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## Oxygen control and improved denitrification efficiency by dosing ferrous ions in the anoxic reactor

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### ABSTRACT

Small concentrations of dissolved oxygen (DO) in the range 0.2–0.4 mg L<sup>-1</sup> normally are present in biological pre-denitrification reactors. This situation causes adverse effects on denitrification rate and, consequently, on the process efficiency. The results presented show the possibility to control the DO in the anoxic reactor by dosing ferrous Fe(II) ions. The experiments were carried out on both batch samples and a pilot plant and proved that oxidation of Fe(II) to Fe(III) is very efficient in the DO control. Moreover, Fe(III) reacts with phosphorus which precipitates as ferric orthophosphate. A dose of 6 mgFe<sup>2+</sup> L<sup>-1</sup> decreased the mean DO concentration from 0.45 to 0.28 mg L<sup>-1</sup>; as a consequence, the denitrification efficiency ( $\eta_{\text{DEN}}$ ) increased from about 65–77%.  $\eta_{\text{DEN}}$  reached up to 89% with 9 mgFe<sup>2+</sup> L<sup>-1</sup> (50% over the stoichiometric for phosphorus removal) thanks to an average DO concentration of 0.08 mgO<sub>2</sub> L<sup>-1</sup> in the denitrification stage. The results also highlighted the strong influence of DO (and consequently the dosage of Fe<sup>2+</sup>) on the specific denitrification rate suggesting to maintain DO concentration in the pre-denitrification reactors lower than 0.2 mg L<sup>-1</sup> in order to achieve high operation efficiencies.

**Keywords:** Biological nitrogen removal; Combined nitrogen and phosphorus removal; Ferrous iron dosing; Dissolved oxygen control; Wastewater treatment plant design

### 1. Introduction

The design of the biological anoxic pre-denitrification reactors is normally made on the basis of the denitrification rate ( $r_{\text{DEN}}$ ), which is defined as the NO<sub>3</sub>-N removal by dissimilation assuming a zero-order kinetics (in relation to both NO<sub>3</sub>-N and organic

substrate) and considering the significant effect of the temperature [1–11].

Biological denitrification efficiency depends on many factors, such as the retention time, the organic load, and the mixed liquor (ML) recycle [1,4,11,12]. In addition, DO (DO<sub>DEN</sub>) control is known to be a very important factor in the denitrification stage.

Average daily concentrations of DO<sub>DEN</sub> in real-scale plants are in the range 0.2–0.4 mg L<sup>-1</sup>, with

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higher values during the day, especially in small sewage treatment plants [13,14]. The inhibitory effect due to the DO concentration found in the anoxic reactors is the result of two opposing factors: on the one hand, the intake of oxygen loads associated with the raw sewage, the sludge recycle and, mainly, the ML recycle; on the other hand, the oxygen consumption determined by the heterotrophic bacteria activity [15].

The effect of dissolved oxygen (DO) on the kinetics of the denitrification process was postulated in 1975 by US-EPA [1] and subsequently highlighted by inserting the inhibition factor  $K'_0/(K'_0 + \text{DO})$  in the expression [16,17]:

$$r_{\text{DEN}} = \left( \frac{1 - 1.42Y}{2.86} \right) \cdot \left( \frac{K \cdot S \cdot X}{K_s + S} \right) \cdot \left( \frac{\text{NO}_3\text{-N}}{K_N + \text{NO}_3\text{-N}} \right) \cdot \left( \frac{K'_0}{K'_0 + \text{DO}_{\text{DEN}}} \right) \cdot \eta \quad (1)$$

where  $Y$  is the heterotrophic bacteria synthesis yield ( $\text{mgVSS mg substrate consumed}^{-1}$ );  $K$  is the maximum specific rate of substrate utilization ( $\text{h}^{-1}$ );  $X$  is the biomass concentration ( $\text{mgMLVSS L}^{-1}$ );  $S$  is the soluble degradable substrate concentration ( $\text{mg L}^{-1}$ );  $K_s$  is the substrate utilization half-velocity coefficient ( $\text{mg L}^{-1}$ );  $\text{NO}_3\text{-N}$  is the nitrate concentration as N ( $\text{mg L}^{-1}$ );  $K_N$  is the nitrate half-velocity coefficient ( $\text{mg L}^{-1}$ );  $K'_0$  is the DO inhibition constant for nitrate reduction ( $\text{mgO}_2 \text{L}^{-1}$ );  $\eta$  is the fraction of heterotrophic bacteria that use nitrate in lieu of oxygen (dimensionless).

Different studies highlighted the inhibitory effect of DO on denitrification efficiency [18–24]. The DO inhibition on the  $r_{\text{DEN}}$  has been observed at  $0.20 \text{ mgO}_2 \text{L}^{-1}$  [18], but on a theoretical basis, the mere presence of  $0.2 \text{ mgO}_2 \text{L}^{-1}$  determines the drop of  $r_{\text{DEN}}$  up to 40% compared to the maximum values obtained in the absence of inhibition [12]. Therefore,  $K'_0$  is considered variable in a wide range ( $0.02\text{--}0.2 \text{ mgO}_2 \text{L}^{-1}$ ), which depends on both the floc size and structure [12].

For practical calculation of the denitrification reactor volume, a semi-empirical relation was proposed [12,25–27]. It correlates the specific denitrification rate (SDNR) at  $20^\circ\text{C}$  ( $\text{SDNR}_{20^\circ\text{C}}$ ,  $\text{gNO}_3\text{-N gMLVSS}^{-1} \text{d}^{-1}$ ) to the sludge loading only referred to the denitrification reactor:

$$\text{SDNR}_{20^\circ\text{C}} = 0.03 \cdot \text{F:M}_{\text{DEN}} + 0.029 \quad (2)$$

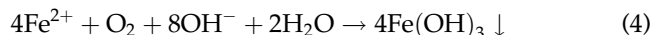
where  $\text{F:M}_{\text{DEN}}$  is the sludge loading in the denitrification stage ( $\text{gBOD}_5 \text{ applied gMLVSS}^{-1} \text{d}^{-1}$ ). The values of SDNR observed in the pre-anoxic reactors of full

scale plants range from 0.04 to  $0.42 \text{ gNO}_3\text{-N gMLVSS}^{-1} \text{d}^{-1}$  [17,24,26]. More recently, Raboni et al. [28] highlighted the strong dependence of SDNR in the sewage pre-denitrification from both DO and  $\text{F:M}_{\text{DEN}}$ :

$$\text{SDNR}_{20^\circ\text{C}} = 0.0864 \left( \frac{K'_0}{K'_0 + \text{DO}} \right) + 0.05 \text{F:M}_{\text{DEN}} \cdot \eta_{\text{BOD}} \cdot \left( \frac{\text{DO}}{0.2 + \text{DO}} \right) \quad (3)$$

where  $K'_0 = 0.18 \text{ mgO}_2 \text{L}^{-1}$  is the DO inhibition constant;  $\eta_{\text{BOD}}$  is the BOD removal efficiency, which depends on  $\text{F:M}_{\text{DEN}}$  ( $\eta_{\text{BOD}} = 0.90$  for  $\text{F:M}_{\text{DEN}} = 0.4 \text{ kg BOD}_5 \text{ kgMLVSS}^{-1} \text{d}^{-1}$ ;  $\eta_{\text{BOD}} = 0.95$  for  $\text{F:M}_{\text{DEN}} = 0.2 \text{ kg BOD}_5 \text{ kg MLVSS}^{-1} \text{d}^{-1}$ ).

Assessed the great dependence of the  $r_{\text{DEN}}$  from DO, the paper shows the possibility of reducing the DO concentration through the dosage of ferrous Fe(II) ions in the anoxic reactor. The oxidation of Fe(II) with oxygen in an aqueous environment is carried out according to the following reaction:



The kinetics of Fe(II) oxidation has been studied extensively [29–33]. It depends on several factors including temperature, pH, concentrations of Fe(II) and DO. Generally, the recognized kinetic expression is the following:

$$\frac{d[\text{Fe}^{2+}]}{dt} = K_{\text{Fe}} \cdot [\text{Fe}^{2+}] \cdot [\text{OH}^-]^2 \cdot p\text{O}_2 \quad (5)$$

where  $p\text{O}_2$  is the partial pressure of oxygen;  $[\text{Fe}^{2+}]$  and  $[\text{OH}^-]$  are the molar concentrations of bivalent iron and hydroxyl ion;  $K_{\text{Fe}}$  is the kinetic constant with values typically ranging from  $1$  to  $6 \text{ E} + 13 \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  [34].

The kinetic equation shows the strong influence of pH on the oxidation rate. Applying Eq. (5) with a DO concentration of  $1 \text{ mgO}_2 \text{L}^{-1}$ , Davison and Seed [32] calculated a half time for  $\text{Fe}^{2+}$  oxidation corresponding to 30 min with a pH value of 7.4 and 100 min at pH equal to 7.0 ( $K_{\text{Fe}} = 2 \text{ E} + 13 \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$ ).

It is worth to note that a biological reduction of both nitrate and nitrite was found to take place in the activated sludge concomitantly with the oxidation of Fe(II) ions [35]. This process seems of potential interest for activated sludge processes, but many aspects should be studied with more detail.

The paper shows the results of batch tests carried out on ML samples collected at the initial stage of the

denitrification reactor in order to verify the influence of Fe(II) dosage on the DO concentration. The effects of Fe(II) on the denitrification process have been also tested on a pilot plant in order to define the optimal DO concentration for improving both the SDNR and the denitrification efficiency.

## 2. Materials and methods

### 2.1. Preliminary batch tests

Batch tests were carried out on samples of ML in order to measure the DO consumption rate. The samples were collected from a pilot plant described in section 2.2. Each test was carried out on four samples (volume: 1.0 L):

- (1) Sample *a*: raw ML collected at the initial stage of the anoxic pre-denitrification reactor ( $ML_{DEN}$ ).
- (2) Sample *b*:  $ML_{DEN}$  with  $Fe^{2+}$  (0% over the stoichiometric dosage for  $P_{tot}$  removal).
- (3) Sample *c*:  $ML_{DEN}$  with  $Fe^{2+}$  (50% over the stoichiometric dosage for  $P_{tot}$  removal).
- (4) Sample *d*: ML recycle.

Samples were mixed slowly in order to avoid solubilization of atmospheric oxygen. Twenty batch tests were carried out with ML at different initial DO concentration. The purpose of the preliminary investigation was to compare the DO consumption rate due to the bacterial respiration in presence of:

- (1) Endogenous carbon only (sample *d*).
- (2) Endogenous carbon and BOD (sample *a*).
- (3) Endogenous carbon and BOD in presence of the chemical reduction due to  $Fe^{2+}$  addition (sample *b*, *c*).

### 2.2. Pilot plant experience

#### 2.2.1. Pilot plant description

An activated sludge pilot plant (Fig. 1) with a biological anoxic pre-denitrification tank (DEN), an oxidation-nitrification stage (OX-NIT) and a final sedimentation (SED) was used for the full scale tests. The pilot plant was fed by pre-treated (screening and aerated grit chamber) sewage from a town of 50,000 inhabitants.

The main features of the pilot plant were as follows:

- (1) DEN: volume 10 m<sup>3</sup>; liquid height 1.8 m; mixing: four slow vertical axis mixers (power input: 11 W m<sup>-3</sup>).

- (2) OX-NIT: volume 20 m<sup>3</sup>; liquid height 1.8 m; aeration: micro-bubble aeration system.
- (3) SED: diameter 2 m; volume 6 m<sup>3</sup>.
- (4) Sewage flow rate:  $Q_{sew} = 2 \text{ m}^3 \text{ h}^{-1}$ .
- (5) ML recycle flow rate:  $Q_{ML} = 6 \text{ m}^3 \text{ h}^{-1}$ .
- (6) Sludge recycle flow rate:  $Q_{SR} = Q_{sew}$ .

#### 2.2.2. Pilot plant operating conditions and testing methods

The pilot plant operating conditions were set in order to verify the impact of  $Fe^{2+}$  dosage on the: (i) average DO concentration in DEN (average  $DO_{DEN}$ , measured as the arithmetic mean of all the DO measurements in DEN) and, consequently, on the denitrification performance expressed as  $N-NO_3$  removal efficiency ( $\eta_{DEN}$ ); (ii) SDNR, calculated as follows:

$$SDNR = \frac{Q \cdot \Delta NO_3 - N}{V_{DEN} \cdot X} \quad (6)$$

where  $Q$  is the sewage flow rate (m<sup>3</sup> d<sup>-1</sup>),  $\Delta NO_3 - N$  is the removed nitrogen, as nitrate, per unit of volume (gNO<sub>3</sub>-N m<sup>-3</sup>);  $V_{DEN}$  is the denitrification reactor volume (m<sup>3</sup>);  $X$  is the biomass concentration.

The pilot plant ran for a continuous period of six months. In this period, the  $F:M_{DEN}$  was maintained within the range 0.2–0.4 kg BOD<sub>5</sub> kgMLVSS<sup>-1</sup> d<sup>-1</sup> (average value: 0.3 kg BOD<sub>5</sub> kgMLVSS<sup>-1</sup> d<sup>-1</sup>) with an average MLVSS concentration kept at 2.0 g L<sup>-1</sup>. DO in OX-NIT was kept in the range 2.0–3.5 mgO<sub>2</sub> L<sup>-1</sup>.

After 90 d, the  $Fe^{2+}$  dosing (as  $FeSO_4$  solution) in the first denitrification tank started. Three different concentrations were used, each for a period of 30 d:

- (1) 6.0 mgFe<sup>2+</sup> L<sup>-1</sup> (0% over the stoichiometric for  $P_{tot}$  removal).
- (2) 7.5 mgFe<sup>2+</sup> L<sup>-1</sup> (25% over the stoichiometric for  $P_{tot}$  removal).
- (3) 9.0 mgFe<sup>2+</sup> L<sup>-1</sup> (50% over the stoichiometric for  $P_{tot}$  removal).

During the experience, the following analytical parameters were measured:

- (1) BOD<sub>5</sub>, COD, TN, NO<sub>3</sub>-N,  $P_{tot}$  and suspended solids concentrations in the pre-treated sewage entering the pilot plant and in the pilot plant effluent (an automatic daily average sampler was used).
- (2) TN and NO<sub>3</sub>-N concentrations entering the DEN and in the filtered samples of the inlet to OX-NIT (automatic daily average samplings).

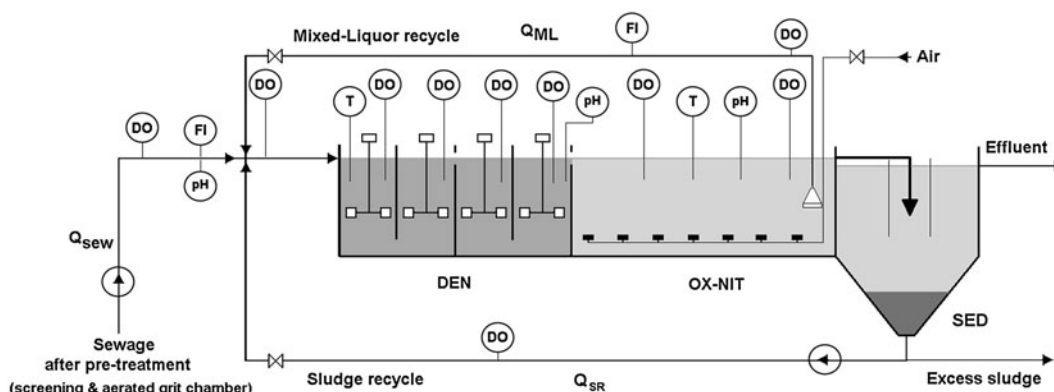


Fig. 1. Scheme of the pilot plant.

- (3) MLVSS and MLSS concentrations in DEN and OX-NIT (manual sampling).
- (4) Temperature in DEN and OX-NIT (fixed probes; accuracy:  $\pm 0.05^\circ\text{C}$ ), as shown in Fig. 1.
- (5) DO concentration in ten measure points (Fig. 1) by means of continuous sampling fixed probes (accuracy:  $\pm 0.01 \text{ mgO}_2 \text{ L}^{-1}$ ; automatic calibration; temperature compensation).
- (6) pH at three measure points (Fig. 1) with continuous sampling fixed probes (accuracy:  $\pm 0.05$ ).

Sampling and analysis were carried out in compliance with official standard methods [36].

### 3. Results and discussion

#### 3.1. Mean quality of the raw sewage and the treated effluent

Table 1 shows the quality of both the raw sewage and the treated effluent collected during the first 90 d (no  $\text{Fe}^{2+}$  addition).

The results indicate a "low strength" sewage. The average efficiency of the plant is 70.8, 90.0, 64.3 and 22% for COD,  $\text{BOD}_5$ , TN and  $P_{\text{tot}}$ , respectively. The removal efficiency of TN is indeed quite poor compared to expectations. This result is largely determined by the excessive presence of DO in DEN (average daily value:  $0.49 \text{ mgO}_2 \text{ L}^{-1}$ ) mainly due to the heavy fluctuations of the sewage quality as shown in [13].

#### 3.2. Preliminary batch tests

Fig. 2 shows two representative results of the investigation carried out on batch tests of  $\text{ML}_{\text{DEN}}$  and

$\text{ML}_{\text{recycle}}$ . Fig. 2(A) and (B) refer to tests with the lowest and highest initial DO concentration, respectively.

The initial values measured at the first stage of DEN (samples *a*, *b* and *c*) show a strong variability of DO concentration of the ML at the inlet of the denitrification stage (range:  $0.97\text{--}0.26 \text{ mgO}_2 \text{ L}^{-1}$ ). This is surely due to the high DO content found in the  $\text{ML}_{\text{recycle}}$  coming from the oxidation stage (samples *d*; DO range:  $2.1\text{--}3.4 \text{ mgO}_2 \text{ L}^{-1}$ ).

Analysing the DO behaviour as a function of time, the curves of the two graphs show similar trends. The comparison between the DO consumption rate of  $\text{ML}_{\text{DEN}}$  (samples *a*) and  $\text{ML}_{\text{recycle}}$  (samples *d*) highlights the influence of BOD content, that is negligible in the  $\text{ML}_{\text{recycle}}$  because of the biological oxidation, and on the contrary high in  $\text{ML}_{\text{DEN}}$ , being this is a combination of raw sewage, ML recycle and sludge recycle. Focusing on the effects of  $\text{Fe}^{2+}$  dosing, the samples *a* show the DO consumption due only to BOD and endogenous carbon while the samples *b* and *c* contain the additional effect of  $\text{Fe}^{2+}$ . Using the stoichiometric doses of  $\text{Fe}^{2+}$  for  $P_{\text{tot}}$  removal (samples *b*), with a contact times of only 5–30 min (depending on the initial DO concentrations), it was possible to bring the DO concentration below  $0.05 \text{ mgO}_2 \text{ L}^{-1}$ . Better results (2–12 min) were obtained with a significant dosage of  $\text{Fe}^{2+}$  (50% over the stoichiometric for  $P_{\text{tot}}$  removal; samples *c*). These results are considerably better than those obtained with no  $\text{Fe}^{2+}$  addition (11–50 min; samples *a*).

#### 3.3. Pilot plant

Fig. 3 shows the performance of biological denitrification as function of the DO average concentration in DEN during the whole experimentation period.

Table 1

Quality of the raw sewage and the treated effluent (mean daily values and standard deviation on 60 samples of pre-treated sewage and treated effluent, respectively)

Parameter	Unit of measurement	Daily values	
		Mean (m)	Standard deviation (SD)
COD in	mg L <sup>-1</sup>	276.5	61.1
COD out	mg L <sup>-1</sup>	80.5	16.9
BOD <sub>5</sub> in	mg L <sup>-1</sup>	129.0	44.0
BOD <sub>5</sub> out	mg L <sup>-1</sup>	12.9	2.1
SS in	mg L <sup>-1</sup>	148.0	49.0
SS out	mg L <sup>-1</sup>	18.5	4.1
TN = TKN in	mg L <sup>-1</sup>	28.6	4.9
TN out <sup>a</sup>	mg L <sup>-1</sup>	10.2	2.8
P <sub>tot</sub> in	mg L <sup>-1</sup>	5.0	1.5
P <sub>tot</sub> out	mg L <sup>-1</sup>	3.9	0.8

<sup>a</sup>All NO<sub>3</sub>-N (TKN in the effluent always less than 0.5 mg L<sup>-1</sup>).

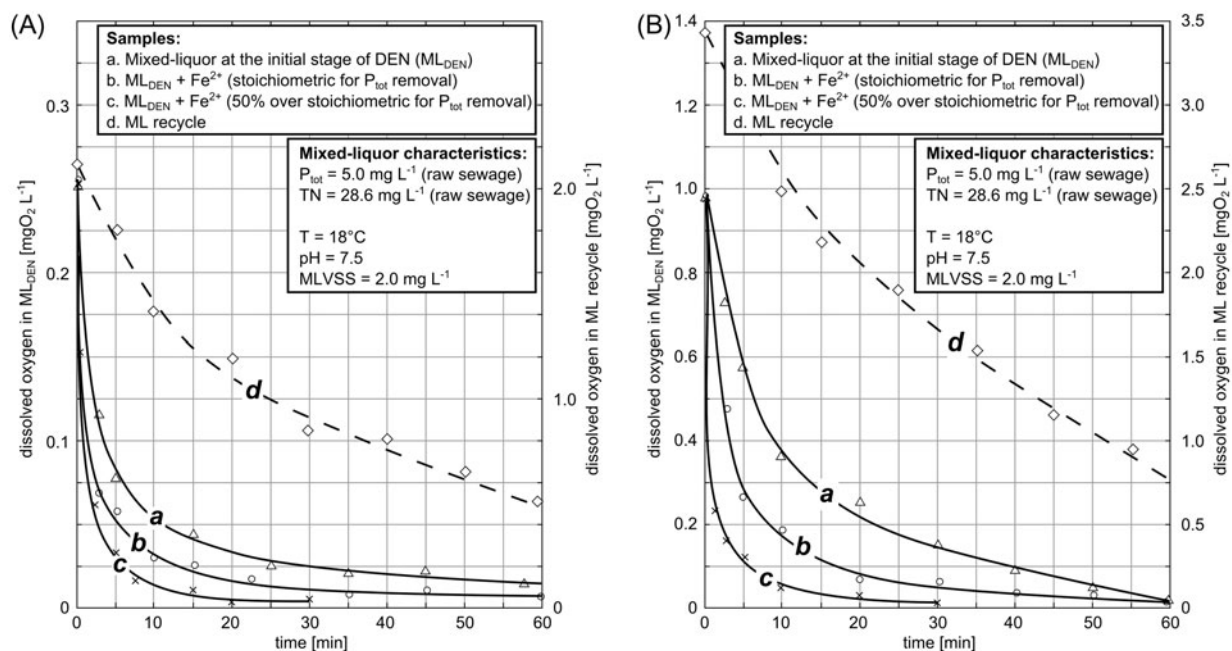


Fig. 2. Trend of DO in the preliminary batch tests carried out on ML samples collected simultaneously in the initial stage of denitrification (ML<sub>DEN</sub>) and in the mixed liquor recycle (ML<sub>recycle</sub>): cases with the lowest (A) and the highest (B) initial DO content.

As stated above, during the first period (no Fe<sup>2+</sup> dosage), high concentrations of DO (mean: 0.49 mgO<sub>2</sub> L<sup>-1</sup>) negatively affected the achievement of good denitrification removal efficiencies (mean: 62%). Another reason of such poor performance was the great variability in average DO<sub>DEN</sub> which was reflected by  $\eta_{DEN}$  (0.34–0.64 mgO<sub>2</sub> L<sup>-1</sup> with performance of 72–53%, respectively).

The Fe<sup>2+</sup> dosing reduced DO<sub>DEN</sub> concentrations up to 0.08 mgO<sub>2</sub> L<sup>-1</sup> smoothing the variability of the denitrification performances: average removal efficiencies of 73, 84 and 89% with 0, 25 and 50% over the stoichiometric dosage for P<sub>tot</sub> removal, were obtained, respectively. It is worth to note that a stoichiometric dosage of Fe<sup>2+</sup> for P<sub>tot</sub> removal reduced average DO<sub>DEN</sub> from 0.49 to 0.30 mgO<sub>2</sub> L<sup>-1</sup>. Therefore, the



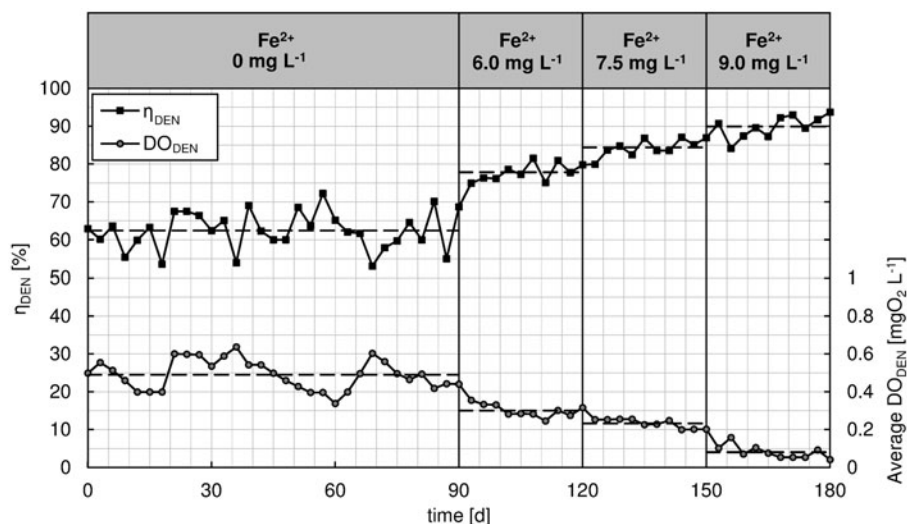


Fig. 3. Denitrification removal efficiency ( $\eta_{DEN}$ ) as function of the average DO content in the denitrification reactor (average  $DO_{DEN}$ ) during the four steps of the experimental period on the pilot plant. Dotted lines represent the mean values of  $\eta_{DEN}$  and  $DO_{DEN}$  in each experimental step.

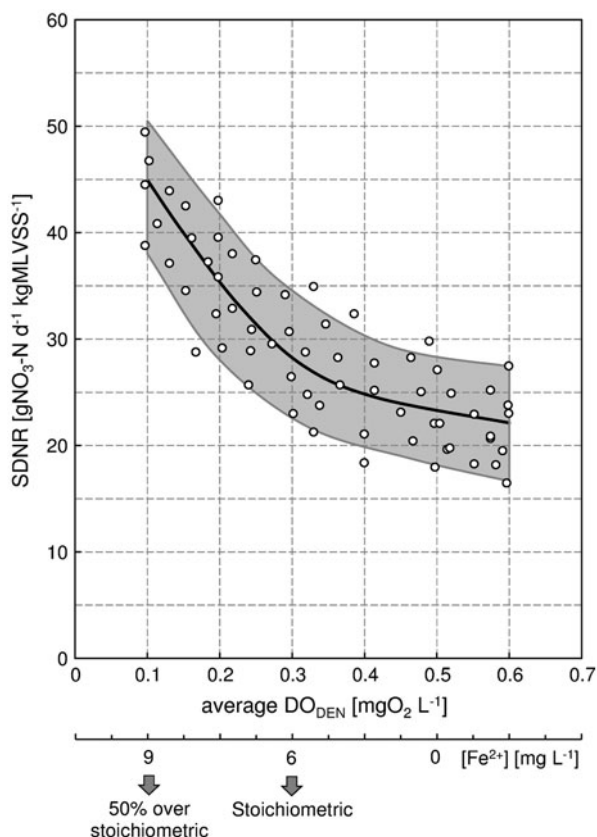


Fig. 4. SDNR as function of the average DO in the anoxic pre-denitrification tank (average  $DO_{DEN}$ ) at  $F:M_{DEN} = 0.3$  kgBOD<sub>5</sub> kgMLVSS<sup>-1</sup> d<sup>-1</sup> (temperature  $T = 18^\circ\text{C}$ ). The additional x-axis shows the concentration of the  $Fe^{2+}$  dosage. The continuous line and the shaded area represent the mean value and the 95% confidence limit, respectively.

results confirmed that the addition of Fe(II) ions in the denitrification stage proves to be very efficient in controlling the DO content. Moreover, Fe(II), once oxidized to Fe(III), also determined the phosphorus removal through the precipitation of ferric orthophosphate.

Fig. 4 shows the SDNR as function of the  $DO_{DEN}$ .

SDNR shows a strong dependence from DO concentration in the range 0.08–0.3 mgO<sub>2</sub> L<sup>-1</sup>, dropping almost linearly from 45 to 27.5 gNO<sub>3</sub>-N d<sup>-1</sup> kgMLVSS<sup>-1</sup>. It is worth to note that such results were obtained with decreasing quantities of  $Fe^{2+}$  ions (Fig. 4). At  $DO_{DEN}$  concentration higher than 0.3 mg L<sup>-1</sup> ( $Fe^{2+}$  dosage: 0% over the stoichiometric for  $P_{tot}$  removal) the influence of DO on SDNR can be considered not so important. Therefore, a good target for plant design operation seems to be an average DO concentration lower than 0.2 mgO<sub>2</sub> L<sup>-1</sup>, which corresponds to a SDNR at 18°C equal to about 35 gNO<sub>3</sub>-N d<sup>-1</sup> kgMLVSS<sup>-1</sup> and a  $Fe^{2+}$  dosage of 25% over the stoichiometric for  $P_{tot}$  removal. Such conditions allow to achieve an average denitrification efficiency equals about 84% (Fig. 3).

#### 4. Conclusions

The presence of DO in the biological denitrification tanks represents a serious limiting factor for the kinetics of the dissimilative reaction and, as a consequence, for the process efficiency. Literature indicates a reduction of the  $SDNR_{20^\circ\text{C}}$  of more than 50% with DO concentration higher than 0.3 mgO<sub>2</sub> L<sup>-1</sup>. The experimental

tests carried out on the pilot plant confirmed that the addition of ferrous ions in the denitrification stage proved to be very efficient in controlling the DO content, as it easily oxidizes the ferric ion. The dosage of  $6 \text{ mgFe}^{2+} \text{ L}^{-1}$  is able to lower the mean DO concentration from 0.45 to  $0.28 \text{ mgO}_2 \text{ L}^{-1}$  improving the denitrification efficiency from 64.8 to 77%. The efficiency was further increased to 84% with  $7.5 \text{ mgFe}^{2+} \text{ L}^{-1}$  (average DO in denitrification:  $0.22 \text{ mgO}_2 \text{ L}^{-1}$ ) and up to 89% with  $9 \text{ mgFe}^{2+} \text{ L}^{-1}$  (average DO in denitrification:  $0.08 \text{ mgO}_2 \text{ L}^{-1}$ ). The results also highlighted the strong influence of DO (as a consequence of  $\text{Fe}^{2+}$  dosing) on the SDNR. In particular, SDNR shows a very pronounced reduction with DO concentration in the range of  $0.05\text{--}0.3 \text{ mgO}_2 \text{ L}^{-1}$ , while it tends to decrease much more slowly at DO values higher than  $0.3 \text{ mgO}_2 \text{ L}^{-1}$ . Therefore, in order to optimize the design of the denitrification stage as well as to achieve high operation efficiencies, average DO values lower than  $0.2 \text{ mg L}^{-1}$  could be suggested as the ideal value.

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