Influence of temperature on denitrification of an industrial high-strength nitrogen wastewater in a two-sludge system

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Abstract

The temperature effect on denitrification rate of a two-sludge system has been studied. An industrial high-strength wastewater and an industrial by-product containing mainly methanol, as external carbon source, were used in this study. The maximum denitrification rate (MDR) was determined at six different temperatures: 6, 8, 10, 15, 20 and 25ºC in batch mode. The temperature coefficient was found to be 1.10 ± 0.01 at temperatures between 10 to 25ºC and 1.37 ± 0.01 at temperatures between 6 to 10ºC. The MDR obtained in the two-sludge system (0.28 mg N·mg VSS^{-1}·d^{-1} at 25ºC) was higher than the one obtained in a single-sludge system with a similar external carbon source. The COD/N ratio required for complete denitrification in the two-sludge system was approximately stoichiometric, which is 3.7 ± 0.9 mg COD·mg N^{-1}.

Introduction

Generally, an excess of nitrates in water is related to public health diseases like methemoglobinemia and carcinogenesis. Therefore, drinking water should not contain more than 10 mg NO_3^--N·ℓ^{-1} (EPA, 1993). For this reason, the removal of nitrates from wastewater is necessary. There are three main methods to remove nitrates from wastewater: ion exchange, reverse osmosis and biological denitrification. Ion exchange is limited due to the lack of resins with high selectivity for nitrate and the problem of regenerating them. The problem of reverse osmosis is low selectivity of the membranes used for nitrate. Due to these limitations for removal of nitrates from industrial wastewater, the most versatile and widely used technology is biological denitrification (Mateju et al., 1992).

The bacteria responsible for the denitrification are classified as facultative heterotrophs and are able to use nitrate as an acceptor of electrons, transforming it into nitrogen gas. During the process, electrons are transferred from a donor, normally an organic substrate, to an acceptor, nitrate or nitrite. Practically any organic compound that can be biologically degraded under aerobic conditions can be used for denitrification. However, denitrification rates will be different depending on the organic compound used.

Denitrification is determined by the stoichiometric ratio between the organic compound used and the nitrate. Industrial wastewater may not offer the appropriate COD/N ratio for carrying out the denitrification process. In order to treat industrial wastewater with a low COD/N ratio it is necessary to add an external organic carbon source. Different external carbon sources are used for denitrification: glucose (Chevron et al., 1997), saccharose (Sison et al., 1995), acetic acid (Oh and Silverstein, 1999), lactic acid (Akunna et al., 1993), ethanol (Hasselblad and Hallin, 1998; Nyberg et al., 1996) and methanol (Bailey et al., 1998; Bilanovic et al., 1999).

Different criteria have been used to choose a specific external carbon source for the denitrification process. First, it is necessary to consider which carbon compound yields the fastest denitrification rate. Published references give conflicting results. Some authors suggest that acetic acid achieves greater rate than glucose, methanol or ethanol (Constantin and Fick, 1997). However, other authors showed similar results with denitrification on acetic acid to those achieved with methanol (Nyberg et al., 1992). Several references indicate that ethanol reaches higher rate than methanol (Andersson et al., 1998; Christensson et al., 1994), although another study indicates that the rate with methanol is greater than that with ethanol (Henze, 1991).

It is also necessary to consider the costs and availability of the external carbon source. If the source is a pure chemical compound (ethanol, methanol, acetic acid), it will be available at a market price. An alternative is to use a by-product as the carbon source, for example the sludge produced in the process. However, the organic matter coming from the sludge is not very biodegradable and therefore a previous chemical or thermal hydrolysis is required. This procedure adds extra cost to the process (Barlindhaug and Odegaard, 1996).

To build an industrial scale denitrification plant, the external carbon source should be cheap and available to guarantee the continuous operation of the wastewater treatment plant. These requirements can be achieved using industrial by-products. In the present study, the feasibility to use a by-product as an external carbon source for the denitrification process was evaluated. This by-product is mainly methanol and the rest is acetone and isopropilic alcohol.

The temperature effect on the denitrification rate is another important feature in the design of a denitrification process. This effect is commonly described using an Arrhenius-type equation (Orhon et al., 2000):

$$r_{D,T1} = r_{D,T2} \cdot \theta^{(T1-T2)} \qquad (1)$$

where:

$r_{D,Ti}$ = denitrification rate at temperature *Ti*,
    mg N-NO_3^-·mg VSS^{-1}·d^{-1}
θ = temperature coefficient

The interest in this topic is reflected in the number of published results on the determination of the effect of temperature on the

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TABLE 1				
Temperature coefficients for different systems				
Temperature coefficient	Technology	Carbon source	Range of temperatures (ºC)	Reference
$\dfrac{1.06}{1.06}$	Single-sludge	$\dfrac{\text{Methanol}}{\text{Ethanol}}$	7-17	Nyberg et al. (1996)
1.06	Single-sludge	Hydrolysed sludge	-	Barlindhaug and Odegaard (1996)
1.06 1.30	Single-sludge	-	7-15 2-7	Oleszkiewicz and Berquist (1988)
$\dfrac{1.11}{1.12}$	Denitrifying pure culture	$\dfrac{\text{Methanol}}{\text{Ethanol}}$	15-25	Christensson et al. (1994)
1.13	Denitrifying pure culture	Methanol	6-30	Timmermans and Van Haute (1983)

TABLE 2	
Composition of industrial wastewater after the nitrification process	
Component	Concentration (mg·ℓ^{-1})
COD	0
N-NO$_3^-$	700-1 900
N-NH$_4^+$	0-10
F$^-$	10-20
Cl$^-$	1 000-1 500
SO$_4^{2-}$	5 000-10 000

denitrification process. In Table 1 some of the different references are summarized but the results are mainly for single-sludge systems or pure denitrifying cultures. There is a lack of data on temperature coefficients for a two-sludge system. This paper focuses on the determination of temperature coefficients of a two-sludge system using a wide range of temperatures.

Experimental

Biomass and two-sludge system

The denitrifying biomass comes from a two-sludge pilot plant with separate nitrification and denitrification stages. The industrial wastewater, with 5 000 mg N-NH$_4^+$·ℓ^{-1}, is fed into the nitrification stage, which is made up of a 27 ℓ aerobic reactor and a settler. Each mechanical unit of the pilot-plant (pumps, level detectors, etc.) is controlled by a PC through a data acquisition card that allows automation of all those elements. Every reactor has in-line sensors (dissolved oxygen (DO), pH, ORP, temperature) connected to probe controllers. The effluent of the nitrification stage and the external carbon source form the influents for the denitrification stage. The external carbon source is needed to denitrify the entire nitrate that has been formed. The denitrification stage is made up of a 27 ℓ anoxic reactor; a 15 ℓ aerated tank and a settler. The nitrogen gas formed in the anoxic reactor is stripped in the aerated tank, enhancing the sedimentation in the settler.

The effect of temperature on the denitrification rate was studied in batch using biomass sampled from the denitrification system of the pilot plant. Prior to this study, the pilot plant was run on the external carbon source for more than 150 d and the biomass was therefore adapted to it (Carrera, 2001).

Industrial wastewater

Table 2 shows the basic composition of the industrial wastewater entering the denitrification stage. As can be seen, the nitrate concentration is 700 to 1 900 mg N-NO$_3^-$·ℓ^{-1} and the ammonium concentration is 0 to 10 mg N-NH$_4^+$·ℓ^{-1}. The industrial wastewater contains high concentrations of chloride and sulphate and does not contain organic matter.

External carbon source

A by-product of an industrial process was used as an external carbon source. The by-product is discharge from a chemical plant, made up of a mixture of methanol, isopropilic alcohol and acetone. The percentage composition is: 60% methanol, 10% acetone, 10% isopropilic alcohol and 20% water. Throughout this study, this by-product is referred to as the 'methanol mixture'.

Laboratory equipment

The batch experiments were done using a Braun Biostat®-Q fermentor unit. Figure 1 shows a diagram of the laboratory equipment. This equipment consists of four 0.5 ℓ reactors. Each reactor has an independent system for control and measurement of temperature, pH, stirring and dissolved oxygen (DO). An external refrigeration system was used to obtain temperatures below 15ºC.

Experimental procedure

The maximum denitrification rate (MDR) was evaluated with six experiments at different temperatures: 6, 8, 10, 15, 20 and 25ºC. Four batch runs were carried out at each temperature (Table 3). The duration of each run was 24 h and pH was maintained between 8.0 and 8.5. The biomass of the Biostat®-Q was replaced with fresh biomass from the denitrifying reactor of the pilot plant in each experiment. The runs were operated with no organic matter or nitrate limitations. Nitrate, COD and VSS concentrations were measured at the end of each run. The nitrite concentration was measured twice in each run to ensure that there was no accumulation. The concentration of nitrite was practically zero in all the runs. The MDR of each run was calculated as:

$$MDR = \frac{\left[N - NO_3^-\right]_{0h} - \left[N - NO_3^-\right]_{24h}}{\left[VSS\right]_{average}} \qquad (2)$$

Analytical methods

The analyses of volatile suspended solids (VSS) were done using

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the methodology described in *Standard Methods* (1995). The analyses of nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) were done by capillary electrophoresis using a WATERS Quanta 4000E CE. The electrolyte used was a WATERS commercial solution. The conditions of the analysis were: temperature of 20°C, 15 kV from a negative source, indirect UV detection at 254 nm and 5 min of retention time.

Results and discussion

Table 3 shows the results of the four runs carried out at each temperature. The range of denitrification rate varied between 0.28 mg N·mg VSS^{-1}·d^{-1} at 25°C to 0.02 mg N·mg VSS^{-1}·d^{-1} at 6°C. These denitrification rates were compared to published results obtained with methanol as external carbon source and are presented in Table 4. The range of denitrification rates in the literature is quite large but all the results, except the pure cultures, are lower than the ones obtained in this study.

The experimental value of the COD/N ratio consumed was calculated as:

$$\frac{COD}{N} = \frac{[COD]_{0h} - [COD]_{24h}}{[N-NO_3^-]_{0h} - [N-NO_3^-]_{24h}} \qquad (3)$$

Figure 1
Diagram of the laboratory equipment

The average value was 3.7 ± 0.9 mg COD·mg N^{-1}. This is close to the stoichiometric ratio proposed for the denitrification process using methanol as carbon source (EPA, 1993; Mateju et al. 1992); although this carbon source is not pure methanol, but a mixture of methanol, acetone and isopropilic alcohol. Nevertheless, other authors found higher experimental denitrification ratios with methanol: 4.6 mg COD·mg N^{-1} (Bilanovic et al., 1999) or 4.45 mg COD·mg N^{-1} (Christensson et al., 1994).

Figure 2 shows the experimental data at six different temperatures and the line of the best fit for the Arrhenius-type equation for the MDR. The influence of temperature depends on the interval of temperatures. The temperature coefficient is 1.10 ± 0.01 between 10 to 25°C, while the coefficient is 1.37 ± 0.01 between 6 to 10°C.

The temperature coefficient for a single-sludge system is generally 1.06 in a range of temperatures from 7 to 17 °C and does not depend upon 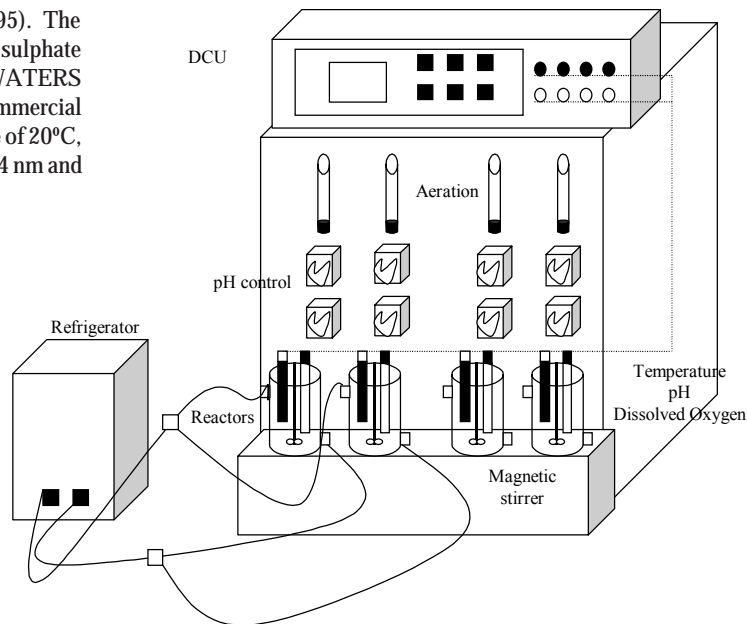the carbon source used (Table 1). On the other hand, the temperature coefficient for systems with pure denitrifying biomass is 1.13 for a range of temperature between 6 to 30°C. Once again, this does not depend upon the carbon source used (Table 1). These values indicate that the effect of temperature on denitrification is more pronounced with pure microbial populations.

The coefficient found by this study for a range of temperatures from 10 to 25°C is closer to the values obtained in systems with pure denitrifying biomass. The coefficient found for temperatures between 6 and 10°C is 1.37, slightly higher than the one given by Oleszkiewicz and Berquist (1988) in a single-sludge system for a range of temperatures from 2 to 7°C. For Oleszkiewicz and Berquist, the change in the temperature coefficient value occurs around 7°C. In this study, this change occurs around 10°C (Fig. 2).

The effect of temperature on the denitrification rate is important in the design of denitrifying reactors. For example, in denitrifying reactors for the treatment of industrial wastewaters, the hydraulic retention time (HRT) will be a function of the nitrogen removed,

TABLE 4				
Maximum denitrification rates with methanol as carbon source				
Technology	**Process**	**Tempera-ture(ºC)**	**MDR (mgN·mgVSS^{-1}·d^{-1})**	**Reference**
Single-sludge	Continuous	-	0.03	Bailey et al. (1998)
Single-sludge	Continuous	12	0.06	Nyberg et al. (1992)
Single-sludge	Continuous	-	0.06	Kang et al. (1992)
Single-sludge	Continuous	30	0.14	Teichgräber and Stein (1994)
Two-sludge	Batch	23 ± 3	0.13	Bilanovic (1999)
Two-sludge	Feedbatch	22 ± 2	0.16	Doyle et al. (2001)
Two-sludge	Batch	20 ± 0.5	0.18	This study
		25 ± 0.5	0.28	
Denitrifying pure culture	Batch	25	1.3	Timmermans and Van Haute (1983)
Denitrifying pure culture	Batch	25	2.2	Christensson et al. (1994)

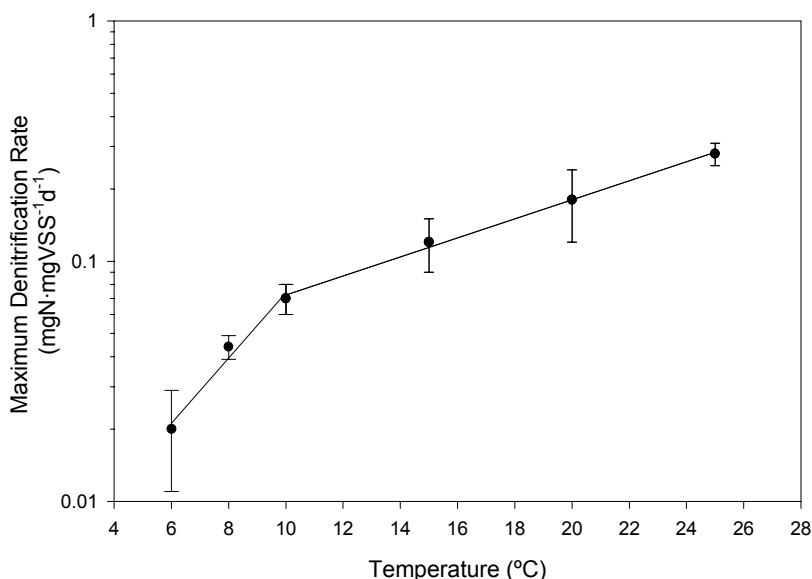| TABLE 3 Batch runs to determine the MDR at six different temperatures							
Temperature (°C)	[N-NO$_3^-$] (mg·ℓ^{-1})		COD (mg·ℓ^{-1})		VSS$_{average}$ (mg·ℓ^{-1})	MDR	MDR$_{average}$
	time		time			(mgN·mgVSS^{-1}·d^{-1})	
	0 h	24 h	0 h	24 h			
25 ± 0.5	1 140	160	4 010	1 130	3 600	0.272	0.28 ± 0.03
	1 050	180	4 370	1 500	3 600	0.242	
	1 760	470	5 830	1 870	4 000	0.323	
	1 400	300	5 530	2 200	4 000	0.275	
20 ± 0.5	1 320	110	4 420	1 030	4 600	0.263	0.18 ± 0.06
	1 880	1 400	6 950	5 570	4 100	0.117	
	1 360	720	4 490	2 740	4 300	0.149	
	1 400	560	6 570	3 760	4 300	0.195	
15 ± 0.5	1 030	530	4 580	2 470	4 000	0.125	0.12 ± 0.03
	1 160	550	5 050	2 750	4 000	0.153	
	1 140	580	5 430	3 380	4 000	0.140	
	950	620	3 990	2 740	4 100	0.080	
10 ± 0.5	1 000	780	5 150	4 370	3 200	0.069	0.07 ± 0.01
	1 090	840	5 080	4 110	3 600	0.069	
	780	490	4 370	3 010	3 300	0.088	
	840	610	4 110	3 020	3 800	0.061	
8 ± 0.5	1 060	840	4 240	3 400	4 400	0.050	0.044 ± 0.005
	710	520	4 580	3 840	4 800	0.040	
	680	480	3 870	3 070	4 900	0.041	
	933	720	4 190	3 420	4 500	0.047	
6 ± 0.5	1 210	1 170	6 140	5 890	4 700	0.009	0.020 ± 0.009
	1 350	1 210	7 000	6 240	4 600	0.030	
	990	920	5 630	5 470	4 300	0.016	
	1 090	990	6 970	6 630	4 300	0.023	

Figure 2
Effect of temperature on the denitrification rate

the biomass concentration and the denitrification rate at the design temperature:

$$HRT = \frac{\left[N - NO_3^- \right]_{removed}}{\left[VSS \right]_{reactor} \cdot r_{D,T}} \qquad (4)$$

where:

HRT = hydraulic retention time, days
$r_{D,T}$ = denitrification rate at temperature of design, mg N-NO$_3^-$·mg VSS^{-1}·d^{-1}

The correlation between the HRT and the temperature can be represented by a decay exponential function ($r^2 = 0.99$) as shows the figure 3 (assuming that the removed nitrate concentration is 1 000 mg N-NO$_3^-$·ℓ^{-1}, the denitrification rate is not limited by substrate and the biomass concentration in the reactor is 4 000 mg VSS·ℓ^{-1}). The dependency of HRT on the temperature is represented by Eq. 5:

Figure 3
Effect of the temperature on the HRT
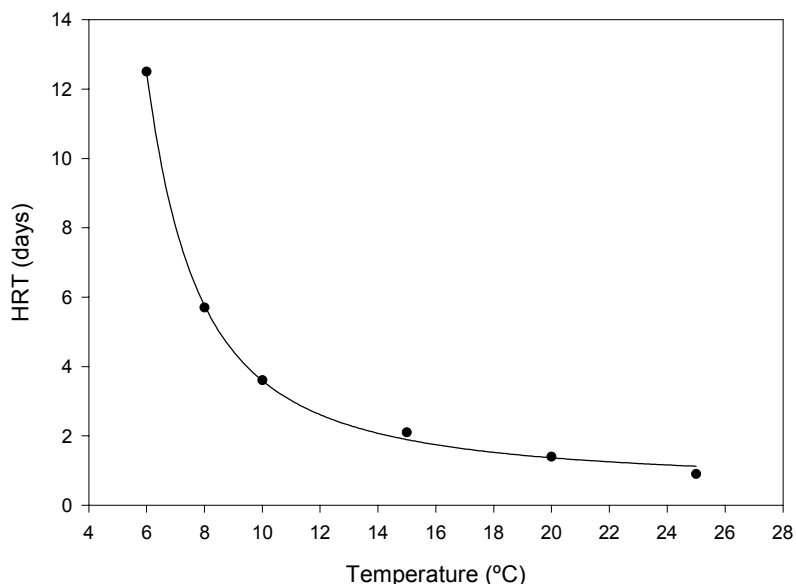
$$HRT = 0.51 \cdot e^{\left(\frac{20.2}{T+0.29}\right)} \qquad (5)$$

where:

T = temperature (^{o}C)

The predicted HRT is 11 times higher at 6°C than 25°C and 3 times higher at 10°C than 25°C. These results indicate the significance of the determination of the minimum temperature on the design of the denitrifying stage of a two-sludge system.

Conclusions

The denitrification rates obtained with the two-sludge system studied are higher than those found in the literature for single-sludge and two-sludge systems using a similar carbon source.
The temperature has an important effect on the denitrification rate of a two-sludge system. The temperature coefficient is 1.10 for the range of temperatures between 10 to 25°C and 1.37 for the range between 6 to 10°C.

Acknowledgements

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