac{G_y}{k_L a P} \quad (3)$$

where G_y is the mole flux of ozone in the gas phase, P the atmospheric pressure and $k_L a$ the overall mass transfer coefficient. The mole flux of ozone (G_y) is related to the gas flow rate (Q_y) and ozone concentration (Y_b) by

$$G_y = \frac{Q_y Y_b}{48 S} \quad (4)$$

with S being the cross-sectional area of the packed bed reactor. The height of the packed bed is finally obtained from

$$Z_T = N_y H_y \quad (5)$$

equations 2-5 can be employed to determine k_{LA} by knowing the reactor size, the operating conditions of experiments and the observed data of ozone concentration.

There are several parameters defined below which were determined from the observed data and employed to quantify the performance characteristics of the nitrification process:

$$\text{NO}_2^- \text{ Removal} = \frac{(X_a - X_b)}{X_a} \times 100\% \quad (6)$$

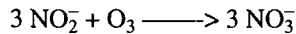
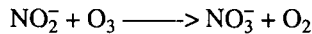
$$\text{Total NO}_2^- \text{ Removal} = Q_x(X_a - X_b)t \quad (7)$$

$$\text{Nitrite Removal Efficiency} = \frac{(X_a - X_b)Q_x}{Y_b Q_y} \times \frac{MO_3}{MNO_2} \times 100\% \quad (8)$$

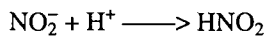
Nitrite removal efficiency defined by equation 8 represents the number of moles of nitrite removed per mole of ozone entering the reactor.

RESULTS AND DISCUSSION

The oxidation reaction between ozone and nitrite can be represented by



The above chemical reactions are relatively simple. However, the nitrite removal depends strongly on the pH conditions as shown in Figure 2. The curves in this figure clearly indicate that there exists an optimum pH around 7. At low pH, some NO_2^- actually combines with H^+ to form HNO_2 according to the reaction



which is not conducive to nitrite removal.

At high pH, the ozone in the aqueous solution can partially decompose to $\text{HO}\cdot$, $\text{HO}_2\cdot$ and $\text{O}\cdot$ free radicals [11, 12] and these free radicals have lower chemical reactivity toward NO_2^- than ozone. This presumably accounts for the decreasing nitrite removal with increasing pH beyond 7.

Figure 2 also displays that as the liquid flow rate increases, the nitrite removal decreases. The result is anticipated because of short contact time between the ozone and nitrite at high liquid flow rate.

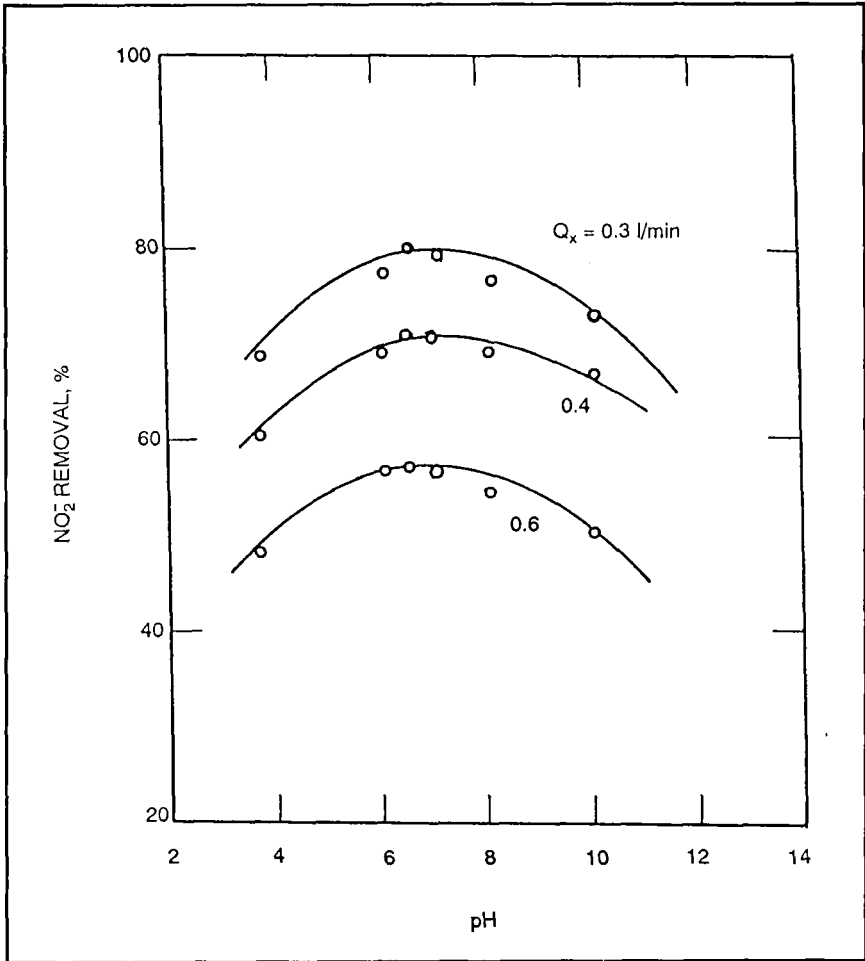


Figure 2. The pH effect on the nitrite removal.

The effect of ozone concentration in the gas stream on the nitrite removal is demonstrated in Figure 3. The nitrite removal becomes increasingly higher as the ozone concentration in the gas stream increases. It is also apparent in this figure that the nitrite removal at pH of 6.7 is significantly higher than the other two pHs. However, it should not be construed that higher nitrite removal at high ozone concentration implies higher ozone utilization. In fact, it is opposite as shown in Figure 4. This is not difficult to comprehend because of the fact that according to equation 8, doubling of the gas phase ozone concentration requires a doubling in the nitrite reduction in the liquid phase in order to maintain the same nitrite

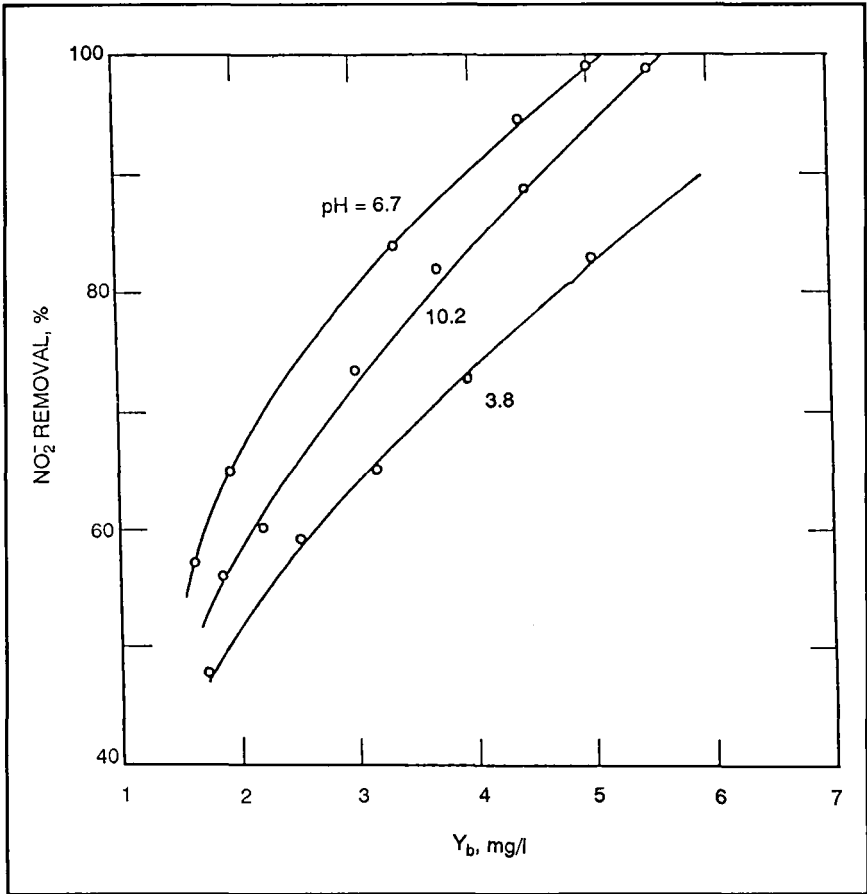


Figure 3. Nitrite removal vs ozone concentration in the inlet gas for various pHs with $Q_x = 0.3$ L/mg, $X_a = 5$ mg/L.

removal efficiency. Figure 3 clearly indicates that this is not the case because nitrite reduction does not increase proportionally to an increase in the ozone concentration in the gas phase.

The effect of inlet nitrite concentration on the nitrite removal is demonstrated in Figure 5. Irrespective of the liquid flow rate, there is a rapid decrease in the nitrite removal for lower inlet nitrite concentration. The decrease in the nitrite removal tends to level off as the nitrite concentration approaches a large value. Figure 6 shows that the total amount of nitrite oxidized by ozone as defined by equation 7 increases with increasing inlet nitrite concentration and liquid flow rate.

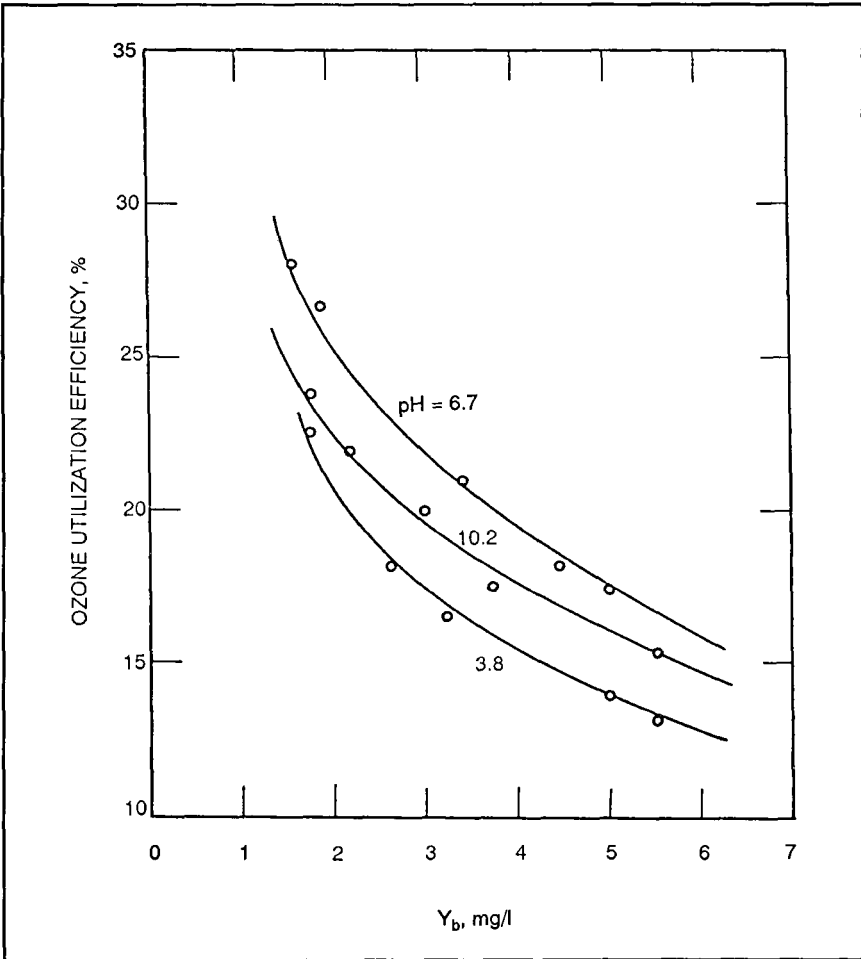


Figure 4. Nitrite removal efficiency vs ozone concentration in the inlet gas with various pHs with $Q_x = 0.3$ L/mg, $X_a = 5$ mg/L.

In practice, many aquacultural activities are conducted using sea water instead of fresh water. Therefore, it would be of interest to know whether ozonation is equally effective when applied to sea water. Figure 7 compares the nitrite removal efficiencies of fresh and sea waters. The pHs of fresh and sea waters were 6.5 and 7.6, respectively, which were close to the optimum operating range. In general, the nitrite removal efficiency for sea water is approximately 10 percent lower than that of fresh water. This is due primarily to the presence of complex salt and minerals in the sea water. In spite of this, the nitrite removal of sea water was

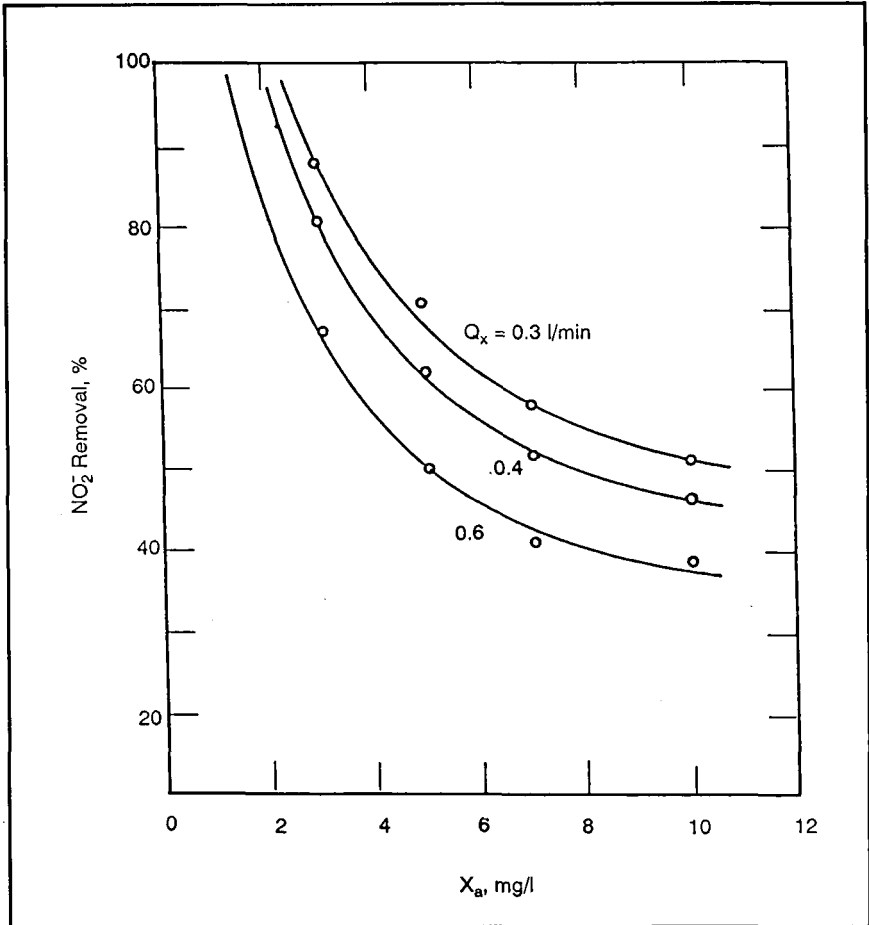


Figure 5. Effect of inlet nitrite concentration on the nitrite removal with $Y_b = 3.46$ mg/L and $pH = 6.7$.

found to be still quite good, implying equal effectiveness of ozonation for nitrification of sea water.

Under the same operating conditions, experiments in the bubble column were performed to test its efficiency for nitrite removal. Comparison of the nitrite removal for the packed bed reactor and the bubble column is displayed in Figure 8. Apparently, the packed bed reactor is significantly more efficient than the bubble column due to considerably improved aeration of the former. For an initial nitrite concentration of 300 mg/L, it took slightly over twenty-three minutes to reduce the nitrite concentration below 0.25 mg/L in a packed bed column, the

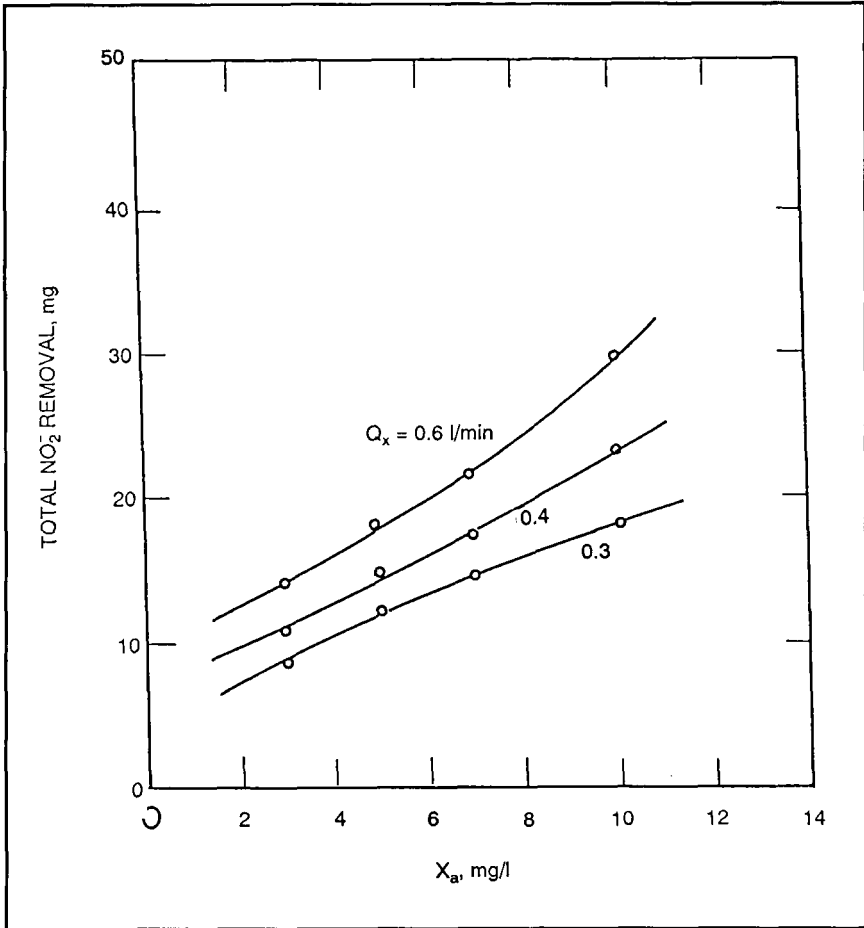


Figure 6. Effect of inlet nitrite concentration on the total nitrite removal with $Y_b = 3.46$ mg/L and $\text{pH} = 6.7$.

acceptable nitrite concentration for aquacultural water. To reach the same level of nitrite concentration in the bubble column, it would require more than thirty-five minutes.

The effects of pH and liquid flow rate on the overall mass transfer coefficient are demonstrated in Figure 9. Again, the pH around 7 had shown better mass transfer efficiency which confirmed the previous observation of optimum nitrite removal around pH of 7. The increasing mass transfer coefficient with increasing liquid flow rate follows the same trend observed by the previous investigators [10].

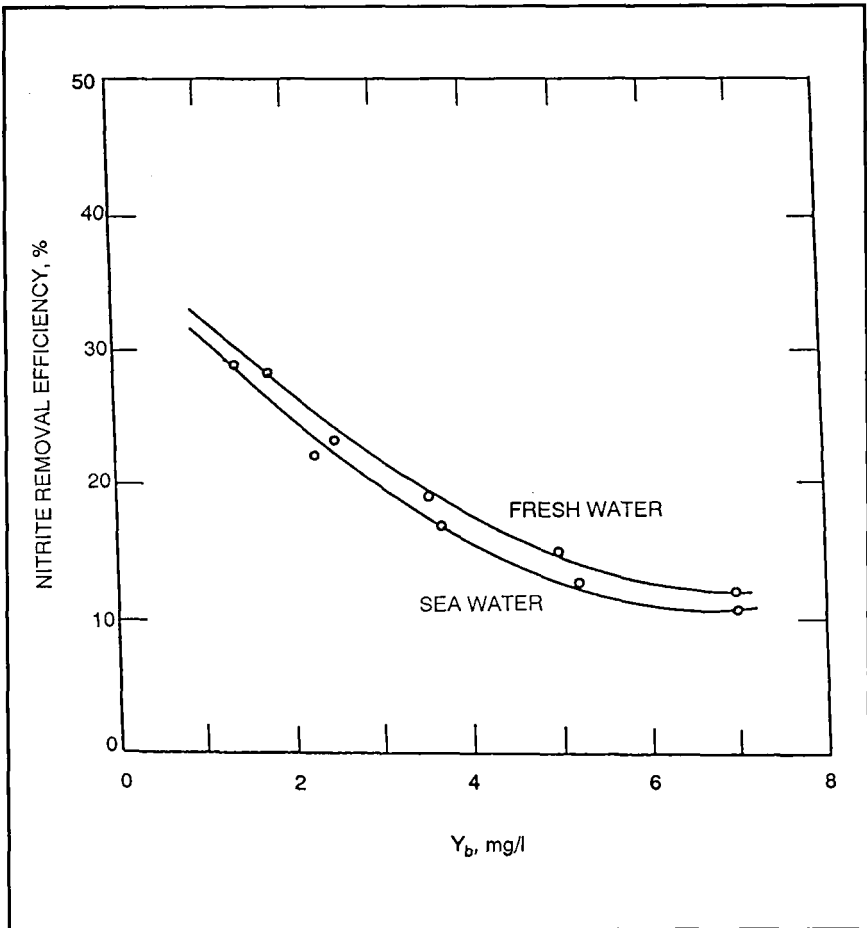


Figure 7. Comparison of nitrite removal efficiencies for fresh and sea waters with pH = 6.5 for fresh water and 7.6 for sea water, $Q_x = 0.3$ L/min and $X_a = 300$ mg/L.

CONCLUSIONS

Nitrite removal from aquacultural water by ozonation in a packed bed reactor was investigated. The experimental data have indicated that an optimum pH around 7 exists for maximum nitrite removal. Since the pH of most aquacultural water fall within the range between 6.5 and 7.5, it does not require pH adjustment for most efficient nitrite removal by ozonation and the pH of the treated water varies only slightly, being within ± 0.2 . In general, fresh water has a higher nitrite

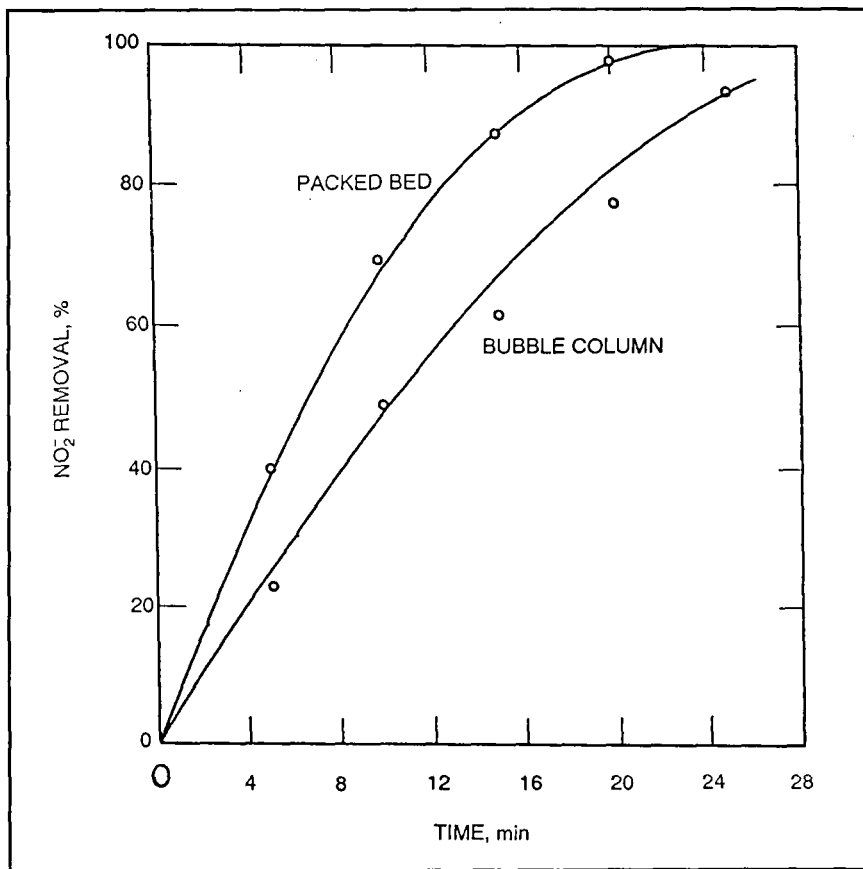


Figure 8. Comparison of nitrite removals for packed bed and bubble columns with $Q_x = 4$ L/min, $X_a = 300$ mg/L, $Y_b = 4.88$ mg/L and $\text{pH} = 6.7$.

removal than sea water. Within the ozone concentration between 1.5 and 6.5 mg/L of the present study, the nitrite removal increases with increasing ozone concentration, but the nitrite removal efficiency decreases.

Under the same operating conditions, the packed bed reactor has been found to be significantly more efficient than the bubble column. The nitrite concentration can be rapidly reduced in such a reactor system to below 0.25 mg/L, an acceptable nitrite concentration level for aquacultural activity. The mass transfer coefficient for the packed bed reactor is found to have the same optimum pH as the nitrite removal. This coefficient is observed to increase with increasing liquid flow rate.

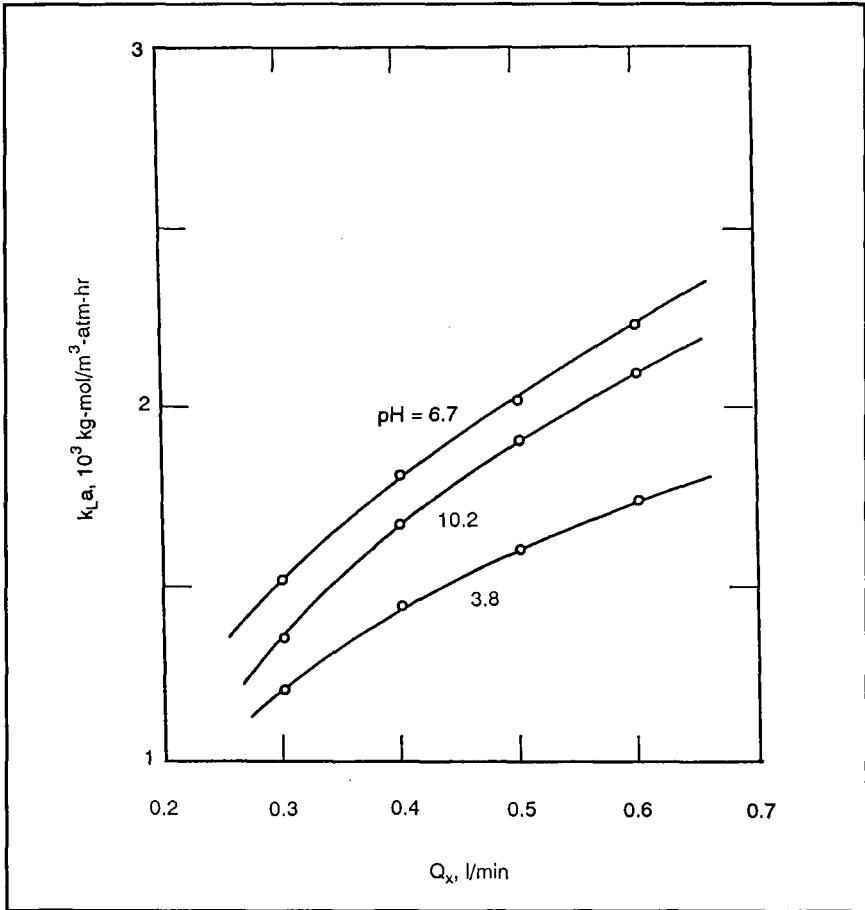


Figure 9. Mass transfer coefficient vs liquid flow rate with $Y_b = 3.48 \text{ mg/L}$.

NOTATION

- G_y molar flux ($\text{g. mol/cm}^2\text{-hr}$)
 H_y height of transfer unit (cm)
 $k_{L,a}$ overall mass transfer coefficient ($\text{g. mol/cm}^3\text{-atm-s}$)
 MNO_2 molecular weight of NO_2^- (g/mol)
 MO_3 molecular weight of ozone (g/mol)
 N_y number of transfer unit
 P atmospheric pressure (atm)
 Q_x liquid flow rate (L/min)
 Q_y gas flow rate (L/min)

S	cross-sectional area of packed bed reactor (cm ²)
X _a	nitrite concentration of inlet liquid (mg/L)
X _b	nitrite concentration of outlet liquid (mg/L)
Y _a	ozone concentration of outlet gas (mg/L)
Y _b	ozone concentration of inlet gas (mg/L)
Y*	equilibrium ozone concentration (mg/L)
Z _T	height of packed bed reactor (cm)

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Direct reprint requests to:

Dr. S. H. Lin
 Department of Chemical Engineering
 Yuan Ze Institute of Technology
 Neili, Taoyuan 320
 Taiwan, ROC