In-situ Determination of Nitrification Kinetics and Performance Characteristics for a Bubble-washed Bead Filter

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ABSTRACT

Intensive recirculating aquaculture systems rely almost exclusively on some form of fixed-film biofilter for nitrification. Currently there is no standardized way to determine and report biofilter performance to facilitate user selection among the numerous options. This type of information is critical for the end user, and also important for both the design engineer and the manufacturer. In an attempt to address this issue, a simple procedure for estimating nitrification reaction rate kinetics is described and applied to a bubble-washed bead filter. Reaction rate kinetics were determined through a series of batch reaction rate experiments with a commercially available 0.06-m^3 (2.0-ft^3) bubble-washed bead filter. Empirical mathematical models for the nitrification of ammonia-nitrogen to nitrate-nitrogen were developed. The kinetics of nitrification were found to fit a simple first-order reaction model, when the ammonia-nitrogen concentration was less than 1 mg NH_4-N/L, and a zero-order reaction when the ammonia-nitrogen concentration was

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greater. The exact breakpoint between first- and zero-order reaction kinetics was found to be a function of the flow rate. In addition, the first-order kinetic reaction rate constants were also a function of the flow rate, reflecting the influence of high nutrient gradients and associated higher nutrient gradient across the biofilm. No effect of flow rate was found for the zero-order reaction rate constants. Kinetic reaction rate parameters, maximum reaction rates, and half-saturation constants were determined for the Monod kinetics model as functions of hydraulic loading rate. Based on these results, an evaluation tool was proposed to help characterize bead filter performance based on reaction rate kinetics. A series of performance characteristic curves were developed to show maximum removal rates as a function of ammonia-nitrogen concentration and flow rates through the bubble-washed bead filter.

INTRODUCTION

All recirculation systems require basic unit operations to remove particulate solid wastes, biological filters to oxidize toxic ammonia and nitrite-nitrogen to nitrate-nitrogen, and aeration or oxygenation of the water to remove carbon dioxide and increase oxygen concentrations (Timmons *et al.* 2002). Additional unit processes can be added depending on the scale of production and the unique water-quality parameters required for each species, such as pH control, foam fractionation, ozone, and disinfection systems (Timmons *et al.* 2002). Over the past few years, numerous solutions have been proposed and developed to handle each one of these unit operations and processes. At the same time, entire recirculation systems and individual components have become available commercially for almost any scale production facility.

This segment of the aquaculture industry relies almost exclusively on some form of fixed film biofilter for nitrification, such as those found in trickling towers, fluidized-bed, floating bead, and rotating biological contactors. The advantages of these forms of biofilter include resistance to short-term toxic loads, ability to perform at low influent concentrations, and high volumetric biomass concentrations (Riefler *et al.* 1998). In addition, the high cell-residence time of a fixed-film biofilter is needed for the low growth rates of both ammonia oxidizing bacteria and nitrite oxidizing bacteria. In November 2004, the Oceanic Institute sponsored a workshop entitled: Design and Selection of Biological Filters for Freshwater and

Marine Applications. During the four-day workshop, numerous papers were presented, reviewing the many types and applications of biological filters in aquaculture. One of the problems discussed was the lack of a standardized way to determine and report biofilter performance to facilitate user selection among the numerous types of biofilters. One entire afternoon was spent discussing standardized evaluation rating of biofilters from the design approach, and the manufacturer's and user's perspectives in relationship to their capital and operational costs. Malone (2004) recommended using a set of standardized conditions for rating biofilter performance consisting of: chemical feed of ammonia-nitrogen, excess dissolved oxygen concentration, alkalinity greater than 150 mg/L $CaCO_3$, pH of approximately 7.5, and temperature of 20°C. In addition, Malone recommended that specialized conditions for low-temperature performance evaluation could be conducted at 10°C. Malone also suggested that biofilter performance be evaluated at several levels of ammonia-nitrogen concentration reflecting his categorization of aquaculture systems as shown in Table 1.

In the past, the selection of the most applicable biofilters for any given species, production level or economic consideration has for the most part been by "rules of thumb" and operating experience based on existing systems. Today, with the commercial availability of standardized families of biofilters, there exists the potential to fully characterize their operating parameters and develop sets of characteristic curves, reflecting ammonia-nitrogen removal rates as a function of operating parameters such as hydraulic loading rates and ammonia-nitrogen concentrations. The overall objective of this study was to develop a simple biofilter evaluation process that could be used to characterize the nitrification removal rate as a function of several simple operating parameters for a bubble-washed bead filter, most importantly, hydraulic loading rate of the biofilter and the operating level of ammonia-nitrogen.

Table 1. Aquaculture systems classification and corresponding ammonia-nitrogen level.

Classification	System	TAN (mg/L)
Ultra Oligatrophic	Larval rearing system	< 0.1
Oligatrophic	Broodstock holding system	< 0.3
Mesotrophic	Fingerling production system	< 0.5
Eutrophic	Growout systems	< 1.0
Hypertrophic	Hardy species growout	< 5.0

BACKGROUND

The concept of using a floating plastic media as biofilter media dates back to the mid-1970s, when they were first used at the Dworshak National Fish Hatchery (Cooley 1979) for the rearing of food and game fish. Although successful, the air-washed bead filter design did not find wide acceptance. In the late 1980s, a hydraulically washed bead filter, which combined both solids capture and biofiltration, was developed at Louisiana State University (Wimberly 1990). Later development of the mechanically washed bead filter (Malone 1992, 1993, 1995) overcame many of the operational difficulties of earlier designs and it proved to be compact and simple to operate (Malone *et al.* 1998, 2000). Malone *et al.* (1993) developed the bubble-washed bead filter initially for the outdoor ornamental or garden-pond market. Since then, the bubble-washed bead filter has found wide application for small aquaculture systems, combining clarification and biofiltration in a single unit. Most recently, an air-driven recirculating system employing a bubble-washed bead filter has been designed and tested by DeLosReyes *et al.* (1997), to minimize the complexity and energy requirements of commercial recirculation systems.

Bead filters are classified as expandable granular biofilters (EGB), which include upflow and downflow sand filters. EGB biofilters offer the competitive advantage of using smaller media with corresponding higher specific surface areas per unit volume when compared to other treatment devices such as trickling filters and RBCs. The higher specific surface area translates into smaller biofilter size. The application of sand filters in aquaculture is limited by the inherent constraint on ammonia conversion due to oxygen limitations in the bed, the high pressure required for fluidization, and the excessively high water use for back flushing. These shortcomings were overcome with low-density plastic beads, which float. Filtration of suspended solids is accomplished by settling, straining, and interception within the granular bead matrix (Malone *et al.* 1993). The plastic beads themselves act as a fixed-bed bioreactor for the growth of nitrifying bacteria on the surface and in the pore spaces between the beads. As the solids and bacterial biomass accumulate, the head loss across the filter bed increases and the hydraulic conductivity decreases. The transfer of oxygen and nutrients to the bacteria is reduced, reducing the nitrification capacity of the filter. During the backwashing cycle, the beads are agitated and homogenized, dislodging trapped solids and shearing off excess biofloc from the beads.

When the floating-bead filter is operated under low solids loading, or frequent backwashing, it should behave like a classical fixed-bed biofilm reactor. Under these conditions, the exchange of soluble substrate between the recirculated water and the attached biofilm is relatively unimpeded and the nitrification process can be described by a simple Monod expression. Malone and Beecher (2000) summarized the performance of floating-bead filters based on the three application categories: broodstock, fingerling, and growout, and listed criteria for the sizing of filters based on feed application rates with the primary method for sizing based on volumetric organic loading rates. Table 2 lists typical values for several performance parameters based on operational filters (Wimberly 1990, Sastry *et al.* 1999). Table 3 presents interim guidelines for the design of systems using floating bead biofilters for both clarification and biofiltration filters (Malone and Beecher 2000).

Table 2. Some typical values for performance parameters for floating-bead biofilters (Malone et al. 1998)

Performance parameter	Broodstock	Fingerling	Growout
Feed loading (kg feed /m^3 media day)	<4	<8	<16
Design TAN (mg/L)	0.3	0.5	1.0
VTR* (g TAN/m^3 media)	35 - 105	70 - 180	140 - 350
O_2 consumption (g O_2/m^3 media day)	0.7 - 2.5	1.4 - 2.5	2.5 - 3.0
Temperature (°C)	20 - 30	20 - 30	20 - 30
pH	6.5 - 8.0	6.8 - 7.0	7.0 - 8.0
Alkalinity (mg/L $CaCO_3$)	>50	>80	>100

**VTR = volumetric TAN removal rate*

Table 3. Interim guidelines for the design of systems utilizing floating bead

Design parameter	Broodstock	Fingerling	Growout
Bead volume (m^3 media /kg of feed day)	0.250	0.125	0.062
Circulation rate (Lpm /kg feed day)	208	83	50
Fish density (kg/m^3)	15	10	60
TAN loading (g/m^3 media day)	84	168	339
Hydraulic loading (Lpm /m^3 media)	832	664	806
HRT (days)	11	16	25
Tank turnover rate (min)	32	40	33

These guidelines were developed by examining a wide range of operating systems of various sizes, species selection, and operation management protocols. In an attempt to standardize the characterization of biofilter performance and in particular, the bubble-washed floating bead filter, a series of batch performance evaluation tests were conducted to characterize the nitrification reaction rates as a function of ammonia-nitrogen concentration and flow rate through the filter. Several nitrification models including simple zero-order and first-order kinetic reaction rates and Monod kinetics were examined to determine how well they fit the experimental data and the corresponding kinetic reaction rate constants were estimated.

MATERIALS AND METHODS

Two commercially available 57-L (2.0-ft^3) bubble-washed bead filters (Model BBF-2P, Aquaculture Systems Technologies, LLC, New Orleans, LA, USA) were employed (Figure 1) for the evaluation trials. The two biofilters were part of a research program, characterizing over time the physical and chemical properties of the solids, dissolved nutrient, and organic substances found in four separate recirculation system designs (Ebeling *et al.* 1998a, Ebeling *et al.* 1998b, Singh *et al.* 1999). Each of the four systems consisted of a fiberglass 2.0-m^3 circular culture tank combined with either a settling basin or a rotating microscreen drum filter with a 60-μm screen and either a trickling tower or a bubble-washed bead filter, forming a 2x2 factorial experimental design. Total volume of each system was estimated at 2.13 m^3. Each system had been initially stocked with 320 hybrid striped bass (average weight 100 g) which were fed a commercial diet at 1.5 to 2 percent of body weight once per day. At the time of the kinetic reaction rate experiments, the filters had been in continuous operation for over 24 months and had a well-established biofilm.

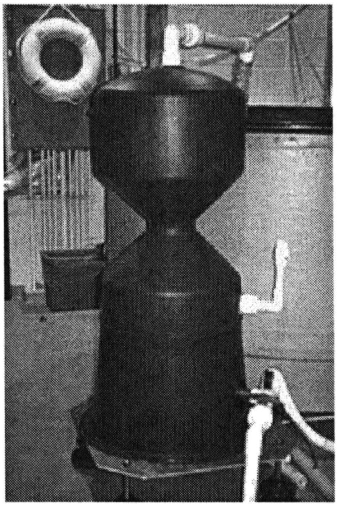

Figure 1. 57 L (2 ft^3) bubble-washed bead filters (Model BBF-2P, Aquaculture Systems Technologies, LLC, New Orleans, LA, USA)

The bubble-washed bead filters have an "hourglass" shaped internal geometry with a constricted washing throat. During continuous filtration, water from the production tank enters from the bottom through a slotted inlet pipe, flows upward through the bed of floating polyethylene beads, and exits through a slotted discharge pipe at the top. The inlet pipe also serves as a sludge discharge line during backwashing. Backwashing consists of completely draining all the water from the filter, causing the beads to be sucked through the washing throat, where they are vigorously scrubbed by cavitation and bubbles from the air inlet valve. The solids-laden water is discharged and the filter refilled, and placed back into operation. Each biofilter contained approximately 57 L of food-grade polyethylene beads, with a mean diameter of 4.4 mm, porosity of 35 percent and a specific surface area of 1050 m^2/m^3 (Sastry *et al.* 1999).

At the conclusion of the above mentioned research project, the fish were removed and the research tanks cleaned and refilled with tap water. The four recirculation systems were then operated for a period of time (approximately 3 weeks) with inorganic ammonia-nitrogen (ammonium chloride) as the sole source of ammonia by a daily addition of approximately 20 to 25 g of NH_4Cl, bringing the ammonia-nitrogen concentration in the tanks to between 2.5 and 3.0 mg-N/L. In addition, each bubble-washed bead filter was backwashed every other day to remove excess biofloc from the system. Heterotrophic bacterial growth was assumed minimal in the biofilters due to the removal of the fish, the backwashing of the systems, and the extended length of time (3 weeks) with little available carbon for their growth.

Each batch nitrification reaction rate trial consisted of spiking each tank with 20 g NH_4Cl and then monitoring water quality in the tanks and the influent and effluent of the individual bead filters at 30-minute intervals until the ammonia-nitrogen concentrations were too low to accurately measure or for a maximum of 8 hours. A range of flow rates through the biofilters was investigated from approximately 10 Lpm to 100 Lpm. These flow rates bracket the design loading rates for the bubble-washed bead filter suggested by Malone and Beecher (2000) from 400 to 800 Lpm/m^3 of beads. All experiments were conducted at room temperature, which varied from 20 to 22°C. Each trial's flow rate was randomly selected from a low flow rate followed by a high flow rate.

The following water quality parameters for the influent and effluent of the biofilter were measured at 30-minute intervals by withdrawing a sample into a 250-mL Erlenmeyer glass flask:

- ammonia-nitrogen (Hach Nessler Method No. 8038 adapted from Standard Methods: 4500-NH_3, APHA 1995) using a HACH DREL/2000 spectrophotometer,
- pH using a Fisher-Scientific Accumet pH Meter 25 (calibrated daily at 4, 7.02, and 10 pH),
- dissolved oxygen and temperature using a YSI Model 58 DO meter (air calibrated method daily),
- alkalinity following standard methods, 2320 B/Titration Method (APHA 1995).

Flow rates through the biofilters were determined by weighing a 20-L bucket of filter discharge water collected over a known time period.

The kinetic reaction rate for the removal of ammonia-nitrogen, r_a, was evaluated based on the change in concentration of ammonia-nitrogen across the filter divided by the hydraulic retention time in the filter, or:

$$r_a = \frac{dC_F}{dt} = \frac{(C_i - C_e)}{V_F / Q} * 1440\,{}^{\text{min}}\!/_{\text{day}} \qquad (1)$$

where: r_a = kinetic reaction rate (g/m^3 day)
dC_F = change in ammonia-nitrogen across biofilter [mg/L]
C_i = concentration in influent to biofilter [mg/L]
C_e = concentration in effluent from biofilter [mg/L]
V_F = volume of biofilter [L]
Q = flow rate through biofilter [Lpm]

Figure 2 shows an example of kinetic reaction rate for the removal of ammonia-nitrogen with respect to influent ammonia-nitrogen concentration for several flow rates through the bubble-washed bead filter.

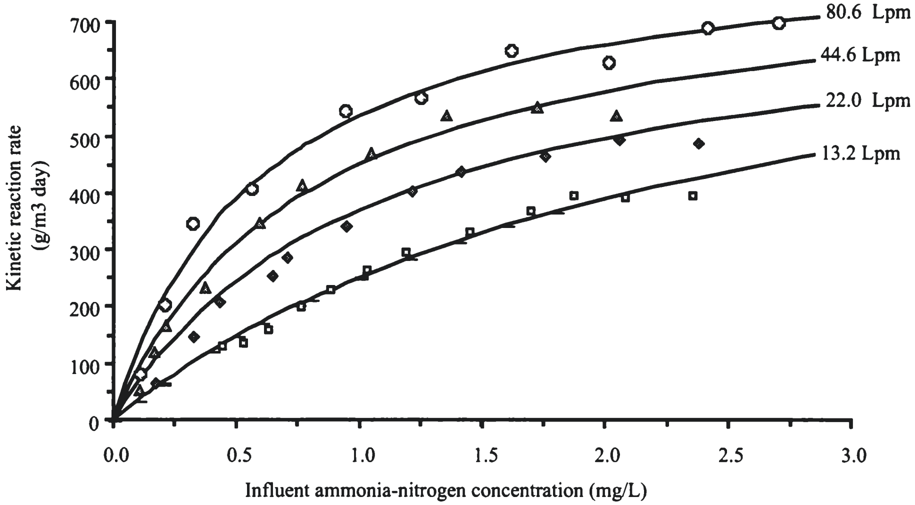

Figure 2. Kinetic reaction rate for the removal of ammonia-nitrogen with respect to influent ammonia-nitrogen concentration for several flow rates after initial spiking with 25 g of NH_4Cl.

RESULTS

Two general approaches to the development of design equations for biological filters have been developed over the past years. The first was to approach the problem from an empirical viewpoint and develop models relating the inlet and outlet concentrations as functions of relevant physical variables such as flow rate, media size, and configuration, dissolved oxygen concentration, pH, and temperature (Wheaton 1985, Metcalf and Eddy 1991). The second approach is to examine the individual processes involved in nitrification, including external mass transfer of ammonia-nitrogen to the biofilm, internal diffusion within the biofilm, and the actual nitrification kinetics (Williamson and McCarthy 1976a,b; Gujer and Boller 1986). Both methods have distinct advantages and disadvantages and are useful in both the design and development of biofilters.

As the aquaculture industry has matured over the past decade, distinct biofilter designs and media are becoming "standards." These include trickling towers, fluidized sand beds, and floating-bead filters. Although a purely theoretical analysis of these filters is useful from an academic research viewpoint, it does little to assist the aquaculture engineer attempting to specify a particular filter design for a given biomass load, system configuration, and economic constraint. Thus, a purely empirical approach is taken here to describe the bead filter's nitrification kinetics as a function of ammonia-nitrogen concentration and flow rate through the filter. From this analysis a series of design curves very similar to pump design curves can be developed that will help the design engineer select the most appropriate filter size and flow rates based on ammonia-nitrogen concentrations desired within the system.

Empirical Model – Reaction Rate Order

The approach used to develop design equations for the biological filters was based on the assumption that the rate of reaction was proportional to the n^{th} power of the concentration:

$$r_a = \frac{dC_a}{dt} = k \times C_a^{\,n} \tag{2}$$

where k is the reaction rate constant, C_a is ammonia-nitrogen concentration, and n is the reaction rate order. The reaction rate order can then be obtained by plotting the log of both sides, or:

$$\log(r_a) = \log(k) + n\log(C_a) \tag{3}$$

Thus, a log-log plot of the experimental data should yield a straight line whose slope corresponds to the order of the reaction rate, n. An example of the resulting plot for the bubble-washed bead filter is shown in Figure 3. This plot and others suggested that the design equation for the rate of reaction could be divided into simple first- and zero-order equations, i.e. $n = 1$ and $n = 0$.

The first- and zero-order data range for these plots was determined by starting at the lowest and highest values of r_a, and then sequentially adding data points one at a time, until there was a significant change in the R^2 value for the two regression lines. Figure 3 demonstrates that near the breakpoint value, the data no longer conform to the simple interpretation outlined above. As Figure 3 shows, at this flow rate and for low concentrations of ammonia-nitrogen, less than 1.0 mg-N/L, the reaction rate order is approximately 1.0. Moreover, for higher concentrations (greater than 1.0 mg-N/L), the reaction rate order appears to be approximately zero. For the purposes of aquaculture system design,

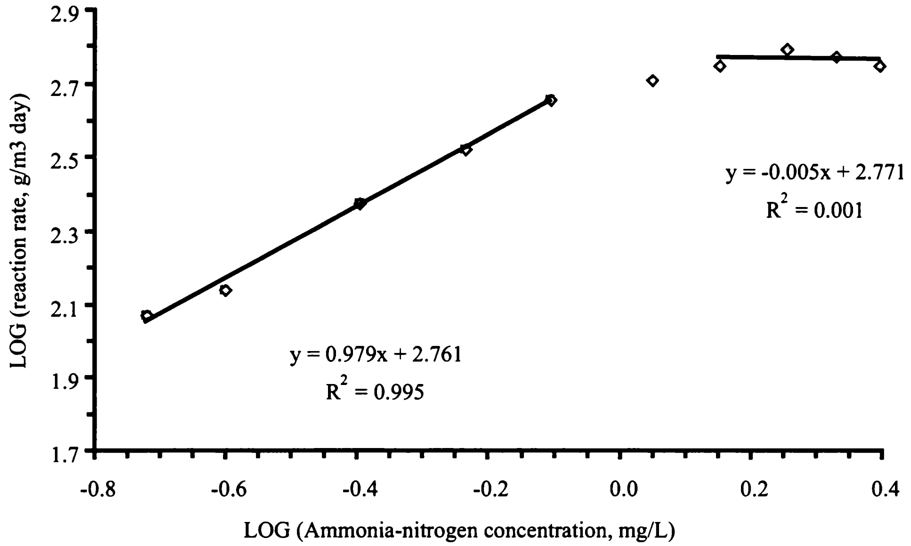

Figure 3. Example of a kinetic reaction rate order analysis for bubble-washed bead filter #1, flow rate of 39.3 Lpm.

this demarcation between first- and zero-order reaction rate corresponds approximately to the two ranges of ammonia-nitrogen concentrations usually encountered in commercial intensive recirculating aquaculture systems. Alternatively, using the classification system proposed by Malone (2004), biofilters designed for larval rearing, fingerling, and broodstock systems would be based on first-order reaction rates, whereas systems designed for growout could be based on either first- or zero-order reaction rates, depending upon species ammonia-nitrogen tolerance.

By extrapolating the linear regression lines for the two rate equations, a breakpoint concentration can be found that corresponds to the concentration where the overall reaction rate shifts from a first-order relationship to a zero-order relationship. The exact value can be found by equating the two regression equations, and solving for the ammonia-nitrogen concentration. Table 4 lists these values as a function of both flow rates through the filters and the corresponding hydraulic retention time. Figure 4 shows the values of the break point as a function of the flow rate through the bubble-washed bead filters.

Table 4. Ammonia-nitrogen concentration break point between first- and zero-order reaction kinetics for the two bubble-washed bead filters.

HRT[1] (min)	Flow (Lpm)	Break point (mg-N/L)
4.32	13.2	1.47
3.80	15.0	1.48
3.63	15.7	1.18
2.60	21.9	1.07
2.59	22.0	1.19
1.87	30.5	0.89
1.82	31.3	0.92
1.45	39.3	1.02
1.28	44.6	0.86
1.05	54.2	0.98
0.88	59.0	0.88
0.95	60.0	0.47
0.77	74.1	0.65
0.71	80.6	0.65

[1] HRT = hydraulic retention time

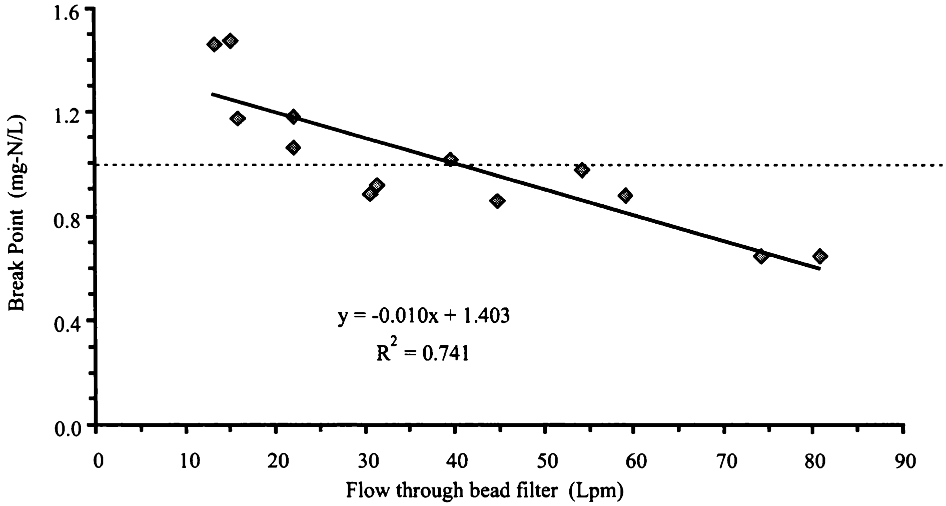

Figure 4. Ammonia-nitrogen break point concentrations between first- and zero-order kinetic reaction rates for the bubble-washed bead filters as flow rate through the biofilter.

Empirical Model – First- and Zero-Order Reaction Rate Constants

Based on the above results, the design equations for the biological filters were divided into either a first- or a zero-order kinetic reaction rate, depending upon the influent ammonia-nitrogen concentration and the break point concentration. Thus where the influent ammonia-nitrogen concentration is relatively low (< 1 mg/L NH_4-N), the reaction rate can be modeled as a first order reaction using Equation 4:

$$\frac{dC_a}{dt} = -k_1 \times C_a \tag{4}$$

where: C_a = ammonia-nitrogen concentration [mg/L]
k_1 = first-order reaction rate constant [day^{-1}]

When the above differential equation is integrated once, a plot of *ln* C_a versus time should yield a straight line with slope equal to the first-order reaction rate constant, k_1. Figure 5 shows several plots at various flow rates through the bead filter. A simple regression analysis of the resulting straight line (Figure 5) less than the break point concentration should correspond to the first-order reaction rate coefficient, k_1. This slope was estimated by starting at the break point between first- and zero-order reactions previously calculated and successively deleting data points to the regression analysis to maximize the R^2 value.

Correspondingly, for higher influent ammonia-nitrogen concentrations (> 1 mg/L NH_4-N), the reaction rate kinetics can be modeled as a zero order reaction rate using Equation 5:

$$\frac{dC_a}{dt} = -k_0 \tag{5}$$

where: k_0 = zero-order reaction rate constant [g/m^3 day]

The zero-order reaction rate coefficient can be estimated by a simple regression analysis of the slope of the straight line found by plotting ammonia-nitrogen concentration versus time, Figure 6, or a mean value and standard deviation could be estimated by averaging the removal reaction rates at ammonia-nitrogen concentrations greater than the break point concentration. Table 5 presents summaries of the first-order and zero-order reaction rate coefficients for the bubble-washed bead filter.

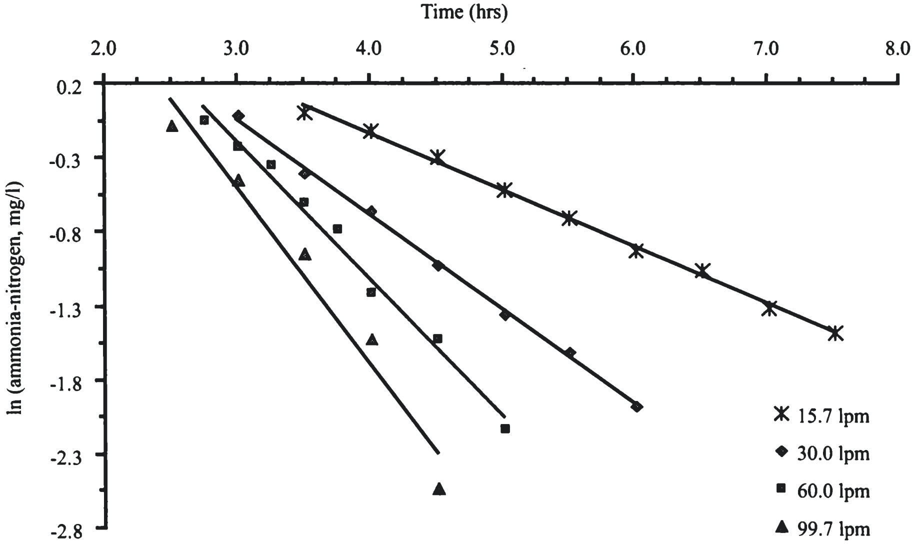

Figure 5. Plot of the graphical solution to determine the first-order reaction rate coefficient for the bubble-washed bead filter #1.

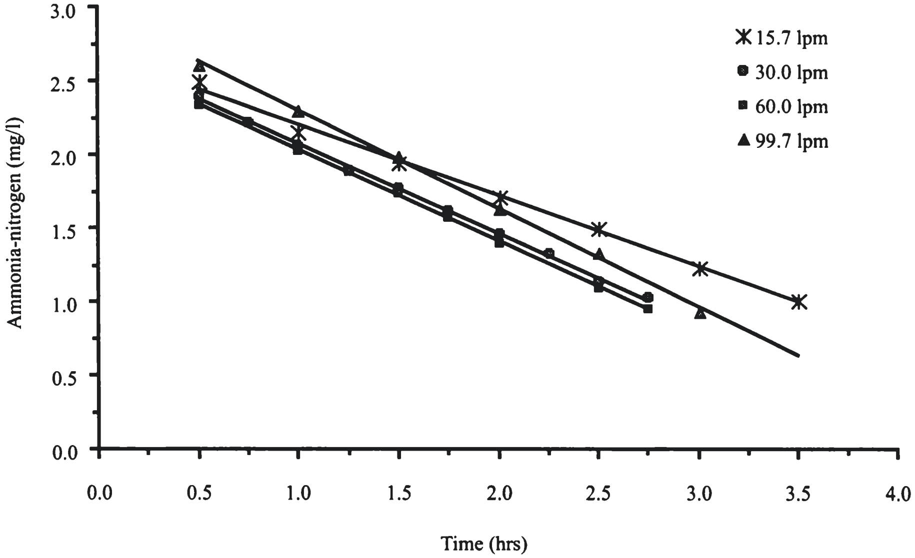

Figure 6. Ammonia-nitrogen concentration as a function of time showing the zero-order reaction rate coefficient.

Table 5. First- and zero-order kinetic reaction-rate coefficients, bubble-washed bead filter

	first-order rate constant		**zero-order rate constant**	
Flow Rate (Lpm)	**k_1 (day^{-1})**	**Regression R-squared**	**k_0 (g/m^3 day)**	**StDev (g/m^3 day)**
Bubble-washed bead filter #1				
13.2	256	0.99	396	87
15.7	283	0.98	433	19
22.0	424	0.96	478	16
30.5	482	0.98	499	12
39.3	586	0.99	588	29
54.2	634	0.98	609	18
60.0	712	0.47	500	48
66.3	681	0.76	427	39
80.6	827	0.83	611	74
99.7	1014	0.99	544	38
Bubble-washed bead filter #4				
15.0	275	0.99	380	22
21.9	332	0.98	439	44
31.3	437	0.99	403	16
44.6	588	0.95	535	46
59.0	681	0.99	525	39
74.1	712	0.89	618	63
92.5	905	—	432	81

Empirical Model – Monod Reaction Rate Parameters

Hagopian and Riley (1998), Williamson and McCarthy (1976a), Srna (1975), and other researchers suggested the use of a single- or double-saturation equation, where either the influent ammonia-nitrogen or dissolved oxygen concentration or both may limit the reaction rate. The overall kinetic reaction rate then becomes:

$$\frac{dC_a}{dt} = -r \tag{6}$$

where:

$$r = r_{\max}\left[\frac{TAN}{TAN + K_{1/2}}\right]\left[\frac{DO}{DO + K'_{1/2}}\right] \qquad (7)$$

and: r = reaction rate [g/m^3 day]
r_{max} = maximum reaction rate [g/m^3 day]
$K_{1/2}$ = half-saturation coefficient for TAN [mg NH_4-N /L]
$K'_{1/2}$ = half-saturation coefficient for DO [mg oxygen /L]
TAN = total ammonia-nitrogen [mg NH_4-N /L]
DO = dissolved oxygen [mg/L]

When $K_{1/2}$ is much smaller than the ammonia-nitrogen or dissolved oxygen concentration, the saturation-rate function appears to be a zero-order reaction and when $K_{1/2}$ is much greater than ammonia-nitrogen or dissolved oxygen, the saturation-rate function appears to be a first-order reaction. In the past, the saturation equations were solved from a Lineweaver-Burke plot of the inverse of the reaction rate versus ammonia-nitrogen concentration. Today, several software programs include solutions to this equation, either as a single- or two-site saturation coefficient. Sigma Plot 2002 (http://www.systat.com) for Windows Version 8.02 graphics software program includes a regression algorithm called Ligand Binding, which allows for the solution of the one- or two-site saturation equation and determination of multiple statistical parameters, including standard error of the measurement. In this study, the single-site saturation equation was used since dissolved oxygen concentrations were maintained above 6 mg/L and was not a rate limiting factor. Table 5 lists the coefficients for the two bead filters and their standard error. It should be noted that for flow rates less than 20 Lpm through the biofilters significant discrepancies were seen. This can be attributed to the difficulty in obtaining accurate measurements of the difference in ammonia-nitrogen across the biofilter at these low flow rates, since the magnitude of the difference is so small.

DISCUSSION

It needs to be pointed out that this analysis of reaction coefficients for nitrification is not the same as is often reported in the literature (Zhu and Chen 1999, 2000, 2002). Rather than analyze a pure strain of *Nitrosomonas* and *Nitrobacter* acclimated to a narrow range of ammonia-nitrogen concentration, this analysis looks at a "real-world" biofilter *in-situ*, with all the confounding factors that affect commercial production biofilters. These include the impact of heterotrophic bacteria, a wide range of influent or system ammonia-nitrogen concentrations due to varying feed rates and times, system upsets, stress and disease of the cultured animals, and numerous other factors. It is the authors' opinion that measurements made on these types of systems will better represent actual "real-world" biofilters. It is interesting to note that the reaction rates determined by pure laboratory systems usually present maximum nitrification rates significantly higher than those seen in "real-world" production systems. This difference is then explained as being due to the impact of total organic carbon, temperature, salinity, or some other mitigating factor.

Empirical Model – Reaction Rate Order

In the application of a first- and zero-order kinetic reaction rate model, one of the parameters of interest in design and sizing of biofilters is the value of ammonia-nitrogen corresponding to the break point between the two models. First-order kinetic reaction rates are directly dependent on the influent ammonia-nitrogen concentration, whereas zero-order rates are independent of influent ammonia-nitrogen concentration. The break point concentration would reflect the change from a diffusion rate limit on nitrification to a reaction rate limit. Experimentally determined break point values for bead filters are plotted versus the flow rate through the biofilter in Figure 4. Two things are of interest, first the almost linear relationship with flow rate, and the range of values from 1.5 mg/L at the lowest flow rates to approximately 0.5 mg/L at the highest rates (R^2 value of 0.74). Second, the decrease in the break point ammonia-nitrogen concentration as the flow rate increases. Based on the guidelines for the design of systems utilizing floating-bead filters, Table 3, (Malone and Beecher 2000), the design hydraulic loading (Lpm/m^3 media) for broodstock and growout would correspond to approximately 47 Lpm. From Figure 4, this would correspond to a break point between first- and zero-order reaction rates at an ammonia-nitrogen concentration of about 0.9 mg-N/L. This would support the concept that for systems requiring ammonia-nitrogen concentrations less than 1.0 mg/L, the bubble-bead filter should be designed based on a first-order reaction rate constant and for growout of hardy species at ammonia-nitrogen concentrations above 1 mg/l with a zero-order reaction rate constant.

Since the external mass transfer of ammonia-nitrogen by diffusion to the biofilm is directly dependent upon the thickness of the stagnant liquid layer surrounding the beads, and that thickness depends on the velocity of the water passing over the beads, it follows that the reaction rate coefficient should be affected by the water flow rate through the filter. Figure 7 shows the first-order reaction rate parameter as a function of the flow rate through the biofilter. It demonstrates nicely the effect of flow rate, in that at low flow rates the reaction rate is significantly lower than that at the highest flow rate. Thus, the first-order reaction rate coefficient at a flow rate, Q (Lpm) for the bubble-washed bead filter can be expressed as:

$$k_1 = (7.9 * Q + 197) \tag{8}$$

and the first-order reaction rate or removal rate becomes:

$$\frac{dC_a}{dt} = -(7.9 * Q + 197) \times C_a \tag{9}$$

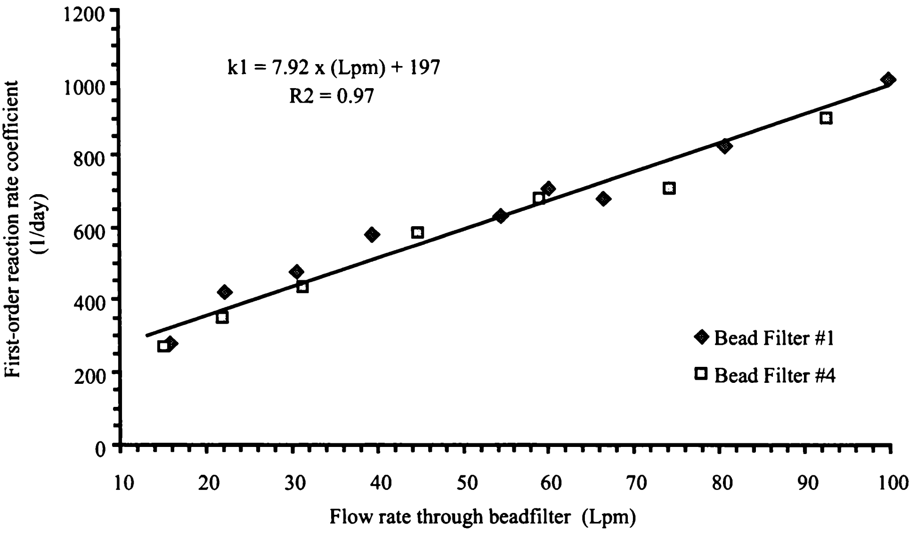

Figure 7. First-order reaction rate coefficient as a function of the flow rate through the bubble-washed bead filter.

Empirical Model – Application of First- and Zero-Order Empirical Model Results

In order to apply the results of this study to the sizing of biofilters, a series of performance characteristic curves were developed, similar to what is commonly used in characterizing pump performance. In this case, the reaction or removal rate (g/m^3 day) is plotted against either flow rate through the biofilters at several values of ammonia-nitrogen or plotted against ammonia-nitrogen concentration for several different flow rates. An example of these performance curves for the bubble-washed bead filter is shown in Figure 8. For this graph, the experimentally derived values for the first-order reaction rate constant as a function of flow rate through the biofilter were used (Eq. 8) and the first-order reaction rate model, solved for the removal rate of ammonia-nitrogen as a function of media volume per day (g/m^3 day). In addition, the experimentally determined reaction rates plotted demonstrate the validity of this model, at least at low ammonia-nitrogen concentrations.

Figure 8 shows clearly the effect of flow rate and ammonia-nitrogen concentration on the performance of the bead filter. The first observation is that at low ammonia-nitrogen concentrations, the impact of flow rate is not as significant as at the higher concentrations. Although the increased

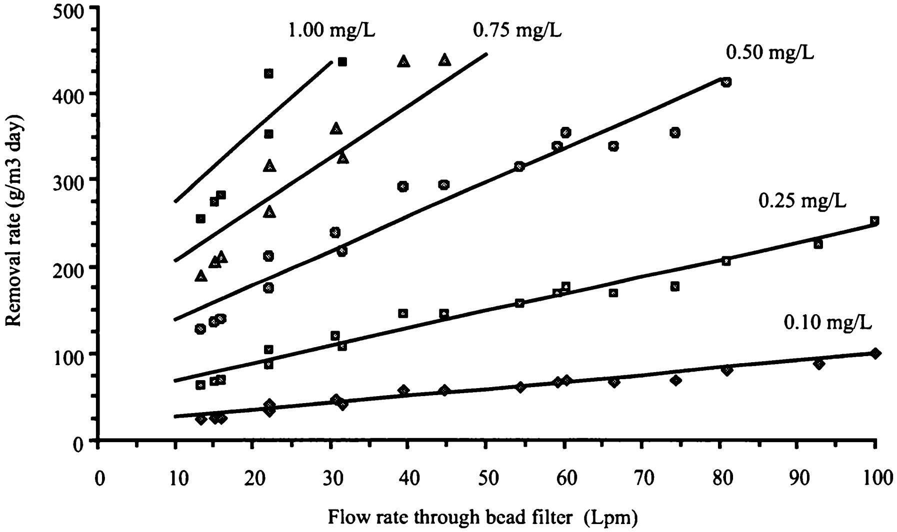

Figure 8. First-order performance characteristic curves for the bubble-washed bead filter as a function of flow rate through the filter and influent ammonia-nitrogen concentration.

flow rate would theoretically reduce the boundary layer between the bulk liquid and the biofilm, increasing external mass transfer, the diffusion rate is also a factor in the concentration gradient. Thus, the high concentrations yield higher gradients, which in turn yield a higher nitrification rate.

The second observation from the results is that as the ammonia-nitrogen concentration increases and, especially at low flow rates through the biofilter, the reaction moves quickly towards a zero-order reaction rate. Under zero-order, the ammonia-nitrogen removal rate is constant and the removal rate is not influenced by the flow rate (Fig. 9). From a design standpoint, this is important since it suggests that the only way to increase the first-order biofilter removal rate is either by increasing the ammonia-nitrogen concentration in the production tanks or, to a limited extent, by increasing the flow rate through the biofilter. The first choice is limited by the species being produced and the second by the hydraulic characteristics of the biofilter, i.e. bursting pressure and the economic cost of pumping.

Figure 9 shows the zero-order reaction rate coefficient as a function of the flow rate through the biofilter. It shows that there appears to be no significant effect of flow rate. This is consistent with the concept that the reaction is kinetic-reaction-rate limited and not a function of the diffusion rate. The mean value for the zero-order reaction rate coefficient is 495 g/m^3 day or assuming a specific surface area of 1050 m^2/m^3, 0.47 g/m^2 day.

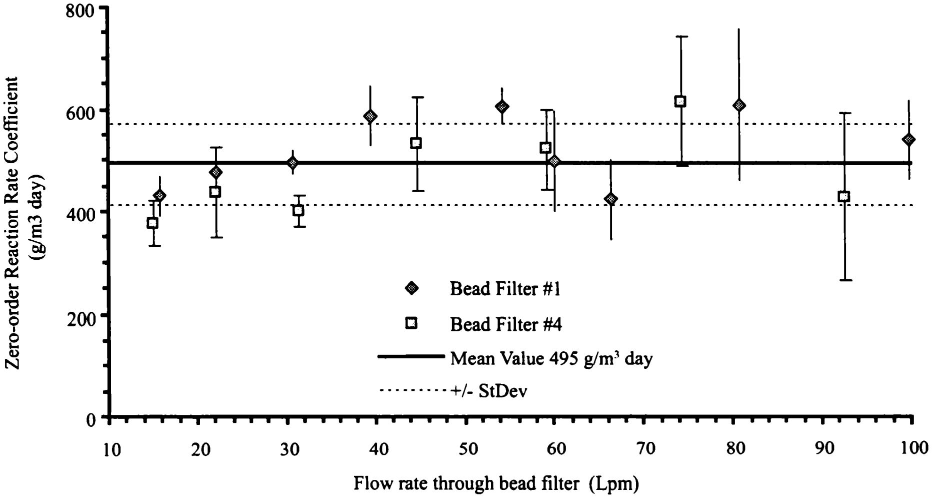

Figure 9. Effect of flow rate on the zero-order reaction rate coefficient, showing the mean value of 495 g/m^3 day ± standard deviation.

Monod Model

The simplified first- and zero-order reaction rate model can be useful in understanding and characterizing biofilter performance for either very low or very high ammonia-nitrogen concentrations. Its major drawback is characterizing the biofilter performance near the break-point between the two models, around 1.0 mg/L ammonia-nitrogen. To overcome this difficulty, most models of biofilms use some form of saturation equation such as the Monod relationship, Equation 6 and 7.

It can be shown that the break point concentration, $C_{bp,}$ determined for the simple empirical kinetic-rate model is approximately equal to the Monod half-saturation coefficient. This is accomplished by equating the Monod equation for high and low values of C in relation to $K_{1/2}$.

Thus, at high values of ammonia-concentration and Equation 7:

$$C_a >> K_{1/2} \qquad \frac{dC_a}{dt} \cong r_{\max} \tag{10}$$

And at low values of ammonia-nitrogen concentration:

$$C_a << K_{1/2} \qquad \frac{dC_a}{dt} \cong r_{\max *} \frac{C_a}{K_{1/2}} \tag{11}$$

Equating the two models at the break-point concentration, C_{bp}, yields:

$$C_{bp} \cong K_{1/2} \tag{12}$$

Thus it becomes possible to estimate the break point between first- and zero-order reaction rates from the Monod reaction rate coefficient. This would suggest that the half-saturation coefficient also would correspond approximately to the break point between kinetics controlled by diffusion across the stagnant layer next to the biofilm and kinetics controlled by the kinetic reaction rates of the bacterial film.

The half-saturation coefficient and the maximum reaction rate coefficient are shown in Figure 10 and 11 in relationship to the flow rate through the biofilter. It is interesting that there appears to be a relationship between the half-saturation coefficient and the flow rate through the biofilter, similar to what was seen for the first-order reaction rate coefficient, although in this case the relationship is reflected in a decrease in value rather than an increase. Similarly with the zero-order reaction rate

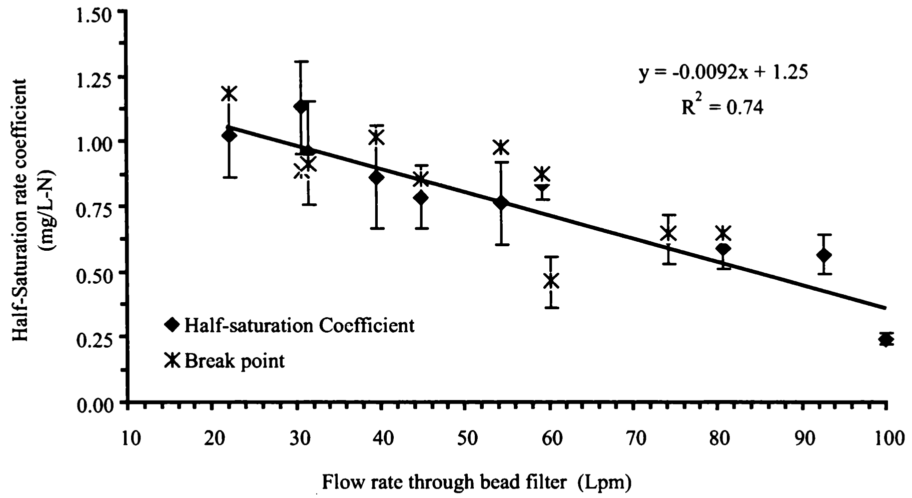

Figure 10. The relationship between the half-saturation coefficient and the flow rate through the bead filter, along with the break point values determined experimentally.

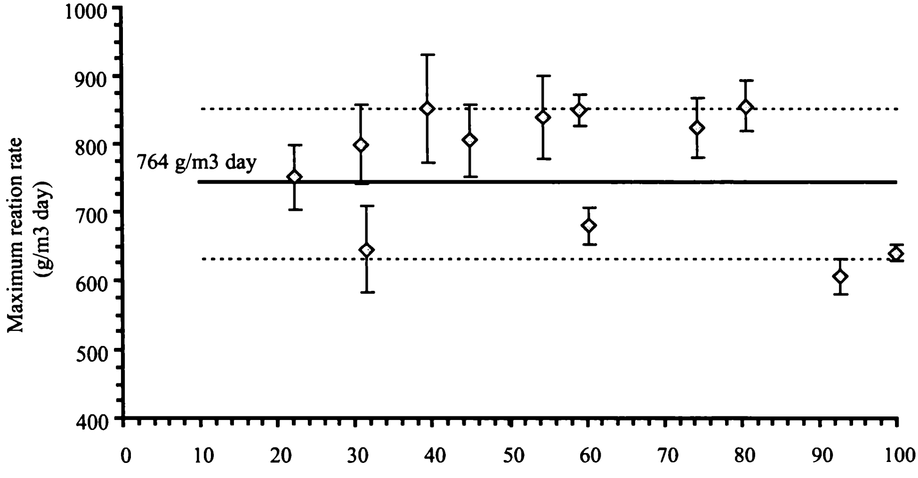

Figure 11. The relationship between the maximum reaction rate coefficient and the flow rate through the bead filter, showing a mean value of 764 g/m³ day and ± one standard deviation (94 g/m³ day).

coefficient, there appears to be no significant impact of flow rate through the biofilter on the maximum reaction rate coefficient, with a mean value of 764 ± 94 g/m^3 day or assuming a specific surface area of 1050 m^2/m^3, 0.73 ± 0.09 g/m^2 day.

Monod Model – Application of the model

The experimentally-derived values for the Monod reaction rate coefficients (Table 6) were used along with Equations 6 and 7 to develop a series of performance characteristic curves as a function of the flow rate through the biofilter and the ammonia-nitrogen concentration, shown in Figures 12 and 13. The chief advantage of these curves is that they

Table 6. Monod kinetic reaction-rate coefficients for the two bubble-washed bead filters for ammonia-nitrogen concentration up to 3.0 mg-N/L.

	Monod Reaction Rate Coefficients			
Flow Rate (Lpm)	**r_{max} (g/m^3 day)**	**Std Error**	**$K_{1/2}$ (mg/L)**	**Std Error**
		Bead filter #1		
13.2	867	90.4	2.44	0.41
15.7	915	73.0	2.30	0.31
22.0	739	40.3	1.10	0.14
30.5	801	58.5	1.14	0.18
39.3	853	79.6	0.87	0.20
54.2	840	61.6	0.77	0.16
60.0	681	27.6	0.47	0.10
80.6	858	37.4	0.60	0.08
99.7	641	11.7	0.25	0.02
		Bead filter #4		
15.0	1095	121	3.23	0.50
21.9	1349	113	3.18	0.37
31.3	647	62.7	0.96	0.20
44.6	807	52.5	0.79	0.12
59.0	851	23.3	0.84	0.05
74.1	825	42.9	0.63	0.09
92.5	608	24.8	0.57	0.07

are applicable over the entire range of ammonia-nitrogen concentrations. The end product of this evaluation technique is a set of design curves that can be used by engineers to properly size a biofilter for a given intensive recirculation system design and production species. In addition, existing systems can be evaluated to determine if they are operating at maximum removal rate for a given flow rate and operating ammonia-nitrogen concentration. From the performance curves, suggestions can be made on how to improve overall removal rate or filter efficiency by modifying the flow rate through the biofilter or adjusting the ammonia-nitrogen concentrations in the production system. However, both modifications have limitations due to the increased cost of pumping either water or species-specific ammonia-nitrogen tolerances.

Figure 12 displays the ammonia-nitrogen removal rate as a function of ammonia-nitrogen concentration based on the Monod relationship for four flow rates. Starting with the loading regime corresponding to broodstock holding or a very light feeding regime, the experimentally determined removal rates span almost exactly the range of volumetric nitrification rates reported by Malone *et al.* (1998). At the recommended flow rate of 11 Lpm, the removal rate at the highest recommended ammonia-

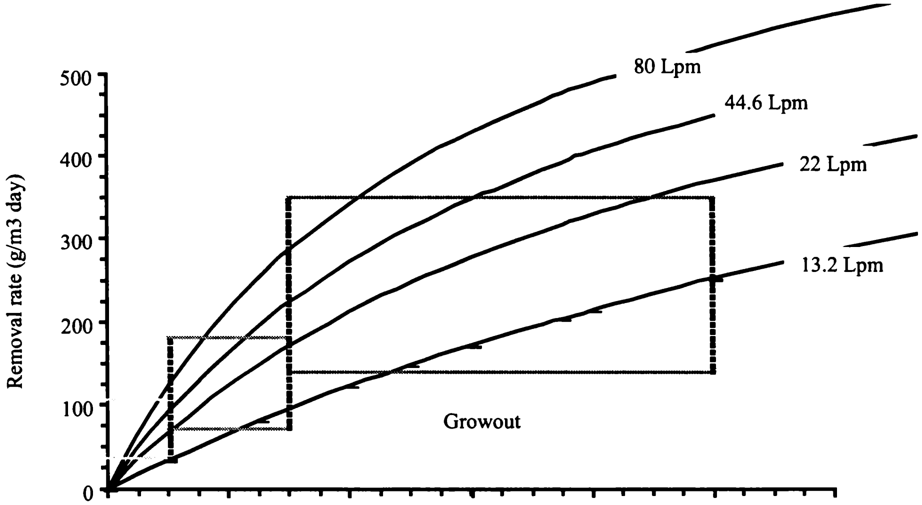

Figure 12. Performance characteristic curves for the bubble-washed bead filters, based on the experimentally determined Monod coefficients as a function of the ammonia-nitrogen concentration, showing the three fish life-stage application levels of ammonia-nitrogen concentration.

nitrogen level is equal to the lower value suggested by Malone *et al.* (1998). For the moderate loading regime of ornamentals, the removal rates corresponding to the recommended flow rate of 22 Lpm curve, bisecting the range of recommended removal rates. Finally, for the growout loading regime or the heavy loading rate, the removal rates corresponding to the recommended flow rate of 45 Lpm covers the full range of reported removal rates from the low end to the high end of 450 g/m^3 day. Malone, *et al.* (1998) reported that, based on their group's experimental data, an ammonia-nitrogen removal rate of 350 g/m^3 day would be expected under normal operation conditions for a production tank TAN concentration of 0.75 mg/L. This is similar to what the experimentally-based performance curves developed in this research suggest as the removal rate for a flow rate of approximately 45 Lpm and TAN concentration of 0.75 mg/L, shown in Figure 13. This graph also shows the recommended flow rates for the three production classifications and the corresponding ammonia-nitrogen removal rates.

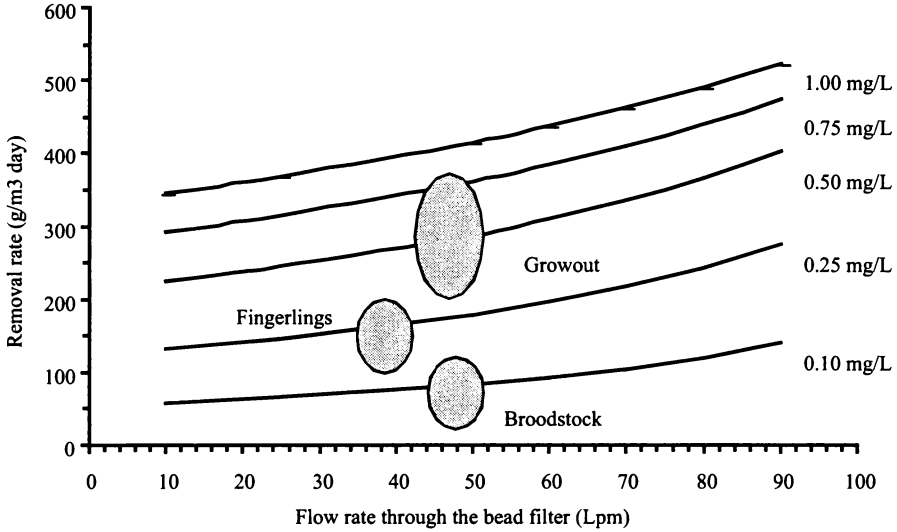

Figure 13. Performance characteristic curves for the bubble-washed bead filters, based on the experimentally determined Monod coefficients as a function of the flow rate through the bead filter.

CONCLUSION

There were no serious difficulties experienced in using a series of batch reaction rate experiments to determine the reaction rate kinetics for a commercially available pilot-scale bubble-washed bead filter. Empirical mathematical models for the nitrification of ammonia-nitrogen to nitrate-nitrogen were developed. The kinetics of nitrification were found to follow a simple first-order reaction model when the ammonia-nitrogen concentration was less than approximately 1.0 mg NH_4-N/L, and a zero-order reaction when the ammonia-nitrogen concentration was greater than 1.0 mg NH_4-N/L. The actual break-point between the two reaction regions was also found to be a function of the flow rate through the biofilter. In addition, the first-order kinetic reaction rate constants were also found to be a function of the flow rate through the filter, reflecting the influence of the fluid velocity on the mass transfer rate across the biofilm.

Using readily available graphical software, the Monod reaction parameters can quickly be determined and from them a series of performance characteristic curves developed as a function of the flow rate through the biofilter and the ammonia-nitrogen concentration. The chief advantage of these curves is that they are applicable over the entire range of ammonia-nitrogen concentrations. The end product of this evaluation technique is a set of design curves that can be used by engineers to properly size biofilters for a given intensive recirculation system design and production species. In addition, existing systems can be evaluated to determine if they are operating at the maximum removal rate for a given flow rate and operating ammonia-nitrogen concentration. From the performance curves, suggestions can be made as how to improve the overall removal rate or filter efficiency by modifying water flow rate through the biofilter or adjusting the ammonia-nitrogen concentrations in the production system.

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