Tr. J. of Engineering and Environmental Sciences
22 (1998) 39-45

Drinking Water Denitrification in a Fixed Bed Packed Biofilm Reactor

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Received: 4 / 10 / 1996

Abstract: In this study the effect of feed solution nitrate content (FNC), which varied between 50 and 200 ppm, and feed solution flow rate (FFR), which was in the range from 25.68 to 535 ml/h, on the nitrate removal performance of an active carbon packed-attached biofilm-fixed bed reactor has been investigated. For this purpose *Paracoccus denitrificans* NRRL B-3784 was used as denitrifier. As a result of this investigation, it was found that up to 200 ppm FNC the present system is able to produce a drinking water with a nitrate content below 20 ppm. On the other hand, up to FFR = 273 ml h^{-1} the present system was also able to produce a drinking water with a nitrate content below 20 ppm. But for higher FFR, the nitrate content of the product water exceeded 50 ppm level required by most of the drinking water standards. The results showed that present system could offer an alternative to systems reported in the available related literature.

Key Words: Active carbon, attached growth, biofilm denitrification, fixed bed, *Paracoccus denitrificans*

Bir Sabit Yataklı Dolgulu Kolon Biyofilm Reaktörde İçme Sularından Nitrat Giderimi

Özet: Bu çalışmada, besleme çözeltisindeki nitrat içeriği (BNİ 50-200 ppm) ve debisinin (BND 25.68-535 ml/h) aktif karbon yüzeyine tutuklanmış biyofilm sabit yataklı reaktörde nitrat giderimine etkileri incelenmiştir. Bu amaçla denitrifiye edici bakteri olarak *Paracoccus denitrificans* NRRL B-3784 kullanılmıştır. 200 ppm BNİ'ye kadarki uygulamalarda 20 ppm altında nitrat içeren içme suyu elde edilmiştir. Diğer taraftan 273 ml/h'e kadarki debilerde nitrat içeriği 20 ppm altında olmasına rağmen çok yüksek BND'de ise 50 ppm in aşıldığı belirlenmiştir. Sonuçlar mevcut sistemin literatürde verilen diğer sistemlere alternatif olabileceğini göstermiştir.

Anahtar Sözcükler : Aktif karbon, biyofilm, nitrat giderme, sabit yatak, yüzey tutuklama, *Paracoccus denitrificans*

Introduction

Contamination of drinking water sources with nitrate may result from over fertilisation (both artificial fertiliser and animal manure) in agriculture, human and animal waste disposal and disposal of the waste water from food processing operations, explosive manufacturing plants, NO_x-absorption in air-washing devices and recorvery of nuclear fuels etc. (Chen and Lin, 1993). Nitrate concentrations may be expressed in terms of nitrate or nitrate-nitrogen. Throughout the present work nitrate and NO^-_3 refer to values expressed as nitrate.

Consumption of nitrate contaminated water may cause health problems. Methemoglobinemia or blue baby syndrome in infants is related to ingestion of water having high nitrate concentrations (Shuvai and Gruener, 1977). Moreover there exists an increasing concern that consumption of water containing high nitrate may lead to some forms of cancer (Weisenburger, 1991 and Crespi and Ramazzoth, 1991). This relationship between health problems and consunmption of nitrate contaminated water led environmental agencies such as US Environmental Protection Agency (US-EPA) and World Health Organisation (WHO) to regulate nitrate concentration standards which in general allow a limit nitrate content of less than 50 ppm in drinking waters (Mateju et al., 1992). Because these standards are difficult to be complied with by controlling the contamination at the source, many municipal water suppliers are inevitably faced with having to meet these standards by employing efficient and economical nitrate removal processes. Several methods with different performance and cost levels are available in the drinking water treatment. Commonly used ones are ion exchange, reverse osmosis and biological denitrification (Mateju et al., 1992).

FIGURES

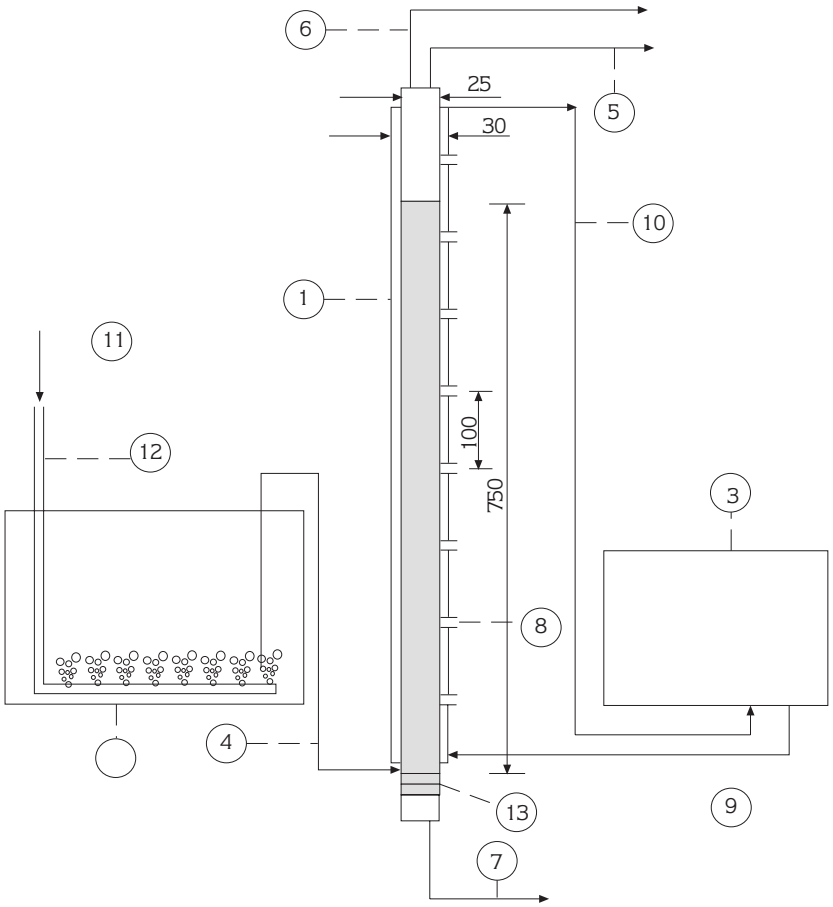

Figure 1. Schematic view of the experimental set-up: 1; active carbon fixed bed bioreactor, 2; feed solution tank, 3; constant temperature water circulator, 4; reactor feed solution inlet line, 5 and 6; product water exit lines, 7; drain, 8; ports for sample collection 9; water for temperature control inlet line, 10; water for temperature control return line, 11; nitrogen gas supply, 12; gas distributor, 13; reactor base.

Biological denitrification for water treatment among others has been shown to be more economical and practical and the most promising and versatile approach (Mateju et al., 1992, Soares et al., 1988 and Gaunlett, 1981). By biological denitrification nitrate in the water is converted into gaseous nitrogen through a number of steps. Known as nitrate respiration (Nurse, 1978) the reaction sequence of this process has been well studied (Painter, 1970 and Payne and Bact, 1973). The disadvantage of the biological denitrification is that it requires additional carbon sources such as methanol, ethanol or acetate for the activity of microorganisms and consequently some post treatments such as filtration, aeration, removal of residual organics and disinfection for eliminating process contaminants.

In recent years biological denitrification has received an increasing attention in the treatment of drinking waters (Lin and Chen, 1995, Yang et al., 1995, Takasaki et al., 1992, Nitisoravut and Yang, 1992 and Wu et al., 1994). Most of the methods employed make use of biosystems immobilised especially with physical or physico-chemical bonds on to the surface of some insoluble base material such as sand, plastic or ceramic (Cizinska et al., 1992).

In this study it is aimed to investigate effects of different parameters on the nitrate removal in a vertical active carbon packed-attached growth biofilm reactor. These parameters are nitrate concentration in feed solution and feed solution flow rate. The active carbon is known to be effective in holding organic substances in water streams. Thus by the use of active carbon bed it is aimed to minimise the contamination of the product water by residual organics.

Materials and Methods

The experimental set-up used in the investigation is shown in Figure 1. The system consisted of an active carbon packed bioreactor, a peristaltic pump, a con-

stant temperature water circulator, a feed solution tank and latex based tubes for liquid flows. *Bioreactor* with eight sampling ports had a water jacket for controlling the temperature of the reactor content. The height of the reactor was 100 cm of which only 75 cm portion was filled with 151 gr. 273 μm mean particle size active carbon. The inner diameter of the reactor was 2.5 cm. The top level of the active carbon bed was between the seventh and eight sampling ports positions. The active carbon is also supposed to act as residual organics removing media. The void volume in the active section of the reactor, V_R=46 ml, was measured experimentally. The total empty volume of the packed section of the reactor V_T was 358 ml again measured experimentally. The contaminated water prepared superficially (feed solution) was fed from the bottom of the reactor and left it from its top. Ethanol was used as carbon source which was added into the solution in such a quantity to give a C/N ratio of 2. Stoichiometric relationship of heterotrophic denitrification with ethanol may be given by following reaction (Mateju et al., 1992):

$$0.613C_2H_5OH+NO_3^{-1} \rightarrow 0.102C_5H_7NO_2+0.7124CO_2 +0.2860H^{-1}+0.98H_2O +0.449N \quad (1)$$

were $C_5H_7NO_2$ is biological cell formula. The coefficient of substrate (C_2H_5OH) to product (N) conversion ($Y_{P/S}$ = gr. N/gr. C_2H_5OH) for the above reaction is 0.446. Mixing in the feed solution tank was provided by Z shape nitrogen gas distributor fixed on the bottom of the tank. An adjustable speed peristaltic pump was used for pumping the feed solution into the reactor.

Paracoccus denitrificans NRRL B-3784 was used as the denitrifying bacteria and obtained from Dr. Lk. Nakamura (Department of Agriculture, Agricultural Resource Service, Midweek Area, National Centre for Agriculture Utilisation Resource, 1815 North University street, Peoria, Illinois, USA). Microorganisms received as lyophilised culture were first activated in a Brain Heart Infusion (BHI) broth and then they were stored in a refrigerator in a sloped agar containing 0.01% yeast extract. Then later they were transferred into fresh media within 30-60 days time periods. Microorganisms were first bred for three days in an erlenmayer flask containing 100 ml metyhlamine and 9.6 mM K_2HPO_4, 6.3 mM KH_2PO_4, 30 mM NH_4Cl, 0.66 mM Na_2MoO_4, 0.26 mM titriplex 1, 0.8 mM $MgSO_4$, 0.01% yeast extract and 1.0 ml trace elements solution as carbon and energy source (Van Spanning et al., 1990) before feeding them into the active carbon packed reactor.

Table 1. Kinetics data for varying feed solution nitrate content

FNC (ppm)	50	75	100	150	200
F (ml h^{-1})	273.76	273.76	273.76	273.76	273.76
X (%)	98.6	99.07	98.6	96.53	91.2
D (h^{-1})	0.7647	0.7647	0.7647	0.7647	0.7647
D_R (h^{-1})	5.95	5.95	5.95	5.95	5.95
L (mg l^{-1} h^{-1})	298	446	595	893	1190
R (mg l^{-1} h^{-1})	293.34	442.09	586.67	861.53	1085.28
P_r (mg l^{-1} h^{-1})	16.81	25.34	33.63	49.38	62.21
t (min.)	10	10	10	10	10

After filling the reactor with the above microbial solution, the reactor was operated in batch mode which enabled attached biofilm to develop on the surface of active carbon particles. When 95% nitrate removal (conversion) was reached, it was assumed that enough biofilm has been developed and the reactor was switched to continuous mode. The test showed that %95 conversion during the batch mode could be reached in two days period.

Samples from each sampling tap were collected at certain time intervals spanning 62 hours operation period for a single test. Nitrate concentrations of these samples collected at different time intervals changed only in the experimental error range (±10%). Thus the data presented here are the average of those obtained at different time intervals.

Collected samples were analysed for their nitrate and nitrite contents. Nitrate analysis were carried out by using an ion analyser of Jenway Model 3040 type fitted with a nitrate electrode and a Double Junction Reference Electrode. Nitrite analysis was done by using a spectrophotometer of Shimadzu UV 160-A type at 543 nm wavelength. As the purpose of the study was only to investigate the nitrate removal performance of the current experimental set-up, no microorganism and organic substance analysis were carried out in the collected samples. In the calculation of the kinetics data (Tables 1 and 2) following expressions were used:

$$X = 100((C_{in}-C_{out})/C_{in}) \quad (2)$$

$$D = F/V_T \quad (3)$$

$$D_R = F/V_R \quad (4)$$

$$L = C_{in}D_R \quad (5)$$

$$P_r = D(C_{in}-C_{out})Y_{P/S} \quad (6)$$

$$R = D_R(C_{in}-C_{out}) \quad (7)$$

$$\tau = 1/D_R \quad (8)$$

Table 2. Kinetics data for varying feed solution flow rate

FNC (ppm)	200	200	200	200	200	200
F (ml h^{-1})	25.68	34.95	51.43	112.5	273.76	535
X (%)	97.3	98.34	97.93	97.82	91.2	65.25
D (h^{-1})	0.072	0.098	0.1437	0.3142	0.7647	1.494
D_R (h^{-1})	0.558	0.76	1.118	2.446	5.95	11.63
L (mg l^{-1} h^{-1})	112	152	224	489	1190	2330
R (mg l^{-1} h^{-1})	109.16	149.47	218.98	478.61	1085.31	1517.72
P_r (mg l^{-1} h^{-1})	6.282	8.596	12.553	27.42	62.21	86.955
t (min.)	107.52	78.96	53.64	24.54	10.08	5.159

Results and Discussions

In this study the effect of feed solution nitrate content (FNC), which varied between 50 and 200 ppm, and feed solution flow rate (FFR), which was in the range from 25.68 to 535 ml/h, on the nitrate removal performance of an active carbon packed-attached biofilm-fixed bed reactor has been investigated. The nitrite content of the product water at the reactor exit was show that it was not detectable using the present measurement technique. It was detectable only up to the tap position 5 and the maximum measured values throughout the peresent work were below 5 ppm (FNC=200 ppm and FFR=25.68 ml/h) and 1.5 ppm (FNC=200 ppm and FFR=273.76 ml/h) for the tap positions 1 and 5, respectively. Therefore in what follows results obtained from only nitrate measurements will be presented here.

The effect of feed solution nitrate content

The effect of FNC on nitrate removal is shown in Figure 2. It is seen that for all FNCs studied after

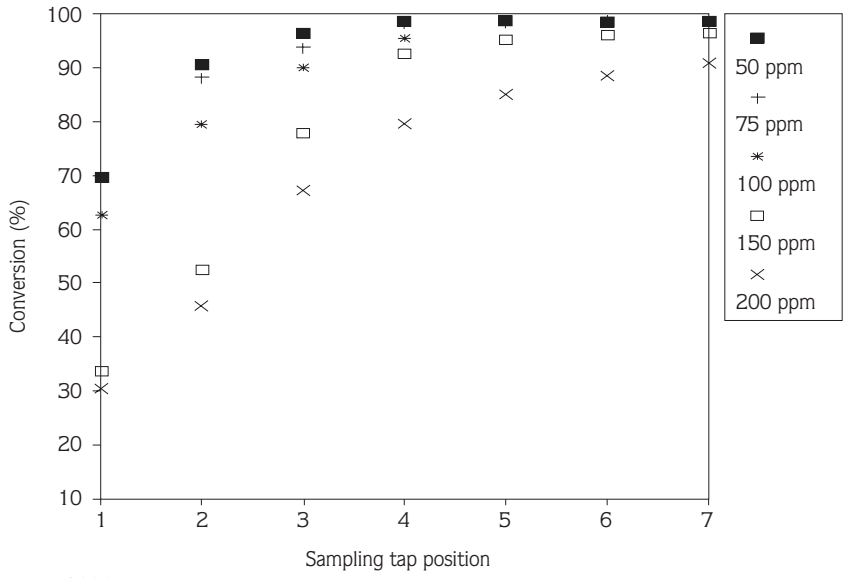

Figure 2. Effect of feed solution nitrate concentration on nitrate removal for a feed solution flow rate of 273.76 ml/h.

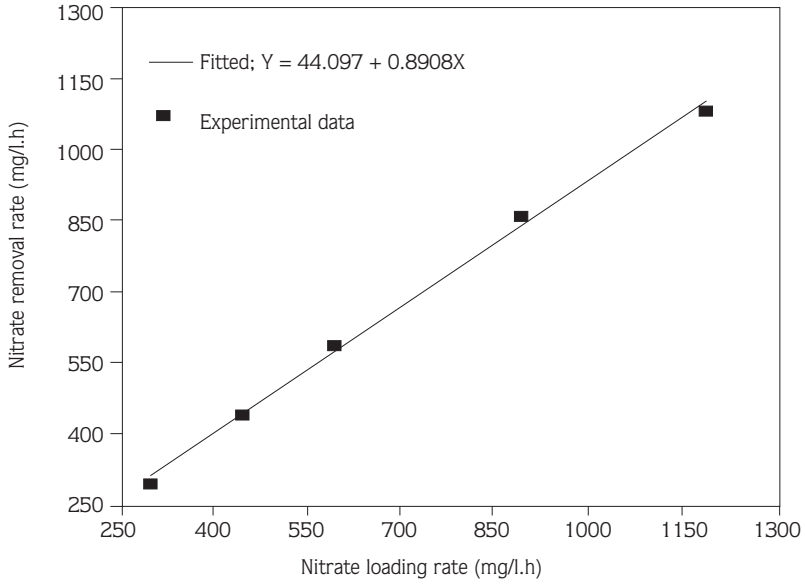

Figure 3. Variation of the nitrate removal rate with the nitrate loading rate (the feed solution nitrate content) for a feed solution flow rate of 273.76 ml/h (Y is the nitrate removal rate and X nitrate loading rate).

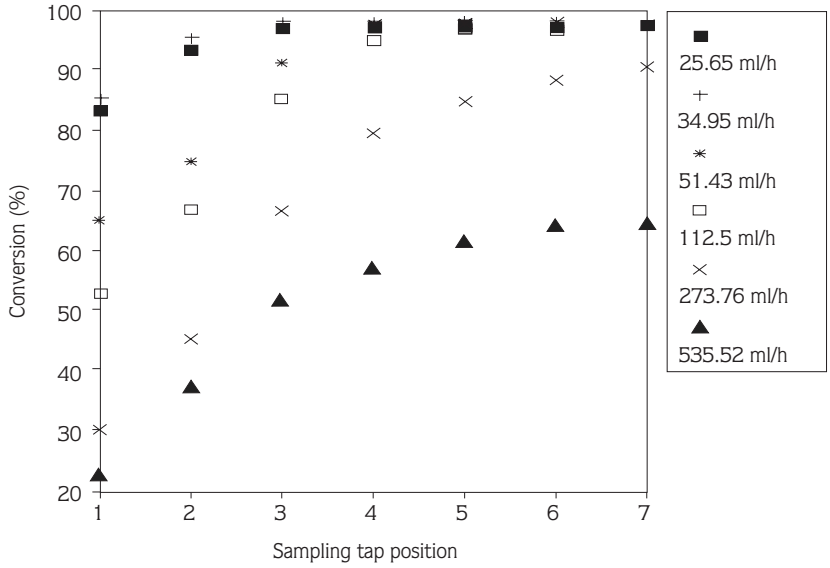

Figure 4. Effect of feed solution flow rate on nitrate removal for a feed solution nitrate concentration of 200 ppm.

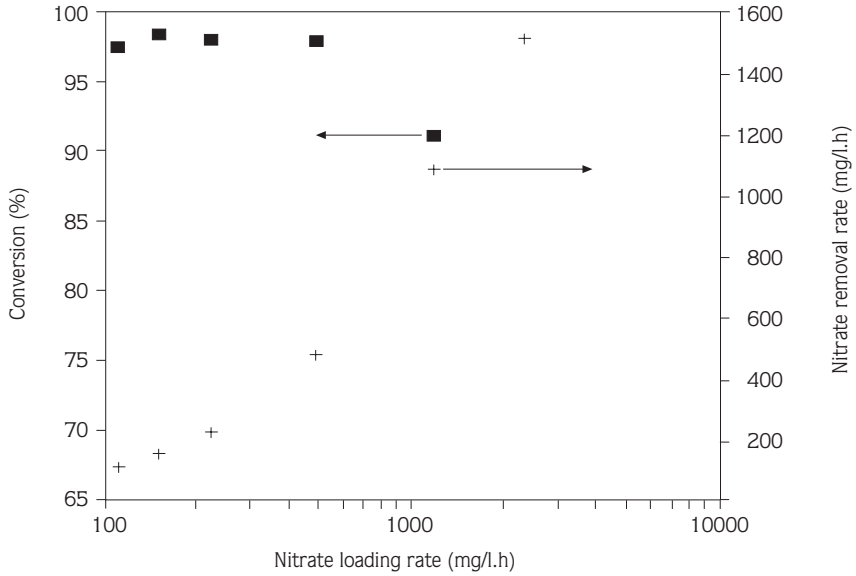

Figure 5. Variation of the conversion and the nitrate removal rate with the nitrate load (the feed solution flow rate) for a feed solution nitrate concentration of 200 ppm.

first few sampling port positions there is not any considerable nitrate removal. For FNC≤75 ppm 90% conversion has already been realised at the beginning section of the reactor, just after the tap position 2. For FNC=100, 150 and 200 ppm 90% conversion is realised at the tap positions 3, 4 and 7, respectively. But for all FNCs the final conversion at the reactor exit is nearly same and product water nitrate concentration (PNC) is below those allowed by environmental standards (US-EPA, WHO). The data implies that the higher the FNC the larger the reactor is required for keeping PNC below allowed limits. The kinetics information calculated using data given in this figure is given in Table 1.

The variation of nitrate removal rate with nitrate loading rate is shown in Figure 3. Since the FFR is constant (273.76 ml h^{-1}) for the data given here, this figure actually shows the effect of FNC on the nitrate removal rate. It is seen from the figure that nitrate removal rate increases linearly with increasing FNC within the range studied. Also shown in this figure is a line and a correlation equation fitted to the experimental data. Numerical form of the data given in this figure is given in Table 1.

The effect of feed solution flow rate

The effect of FFR on nitrate removal is shown in Figure 4. It is clear form the figure that for all tap

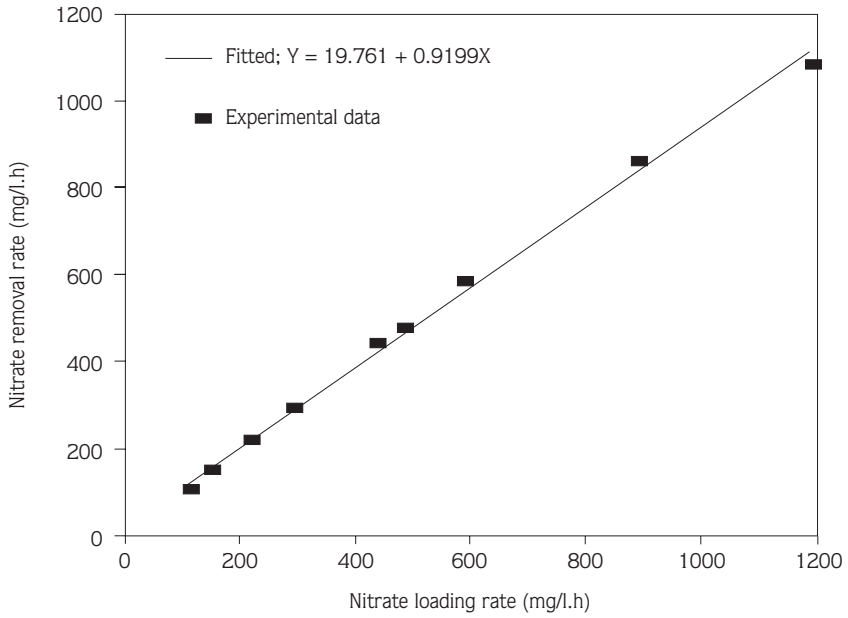

Figure 6. Variation of the nitrate removal rate with the nitrate loading rate for varying the feed solution nitrate concentrations (50-200 ppm) and the flow rates(25.68-273.76 ml h-1) (Y is the nitrate removal rate and X nitrate loading rate.

position conversion decreases with increasing flow rate. Except the highest flow rate being studied, 535.52 ml/h, PNC at the exit from the reactor for all FFRs is below allowed limits. For FFR=25.65 and 34.95 ml h^{-1}, 90% conversion is realised just before the tap position 2, for FFR=51.43 and 112.5 ml h^{-1}, around the tap position 3, for FFR=273.76 ml h^{-1}, just after the tap position 6 and while for FFR=535.52 ml h^{-1}, 90% conversion is never realised. This indicates that for higher FFRs larger reactors are needed to comply with the water standards. The kinetics information calculated using data given in this figure is given Table 2.

Figure 5 shows the variation of total conversion and total nitrate removal rate with nitrate loading rate. Because FNC is constant (200 ppm) for all the data given here this figure represents the effect FFR. Numerical form of the data given in this figure is given in Table 2. As expected nitrate removal rate increases with increasing FFR. The conversion remains constant for FFR≤112.5 but after that it decreases sharply with increasing FFR. The maximum nitrate removal rate, 1517.72 mg l^{-1} h^{-1}, was obtained for FFR=535 ml h^{-1} which is the highest FFR being investigated. For this, as it is seen from table 2, reactor residence time and the dilution rate have been found to be 5.159 minutes and 11.63 h^{-1}, respectively. This figure indicates that one needs to be very careful when designing a reactor. If a high conversion is required, FFR should be kept below a certain limit. But if a high nitrate removal rate is required, higher FFRs should be chosen.

Figure 6 shows the variation of the nitrate removal rate with the nitrate loading rate for varying feed solution nitrate concentrations (50-200 ppm) and flow rates (25.68-273.76 ml h^{-1}). Also shown in this figure is a line and a correlation equation fitted to the experimental data. Numerical form of the data given in this figure is given in Tables 1 and 2. It is clear from the data that nitrate removal rate linearly increases with increasing nitrate load within the range studied.

Conclusions

Denitrification performance of attached growth biofilm of *Paracoccus denitrificans* cells on active carbon in a packed bed vertical reactor system has been investigated as function of FNC and FFR. Conclusions derived from this work may be summarised as follows:

- Up to 200 ppm FNC the present system is able to produce a drinking water with a nitrate content below allowed limits. For a fixed FFR although nitrate removal rate increases with increasing FNC, the quality of the product water becomes poorer.

- Up to FFR=273 ml h^{-1} the present system is also able to produce a drinking water with a nitrate content below allowed limits. But for higher FFR the quality of the product water becomes exceeds the allowed limit level. The nitrate conversion remains constant for FFR≥273 ml h^{-1} but then after it decreases

very sharply with increasing FFR, while nitrate removal rate always increases with increasing FFR.

• The nitrate removal rate has been correlated as function of the nitrate loading rate for a FNC range from 50 to 200 ppm and FFR range from 25.68 to 273.76 ml h^{-1}. The resultant equation was Y=19.761+0.9199X (Y is the nitrate removal rate and X the nitrate loading rate).

• The nitrite content of the product water at the reactor exit was so low that it was undetectable by the present measurement technique.

Nomenclature

C :	Concentration	ppm
D :	Dilution rate	h^{-1}
F :	Feed solution flow rate	ml h^{-1}
L :	Nitrate loading rate	mg l^{-1} h^{-1}
P :	Efficiency	mg l^{-1} h^{-1}
R :	Nitrate removal rate	mg l^{-1} h^{-1}
X :	Conversion	%
Y :	Conversion coefficient	-
τ :	Reactor residence time	h

Subscripts:

in :	Inlet conditions
out :	Outlet conditions
P/S :	Product to substrate
R :	Real
r :	Reactor
T :	Total

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