

## MOLASSES AS A CARBON SOURCE FOR DENITRIFICATION

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**Abstract:** The paper presents the results of an experiment with sugar-industry waste (molasses) as an organic carbon source for denitrification. The investigations concern the influence of untreated molasses and molasses after pretreatment (hydrolyzed molasses) and variable COD/N ratio (6.0; 5.0; 4.0) on denitrification efficiency and kinetics. Moreover, sludge production, in dependence on tested carbon source, was estimated. At COD/N ratio 6 and 5, regardless of applied organic carbon source (untreated molasses, hydrolyzed molasses), the denitrification efficiency was over 98%. However, from kinetic analysis it results that a kind of carbon source and COD/N ratio have an effect on denitrification rate. The highest nitrate removal rate – 9.5 mg  $N_{NO_3}/(dm^3 \cdot h)$  was obtained at COD/N = 6 in the reactor with hydrolyzed molasses as a carbon source and the lowest – 5.14 mg  $N_{NO_3}/(dm^3 \cdot h)$  in reactor with untreated molasses at COD/N = 5.0. The lowering of COD/N ratio to 4 caused decrease of the process efficiency to 27.6% (untreated molasses) and 44.3% (hydrolyzed molasses). Hydrolyzed molasses as a carbon source caused higher production of activated sludge. In reactors with untreated molasses  $Y_{obs}$  equals 0.40 mg VSS/mg COD at COD/N ratio 6 and 0.31 mg VSS/mg COD at COD/N ratio 5. In reactors with molasses after hydrolysis  $Y_{obs}$  were 1.35-fold and 1.5-fold higher, respectively. Since, the molasses hydrolysis results in rising costs of wastewater treatment and cause higher sludge production, untreated molasses seems to be a more suitable carbon source for denitrification.

## INTRODUCTION

The biological oxidation of nitrogen compounds occurring in wastewater leads to nitrates as the final products. The biological removal of nitrate can be achieved via heterotrophic denitrification, which requires a carbon source as an electron donor. In the case of wastewater, especially with a low COD/N ratio, the readily biodegradable organics can be a limiting factor for complete nitrate removal.

From the review of the literature, it can be concluded that short-chain fatty acids and low molecular weight alcohols are the most often applied as an external carbon source in denitrification [5, 7, 9, 10, 11, 15, 20]. In the case of wastewater containing high concentrations of nitrate, the use of commercially available chemicals represents a critical cost in the process. Therefore, researchers use waste materials as an alternative carbon source, e.g. industrial effluents, primary sludge, supernatant of thermally treated wastewater sludge or organic fraction of municipal solid waste [2, 3, 18, 21, 27].

In spite of a multiplicity of investigations, the dose of an external organic carbon source required for denitrification process, has not been established. The main reason is that the process efficiency depends on many factors, such as the kind of external carbon

source, the type of reactor used and the microorganisms used in the process (pure cultures, mixed populations). So, it can be concluded that the optimal C/N ratio for the denitrification system for treating by different wastewater must be experimentally determined.

Nowadays, with the rising costs of sludge disposal, the minimization of sludge production during wastewater treatment has become of an increasing importance. However, studies concerning denitrification with an external carbon source have dealt with process efficiency without the examination of activated sludge production. Therefore, the aim of this study was to examine sugar-industry waste (molasses) as an organic carbon source for denitrification, to determine process efficiency and kinetics in dependence on the pre-treatment of molasses and COD/N ratio and to determine the define sludge production in term of  $Y_{obs}$ .

## METHODS

### **Process configuration**

Experiments were carried out in sequencing batch reactors SBRs with the working volume of 2.5 dm<sup>3</sup>. The reactors were operated in a 24-h cycle mode (filling 0.25 h, anoxic 23 h, settling 0.5 h and decantation 0.25 h).

Three series were carried out (series 1–3) differed in COD/N ratio in the influent, i.e. 6.0 (series 1), 5.0 (series 2) and 4.0 (series 3). At each series the investigations were conducted in parallel research stations (SBR 1 and SBR 2) with untreated molasses and molasses after pretreatment (hydrolyzed molasses) as an organic carbon source (Tab. 1).

Table. 1. Technological parameters in series 1–3

Technological parameters	SBR 1	SBR 2
Carbon source	molasses	hydrolyzed molasses
Hydraulic retention time (HRT) [d]	1.25	1.25
Volumetric exchange rate [-]	0.8	0.8
$C_{0,N-NO_3}$ [mg N <sub>NO<sub>3</sub></sub> /dm <sup>3</sup> ]	100	100

All reactors were operated at a room temperature ( $19 \pm 3^\circ\text{C}$ ) for 2 months at each COD/N ratio.

### **Wastewater and carbon source characterization**

SBRs were supplied with the activated sludge from anoxic chamber of municipal wastewater treatment plant. The initial MLVSS concentration in SBRs was 3.5 g/dm<sup>3</sup>. The reactors were fed with synthetic wastewater – composition and concentration of micronutrients were taken from Coelho *et al.* [4] (modification, without NH<sub>4</sub>Cl). As a consequence, the treatment process was not limited by the lack of these components.

As a nitrate source KNO<sub>3</sub> was used in specific amount to maintain its concentration on the level of 100 mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup> at the beginning of SBR cycle. As an external carbon source in SBR reactors sugar beet molasses (untreated and hydrolyzed) were used.

### *Hydrolysis of molasses*

To increase susceptibility of molasses to biodegradation, it was hydrolyzed. A portion of 240 g molasses was dissolved in 760 g of deionised water and hydrolyzed for 30 min at 100°C and at pH 1.5 (adjusted with 98% H<sub>2</sub>SO<sub>4</sub>). Next, the solution was cooled to about 60°C and neutralized to pH 7.5 with Ca(OH)<sub>2</sub>. After 12 hours, it was centrifuged at 4500 rpm for 10 min. to remove precipitated CaSO<sub>4</sub>.

### *Preparation of stock solutions*

Depending on COD/N ratio, an established amount of molasses stock solution was put into SBR 1 or hydrolyzed molasses was put to SBR 2, prepared as follows: 260 g of molasses was filled up with deionised water to 1 dm<sup>3</sup> and diluted 200-times. Stock solution of hydrolyzed molasses was prepared in similar way. The characteristic of stock solutions is given in Table 2 (chapter *Carbon source characterization*).

### *Analytical methods*

The influents and effluents from the SBRs were subjected to measurements with the following parameters:

- organic compounds expressed as COD (dichromate reflux method) – according to Standard Methods (1997) [25] and BOD<sub>5</sub> – according to DIN EN 1899-1/EN 1899-2 official EPA method using OxiTop® made by WTW company,
- nitrogen compounds (nitrite nitrogen (colorimetric method with sulfanilic acid and 1-naphthylamine) and nitrate nitrogen (colorimetric method with phenolsulfonic acid) – according to the Standard Methods (1997) [25],
- volatile suspended solids (VSS) and total suspended solids (TSS) in the settled effluent (according to the to the Standard Methods, 1997) [25].

The mixed reactor content was measured for the mixed liquor total suspended solids (MLTSS) and volatile suspended solids (MLVSS) (according to the Standard Methods, 1997) [25].

## RESULTS AND DISCUSSION

### *Carbon source characterization*

Molasses hydrolysis caused increase of biodegradability in comparison with untreated molasses. It was confirmed by higher BOD<sub>5</sub>/COD ratio and value of constant rate of oxygen uptake  $k$ , which in the case of molasses were 0.58 and 0.203 1/d, respectively. However, for hydrolyzed molasses they were 1.3- and 1.5-fold higher, respectively (Tab. 2).

Table. 2. Characteristics of the carbon sources

Parameter	Unit	Molasses		Hydrolyzed molasses	
COD	[mg/dm <sup>3</sup> ]	918	± 9.07	917	± 11.76
BOD <sub>5</sub>	[mg/dm <sup>3</sup> ]	533	± 7.9	721	± 6.98
BOD <sub>5</sub> /COD	[-]	0.580	± 0.012	0.79	± 0.014
$k$	[1/d]	0.203	± 0.006	0.303	± 0.010

In the literature, it is usually stated that the value of  $k$  depends primarily on the rate at which the organic substances can be biologically oxidized. Thus, for instance, in raw

municipal wastewater, values of  $k$  are much higher (0.3–0.5 1/d) than in some industrial wastewater containing primarily slowly degradable compounds (0.2 1/d) [23].

### The efficiency and rate of denitrification

#### The efficiency of denitrification

The efficiency of denitrification was investigated in 3 series differed in COD/N ratio in raw wastewater, which in individual series was 6.0 (series 1), 5.0 (series 2) and 4.0 (series 3). In each series, the research was conducted in 2 SBR reactors, with carbon source in a form of untreated molasses (SBR 1) and hydrolyzed molasses (SBR 2).

Nitrate and nitrite concentrations in treated wastewater are given in Table 3. From the data obtained, it is clear that in the effluent from SBR reactors both at COD/N = 6.0, and COD/N = 5.0 nitrite and nitrate concentrations did not exceed 1 mg  $N_{NO_x}/dm^3$ .

Table 3. Concentrations of nitrite and nitrate in the effluent

Carbon sources	COD/N = 6 (series 1)		COD/N = 5 (series 2)		COD/N = 4 (series 3)	
	$N_{NO_2}$ [mg/dm <sup>3</sup> ]	$N_{NO_3}$ [mg/dm <sup>3</sup> ]	$N_{NO_2}$ [mg/dm <sup>3</sup> ]	$N_{NO_3}$ [mg/dm <sup>3</sup> ]	$N_{NO_2}$ [mg/dm <sup>3</sup> ]	$N_{NO_3}$ [mg/dm <sup>3</sup> ]
Molasses (SBR 1)	0.03 ± 0.001	0.28 ± 0.03	0.9 ± 0.024	0.29 ± 0.007	56.3 ± 3.84	16.2 ± 1.05
Hydrolyzed molasses (SBR 2)	0.05 ± 0.002	0.26 ± 0.03	0.61 ± 0.02	0.11 ± 0.011	43.1 ± 2.75	12.4 ± 0.92

Lowering of COD/N ratio to 4.0 caused increase of the sum of nitrite and nitrate concentration in the effluent to 72.5 mg  $N_{NO_x}/dm^3$  (molasses) and 55.5 mg  $N_{NO_x}/dm^3$  (hydrolyzed molasses), what responded to the denitrification efficiency of 27.6% and 44.3%, respectively. *Æsøy et al.* [1] stated that obtaining complete denitrification of nitrate (25 mg  $N_{NO_3}/dm^3$ ) in biological bed was possible at COD/N ratio of 8–10 mg COD/mg  $N_{NO_3}$  and when organic fraction of municipal waste was used as carbon source. The investigations of *Tsonis* [26] with use of wastewater from olives processing in modified Bardenpho system revealed that demand for that substrate was from 4.6 to 5.4 mg COD/mg  $N_{NO_3}$ . *Quan et al.* [24] examined removal of nitrate with use of hydrolyzed molasses as a carbon source. The authors stated that the content of readily accessible organics in molasses after acid hydrolysis was 47.5%, what allowed to achieve 91.6% efficiency of denitrification at COD/ $N_{NO_3}$  4.8–5.3. Thus, the authors demonstrated that hydrolyzed molasses can be an effective carbon source in denitrification process. From our investigations it is clear that at similar COD/N ratio complete denitrification can be achieved using both hydrolyzed molasses and molasses without pretreatment.

#### Denitrification rate

In series 1 (COD/N = 6.0) and 2 (COD/N = 5.0), for which complete denitrification was achieved, after attainment of steady-state conditions in both reactors, kinetic analysis was performed. On the basis of changes in nitrite and nitrate concentrations in the SBR operating cycle, a reaction rate was estimated.

The analysis of experimental results showed that denitrification was a zero-order kinetics defined by the following differential equation:

$$r_{deni,NO_x} = -\frac{dC_{NO_x}}{dt} = -k_{deni,NO_x} \quad (1)$$

The solution for this could be fitted to the experimental data according to (2):

$$C_{NO_x} = -k_{deni,NO_x} \times t + C_{0,NO_x} \quad (2)$$

where:

$r_{deni,NO_x}$  – denitrification rate [ $\text{mg N}_{NO_x}/(\text{dm}^3 \cdot \text{h})$ ],

$k_{deni,NO_x}$  – constant of denitrification rate [ $\text{mg N}_{NO_x}/(\text{dm}^3 \cdot \text{h})$ ],

$C_{NO_x}$  – sum of nitrite and nitrate concentration after time  $t$  [ $\text{mg N}_{NO_x}/\text{dm}^3$ ],

$t$  – time [h],

$C_{0,NO_x}$  – sum of nitrite and nitrate concentration at the beginning of the SBR operating cycle [ $\text{mg N}_{NO_x}/\text{dm}^3$ ].

The changes of nitrite and nitrate concentration in SBR operating cycle, depending on applied carbon source at COD/N equal 6.0 is presented in Figure 1. Denitrification rate was  $8.4 \text{ mg N}_{NO_x}/(\text{dm}^3 \cdot \text{h})$  (molasses) and  $9.5 \text{ mg N}_{NO_x}/(\text{dm}^3 \cdot \text{h})$  (hydrolyzed molasses). By the first hours of the cycle an increase of nitrite concentration was observed in both reactors (Fig. 1), and their highest concentrations  $39.7 \text{ mg N}_{NO_2}/\text{dm}^3$  (SBR 1) and  $34.5 \text{ mg N}_{NO_2}/\text{dm}^3$  (SBR 2) were noted at 7<sup>th</sup> and 3<sup>rd</sup> h of the cycle, respectively. Complete reduction of nitrate and nitrite was stated during 12 h of the cycle.

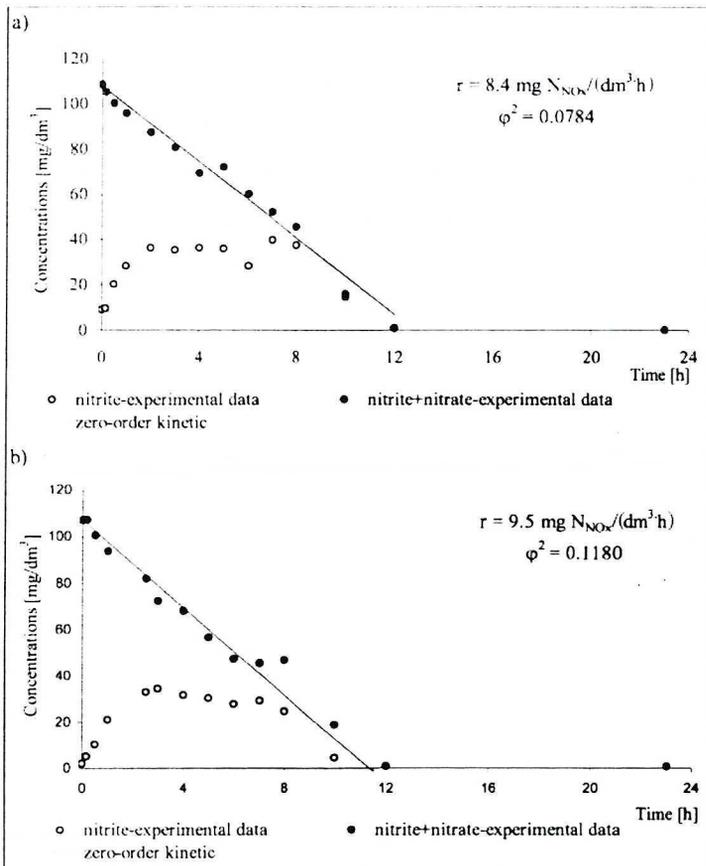


Fig. 1. Concentrations profile of nitrite and sum of nitrite and nitrate and reaction rates described by zero-order kinetics at COD/N = 6.0 a) – molasses, b) – hydrolyzed molasses

In Figure 2, changes of nitrite and nitrate concentration in SBR operating cycle, depending on type of carbon source at COD/N = 5.0 are shown.

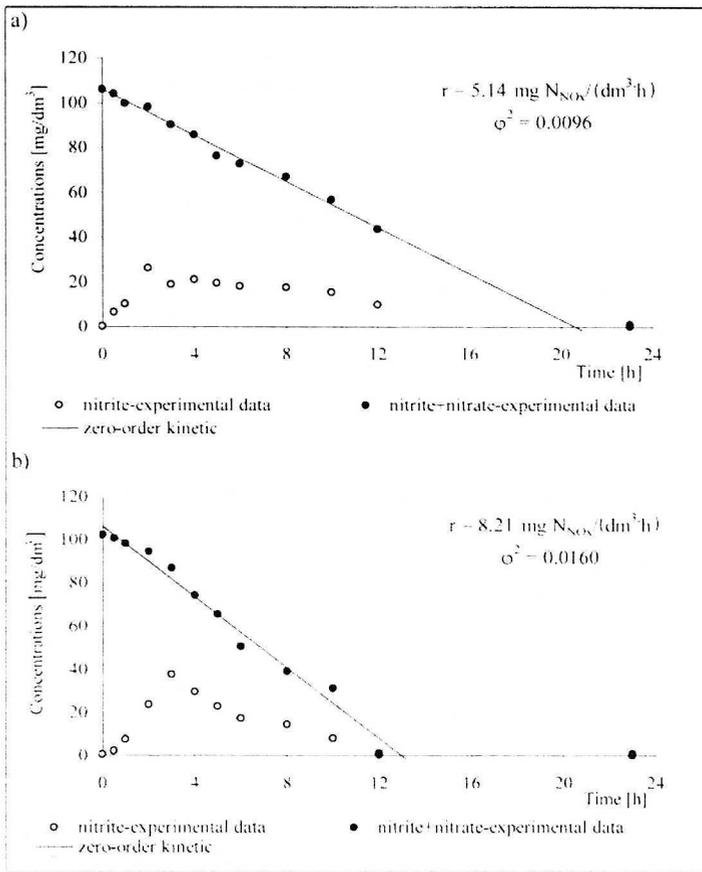


Fig. 2. Concentrations profile of nitrite and sum of nitrite and nitrate and reaction rates described by zero-order kinetics at COD/N = 5.0 a) – molasses, b) – hydrolyzed molasses

Higher denitrification rate at this COD/N ratio was obtained in SBR 2 (hydrolyzed molasses) (Fig. 2b). It was  $8.21 \text{ mg N}_{\text{NOX}}/(\text{dm}^3 \cdot \text{h})$  and 1.6-fold higher in comparison with SBR 1 (Fig. 2a), where untreated molasses was a carbon source.

In reactor with hydrolyzed molasses (SBR 2), after 10 h of the cycle, the concentration of the sum of nitrite and nitrate concentration was on the level of about  $30 \text{ mg N}_{\text{NOX}}/\text{dm}^3$ , and after next 2 h decreased to about  $1 \text{ mg N}_{\text{NOX}}/\text{dm}^3$  (Fig. 2b). It means that already after 12 h of the cycle complete denitrification was obtained. However, in the case of molasses without hydrolysis the decrease of the sum of nitrite and nitrate concentration reached 58%.

A significant lowering of the denitrification rate with untreated molasses as a carbon source after decreasing of COD/N<sub>NO3</sub> from 6 to 5, is very significant because of practical use. At the rate of  $5.14 \text{ mg N}_{\text{NOX}}/(\text{dm}^3 \cdot \text{h})$ , the time necessary to complete reduction of nitrite and nitrate is about 20 h, which poses over 80% of the cycle length. It means that

Table. 4. Denitrification rate for various carbon-utilizing technologies according to literature data

Carbon source	C/N ratio	Kind of wastewater	Reactor system	Denitrification rate	Reference
Methanol	$\text{CH}_3\text{OH}/\text{N}_{\text{NO}_3} > 2.5$	synthetic wastewater	continuous-flow stirred reactor	4.35 mg/(g VSS·h)	Foglar, Briski [9]
Methanol	3.9 g COD/g N	wastewater	single activated sludge	3 mg/(g VSS·h)	Nyberg <i>et al.</i> [20]
Methanol	8 mg $\text{CH}_3\text{OH}/\text{dm}^3$	wastewater	SBR	0.8 mg/(g VSS·h)	Louzeiro <i>et al.</i> [15]
Methanol	–	wastewater	predenitrification system	3.2 mg/(g VSS·h)	Peng <i>et al.</i> [22]
Methanol	1.8–7.3 mg COD/mg $\text{N}_{\text{NO}_3}$	landfill leachate	SBR	39.9–48.4 mg/(dm <sup>3</sup> ·h)	Kulikowska, Klimiuk [12]
Ethanol	C/N = 6.0	synthetic wastewater	columns with beads of immobilized <i>Pseudomonas butanovora</i>	67.9 mg/(dm <sup>3</sup> ·h)	Kesserü <i>et al.</i> [11]
Ethanol	4.4 g COD/g N	wastewater	single activated sludge	10 mg/(g VSS·h)	Nyberg <i>et al.</i> [20]
Ethanol	–	wastewater	predenitrification system	9.6 mg/(g VSS·h)	Peng <i>et al.</i> [22]
Ethanol	$\text{COD}/\text{N}_{\text{utilization}} = 7.4$	landfill leachate	SBR	6.67 mg/(g VSS·h)	Doyle <i>et al.</i> [6]
Acetate	–	wastewater	predenitrification system	12.0 mg/(g VSS·h)	Peng <i>et al.</i> [22]
Acetate	$\text{COD}/\text{N}_{\text{utilization}} = 7.4$	landfill leachate	SBR	6.67 mg/(g VSS·h)	Doyle <i>et al.</i> [6]
Acetic acid	C/N = 6.0	synthetic wastewater	columns with beads of immobilized <i>P. butanovora</i>	63.75 mg/(dm <sup>3</sup> ·h)	Kesserü <i>et al.</i> [11]
Acetic acid	2.7 mg COD/mg $\text{N}_{\text{NO}_3}$	landfill leachate	SBR	7.14 mg/(g VSS·h)	Kulikowska, Racka [13]
Acetic acid + propionic acid 1:1	2 mg C/mg $\text{N}_{\text{NO}_3}$	synthetic wastewater	batch experiment	0.35–1.75 mg/(g·h)	Elefsiniotis, Li [7]
Propionic acid	2 mg C/mg $\text{N}_{\text{NO}_3}$	synthetic wastewater	batch experiment	0.058–1.2 mg/(g·h)	Elefsiniotis, Li [7]
Propionic acid	5.3 mg COD/mg $\text{N}_{\text{NO}_3}$	landfill leachate	SBR	5.08 mg/(g VSS·h)	Kulikowska, Racka [13]
Butyric acid	5.1 mg COD/mg $\text{N}_{\text{NO}_3}$	landfill leachate	SBR	12.2 mg/(g VSS·h)	Kulikowska, Racka [13]
Maltose	$\text{COD}/\text{N}_{\text{utilization}} = 7.4$	landfill leachate	SBR	7.08 mg/(g VSS·h)	Doyle <i>et al.</i> [6]
Succinic acid	C/N = 6.0	synthetic wastewater	columns with beads of immobilized <i>P. butanovora</i>	48 mg/(dm <sup>3</sup> ·h)	Kesserü <i>et al.</i> [11]

with a slight increase of nitrate concentration in the influent, the length of the cycle may turn out to be insufficient to complete nitrate reduction and may lead to loss of process stability.

From the review of the literature, it is clear that values of denitrification rate using fatty acids and alcohols as an external carbon source are numerous. However, the data obtained by individual authors differed by order of magnitude even for the same carbon source (Tab. 4). The differences could result from the fact that individual experiments varied from each other by operational conditions, dosage of organic carbon, reactor type, and kind of treated wastewater (industrial, municipal or synthetic). On the other hand, the literature data concerning denitrification rate with the use of alternative carbon sources are sparse. Barlindhaug, Ødegaard [3] noticed denitrification rate of 1.4 kg  $N_{NO_3}/(m^3 \cdot d)$  at  $COD/N_{NO_3} = 8.0$  in a biological bed with hydrolyzed excessive sludge as a carbon source. Usage of a similar carbon source (a mixture of hydrolyzed sludge and organic fraction of municipal waste) and  $COD/N_{NO_3}$  Esøy *et al.* [1] enabled to achieve a denitrification rate nearly 2-fold higher. Elefsiniotis *et al.* [7] investigated the ability of VFA generated from anaerobic digester (treating a mixture of starch rich industrial and municipal wastewater) to act as a carbon source for denitrification. According to the authors the mean denitrification rate was 0.0111 g  $N_{NO_3}/g$  VSS d.

#### Observed biomass yield coefficient

In present study an observed biomass yield coefficient  $Y_{obs}$  was determined, depending on the type of organic carbon source and COD/N ratio in raw wastewater. The value of the  $Y_{obs}$  corresponds to net biomass yield coefficient and can be calculated from the following equation (4):

$$Y_{obs} = \frac{X_{org} \cdot (V_w / t_c) + X_e \cdot (V_{eff} / t_c)}{(C_s - C_e) \cdot (V_m / t_c)} \quad (4)$$

where:

$Y_{obs}$  – observed biomass yield coefficient [mg VSS/mg COD],

$X_{org}$  – volatile suspended solids in SBR [mg VSS/dm<sup>3</sup>],

$V_w^{org}$  – volume of suspended solids disposed in SBR operating cycle [dm<sup>3</sup>],

$t_c$  – time of SBR operating cycle [d],

$X_e$  – effluent volatile suspended solids concentration [mg VSS/dm<sup>3</sup>],

$V_{eff}$  – volume of wastewater effluent in SBR operating cycle [dm<sup>3</sup>],

$V_{in}$  – volume of wastewater influent in SBR operating cycle [dm<sup>3</sup>] ( $V_{in} = V_{eff} + V_w$ ),

$C_s$  – concentration of COD in raw wastewater [mg COD/dm<sup>3</sup>],

$C_e$  – concentration of COD in the effluent [mg COD/dm<sup>3</sup>].

The values of observed biomass yield coefficient  $Y_{obs}$  depending on carbon source and COD/N ratio in raw wastewater calculated from equation 4 are given in Table 5.

Table 5. Observed biomass yield coefficient ( $Y_{obs}$ )

$Y_{obs}$ [mg VSS/mg COD]	COD/N = 6.0		COD/N = 5.0	
	molasses	hydrolyzed molasses	molasses	hydrolyzed molasses
	0.40	0.54	0.31	0.47

Higher values of  $Y_{\text{obs}}$  were stated in reactors, where hydrolyzed molasses was applied as a carbon source – 0.54 mg VSS/mg COD (COD/N = 6.0) and 0.47 mg VSS/mg COD (COD/N = 5.0). It means that in the case of hydrolyzed molasses 47–54% of COD was converted to biomass during the denitrification process. In reactors with untreated molasses  $Y_{\text{obs}}$  was 1.35-fold and 1.52-fold lower, respectively.

It is known that pretreatment of molasses enables better assimilation of substrate by activated sludge microorganisms. On the other hand, readily biodegradable substances give more biomass growth [23].

In the effluent from SBRs with molasses and hydrolyzed molasses concentrations of organics expressed as COD were similar and equalled 112 mg COD/dm<sup>3</sup> (molasses) and 108 mg COD/dm<sup>3</sup> (hydrolyzed molasses) at COD/N = 6.0 and 98 mg COD/dm<sup>3</sup> and 89 mg COD/dm<sup>3</sup>, respectively, at COD/N = 5.0. Therefore, it may be supposed that polysaccharides (the major components in molasses) have carbon chains that are too long to be used by microorganisms. On the other hand, the main product of hydrolyzed molasses are reduced sugars – glucose or sugars similar to glucose [19], which are considered as readily biodegradable organics and it is known that this type of substances gives higher biomass growth. Therefore, in the case of hydrolyzed molasses  $Y_{\text{obs}}$  was higher than for untreated molasses.

Majone *et al.* [16] studied the removal mechanisms and sludge production during the pre-denitrification in anoxic/aerobic sequencing process with different substrates (commercially available acetate, ethanol, glucose, glutamic acid as carbon source). According to the authors, the observed biomass yield coefficient for glucose was the highest among applied substrates – 0.74 g COD/g COD (0.5 g VSS/g COD) and was comparable with the results obtained from our own research for hydrolyzed molasses.

In the literature, there are conflicting reports on biosolids production. It is known that the value of  $Y_{\text{obs}}$  depends on a type of substrate [23]. According to the authors, values of  $Y_{\text{obs}}$  for aerobic heterotrophs in a system with plug flow pattern and in completely mixed system changed in the range of 0.53–0.62 g COD/g COD for glucose, 0.35–0.49 g COD/g COD for acetic acid, 0.25–0.48 g COD/g COD for methanol and 0.35–0.37 g COD/g COD for ethanol. McClintock *et al.* [17] have found that biosolids production is lower when anoxic conditions are incorporated in the process. However, from other author's researches it results that sludge production in anoxic system was the same or higher than in aerobic system (Lishman *et al.* [14] (after Smyth 1994).

## CONCLUSIONS

On the basis of the obtained results the conclusions are as follows:

1. Molasses hydrolysis caused increase in organics biodegradability. The values of  $BOD_5/COD$  ratio and rate constants of oxygen consumption  $k$  for hydrolyzed molasses were 1.3-fold and 1.5-fold higher, respectively, in comparison with non-hydrolyzed molasses.
2. Complete denitrification (the efficiency above 98%), irrespective of organic carbon source (untreated molasses, hydrolyzed molasses) was obtained both at COD/N ratio of 6.0 and 5.0. Decreasing of COD/N ratio to 4.0 caused decline of denitrification efficiency to 27.6% (untreated molasses) and to 44.3% (hydrolyzed molasses).
3. Denitrification rate at COD/N ratio of 6.0 was 9.5 mg  $N_{\text{NOx}}/(dm^3 \cdot h)$  in the reactor

with hydrolyzed molasses and  $8.4 \text{ mg N}_{\text{NOX}}/(\text{dm}^3 \cdot \text{h})$  in reactor with non-hydrolyzed molasses. It means that in both cases complete denitrification proceeded within 12 h of the cycle. After decreasing of COD/N ratio to 5.0, the time necessary to reduction of nitrate for hydrolyzed molasses remained unchanged. However, in case of non-hydrolyzed molasses it lengthened to 20 h.

4. Sludge production was dependent on the substrate used. In reactors with untreated molasses, the value of observed yield coefficient was 1.35-fold (COD/N = 6.0) and 1.52-fold (COD/N = 5.0) lower in comparison with hydrolyzed molasses.
5. Taking into account the economical aspects (molasses hydrolysis increases the cost of wastewater treatment) and the fact that molasses after hydrolysis causes higher sludge production, untreated molasses seems a more suitable carbon source for denitrification.

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#### MELASA JAKO ŹRÓDŁO WĘGLA W PROCESIE DENITRYFIKACJI

Praca zawiera wyniki badań dotyczące możliwości wykorzystania melasy – produktu odpadowego powstającego w przemyśle cukrowniczym – jako źródła węgla organicznego w procesie denitryfikacji. Badano wpływ hydrolizy melasy oraz stosunku ChZT/N (6,0; 5,0; 4,0) na efektywność i kinetykę procesu. Określono również przyrost osadu czynnego w zależności od rodzaju źródła węgla (melasa, melasa zhydrolizowana) oraz stosunku ChZT/N. Przy stosunku ChZT/N wynoszącym 6,0 i 5,0, niezależnie od formy występowania źródła węgla organicznego (melasa, melasa zhydrolizowana), efektywność denitryfikacji przekraczała 98%. Badania kinetyki procesu wykazały natomiast, że rodzaj źródła węgla oraz stosunek ChZT/N wpływały na szybkość denitryfikacji. Najwyższą szybkość procesu –  $9,5 \text{ mg N}_{\text{NO}_x}/(\text{dm}^3 \cdot \text{h})$  odnotowano przy ChZT/N wynoszącym 6,0 w reaktorze z melasą zhydrolizowaną a najniższą –  $5,14 \text{ mg N}_{\text{NO}_x}/(\text{dm}^3 \cdot \text{h})$  w reaktorze z melasą niezhydrolizowaną przy ChZT/N wynoszącym 5,0. Obniżenie stosunku ChZT/N do 4,0 spowodowało spadek efektywności procesu do 27,6% (melasa niezhydrolizowana) oraz 44,3% (melasa zhydrolizowana). Zastosowanie melasy zhydrolizowanej powodowało wyższy przyrost osadu czynnego. W reaktorach, gdzie źródłem węgla była melasa niezhydrolizowana  $Y_{\text{obs}}$  wynosił  $0,4 \text{ mg smo}/\text{mg ChZT}$  przy stosunku ChZT/N wynoszącym 6,0 i  $0,31 \text{ mg smo}/\text{mg ChZT}$  przy stosunku 5,0. W reaktorach z melasą zhydrolizowaną  $Y_{\text{obs}}$  był odpowiednio 1,35-krotnie i 1,5-krotnie wyższy. Biorąc pod uwagę, że hydroliza melasy podnosi koszty oczyszczania ścieków oraz przyczynia się do wyższej produkcji osadu nadmiernego, melasa niezhydrolizowana wydaje się być lepszym źródłem węgla organicznego w procesie denitryfikacji.