Denitrification potential enhancement by addition of anaerobic fermentation products from the organic fraction of municipal solid waste

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Abstract The aim of this study is to demonstrate the denitrification potential enhancement determined by the addition of the anaerobic fermentation products from the organic fraction of municipal solid waste in BNR wastewater treatment plants. The denitrification potential rose from 6 to 17 mgNO$_3$-N/l thanks to the good performances showed by the fermentation products in the denitrification step: a typical maximum denitrification rate of about 5 mgN/gVSS d was observed. This value is similar to those obtained by using pure organic substrates. The denitrification capacity increase is determined by a significant increase of S$_s$ and X$_s$ availability in the influent due to the anaerobic fermentation products addition which leads to an influent COD increase equal to 68% of the total load: this value is significantly higher than the one obtained by fermentation of primary and/or waste activated sludge (3–5%).

Keywords Denitrification potential; fermentation; Nitrogen Utilisation Rate test; organic fraction of municipal solid wastes; RBCOD

Introduction

Following the approach given by the 91/271/EC Directive about nitrogen and phosphorus standards in treated wastewater discharges, the planning and upgrading of the WWTPs in European Countries must be more and more oriented towards BNR approaches. Nitrogen removal is often incomplete because of low organic loading in sewers. In particular, the denitrification potential of wastewater is primarily a function of the available organic carbon, which is usually expressed as COD/N or BOD/N ratio. As much as it concerns N removal it is important to underline that, besides easily biodegradable COD availability, also other aspects such as the configuration of the plant (pre-denitrification, simultaneous denitrification) and activated sludge characteristics (sludge age, organic loading rate) play an important role in the denitrification step. Many studies report a wide range of COD/N ratios required for satisfactory or complete denitrification processes between 4 and 15 gCOD/gN. If the COD/N ratio in inlet wastewater is not enough, an external carbon source is needed for a satisfactory denitrification step. This external carbon source can be either chemical (acetic acid or methanol), a primary settled hydrolysed sludge (Lötter and Pitman, 1992; Kristensen *et al.*, 1992; Isaacs & Henze, 1995) or the anaerobic fermentation products from the organic fraction of municipal solid waste (OFMSW) (Cecchi *et al.*, 1994; Pavan *et al.* 1998; 2000).

Following the last approach, in use within the AF-BNR-SCP process, proposed for the first time in Cecchi *et al.* (1994) and now existing in full-scale size in Treviso (Italy), easily biodegradable organic compounds (RBCOD) are produced by the anaerobic fermentation (AF) of OFMSW. The liquid fraction coming from the anaerobic fermentation (AF) step is fed into the BNR plant along with the incoming stream of wastewater for the enhancement of RBCOD availability to promote nitrogen and phosphorus biological removal. The solid fraction from the anaerobic fermenter is then blended with the excess activated sludge from the BNR treatment plant and fed into an anaerobic co-digestion unit. The phosphorus in the

anaerobic digestion supernatant flow is removed and recovered by the struvite crystallisation process (SCP) without any chemicals addition (Battistoni *et al*., 1998a).

In this study the denitrification potential enhancement after OFMSW anaerobic fermentation products addition is investigated, while considering NUR tests performed using synthetic RBCOD source. The comparison of the effect of these additions gives important information about the real benefits coming from the integrated approach (AF-BNR-SCP) mentioned before.

Materials and methods

The 0.8 m^3 – CSTR fermenter was electrically heated and fed once a day by a membrane pump with the source collected substrate coming from some supermarkets of Treviso municipality (Veneto region, Italy) shredded by a hammer mill and homogenised in a stirred tank before feeding. The effluent from the fermenter was screened by a 1 mm sieve-screw press (Pavan *et al*., 1994). Typical characteristics of the anaerobic fermentation products are shown in table 1 (see also Battistoni *et al*., 1998b and Traverso *et al*., 2000).

According to the individual daily OFMSW and wastewater productions, respectively 300 g/PEd for OFMSW and to 250 1/PEd for wastewater and supposing a screw-press efficiency in the anaerobic fermentation process between 0.6 and 0.75, a COD increase in the inlet of the BNR treatment plant between 56 and 74 mg O$_2$/l is expected, mainly due to the readily biodegradable fraction (Table 2).

On the basis of typical N and P concentration values in the anaerobic fermentation liquid effluent no nutrients increase was observed in the BNR inlet (Battistoni *et al*., 1998b). The characteristics of the wastewater, before and after the anaerobic fermentation products addition, are summarised in Table 2.

The activated sludge used for tests was taken from a BNR pilot-plant working at a sludge organic loading of 0.015 kgCOD/kgMLSSd and a COD/N ratio in the inlet between 9 and 11. Nitrates Utilisation Rate (NUR) tests were carried out in a 10 l-stirred vessel in the pulse mode. According to Kujawa and Klapwijk (1999), activated sludge in anoxic and endogenous conditions was added of about 20–30 mg NO$_3$-N/l. On the basis of the typical operational conditions of the BNR pilot plant a wastewater/activated sludge ratio (f$_{WW}$) of 0.2 was used which was the same as the BNR pilot plant anoxic step one. When dissolved oxygen concentration in the bulk dropped to low values (< 0.1 mgO$_2$/l) wastewater was added in the pulse mode.

The trends of NO$_2$-N, NO$_3$-N, and PO$_4$-P were followed by ionic chromatography analysis (Dionex DX-300, AS-4 column) on sieved samples filtered through black ribbon paper filters. All other analytical parameters were determined according to APHA (1992).

Table 1 Anaerobic fermented OFMSW characteristics

Parameter	Unit	Typical range values
COD total	mgO$_2$/l	60000–80000
COD soluble	mgO$_2$/l	35000–50000
RBCOD	mgO$_2$/l	34000–39000
Acetic Acid	mgO$_2$/l	5800–19200
VFA (C2-C5)	mgO$_2$/l	7000–25000
Lactic Acid	mgO$_2$/l	8100–23500
TKN	mgN/l	100–600
NH$_3$-N	mgN/l	65–500
NO$_3$-N	mgN/l	0–1
P total	mgP/l	125–450
PO$_4$-P	mgP/l	70–400
TS	mg/l	25000–45000

188

Table 2 Treviso City wastewater characteristics before and after the addition of the anaerobic fermention products of the organic fraction of municipal solid wastes

Parameter		Wastewater	Wastewater + OFMSW fermented	Average COD, N, P increase, %
TSS	mg/l	36 ± 15	53 ± 9	68
COD total	mgO_2/l	120 ± 12	175 ± 10	68
COD soluble	mgO_2/l	57 ± 9	97 ± 12	59
RBCOD	mgO_2/l	18 ± 12	82 ± 20	219
TKN	mgN/l	12.4 ± 1.8	12.5 ± 1.8	0.01
NH_3-N	mgN/l	7.3 ± 2	7.3 ± 1.8	0
NO_3-N	mgN/l	1.0 ± 0.3	1.0 ± 0.3	0
P total	mgP/l	1.6 ± 0.3	1.7 ± 0.6	0.06
PO_4-P	mgP/l	0.8 ± 0.2	1.0 ± 0.4	20

D. Bolzonella et al.

Results and discussion

During the denitrification step using a typical wastewater as carbon source, three different rates can be generally recognised: the first, the highest, is firstly determined by the soluble readily degradable COD (S_s) availability, the second by the particulate slowly biodegradable COD (X_s) and the lowest in endogenous conditions (Kujawa and Klapwijk, 1999). In domestic wastewaters the RBCOD fraction (S_s) generally accounts only for 10–20% of total COD (Henze *et al*., 1994) and its contribution in the overall denitrification rate is not prevailing; therefore the particulate COD fraction (X_s) determines the overall denitrification potential of a wastewater. Since only low weight organic molecular compounds are readily used in the denitrification step, the denitrification rate on X_s is determined by the hydrolytic and fermentation phenomena occurring in the anoxic step (or even anaerobic, if present) of a BNR system by which the conversion of particulate COD (X_s) into soluble COD (S_s) is carried out.

In Figure 1 the typical nitrates course during a NUR test is presented after the addition of the Treviso treatment plant raw wastewater.

The total denitrification rate allows a typical value of 0.5 mgN/gMLVSS h (at 20°C). This is the result of two different denitrification rates: the first depending on the particulate COD (X_s) and the second on the endogenous respiration (see Table 4). The denitrification
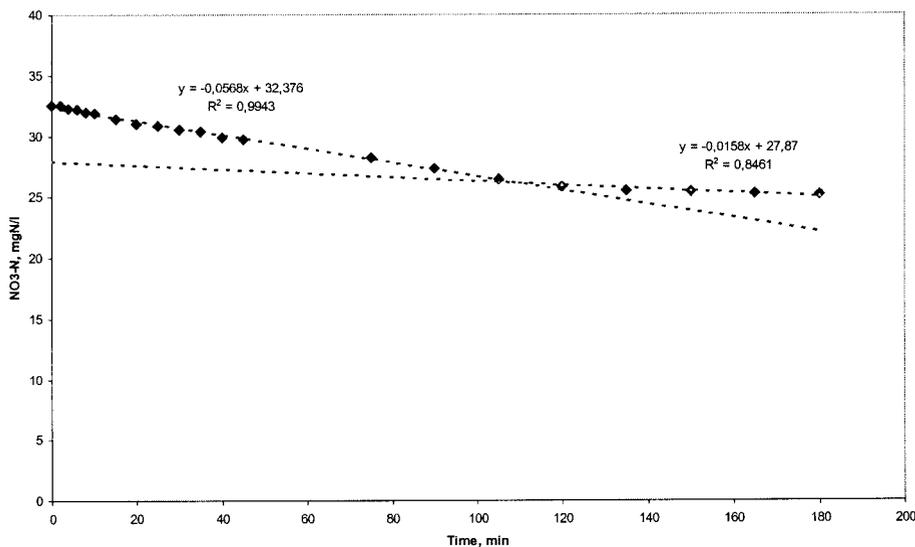

Figure 1 Typical trend of nitrates after a pulse dose of domestic wastewater in Treviso WWTP

189

step depending on soluble COD (S_s) is absent. In this case no real contribution is given by the readily biodegradable COD fraction, therefore only the particulate COD and the endogenous activity determine the overall denitrification potential of this wastewater. Thus the hydrolysis rate is the limiting step, because it is the only way to increase the S_s availability. It is clear that no satisfactory nitrogen removal can be achieved in these conditions.

If the anaerobic fermentation products from the OFMSW are added to the wastewater a totally different nitrate trend can be observed (Figure 2).

In all the NUR tests the fermentation products addition was done according to the typical daily per capita production of 300 g of OFMSW and 250 l of wastewater, as mentioned above. The results obtained with the fermentation products addition were confirmed and evaluated in a wider range of conditions, considering different amount of addition and comparing these data with other synthetic RBCOD sources, such as methanol, acetic acid and lactic acid. From the denitrification rate values (Table 3) it was possible to outline that the anaerobic fermentation products from the OFMSW are comparable with acetate as electron donor in denitrification processes. Furthermore, the maximum denitrification rates obtained in this study with the use of fermentation products, are smaller than the ones reported in Pavan *et al.* (1998), probably because of the different characteristics of the activated sludge used in the NUR batch tests.

The total denitrification rate allows 1.3 mgN/gMLVSS h, determining a 3 times increase over that with wastewater as the unique electron donor. This value is the overall result of three different rates: the first, which is the highest, is due to the OFMSW fermentation products addition and depends on the S_s larger availability (220% of RBCOD increase, see Table 2). With the fermentation products addition, the maximum denitrification rate is characteristically close to 5 mgN/gMLVSS h and similar to those obtained using pure carbon sources such as methanol or acetate, as confirmed by this study by means of some tests performed with these substrates in the same experimental conditions (see Table 3).

The second denitrification rate relies on X_s: this value is higher than the ones obtained exclusively with wastewater as electron donor. This is because the OFMSW fermentation products addition leads to an increase of this substrate fraction and the hydrolysis phenomena, which convert Xs into Ss, are not limited. The endogenous denitrification rate is the same as for the wastewater experiment (see Table 4). A keynote is that no phosphorus release was observed during NUR tests, therefore the available RBCOD was used only for nitrogen removal.
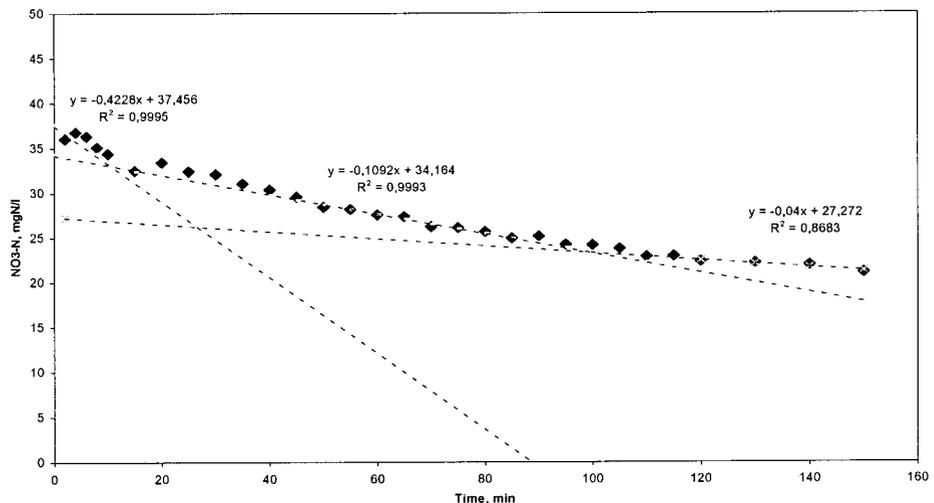

Figure 2 Trend of nitrates after a pulse dose of domestic wastewater and fermented OFMSW

190

Table 3 Carbon sources and observed maximum denitrification rates

Max denitrification rate, mgN/mgMLVSS h[a]	Carbon source	References
2.3–4	Acetate	This study
0.4–1	Methanol	This study
1–1.1	Lactic Acid	This study
3–5.5	Anaerobic fermented of OFMSW	This study
7–11	Anaerobic fermented of OFMSW	Pavan *et al.* (1998)
3.2	Acetate	Isaacs and Henze (1995)
4.1	Sludge hydrolysed	Isaacs and Henze (1995)
3.6	Acetate	Kujawa and Klapwijk (1999)
1–3	S_s	Kujawa and Klapwijk (1999)

(a) Rates expressed at 20°C by the formula $K_{D,T} = K_{D,20} \cdot \vartheta^{(T-20)}$, where $\vartheta = 1.123$

Table 4 Typical denitrification rates observed during NUR tests

Denitrification rates[a], mgN/gVSS h	Wastewater	Wastewater + OFMSW fermented
k_{D1}	–	5
k_{D2}	0.5	1.2
k_{D3}	0.2	0.3
k_D observed	0.5	1.3

(a) Rates expressed at 20°C by the formula $K_{D,T} = K_{D,20} \cdot \vartheta^{(T-20)}$, where $\vartheta = 1.123$

In view of the fact that nitrites utilisation was negligible, the volumetric denitrification rates are given by

$$r_D = \frac{\Delta(NO_3 - N)}{\Delta t}, \quad \text{mgN} / l \cdot h \tag{1}$$

On Eq. (1) basis, the different volumetric denitrification rates can be defined for the wastewater different COD fractions. Specifically, the total rate r_{D1}, which is the sum of the denitrification rates on S_s, X_s and the one on endogenous respiration, is given by:

$$r_{D1} = r_{D, Ss} + r_{D, Xs} + r_{D, end} \tag{2}$$

while the denitrification rate on X_s and on endogenous conditions, is given by r_{D2}:

$$r_{D2} = r_{D, Xs} + r_{D, end} \tag{3}$$

and the denitrification rate in endogenous condition, r_{D3}, is given by:

$$r_{D3} = r_{D, end} \tag{4}$$

The specific denitrification rate is given by:

$$k_D = \frac{r_D}{X_V}, \quad \text{mgN} / \text{mgMLVSS h} \tag{5}$$

where X_V is the biomass concentration (mg/l).

By reason of Eq. (5) the different denitrification rates can be estimated. Table 4 reviews the main results obtained during NUR tests. It can be noticed that the denitrification rate on X_s is just about the same as the total rate. This is because X_s is the most abundant COD

available fraction for the biological denitrification process after it has been hydrolysed into soluble compounds.

The value of the OFMSW anaerobic fermentation products for the denitrification process can also be estimated by means of the comparison of the specific utilisation, expressed in terms of $mgCOD/mgNO_3$-N, among different carbon sources. This attitude was evaluated on the basis of the reduced amount of nitrates in NUR tests carried out with an initial concentration of different carbon sources of 500 mgCOD/l. Table 5 summarises the obtained results.

Denitrification potential

According to Kujawa and Klapwijk (1999) the denitrification potential of a wastewater can be described as the amount of nitrates, expressed as mg NO_3-N/l, which can be denitrified on the COD fractions S_s and X_s:

$$DP_{S_s} = \frac{\Delta(NO_3^- N + 0.6 NO_2^- N)}{f_{ww}}; \quad mgNO_3^- N / l \tag{6}$$

and

$$DP_{X_s} = \frac{\Delta(NO_3^- N + 0.6 NO_2^- N)}{f_{ww}}; \quad mgNO_3^- N / l \tag{7}$$

were f_{WW} is the wastewater/activated sludge ratio and 0.6 is the conversion factor from nitrites to nitrates nitrogen. The denitrification potential of the wastewater fractions does not rely on the mixed liquor biomass concentration. Even with different MLSS levels the amount of nitrate that can be denitrified on the subsequent wastewater fractions, S_s and X_s, is always the same and only the reduction rate is changing. If the S_s and X_s fractions are not adequate for the denitrification process, the endogenous denitrification is also needed to accomplish the effluent standards for total nitrogen.

The denitrification potential for endogenous conditions depends on the total denitrification volume and is given by:

$$DP_{end} = \frac{r_{D,end} V_D}{Q_{IN}}; \quad mgNO_3^- N / l \tag{8}$$

where V_D represents the denitrification step volume and Q_{IN} the wastewater inflow rate; thus, this ratio is, in other words, the hydraulic retention time (HRT) of the anoxic zone.

If the biomass concentration in the denitrification step should vary, the specific endogenous denitrification potential is to be used:

$$DP_{end} = \frac{r_{D,end} V_D}{Q_{IN} X_V} = \frac{k_{D,end} V_D}{Q_{IN}}; \quad mgNO_3^- N / l \tag{9}$$

where X_V is the biomass concentration (mg/l) in the anoxic step.

Ultimately, the total denitrification potential of the system depends, firstly, on the wastewater characteristics and, secondly, on the basic denitrifying activity of the sludge:

Table 5 Specific utilisation of different carbon sources

Carbon source	Specific consumption, mgCOD/mg NO_3-N
OFMSW anaerobic fermented	1.6–2.4
Acetate	2.9–3.6
Lactic acid	5.5–6.0
Methanol	5.0–6.2

$$\Sigma DP = DP_{Ss} + DP_{Xs} + DP_{endog, spec} \cdot X_V \cdot (V_D)$$ (10)

In this study no significant variations of nitrites concentration were observed, therefore the nitrates variation can totally explain the denitrification potential of the wastewater.

Table 6 summarises the denitrification potential of the wastewater with and without the anaerobic fermentation products addition. As can be seen, in this latter case the denitrification potential, SDP, is nearly three times greater as both the S_s and X_s COD fractions increased thanks to the anaerobic fermentation products addition, while the denitrification potential on the endogenous activity was the same (Table 6).

Table 6 Denitrification potential

Denitrification potential		Wastewater	Wastewater with OFMSW fermented
DP_{Ss} ,	$mgNO_3$-N/l	0	7
DP_{Xs} ,	$mgNO_3$-N/l	6	10
DP_{end} ,	$mgNO_3$-N/l	0.1	0.1
ΣDP,	$mgNO_3$-N/l	6.1	17.1

Conclusions

The investigation described in this paper has brought some important information about the advantages of embracing an integrated MSW-wastewater cycles strategy, on the basis of the denitrification potential evaluation. In particular:

- The comparison between the sole wastewater and the wastewater with fermentation products addition on a mass balance basis has demonstrated a global COD increase near to 70%, and of 220% in terms of RBCOD. These values are much larger than the ones obtained by primary sludge anaerobic fermentation (3–5%, Rabinowitz, 1998);
- No valuable increases in the inlet nutrients content were observed after the addition of the fermentation products and, subsequently, the C/N and C/P ratios were significantly enhanced;
- Maximum values of denitrification rates obtained using the proposed approach are very appealing, especially when compared with the ones coming from synthetic substrates such as methanol or acetate: values up to 5.5 mgN/mgVSS h were achieved compared with 2.3 mgN/mgVSS h obtained with acetate addition;
- A real denitrification potential enhancement can be accomplished by the addition of the anaerobic fermentation products from the OFMSW: a nearly 3 times increase (from 6 to 17 $mgNO_3$-N/l) of this value was observed.

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D. Bolzonella et al.

194