EFFECT OF NITRATE ON NITRIFICATION OF CONCENTRATED NITROGENOUS WASTEWATERS IN ROTATING BIOLOGICAL CONTACTOR AND AEROBIC EXPANDED BED REACTORS

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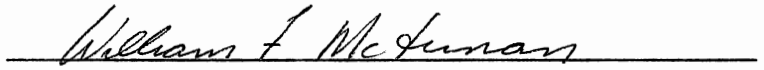

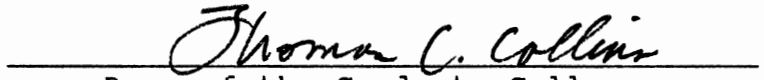

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CHAPTER I

INTRODUCTION

1.1 Development of this Research

This research was undertaken to investigate the feasibility of biological nitrification treatment of fertilizer wastewater, which contains ammonia-N and nitrate-N at concentrations up to 3020 mg/l and 1620 mg/l, respectively (Clarkson, 1990). High nitrogenous waste streams are generated from industries such as munitions, fertilizers, oil refineries, semiconductor, meat and milk processing, with ammonia as a typical component.

Discharge of ammonia in large amounts could give rise to some environmental problems. A significant oxygen demand could be exerted by the oxidation of ammonia to nitrate in receiving waters. Excessive nitrogen from industrial wastes would cause eutrophication in lakes and other slow-flow water courses where nitrogen is the limiting nutrient, leading to exhaustion of DO and severe odor problems. Ammonia is toxic to aquatic organisms, especially the higher forms such as fish. For some fish like rainbow trout the 24-hr ammonia LC_{50} is even as low as 0.2 mg/l (National Research Council, 1979). Ammonia discharged into ground

water may accumulate in nitrite and nitrate forms in aquifers and present a potential threat to the surrounding water sources. Ammonia may also be discharged to the air from industrial discharges or from the treatment of liquid waste streams by stripping. In order to protect the receiving environment from being subjected to the problems caused by nitrogenous wastes, ammonia in industrial waste streams should be removed or converted to other innocuous forms.

Biological nitrification is a well established treatment process to eliminate the nitrogenous oxygen demand and the ammonia toxicity in both municipal and industrial wastewaters. It is also the first step in the nitrification-denitrification process, by which nitrogenous pollutants can be biologically removed from wastewater or secondary effluent. In the nitrification process, ammonia-N is converted to nitrate-N by nitrifying bacteria. Biological nitrification is commonly used for low-strength nitrogenous wastewater treatment, but recent research has demonstrated the potential success of this process in treating high-strength industrial wastes with different high-rate biological reactors (Collins, Clarkson and Vrona, 1988; Collins, Clarkson and Florio, 1989).

Suspended growth and fixed-film biological systems have been successfully used for biological nitrification in laboratory-scale, pilot-scale and full-scale treatment

plants (Antonie, 1976; Collins et al., 1988; Collins et al., 1989; Jeris, Owens, Hickey and Flood, 1977; Lue-Hing, Obayashi, Zenz, Washington and Sawyer, 1976). With advantages such as shorter hydraulic retention times, higher biomass concentrations, smaller reactor volume, better resistance to loading fluctuation and toxicants, less need for effluent clarifier, no need for sludge recycling, and better economics, the fixed-film system has proven superior to suspended growth systems. Trickling filters, rotating biological contactors, activated bio-filtrations, packed bed and fluidized-bed reactors are examples of fixed-film systems. Of these processes, the rotating biological contactor (RBC) has been demonstrated to perform well, while some recent research showed that aerobic expanded bed (AEB) is also a promising process for high-strength industrial wastes, with advantages such as small treatment volume and high efficiency (Jewell, 1981). RBC and AEB were, therefore, chosen to be used in this research.

In some nitrogenous wastewaters (e.g. fertilizer production wastewater), nitrate ions and ammonia are discharged together. Theoretically, there may be some product inhibition of nitrate to nitrification of ammonia. Little information on this problem is available in the literature.

1.2 Objectives of this Research

Based on the previous research results of the RBC and AEB reactors and the characteristics of nitrogenous fertilizer wastewater, investigating the following problems were the principal objectives of this research:

(a) the effects of pre-existing nitrate ions at high concentration on the biological oxidation of ammonia and nitrite to nitrate;

(b) the upper loading limit of ammonia-N in aerobic expanded bed reactor;

(c) the optimal feeding regime for the efficient use of RBC surface area;

(d) the effects of disc rotation speed on the performance of RBC.

CHAPTER II

BACKGROUND THEORY AND LITERATURE REVIEW

2.1 Biochemistry of Nitrification

The overall stoichiometric reactions of the oxidation of ammonia to nitrate can be written as follows (EPA, 1975; Painter, 1970):

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^- + (58\text{-}84\ Kcal) \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- + (15.4\text{-}20.9\ Kcal) \quad (2)$$

The reaction of ammonia oxidation is actually much more complex than presented in Equation 1, involving the formation of hydroxylamine and other unstable intermediates which have yet to be determined (Painter, 1970; Grady & Lim, 1980). The reaction of formation and oxidation of hydroxylamine can be written as follows (Aleem, 1970):

$$NH_4^+ + 0.5O_2 \rightarrow NH_2OH + H^+ \quad (1.1)$$

$$NH_2OH + O_2 \rightarrow H^+ + NO_2^- + H_2O + energy \quad (1.2)$$

The energy released in these reactions is used by the nitrifying organisms in synthesizing their cell mass from inorganic carbon sources such as carbon dioxide, bicarbonate and carbonate. The assimilation of carbon dioxide is completed via the Calvin cycle (Sharma & Ahlert, 1977). For convenience the reactions 1 and 2 are named

nitritification and nitratification, respectively (Prakasam & Loehr, 1972). Nitritification is carried out principally by organisms of the genera Nitrosomonas (N.europaea and N.monocella) and Nitrosococcus. Because Nitrosomonas, especially N.europaea, have been the species most commonly isolated from wastewater treatment environments, the generic term Nitrosomonas has been used to represent organisms capable of oxidizing ammonia. Nitratification is effected principally by members of the genera Nitrobacter (N.agilis and N.winogradskyi) and Nitrosocystis. For a similar reason as in the case of ammonia oxidation, the term Nitrobacter has been used as an all-embracing term for nitrite oxidizers (Barnes & Bliss, 1983).

Some features of the autotrophic nitrifying bacteria, Nitrosomonas and Nitrobacter, are summarized in Table 1 (Sharma & Ahlert, 1977).

Assuming the empirical formulation $C_5H_7NO_2$ for the gross composition of Nitrosomonas and Nitrobacter, the stoichiometry of cell growth can be written as follows (EPA, 1975):

$$15CO_2 + 13NH_4^+ \xrightarrow{\text{Nitrosomonas}} 10NO_2^- + 3C_5H_7NO_2 + 23H^+ + 4H_2O \quad (3)$$

$$5CO_2 + NH_4^+ + 10NO_2^- + 2H_2O \xrightarrow{\text{Nitrobacter}} 10NO_3^- + C_5H_7NO_2 + H^+ \quad (4)$$

TABLE I

SOME CHARACTERISTICS OF NITRIFYING BACTERIA

	Nitrosomonas	Nitrobacter
Estimated Generation Time (hours, strong function of temperature)	8-36	12-59
Autotroph	Obligate	Facultative
DO requirement to Nitrify	Strict Aerobe	Strict Aerobe
Y (g VSS grown/g substrate -N oxidized)		
Experimental	0.04-0.13	0.02-0.07
Theoretical	0.29	0.084

Carbon dioxide exists in aqueous systems in equilibrium with other species as in the following equations:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{-2} \quad (5)$$

The free acid (H^+) produced in Reactions 1, 3 and 4 reacts with bicarbonate in the typical pH range of biological activity (neutral to slightly alkaline) according to Equation 5. Equation 5 can be incorporated into equations 1, 3 and 4 to give the following:

$$NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NO_2^- + 2H_2CO_3 + H_2O + (58\text{-}84\ Kcal) \quad (6)$$

$$13NH_4^+ + 23HCO_3^- \rightarrow 8H_2CO_3 + 10NO_2^- + 3C_5H_7NO_2 + 19H_2O \quad (7)$$

$$NH_4^- + 10NO_2^- + 4H_2CO_3 + HCO_3^- \rightarrow 10NO_3^- + 3H_2O + C_5H_7NO_2 \quad (8)$$

On the assumption of a cell yield of 0.15 (g VSS/g NH_4^+-N) for Nitrosomonas (EPA, 1975), combining Equations 6 and 7 gives:

$$55NH_4^+ + 76O_2 + 109HCO_3^- \xrightarrow{\text{Nitrosomonas}} C_5H_7NO_2 + 54NO_2^- + 57H_2O + 104H_2CO_3 \quad (9)$$

Similarly, Equations 2 and 8 can be combined, assuming a Nitrobacter cell yield of 0.02 (g VSS/g NO_2^--N oxidized), to give the following equation for Nitrobacter growth:

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7NO_2 + 3H_2O + 400NO_3^- \quad (10)$$

The assumptions for yields are based on representative measurements. Combining Equations 9 and 10 yields the overall reaction for nitrifier synthesis and oxidation as presented in Equation 11:

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7NO_2 + 1.041H_2O + 0.98NO_3^- + 1.88H_2CO_3 \quad (11)$$

Equation 11 reveals three factors of particular importance to nitrogenous wastewater treatment: (a) the very low cell yield per unit of ammonia nitrogen oxidized; (b) the large requirement for oxygen, amounting to approximately 4.3 g O_2 for each g NH_4^+-N oxidized all the way to nitrate-N; (c) the requirement for alkalinity (HCO_3^-) to buffer the system against hydrogen ions produced in the nitrification and to provide carbon for cell synthesis, amounting to 7.14 g alkalinity (as $CaCO_3$) for each g NH_4^+-N

oxidized.

2.2 Factors Affecting Nitrification

There are many factors affecting nitrification reactions. Only those factors of special importance to this research are discussed below.

Dissolved Oxygen. Oxygen is utilized in the oxidation reactions by nitrifying bacteria for accepting electrons and in a small quantity for synthesizing cell mass. The theoretical nitrogenous oxygen demand is 4.57 g per g of NH_4^+ oxidized to nitrate according to Eqs. 1 and 2. Based on 120 BOD bottle studies, Wezernak & Gannon (1967) found that 4.33 parts of oxygen are required for each part of NH_3-N oxidized to NO_3^--N. Dissolved oxygen concentrations higher than 1-2 mg/l are enough to keep the nitrification a zero-order reaction with respect to nitrogen (Schoberl & Engel,1964; Knowles, Downing & Barrett, 1965), therefore 2 mg/l of DO has been widely suggested as a minimum for nitrification (EPA, 1975; Benefield & Randall, 1980; Metcalf and Eddy Inc., 1979). Some observations show that higher DO concentrations of 3-4 mg/l can significantly enhance nitrification efficiency (Benefield & Randall, 1980; Bliss, Barnes & Windschuttel, 1981; Ministry of Technology of UK, 1965), but relatively little further improvement can be achieved at 5-6 mg/l of DO (Bliss et al., 1981). Haug & McCarty (1972) reported that there is no

inhibition by DO at concentration up to 60 mg/l. In submerged biofilm reactors like the AEB, providing enough DO is of special importance for successful operation.

Temperature. Temperature has a profound influence on nitrification. The optimal temperature ranges from 28° C to 36° C with an overall range of approximately 4-50° C over which growth of various species of nitrifying bacteria can occur (Painter, 1970). Nitrification reactions closely follow the van't Hoff-Arrhenius law up to 30° C (Focht & Chang, 1975). Stankewich (1972) summarized the results of several researchers to give the general equation determining the effect of temperature on the maximum specific growth rate:

$$u_{mT} = u_{m15} \exp[K(T-15)] \qquad (12)$$

where u_{mT} is the maximum specific growth rate at any temperature T (° C) and u_{m15} the rate at 15° C. The reported values of K are 0.095-0.12 for Nitrosomonas and 0.56-0.69 for Nitrobacter. The saturation constants for both Nitrosomonas and Nitrobacter, with respect to both inorganic nitrogen and DO, were found to increase with increasing temperature (EPA, 1975). For RBC, low temperature should be avoided during the start-up period, otherwise it is difficult to build up enough quantity of biomass (Antonie, 1976). Temperature also affects the equilibrium of nitrogen forms between NH_3 and NH_4^+ in water, with higher temperature in favour of NH_3 form.

pH. Various pH optima for nitrification have been reported in the literature. There appears to be a general agreement, however, that as the pH decreases into the acidic range the rate of nitrification declines (EPA, 1975). The optimum pH values were considered between 7.1 and 9.0 for various fixed-film studies (Collins et al, 1988). One of the factors contributing to the effect of pH is that pH affects the concentrations of the un-ionized substrate nitrogen, free ammonia (FA) and free nitrous acid (FNA). Anthonisen, Loehr, Prakasam & Srinath (1976) found that the ranges of FA concentrations that begin to inhibit the nitrifying organisms are: FA inhibition to Nitrosomonas, 10 to 150 mg/l and FA inhibition to Nitrobacter, 0.1 to 1.0 mg/l; FNA begins inhibition to nitrifying bacteria at concentrations between 0.22 and 2.8 mg/l. FA can be determined by the following equations (Water Pollution Control Federation, 1983):

$$NH_3 + H^+ \text{ <--> } NH_4^+ \quad (13)$$

$$NH_3 \text{ (mg/L as N)} = n / (1 + 10^{-pH-pK}) \quad (14)$$

$$pK = -3751.5 / T + 6.6495 - 0.011032 * T \quad (15)$$

$$n \text{ (mg/L as N)} = 14{,}000 * ([NH_3] + [NH_4^+]) \quad (16)$$

where T is the water temperature in °K. NH_4OH also exists in water, but in very small quantity, and therefore can be neglected in making the above calculations.

In nitrification treatment processes, pH is often controlled by adding carbonate or bicarbonate which also

provide necessary carbon source.

Nitrate-N. Little attention has been given to the effect of nitrate ions on the oxidation of ammonia to nitrate. From the viewpoint of biochemistry, some product inhibition by nitrate ions can be expected. Boon & Laudelout (1962) reported that nitrate-N non-competitively inhibited oxidation of 224 mg/l nitrite-N, with 50% inhibition at 2,800 mg/l nitrate-N. In their experiment, Nitrobacter winogradskyi was employed. The cell suspension, nitrite and nitrate were added to a flask and oxygen uptake rate was measured. Some industrial wastewater contains both ammonia-N and nitrate-N at high concentrations. Short term samples of fertilizer wastewater, for example, contained nitrate-N up to 1620 mg/l and the ratio of NH_3-N:NO_3^--N averaged 1.9:1 (Clarkson, 1990). The concentrations of NH_3-N and NO_3^--N are independent in fertilizer wastewater. This is just a ratio of average values taken over a short time. Occasionally this ratio could be much higher. Therefore the effect of nitrate ions on the nitrification reaction deserves some investigation.

2.3 RBC for Nitrification

RBC is a wastewater treatment system using a series of rotating discs mounted on a central shaft. The discs provide large surface area for attached biomass growth and are partially submerged in the wastewater. RBC has been

proven an effective reactor for nitrification treatment of both domestic and industrial wastewater. In studies compiled by Collins et al. (1988), the concentration of ammonia-N ranged from 3 mg/l to 893 mg/l, and high nitrification rates, up to 99% in some cases, were achieved. The maximum mass loading rate applied to an RBC was 4.1 g NH_3-N/sq.m/d with a minimum of 0.29 g/m^2*d.

Although the RBC is a well established wastewater treatment reactor, some attention should be given to the areas discussed below:

The popular feeding regime is that the wastewater is introduced into the first stage and flows through RBC stagewisely. Some researchers (Collins et al., 1988; Lue-Hing et al., 1976) found that in many cases almost all nitrification can be achieved in the first stage. This implied that certain changes in the feeding regime could be made to better use the surface of RBC.

Disc rotational velocity affects wastewater treatment in several ways: it provides contact between the biomass and the wastewater, it aerates the wastewater, and it provides energy to thoroughly mix the wastewater in each stage. Increases in rotational velocity enhance the effect of each of these factors. However, there is an upper rotational velocity above which there is no further benefit (Antonie, 1976). Based on experiments with domestic wastewater, Antonie suggested that the optimum peripheral

velocity of disc BOD removal and nitrification in domestic wastewater is about 0.3 m/sec. Weng & Molof (1974) used a six-stage RBC reactor to carry out COD removal and nitrification together. When the disc peripheral velocity was 0.16 m/sec (20 rpm), COD was high enough to inhibit nitrification. The NH_3-N concentration was reduced from 26.6 mg/l to 22.7 mg/l in the last stage, achieving a removal rate of 17 %, as the disc peripheral velocity was increased to 0.24 m/sec (30 rpm). As the disc peripheral velocity was further raised to 0.33 m/sec (42 rpm), the NH_3-N concentration in the last stage was reduced to 17.1 mg/l and the removal rate was increased to 36%.

There is usually a net loss of nitrogen through RBC systems, of the order of 20% (Barnes & Bliss, 1983). Some researchers believe that this is due to some denitrification at the media/biomass interface (Ellis & Banaga, 1976), while Votes, Vanstaen & Verstraete (1975) reported that denitritification (reduction of nitrite to gaseous nitrogen) probably takes place under both anaerobic and aerobic conditions.

Friedman, Robbins & Woods (1979) reported that a water temperature drop of 2-3°C below the atmospheric temperature was found and seemed to be independent of rotational speed and hydraulic loading rate. This temperature drop was attributed to evaporative cooling. No literature about water loss through the RBC reactor is available.

2.4 AEB for Nitrification

AEB reactors are submerged fixed-film biological wastewater treatment units utilizing very small biomass support particles with continuous recycle. It has demonstrated potential success in some research (Collins et al., 1989). Collins et al. applied AEB to nitrification treatment of semiconductor wastewater. In their research, the ammonia-N concentration was higher than 180 mg/l, and the nitrification rates were over 94% under loadings between 1.27 and 11.52 g/l bed*d with four reactors in which static bed volumes range from 45 to 450 ml. DO in influent was between 8.50-8.97 mg/l and in effluent 1.04-2.57 mg/l. DO destroyed (mg) per mg NH_3-N oxidized to nitrate ranged from 2.74 to 3.38, nitrogen loss was between 9.4% and 20.5%. The highest attached VS reached 42.5 g VS/l bed. Diatomaceous earth particles were employed as biofilm support media, with a high surface area to volume ratio of 5780 sq.m/cubic m. These researchers found that because of the high biomass concentration, DO concentration is the limiting factor in further improving AEB's performance. They suggested that for even better performance, denser biomass support media could be substituted so that the recycle rate could be increased, or the system could be converted to pure oxygen. Biological fluidized-bed has been successfully used for BOD and nitrogen removal in many plants (Jeris et al., 1977), and the AEB and fluidized-bed

are similar reactors. The principal difference between AEB and fluidized-bed is at the bed expansion rate. Some researchers claimed that the AEB reactor should not have a bed expansion rate higher than 20% (Jewell, 1981). In the research by Collins et al. (1989) bed expansion rates higher than 60 % (similar to fluidized bed) were used. The upper nitrogen mass loading limit while oxygen is not the limiting factor in AEB is of principal interest in this research.

CHAPTER III

MATERIALS AND METHODOLOGY

3.1 Experimental Apparatus

3.1.1 Rotating Biological Contactor Reactor

The rotating biological contactor reactor, which is shown in Figures 1 and 2, consisted of a semicircular tank divided into five compartments of roughly equal volume. The net liquid volume provided by the reactor was 6.97 L. Thirty 17.5-cm-diameter plastic discs mounted on a shaft were divided into five stages by bulkheads, each consisting of five discs. Discs were fixed 1.2 cm apart from each other to avoid possible clogging. The plastic discs provided 1.44 sq.m of total surface area for biomass growth and were submerged in the tank to about 40 percent of the disc diameter. The shaft bearing the discs was driven by a electric motor (model No. 7553-30, Cole-Parmer Instrument Co.).

In common RBC reactors, the feed solution is introduced into the first stage and flows stagewise through the whole reactor. In order to make better use of the disc

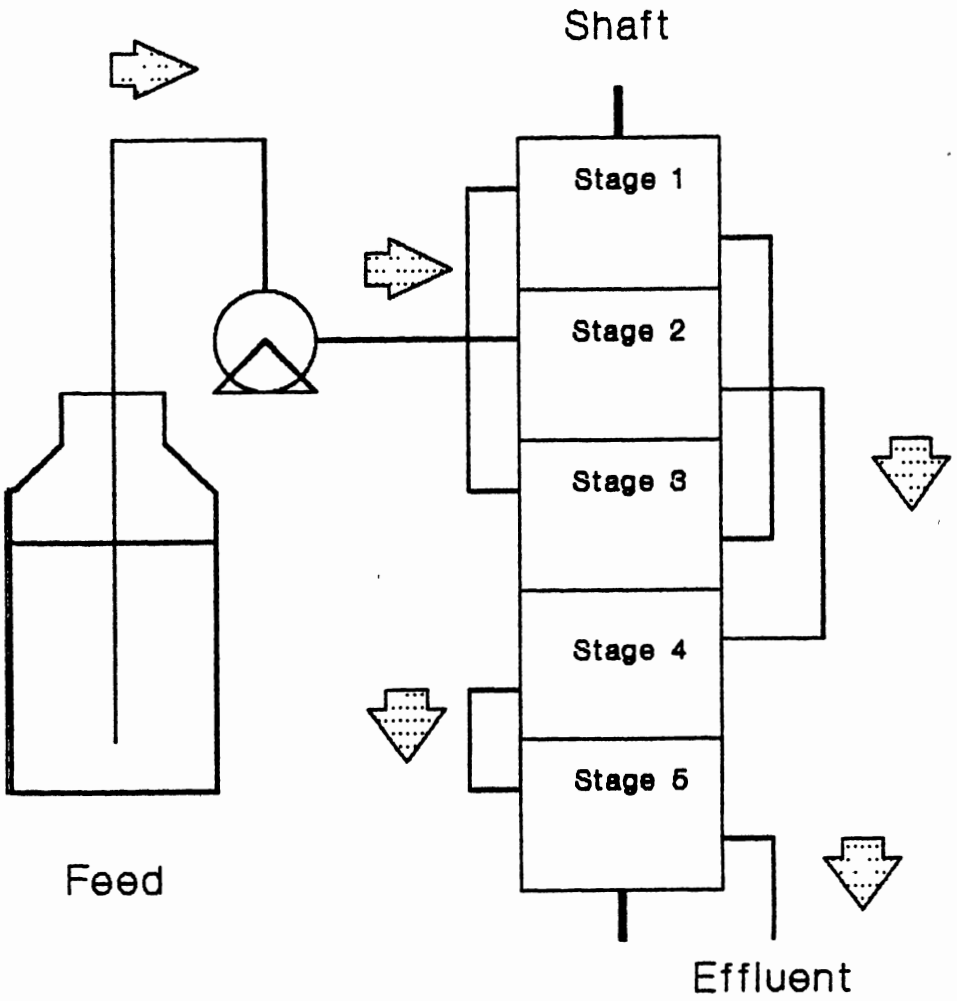

Figure 1. Schematic Diagram Of RBC System

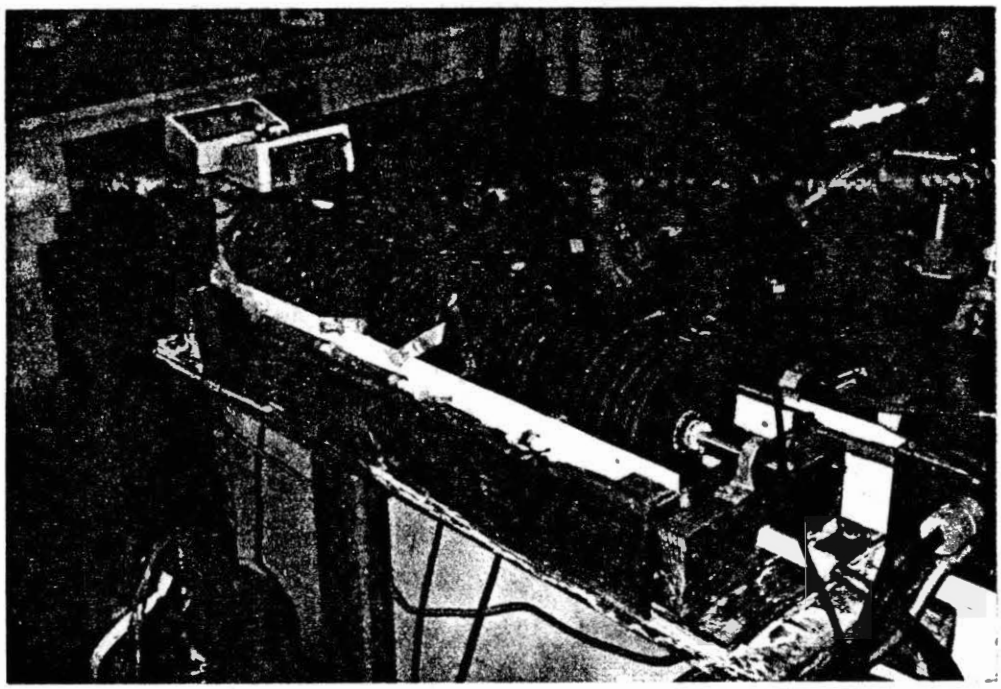

Figure 2. Photograph Of RBC Reactor

surface area, a new feeding regime was adopted for this reactor, i.e., influent was evenly pumped from a 25 L container into the first four stages, and the effluent from the first four stages was collected in a PVC plastic piping and discharged into the fifth stage, which was used as polishing unit. The polished water was discharged from the reactor through an overflow opening in the fifth stage. Four positive displacement Masterflex pumps (model No. 7520-10, Cole-Parmer) fitted with standard pump heads (model No. 7014-20) were employed for feeding. In the latter part of the experiment, the fourth and fifth stages were used as polishing units while the total RBC mass loading was kept the same as before, but was introduced only to the first three stages simultaneously.

In the start-up phase of this experiment, the biomass growth was hindered by the low water temperature (lower than 16 °C). To overcome this problem, an electric hot water bath (MW-1120A, Blue M electric Co.) was used to heat the water in the RBC.

3.1.2 Aerobic Expanded Bed

The aerobic expanded bed system is shown in Figures 3 and 4. The AEB reactor consisted of a calibrated cylindrical glass cylinder, which was 41 cm long and 2.5 cm in inner diameter with a volume of 200 ml. The effluent from the top of the expanded bed reactor was introduced to

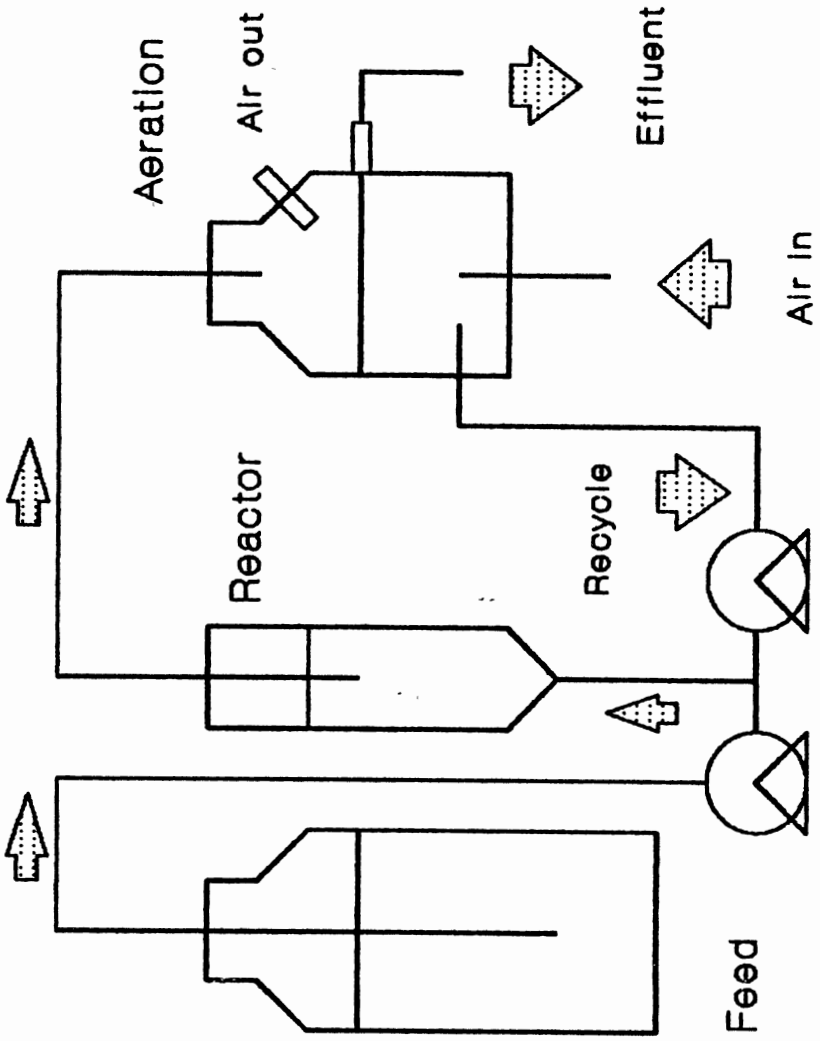

Figure 3. Schematic Diagram Of AEB System

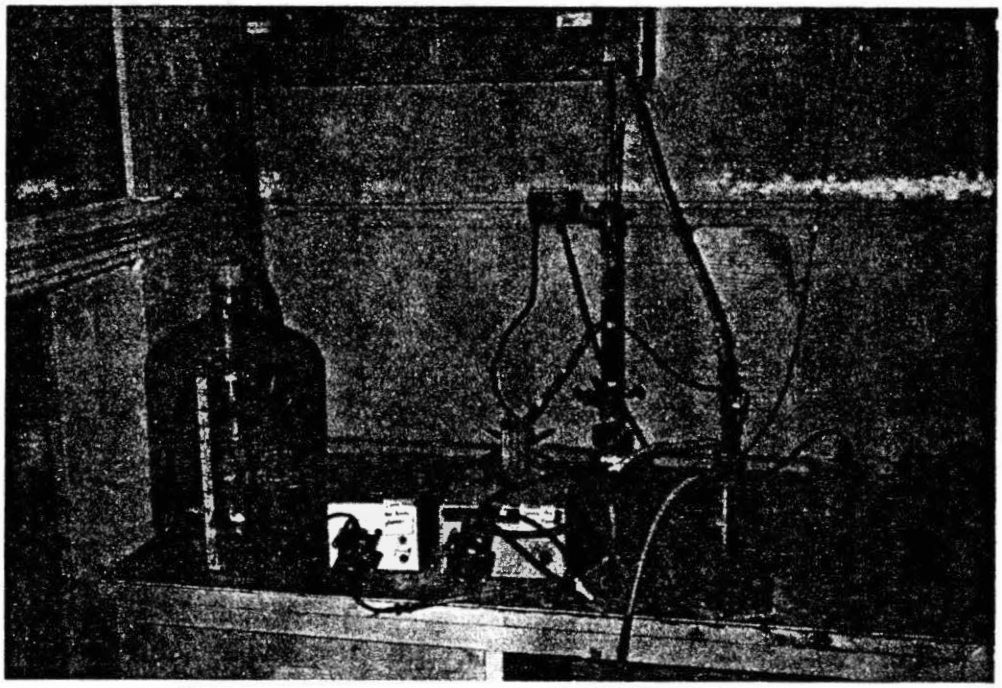

Figure 4. Photograph Of AEB Reactor

a 500-ml aeration bottle in which the effluent was aerated by air. Effluent recycling was carried out to increase the dissolved oxygen and expand the bed in the reactor. A positive displacement pump (7553-50, Cole-Parmer) was used to recycle the aerated effluent to the bottom of the reactor. The pump was fitted with two model 7015-20 pump heads (Cole-Parmer Instrument Co.). Treated water left the system through an overflow opening located at the upper part of the aeration bottle. The feeding solution from a 25 L container was pumped to the bottom of the reactor by a Cole-Parmer model 7553-50 pump fitted with a positive displacement pump head (model 7016-20). The feed and the recycled effluent joined together in a plastic tubing leading to the bottom of the reactor. The biofilm support media in the reactor consisted of diotamaceous earth particles(diameter averaging about 1 mm), which provide a high surface area to volume ratio (up to 5780 m^2/m^3 in this case) and have a bulk density of 0.35 g/cm^3. The support media bed was expanded by the mixture of the feed and the recycled effluent, and the expansion rate was adjusted through changing the recycle rate.

3.2 Feed Solution

Synthetic substrate was used in this research to simulate the nitrification process of the fertilizer nitrogenous wastewater. The composition of the feed

solution was determined mainly based on the stoichiometric equations described in Chapter 2 with respect of the biomass growth requirements for trace nutrients. Nitrate was added to feed solution in the latter part of the experiment. The concentrations of the feed solution were different for the RBC and AEB reactors at different experimental stages, but the dose of each chemical was proportionally increased or decreased in feed solutions of different concentrations. The composition of 500 mg NH_3-N/L feed solution is, for example, given in Table 2. All chemicals were dissoived separately in tap water and then mixed well in a 25 L glass bottle; pH ranged from 7.6 to 7.9 in all the feed solutions used in this experiment.

TABLE II

COMPOSITION OF 500 mg NH_3-N/L FEED SOLUTION

Ingredients	Concentration, g/L
Ammonium Sulfate	2.360
Sodium Bicarbonate	5.920
Potassium Dihydrogen Phosphate	0.160
Ferrous Sulfate	0.005
Magnesium Sulfate	0.005

3.3 Start-up Procedure

3.3.1 Rotating Biological Contactor

The inoculum for autotrophic nitrification was collected from an anaerobic expanded bed unit employed to carry out denitrification process in this laboratory at Oklahoma State University. The composition and concentration of the feed were the same as those listed in Table II, except that the concentration of sodium bicarbonate was 39 % lower. For more than a month, little attached biomass was developed. The concentration of sodium bicarbonate was then increased to 5.92 g/L, the same as listed in Table II. The RBC mass loading rate was 2.65 g NH_3-N/m^2*d. Although much more biomass attached onto the discs after the increase in sodium bicarbonate concentration, the growth rate was still low. The low water temperature (about 16°C) was considered to cause the slow growth, therefore a hot water bath was used to heat the water to room temperature (about 24°C). Within a month the ammonia conversion rate increased from 35 % to over 60 % under a mass loading rate of 4.76 g NH_3-N/m^2*d and a disc rotation speed of 6 RPM. The concentration of nitrite ion was less than 10 mg/L, indicating a balanced growth of Nitrosomonas and Nitrobacter.

3.3.2 Aerobic Expanded Bed

The seed for autotrophic nitrification in the AEB reacor was collected from an activated sludge aeration tank of the sewage treatment plant of Ponca City, Oklahoma. The activated sludge was contained in a 25 L glass bottle. Every day the supernatant was drained and replenished with feed solution containing 185 mg NH_3-N/L. The initial bed volume of diatomaceous earth particles was 70 ml and the bed expansion rate was kept at about 40 %. The feed solution contained 185 mg NH_3-N/L along with necessary nutrients and was pumped to the reactor from the substrate container.

The adapted sludge from the activated sludge bottle was added into the reactor through the aeration bottle three times a day, 5 to 10 ml per addition, which was later increased to five times a day, 10 ml per addition. Some biomass from RBC reactor was also added to the AEB reactor during a period of 20 days. The biofilm attachment of nitrifying bacteria occured first at the upper region of the bed and then developed down to the bottom. Some media were taken out of the reactor at times to keep a bed volume of about 80 ml. In two months ammonia conversion rates over 70 % were achieved under mass loadings of about 14.4 g NH_3-N/L bed*d. The high mass loading was intended to promote biomass growth. The biomass attachment was stratified with less biomass coating the media particles in the lower

region of the bed. This was eliminated by increasing the bed expansion rate to about 65 %.

3.4 Analytical Techniques

3.4.1 Ammonia Nitrogen

Concentration of ammonia nitrogen was measured according to the methods described in Standard Methods (APHA, AWWA & WPCF, 1985), Section 417 B. Direct nesslerization method was used, and its validity was checked by the distillation method with one sample out of each sample set. The difference between these two methods never exceeded 1 % in the whole experiment. EDTA was used to inhibit the precipitation of residual calcium and magnesium. Samples were diluted with distilled water. A DR/3 Spectrophotometer (HACH Co.) was used to measure color.

3.4.2 Nitrite and Nitrate

The techniques used for determinations of concentrations of nitrite and nitrate were given in Standard Methods, Section 429 (APHA et al., 1985). A Dionex ion chromatograph, series 2000i/sp, was used for the measurements. Standard solutions were prepared for each analysis.

3.4.3 Total Suspended Solids

Total suspended solids were measured according to the methods described in Standard Methods (APHA et al.,1985), Section 209 C. Filtered solids were dried at 103-105°C.

3.4.4 Volatile Suspended Solids

The procedures described in Standard Methods (APHA et al., 1985), Section 209 D, were followed for determination of volatile suspended solids. The residue from total suspended solids determination was used for the determination of volatile suspended solids.

3.4.5 Attached Biomass in AEB Reactor

The procedures described by Clarkson (1986) were followed to determine the attached biomass in AEB reactor. Samples were taken from the center of the expanded bed reactor using a wide mouth pipet and transfered to 10 ml wide bore graduated cylinders. The cylinders were then tapped and spun several times to consolidate the samples. During this process of consolidation, particles were added or removed and the tamping procedure followed until each sample contained exactly 5.0 ml of packed particles. Supernatant was decanted and the sample was transfered to an ashed, preweighed porcelain drying dish by sluicing it out with a stream of distilled water from a wash bottle. The jet of water from the wash bottle was used to agitate

the particles vigrously. The supernatant containing loose solids was transfered to other drying dishes. Care was taken not to remove support particles from their original dish. This process was repeated until further washing produced no further loose biomass.

The dishes containing these samples were subjected to the total suspended solids procedure described in Section 3.4.3. Blanks consisted of biomass-free diatomaceous earth particles prepared along with those used for the expanded bed but stored in a buffer solution at room temperature. Blank samples were necessary to correct for hygroscopically bound water in the diatomaceous earth in performing the solids calculations. After the samples were ashed finally, the particles were rehydrated with distilled water, transferred to the graduated cylinders, and the final volume of sample was taken. The samples were tamped well before the final volume of the rehydrated sample was recorded.

3.4.6 Attached Biomass in RBC Reactor

Samples for determination of the attached biomass in RBC were taken from disc surface with knife, and then were subjected to a procedure similar to that described in Section 3.4.4. Four samples were taken from each stage at different locations. The surface area of each sample was measured. The average of the four samples and the surface

area measured were used for calculating the total biomass in that stage.

3.4.7 pH

pH values of samples were measured with a model 900 Accumet pH meter (Fisher Scientific Co.). This meter was calibrated with standard solution each time when used on every set of samples.

3.4.8 Alkalinity

Alkalinity was measured according to the procedures described in Standard Methods (APHA et al., 1985), Section 403. Sulfuric acid of 0.1 N was used for titration. The end point of pH 4.5 of titration was determined with a model 900 Accumet pH meter (Fisher Scientific Co.).

3.4.9 Dissolved Oxygen

DO was measured with a model 97-08-00 O_2 electrode (Orion Research Co.). Procedures described in Standard Methods (APHA et al., 1985), Section 421 C, were followed to check the results measured with O_2 electrode once a week. The difference between the results from these two methods was always smaller than 0.2 mg/l of DO.

CHAPTER IV

EXPERIMENTAL APPROACHES AND RESULTS

4.1 Aerobic Expanded Bed

4.1.1 AEB under Basic Operational Conditions

After attached biofilm had been well established in the AEB reactor, a steady state operation was kept for 10 days before various tests were carried out. It had been found that the system could reach a new steady state well within two days after operational conditions had been changed, because the HRT was only about 0.75 hr. In this AEB system, a steady state meant the variation in the conversion rates was smaller than 5 % of the average of the data observed in at least two consecutive days. All the operational conditions and the analytical results are shown in Table III in which the averages of six samples are tabulated.

Feed solution was prepared at concentration of 185 mg NH_3-N/L and pumped into the reactor at a calculated rate of 3.02 L/d. Static bed volume was 80 ml. A bed expansion rate of 70 % was maintained by a recycle rate at about 490 L/d.

TABLE III

AEB BASIC OPERATIONAL CONDITIONS AND RESULTS

Items	Data
Static Bed Volume (ml)	80
Bed Expansion Rate (%)	70
Recycle Rate (L/d)	490
Substrate Flow Rate (L/d)	3.02
Hydraulic Retention (hrs)	0.75
Influent Ammonia-N (mg NH_3-N/L)	180
Effluent Ammonia-N (mg NH_3-N/L)	5.4
Nitrification Efficiency (%)	97
Specific Mass Loading (g NH_3-N/L bed*d)	7
Influent Nitrite (mg NO_2^--N/L)	<1
Effluent Nitrite (mg NO_2^--N/L)	<1
Influent Nitrate (mg NO_3^--N/L)	<1
Effluent Nitrate (mg NO_3^--N/L)	173.5
N Balance (%) [a]	0.6
Attached VS (g VS/L static bed)	46.7
Entrapped VS (g VS/L static bed)	1.51
Specific NH_3-N Conversion Rate (g NH_3-N/g VS*d)	0.141
Influent DO (mg/L)	7.2
Effluent DO (mg/L)	4.2
Oxygen Destroyed (mg) per mg of NH_3-N Converted to Nitrate	2.75
Alkalinity Consumed (mg) per mg of NH_3-N Converted to Nitrate	7.83
Effluent TSS (mg/L)	4.65
Effluent VS (mg/L)	3.05
Influent pH	7.6
Effluent pH	7.35
Water Loss Through System (%) [b]	1.4

[a] N balance (%) = $[(N_{out} - N_{in})/N_{in}]*100\%$

[b] All measured and calculated data were not corrected with the water loss datum

The high expansion rate maintained DO in effluent much higher than 2 mg/L necessary for nitrification, and it also provided longer contact time between the biomass and substrate by prolonging the hydraulic retention time. Mass loading was kept at about 7.0 g NH_3-N/L bed*day, which was calculated on the basis of static bed volume. Hydraulic retention time was about 0.75 hr, calculated from the feed flow rate and the liquid volume in the expanded bed. Because of unstable feeding pump rate and the fluctuation in feed solution concentration, both the mass loading rate and the hydraulic retention time could not be kept exactly constant. The feed solution concentration was found to decrease 2 mg NH_3-N/L per day on average, while concentrations of nitrate and nitrite ions in the feed solution increased slightly.

A high ammonia-N conversion rate of 97 % was achieved with ammonia-N in the effluent lower than 7 mg/L. Nitrite ion in the effluent was measured at concentration lower than 1 mg/L, indicating a balanced development of bacteria species. Oxygen destroyed (mg) per mg of NH_3-N converted to nitrate averaged about 2.75, much lower than theoretical value of 4.3. It is possible that gaseous oxygen of small air bubbles in the aerated recycle water could continue to dissolve into the water in the reactor, so that extra DO besides that measured was available for reaction. Denitritification (reduction of nitrite to gaseous

nitrogen) might contribute a little in this phenomenon. DO in the effluent was above 4.0 mg/L, not being the reaction limiting factor. Alkalinity consumed (mg) per mg of NH_3-N converted to NO_3^- was 7.83, a little higher than theoretical value of 7.14. pH values in the substrate and the effluent of the reactor were about 7.6 and 7.35, respectively, falling in the optimum range of 7.1-9.0, indicating that the dose of bicarbonate determined from the stoichiometry provided enough pH buffering capacity in this system. The biomass particles were ball-shaped and the biofilm coating the support particle was about 0.3 mm thick.

4.1.2 Effects of Nitrate on AEB Performance

Nitrate ions were provided by dissolving potassium nitrate in tap water separately and mixing well with the original feed solution. The nitrate-containing feed solutions were prepared according to ratios of NH_3-N:NO_3^--N ranging from 6:1 to 1:12. The ratio of NH_3-N:NO_3^--N in the fertilizer wastewater from the Agricultural Minerals Corporation plant averaged only 1.9:1 (Clarkson,1990), but occasionally was much higher. The concentration of nitrate was increased step by step until the ratio of 1:12 was reached. A steady operation condition was maintained for at least two days at each nitrate addition level. During the

period of this test, all the operational conditions were kept as constant as possible: bed volume 85 ml, bed expansion 66 %, substrate flow rate 3.02 L/d and ammonia-N mass loading 6.0 g NH_3-N/L bed*d. All the operational conditions and the averages of three samples are shown in Table IV and Figure 5.

TABLE IV

EFFECTS OF NITRATE ON AEB PERFORMANCE

Items	Time (days)						
	1-4	5-7	8-10	11-14	15-16	17-18	19-20
Bed Volume (ml)	85	85	85	85	85	85	85
Bed Expansion (%)	66	66	66.2	66.3	66	66.5	66.1
Recycle Rate (L/d)	386	386	389	340	385	387	384
Influent NH_3-N (mg/L)	178	178	174	177	170	171	170
Effluent NH_3-N (mg/L)	10	10.5	11	11.5	12.4	12.5	12.8
NH_3-N Conversion (%)	94.4	94.1	93.7	93.5	92.7	92.7	92.5
Mass Loading (g NH_3-N/L bed/d) [a]	6.3	6	5.9	6.1	5.8	6.1	6.05
Feed Flow Rate (L/d)	3.02	2.88	2.88	2.95	2.88	3.02	3.02
HRT (hrs)	0.77	0.8	0.81	0.79	0.8	0.77	0.77
Influent NO_3^--N(mg/L)	0	33	93	192	365	1140	2110
Effluent NO_3^--N(mg/L)	176	204	230	392	563	1430	2075
Influent NO_2^--N(mg/L)	0	0	0	0	0	0	0
Effluent NO_2^--N(mg/L)	0	8	0	0	0	0	0
Total N in (mg/L)	178	211	267	369	535	1311	2280
Total N out (mg/L)	186	217	241	404	575	1443	2088
N Balance (%) [b]	4.5	2.9	-9.7	9.3	7.6	10	-8.4

[a] Static bed volume was used for calculation

[b] N balance (%) = $[(N_{out} - N_{in})/N_{in}] * 100$ %

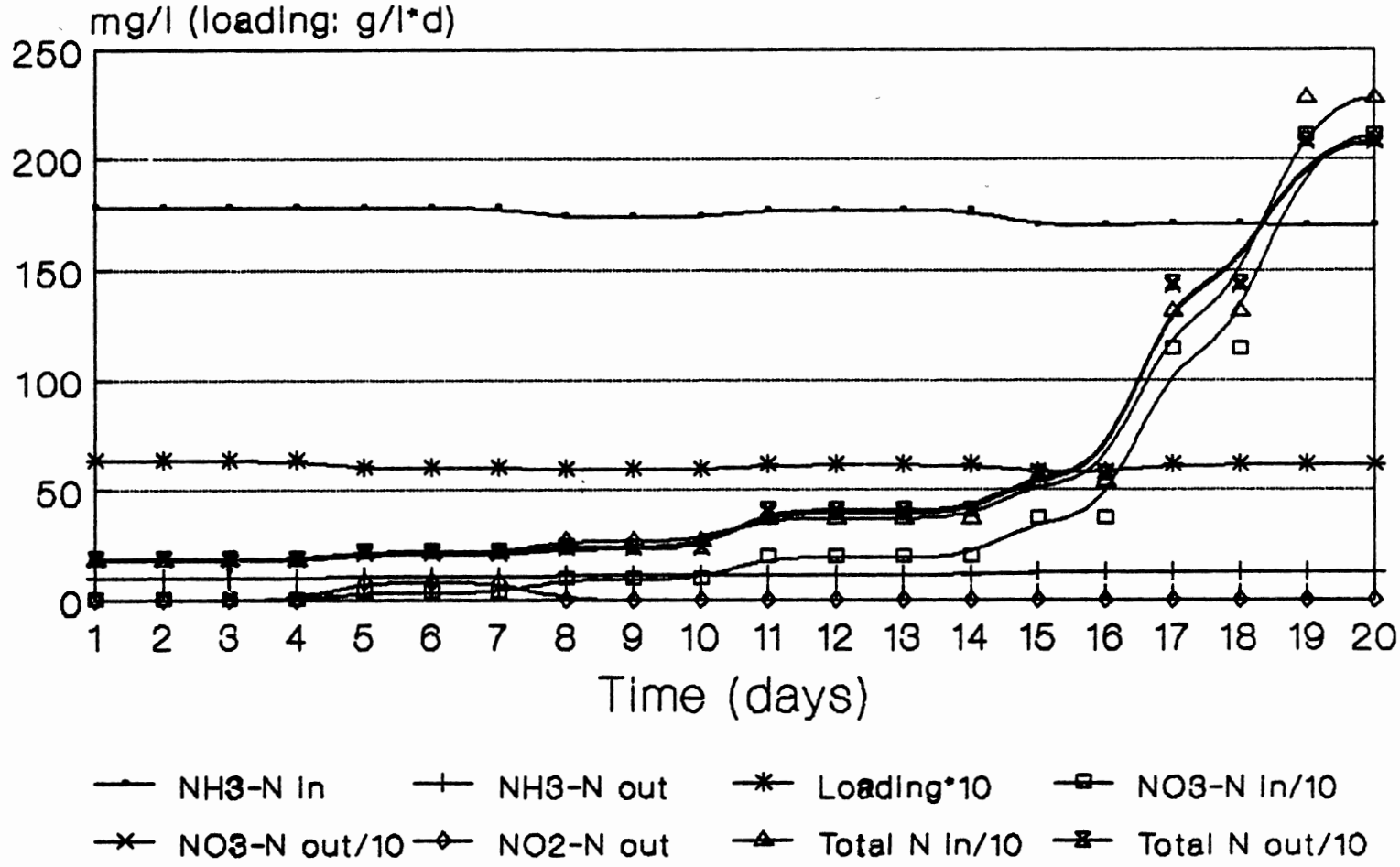

Figure 5. Effects of Nitrate on AEB Performance

Before the addition of nitrate ions, the ammonia-N conversion rate was 94.4 %. When the concentration of nitrate-N in the feed solution reached 2110 mg/L, the ammonia-N conversion rate dropped slightly to 92.5 %. Nitrite-N in the effluent was detected only when nitrate ions were first added (NH_3-N:NO_3^--N = 6:1), at a concentration 8 mg/L.

4.1.3 Upper Mass Loading Limit

The NH_3-N loading rate was increased by increasing the feed concentration from 185 to 370 mg NH_3-N/L, while other operational conditions were kept constant. The feeding flow rate was about 3.1 L/d, the static bed volume 90 ml, the bed expansion rate 63 %, and the hydraulic retention time 0.77 hr. DO in effluent was kept above 3 mg/L by a high recycle rate of 461 L/d, so that the DO was not reaction limiting factor. The reactor was operated at steady state for three days under each mass loading rate, and analyses for the influent and effluent were made daily. All the measured data are presented in Table V and Figure 6. They are averages of three samples.

The ammonia-N conversion rate was 94 % when the feed solution concentration was 177 mg NH_3-N/L and the mass loading rate was maintained at 6.2 g NH_3-N/d*L static bed. The conversion rate remained satable at 93 % as the feed solution concentration and the mass loading rate increased

TABLE V

AEB PERFORMANCE UNDER DIFFERENT LOADINGS

Items	Time (days)			
	1-3	4-6	7-9	9-15
Static Bed Volume (ml)	90	90	90	90
Bed Expansion Rate (%)	62	63	63	63.3
Recycle Rate (L/d)	458	461	461	458
Flow Rate (L/d)	3.15	3.08	3.12	3.14
HRT (hrs)	0.75	0.77	0.77	0.77
Influent NH_3-N (mg/L)	177	220	248	345
Effluent NH_3-N (mg/L)	10	12	18	96
NH_3-N Conversion Rate (%)	94	94	92.7	72.2
Mass Loading Rate (g NH_3-N/d*L static bed)	6.2	7.5	8.6	12
Influent DO (mg/L)	7.7	7.7	7.7	7.7
Effluent DO (mg/L)	3.7	3.65	3.6	3.33
Influent pH	7.6	7.65	7.7	7.8
Effluent pH	7.35	7.8	8.1	8.35

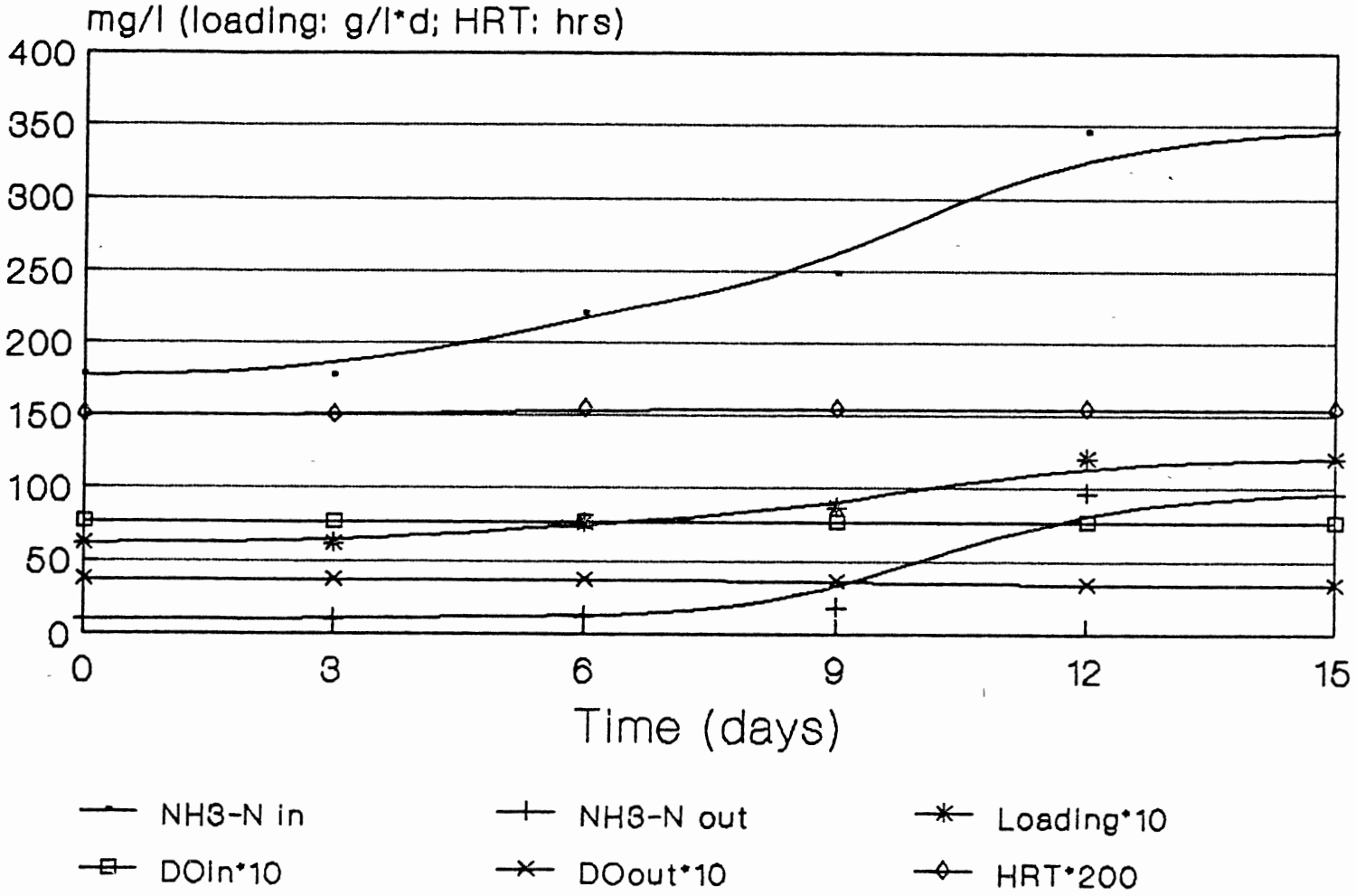

Figure 6. AEB Performance under Different Loadings (refer to Table V for schedule of mass loading rate versus time)

to 248 mg NH_3-N/L and 8.6 g NH_3-N/d*L static bed, respectively. But the ammonia-N conversion rate decreased sharply to 72 %, when the feed solution concentration was raised to 345 mg/L and the mass loading rate was 12 g/d*L. The DO in influent maintained at about 7.7 mg/L during this test, while the effluent DO decreased from 3.7 to 3.3 mg/L as the mass loading increased. This was still much higher than the 2 mg/L limit for nitrification. The pH in the reactor increased from 7.35 to 8.35 with the increase in feed solution concentration, still falling within the optimum range of 7.1 to 9.0.

4.2 Rotating Biological Contactor

4.2.1 RBC under Basic Operational Conditions

Before various tests were carried out, a steady state operation was maintained for twenty days. For this system a steady state could be established within three days. The HRT used in this experiment was about 12 hrs.In this RBC system, a steady state was considered reached when the variation of the conversion rates was smaller than 5 % of the average of the data observed in at least three consecutive days. The feed solution was prepared at 630 mg NH_3-N/L, and three pump heads of same size were used to pump the feed solution to disc stages 1, 2, and 3. This feeding regime was used in all other tests of RBC. The flow

rate to each stage was 3.312 L/d, resulting in a total flow rate of 9.936 L/d to the RBC reactor. The disc stages 4 and 5 were used as polishing units in series. Effluents from stages 1, 2, and 3 were introduced into stage 4. The polished effluent of the RBC left the reactor from stage 5 through an overflow port. Analyses were made about every three days. The averages of six samples are tabulated in Table VI.

A high ammonia-N conversion rate of 98 % was achieved under a total RBC mass loading rate of 4.3 g NH_3-N/d*m^2 disc surface. The mass loading rate of the stages 1, 2, and 3 was 7.1 g NH_3-N/d*m^2 disc surface. Nitrite-N in the effluent was detected at less than 1 mg/L. The hydraulic retention time of the RBC reactor was 12.3 hrs under a total flow rate of 9.936 L/d. The total reactor liquid volume was 5.085 L, almost 1.9 L lower than the initial volume due to the biomass growth and heating tubing installation. The datum of 5.085 L was used for calculating the hydraulic retention time.

4.2.2 Effects of Disc Rotation Speed

This test was carried out to examine the comprehensive effects of disc rotation speed on the performance of the RBC reactor. Antonie (1976) found that the optimum disc peripheral velocity for domestic wastewater treatment is 0.3 m/sec, despite how large the disc diameter is. In this

TABLE VI

RBC UNDER BASIC OPERATIONAL CONDITIONS

Items	Data
Ammonia-N in Influent (mg/L)	619
in Stages 1, 2 & 3 (mg/L)	178
in Stage 4 (mg/L)	88
in Effluent (mg/L)	12.4
Ammonia-N Conversion Rate (%)	98
RBC Mass Loading Rate (g NH_3-N/d*m^2)	4.3
Mass Loading Of Stages 1, 2 and 3	7.1
Flow Rate (L/d)	9.936
RBC Liquid Volume (L)	5.085
Hydraulic Retention Time (hrs)	12.3
Influent Nitrate-N (mg/L)	< 1
Effluent Nitrate-N (mg/L)	705
Influent Nitrite-N (mg/L)	< 1
Effluent Nitrite-N (mg/L)	< 1
Water Loss (%)	16
N Balance (%)[a]	
(1)[b]	15.9
(2)[c]	-2.6
pH in Influent	7.8
in Stages 1, 2 & 3	8.25
in Stage 4	8.2
in Effluent	8.0
DO in Stages 1, 2 & 3	4.1
in Stage 4	4.0
in Stage 5	4.1
Influent Alkalinity (mg/L as $CaCO_3$)	5222
Effluent Alkalinity (mg/L as $CaCO_3$)	744
Alkalinity Destroyed (mg) per mg NH_3-N Converted to Nitrate	7.1
Water Temperature (°C)[d]	25
Room Temperature (°C)	25
Disc Rotational Speed (revolutions/min)	10

[a] N Balance(%) = $[(N_{out} - N_{in})/N_{in}]*100\%$
[b] Water loss was not taken into consideration
[c] Water loss was taken into consideration
[d] Hot water bath was used to maintain the temperature

test, the disc peripheral velocity was increased from 0.0073 m/sec (0.8 rpm) to 0.42 m/sec (46 rpm) step by step, while the mass loading rate and flow rate were kept at about 4.75 g NH_3-N/d*m^2 and 11.06 L/d, respectively. The feed solution was 630 mg NH_3-N/L. The hot water bath was turned off in this test. The reactor was operated under steady state for four days at each disc rotation speed, and analyses for ammonia-N conversion rate, DO, and other parameters were made. The averages of three samples are shown in Table VII and Figure 7.

The ammonia-N conversion rate was 66 % at 0.0073 m/sec (0.8 rpm), and it increased with the increase in disc peripheral velocity. The conversion rate reached 88.7 % at 0.23 m/sec (25 RPM), and after this point seemed not to be sensitive to the increase in disc peripheral velocity. Only 0.8 % increase in ammonia-N conversion rate was achieved by increasing the peripheral velocity from 0.23 m/sec (25 RPM) to 0.33 m/sec (36 RPM). DO in reactor also increased with the increase in disc peripheral velocity, from about 2.1 mg/l at 0.0073 m/sec (0.8 RPM) to 5.0 at 0.33 m/sec (36 RPM). Biofilm detached from the disc surface and much water was spilled out of the reactor as the disc peripheral velocity was finally increased to 0.42 m/sec (46 RPM). The water temperature drop and water loss were observed at ranges of 3.0-6.5 °C and 7.3-11 %, respectively. Their increases seemed not strongly related to the increase in

TABLE VII

EFFECTS OF DISC ROTATION SPEED

Items	Rotation Speed (RPM)								
	0.8	3	6	9.5	15	21	25	33	36
Flow Rate(L/d)	11.0	11.0	11.0	11.0	11.0	11.0	11.1	11.1	11.1
Loading(g/m^2*d)									
Stages 1-3	7.93	7.9	7.92	7.89	7.92	7.9	7.95	7.91	7.92
RBC	4.76	4.74	4.75	4.73	4.75	4.74	4.77	4.75	4.75
HRT (hrs)	11.1	11.1	11.1	11.1	11.1	11.1	11.0	11.0	11.0
NH_3-N (mg/L)									
In Influent	621	619	620	618	620	619	620	617	618
In Effluent	211	181	172	155	108	80	70	66	65
Conversion Rate(%)	66.0	70.8	72.3	74.9	82.6	87.1	88.7	89.3	89.5
pH									
In Stages 1-3	8.46	8.46	8.5	8.45	8.3	8.3	8.25	8.25	8.2
In Stage 4	8.5	8.5	8.5	8.45	8.3	8.25	8.25	8.25	8.25
In Stage 5	8.46	8.45	8.45	8.4	8.2	8.2	8.2	8.2	8.2
DO (mg/L)									
In Stages 1-3	2.1	3.75	3.8	3.9	4.5	4.6	4.7	4.95	5.0
In Stage 4	2.3	3.7	3.7	3.7	4.36	4.5	4.6	4.8	4.9
In Stage 5	2.2	3.8	3.8	3.9	4.4	4.6	4.7	4.95	5.05
Room T (°C)	20.0	22.4	21.9	20.0	22.3	22.3	23.0	23.0	22.0
Water T (°C)	16.8	19.4	18.4	17.0	18.2	18.1	18.0	16.5	16.0
T Drop (°C)	3.2	3.0	3.5	3.0	4.1	4.2	5.0	6.5	6.0
Water Loss (%)	9.2	7.3	9.4	8.0	9.0	9.9	10.4	11.0	11.0
N Balance (%)[a]									
(1)[b]	-15	-4.4	1.1	3.9	7.2	9.1	10.9	13.0	12.5
(2)[c]	-22	-11	-7.6	-3.8	-1.7	-0.7	0.1	1.8	1.4
Effluent VSS(mg/L)	1.5	1.7	1.7	1.9	2.0	2.7	3.3	4.5	5.1

[a] N Balance (%) = $[(N_{out} - N_{in})/N_{in}] * 100\%$

[b] Water loss was not counted in balancing

[c] Water loss was counted

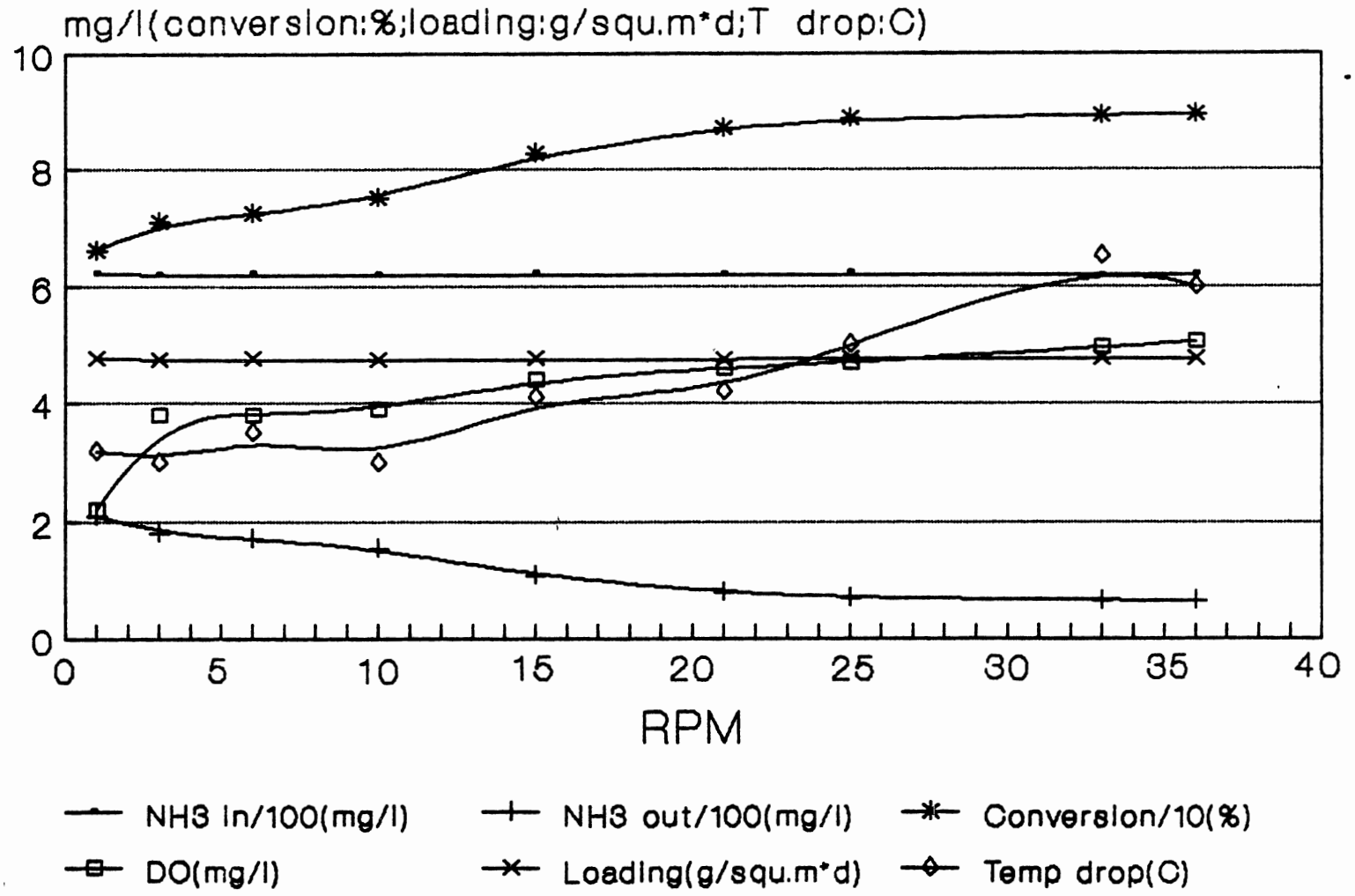

Figure 7. Effects of Disc Rotation Speed

disc rotation speed. pH in the reactor decreased from about 8.46 to 8.2 as the rotation speed increased. Nitrogen loss through the reactor was 22 % at 0.0073 m/sec (0.8 RPM), and decreased to almost zero when the peripheral velocity was increased to over 0.23 m/sec (25 RPM). As the disc peripheral velocity was increased from 0.0073 m/sec (0.8 RPM) to 0.33 m/sec (36 RPM), VSS in the RBC effluent increased from about 1.5 mg/L to 5.1 mg/L. The biofilm thickness was 1 mm in stages 1-4 and 0.6 mm in stage 5.

4.2.3 Effects of Nitrate on RBC Performance

The effects of nitrate ions on the reactor performance was examined by adding potassium nitrate to the feed solution, while other operational conditions remained constant. The nitrate-N concentration in feed solution was tested from 0 to 3600 mg/L in six steps, finally reaching a NH_3-N:NO_3^--N ratio of 1:5.7. No analyses were made at one interim addition of nitrate-N (2700 mg/l). The reactor was operated under ateady state for at least four days at each nitrate-N concentration. Less than three days were needed to reach a steady state. The feed solution containing 630 mg NH_3-N/l and nitrate ions was pumped into the reactor at a flow rate of 10.4 L/d, giving a total RBC hydraulic retention time of 11.8 hrs. The RBC ammonia-N mass loading was maintained at about 4.4 g/m^2*d. The disc rotation speed

was kept at 10 RPM. The hot water bath was in use during this test. The operational conditions and the measured data are shown in Table VIII and Figure 8 in which the averages of three samples are tabulated.

TABLE VIII

EFFECTS OF NITRATE ON RBC PERFORMANCE

Items	Time (days)					
	1-4	5-8	9-12	13-16	17-20	21-24
Influent Ammonia-N (mg/L)	611	616	618	614	615	615
Effluent Ammonia-N (mg/L)	38.8	41.0	42.0	46.5	57.5	66.8
Conversion Rate (%)	93.6	93.3	93.2	92.4	90.7	89.1
Influent Nitrate-N (mg/L)	0	108	308	895	1810	3593
Effluent Nitrate-N (mg/L)	621	761	1007	1642	2540	4801
Influent Nitrite-N (mg/L)	0	0	0	0	0	0
Effluent Nitrite-N (mg/L)	0	0	0	0	0	0
Water Loss (%)	23	23	23	23	22.5	22.5
Total N_{in} (mg/L)	611	724	926	1509	2425	4208
Total N_{out} (mg/L)	660	802	1049	1689	2598	4868
N Balance (%)[a]						
(1)[b]	8.0	10.8	13.3	11.9	7.1	15.7
(2)[c]	-17	-15	-13	-14	-17	-10
Flow Rate (L/d)	10.4	10.4	10.4	10.4	10.4	10.4
HRT (hrs)	11.8	11.8	11.8	11.8	11.8	11.8
RBC Ammonia-N Loading ($g/d*m^2$)	4.4	4.44	4.45	4.42	4.43	4.43
Influent pH	7.8	7.8	7.85	7.85	7.9	7.9
Effluent pH	7.85	7.85	7.9	7.9	7.95	7.7
DO average (mg/L)	3.8	3.8	3.85	3.8	3.9	3.85
Room T (°C)	25	24.5	23	24	24	25
Water T (°C)	24.5	23.5	23	24.5	23	24.5
Disc Rotation Speed (RPM)	10	10	10	10	10	10

[a] N Balance(%) = $[(N_{out} - N_{in})/N_{in}] * 100\%$
[b] Water loss was not counted in calculation
[c] Water loss was counted in calculation

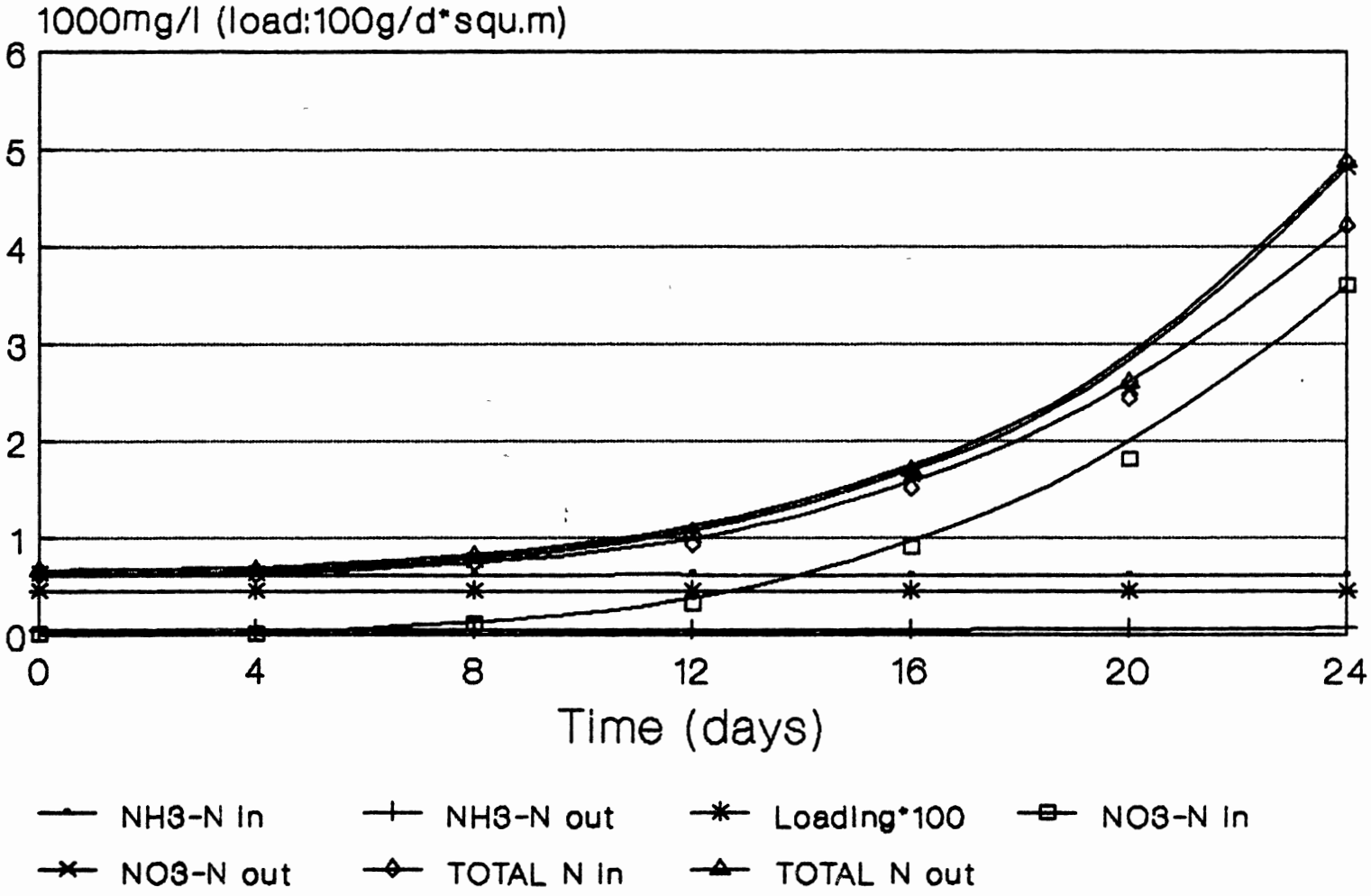

Figure 8. Effects of Nitrate on RBC Performance

Before potassium nitrate was added to the feed solution, the effluent ammonia-N was 38 mg/L, giving a conversion rate of 94 %. With the addition of nitrate ions to feed solution, the conversion rate declined only slightly. When the nitrate addition finally reached 3600 mg NO_3^--N/L, the ammonia-N conversion rate decreased to 89 %, showing no significant inhibition of nitrification reaction by nitrate ions up to this strength tested. No nitrite ions in the RBC effluent were detected throughout this test. Nitrite-N of 8 mg/L was found in the effluent when nitrate was first introduced into the AEB feed solution.

4.2.4 RBC Performance under Different Loadings

This test was carried out to examine the RBC performance under three different mass loadings. Feed solution concentration was kept at 630 mg NH_3-N/L, but flow rate was changed to impose different mass loadings to the reactor. The changed flow rates were 9.9 L/d, 11.2 L/d and 13.2 L/d, giving hydraulic retention times of 12.3 hrs, 10.9 hrs and 9.2 hrs, respectively. The reactor was operated for at least one week at each flow rate. Disc rotation speed was kept at 10 RPM. Hot water bath was used in this test to keep the water temperature at about 25 °C. The operational conditions and measured results are presented in Table IX and Figure 9. They are all averages

of four samples.

TABLE IX

RBC PERFORMANCE UNDER DIFFERENT LOADINGS

Items	Loadings (g NH_3-N/d*m^2)		
	4.3	4.8	5.6
Flow Rate (L/d)	9.9	11.2	13.2
Hydraulic Retention (hrs)	12.3	10.9	9.2
Disc Rotation Speed (RPM)	10	10	10
Influent Ammonia-N (mg/L)	619	610	613
Effluent Ammonia-N (mg/L)	12	54	92
Conversion Rate (%)	98	91	85
Influent pH	7.8	7.8	7.8
Effluent pH	8.0	8.15	8.35
DO average	4.1	4.2	4.0
Room Temperature (°C)	25	25	25.5
Water Temperature (°C)	25	24	25.5
Water Loss (%)	16	16	16

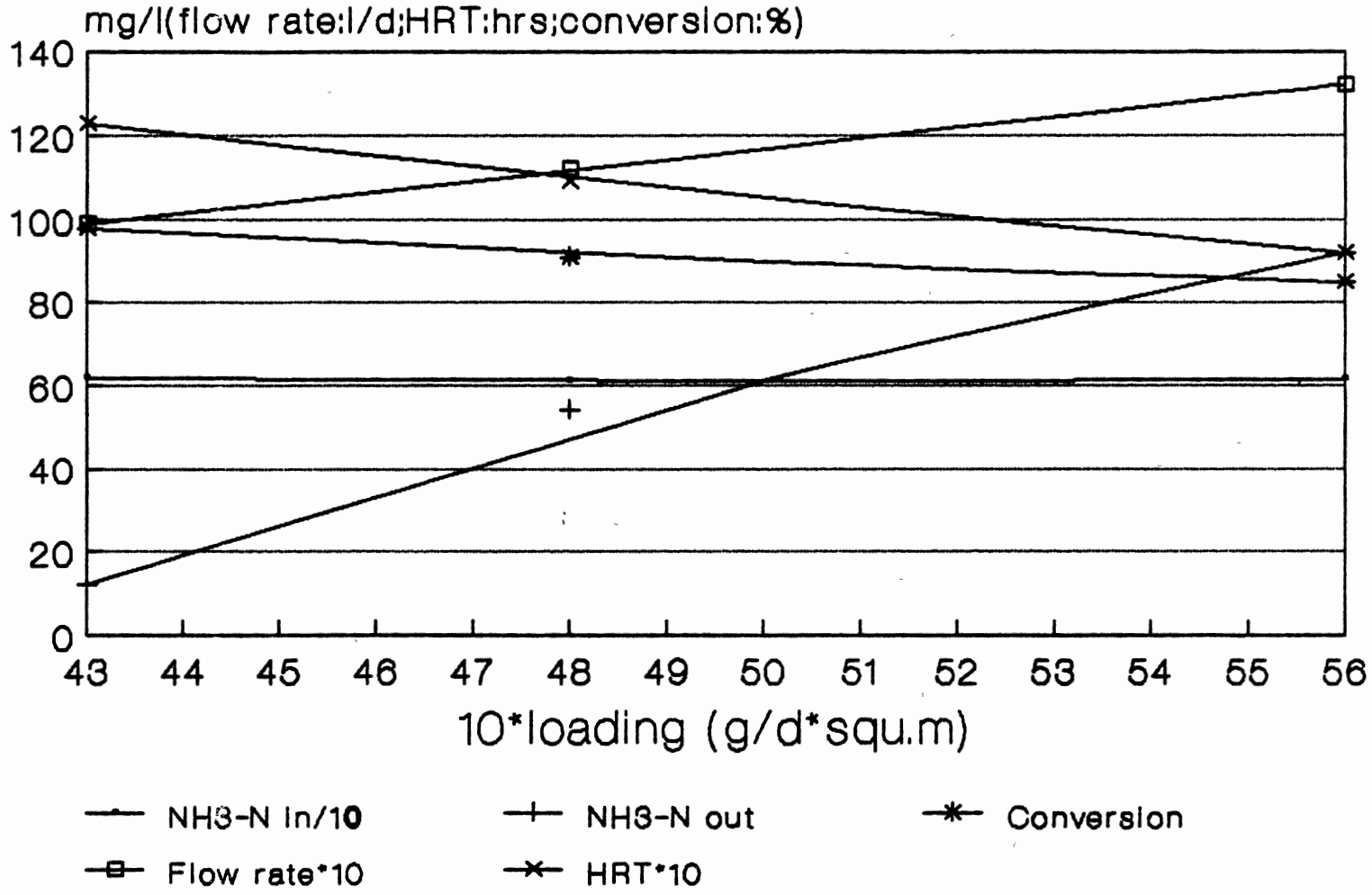

Figure 9. RBC Performance under Different Loadings

With the increase in flow rate the ammonia-N conversion rate decreased. At the flow rate of 9.9 L/d, a high ammonia-N conversion rate of 98 % was achieved with an ammonia-N mass loading rate of 4.3 g/d*m^2. As the flow rate increased to 11.2 L/d, the ammonia-N loading rose to 4.8 g/d*m^2, and the conversion rate decreased to 91 %. The flow rate of 13.2 L/d imposed an ammonia-N mass loading of 5.6 g/d*m^2 to the reactor and caused the ammonia-N nitrification to drop further to 85 %.

4.3 Miscellaneous Observations

During the test of AEB performance under different mass loadings, the sodium bicarbonate concentration should have been 2.72 g/L for a 230 mg NH_3-N/L feed solution, which was determined from stoichiometry. But by mistake a feed solution containing only 2.19 g/L of sodium bicarbonate was used for two days. The shortage in bicarbonate caused the effluent pH to drop from 7.8 to 6.9, and the ammonia-N nitrification rate decreased from 94 % to 77 %. After the right feed solution was provided, the system resumed the original state, demonstrating the critical importance of buffering capacity to nitrification stability.

After the RBC reactor had been operated for 150 days, fly larvae were detected consuming the nitrifying biomass above and along the water surface, but they could not

survive in the area submerged under the water. They existed throughout the rest of the RBC operation, but no appreciable hindrance of the nitrification process by the fly larvae was found.

The RBC was once operated at a feed solution flow rate of 17.9 L/d with the mass loading rate being 5.43 g NH_3-N/d*m^2. The nitrification rate was 65.4 % at a disc rotation speed of 8 RPM (peripheral velocity 0.073 m/sec). The above operational conditions were later changed to disc rotation speed 10 RPM (peripheral velocity 0.092 m/sec), flow rate 12.8 L/d and mass loading of 6.26 g NH_3-N/d*m^2, all other operational conditions remaining the same. As a result, average DO in reactor increased from 4.1 mg/L to 4.5 mg/L, and the nitrification rate was raised to 77 %, even though the loading rate had increased. Obviously the increase in disc rotation speed made the difference. This result coincided with those obtained in the subsequent test for effects of disc rotation speed on RBC performance.

After all tests were completed, the biomass attached onto the RBC disc surface was measured. In stages 1, 2, and 3, the biofilm was 1 mm thick, the biomass (VS) in each stage was 24.23 g, and the biomass concentrations were 84 g VS/m^2 and 0.084 g VS/cm^3 biofilm. In stage 4, the biofilm was 1 mm thick, biomass was 21.64 g, and biomass concentrations were 75 g VS/m^2 and 0.075 g VS/cm^3 biofilm, while in stage 5, the biofilm thickness was 0.6 mm, the

biomass was 19.33 g, and the biomass concentrations were 67 g/m^2 and 0.11 g/cm^3 biofilm. The biofilm compositions measured as percentage of VS were 60 % in stages 1-3, 63 % in stage 4, and 67 % in stage 5. The total biomass attached on the discs of this reactor was 113.66 g.

CHAPTER V

DISCUSSION AND CONCLUSIONS

5.1 Effects of Nitrate on Nitrification

Theoretically, there may be a certain amount of product inhibition of nitrate ions to nitrification, but to what extent is unknown. The effects of nitrate ions on the nitrification of ammonia were tested in both AEB and RBC systems. In AEB, the concentration of nitrate-N in influent was increased stepwise from 0 to 2100 mg/l, and the ammonia conversion rate was slightly decreased from 94.4 % to 92.5 %. Nitrite ions of 8 mg NO_2^--N/l were found in the effluent in the first day when nitrate-N was added to the feed solution at a concentration of 33 mg/l, and the specific mass loading was 23.94 mg NO_3^--N/g VS*d. After that there was no nitrite detected in the effluent in spite of the increasing nitrate-N concentration in the feed solution. These results indicated that nitrifying bacteria can acclimate to a circumstance where nitrate ions exist. With a 95 % confidence level, analysis of variance indicated no difference between 94.4 % and 92.5 %. Nitrate ions up to 2100 mg NO_3^--N/l had no significant effect on the oxidation of ammonia to nitrate in the AEB system.

In the RBC system, the ammonia conversion rate was reduced from 93.6 % to 89.1 % when the concentration of nitrate ions in the feed was increased from 0 to 3600 mg NO_3^--N/l. There was no nitrite produced in the effluent throughout the test. The much longer hydraulic retention time (11.8 hrs) than that (0.77 hrs) in AEB system may explain why no nitrite was detected when nitrate ions were first added to the influent. Analysis of variance was carried out with a 95 % confidence level, and the result showed no difference between 93.6 % and 89.1 %. All these results proved that there are no significant effects by nitrate ions on the nitrification of ammonia all the way to nitrate, up to a nitrate concentration of 3600 mg NO_3^--N/l, in the RBC system.

Contrary to the above results, Boon & Laudelout (1962) reported that in a flask experiment, nitrate-N non-competitively inhibited oxidation of 224 mg/l nitrite-N, with 50 % inhibition at 2,800 mg/l nitrate-N. Nitrobacter winogradskyi was used in their experiment, which tested only the second conversion step in nitrification. Cell suspension, nitrite and nitrate ions were added to test flasks, with no ammonia present. Possible explanations for the difference between these experiments are: (a) Nitrobacter agilis instead of Nitrobacter winogradskyi is the species most commonly encountered in wastewater treatment systems (Barnes & Bliss, 1983). They most

probably have different abilities of resistance against nitrate inhibition; (b) Gee, Pfeffer & Suidan, (1990) found that the oxidation ability of Nitrobacter was largely reduced in the absence of ammonia and Nitrosomonas. Nitrobacter with lowered substrate oxidation ability may be more susceptible to the nitrate inhibition. More detailed efforts are needed to thoroughly resolve these problems.

5.2 Upper Mass Loading in AEB

A minimum of 2 mg/l of dissolved oxygen has been widely suggested as requirement for nitrification (EPA, 1975). In this test, DO in the effluent was kept between 3.33 and 3.7 mg/l, therefore DO was not the limiting factor for nitrification. By examining Table V and Figure 6, it can be suggested that the upper mass loading for the AEB system in these experiments is 7.5 g NH_3-N/l bed*d while maintaining an acceptable conversion rate and effluent quality.

5.3 Optimization of RBC Feeding Regime

The prevailing feeding regime for RBC systems is that the total wastewater flow is introduced into the first stage and flows through the RBC from stage to stage in sequence. With this feeding regime, Collins et al. (1988) achieved a ammonia conversion rate of 97 % under a loading rate of 3.0 g NH_3-N/m^2*d in synthetic semiconductor

wastewater. The disc rotation speed was 3 rpm, corresponding to a peripheral velocity of 0.094 m/sec. Lue-Hing et al. (1976) treated sludge supernatant with 99.8 % ammonia removed under a mass loading rate of 4.0 g NH_3-N/m^2*d, which was the maximum mass loading rate reported in the literature. In their experiments, the disc rotation speed was 13 rpm and the peripheral velocity was not reported (probably higher than 0.2 m/sec, estimated from tank volume and disc surface area). In both cases, over 96 % of ammonia conversion took place in the first stage, implying that changes can be made in the feeding pattern to better use the disc surface area.

In this research, the feeding regime was changed so that the influent was introduced into the first three stages simultaneously, while the fourth and fifth stages were used in series as polishing units. Results presented in Table VI show that 98 % ammonia conversion was achieved under a mass loading of 4.3 g NH_3-N/m^2*d. Comparisons among results are shown in Table X. It can be easily seen from Table X that the new feeding regime made better use of the disc surface. With comparable conversion rates, the new feeding regime increased the mass loading rates by 47.8 % and 7.5 % from those of Collins et al. and Lue-Hing et al., respectively.

TABLE X

COMPARISON OF DIFFERENT FEEDING REGIMES

Items	Collins et al.(1988)	*Lue-Hing et al.(1976)	This Experiment
Influent NH_3-N (mg/l)	827	714	619
Conversion Rate (%)	97	99.8	98
Loading (g NH_3-N/m^2*d)	3.0	4.0	4.3
Disc Rotation (RPM)	3	13	10
Peripheral Velocity(m/s)	0.094	0.2(?)	0.092
HRT (Hrs)	40.8	24	12.3
Water Temperature (°C)	18.8-21.8	19-23	23.5-25

*103 % sludge recycle was used. Results from Lue-Hing et al. indicated that without the sludge recycle the conversion rate would be much lower.

5.4 Effects of Disc Rotation Speed

Disc rotation speed affects wastewater treatment principally in three ways: it provides contact between the biomass and the water; it aerates the wastewater; and it provides energy to thoroughly mix the wastewater in each stage. The detailed effects were tested by increasing the disc rotation speed from 0.8 rpm to 36 rpm in nine steps. The RBC reactor failed due to biomass loss and water spilling out of the reactor when the disc rotation speed increased to 46 rpm. At a disc rotation speed of 0.8 rpm, the conversion rate of ammonia was 66% and increased with rotation speed all the way to 89.5 % when the disc rotation speed reached 36 rpm.

From Figure 7 it can be seen that the conversion rate

quickly increased with the increase in the disc rotation speed until the rotation speed reached 25 rpm (disc peripheral velocity 0.23 m/sec), averaging an increase of 0.94 % in conversion rate per 1 rpm in the disc rotation speed. After that, the increase in the conversion rate slowed down. Between 25 rpm (0.23 m/sec) and 33 rpm (0.3 m/sec), the conversion rate rose at a rate of 0.075 % per 1 rpm. Between 33 rpm (0.3 m/sec) and 36 (0.33 m/sec), every 1 rpm increase in the rotation speed caused only 0.067 % increase in the conversion rate. Based on these results, it appears the optimum peripheral velocity of disc for nitrification in industrial nitrogenous wastewater falls within the range of 0.23 m/sec and 0.3 m/sec. Further increase in the rotation speed will lead smaller incremental conversion rate increases. This result roughly coincides with that by Antonie (1976). Antonie believed that there is an upper rotation velocity above which there is no further benefit, and based on experiments he suggested that the optimum peripheral velocity of disc for BOD removal and nitrification in domestic wastewater is about 0.3 m/sec.

DO in stages was increased by increased disc rotation speed. The average DO was 2.2 mg/l at the rotation speed of 0.8 rpm, and it increased to 4.98 mg/l when the rotation speed reached 36 rpm. There is no doubt that the increased DO contributed to increasing the conversion rate. From

Figure 7 it can be seen that after the DO reached 4.65 mg/l, the increase in the ammonia conversion rate was very limited, although the DO continued to increase with the increase in the disc rotation speed. It has been found that higher DO concentration of 3-4 mg/l can significantly enhance nitrification efficiency (Benefield & Randall, 1980; Bliss et al., 1981; Ministry of Technology of UK, 1965), but relatively little further improvement can be achieved at 5-6 mg/l of DO (Bliss et al., 1981). The enhancement of water mixing and contact between water and biomass by rotation speed increase also helped increase the nitrification efficiency, although the enhancement is not measurable in this experiment. The increase of conversion efficiency in this experiment cannot be attributed only to the increased DO.

5.5 Nitrogen Loss through RBC Reactor

Nitrogen loss through the RBC reactor was observed in this experiment. The nitrogen loss accounted for 2.6 % of the influent nitrogen under the basic operation conditions. When the rotation speed was 10 rpm, the average DO was 4.07 mg/l and the average pH was 8.15. In the set of experiments for testing disc rotation speed effects, the highest nitrogen loss was 22 %, which occurred when the disc rotation speed was 0.8 rpm, the average DO was 2.2 mg/l and the average pH was 8.47. Barnes & Bliss (1983) reported

that there is usually a net loss of nitrogen through RBC systems of the order of 20 %. Some explanations can be made for this phenomenon.

NH_3 volatilization by aeration may cause some nitrogen loss. Air stripping of ammonia has been practiced at a high pH (usually 10.5 to 11.5) (Water Pollution Control Federation, 1983). Votes et al. (1975) reported that no significant ammonia volatilization occurs below pH 8.0 in an activated sludge system aerated by air. Table XI shows that the N balances were -22 % and 0.1 % when the disc rotation speed was 0.8 rpm and 25 rpm, respectively. The data shown in Table XI were based on those from Table VII, and the equations 13 to 16 were used to calculate the ammonia concentration. From the results presented in Table XII, it can be seen that the N balance (%) changed from -22 % to 0.1 % (22.1 % difference)and the percent of NH_3-N calculated decreased from 8.7 % to 5.7 % (3 % difference), as the disc rotation speed increased from 0.8 rpm to 25 rpm. Also aeration was enhanced, and the pH decreased from 8.47 to 8.23. Ammonia volatilization was not significant in causing the nitrogen loss in this case, even with an assumption that all ammonia nitrogen in the RBC was lost by disc rotation aeration, which is much weaker than aeration by compressed air. Some other factor evidently has more weight in the nitrogen loss process.

TABLE XI

EFFECTS OF AMMONIA VOLATILIZATION

Items	Rotation Speed (RPM)	
	0.8	25
Influent N (NH_3-N+NH_4^+-N)(mg/l)	621	620
Average pH	8.47	8.23
Water T (°C)	16.8	18
N balance (%)	-22	0.1
NH_3-N In Stages (mg/l)[a]	54.4	35.4
Percent Of NH_3-N (%)[b]	8.7	5.7

[a] calculated assuming the concentration of NH_3-N and NH_4^+-N in stages the same as that in influent. In fact, it is much lower than that in influent

[b] counted the NH_3-N in stages as percent of influent N (NH_3-N + NH_4^+)

Some researchers believe that the nitrogen loss through RBC systems is due to some denitrification at the media/biomass interface (Ellis & Banaga, 1976; Water Pollution Control Federation, 1983). The existence of an oxygen gradient within the biomass results in low dissolved oxygen concentration in deep biomass, while the DO in bulk liquid remains high enough to suppress the denitrification. Votes et al. (1975) reported that denitritification (reduction of nitrite to gaseous nitrogen) probably takes place under both anaerobic and aerobic conditions. The redox potentials ($E_h°$) of O_2/H_2O, NO_3^-/N_2, and NO_2^-/N_2 amount, respectively, to 808, 408 and 966 mV, implying that nitrite might compete with oxygen as an alternative

electron acceptor for microbial respiration processes. Results of this experiment proved the possibilities of both denitrification and denitritification in the RBC process. As presented in Table VII, the N balance changed from -22 % to 1.4 % when the DO in the bulk liquid increased from 2.2 mg/l to 4.98 mg/l due to the increased disc rotation speed. According to this theory, when the DO was low, denitrification and denitritification took place near the disc surface and nitrogen was lost as gaseous nitrogen. With the increase in DO in the bulk liquid, the DO within the biofilm also increased and both denitrification and denitritification were suppressed, leading to little nitrogen loss through gaseous nitrogen production. It is unknown from the results which reaction, denitrification or denitritification, contributed more to the nitrogen loss. The nitrogen loss through by denitrification and denitritification suggests the possibility that the ammonia nitrogen removal can be achieved in a single reactor.

5.6 Water Loss through RBC Reactor

Some water will be lost to air by evaporation which is enhanced by disc rotation. Water loss in this experiment ranged from 7.3 % to 23 %. The water loss seemed higher when air temperature and disc rotation speed were higher. No data available in literature can be used to compare these results.

5.7 Attached VS on RBC Disc Surface

The attached VS on the RBC disc surface basically fell in the range of 7.5-48 g/m^2 (Collins et al, 1988). In the experiment by Collins et al. (1988), the traditional feeding pattern was used and the mass loading rate was 3.02 g NH_3-N/m^2*d. They found that the biofilm solids composition was 68.5 % volatile, and the average attached VS decreased by 89.5 % from stage 1 (22.8 g/m^2) to stage 4 (2.4 g/m^2), indicating ineffective use of the disc surface in the latter stages. In this experiment, the new feeding pattern was used and the mass loading rate was 4.3 g/m^2*d. The biofilm composition ranged from 60 to 67 % as percentage of VS, similar to that in Collins et al. The attached VS was 84, 75 and 67 g/m^2 in stages 1-3, 4 and 5, respectively. From stage 1-3 to stage 5 the VS decreased by only 20 %, indicating much better use of the disc surface. The much higher VS concentration contributed to increasing the mass loading limit.

5.8 Conclusions

With a synthetic industrial nitrogenous wastewater (containing little organic carbon), various tests were carried out in both RBC and AEB systems. Based on the results from these tests, the following conclusions can be drawn:

1. Pre-existing influent nitrate ions had no

significant effects on the nitrification of ammonia, up to the concentrations of 2100 and 3600 mg NO_3^--N/l, in the AEB and RBC systems, respectively.

2. When DO was not the limiting reaction factor in the AEB reactor, the upper mass loading rate was 7.5 g NH_3-N/l bed*d with a static bed volume of 90 ml.

3. In an RBC system devoted exclusively to nitrogen oxidation, introducing feed into the first several stages simultaneously can make better use of the disc surface area by creating more even attached biomass distribution through the RBC stages and sustaining high biofilm VS concentrations (ranging from 67 to 84 g/m^2 in this experiment).

4. Increasing the RBC disc rotation speed can achieve higher nitrification efficiency until a disc peripheral velocity of 0.3 m/sec is reached. The optimal disc peripheral velocity is between 0.23 and 0.3 m/sec.

5. Nitrogen loss through RBC reactors can be caused by both denitrification and denitritification taking place within the biofilm, and both reactions can be suppressed by high DO in bulk liquid.

6. Water loss caused by evaporation can be significant in RBC systems (up to 23 % in these experiments).

CHAPTER VI

FURTHER RESEARCH NEEDS

6.1 Nitrogen Removal in A Single Reactor

The results from this experiment indicated that 22 % nitrogen removal could be achieved by the denitrification and denitritification taking place in the RBC and AEB reactors. Further increase in the nitrogen removal rate can be expected, but more research is needed to investigate the operational conditions which facilitate denitrification and denitritification while nitrification is completed. For example, DO, necessary reducing agent, and carbon source additions may deserve further attention.

6.2 Nitrate Effect on Specific Species of Nitrifier

As discussed in the previous chapter, the results from this experiment and Boon & Laudelout (1962) showed that the effects of nitrate ions on different species of nitrifier may be largely different. Further attention can be focused on the effect of nitrate ions on individual nitrifying bacterial species, and proper operational conditions could

be developed to promote those species which have stronger resistance to the nitrate inhibition.

6.3 Nitrification in Wastewater with High Organic Carbon Concentration

This research showed that complete nitrification can be achieved in concentrated nitrogenous wastewater containing no source of organic carbon. Some other research (Lue-Hing et al, 1976; Antonie, 1976; Barnes & Bliss, 1983) indicated complete nitrification with wastewater containing high organic carbon and low ammonia or low organic carbon and high ammonia concentrations (extra alkalinity is added in influent) in RBC systems. These studies also revealed suppression of nitrifier growth by heterotrophs when BOD is high. Barnes & Bliss (1983) believed that the heavy growth of heterotrophs on the disc surface can physically cover the nitrifiers and cause local depletion of dissolved oxygen, thereby hindering the nitrification reaction. When BOD is reduced to 8-10 mg/l, complete nitrification could be achieved in low ammonia wastewater (no alkalinity addition is needed). In the treatment of wastewater containing organic carbon and ammonia both at high strength in a single reactor, alkalinity addition may be needed for completing the nitrification after the organic carbon removal has been finished. Further work on this kind of wastewater treatment is needed.

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