## Desalination and Water Treatment

# www.deswater.com

1944-3994/1944-3986 $^{\odot}$  2011 Desalination Publications. All rights reserved

0 doi: 10/5004/dwt.2011.2476

# Laboratory operation of MBR and SBR models with selected inhibitors of nitrification

# Andrea Blšťáková, Igor Bodík\*, Stanislav Sedláček, Miloslav Drtil

Institute of Chemical and Environmental Engineering, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic Tel. +421 259325 384; Fax: +421 259325 792; email: igor.bodik@stuba.sk

Received 11 November 2010; Accepted 14 June 2011

## ABSTRACT

Presented contribution is focused on long-term laboratory operation (11 mon) of membrane bioreactor (MBR) and sequencing batch reactor (SBR) operated with selected organic compounds that were supposed to be strong inhibitors of nitrification process. The first term of operation with selected inhibitor diphenylamine (DPA), the second term of operation with 4-aminodiphenylamine (ADPA) and the third term of operation with benzothiazole (BT) were tested. The effect of two different sludge ages and the different kinds of treatment models was examined. In SBR model, the nitrification process occurred only to the first step (high NO<sub>2</sub>–N concentrations) with tested inhibitors DPA and ADPA. At BT concentrations in substrate in the range of 2–6 mg/l, slender nitrification was observed and high  $NH_4$ –N effluent concentrations were measured. On the other hand, in the MBR model the nitrification was completed to the second step (high NO<sub>3</sub>–N concentration) almost during the whole period of operation.

*Keywords:* Benzothiazole; Nitrification; MBR; Inhibitors of nitrification; Industrial wastewater; Diphenylamine

## 1. Introduction

Nitrification is the term used to describe the two-step biological process in which ammonium cation  $(NH_4^+-N)$  is oxidized to nitrite  $(NO_2-N)$  and nitrite is oxidized to nitrate  $(NO_3-N)$  by means of autotrophic microorganisms. The need for nitrification in wastewater treatment arises from water quality concerns over:

- the effect of ammonia on receiving water with respect to dissolved oxygen concentrations and fish toxicity,
- the need to provide nitrogen removal to control eutrophication, and
- the need to provide nitrogen control for water-reuse applications including groundwater recharge [1].

Nitrifying organisms are sensitive to a wide range of organic and inorganic compounds at concentrations well below those that would affect aerobic heterotrophic organisms. Toxic compounds include solvent organic chemicals, amines, proteins, tannins, phenolic compounds, alcohols, cyanates, ethers, carbamates, and benzene. The most significant inhibitory effects have those organic compounds that contain both nitrogen and sulphur in their molecules (mercaptobenzothiazole, thiourea, allylthiourea etc.) [2–4].

Nitrification is also inhibited by un-ionized ammonia (NH<sub>3</sub>) or free ammonia, and un-ionized nitrous acid (HNO<sub>2</sub>). The inhibition effects are dependent on the total nitrogen species concentration, temperature and pH. At free ammonia concentrations in the range of 10 to 150 mg/l, inhibition of first step of nitrification was observed to result in an increase in ammonium concentration in the

PERMEA 2010 – Membrane Science and Technology Conference of Visegrád Countries (Czech Republic, Hungary, Poland, Slovakia), September 4–8, 2010, Tatranské Matliare, Slovakia

35 (2011) 185–194 November

<sup>\*</sup>Corresponding author.

reactors. On the other hand, the second step of nitrification was also inhibited at free nitrous acid concentration from 0.2 mg/l to 2.8 mg/l. The availability of free ammonia and free nitrous acid are function of pH and solution concentration of ammonium and nitrite. The concentrations of free ammonia and free nitrous acid can be determined from the equations and graphs presented first by Anthonisen and then by many other authors [5–8].

Very important source of nitrifying inhibitors are industrial wastewaters containing nitrogen and sulphur (thiourea, cyanide, phenols, aniline, etc.) and heavy metals (Zn, Pb, Ni, Cr, Cd, etc.) [6]. According to Knapp et al. 7 mg/1 benzothiazole (BT) causes a 50% and 54 mg/1 a 100% inhibition of ammonia oxidation, while nitrite utilization is not affected [9]. The benzothiazole inhibits activated sludge respiration at a concentration of 650 mg/1 [10,11]. Other authors examined the biodegradability of several benzothiazoles using a degradation test. In these conditions, only 2-hydroxybenzothiazole was biodegraded and 2-mercaptobenzothiazole, benzothiazole SO<sub>3</sub>, 2-aminobenzothiazole and 2-(methylthio) benzothiazole were not [12–14].

Puig et al. identified forty-six different compounds in wastewater resulting from the manufacture of rubber antioxidants and accelerators. They studied their reaction when subjected to techniques of chemical oxidation using ozone. With regard to the benzothiazole group, after ozonation, the heterocyclic compounds like 2-benzothiazoleamine, benzothiazole, 2-(methylthio)- or 2-mercaptobenzothiazole with activating substituting groups were completely removed. The concentration of 2-methylbenzothiazole and 1,2-benzisothiazole, 3-methyl were decreased by 82.3% and 79.7%. The concentration of benzothiazole without any substituting group was decreased by 66% [15].

One of the most promising newer technologies for wastewater treatment is membrane bioreactors (MBRs), which combine membrane filtration with biodegradation processes. Solid materials, biomass and pathogenic bacteria and even macromolecules are retained while allowing water and smaller solution species to pass through the membrane, so that the very high quality of the effluent is reached. The advantages offered by MBRs over the conventional activated sludge process include the very high quality of the effluent, separation of solid retention time (SRT) from hydraulic retention time (HRT) in an MBR system, long SRT and low sludge loading rate. The performance of nitrification in such systems is much more effective and less sensitive on inhibitors. It was demonstrated that the microbial populations in an MBR are capable of degrading a wider range of organic substances than a culture from a conventional sludge system [16,17].

However, it is important to highlight that biological treatment processes for industrial wastewater may heavily influence the selection process, especially for the nitrifying biomass, because of the presence of salts, heavy metals and organic inhibitors. In the context of a wider experimental investigation on the efficiency and viability of MBR for the treatment of industrial wastewater, this paper presents a comparison of a laboratory MBR and sequencing batch reactor (SBR) treatment plant. Both tested plants were fed with the same industrial wastewater with high content of organic inhibitors of nitrification, not only in terms of process efficiency in the removal of pollutants, but also in terms of nitrification efficiency. The main goal of this study is to find out effects of three tested compounds (diphenylamine, 4-amino-diphenylamine and benzothiazole) on nitrification process using two models (MBR and SBR operated with different SRT) in period from January to December 2009. The research was performed at Institute of Chemical and Environmental Engineering (ICHEE) of Slovak University of Technology (SUT).

#### 2. Materials and methods

## 2.1. Description of tested compounds and laboratory models

For the purposes of this study three potential nitrification inhibitors were selected and used: diphenylamine, 4-amino-diphenylamine and benzothiazole. The selection of inhibitors was realized on the basis of long term experiences with inhibition of nitrification at biological wastewater treatment plant (WWTP) in one of the important Slovak chemical industrial factories. Nowadays, the reconstruction of WWTP is being prepared and the question of MBR installation is very actual. The results of this study should be useful for selection of appropriate treatment technology.

Diphenylamine (DPA; structure see Fig. 1) is a compound from the third European Union (EU) list of priority pollutants. It was assigned by the EU to Germany to assess and control its environmental risks. DPA and its derivatives are most commonly used as stabilizers in nitrocellulose-containing explosives and propellants, in the perfumery, and as antioxidants in the rubber and elastomer industry. Diphenylamines are still produced by the chemical industries. The worldwide annual production of DPA in the 1980s was about 40,000 *t* of which nearly 4000 *t* were produced in Germany [18,19]. This compound still has an industrial significance, so the current annual production may be even higher. This is especially supported by published values showing



high production rates for this compound in the eastern countries of Europe (for example, the Slovak Republic produced more than 10,000 t/y) [20].

Some ecotoxicological studies demonstrated the potential hazard of various diphenylamines to the aquatic environment and to bacteria and animals. Studies on the biodegradability of DPA and its derivatives are very rare. Therefore, further investigation is required to determine the complete dimension of the potential environmental hazard and to introduce possible (bio)remediation techniques for sites that are contaminated with this class of compounds [21].

4-amino-diphenylamine (ADPA; structure see Fig. 2) is used in the production of hair dyes and other dyes, is a precursor and intermediate for the synthesis of various chemicals for photography and for pharmaceutical products, and is used in rubber compound manufacture. Additionally, ADPA is an azo reduction metabolite of the widely used food dye Metanil Yellow [21].

Benzothiazole (BT, structure see Fig. 3) and its derivatives are manufactured worldwide for a wide variety of applications. They are used, among other things, as slimicides in the paper and pulp industry, as fungicides, as herbicides or as anti-algal agents. They are applied as corrosion inhibitors in cooling water and in antifreeze for automobiles. Their main use is as vulcanization accelerators in rubber production, catalysing the formation of sulphide linkages between unsaturated elastomeric polymers in order to obtain a flexible and elastic cross linked material. Benzothiazoles, although found in minor concentrations in natural products, are now more widely released into the environment as industrial xenobiotics. This raises questions about their biodegradability, their behaviour in activated sludge systems and their general toxicity [12].

For the purposes of this study the synthetic wastewater was prepared daily in our laboratory. Composition of synthetic wastewater met basic composition parameters of wastewater from real Slovak industrial WWTP, where long term inhibition of nitrification has been observed.



Fig. 2. Molecular structure of ADPA.



Fig. 3. Molecular structure of BT.

For preparing of 100 l/d of synthetic wastewater (substrate), these volumes or amounts of selected substances were needed: 200 ml methanol, 20 g peptone, 11 ml toluol, 13 ml isopropanol, 100 g  $NH_4$ –N, 400 g NaCl, 120 g  $Na_2CO_3$ , 170 ml P (phosphorus solution concentration 10 g/l) and tested inhibitor (DPA or ADPA or BT) e.g.: for concentration of inhibitor 10 mg/l it was dose of 1 g. The basic parameters of substrate and models are reported in Table 1. Such prepared substrate was used as feed for both (MBR and SBR) treatment models.

Basic parameters of both laboratory models are presented in Table 1. Membrane bioreactor (MBR, Fig. 4) model consisted basically of activated sludge tank (300 l) with immersed flat-sheet membrane module (surface area 6.25 m<sup>2</sup>, supplied by Martin-Systems Company, Germany, Fig. 5). MBR model was inoculated by real activated sludge from mentioned industrial WWTP in volume of 150 l and was filled with water to 200 l. The initial sludge concentration in MBR model after inoculation was 11 g/l. Activated sludge in MBR model was aerated using aerator and compressor. Daily, 100 l of substrate was pumped into

Table 1

Basic technological parameters of SBR and MBR model operation

1			
Parameter	Unit	MBR	SBR
Volume of reactor	1	300	3.0
Load Bv (COD)	kg/m³d	0.86	0.86
Sludge age θx	D	50	20
(predetermined)			
COD substrate	mg/l	3000	3000
NH₄–N substrate	mg/l	400	400
Total salinity	g/l	6.0	6.0



Fig. 4. MBR model.

Table 2



Fig. 5. Flat-sheet module.



Fig. 6. SBR model.

the MBR model continually for 20 h/d. Once a day, 100 l of permeate (treated water from MBR model) was drained into the sewage. Predetermined sludge age in MBR model was 50 d (61 of excess sludge).

The initial sludge concentration in sequencing batch reactor (SBR, Fig. 6) after inoculation was 7 g/l. Daily, one litre of substrate described above - influent was pumped into the SBR model discontinually during 21 h/d. Once a day, after two hours of activated sludge sedimentation, 850 ml of supernatant (treated water from SBR model) was drained into the sewage. Predetermined sludge age in SBR model was 20 d (150 ml of excess sludge).

## 2.1.1. Sampling and chemical analysis

The samples of influent (substrate), permeate, SBR supernatant (effluent, treated waste water), MBR and SBR activated sludge were sampled regularly two times per week and analysed in laboratory of ICHEE according

Date	Day of operation	Action	Inhibitor conc. [mg/l]
16th Jan		Sludge inoculation of MBR and SBR	0
19th Jan	1st	The beginning of substrate dosing	0
26th Jan	8th	The beginning of DPA dosing	10
9th Feb	22nd	The beginning of oil dosing	20 ml*
6th March	47th	Increase of DPA concentration	25
30th March	71st	Increase of DPA concentration	50
4th May	106th	The beginning of period without	0
3rd June	136th	The beginning of ADPA dosing into	10
22nd July	185th	Increase of ADPA	25
17th Aug	211th	Increase of ADPA concentration	50
31st Aug	240th	The beginning of period without inhibitor dosing	0
16th Oct	266th	The beginning of BT dosing into substrate	2
12th Nov	293rd	Increase of BT concentration	6
16th Dec	326th	The end of operation	6

Important dates of MBR and SBR operation

\* The beginning of 20 ml/d oil dosing directly into the MBR model with aim to eliminate foaming of activated sludge.

to standard methods [22]. During the operation the basic quality parameters (temperature, pH, oxygen concentration, chemical oxygen demand COD,  $NH_4$ –N,  $NO_2$ –N,  $NO_3$ –N,  $N_{total}$ , suspended solids etc.) of influents and effluents were determined. The inhibitor concentrations in each sample of influents, effluents and activated sludges were analysed using chromatographic techniques in laboratories of Research Institute of Chemical Technology RICHT Inc. (in Slovak VUCHT a.s.).

#### 2.1.2. The important dates of MBR and SBR operation

In Table 2, the important dates of MBR and SBR operation during the 2009 are presented.

## 3. Results and discussion

In this part of contribution individual quality parameters of MBR and SBR models, activated sludge,

189

influents and effluents during the whole operation periods are discussed.

#### 3.1. Temperature

The temperature values of activated sludges of laboratory models were in interval between 17.9 to 28°C as a consequence of temperature adaptation in MBR and SBR model to air temperature in laboratory during the operation. The temperature range in laboratory conditions met the range of temperature on real WWTP during summer and winter conditions.

#### 3.2. Oxygen concentration

During the whole operation no problems with oxygen dosing into the MBR and SBR activated sludge were observed. The oxygen concentrations were on high level in interval between 6.8 to circa 7.5 mg/l. During the period of BT dosing into substrate of SBR model, a slightly higher decrease of oxygen concentration (5 mg/l) was observed, even though the oxygen concentration in SBR sludge was still high enough.

## 3.3. pH

The pH values in MBR and SBR sludge were in interval between 6.0 to 9.0. Sometimes, as a consequence of  $H^+$  ions formation, the decrease of pH occured. In this case, pH was regulated by sodium carbonate  $Na_2CO_3$  dosing in adequate amount to obtain pH in interval 7 to 9 in MBR and SBR models, which corresponds with pH values in real industrial WWTP.

## 3.4. Sludge concentration

The MBR and SBR sludge concentration X<sub>2</sub> changed significantly during the operation (Fig. 7). The membrane separation enabled higher sludge concentration in the MBR model (3-4 g/l) compared to SBR model (2-3 g/l). The reasons of the lower sludge concentration in both models could be explained with several phenomena: (i) disintegration of sludge flocks due to inhibition and/or toxicity of substrate compounds as methanol, toluene, isopropanole, diphenylamine, benzothiazole etc.; (ii) high salinity of substrate -6 g/l (but comparable with real WWTP conditions); (iii) absence of suspended solids in substrate (contrary to real WWTP conditions); (iv) low sludge load of systems. Probably because of these phenomena the decay of activated sludges in both laboratory models occurred. Part of the sludge flocks were disintegrated and solubilised in activated sludge and afterwards partially oxidised by viable sludge flocks. This phenomena of sludge flocks disintegration occurred also at real industrial WWTP, nevertheless, the sludge concentration at real WWTP is higher (ca 6-8 g/l).



Fig. 7. Sludge concentrations in MBR and SBR model.

The predetermined sludge age in MBR model was 50 d, but the real value was circa 35 d, which is a higher value in compare with the sludge age of SBR model. The predetermined sludge age in SBR model was 20 d, but the real value decreased to circa 10 d.

## 3.5. Chemical oxygen demand

In Table 3, the average COD values of effluents of MBR and SBR model for periods with inhibitor dosing into substrate during the whole operation are presented. The highest COD value achieved unfiltered SBR effluent, its average value was 609 mg/l. The best effluent was MBR

#### Table 3

Average COD values of MBR and SBR effluents during the whole operation

Inhibitor	Conc. [mg/l]	MBR filt [mg/l]	MBR permeate [mg/l]	SBR unfilt [mg/l]	SBR filt [mg/l]
DPA	10	456	120	740	638
DPA	25	394	80	442	371
DPA	50	472	40	454	362
ADPA	10	740	263	773	535
ADPA	25	383	40	986	713
ADPA	50	367	37	981	707
BT	2	170	75	257	124
BT	6	191	33	241	120
Average		397	86	609	446

permeate, that achieved the average COD value during the periods of inhibitor dosing into substrate 86 mg/l (see Table 3). To compare the quality of membrane ultrafiltration effluent, parallel samples from permeate (MBR permeate) and sludge mixture directly from MBR model filtered "only" through laboratory filtration paper (MBR filt) were regularly measured. The quality of permeate was much higher during whole tested periods. The COD concentration from SBR model should be analogous to effluents from real WWTP (with sedimentation tanks). All SBR effluent values (also filtered) were significantly higher then MBR permeate values and were comparable with effluents from real industrial WWTP (average COD = 310 mg/l). From this point of view (COD removal) the application of MBR system into real industrial WWTP is very effective.

## 3.6. Permeate flux

During the MBR model operation no membrane clogging was observed, even though vegetable oil was dosed on the sludge surface in volume of 20 ml per day to eliminate foam that could overflow MBR model, if oil would have not been dosed. Predetermined flux from MBR model was 10 l/m<sup>2</sup>h. During the whole year operation of MBR was measured flux in interval 9 to 10 l/m<sup>2</sup>h.

#### 3.7. Nitrification process in MBR model

On Fig. 8, nitrification process of MBR model during the whole operation is presented. For MBR permeate



Fig. 8. Nitrification process in MBR model.

total nitrogen was in range 400–500 mg/l. NH<sub>4</sub>–N concentrations in the effluent were much lower than 10 mg/l during the whole operation, only in the period when inhibitor was changed, NH<sub>4</sub>-N concentrations increased a little. At the time of activated sludge adaption on substrate with selected inhibitor DPA and ADPA, NO<sub>2</sub>-N concentrations in effluent were higher. After few days of sludge adaption on inhibitor in substrate, NO2-N concentrations decreased again to zero values. The opposite course was in case of NO<sub>3</sub>–N concentrations. In first days of sludge adaption on substrate, NO<sub>3</sub>-N concentrations continually increased to values around 400 or more mg/l. Thus, in MBR model the nitrification process was inhibited only during the initial days of sludge adaption on substrate with selected inhibitor DPA and ADPA. During the rest of period of operation, nitrification process with DPA, ADPA and BT was completed to second step. The NO<sub>2</sub>-N concentration increased to 50 mg/l during the second period without inhibitor dosing into substrate. Long term operation of MBR confirms the very low inhibition of tested organic compounds on nitrification process.

#### 3.8. Nitrification process in SBR model

On Fig. 9 nitrification process of SBR model during the whole operation is presented. In SBR supernatant - effluent (filtered treated wastewater) total nitrogen was in interval 350–450 mg/l. The  $NH_4$ –N concentrations were very low (under 10 mg/l) during the whole operation with DPA dosing into substrate, i.e., the first step of nitrification (nitrite production) was not negatively affected. Partial inhibition of second step of nitrification occurred at DPA inhibitor concentration of 10 mg/l. On the other hand, the second step of nitrification was heavily inhibited by higher a DPA concentration which is evident from NO<sub>2</sub>–N and NO<sub>3</sub>–N concentration courses.

In the period when tested inhibitor was ADPA, effluent  $NH_4$ –N concentrations increased to 30 mg/l, which represented slight (10–20%) inhibition of the first nitrification step. The second step of nitrification was also strongly inhibited by ADPA but inhibition was not so serious compared with DPA using. It is indicated by slight decrease of nitrite and also by increasing of nitrates in this period.

The inhibition of the first nitrification step intensively started already in case of low BT dosing followed by sharp increasing of  $NH_4$ –N concentrations in effluent. After increase of BT concentration to 6 mg/l in substrate, a slender nitrification (low  $NO_2$ –N and  $NO_3$ –N concentrations) was observed. High  $NH_4$ –N concentration values (300–350 mg/l) were measured during the period at BT concentration 6 mg/l in substrate. It follows, that BT at both tested concentrations was the sturdiest inhibitor of nitrification process in the first step, but the second step was not so severely influenced, which was confirmed by results from Knapp [9].



Fig. 9. Nitrification process in SBR model.

Table 4

UNL – under measured mint()							
	Teor. Conc. in Substr. [mg/l]	Real Conc. in Substr. [mg/l]	SBR Unf. effluent [mg/l]	SBR sludge [mg/g]	MBR Perm. [mg/l]	MBR sludge [mg/g]	Sample`s day
DPA	10	10	0.05	0.185	0.05	0.170	25th
	10	9.3	UML	UML	UML	0.05	44th
	25	30.4	UML	UML	UML	UML	65th
	50	52.7	UML	0,04	UML	0.02	95th
ADPA	10	11.5	UML	UML	UML	0.0428	156th
	10	10.9	UML	UML	UML	0.1994	184th
	25	22.6	UML	UML	UML	0.2940	198th

Measured DPA and ADPA concentrations in activated sludges and effluents of both laboratory models (abbreviation UML – under measured limit)

Table 5

Calculated real and implicit DPA and ADPA concentrations in activated sludge of MBR and SBR model

	Teor. Conc. Substr. [mg/l]	Real Conc. Substr. [mg/l]	SBR real [mg/l]	SBR implicit [mg/l]	MBR real [mg/l]	MBR implicit [mg/l]	Sample`s day
DPA	10	10	0.68	57	1.33	57	25th
	10	9.3	0	117	0.21	117	44th
	25	30.4	0	280	0	280	65th
	50	52.7	0.079	730	0.074	730	95th
ADPA	10	11.5	0	70	0.15	70	156th
	10	10.9	0	163	0.701	163	184th
	25	22.6	0	279	1.02	279	198th

## 3.9. Inhibitor concentration in samples

In Table 4 and 5, DPA and ADPA concentrations of activated sludges, influent and effluents for both models are presented. In case of BT no inhibitor concentration measurements in samples were performed.

From Table 4 can be seen, that almost every measured inhibitor concentration in both activated sludges and effluents of MBR and SBR model was under measured limit or near to zero values. It means, that both inhibitors are biodegradable and are not accumulated into sludge.

From Table 5 can be seen, that real measured inhibitor concentrations in both activated sludges of laboratory models were near to zero values. On the other hand, implicit calculated inhibitor concentrations were very high in compare with real measured inhibitor concentrations. It follows, that DPA and ADPA inhibitors in activated sludges of both laboratory models were removed.

## 4. Conclusions

Based on year operation (16th Jan–16th Dec 2009) of laboratory MBR and SBR models with tested inhibitors of nitrification, diphenylamine DPA, 4-amine-diphenylamine ADPA and benzothiazole BT following conclusions can be stated:

#### 4.1. MBR model

- By using of membrane filtration the permeate COD concentration decreased to 30–40 mg/l. Average permeate COD concentration during the whole operation with inhibitor dosing into substrate was 86 mg/l.
- The suspended solids concentrations in permeate were under measured limit.
- The decrease of permeate colour in compare with influent colour occurred thanks to membrane filtration.
- At higher sludge age as in case of MBR model (predetermined 50 d), complete nitrification into the both steps at each inhibitor in substrate was achieved. In MBR model nitrification process was inhibited only during the first days of sludge adaption on substrate with selected inhibitor DPA and ADPA. The rest of the period of operation, nitrification process with DPA, ADPA and BT was completed to second step.
- Despite of membrane filtration sludge concentration decreased from initial 11 g/l to final 3–4 g/l. Probably due to the high salinity concentration (6 g/l), methanol, toluene, isopropanole and presence of inhibitors in substrate, the decay of activated sludge occurred. The predetermined sludge age in MBR model was 50 d, but the real value was circa 35 d.
- DPA and ADPA concentrations in permeate were under the measured limit. The DPA and ADPA real

measured sludge concentrations were near to zero values in comparison with implicit calculated sludge concentrations during the whole operation. It follows, that inhibitors DPA and ADPA were biologically removed.

 From the long point of view can be alleged, that the measured permeate flux values were stable in interval 9–10 l/m<sup>2</sup>h.

## 4.2. SBR model

- The average unfiltered supernatant COD concentration during the whole operation with inhibitor dosing into substrate was 609 mg/l. The lower sludge age of SBR model had positive effect on sludge sedimentation. Despite of that, the values of unfiltered COD concentration of SBR model were high. It was caused by unsedimentated suspended solids (circa 150 mg/l), by presence of dispersed sludge flocks and unsedimentated turbidity in supernatant-effluent. The average filtered effluent COD concentration of SBR model was in interval 300–700 mg/l during the whole operation with inhibitor dosing into substrate.
- At lower sludge age (20 d), at DPA concentration of 10 mg/l in the substrate, slow but progressive nitrification into the second stage (50–80%) was accomplished. After DPA concentration increased in the substrate to 25 mg/l and later 50 mg/l, a significant (almost 100%) inhibitive effect on second step of nitrification was achieved.
- With tested inhibitor ADPA the nitrification course was similar to nitrification with tested inhibitor DPA. The change occurred in case of BT dosing into substrate. The nitrification into the second step was observed only at BT concentration 2 mg/l in substrate. At BT concentration 6 mg/l in substrate, the NO<sub>3</sub>–N concentrations decreased from 350 mg/l to 50 mg/l and at these values persevered till the end of operation. High NH<sub>4</sub>–N concentration values (300–350 mg/l) were measured during the period at BT concentration 6 mg/l in substrate. It follows, that BT at concentration 6 mg/l was the sturdiest inhibitor of nitrification.
- The sludge concentration decreased from initial 7 g/l to final 1.5 g/l, which can be explained by higher suspended solids concentration in the effluent. Probably because of high salinity concentration (6 g/l), methanol, toluene, isopropanole and presence of inhibitors in substrate, the decay of activated sludge occurred. The predetermined sludge age in SBR model was 20 d, but the real value was circa 10 d.
- DPA and ADPA concentrations in the effluent were similar to the findings with MBR model.

The long term testing of selected nitrification inhibitors confirmed the positive influence of membrane filtration on nitrification process stability. The higher sludge age, higher sludge concentration in MBR, high sludge separation on membrane creates optimal technological conditions for reduction of inhibitors influence on nitrification process. On the other hand, SBR system (as analogy to the classic activated sludge system with sedimentation tanks) showed high nitrification sensitivity on tested organic inhibitors. By arrangement of membrane filtration into real technological line of industrial WWTP, the complete nitrification into the both steps and good quality effluent could be achieved.

#### Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0144-07.

#### References

- Metcalf and Eddy, Inc. Wastewater Engineering, Treatment and Reuse, International edition, Published by McGraw Hill, 2004.
- [2] U. Pagga, J. Bachner and U. Strotmann, Inhibition of nitrification in laboratory tests and model wastewater treatment plants, Chemosphere, 65 (2006) 1–8.
- [3] S. Martinez/Hernández, A.-C. Texier, F. de Maria Cuervo-Lopéz and J. Goméz, 2-Chlorphenol consumption and its effect on the nitrifying sludge, J. Hazard. Mater., 185 (2011) 1592–1595.
- [4] A.M. Eilersen, E. Arvin and M. Henze, Monitoring toxicity of industrial wastewater and specific chemicals to green alga, nitrifying bacteria and an aquatic bacterium, Water Sci. Technol., 50 (2004) 277–283.
- [5] A.C. Anthonisen, R.C. Loehr, T. Prakasam and E.G. Srinath, Inhibition of nitrification by ammonia and Nitrous acid, J. Wat. Poll. Cont. Fed., 48 (1976) 835–844.
- [6] M. Henze, M.C. van Loosdrecht, G.A. Ekama and D. Brdjanovic, Biological wastewater treatment – principles, modelling and design, IWA publishing, 2008.
- [7] J.-H. Kim, X. Guo and H.-S. Park, Comparison study of the effects of temperature and free ammonia concentration on nitrification and nitrite accumulation, Process Biochem., 43 (2008) 154–160.
- [8] S. Park and W. Bae, Modeling kinetics of ammonium oxidation and nitrite oxidation under simultaneous inhibition be free ammonia and free nitrous acid, Process Biochem., 44 (2009) 631–640.
- [9] J.S. Knapp, A.G. Callely and J. Mainprize, The microbial degradation of morpholine, J. Appl. Bacteriol., 52 (1982) 5–13.
- [10] V.I. Repkina, S.A. Dokudovskaya, R.A. Umrikhina and V.A. Samokhina, Maximum permissible concentrations of benzothiazole and 2-mercaptobenzothiazole during biochemical treatment of wastewaters, Khim. Prom-st., 10 (1983) 598–599 (in Russian).
- [11] J.D. Walker, Effects of chemicals on microorganisms, J. WPCF, 61 (1989) 1077–1097.
- [12] H. De Wever and H. Verachtert, Biodegradation and toxicity of benzothiazoles, Wat. Res., 31 (1997) 2673–2684.
- [13] J. Chudoba, F. Tucek and K. Zeis, Biochemischer Abbau yon Benzthiazolderivaten, Acta Hydroch. Hydrob., 5 (1977) 495–498.

- [14] P. Pitter, Determination of biological degradability of organic substances, Water Res., 10 (1966) 231–235.
- [15] P. Puig, P. Ormad, J. Roche, E. Sarasa, P. Gimeno and J.L. Ovelleiro, Wastewater from the manufacture of rubber vulcanization accelerators: characterization, downstream monitoring and chemical treatment, J. Chromatogr. A, 733 (1996) 511–522.
- [16] S. Judd, The MBR book Principles and Applications of MBR in Water and wastewater treatment, Elsevier, London, 2006.
- [17] G. Munz, M. Gualtiero, L. Salvadori, B. Claudia and L. Claudio, Process efficiency and microbial monitoring in MBR and CASP treatment of tannery wastewater, Bioresour. Technol., 99 (2008) 8559–8564.
- [18] BUA (Berategremium für Umweltrelevante Altstoffe der Gesellschaft Deutscher Chemiker). BUA-Stoffbericht 114 (Ergänzungsberichte I.), Diphenylamin (Nr. 15). S. Hirzel Verlag, Stuttgart, Germany, 1993.

- [19] G. Rippen, Handbuch Umweltchemikalien: Diphenylamin. In: Ergänzungslieferung (12/97), Ecomed Verlag, Landsberg, Germany, 41 (1997) 1–8.
- [20] M. Murin, J. Gavora, I. Drastichová, E. Dušková, T. Madsen, J. Tørsløv, A. Damborg, H. Tyle and F. Pedersen, Aquatic hazard and risk assessment of two selected substances produced in high volumes in the Slovak Republic, Chemosphere, 34 (1997) 179–190.
- [21] O. Drzyzga, Diphenylamine and derivatives in the environment: a review, Chemosphere, 53 (2003) 809–818.
- [22] APHA AWWA WPCF, In L.S. Clescerl, A.E. Greenber, A.D. Eaton (Eds.) Standard methods of examination of water and wastewater, 20th Ed., Washington DC: American Public Health Association, 1999.