

Scientific paper

# Industrial Wastewater as a Source of External Organic Carbon for the Biological Nutrient Removal

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## Abstract

Addition of external organic carbon source for denitrification is generally used in wastewater treatment plants (WWTPs) to intensify nitrogen removal processes. The aim of the laboratory survey was to measure the composition of concentrated industrial wastewater, determine the possibilities of its use as an external denitrification substrate, and assess its overall impact on WWTP. The obtained results demonstrate that the analysed industrial wastewater is biodegradable, and can be used as a denitrification substrate without special adaptation of biomass. The denitrification rates with tested wastewater were in the range of 1.6 to 1.9 mg<sub>N</sub>/g-h. Negative influence of long-term dosing of industrial wastewater on activated sludge were not confirmed. The effect of imported wastewater on WWTP must be assessed comprehensively, including the impact of heavy metals from wastewater on the sludge quality. The instructions on how to calculate this balance are provided in the article.

**Keywords:** Biodegradability of industrial wastewater, biological wastewater treatment, heavy metals in sludge, denitrification rate, semicontinuous bioreactors

## 1. Introduction

Over the years, considerable effort has been made to advance and optimize the technologies for effective biological nitrogen removal at wastewater treatment plants (WWTPs).<sup>1,2</sup> Heterotrophic denitrification is an efficient process in which, through microbiological activity, a reduction of nitrates and nitrites to nitrogen gas occurs.<sup>3</sup> It has a unique place in the biological removal of nitrogen from wastewater. This is because during the denitrification, nitrogen passes from water into the air. Anoxic zones without dissolved oxygen, in which the redox potential values are in the range of approximately –50 mV to 50 mV for calomel electrode and approximately 150 mV to 250 mV for standard hydrogen electrode, are necessary for this process.<sup>4</sup> Denitrification is most often used in wastewater treatment, where the sources of electrons for nitrogen reduction are organic compounds.<sup>5</sup> The process takes place even in the absence of exogenous organic carbon (C<sub>org</sub>) but its rate is significantly lower. In this case, bacteria use their internal organic compounds as a source of electrons (endogenous process).

In many WWTPs, the absence of readily biodegradable organic substrate in the wastewater is a limiting factor for successful removal of higher nitrogen concentrations. This occurs mainly due to the long sewerage networks in which organic compounds are anaerobically decomposed, while nitrogen remains in the wastewater. Groundwater leakage into the sewer system<sup>6</sup> can also be a contributor of excess nitrogen in the wastewater, although this problem is not commonly reported. In the groundwater of the Slovak Republic, there is NO<sub>3</sub><sup>–</sup> usually present at dozens mg/l.<sup>7</sup> The average groundwater infiltration into the damaged pipes is 36.85% of the total wastewater volume.<sup>8</sup> If the leakage of the groundwater into sewerage is too high, then this nitrogen source is certainly interesting. Increased nitrogen input into wastewater can be also a consequence of the changes in eating habits of a population. While in the Slovak standard<sup>9</sup> nitrogen production is reported at the level of 11 g/d per capita, Pitter<sup>4</sup> already stated the production at 12 g/d per capita and it is possible to find in the literature the production up to 14 g/d per capita.<sup>10</sup>

In the case of insufficient concentrations of C<sub>org</sub> in the wastewater, or too short retention time of wastewater

under anoxic conditions at WWTP, a possible solution is the dosing of suitable external organic substrate into the denitrification reactor (to increase the denitrification rate).<sup>11</sup>

Composition of organic compounds has a strong effect on the presence of denitrifying microorganisms and thus on denitrification efficiency. Available external sources of  $C_{org}$  are alcohols, especially methanol (cost-effective, although it requires some adaptation of biomass and increased demands on operational safety because it is toxic and explosive) or ethanol (does not require such adaptation of biomass but is more expensive).<sup>4</sup> Organic acids (mainly acetic acid) also require less problematic adaptation because the biomass at the WWTP recognizes them (they are formed by acidogenesis and acetogenesis in the sewerage system), but they are also more expensive. Another option is saccharides (e.g., glucose, amyloid, sucrose).<sup>12</sup> The use of alternative  $C_{org}$  sources such as concentrated wastewater from industries are an interesting option.<sup>13,14</sup> In any case, these wastewaters must be treated, and therefore their import to WWTPs, where they increase the efficiency of denitrification, will bring double benefits. The usability of wastewater from the agro-food industry (e.g., milk bottling industries, potato processing industries, wastewater from winery industries) is commonly reported<sup>15</sup>, however other industries also produce external organic substrates.

The specific denitrification rates reported in  $mg_N/g\cdot h$  vary considerably – mostly from tenths up to  $20\ mg_N/g\cdot h$  (referred to g of dry solids).<sup>12,16–22</sup> For activated sludge adapted to sewage, acetate is reported as the substrate with the highest denitrification rates. Denitrification rates are affected by test conditions. The optimal reaction temperatures were 15–35 °C in which complete denitrification was achieved and nitrite accumulation was observed at 10 °C indicating the incomplete denitrification at low temperature.<sup>23</sup> Temperature change from 10 °C to 20 °C exerted a more significant positive effect on both the specific denitrification and carbon consumption rates than a further temperature increase from 20 °C to 30 °C.<sup>24</sup> The denitrification rate is also positively related to the pH value. At lower pH values, the nitrogen oxidoreductases were progressively inhibited in such way, that the overall rate of denitrification decreased and  $N_2O$  produced increased.<sup>25</sup> The process was stable in the neutral pH range and the highest denitrification rates were obtained at the pH values from 7.1 till 7.8.<sup>26</sup> In Cao et al.<sup>27</sup> maximum denitrification rates were measured at pH of 6.6–7.5 with inhibited denitrification at pH increased to 8.5 and 9.2.

The values of the rates also depend on the composition of the biomass during the tests, adaptation, and sludge retention time (SRT) (the higher the SRT values, the higher the increase in volumetric rates, but the specific rates related to the unit amount of biomass may also decrease).<sup>11</sup> If denitrification rates are measured in batch kinetic tests, then the test conditions are different from those in the activated sludge reactor. In the batch test, there is

a substrate concentration gradient (i.e., at the beginning of the test there are high substrate concentrations, and they only gradually decrease). According to the so-called Monod kinetics, the substrate removal rate decreases with decreasing substrate concentration.<sup>28,29</sup> When assessing denitrification rates, it is also necessary to consider whether the organic substrate is single- or multicomponent. According to Henze et al.<sup>29</sup> and Phillips et al.<sup>30</sup>, the denitrification rates achieved in batch kinetic tests are divided into 3 parts. In the first phase of the tests, the rate is the highest because an easily degradable organic substrate enters the denitrification; in the second phase of the test, the rate is slower because high molecular weight and insoluble organic compounds requiring hydrolysis are denitrified; and finally in the third phase, the rate is the lowest because only endogenous denitrification takes place. The rates calculated according to the recommendations of the technical standards<sup>9,11</sup> are on the level of 0.5–3  $mg_N/g\cdot h$ . Such rates are observed also at real WWTPs<sup>31</sup>. According to Henze et al.<sup>5</sup> the denitrification rates valid for temperatures 10–20 °C are 0.1–0.2  $mg_N/g\cdot h$  for endogenous denitrification, 0.6–2  $mg_N/g\cdot h$  for raw wastewater, and 1–9  $mg_N/g\cdot h$  for methanol and acetate. In summary, denitrification rates measured with a given substrate above 1  $mg_N/g\cdot h$  can be considered a positive result.

Organic matter is an essential factor for microbial growth and development. In addition to the biodegradability, price and storage options<sup>12</sup>, choice of external organic substrate is influenced also by the following factors: the highest possible chemical oxygen demand ( $COD_{Cr}$ ) and specific  $COD_{Cr}$  expressed in  $mg\ COD_{Cr}/mg$  substrate; efficiency at which the bacteria are able to use it; toxicity of intermediates or substrate itself; composition stability (with the best possible homogeneity)<sup>4,5</sup>. The next factors are the lowest possible portion of nitrogen in the substrate; the highest possible portion of compounds in the substrate entering the denitrification reaction; low portion of compounds entering the assimilation reaction associated with the growth of new biomass; and the lowest possible ratio of high molecular weight and undissolved compounds.<sup>4,5,11</sup>

The objectives of this study were to analytically determine the content of components present in industrial wastewater with a high COD concentration, monitor its impact on the biological stage of WWTPs, and to present the possibilities of using concentrated industrial wastewater as an external source for the denitrification (e.g., at municipal WWTPs with the lack of denitrification capacity, where the accelerating of denitrification could help to achieve the legal requirements on treated wastewater and to reduce the payment of fees for discharged nitrogen).<sup>32,33</sup>

## 2. Materials and Methods

The analysed parameters, their abbreviations, respective symbols, and the method of determination are

shown in Table 1. All analyses were performed according to standard procedures.<sup>34</sup>

Activated sludge for denitrification and respirometry tests was cultivated in three long-term semicontinuous lab-scale bioreactors<sup>35</sup> (designated R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>) with a total volume of 1 litre placed on magnetic stirrers. Mixing and aeration of the activated sludge in models R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> were set up in the following way: 5 hours after the addition of the substrate mixing (i.e., denitrification) followed by 17 hours aeration (i.e., nitrification and oxidation of residual organic compounds with O<sub>2</sub>), and 2 hours sedimentation and draw off effluent and dosing of the substrate. The volumetric load expressed in kg COD<sub>Cr</sub> was maintained at 0.88 kg/m<sup>3</sup>·d. The hydraulic retention time was 1.8 days and the set SRT was 15 days. Reactors were operated at the laboratory temperature 27–30 °C (experiments performed during summer months). Such temperatures were higher than typical municipal wastewater temperatures in Slovakia (approx. 10 °C during winter and 20–25 °C during summer<sup>8</sup>). However, these differences were neglected, because biological heterotrophic processes (like denitrification) are not significantly influenced by temperature. In addition, the main aim of the research was not to measure absolute values of denitrification rates but to evaluate biodegradability under anoxic conditions from the differences between endogenous, exogenous and total rates.

The substrate was dosed every 24 hours. Substrate for the reactor R<sub>1</sub> (i.e., reference reactor) contained glucose, peptone, and starch. The substrate consisting of glucose, peptone, starch, and industrial wastewater was dosed into reactor R<sub>2</sub> in a ratio of 1:1 (mg COD<sub>Cr,glucose + peptone + starch</sub> : mg COD<sub>Cr, industrial wastewater</sub>). Only the industrial wastewater was dosed into reactor R<sub>3</sub>. Total concentration of COD<sub>Cr</sub> in each substrate was 1,600 mg/l. Nutrients (N and P) were dosed in the form of NH<sub>4</sub>Cl and KH<sub>2</sub>PO<sub>4</sub>. The concentrations of TKN (N-NH<sub>4</sub> + N<sub>org</sub>) were at the level of 55 mg/l and P-PO<sub>4</sub> at the level of 12 mg/l. To ensure the supply of micronutrients for activated sludge, reject water from dewatering of digested sludge at real municipal WWTP was added (30 ml<sub>reject water</sub>/l<sub>of substrate</sub>). The pH was adjusted with a sodium hydro-carbonate solution to 7.

Denitrification tests were performed on the 0, 7<sup>th</sup>, and 22<sup>nd</sup> day of operation of the laboratory reactors R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>. 22 days represent 1.5 times the value of SRT;

within 22 days the original activated sludge (inoculum) with SRT of 15 days is completely replaced. For more complicated substrates, due to slower adaptation and slower growing biomass, it is possible to recommend higher SRTs and longer duration of experiments.<sup>35</sup> In this research, the 3 week duration of the experiments was also set according to the requirements of the industrial wastewater producer.

Before the denitrification test, activated sludge was taken from the reactors R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> (taken as an excess sludge), diluted to a concentration of 1 g/l and poured into biochemical oxygen demand (BOD) bottles D<sub>1</sub>, D<sub>2</sub>, and D<sub>3</sub>. After a 2-hour aeration to remove residual degradable organic compounds, aeration was replaced by a slow stirring and the tested substrate was added. Initial N-NO<sub>3</sub> concentration in all 3 bottles was 30 mg/l. Organic exogenous substrate wasn't added to the bottle D<sub>1</sub> (this denitrification test was comparative and only endogenous denitrification was performed). Organic substrate was added to the BOD bottles D<sub>2</sub> and D<sub>3</sub> to allow comparison of endogenous and total denitrification rates. If total respiration rates in bottles D<sub>2</sub> and D<sub>3</sub> were higher than the endogenous rate in D<sub>1</sub>, the organic substrate was degradable and usable in denitrification. Glucose was added to bottle D<sub>2</sub> in the ratio COD<sub>Cr</sub> : N-NO<sub>3</sub> = 15 mg/mg (COD<sub>Cr</sub> = 450 mg/l). Organic substrate was added excessively with the aim to eliminate denitrification rate limitation. The tested industrial wastewater was added to bottle D<sub>3</sub>, also in the ratio of COD<sub>Cr</sub> : N-NO<sub>3</sub> = 15 mg/mg. By comparing the rates in bottles D<sub>2</sub> and D<sub>3</sub>, denitrification with industrial wastewater and a standard biodegradable compound was assessed. At the same time, nutrients N and P were added to bottles D<sub>2</sub> and D<sub>3</sub> to avoid limiting the denitrification by their absence.

During the tests, changes in pH were also monitored and their values were continuously adjusted to the neutral range of 6.8–7.3 (with a diluted acid or alkali). During denitrification in a closed reactor, the pH can rise, but also fall slightly.<sup>36</sup> Except for the decrease in N-NO<sub>3</sub>, the decrease in COD<sub>Cr</sub> and the possible formation of N-NO<sub>2</sub> as an intermediate product of incomplete denitrification were also monitored. Tests lasted for 24 hours and the samples for analysis were taken in 3 hour intervals (during the first 9 hours, 4 samples, including taking sample at time 0); the last sample was taken after 24 hours (the significance of

**Table 1.** Analysed parameters, their abbreviations (symbols), and the method of determination.

Gravimetric methods	Spectrophotometric methods	Atomic absorption spectrometry
total solids (TS) total	chemical oxygen demand (COD <sub>Cr</sub> )	cadmium (Cd)
suspended solids (TSS)	ammonium nitrogen (N-NH <sub>4</sub> )	chromium (Cr)
volatile solids (VS) activated	total Kjeldahl nitrogen (TKN)	copper (Cu)
sludge concentration (X <sub>c</sub> )	nitrite nitrogen (N-NO <sub>2</sub> )	nickel (Ni)
sludge volume index (SVI)	nitrate nitrogen (N-NO <sub>3</sub> )	lead (Pb)
	phosphate phosphorus (P-PO <sub>4</sub> )	zinc (Zn)

Note: Spectrophotometer HACH DR5000 and atomic absorption spectrometer ContrAA 700 Analytik Jena were used

this sample was only a control). Denitrification rates and organic substrate consumption were evaluated according to the decline in  $\text{N-NO}_3$  and  $\text{COD}_{\text{Cr}}$  concentrations. For the first 9 hours of the test, the denitrification rate was not limited by the absence of organic substrate and the decline in concentrations was linear. The specific denitrification rates in  $\text{mg}_\text{N}/\text{g}\cdot\text{h}$  could thus be calculated from the slope of decrease of the concentrations divided by time and sludge concentration. The principle of such batch denitrification tests with further details is given in Bodík et al.<sup>35</sup>

Respirometric determination of biomass activity from individual reactors  $R_1$ ,  $R_2$ , and  $R_3$  was also performed by measuring oxygen consumption rates<sup>34,37</sup> and comparing endogenous ( $r_{\text{X,ox,en}}$ ), total ( $r_{\text{X,ox,t}}$ ), and substrate (exogenous) respiration rates ( $r_{\text{X,ox}}$ ) in 300 ml closed BOD bottles. The tests of anoxic biomass activity from denitrification tests were thus supplemented with information about oxic activity.

Respirometric measurements were performed on days 0 and 22. On day 0, only one respirometric measurement was performed, with the exogenous substrate glucose. The aim was to obtain information about the activity of the sludge before the addition of industrial wastewater. On day 22, three respirometric measurements with activated sludge from reactors  $R_1$ ,  $R_2$ , and  $R_3$  were performed to assess changes in oxic activity in all 3 reactors (especially in reactors  $R_2$  and  $R_3$ , where the biomass was exposed for 22 days to industrial wastewater). Before the respirometric tests, sludge taken as excess sludge from reactors  $R_1$ ,  $R_2$ , and  $R_3$  was aerated for 2 hours to remove residual exogenous organic compounds. The biomass was diluted to 1 g/l and the allylthiourea (10 mg/l) was added to suppress oxygen consumption by nitrification. For the first 5 minutes,  $r_{\text{X,ox,en}}$  was measured and then, for  $r_{\text{X,ox,t}}$  measurements, the following exogenous substrates were injected into the system: on day 0, glucose was added to the sludge; on day 22, glucose was used for the biomass from reactor  $R_1$ , glucose and industrial wastewater in the ratio  $\text{COD}_{\text{Cr}} = 1:1$  for biomass from reactor  $R_2$  and only industrial wastewater for biomass from reactor  $R_3$ . The concentration of exogenous  $\text{COD}_{\text{Cr}}$  in the BOD bottles after substrate dosing in all three cases was 17 mg/l. Respirograms were created by evaluating the respirometric measurements from which

the respiration rates  $r_{\text{X,ox,en}}$ ,  $r_{\text{X,ox,t}}$ ,  $r_{\text{X,ox}}$  in  $\text{mg}_{\text{O}_2}/\text{g}\cdot\text{h}$ , and substrate consumption rate  $r_{\text{X}}$  in  $\text{mg}_{\text{CHSKCr}}/\text{g}\cdot\text{h}$  were calculated according to Bodík et al.<sup>35,37</sup>

### 3. Results and Discussion

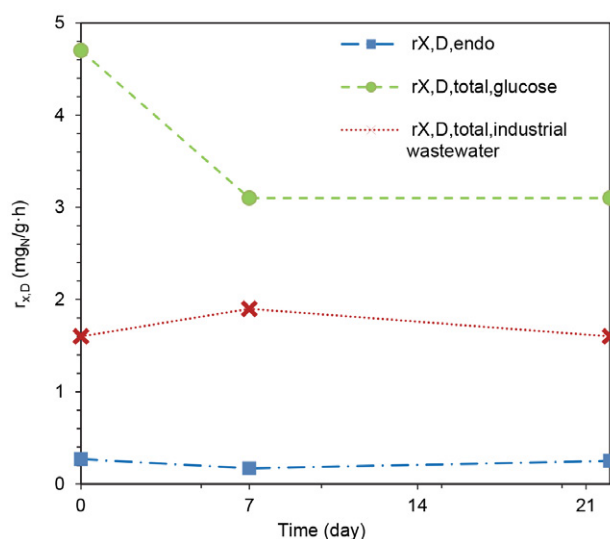
The sample of industrial wastewater (from the automotive industry) was partially turbid, grey in colour, and had a faint odour in concentrated form. The tested sample had concentrations of  $\text{COD}_{\text{Cr}} = 40.3$  g/l,  $\text{BOD}_5 : \text{COD}_{\text{Cr}} = 0.37$ ,  $\text{BOD}_5 = 14.8$  g/l (measured with unadapted inoculum),  $\text{N-NH}_4 = 16$  mg/l,  $\text{N-NO}_3 = 11$  mg/l,  $\text{P-PO}_4 = 21$  mg/l,  $\text{TS (105 }^\circ\text{C)} = 41.5$  g/l,  $\text{TSS (105 }^\circ\text{C)} = 2.1$  g/l,  $\text{VS (550 }^\circ\text{C)} = 68\%$ , and  $\text{pH} = 6.2$ . Solvents based on glycol are the main fraction in the wastewater (the detailed composition of organic compounds is confidential; request of the producer). The concentration of heavy metals is in Table 2, focusing on the metals included in the Act on the application of sewage sludge to soil no. 188/2003<sup>38</sup>, as there is an assumption that the metals present in the wastewater will be adsorbed into activated sludge and can thus influence its treatment and handling. According to their toxicity and bioaccumulation tendency, high concentrations of metals in sewage sludge can be also obstacle to its reuse.<sup>39,40</sup> The other metals listed in the Act of Slovak Republic (no. 188/2003)<sup>38</sup> (As, Hg) were not determined; their occurrence in industrial wastewater according to its producer can be neglected. Table 2 also shows the real concentrations of metals in sludge from Slovak municipal WWTPs (average values valid for Slovak WWTPs according to Kozáková et al.<sup>41</sup>). These concentrations were used in the calculations to assess the acceptable amount of industrial wastewater imported to the WWTP as an external denitrification substrate.

Results of the denitrification tests are shown in Fig. 1. Day 0 assays inform about immediate response of non-adapted biomass to the addition of industrial wastewater (i.e., biomass that has been previously fed only with glucose, peptone, and starch). Subsequently, these tests were repeated on days 7 and 22 to see how the characteristics and parameters of biomass change after long-term exposure to industrial wastewater. The comparison of values

**Table 2.** The concentrations of heavy metals in industrial wastewater, real concentrations of metals in sludge from Slovak WWTP<sup>41</sup>, and limit concentrations of metals in sludge from WWTP applied to soil.<sup>38</sup>

Parameter	Industrial wastewater (mg/l)	Real concentrations of metals in sludge (mg/kg sludge dry matter)	Limit concentrations of metals in sludge (mg/kg sludge dry matter)
Cd	≤ 0.1	0.8	10
Cr	0.4	41	1,000
Cu	0.2	168	1,000
Ni	1.8	25	300
Pb	≤ 0.1	38	750
Zn	38.1	979	2,500

measured on day 0 ( $r_{X,D,endo} = 0.27 \text{ mg}_N/\text{g}\cdot\text{h}$ ;  $r_{X,D,total,industrial \text{ wastewater}} = 1.6 \text{ mg}_N/\text{g}\cdot\text{h}$ ) shows the immediate biological degradation of organic substances and no need for special adaptation of the biomass. Denitrification tests performed on day 7 and 22 show that industrial wastewater remains degradable for denitrification purposes even after long-term exposure (rates  $r_{X,D,endo} = 0.17 \text{ mg}_N/\text{g}\cdot\text{h}$  vs.  $r_{X,D,total,industrial \text{ wastewater}} = 1.9 \text{ mg}_N/\text{g}\cdot\text{h}$  and  $r_{X,D,endo} = 0.25 \text{ mg}_N/\text{g}\cdot\text{h}$  vs.  $r_{X,D,total,industrial \text{ wastewater}} = 1.6 \text{ mg}_N/\text{g}\cdot\text{h}$ ). Industrial wastewater did not deactivate the biomass. Denitrification rates measured with industrial wastewater were lower than the rates measured with glucose as a standard organic substrate ( $r_{X,D,total,industrial \text{ wastewater}} = 1.6\text{--}1.9 \text{ mg}_N/\text{g}\cdot\text{h}$  vs.  $r_{X,D,total,glucose} = 3.1\text{--}4.7 \text{ mg}_N/\text{g}\cdot\text{h}$ ). Nevertheless, industrial wastewater can be used as external organic substrate for denitrification at WWTP. The intermediate  $\text{N-NO}_2$  and its undissociated form  $\text{HNO}_2$  were not accumulated in any of the denitrification tests with industrial wastewater. The  $\text{COD}_{Cr} : \text{N-NO}_3$  ratio (ratio of  $\text{mg COD}_{Cr}$  in industrial wastewater consumed in denitrification of  $1 \text{ mg N-NO}_3$ ) was 9. According to stoichiometry of denitrification reaction involving both dissimilation and assimilation, standard ratios are in the range of 5–7 (consumption of  $\text{COD}_{Cr}$  calculated for the reduction of  $\text{N-NO}_3$  to  $\text{N}_2$  is  $2,86 \text{ mg}_{\text{COD}}/\text{mg}_N$ ; the next  $\text{COD}_{Cr}$  is consumed for a growth of new biomass, which depends on the bacteria involved in denitrification and which can not be stoichiometrically calculated).<sup>4,11</sup>



**Figure 1.** Rates of endogenous denitrification  $r_{X,D,endo}$  (test D<sub>1</sub>), total denitrification  $r_{X,D,total,glucose}$  with glucose as organic substrate (test D<sub>2</sub>), and total denitrification  $r_{X,D,total,industrial \text{ wastewater}}$  with industrial wastewater as organic substrate (test D<sub>3</sub>).

The long-term impact of industrial wastewater on activated sludge and biomass adaptation was also evaluated from the concentrations of  $\text{N-NH}_4$  and  $\text{COD}_{Cr}$  in the effluent of models R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>. These indicators were

used to monitor the influence on the nitrification and the concentration of residual and non-biodegradable organic matter from industrial wastewater (Table 3). At the same time, the values of volatile suspended solids (VSS) (as a share of organic matter in activated sludge) and sludge volume index (SVI) were evaluated (Table 3). All these parameters are important for WWTP as they influence a possible deterioration of the effluent from the WWTP, where industrial wastewater would be considered as an external denitrification substrate. Nitrification was efficient throughout the whole experiment, as confirmed by  $\text{N-NH}_4$  concentrations in the effluents from all 3 models (differences of 1.9 to 3.7  $\text{mg/l}$  can be neglected). An important parameter in terms of fees for treated wastewater<sup>33</sup> is the residual  $\text{COD}_{Cr}$ . If the industrial wastewater contains hardly or non-biodegradable organic compounds, it is necessary to quantify the possible increase of  $\text{COD}_{Cr}$  concentration in the effluent from the WWTP. The increase of  $\text{COD}_{Cr}$  concentration occurred in models R<sub>2</sub> and R<sub>3</sub> with dosed industrial wastewater, where the average concentration increased from 59  $\text{mg/l}$  to 129 and 145  $\text{mg/l}$ . If we balance the average values of  $\text{COD}_{Cr}$  from industrial wastewater in the influent to models R<sub>2</sub> and R<sub>3</sub> (800  $\text{mg/l}$  in model R<sub>2</sub> and 1,600  $\text{mg/l}$  in model R<sub>3</sub>) and  $\text{COD}_{Cr}$  increase in the effluent from these models, the impact is as follows:

- In model R<sub>2</sub>, every 100  $\text{mg/l}$  of  $\text{COD}_{Cr}$  from industrial wastewater added to the activated sludge reactor increased the concentration of effluent  $\text{COD}_{Cr}$  by 8.8  $\text{mg/l}$  (calculated as  $(129 \text{ mg/l} - 59 \text{ mg/l}) / 800 \text{ mg/l} / 100 \text{ mg/l}$ )
- In model R<sub>3</sub>, every 100  $\text{mg/l}$  of  $\text{COD}_{Cr}$  of liquid waste added to the activated sludge reactor increased the concentration of effluent  $\text{COD}_{Cr}$  by 5.4  $\text{mg/l}$  (calculated as  $(145 \text{ mg/l} - 59 \text{ mg/l}) / 1,600 \text{ mg/l} / 100 \text{ mg/l}$ )
- If we assume that for denitrification of 10  $\text{mg/l}$   $\text{N-NO}_3$  it is necessary to add industrial wastewater with  $\text{COD}_{Cr}$  of 90  $\text{mg/l}$  (ratio  $\text{COD}_{Cr} : \text{N-NO}_3 = 9$  measured in denitrification tests D<sub>3</sub>), then reduction of 10  $\text{mg/l}$   $\text{N-NO}_3$  in the effluent from WWTP is connected with  $\text{COD}_{Cr}$  increase 4.9–7.9  $\text{mg/l}$  ( $5.4 \text{ mg/l} \cdot 90 \text{ mg/l} / 100 \text{ mg/l}$ ;  $8.8 \text{ mg/l} \cdot 90 \text{ mg/l} / 100 \text{ mg/l}$ ).

**Table 3.** Average effluent concentrations and their range for reference model R<sub>1</sub>, model R<sub>2</sub> with glucose and industrial wastewater, and model R<sub>3</sub> with only industrial wastewater dosing.

Parameter	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
$\text{N-NH}_4$ ( $\text{mg/l}$ )	1.9 0.2–6	3.5 0.4–6	3.7 1.6–5.3
$\text{COD}_{Cr}$ ( $\text{mg/l}$ )	59 49–97	129 87–169	145 61–167
VSS (%)	79 81–82	75 71–86	75 70–82
SVI ( $\text{ml/g}$ )	52 45–60	48 43–49	51 45–64

Table 4. Results of respirometric measurements.

Respirometric rates	Typical values according to Bodík et al. <sup>35</sup>	Day 0 <sup>a)</sup>	Day 22 <sup>b)</sup>		
		(Model R <sub>1</sub> )	(Model R <sub>2</sub> )	(Model R <sub>3</sub> )	
r <sub>X,ox,en</sub> (mgO <sub>2</sub> /g·h)	1–10	3	4	3	4
r <sub>X,ox</sub> (mgO <sub>2</sub> /g·h)	10–100	20	22	22	20
r <sub>X,max</sub> (mgCOD/g·h)	30–200	71	68	65	61

<sup>a</sup> Reference measurement with glucose as an exogenous substrate; measured with biomass used as a common inoculum for models R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>

<sup>b</sup> Exogenous substrates: glucose for activated sludge from model R<sub>1</sub>, glucose + industrial wastewater (1:1) for activated sludge from model R<sub>2</sub>, industrial wastewater for activated sludge from model R<sub>3</sub>

The impact of industrial wastewater on biomass was also monitored using the parameters VSS and SVI. The differences between models R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are insignificant (negligible accumulation of inorganic compounds and activated sludge retained the formation of compact flocs with good sedimentation properties).

Results from respirometric measurements obtained during testing industrial wastewater are shown in Table 4. The results confirm that oxic respiration activity (i.e., ability to remove glucose as a reference substrate and industrial wastewater) has changed minimally during the operation of models R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>. The main conclusion is that industrial wastewater was not toxic to the biomass. The measured respiration rates in Table 4 are also compared with the recommended rates and even though they are at the lower end of the typical values from literature<sup>35</sup>, they are still acceptable and do not affect the previous statement.

In the case of additional industrial wastewater to the denitrification reactor, it is also important to assess how many m<sup>3</sup> can be imported to the WWTP so that the permitted concentration limits of heavy metals in sludge are not exceeded. Heavy metals in the wastewater are at the WWTP mostly adsorbed into the primary and activated sludge, and subsequently, remain in the digested sludge removed from the WWTP. The legislation defines these concentrations for cases where the sludge from WWTP is applied to the soil.<sup>38</sup> Application to the soil, either directly or as a compost from composting plants, is currently still the most common method of sludge management in Slovakia.<sup>41</sup> The following calculation shows an example of how to evaluate such balance for specific heavy metals and specific WWTP. The calculation assumes Cr in industrial wastewater, import of wastewater to WWTP with a capacity of approximately 10,000 inhabitants, inflow of 150 l/d per capita, specific production of sludge dry matter of 40 g/d per capita<sup>9,11</sup>, and concentrations of metal according to Table 2:

- WWTP inflow = 10,000 inhabitants · 150 l/d = 1,500 m<sup>3</sup>/d
- Daily sludge production = 10,000 inhabitants · 40 g/d = 400 kg/d

- Limit concentration of Cr in sewage sludge defined by Slovak legislation = 1,000 mg/kg
- Average background concentration of Cr in sludge at Slovak WWTPs: 41 mg/kg
- Capacity of sludge to adsorb Cr (the limit concentration defined by legislation is not to exceeded) = 1,000 mg/kg – 41 mg/kg = 959 mg/kg
- Possibility to import Cr in industrial wastewater to the WWTP = 400 kg/d · 959 mg/kg = 383,600 mg/d = 3.84 kg/d
- Concentration of Cr in industrial wastewater = 0.4 mg/l
- Volume of industrial wastewater with 383,600 mg/d of Cr = 383,600 mg/d / 0.4 mg/l = 959,000 l/d = 959 m<sup>3</sup>/d
- Conclusion of the example calculation for Cr: at a WWTP with a capacity of 10,000 inhabitants, 959 m<sup>3</sup>/d of industrial wastewater can be imported as an external denitrification substrate and the Cr concentration in sludge will not exceed the limit of 1,000 mg/kg. This consideration includes simplification that Cr from industrial wastewater is completely absorbed to the sludge. The volume of industrial water (959 m<sup>3</sup>/d) represents 64% of the WWTP inflow (1,500 m<sup>3</sup>/d).

The percentage of industrial wastewater imported to the WWTP with a capacity of 10,000 inhabitants calculated for other heavy metals from Table 2 are given in Table 5.

Table 5. The percentage of industrial wastewater to the WWTP (with a capacity of 10,000 inhabitants) for selected heavy metals.

Heavy metal	Volume of liquid waste (m <sup>3</sup> /d)	Percentage of liquid waste according to WWTP inflow (%)
Cr	959	64
Cd	36.8	2
Cu	1,664	111
Ni	61.1	4
Pb	2,835	189
Zn	15.9	1

According to these balances, Zn represents the worst case since it reduces the percentage of daily imported

volume of industrial wastewater to only 1% (15.9 m<sup>3</sup>/d). However, this amount of industrial wastewater is still interesting. It represents approximately 424 mg/l COD<sub>Cr</sub> and this concentration has a potential to denitrify 47 mg/l N-NO<sub>3</sub> (COD<sub>Cr</sub> of industrial wastewater = 40.3 g/l; ratio COD<sub>Cr</sub> : N-NO<sub>3</sub> = 9).

## 4. Conclusion

The main results emerging from the testing of industrial wastewater as a possible external denitrification substrate imported to the municipal WWTP to increase the rate and efficiency of denitrification are as follows:

- Industrial wastewater is biodegradable, also for non-adapted biomass
- Denitrification resulted in nitrogen gas production without accumulation of intermediate products
- The denitrification rates with industrial wastewater as an external substrate were in the range of 1.6 to 1.9 mg<sub>N</sub>/g·h. Addition of this substrate improves denitrification efficiency
- Negative impact of long-term dosing of industrial wastewater on activated sludge was not confirmed
- Partial increase of COD<sub>Cr</sub> concentration in the effluent from activated sludge reactor was measured (small amount of organic compounds in industrial wastewater was non-biodegradable). The addition of industrial wastewater with COD<sub>Cr</sub> concentration of 100 mg/l increased the COD<sub>Cr</sub> concentration in the WWTP effluent by 5–9 mg/l. This problem can be regulated by the amount of industrial wastewater applied into the denitrification reactor.
- The impact of the imported industrial wastewater as an external denitrification substrate for WWTP must be assessed comprehensively, including details such as the accumulation of heavy metals from the wastewater in the activated sludge. The instructions on how to calculate this balance are provided in the article.

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## Povzetek

Dodatek zunanjega vira organskega ogljika za denitrifikacijo se običajno uporablja v čistilnih napravah odpadnih vod za namen intenziviranja procesov odstranjevanja dušika. Cilj laboratorijske raziskave je bil izmeriti sestavo koncentrirane industrijske odpadne vode, ugotoviti možnosti njene uporabe kot zunanjega substrata za denitrifikacijo in oceniti njen celoten vpliv na čistilno napravo. Dobljeni rezultati kažejo, da je analizirana industrijska odpadna voda biološko razgradljiva in se lahko uporablja kot denitrifikacijski substrat brez posebne prilagoditve biomase. Stopnje denitrifikacije pri testirani odpadni vodi so bile v območju od 1,6 do 1,9 mg N/g·h. Negativni vpliv dolgotrajnega doziranja industrijske odpadne vode na aktivno blato ni bil potrjen. Vpliv uvožene odpadne vode na čistilno napravo je treba oceniti celovito, vključno z vplivom težkih kovin iz odpadne vode na kakovost blata, kar je navedeno tudi v tej raziskavi.



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