J. Indian Chem. Soc.,
Vol. 96, December 2019, pp. 1493-1497

Comparative study on denitrification kinetics of nitrified effluent with and without organic carbon by activated sludge process

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Manuscript received online 19 August 2019, revised and accepted 02 December 2019

Denitrification studies were conducted in a lab scale batch activated sludge reactor with and without external organic carbon source using nitrate to biomass ratio of 0.1 and 0.2 at (36±0.5)°C. Kinetic parameters for both cases were evaluated following Monod's approach and compared to understand the impact of organic carbon in dentrification reaction. A comparison of various kinetic parameters showed that half velocity constant and maximum specific nitrate utilization rate in case of studies with methanol as organic carbon were higher than those obtained without organic carbon. Similar trend has been observed for yield coefficient and endogenous decay constant exhibiting greater values for addition of methanol. The values of half velocity constant (K_s) and specific substrate utilisation rate (k) for studies without external carbon source were determined as 4.68 mg/L and 0.280 day^{-1} respectively. When methanol with concentration 1.9 times that of nitrate nitrogen was used, those resulted in a value of 11.69 mg/L and 0.312 day^{-1} respectively. The yield coefficient (Y) for the denitrifying microorganisms from the studies with and without adding external organic carbon was evaluated as 0.143 mg VSS/mg NO_3^--N and 0.121 mg VSS/mg NO_3^--N respectively and decay coefficient (k_d) was evaluated as 0.102 day^{-1} and 0.0687 day^{-1} respectively.

Keywords: Denitrification kinetics, nitrified effluent, activated sludge, kinetic coefficients, methanol addition, endogenous decay.

Introduction

Nitrogen in the form of nitrates present in water concerns with environmental issues including eutrophication which undergoes further conversion to carcinogenic nitrosamines and nitrosamides[1]. Nitrate concentration in wastewater can be economically lowered using biological denitrification[2], which follows anoxic reduction of nitrate to nitrogen gas via nitrite. Biological denitrification of wastewater is usually slow and is recorded to last for several days. Earlier studies undertaken for determination of kinetic coefficients pertaining to dentrification involved presence of organic carbon in the wastewater.

Heterotrophic denitrification requires organic carbon source because the microorganisms utilise nitrate as terminal hydrogen acceptor and carbon is assimilated into the cell[3]. Thus, organic carbon should be supplied externally if not present. In the absence of any organic carbon, endogenous decay of biomass present in the reactor may also contribute to organic carbon requirement[4]. The nature and the amount of the organic substrate used as exogenous carbon source play an important role in the success and cost of denitrification[5]. Methanol is most widely used carbon source (Barth *et al*., 1968; McCarty *et al*., 1969; Grady and Lim, 1981) followed by internal carbon source obtained from endogenous respiration[6].

Comparing the effects of different organic carbon sources on denitrification rate, Mokhayeri *et al*.[7] observed the denitrification rates with acetate and ethanol to be higher than that obtained in case of methanol. The ratio of organic carbon to nitrate nitrogen is often kept between 5 and 10 for efficient denitrification[8]. Methanol consumption (in mg) per mg NO_3^--N reduced to nitrogen gas is theoretically estimated to be 1.91[4], although in practice, the value is observed to be much higher.

For cost-effective and efficient denitrification, an optimal methanol to nitrogen/nitrate ratio seems to be an advantageous parameter under minimal accumulation of nitrite ions[5]. In case of nitrate degradation of wastewater characterized by low carbon and high nitrogen content, successful denitrification requires addition of external organic carbon which in turn increases the treatment cost. In order to understand and quantify the effect of absence of external organic carbon on denitrification rates, kinetic parameters can be compared between the studies with and without organic carbon addition. It is confirmed that the reaction when utilizes endogenous decay as the sole organic carbon source, has slower reaction rates, but the rate is acceptable from process economy point of view[9]. No attempt has yet been taken to express the kinetics of denitrification for wastewaters having low C:N ratio without adding any external carbon source. The present study aims to determine and compare the kinetic coefficients evaluated for denitrification reaction using synthetic wastewater with and without the addition of external organic carbon source.

Experimental

The synthetic nitrified effluent was collected from a biological nitrifying Activated Sludge Reactor, which is under operation in the Environmental Engineering Laboratory of the Civil Engineering Department, IIEST, Shibpur. Several laboratory scale batch denitrification studies were conducted using cylindrical reactors with a working volume of 1 L. Denitrifying biomass was taken from a suspended growth biological system treating synthetic wastewater enriched with NO_3^--N. Synthetic nitrified effluent having initial NO_3^--N concentration in the range of 50–250 mg/L was used, under nitrate to biomass ratio of 0.1 and 0.2 and at pH of 7.5–8.0. Total 20 batch studies were conducted with initial substrate conditions (nitrate concentration) as given in Fig. 1[9]. All the batch studies were continued for 6 h duration and effluent samples were collected at every 30 min interval to monitor MLSS and NO_3^--N concentration. All the chemicals used during the study were of reagent grade. COD was analysed by closed reflux method in model no. WTW CR 3200 and Systronics UV-Vis spectrophotometer 117 was used for determination of nitrate and nitrite.

Nitrate, nitrite, DO and COD concentrations for all batches were monitored periodically complying analytical methods as mentioned in APHA (1995). The kinetic coefficients for denitrification reaction were evaluated following Monod's kinetic equations as under. The growth rate constant for denitrifying organisms can be evaluated as[4]:

$$\mu = \mu_{max} \frac{S}{K_s + S} \tag{1}$$

where, μ_{max} = maximum growth rate constant, h^{-1}, S = nitrate concentration in the solution at a particular time, expressed as mg/L and K_s = half velocity constant, i.e. nitrate concentration at which specific growth rate of denitrifiers equals to half of their maximum specific growth rate, mg/L.

Now, rate of denitrifier's growth can be written as

$$r_g = \frac{dx}{dt} = -Y.\, r_{su}$$

where, Y = growth yield coefficient = fraction of nitrate converted to denitrifiers, expressed as mg/L biomass produced/ mg/L nitrate utilized.

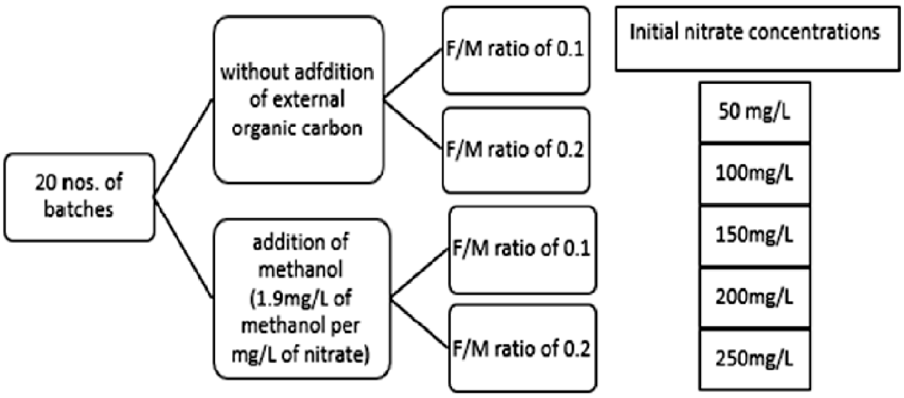

Fig. 1. Scheme of batch studies with various initial nitrate concentrations.

or,

$$\mu X = \frac{(S_0 - S)}{\theta} Y$$

where, S_0 = initial nitrate concentration, mg/L, θ = batch period, day and X = biomass concentration of the denitrifiers.

$$\text{Therefore, } \mu_{max} = \frac{S}{K_s + S} X = \frac{(S_0 - S)}{\theta} Y$$

or,

$$\frac{(S_0 - S)}{\theta . X} = \frac{k.S}{K_s + S}$$

where, k = specific nitrate utilization rate

$$= \frac{\mu_{max}}{Y}, \text{ mg/L}$$

or,

$$\frac{\theta X}{(S_0 - S)} = \frac{K_s}{k} . \frac{1}{S} + \frac{1}{k} \qquad (2)$$

From the results of batch study, the values of $\frac{\theta . X}{(S_0 - S)}$ can be plotted with respect to those of $\frac{1}{S}$ to determine the values of the two important kinetic parameters k and K_s. k is obtained from Y-axis intercept and K_s is calculated from the slope of the curve. As dentrifiers grow, they consume nitrate present in the reactor and their endogenous decay also takes place simultaneously. The endogenous decay is also proportional to denitrifier biomass present in the reactor.

Hence, the net rate of dentrifier biomass growth

$$= Y . \frac{\mu_{max} S X}{K_s + S} - k_d X,$$

k_d = endogenous decay constant, day^{-1}

or,

$$= \frac{(X' - X)/X}{\theta} = \frac{S_0 - S}{X\theta} Y - k_d . \qquad (3)$$

where, X′ = final dentrifier biomass over a batch period θ.

From the results of batch study, the values of $\frac{(X' - X)/X}{\theta}$ can be plotted with respect to those of $\frac{S_0 - S}{X\theta}$ to determine the kinetic parameters Y and k_d. k_d is obtained from Y-axis intercept and Y is determined from the slope of the curve.

Results and discussion

The batch studies performed by varying initial nitrate concentration shows better removal in terms of nitrate nitrogen for those with methanol than the studies without external organic carbon source when all other experimental parameters were kept constant. The percentage removal of NO_3^--N for each of the batch studies are presented in Table 1. It is quite predictable that denitrification would be higher in presence of methanol, an external organic carbon source. It is to note from the experimental data that initial nitrate concentration also affects the removal efficiency apart from the concentra-

Table 1. Percentage removal of nitrate nitrogen (NO_3^--N) under batch studies

Organic carbon source	Nitrate to biomass ratio	Initial nitrate (NO_3^--N) concentration (mg/L)	Percentage removal of NO_3^--N
No external organic carbon	0.1	50	54.1
		100	29.8
		150	34.9
		200	37.3
		250	28.6
	0.2	50	15.8
		100	10.7
		150	17.7
		200	10.4
		250	10.9
Methanol as organic carbon	0.1	50	91.7
		100	53.0
		150	44.8
		200	39.7
		250	37.5
	0.2	50	86.6
		100	52.4
		150	40.1
		200	32.9
		250	37.0

tion of organic carbon and the relationship is not linear. Often an increasing F/M ratio is detrimental to the efficiency of nitrogen removal and may also cause elevated BOD in the effluent[6]. As reported by Dold *et al.*[10], improved growth rate for denitrifiers can be obtained by decreasing the amount of initial biomass concentration. It is observed that percentage removal of NO_3^--N decreases with the increase in influent concentration for a specific nitrate to biomass ratio, which is quite expected. It also decreases with the increase in nitrate to biomass ratio for any specific influent NO_3^--N concentration. There is considerable increase in percentage removal of NO_3^--N for addition of methanol as a source of organic carbon, but the extent of increase is marginal under high concentration of NO_3^--N. In case of no addition of methanol, the percentage removal of NO_3^--N is extremely low under nitrate to biomass ratio 0.2, especially for higher initial NO_3^--N concentration.

The kinetic parameters were evaluated based on Monod's growth kinetics for denitrification reactions without and with organic carbon. The results are shown in Figs. 2a, 2b, 3a and 3b respectively. From the figures, the values of half velocity constant (K_s) and specific substrate utilisation rate (k) were determined as 4.68 mg/L and 0.280 day^{-1}, respectively for the studies conducted without using any external carbon source. Those kinetic constants yielded a value of 11.69 mg/L and 0.312 day^{-1}, respectively from the batch studies conducted using methanol with concentrations 1.9 times the concentration of nitrate nitrogen. The yield coefficient (Y) for

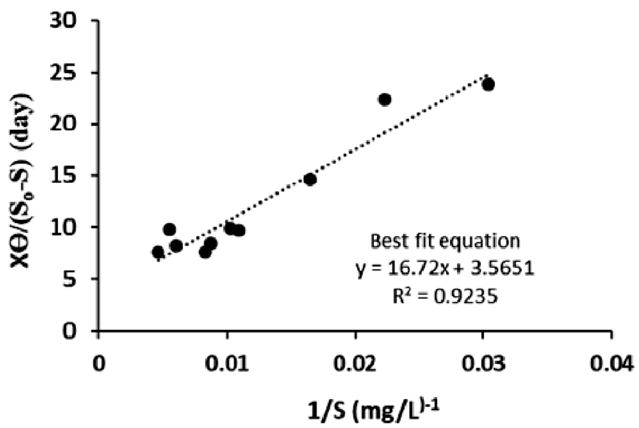

Fig. 2a. Determination of K_s and k for studies without external organic carbon.

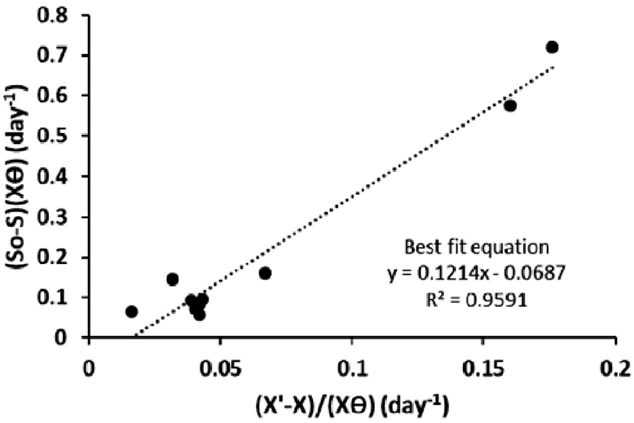

Fig. 2b. Determination of Y and k_d for studies without external organic carbon.

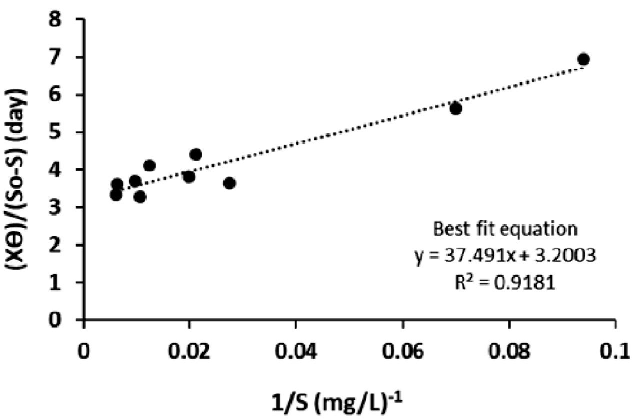

Fig. 3a. Determination of K_s and k for studies with methanol as organic carbon.

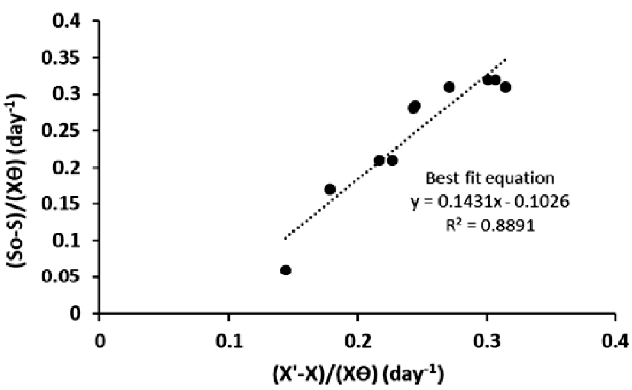

Fig. 3b. Determination of Y and k_d for studies with methanol as organic carbon.

the denitrifying microorganisms from the studies without addition of any external organic carbon was evaluated as 0.121 mg VSS/mg NO_3^--N and decay coefficient (k_d) was evaluated as 0.0687 day^{-1}. From the studies using methanol, the values of these coefficients were evaluated as 0.143 mg VSS/mg NO_3^--N and 0.102 day^{-1} respectively.

Moore and Schroeder[11] reported that the yield coefficient of cell growth for denitrification with methanol to nitrate ratio 10 was 0.55. In the present study the yield coefficient is calculated as 0.121 and 0.143 for without methanol and with methanol respectively. The values of yield coefficient are in lower side due to the fact that methanol addition was only 1.9 times of the influent nitrate concentration. The half saturation constant for the present study with methanol was found to be more than that without external organic carbon. The half saturation constants reflected the magnitude of the DO and nitrogen concentrations required to create the driving force for mass diffusion. All the half-saturation constants are observed to be considerably higher than that reported by Moore and Schroeder[11]. This gross variation may be attributed to the fact that high rate of denitrification occurred on account of significant addition of methanol in the tune of 10 times of nitrate. The endogenous decay coefficient increased with the addition of methanol in the present study although its value is not at par with that reported by Moore and Schroeder[11]. In their study the endogenous decay coefficient was observed to be about 3 times of that in case of methanol addition in the present study. This high magnitude of endogenous decay coefficient is presumably due to considerable denitrifying biomass growth by virtue of significant addition of methanol. Hence, the results obtained from the present study are found to marginally corroborate with the data as obtained from a typical study on dentrification.

Conclusions

Experimental data obtained from batch denitrification studies with and without external organic carbon was used to determine the kinetic coefficients as per Monod's approach. The values of half velocity constant (K_s) and specific substrate utilisation rate (k) were determined as 4.68 mg/L and 0.280 day^{-1}, respectively for studies without using external carbon source. Those kinetic constants resulted in the value of 11.69 mg/L and 0.312 day^{-1}, respectively when methanol with dosage 1.9 times the concentration of nitrate nitrogen was added. The yield coefficient (Y) and endogenous decay coefficient (k_d) for the denitrifying microorganisms from the study without adding external organic carbon was evaluated as 0.121 mg VSS/mg NO_3^--N 0.0687 day^{-1}. From the studies using methanol, the values of these coefficients were evaluated as 0.143 mg VSS/mg NO_3^--N and 0.102 day^{-1} respectively. Although addition of methanol enhances the rate of dentrification, it can also be accomplished partially by adopting low nitrate to biomass ratio, in turn by increasing the biomass concentration for a given amount of nitrate concentration.

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