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AEROBIC TREATMENT OF AMMONIUM FERTILIZER EFFLUENT IN A FIXED-FILM BIOLOGICAL SYSTEM

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ABSTRACT

A fertilizer plant effluent that contains high levels of ammonia was treated using a four-stage, fixed-film aerated bioreactor in a pilot plant design. Ammonia concentrations in the influent wastes were maintained up to 480 mg L^{-1} NH_3-N and reactor hydraulic loading rates were varied up to 0.14 m^3 m^{-2} d^{-1} during continuous operation. Process performance was satisfactory and nitrification rates were determined based on steady-state operation. Ammonia removal was not inhibited by the organic content and the high ammonia concentrations of the influent waste. Removal rates obtained at 20°C ranged between 0.49 to 3.23 NH_3-N per day per g volatile solids of attached biomass, which are considerably higher than those reported for the activated sludge and RBC processes under similar operating conditions. This could be attributed to the good oxygen transfer capacity and the large quantity of attached biomass attained in the studied reactor. The rate of nitrification in this system apparently follows first-order kinetics. Design relationships were developed for nitrification of fertilizer effluent and an optimum design loading of 25 g NH_3-N $m^{-2}d^{-1}$ is recommended to achieve higher than 90% ammonia removals.

KEYWORDS

Fertilizer effluent; ammonia-rich waste; fixed-film reactor; nitrification; process design.

INTRODUCTION

Industrial wastewater effluents generated from the manufacture of urea and ammonia fertilizers usually contain considerable amounts of ammonia nitrogen. When such effluents are discharged to the environment, depletion of receiving-water oxygen resources can occur as the ammonia is oxidized to nitrate. This depletion of oxygen can be eliminated if the ammonia is first oxidized to nitrate before it is discharged. Biological nitrification is the process commonly used to accomplish this objective. In this process, the ammonium ion is aerobically converted to nitrite and finally to nitrate in two steps by nitrifying autotrophic bacteria.

Nitrification will occur in most aerobic biological treatment processes when the operating and environmental conditions are suitable (Metcalf & Eddy, 1979). One of the important controlling variables is the solids residence time (SRT), i.e. sludge age. Since longer residence times are required for more effective nitrification, it is important to retain nitrifying bacteria

and avoid excessive wash-out of these microorganisms in biological treatment systems. Therefore, attached-growth systems appear more applicable than suspended-growth systems. However, in the literature, the nitrification process is reasonably well defined for suspended-growth systems than for attached-growth systems (Barnes and Bliss, 1983).

Biological treatment of ammonia-rich wastewaters has been investigated using suspended-growth systems such as the activated sludge process (Hutton and LaRocca, 1975; Pascik and Mann, 1983; Thiem and Alkhatib, 1988). These studies showed that the activated sludge process can be optimized for nitrification of high ammonia concentrations (up to 1000 mg $L^{-1}NH_4^+$-N)at long SRT's in a two-stage treatment scheme. Efficient aeration systems and long SRT were required for this purpose. Such treatment schemes will result in a substantial increase in treatment costs. On the other hand, attached-growth systems such as the rotating biological contactor (RBC) and the expanded bed reactor proved to be very effective in treating concentrated ammonia effluents in a single-stage treatment scheme (Lue-Hing et al., 1976; Collins et al., 1988). It is estimated that 4.6 kg of oxygen are theoretically required in order to oxidize 1 kg of ammonia-nitrogen by biological nitrification. Therefore, additional oxygen must be provided for the nitrification of ammonia-rich wastewaters especially in attached-growth systems. An aerated stationary fixed-film (ASFF) biological system (Hamoda and Abd-El-Bary, 1987) appears to be a viable alternative. This study was initiated to determine the effectiveness of nitrification in the ASFF biological system as a means of treating ammonia-rich wastewater effluent from a chemical fertilizer plant in Kuwait.

MATERIALS AND METHODS

Wastewater Characteristics

Wastewaters generated from the fertilizer manufacturing plants at Shuaiba which are owned and operated by the Petrochemical Industries Company of Kuwait are considered in this study. The plants produce liquid ammonia, prilled urea and sulfuric acid and generate two major effluent streams. One stream is diluted with the cooling seawater and discharged into the Arabian Gulf waters. The other stream, containing urea and ammonia, is collected in a neutralizing pit and a hydrolyzer is used for purifying this stream before being pumped to two large lagoons for storage prior to reuse in irrigation of forestry and agricultural lands. The quality of the effluent pumped to the lagoon is regulated as neat as possible to contain about 200 mg L^{-1} ammonia-nitrogen and urea depending on the efficiency of the hydrolyzer. Approximately 500 to 1000 m^3 d^{-1} of the effluent is directed to the lagoon for reuse. This effluent stream, which requires further treatment in order to reduce its ammonia content to acceptable levels, was the subject of this study. Its characteristics, as determined during the study, are shown in Table 1. The average

TABLE 1 Characteristics of the Fertilizer Plant Effluent During the Study

Parameter(1)	Average(2)	Minimum	Maximum
COD	190	92	360
Urea-N	140	38	220
NH_3-N	230	72	430
(NO_2+NO_3)-N	22	5	40
Oil	6.5	3	9
pH	8.7	7.6	9.2
Turbidity	25	13	42
TDS	1205	1025	1820
SS	35	20	45
Conductivity	1350	1100	2000
Cu	0.02	ND(3)	ND
Cr	0.03	ND	ND
Pb	0.01	ND	ND

(1) All values are in mg L^{-1} except for pH and for conductivity (μmhos cm^{-1})
(2) No. of observations = 78
(3) Not determined.

concentrations of urea-nitrogen and ammonia-nitrogen were relatively high whereas chemical oxygen demand (COD) was relatively low and suspended solids concentrations were extremely low. These concentrations were generally stable although a range of values was observed (Table 1). The ratio of ammonia-nitrogen to urea-nitrogen in the effluent was almost constant.

Experimental Procedures

An in-house pilot plant of 1.5 $m^3 d^{-1}$ capacity was constructed in the Shuaiba industrial complex to treat the fertilizer plant effluent. The pilot plant consisted of a covered feed storage tank, a feed pump, a continuous-flow ASFF reactor, and an effluent collection tank. Three identical ASFF reactors made of plexiglas were used. Each reactor has a net liquid volume of 50 l and was divided into four stages (equal-size compartments) in series as shown in Fig. 1. There were 10 ceramic (tile) media plates in each stage providing a sur-

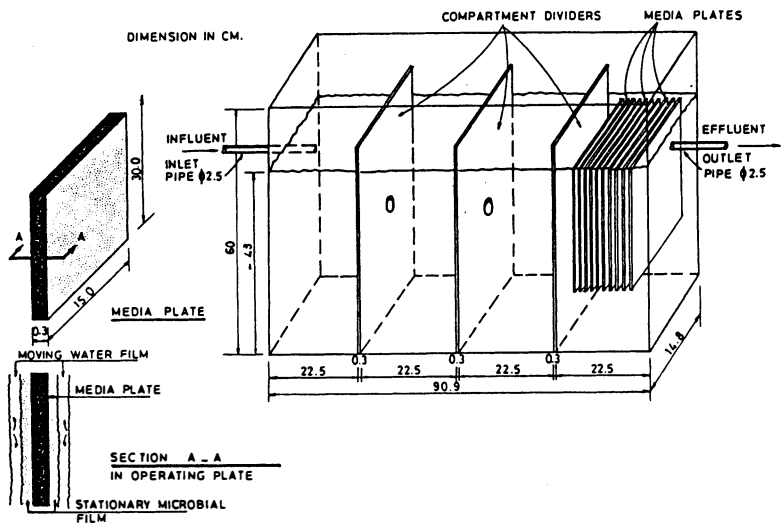

Fig. 1. Schematic of the ASFF reactor.

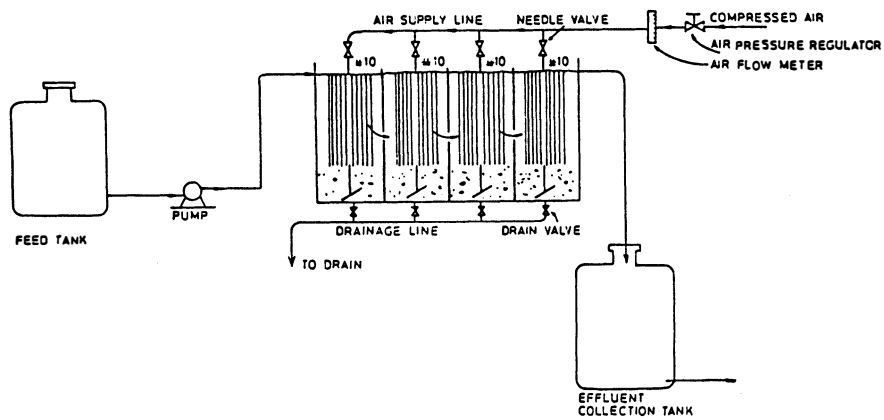

Fig. 2. Experimental set-up

face area of 0.9 m^2 per stage for microbial attachment and a surface area-to-volume ratio of 72. The media plates were held in place by equally spaced grooves to form an array. Sufficient compressed air was introduced, at a regulated rate, through two porous-tube diffusers placed at the bottom of each compartment so as to create rising air bubbles in the spaces between media plates and maintain dissolved oxygen levels at approximately 90% of saturation. The reactor operated as a continuous-flow system in the experimental set-up shown in Fig. 2. The wastewater was pumped from the feed tank to the reactor at a measured and controlled flow rate and effluent from the reactor flowed by gravity to the collection tank.

Activated sludge cultures containing nitrifying bacteria were obtained from a local municipal wastewater treatment plant and used as initial seed for the development of biological films of nitrifying bacteria on the plates of the reactor. Biofilm development took about four weeks during which the reactors were fed the fertilizer plant effluent on a semi-continuous basis. After the development of biofilms, the reactors were operated as continuous-flow systems for six months at room temperature (20 ± 2°C).

Each reactor was operated at a different influent nitrogen concentration covering the range of concentrations found in the fertilizer plant effluent so as to examine the effect of concentration on reactor performance. The basic feed to the reactors was fertilizer plant effluent. Feed nitrogen and COD concentrations were adjusted as required by dilution with tap water or by the addition of synthetic ingredients to achieve certain nitrogen and COD levels. The wastewater feed to each reactor was supplemented with phosphorus and micronutrients required for adequate microbial growth. The continuous-flow reactors were operated at four different flow rates to attain different hydraulic retention times (HRTs) and mass loading rates. Varying the operating conditions permitted the development of design criteria for the ASFF system.

Analytical Methods

Filtered chemical oxygen demand (COD), ammonia, nitrites plus nitrates, and total nitrogen were regularly determined in the samples taken, whereas suspended solids (SS), dissolved oxygen (DO), pH and temperature were measured occasionally. Analytical procedures followed in COD, total Kjeldahl nitrogen, ammonia and SS determinations were those outlined in Standard Methods (APHA, 1975). Nitrite plus nitrate (NO_2 + NO_3) nitrogen was determined by a sulphanilamide method using a Skalar Auto-analyzer (Model 5101) with automatic sampler. Nitrate nitrogen concentration was also checked using a selective electrode on a Corning Ion Analyzer (Model 150). At the end of each experimental run, the total amount of biomass attached to plates in each stage was measured by calculating the dry weight of biomass scraped from a known area of each plate (oven-dried at 105°C). From the dried biomass, several samples were taken to determine the volatile fraction (VS) according to Standard Methods (APHA, 1975).

RESULTS AND DISCUSSION

Process Performance

Long-term experimental runs generated reasonably good steady-state data. These data were analysed to evaluate overall ammonia removal efficiency and percentage nitrification at different influent NH_3-N concentrations and hydraulic loading rates (or HRTs) as shown in Fig. 3. Ammonia removal efficiency decreased as the hydraulic loading rate was increased (HRT decreased) in almost a linear form. Since the ammonia transformed shows up as nitrites (NO_2) and nitrates (NO_3) during biological oxidation, the percentage nitrification can be expressed as:

$$\% \text{ Nitrification} = \frac{(NO_2\text{-}N) + (NO_3\text{-}N)}{\text{Total N}} \times 100. \quad (1)$$

Fig. 3 shows similar trends for both percentage nitrification and ammonia removal as a function of the hydraulic loading rate which indicate that ammonia removal in the ASFF system occurred primarily through biological nitrification. However, since nitrification was monitored concurrently with COD removal during reactor operation, a small portion of ammonia could have been removed through biological assimilation by heterotrophic microorganisms. It is also possible that ammonia could have been gained by biodegradation of

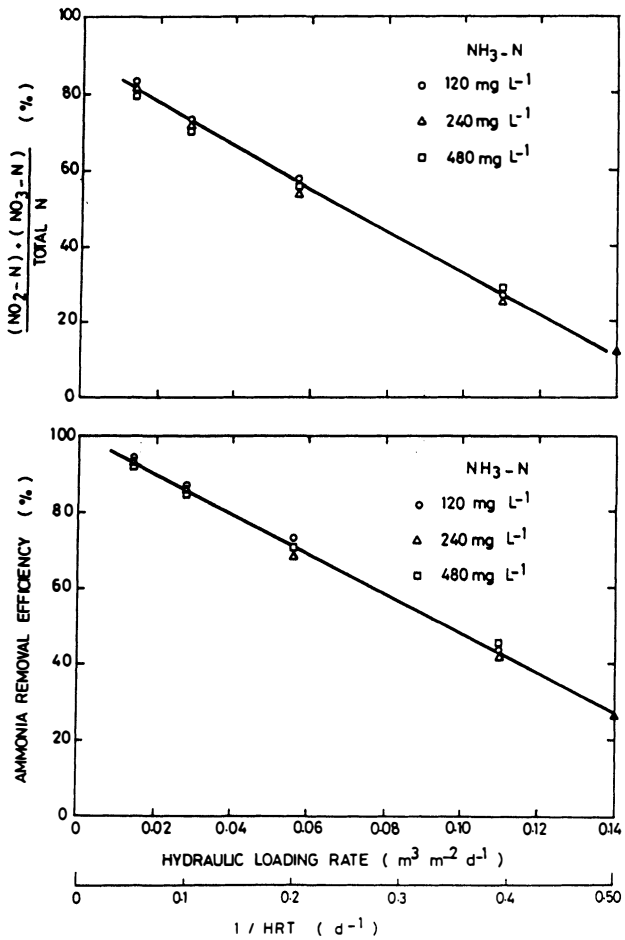

Fig. 3. Effects of hydraulic loading and retention time on nitrification.

urea. Nitrogen could have been lost through the system by some denitrification at the media/biomass interface, even though aerobic conditions prevailed. This makes theoretical interpretation of ammonia transformation more difficult. Meanwhile, the decrease in ammonia removal and percentage nitrification at higher hydraulic loading rates (shorter HRTs) is presumably due to the shorter SRTs obtained under increased loading conditions (Hamoda, 1989).

Fig. 3 shows that data on ammonia removal and nitrification percentages at different influent ammonia concentrations can be fitted by a single line in each case when plotted as a function of hydraulic loading rate or 1/HRT. This indicates that influent ammonia concentration has practically an insignificant effect on nitrification efficiency in the ASFF reactor at the range of concentrations studied.

It should be mentioned that pH in the ASFF reactors was in the range of 6.1 to 8.0, which is close to the optimum range for nitrification. The amount of ammonia removed by stripping during aeration under these pH conditions is considered insignificant. The microbial conversion causes a drop in pH but the adequate buffering capacity of the system resulted in only a moderate drop in the pH. Meanwhile, the dissolved oxygen concentrations observed in the reactors during the experiments were consistently higher than 6 mg L^{-1}. The wastewater feed used in this study contributed COD because of its urea content. The COD/N ratio of the feed was about 0.75 indicating a nitrogen-rich wastewater. Meanwhile, the TOC/COD ratio of the wastewater was approximately 0.8. The organic content of the wastewater was reduced during treatment in the ASFF reactor because of biological oxidation. The overall COD removal efficiencies in the reactors during the nitrification experiments were in the range of 60 to 85 percent, with the higher efficiencies being observed at lower organic loadings. The organic loadings applied were in the range of 1.2 to 34 g COD $m^{-2}d^{-1}$ and the corresponding nitrogen loadings ranged between 1.5 and 45 g N $m^{-2}d^{-1}$. Removal of organics in these studies indicates that heterotrophic bacteria were present in the ASFF reactors along with the autotrophic nitrifying bacteria. Meanwhile, it is interesting to note that the high ammonia removal efficiencies reported in the experiments were obtained at such a wide range of organic loadings applied. This indicates that nitrification was not inhibited by the organic carbon source.

Figure 4 shows the mean steady-state nitrite plus nitrate nitrogen concentrations in the four stages of the ASFF reactor. Analyses of the data obtained show that, in general, the majority of nitrification occurred in the

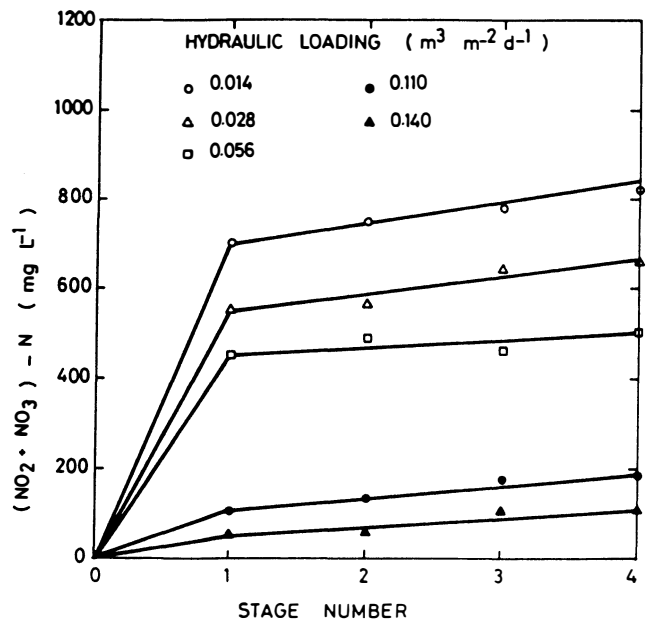

Fig. 4. Nitrite plus nitrate concentrations in the stages of the reactor at different hydraulic loadings.

first stage where considerable ammonia nitrogen and COD removals were observed. The first stage contained the highest ammonia nitrogen concentrations in all experiments. This indicates that nitrification was not inhibited by the higher ammonia nitrogen concentrations present in the first stage and was accompanied by organic carbon removal. It can be seen from Fig. 4 that higher (NO_2+NO_3) nitrogen concentrations were reported at higher hydraulic (or mass) loadings due to the increased amounts of ammonia nitrogen being oxidized. Meanwhile, occasional checking of NO_3 in the system by ion selective electrode compared to (NO_2+NO_3) values indicated that these values were almost contributed by NO_3 alone.

The ASFF reactor optimized for nitrification (nitrogenous substrate removal) in these experiments retained lower attached biomass compared to reactors performing primarily carbonaceous substrate removal (e.g. sugar) reported earlier (Hamoda and Abd-El-Bary, 1987) at similar organic loadings. This could be attributed to the slow growth of the autotrophic nitrifying bacteria responsible for nitrification in the former reactor compared to the rapid growth of the heterotrophic bacteria oxidizing carbonaceous material in the latter reactors. Although organic carbon removal was also observed in the nitrification reactor, the complex nature of urea as an organic substrate seems to be hardly able to support appreciable heterotrophic bacterial growth in the system. Meanwhile, the ammonia removal rates calculated from the experimental results of the ASFF reactor ranged between 0.49 to 3.23 g NH_3-N removed per day per g VS of attached biomass. These removal rates are considerably higher than the range of 0.006 to 0.6 g NH_3-N removed per day g MLVSS reported for the activated sludge process treating concentrated ammonia wastewaters (Hutton and LaRocca, 1975). This could be attributed to the longer SRTs attained in the ASFF reactor compared with the activated sludge aeration tank. Meanwhile, there was no apparent inhibition of nitrification in the ASFF reactor from organic matter or heavy metals present in the wastewater.

Design Considerations

To date, the most common approach to design attached-growth processes has been to use loading factors (Antonie, 1976). Assuming that sufficient air can be supplied in the system, nitrification can be generally assured at a moderate temperature but is enhanced at higher temperatures within the mesophilic range. A longer SRT or HRT (i.e. lower hydraulic loading rates) must be used if nitrification is to be accomplished beyond those necessary for the stabilization of the organic matter. Nitrifying bacteria, which are strict autotrophs, have a growth rate that is much slower than that of the heterotrophic bacteria responsible for the degradation of the organic matter. Because microbial conversion causes a drop in pH, provision should be made for lime or caustic addition with low-alkalinity wastewaters.

Design relationships were developed for nitrification of the fertilizer plant effluent in the ASFF reactor as shown in Fig. 5. The surface area required can be computed from this figure. On the other hand, the loading rates required for the operation of the ASFF reactor to obtain certain effluent quality (ammonia content) can be also determined from Fig. 5. With a design loading of 25 g NH_3-N $m^{-2}d^{-1}$ (i.e. 0.063 m^3 $m^{-2}d^{-1}$ in combination with an influent NH_3-N content of 400 mg L^{-1}) ammonia removals greater than 90% can obtained. It is to be noted that these relationships were developed based on pilot-plant data obtained at 20°C. Higher nitrification rates are expected at higher temperatures (Hall and Murphy, 1985) but temperatures above 35°C are beyond the optimum range (Metcalf & Eddy, 1979).

Process design loadings may be established if an adequate SRT is maintained. A shift in SRT may significantly change the design base since SRT is very critical in achieving effective ammonia transformation. In the studied ASFF reactor, SRT is related to loading rates to the system (Hamoda, 1989). The SRT was calculated as sludge in the system (g VS of attached biomass) divided by wasted sludge (g VS escaping in the effluent per day). SRT values ranged between 30 to 150 d which are markedly higher than maximum SRTs attained in the activated sludge process optimized for nitrification of concentrated ammo-

nia wastewaters (Hutton and LaRocca, 1975). This shows the capability of the ASFF reactor in retaining considerably large amounts of attached biomass.

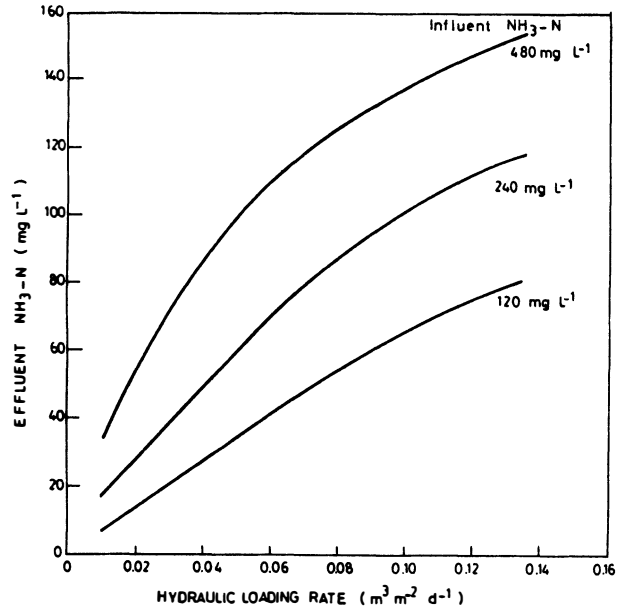

Fig. 5. Design relationships for nitrification of fertilizer plant wastewater.

Since the effluent from the ASFF reactor contains relatively high nitrate concentrations, further polishing of this effluent may be required in order to remove nitrates. This could be achieved by denitrification under anoxic conditions in the fixed-film reactor so as to convert the nitrates into nitrogen gas. Effluent quality requirements will determine whether denitrification is needed in each case.

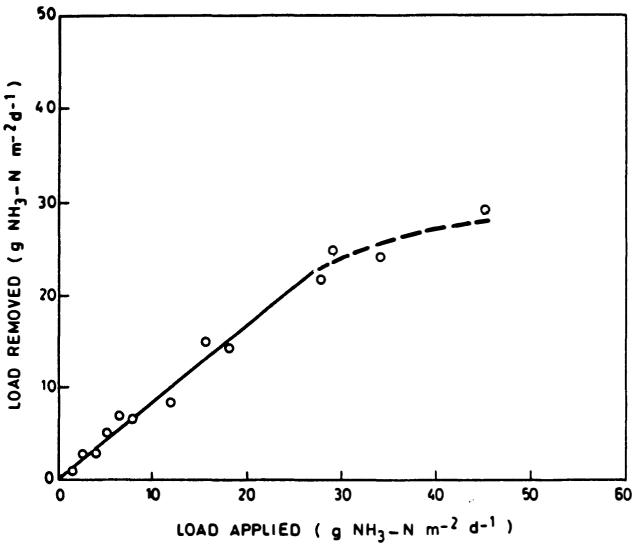

Fig. 6. Applied vs. removed ammonia nitrogen loadings.

There is some disagreement in the literature (Barnes and Bliss, 1983) as to whether the rate of nitrification in attached-growth systems follows zero-order, half-order, or first-order kinetics with respect to ammonia concentration. The results shown in Fig. 3, where percent ammonia nitrogen removal is shown as a function of overall hydraulic loading rate in the system for various influent ammonia concentrations, show that the concentration lines coincide. It may imply that ammonia nitrogen removal in the system is a first order reaction, which is supported by the relationship obtained in Fig. 6 at one hydraulic loading but different ammonia concentrations showing that ammonia nitrogen removal rates per unit biofilm surface area increased linearly with increasing ammonia nitrogen application rates. This is true up to a certain loading limit beyond which the order of the reaction decreased, approaching zero-order (shown by the dashed line), i.e. it follows Monod-Kinetics. Low reaction orders were reported in the literature at high concentrations of ammonia (Barnes and Bliss, 1983). Because the amount of nitrifying biomass that develops on the media plates in the reactor increases by increasing the ammonia nitrogen concentration, the amount of ammonia nitrogen removed also continues to increase but up to a limit determined by the substrate (ammonia nitrogen) concentration and oxygen transfer in the system.

It can be seen from Fig. 6 that ammonia-nitrogen removal rates up to 30 g NH_3-N $m^{-2}d^{-1}$ were obtained at 20°C. These rates are considerably higher than removal rates of 10 g $m^{-2}d^{-1}$ at 20°C reported by Lue-Hing et al. (1976) for the RBC system treating wastewaters containing high concentrations of ammonia (approximately 800 mg L^{-1}). Good oxygen transfer capacity and biomass retention in the ASFF reactor contributed to its adequate performance during nitrification.

CONCLUSIONS

1. Treatment of fertilizer plant effluent containing ammonia nitrogen concentrations up to 480 mg L^{-1} was successfully accomplished in the ASFF system. Ammonia nitrogen removals greater than 90% were obtained at loading rates up to 25 g NH_3-N $m^{-2}d^{-1}$. However, ammonia removal efficiencies decreased as the loading rate was increased.

2. Ammonia removal rates obtained ranged between 0.49 to 3.23 g NH_3-N per day per g volatile solids of attached biomass which are considerably higher than those reported for the activated sludge process treating high ammonia wastewaters.

3. The rate of nitrification in the ASFF system apparently follows first-order kinetics with respect to ammonia at lower concentrations but approaches zero-order at higher concentrations.

4. Design relationships were developed for nitrification of the fertilizer plant effluent in the ASFF system. These relationships can be used to determine the required hydraulic loading rate for a particular influent ammonia nitrogen concentration depending on effluent quality requirements.

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