ELSEVIER

Biological nitrate removal from wastewater of a metal-finishing industry

Carmen Gabaldón, Marta Izquierdo, Vicente Martínez-Soria, Paula Marzal,
Josep-Manuel Penya-roja*, F. Javier Alvarez-Hornos

Department of Chemical Engineering, University of Valencia, Dr. Moliner, 50, 46100 Burjassot, Spain

Abstract

An upflow packed bed reactor at laboratory scale has been operated for a continuous period of 5 months to investigate the technical feasibility of biological nitrate removal applied to the effluent of the coagulation–sedimentation wastewater of a metal-finishing industry. The reactor was fed with industrial wastewater in a five-fold dilution to reproduce the global spill in the factory (20/80, industrial wastewater/domestic wastewater) with a concentration of nitrate between 141 and 210 $g\ NO_3$-N/m^3. Methanol was added as a carbon source for denitrification. Inlet flow rate was progressively increased from 9 to 40 L/day (nitrogen input load from 45 to 250 $g\ NO_3$-$N/(m^3\ h)$). The highest observed denitrification rate was 135 $g\ NO_3$-$N/(m^3\ h)$ at a nitrate load of 250 $g\ NO_3$-$N/(m^3\ h)$, and removal efficiencies higher than 90% were obtained for loads up to 100 $g\ NO_3$-$N/(m^3\ h)$. A mass relation between COD consumed and NO_3-N removed around 3.31 was observed. Better results were achieved in a previous stage using tap water with nitrate added as a sole pollutant as a synthetic feed (critical load of 130 $g\ NO_3$-$N/(m^3\ h)$ and denitrification rate of 200 $g\ NO_3$-$N/(m^3\ h)$ at a nitrate load of 250 $g\ NO_3$-$N/(m^3\ h)$). This fact could indicate that the chemical composition of the industrial source hinders to some extent the performance of the biological process. Whatever case, results demonstrated the viability of the denitrification process for the global industrial wastewater. A simple model based on Monod kinetics for substrate consumption, and constant biomass concentration was applied to model the industrial wastewater treatment, and a reasonably good fitting was obtained.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Biological nitrate removal; Denitrification; Metal-finishing process; Industrial wastewater; Fixed-bed biological reactor

1. Introduction

Industrial wastewater from metal-finishing processes contains heavy metals and cyanide as main toxic compounds. Conventional treatments used to remove these hazardous materials include physical–chemical methods such as cyanide oxidation, reduction of hexavalent chromium, and coagulation–flocculation followed by sedimentation for heavy metals removal. In some metal surface-finishing industries, the acid pickling step generates high levels of nitrate and/or sulphate which increase the conductivity values of the wastewater streams. As nitrate and sulphate are very high soluble substances, they cannot be removed by conventional physical–chemical treatments. Nitrogen discharge to ponds and lakes could contribute to enhance the eutrophication process, so many regions

including EU countries, have developed restricted regulations for nitrogen concentration in wastewater effluents.

Among several non-biological available methods, selective inorganic ion exchangers can be used to remove nitrate ions from metal-finishing wastewaters, but this technique is expensive and generates a saline waste from resin regeneration which becomes difficult to dispose of. By other side, biological methods are low cost and non-generating hazardous residues. Nitrogen removal via biological nitrification–denitrification processes are usually applied for municipal wastewater treatment with a high number of world-wide applications [1].

In the last decade, studies on biological nitrogen removal using synthetic wastewater to simulate industrial discharges have been performed in order to evaluate the potential application of the nitrification–denitrification process to industrial wastewaters [2], but few studies focused on real industrial wastewater have been published in the metal-processing industry. Schuch et al. [3] and Buchhesiter et al. [4] operated a pilot plant for nitrification and denitrification of different industrial

wastewater streams from a metal working industry, obtaining that released ammonia from ethanolamines of the permeate in the denitrification stage could only be nitrified during aerobic treatment if it was co-treated together with a non-toxic wastewater stream from other sources in the factory. These authors also showed that a complete biological nitrogen removal of an industrial wastewater with high amount of nitrate and without carbon sources for biological degradation, could be achieved just by mixing it with other wastewater streams with enough amount of biodegradable carbon [4]. Hirata et al. [5] reported a maximum nitrogen volumetric rate of 0.24 kg NO_3-N/(m^3 day) (10 g NO_3-N/(m^3 h)) by using an anaerobic aerobic circulating bioreactor system to remove ammonia and nitrate from two- to five-fold diluted industrial wastewater discharged from metal recovery processes. Kasia et al. [6] used an aerobic continuously stirred tank reactor for nitrification followed by upflow gravel packed column for denitrification applied to a wastewater generated by a metal refining company. They have obtained high ammonia removal efficiencies (up to 89%), but the nitrate removal (maximum 15% removal efficiency) did not meet the expectations previously projected by Koren et al. [2] using synthetic wastewater. The failure of denitrification was explained on the basis of the used carbon source, a sewage that contained a variety of unknown substances including surfactants that could have inhibited the biological process.

Typical volumetric NO_3-N loadings for upflow denitrification filters are in the range from 3.0 to 4.0 kg NO_3-N/(m^3 day) (125–167 g NO_3-N/(m^3 h)) to achieve effluent concentrations below 5.0 g NO_3-N/m^3 [7]. Municipal wastewater contains sufficient carbon and phosphorous as nutrients, but some industrial wastewaters often do not. For the wastewater of low C/N ratio, organic compounds such as methanol have to be added to the system. Typical C/N ratio values reported are ranged between 3.7 [8] and 4.5–5.3 g COD/g NO_3-N [1].

The purpose of this study is to investigate the technical feasibility of an upflow packed bed for biological nitrate removal applied to the effluent of the coagulation–sedimentation wastewater plant of a metal-finishing industry. Furthermore, operation conditions such as nitrate loading, empty bed residence time and carbon source requirements have been enclosed in order to achieve effluent NO_3-N concentrations below 20 g/m^3, which have been established as the local discharge regulation. To reveal possible inhibition associated with the industrial wastewater composition (heavy metals, salinity and surfactants) a preliminary study using a synthetic wastewater containing nitrate as sole pollutant was performed.

2. Materials and methods

2.1. Experimental system

A methacrylate column with a total height of 45 cm and an internal diameter of 6.2 cm has been used as reactor followed by a 1-L sedimentation tank. The column was filled with 42.5-cm depth of nylon rings (4- to 6-mm of height, 5.9-mm internal diameter and 7.8-mm external diameter). The specific surface area of the packed material was 530 m^2/m^3.

2.2. Characteristics of wastewater

The studied metal processing industry manufactures faucets and metal fittings. Manufacturing process includes a sulfo-nitric acid pickling unit generating wastewater, which is discharged to the coagulation–sedimentation plant along with the others industrial spills to remove heavy metals. The coagulation–sedimentation process includes a metal hydroxide precipitation at basic pH conditions, a separation of clarified wastewater and a final pH neutralization step (effluent pH around 8.0). Besides, another wastewater source is generated in the factory related to grey water and black water production, which could be considered as domestic wastewater. Both effluents are discharged in conjunction to the municipal sewer, with a contribution of about 20/80 for the industrial/domestic sources. The characteristics of the industrial and the global wastewater discharge are shown in Table 1. Industrial wastewater contains high concentrations of ions such as nitrate, sulphate, sodium, as well as several metal ions such as copper, lead and zinc. Main problem associated to this final effluent is related to the high nitrate concentration as local regulation has recently imposed 20 g/m^3 NO_3-N as maximum average concentration for discharges to the municipal sewer. By other hand, industrial and domestic wastewaters co-treatment could facilitate the nitrogen removal as the domestic spill can be used as a carbon source, and can reduce the possible inhibitory effects due to the high salinity or to the heavy metal concentrations associated to the industrial wastewater.

2.3. Operation conditions

Experiments were carried out in two phases. In the first stage, tests were designed to evaluate the process behaviour (maximum nitrate loading, transient responses, etc.) in absence of inhibitory effects due to the presence of toxic compounds. For this purpose, tap water matrix including nitrate as sole pollutant was used as synthetic feed. Phosphate was supplied

Table 1
Characteristics of the industrial wastewater and the global discharge of the metal-finishing industry

Parameter	Industrial source	Global effluent
Average flowrate (m^3/day)	2.8	13.9–14.5
pH	7.8–8.4	7.2–8.0
Conductivity (mS/cm)	7.78–9.42	2.0–2.8
COD (g/m^3)	75–115	210–320
BOD_5 (g/m^3)	10–30	105–130
NO_3-N (g/m^3)	700–1000	125–220
SO_4^{2-} (g/m^3)	6500–7500	1420
PO_4-P (g/m^3)	<0.02	3.1–3.8
Cd (g/m^3)	n.d.	0.02–0.06
Cr^{3+} (g/m^3)	<0.05	<0.05
Cu (g/m^3)	2.53–6.97	1.06–1.51
Ni (g/m^3)	0.21–0.92	0.03–0.13
Pb (g/m^3)	n.d.	0.1–0.12
Zn (g/m^3)	3.50–9.56	0.65–2.13
CN (g/m^3)	n.d.	<0.02

n.d.: not determined.

to avoid nutrient limitations (0.022 P/COD mass ratio) and methanol was added as the biodegradable organic source. The average COD/NO$_3$-N mass ratio was selected as 3.7 [8]. The pH was adjusted around 7.0. Prior to operation, inoculation of the reactor was performed by pumping 2 L of a settled activated sludge coming from the anoxic suspended growth reactor of a nitrification–denitrification municipal wastewater treatment plant. The system was operated at a constant flow rate of 24 L/day (1.28 h hydraulic empty bed retention time) for a total period of 6 weeks. Three increasing inlet nitrate loads were applied, with conductivity values varying from 2.0 to 3.0 mS/cm.

In the second stage, the treatment of the real industrial effluent has been evaluated for a 4-month period to determine the technical feasibility of the process and the optimum operation conditions. All experiments were performed by using as feed a five-fold diluted industrial effluent in tap water to simulate similar physical–chemical characteristics related to toxic compounds and salinity than those involved to apply the denitrification process to the industrial effluent in conjunction with the domestic wastewater of the factory. This situation corresponds to treat directly the global discharge of the industrial site. Phosphate as major nutrient and methanol as the biodegradable organic source were added to the influent by using similar ratios to those of the synthetic wastewater. The pH was adjusted around 7.0. Conductivity values were in the range of 2.5–2.9 mS/cm. The influent was pumped in upflow mode at rates of 9–40 L/day, resulting in a range of 0.8–3.5 h of hydraulic empty bed retention time.

2.4. Analytical methods

Samples were filtered before water quality measurements. Conductivity, pH, alkalinity and phosphate concentration were determined according to the Standard Methods for Examination of Water and Wastewater [9]. Nitrate and COD concentrations in the influent and effluent were measured using test kits. The kits used were Merck Spectroquant kits 14773 (nitrate) and 14539 (COD).

3. Results and discussion

3.1. Stage 1: synthetic wastewater

The time course of the denitrification process for the synthetic wastewater is shown in Fig. 1, where the step variation of the influent and the effluent concentrations for NO$_3$-N and COD, along with the removal efficiencies at a constant flow rate of 24 L/day can be observed. Influent and effluent pHs are also shown.

The effect of nitrate load was studied by changing the influent nitrate concentration step by step from about 100 to 400 g NO$_3$-N/m^3. The nitrate levels in the effluent were high for the first 8 days, and gradually decreased until day 12 when then nitrate reached levels below 20 g NO$_3$-N/m^3. This period corresponds to the biomass acclimatization period and the biofilm's growth around the packed material. From day 11, nitrate removal efficiencies stayed in values higher than 80%, but at day 22, removal efficiency decreased below 80% with deterioration in the qual-
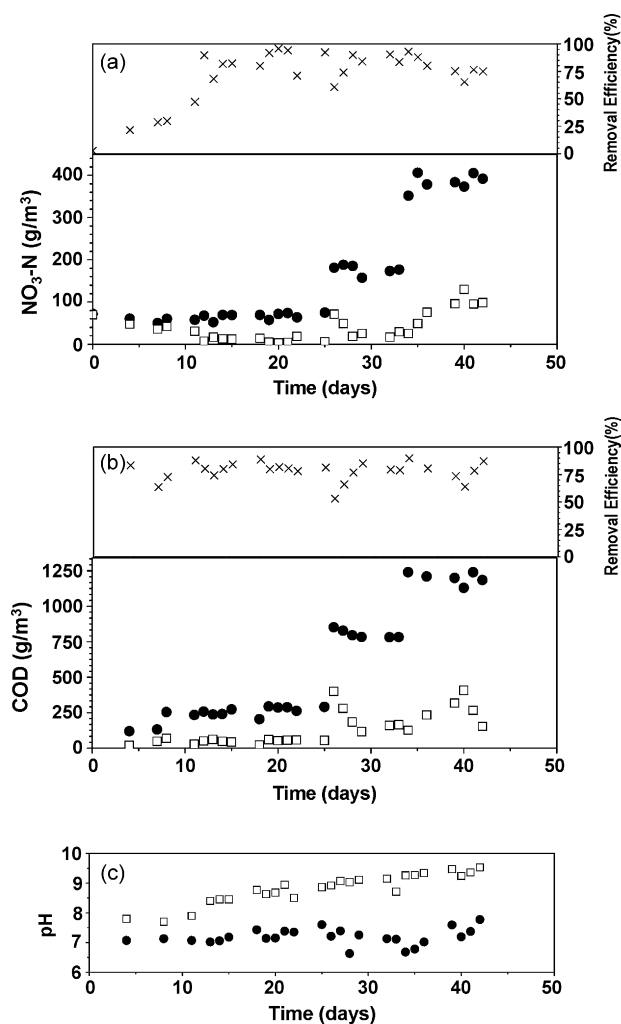

Fig. 1. Continuous denitrification of synthetic wastewater at a constant flow rate of 24 L/day. (●) Influent concentration; (□) effluent concentration; (×) removal efficiency: (a) NO$_3$-N; (b) COD; (c) influent (●) and (□) effluent pH.

ity effluent. This phenomenon was accompanied by an increase in the pressure drop up to 2 m H$_2$O m^{-1} (19.6 kPa m^{-1}) indicating an excessive biomass accumulation, so the filter material was removed and washed. On restoration of the operation, removal efficiency was recovered. In order to avoid this problem, a wash procedure was carried out once a week: a high water flow (200 L/h) was introduced down trough the packed bed during 15 min. The excess biomass produced on the packing was flushed out, and the pressure drop was kept below 0.5 m H$_2$O m^{-1} (4.9 kPa m^{-1}) for the rest of the experimentation. The increase in the nitrate load (day 26) caused initially a decrease in the removal efficiency to 60%, but this was a transitory behaviour and removal efficiencies were fast recovered and kept around 80–90% since day 28. By doubling the nitrate load (day 34), the nitrate reduction activity reached a stable value around 70–80% in 2 days, indicating that biodegradation limitation appeared. The denitrification process caused a pH's rise that cannot be buffered by the alkalinity of the synthetic wastewater. This effect was more relevant as the inlet concentration increased; it has been reported that pH values between 7.0 and 8.0 have no significant effects on denitrifica-
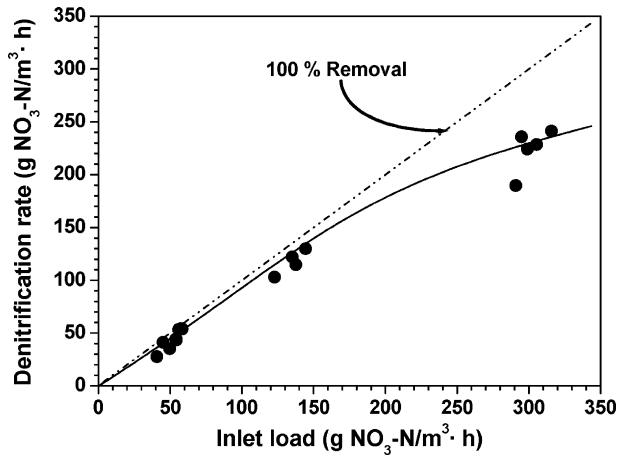
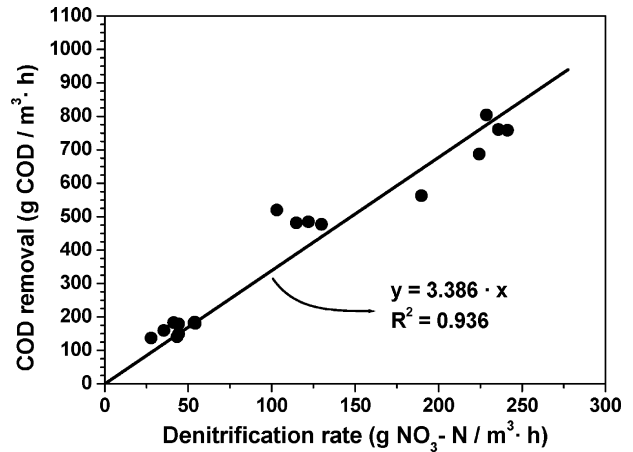Fig. 2. Denitrification rate vs. NO₃-N load for the synthetic wastewater.

Fig. 3. COD removal vs. denitrification rate for the synthetic wastewater.

tion rate [1]. In this study high removals were even possible for pH above 9.0. The decrease in the nitrate removal obtained for the greater influent nitrate concentration (400 g NO₃-N/m³, loading of approx. 300 g NO₃-N/(m³ h)) could be associated to the pH inhibition, since effluent pHs higher than 9.5 were reached. The addition of methanol (measured as COD) was shown enough to assure a 100% nitrate removal. At industrial scale, for high nitrate loads where removal efficiency decreases, the methanol load must be optimized to avoid effluent concentrations greater than 125 g COD/m³ in order to fulfil environmental regulations.

Denitrification rates for the different NO₃-N loading values are shown in Fig. 2. Data from days 1 to 11, 26, 27, 34 and 35 are excluded as they can be considered as transient responses. The maximum nitrate load for elevated nitrogen elimination was around 130 g NO₃-N/(m³ h). The highest observed denitrification rate was 230 g NO₃-N/(m³ h) for a nitrate load of 300 g NO₃-N/(m³ h). These values are comparative to those previously reported for high load studies [7,10], indicating that the selected retention time of 1.28 h is adequate to assure the denitrification performance. Reported NO₃-N loadings for upflow packed-bed postanoxic denitrification reactors are in the range from 125 to 166 g NO₃-N/(m³ h) to achieve effluent NO₃-N concentrations below 5.0 g/m³ [7,10].

Fig. 3 shows simultaneous denitrification rate and COD removal. The slope of the linear regression indicates the stoichiometric coefficient: 3.39 g COD consumed/g NO₃-N removed. Typical stoichiometric coefficient for the denitrification process between methanol (measured as COD) and nitrate are in the 3.5–4.1 range [11].

3.2. Stage 2: diluted industrial wastewater

The effect of nitrate loading for the industrial wastewater was studied in continuous column operation by changing the flow rate from 9 to 40 L/day, step by step (days 43–135), thus corresponding a step decrease in the empty bed residence time from 3.5 to 0.8 h. Fig. 4 shows the time course of the continuous denitrification process. The normal influent nitrate concentration values were in a range of about 140–210 g NO₃-N/m³ by

five-fold dilution of the industrial effluent periodically supplied to the laboratory according to the normal variability in the factory, only nitrate levels in the influent between day 120 and 126 were so low due to abnormal performance in the factory. As can be observed, as flow rate increased, efficiency removal
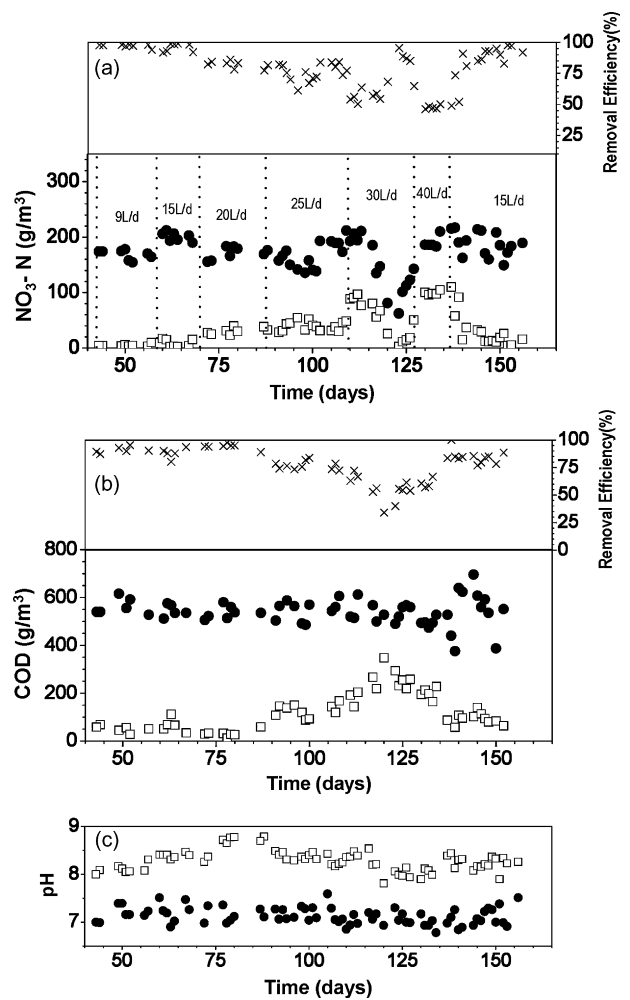

Fig. 4. Continuous denitrification of industrial wastewater with various flow rates. (●) Influent concentration; (□) effluent concentration; (×) removal efficiency: (a) NO₃-N; (b) COD; (c) influent (●) and (□) effluent pH.

decreased. For flow rates of 30 and 40 L/day the efficiency removal decreased to values around 45–55%, indicating that a limitation in the denitrification rate was reached. The maximal flow rate to assure effluent concentrations below 20 g NO_3-N/m^3 was 15 L/day, thus corresponding to a maximum nitrate load of 100 g NO_3-N/(m^3 h). This result indicates that the denitrification process for the industrial source was not working as well as for the synthetic wastewater. The industrial wastewater presented more buffering capacity than the synthetic one; effluent pH remained in the range 7.8–8.7, so the poorer performance cannot be attributed to high pHs. The decrease in the efficiency could be related to the small amount of toxics substances that the industrial source contains, since these compounds could inhibit in some extent the denitrification process. Whatever case, results obtained are good enough to demonstrate the viability of the denitrification process of the industrial wastewater by treating the global effluent (industrial and domestic sources) previously to its outflow. For all the experiments, COD effluent concentrations indicate that organic source was not limiting the process. Effluent COD concentrations are kept between 25 and 125 g/m^3, only for higher flow rates, with removal efficiencies lower than 60%, effluent COD concentrations reached values greater than 150 g/m^3, so the addition of methanol should be adjusted in relation to the denitrification rate. The stoichiometric coefficient was 3.31 g COD consumed/g NO_3-N removed (standard deviation of 0.47), similar to that obtained in the synthetic wastewater treatment. Considering that the global effluent of the industrial site has a COD concentration of about 210–320 g/m^3, mainly coming from the domestic spill, the methanol supply as extra carbon source should vary approximately between 50 and 280 g of methanol/m^3. Therefore, the implementation of the denitrification process at industrial scale implies careful control of the COD and nitrate concentrations of the influent, to save costs and to avoid high COD concentrations in the final effluent of the industrial site.

In order to verify the process stability, during the last 1 month of the experimental study (days 135–160), the system was operated at a constant flow rate of 15 L/day, which has been shown suitable to guarantee effluent nitrate concentration below 20 g NO_3-N/m^3. Results of the evolution of the process have been also presented in Fig. 4, where it can be observed that the biological reactor remained nearly stationary after a short transitory period.

Denitrification rates versus the nitrate load are presented in Fig. 5 for the experimental data corresponding to 43–135 days. As can be seen, under low load conditions, the denitrification rate essentially equals the load, with removal efficiencies close to 100%. The critical nitrate load, that is, the lowest value that generates removal efficiencies lower than 100%, was about 100 g NO_3-N/(m^3 h). The highest observed denitrification rate was 135 g NO_3-N/(m^3 h) at a nitrate load of 250 g NO_3-N/(m^3 h). By comparison with the obtained values from the synthetic wastewater treatment (critical load of 130 g NO_3-N/(m^3 h), denitrification rate of 200 g NO_3-N/(m^3 h) at a nitrate load of 250 g NO_3-N/(m^3 h)) indicates that the chemical composition of the industrial source hinders to some extent the performance of the biological process. The operational flow rate
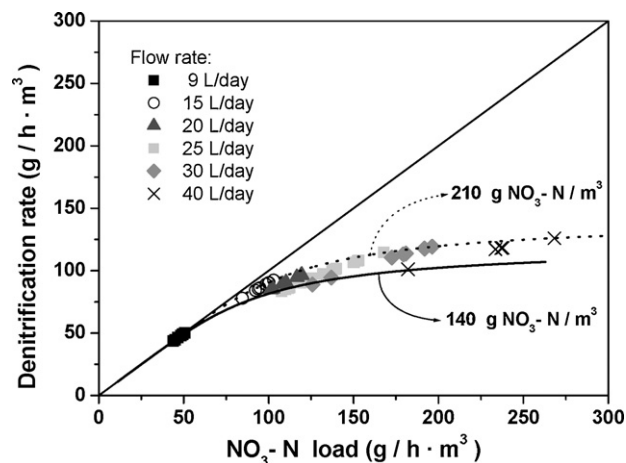

Fig. 5. Denitrification rate vs. NO_3-N load of the industrial wastewater. Symbols denote experimental data at different flow rates, and lines denote model simulation for nitrate inlet concentrations of 140 (solid line) and 210 (dashed line) g NO_3-N/m^3.

for the last 3 weeks was selected in order to maintain a nitrate load equal to the critical nitrate load obtained.

A simplified model development was used to simulate the experimental results. Assuming plug-flow regime, Monod kinetic for substrate consumption, and constant biomass concentration, the nitrate balance for the reactor is as follows:

$$\frac{dS}{d\tau} = r(s) = -k\frac{S}{K_s + S} \qquad (1)$$

where S is the nitrate concentration; τ the empty bed residence time; k the maximum denitrification rate; K_s is the Monod or half-saturation constant. Notice that the units of k are in reference to the limiting substance; in this case the units of k are g NO_3-N removed/(m^3 reactor h). The kinetic parameters, k and K_s, correspond to the observed behaviour of the system under the operational conditions tested, and include not only the biomass activity but also the mass transfer limitations.

Integrating the nitrate balance throughout the whole reactor height:

$$K_s \ln\frac{S_0}{S} + (S_0 - S) = k\tau \qquad (2)$$

and substituting the effluent concentration, S, by the denitrification rate (DR) defined as

$$DR = \frac{S_0 - S}{\tau} \qquad (3)$$

The kinetic parameters were determined by least squares fitting technique applied to the experimental denitrification rates corresponding to those obtained in the variable flow rate period (days 43–135). The calculated parameters are $k = 217$ g NO_3-N removed/(m^3 h) and $K_s = 112$ g NO_3-N/m^3. The Monod constant, K_s, is significantly higher than the values usually reported from experiments performed on microorganisms in stirred suspensions [1], which could indicate that the kinetic constants integrated both process: biodegradation and diffusion mass transfer.
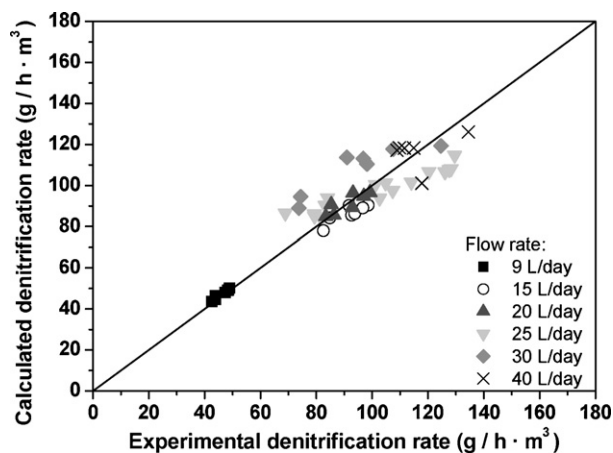
Fig. 6. Comparison between experimental and estimated denitrification rates of the industrial wastewater.

The theoretical curves of the denitrification rate as a function of nitrate load (S_0/τ) can be calculated with the calibrated parameters of the model by applying Eqs. (2) and (3). As can be observed, the denitrification rate depends on two variable parameters: S_0 and τ. As the industrial wastewater presented a great variability in its nitrate concentration, resulting in a broad range of about 140–210 g NO$_3$-N/m^3 in the influent nitrate concentration to the bioreactor, the curves have been calculated for the two extreme influent concentrations: 140 and 210 g NO$_3$-N/m^3. It is observed that reactor performance can be reasonably predicted by the mathematical model. The experimental denitrification rate has been compared with that calculated by using the kinetic parameters. Calculated values versus experimental data have been plotted in Fig. 6. As can be observed, the denitrification rate reasonably corresponds to that expected from the measured one. Mean relative deviations between measured and estimated values was found in 8.4%.

4. Conclusions

The experiments developed in laboratory showed that nitrate removal via biological denitrification from a global wastewater of a metal-finishing factory (20/80, industrial wastewater/domestic wastewater) can be carried out successfully in an upflow packed bed reactor. High removal efficiencies (higher than 90%) were achieved for NO$_3$-N loads up to 100 g NO$_3$-N/(m^3 h). The highest observed denitrification rate was 135 g NO$_3$-N/(m^3 h) at a nitrate load of 250 g NO$_3$-N/(m^3 h). Methanol was added as a carbon source with an observed mass relation between COD consumed and NO3-N

removed around 3.31. Better results were achieved in a previous stage using tap water with nitrate added as a sole pollutant (critical load of 130 g NO$_3$-N/(m^3 h) and denitrification rate of 200 g NO$_3$-N/(m^3 h) at a nitrate load of 250 g NO$_3$-N/(m^3 h)). This fact could indicate that the chemical composition of the industrial source hinders to some extent the performance of the biological process.

A simple model based on Monod kinetics for substrate consumption, and constant biomass concentration was applied to model the industrial wastewater treatment, and a reasonably good fitting was obtained.

Acknowledgments

References

[1] Metcalf and Eddy Inc., in: G. Tchobanoglous, F.L. Burton, H.D. Stensel (Eds.), Wastewater Engineering—Treatment, Disposal and Reuse, fourth ed., McGraw-Hill, New York, 2002.
[2] D.W. Koren, W.D. Gould, P. Bedard, Biological removal of ammonia and nitrate from simulated mine and mill effluents, Hydrometallurgy 56 (2000) 127–144.
[3] R. Schuch, R. Gensicke, K. Merkel, J. Winter, Nitrogen and DOC removal from wastewater streams of the metal-working industry, Water Res. 34 (2000) 295–303.
[4] F. Buchhesiter, R. Schuch, J. Winter, Biological nitrogen removal from wastewater of the metal-working industry, Chem. Eng. Technol. 23 (2000) 967–971.
[5] A. Hirata, Y. Makamura, S. Tsuneda, Biological nitrogen removal from industrial wastewater discharged from metal recovery processes, Water Sci. Technol. 44 (2001) 171–179.
[6] J.M. Kasia, J.R. Duncan, J.E. Burgess, Biological removal of nitrogen species from metal-processing wastewater, Water S.A. 31 (2005) 407–412.
[7] R. Pujol, M. Hamon, X. Kendel, H. Lemmel, Biofilters: flexible, reliable biological reactors, Water Sci. Technol. 29 (1994) 33–38.
[8] W.W. Eckenfelder, Y. Argaman, Principles of biological and physical/chemical nitrogen removal, in: R. Sedlak (Ed.), Phosphorus and Nitrogen Removal from Municipal Wastewater. Principles and Practice, 2nd ed., Lewis Publishers, New York, 1991, pp. 3–42.
[9] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington, 1999.
[10] V.R. Borregaard, Experience with nutrient removal in fixed-film system at full scale wastewater treatment plants, Water Sci. Technol. 36 (1997) 129–137.
[11] M. Henze, P. Harremoes, J.I. Cour Jansen, E. Arvin, Wastewater Treatment. Biological and Chemical Processes, third ed., Springer, Berlin, 2002.