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Operation of MBR pilot plant–industrial wastewater treatment in Duslo Šal'a Inc.

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ABSTRACT

The aim of presented study is testing of pilot plant for industrial wastewater treatment by using of membrane bioreactor with submerged hollow fibre membranes. During the almost two years long operation the various operation statuses were studied and recorded. The chemical regeneration process was optimised and it was investigated, that important and integral part of chemical regeneration was acidous step. Presented tests pointed at significant quality improvement of treated wastewaters, above all values of organic compounds (chemical oxygen demand, biochemical oxygen demand) in compare with real WWTP in Duslo Šal'a a.s. After application of membrane separation also nitrogen removal was more effective, especially nitrification process.

Keywords: Industrial wastewater; Inhibition of nitrification; Membrane regeneration; Organic chemistry production; Permeability; Hollow-fibre membrane; Duslo a.s. Šal'a

1. Introduction

Membrane processes are successfully utilised in many branches of industry. First pilot plant experiments were carried out in 80–90´s, when production of membrane materials had reached certain development. Despite of that, membrane price, capital and operational costs of this technology did not allow its wider application. On the other hand, by 2006, around 300 large industrial plants with a capacity >20 m^3/d were in operation in Europe. Membrane bioreactor (MBR) technology has not only attracted increasing interest for the set up of new wastewater treatment systems but also it has high potential looking at upgrading tasks of already existing wastewater treatment plants (WWTPs) [1–6].

For instance, the largest industrial MBR Sobelgra plant in Belgium (as of 2005) was commissioned in November 2004 and is equipped with 16 PURON® modules providing total membrane area of 8000 m^2. The MBR plant was selected as a result of the plant capacity being extended from 110 to 250 ktonne per annum. The MBR was retrofitted into the existing aeration tank, which was divided into two parts to provide and aeration tank and a separate membrane tank. The MBR plant treats effluent from a malting operation, which is being very high in organic content and with a relatively low

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biochemical/chemical oxygen demand (BOD/COD=0.4) ratio. The wastewater (feed) and treated water (effluent - permeate) quality comparison showed interesting values of water quality parameters and efficiency of treatment process [7].

In Koch Membrane Systems, the membrane element is the submerged hollow-fibre (HF), the membrane material is PES. A unique feature of the PURON® system is the securing of the fibres only at the base, with the membrane filaments individually sealed at the top. Scouring air is injected between the filaments intermittently by means of a central air nozzle at the module base so as to limit the degree of clogging at the module base. The free movement of filaments at the top of the module is designed to allow gross solids, such as hair and agglomerated cellulose fibres, to escape without causing clogging in this region [7].

Modern industry exploits various synthetic organic compounds, which are biorefractory, bioaccumulatory and/or carcinogenic. Unfortunately, many of the concentrated streams from e.g. organic chemical synthesis, exhibit extremes of pH, high concentrations of salts (up to 20% w/v), and carried-over catalysts, one or all of which may inhibit microbial growth. Biorefractory organics which often occur in this type of effluent, and which would be amenable to treatment using this process are for example Phenol, 2,4-Dichlorophenol, Pentachlorophenol, 2-Nitrophenol, 2,4-Dinitrophenol, Aniline, *o*, *m* and *p* - Phthalic acid, and etc. Combination of biodegradation and membrane technology could be sufficient process for treatment such streams [8 –13].

DUSLO a.s. Šal'a (a.s. = joint-stock company) is one of the most important producers of industrial fertilizers in Central Europe. At the same time DUSLO a.s. produces a wide range of organic chemicals, especially rubber additives and pesticides. Inorganic forms of nitrogen are among the pollutants present in the wastewater. Great attention is paid to the removal of these pollutants. However, high concentrations of inorganic forms of nitrogen are still present in the effluent from wastewater.

Presented contribution summarises main results from the operation of MBR pilot plant, which aim is to confirm facilities of MBR utilisation in the process of industrial WWTP Duslo Šal'a reconstruction as the first application of MBR in the Slovak Republic. Effectual integration of MBR into the technological line of WWTP Duslo Šal'a would markedly increase quality of discharged wastewater and consequently, the quality of recipient - the river Váh in its below flow would be improved. In the term of social relevance, this appears as major aim of given project. For this purpose, Koch Membrane Systems - PURON® was selected and long-term tested for the operation of MBR pilot plant Duslo Šal'a.

2. Materials and methods

2.1. Description of Industrial WWTP Duslo Šal'a a.s.

Duslo, a.s. Šal'a is one of the most significant chemical industry companies in Slovakia. The company produces wide scale of industrial fertilizers, rubber industry chemicals, dispersions and glues as well as special products of organic and inorganic chemistry. The wastewater contains wide scale of biodegradable substances (methanol, toluene, aniline, acetone, isopropanol, hexalin, phthalic acid, etc.), inorganic nitrogen compounds as well as slowly biologically degradable substances, for example derivatives of diphenylamine. The wastewater treatment is realised in mechanical-biological WWTP that was built in 70 – 80´s of the last century on plot of company [14].

Recent technological arrangement of WWTP (Fig. 1) represents two-stage activated sludge system with oxic (N) and anoxic (D) zones. The volume of the first stage is nearly double in comparison with the second stage. Suggested changes of WWTP (Fig. 2) compared with recent

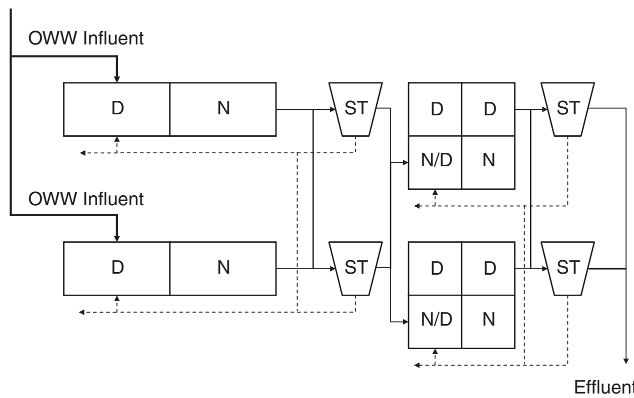

Fig. 1. Technological scheme of recent biological WWTP Duslo Šal'a a.s.

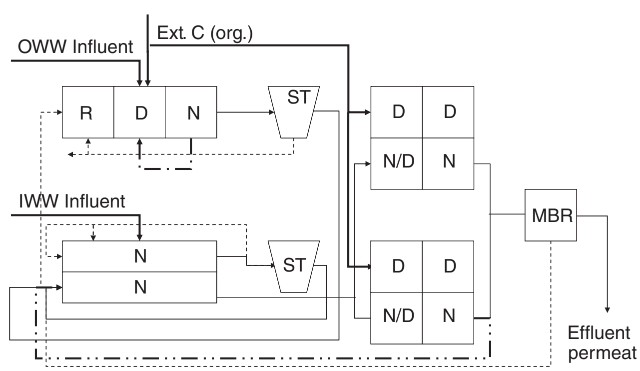

Fig. 2. Proposal of new technological arrangement of WWTP Duslo Šal'a a.s. OWW – organic waste water, IWW – inorganic waste water, R- regenerator, D – denitrification, N – nitrification, ST – sedimentation tank, MBR – membrane bioreactor.

a) b) c)

Fig. 3. Photo documentation: A - overview of pilot model unit, B - module after chemical regeneration, C - module before chemical regeneration.

technological arrangement are as follows: complement of regeneration zone, first stage reduction by 50% of recent stage, technology enhancement for nitrification of inorganic wastewater (within change of WWTP conception, the selected flows of inorganic wastewater from production of fertilizers are going to be treated in biological WWTP), the utilisation of 25% of recent first stage on nitrification process in second stage and integration of MBR behind the recent second stage or its insertion into the second stage.

2.2. Description of the MBR pilot plant

The operation of MBR pilot plant (Fig. 3A) was started up on 19th June 2008 and its basic parameters are described in the Table 1. The MBR model unit was designed in the scaling factor 1:1900 to the proposal of new WWTP (Fig. 2). Supplier and operating supervisor of pilot plant is company Envi-pur, Ltd.

3. Results and discussion

3.1. MBR Pilot plant operation - Phase 1 (June 2008 – January 2009)

After construction and test period the real operation of MBR unit started up in June 2008. Initial hydraulic loading was set up on flow 360 – 380 l/h gross (11.6 – 12.4 l/m^{2}h = LMH gross flux) or 355 l/h net (11.4 LMH). In text written bellow measured parameters of various operating conditions are described.

Table 1
Basic technological parameters of real WWTP and MBR pilot plant in DUSLO Šal'a

		Real WWTP Duslo Šal'a	MBR unit of Duslo Šal'a
Parameter	unit	value	value
Total volume of reactors	m^3	21 500	10.8
Design inflow of wastewater	m^3/h	700	0.36
Hydraulic retention time 1st stage	h	19.3	12.7
Hydraulic retention time 2nd stage	h	9.9	16.8
Sludge concentration	g/l	4–8	6–18
Solid retention time - SRT	d	25–30	35–40
Dissolved oxygen concentration	mg/l	3–5	3–6
Membrane surface area	m^2	-	31 (62)
Design flux	LMH	-	11.6

3.2. Membrane fouling during initial operation

Until 80th (8th September) day from start up the membrane separation was operated with flow 360 – 380 l/h gross (11.6 – 12.4 LMH), which represents 335 – 355 l/h net (10.8 – 11.4 LMH). Because of problems with heavy

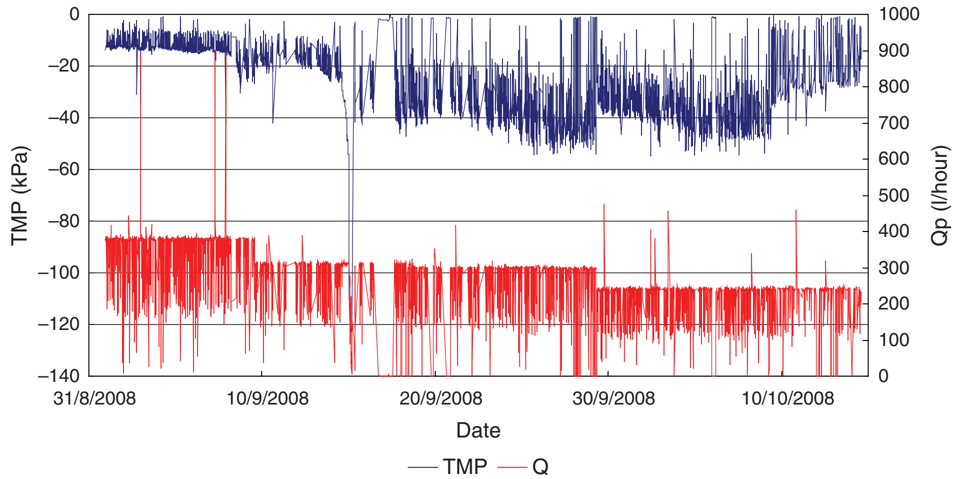

Fig. 4. TMP and permeate flow evaluation during the first phase.

membrane fouling, it was obliged to decrease permeate flow on 310 l/h gross and later on 240 L/h gross. Step by step flow decreasing was necessary because of continuous increasing of trans-membrane pressure (TMP) with unsustainable value under – 50 kPa (see Fig. 4).

3.3. Chemical cleaning of MBR pilot plant and TMP decreasing

In this phase of research the permeate flux and membrane fouling were investigated. Till 7th November 2008 (142nd day - Fig. 5) the permeate flow was stable at 350 l/h gross (flux 10.3 LMH) during next two weeks. The values of TMP were also stable during this period (–10 kPa) and the membrane process did not show any significant fouling sign. With the aim to lengthen of operation time without regeneration the permeate flow was decreased on 8th November (143rd operation day) to 280 l/h gross (flux = 9.0 LMH) for the next ten days. On 152nd day the permeate flow increased to 420 l/h gross (flux =13.5 LMH) for a one day and on 153rd day decreased to 340 l/h gross (flux = 11.0 LMH). These short-term higher permeate flows caused immediately decreasing of TMP values. The TMP had been also decreasing during the period with higher permeate flows more rapidly than in the case of initial long-term permeate flow 280 l/h (gross). By reason of increased TMP, on 154th day the oxidative regeneration (by sodium hypochlorite) was accomplished.

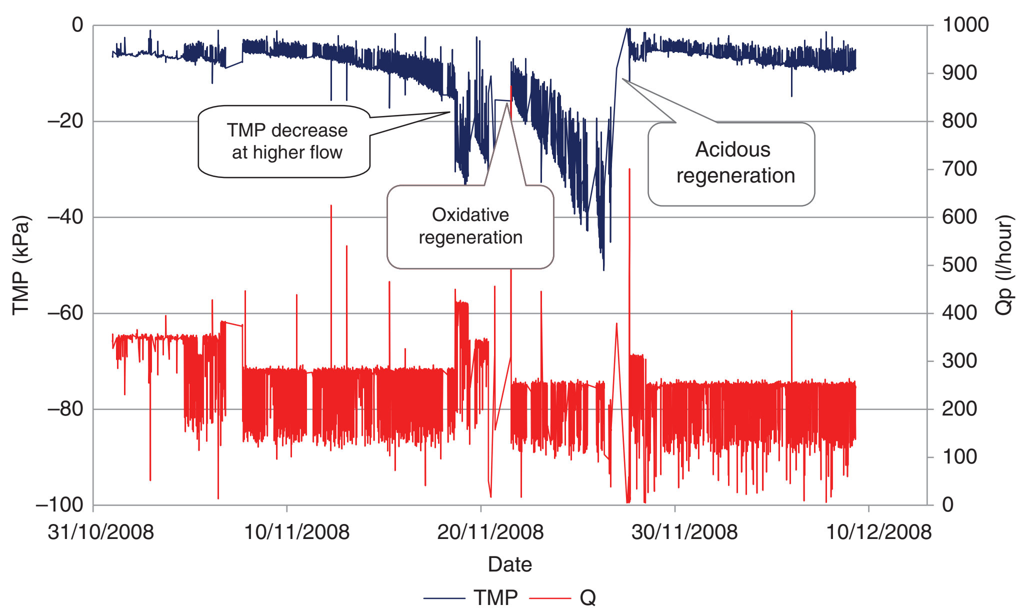

Fig. 5. Evolution of permeate flow and TMP before and after chemical cleaning.

Table 2
Membrane permeability before and after oxidative and acid regeneration

Membrane permeability	Oxidative regeneration	Acid regeneration
Membrane permeability before regeneration at 20°C	42 LMH/bar	19 LMH/bar
Membrane permeability after regeneration at 20°C	84 LMH/bar	259 LMH/bar
Initial membrane permeability of new membrane at 20°C	89 LMH/bar	389 LMH/bar
Permeability ratio after and before regeneration	(84/42)x100 = 200%	(259/19)x100 = 1 319%
Permeability recover to initial permeability of new membrane	(84/389)x100 = **21.5%**	(259/389)x100 = **67%**

As it is evident from the Fig. 5, despite of reduced permeate flows (on 260 l/h gross) the oxidative regeneration did not improve TMP values and increasing of TMP followed up to −50 kPa on 160th day of operation. From this reason the acid regeneration (by citric acid) was carried out and on 161st day. After acid regeneration, the permeate flow was operated at 260 l/h gross (flux = 8.4 LMH) and the operation at this permeate flow was performed during 3–4 weeks without any technological problems. In Table 1 membrane permeability before and after oxidative and acid regeneration is presented and evaluated.

The results in Table 2 show that oxidative regeneration was not so effective in permeability recovery. Permeability was recovered more effectively by acid regeneration. This finding has confirmed that increasing of membrane´s resistance during standard operation was caused mainly by inorganic substances found in wastewater. Total salinity in Duslo Šal'a a.s. wastewater is very high (6 g/l) with high concentration of chlorides, carbonated ions, fluorides, sulphates and other ions predominantly causes membrane scaling. The better effectivity of acid regeneration compare to oxidative regeneration was confirmed also in the followed operation of pilot plant in Duslo Šal'a a.s.

3.4. MBR Pilot plant operation - Phase 2 (February 2009 – November 2009)

The aim of the second phase was to achieve sustainable long-term TMP development with minimal periodicity of chemical regeneration. Hence the second membrane module was installed into pilot-scale system. This configuration has been operated from 10th March 2009. Total filtration surface of membrane module was increased to 62 m^2 (31 + 31 m^2). During second phase the tested plant was operated on full hydraulic performance (approx 9 m^3/d) and with the average flux on 6.1 LMH net.

Operation in period February 2009 – November 2009 was characterised by very slow permeability decrease. On Fig. 6 and Fig. 7 the TMP values and flux are presented.

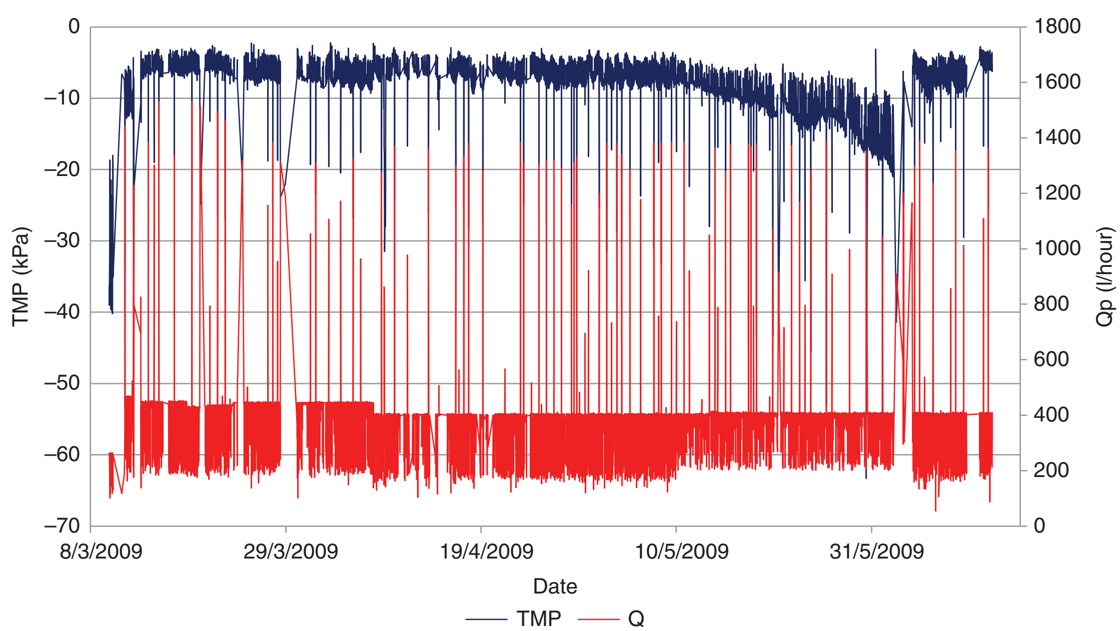

Fig. 6. TMP and permeate flow during the stable operation through the March – June 2009.

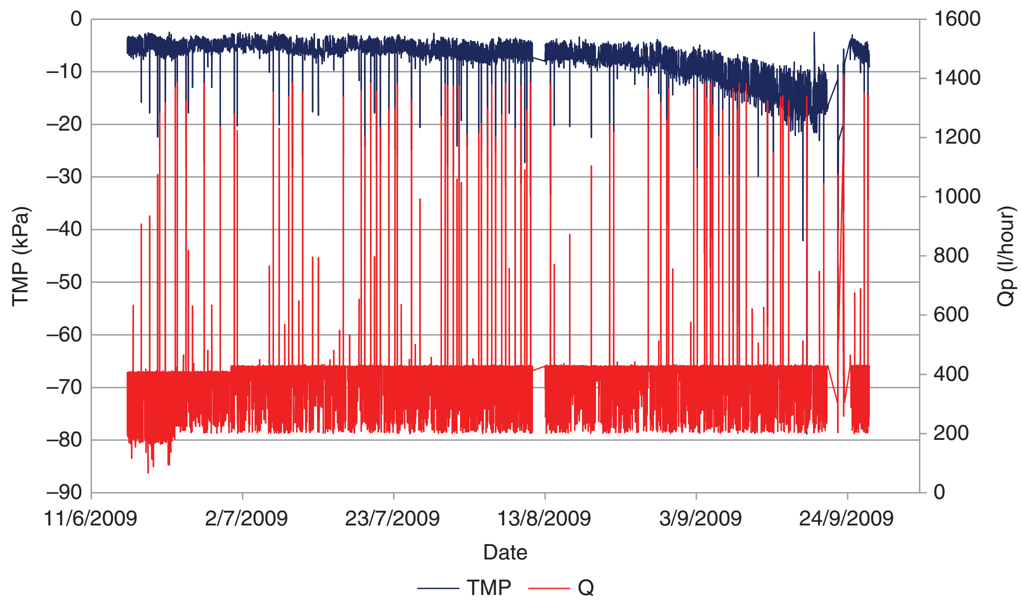

Fig. 7. Evolution of TMP and permeate flow through the June – September 2009.

TMP moved in range −5 up to −20 kPa. Gross flux was maintained between 6.9 – 6.5 LMH (430–400 l/h) during whole nine months operation period. Generally, we can characterise this period of operation as very stable without relevant technical problems. Set-up technological parameter seems to as optimal also for future real operation of membrane treatment plant.

Achieved period between two chemical regenerations was three months. On Figs. (8,9) the permeability courses during the second phase are presented. Permeability after chemical regenerations was maintained between 1.5 – 2 LMH/kPa at 20°C. During operation it was recorded slowly decreasing of values around 0.5 LMH/kPa at 20°C. This value was set up as threshold

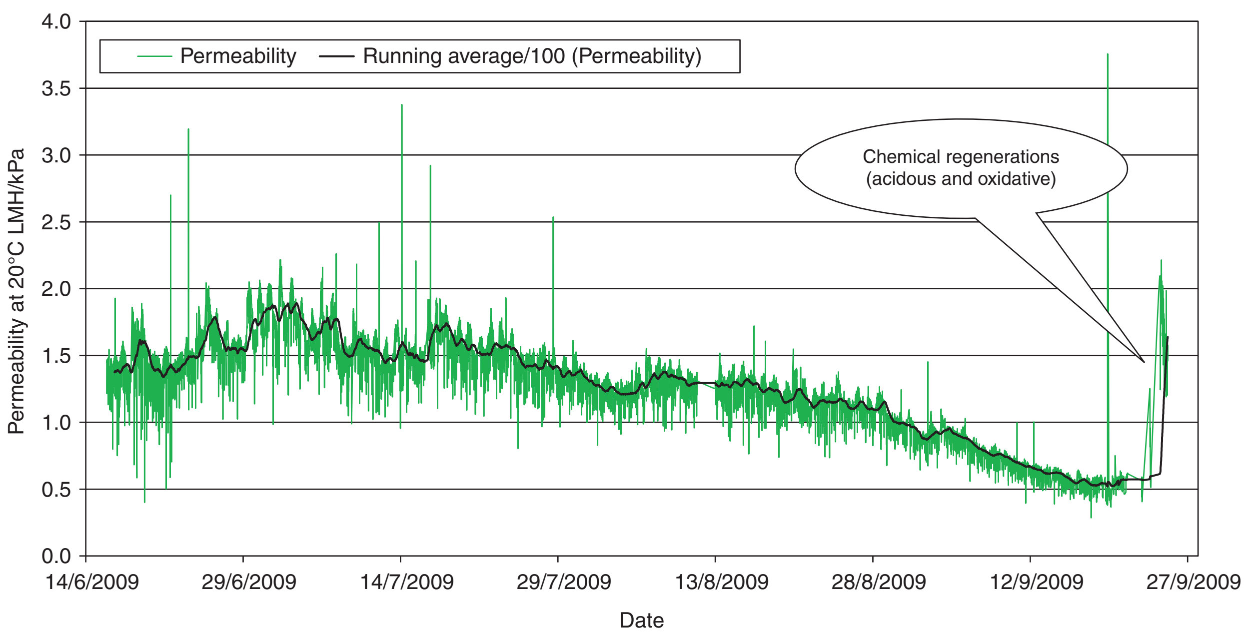

Fig. 8. Evolution of permeability through the March–June 2009.

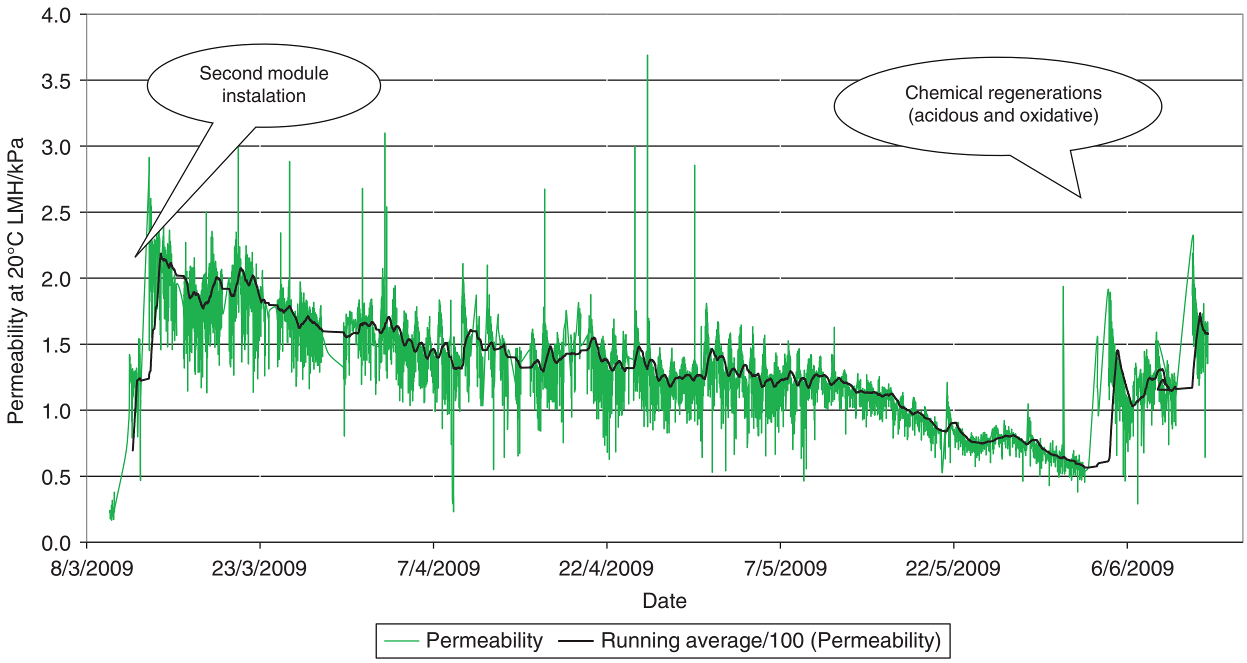

Fig. 9. Evolution of permeability through the June – September 2009.

for regeneration, although operation was possible down to 0.2 – 0.3 LMH/kPa at 20°C for probably next few weeks. Chemical regeneration for permeability recovery consisted from both, acidous and also oxidative steps.

3.5. Comparison of influent and effluent quality parameters in MBR pilot plant of Duslo Šal'a Inc.

Quality evaluations of wastewater treatment were performed by analysis of wastewater as influent (raw wastewater) and effluent (permeate - treated wastewater from MBR pilot plant) during whole year 2009 (ca 70 samples) – see Table 3. Received values were compared with data from existing real WWTP in Duslo Šal'a also from year 2009 (ca 100 samples). Obtained results confirmed the information from previous experimental works concerning COD decrease in treated wastewater. Effluent COD of treated wastewater from real WWTP Duslo Šal'a Inc. was in average more than 300 mg of COD/L and permeate COD from pilot plant was less

Table 3
Influent and permeate quality parameters in MBR pilot model unit and in real WWTP in Duslo Šal'a during year 2009

	Real WWTP Duslo Šal'a			Pilot model unit of Duslo Šal'a		
Parameter	Influent (mg/l)	Effluent (mg/l) Average (min-max)	Efficiency (%)	Influent** (mg/l)	Permeate (mg/l) Average (min-max)	Efficiency (%)
COD	1105	310 (185–455)	72	1210	92 (52–125)	93
BOD_5	302	17 (12–28)	94	334	14 (8–22)	96
NH_4-N	73	85 (65–124)	–14	85	19 (8–39)	77
NO_3^-N	45	2.3 (0.1–5.6)	95	50	10 (6–18)	80
NO_2^-N	8	12 (2.2–30.5)	–50	8	37 (15–58)	–362
N_{inorg}	126	99 (74–144)	21.2	143	66 (41–88)	53,5
MLSS	178	75 (54–92)	57.9	185	<3	>98
Absorbance*	-	1.189 (1.011–1.325)	-	-	0.108 (0.081–0.129)	-

*Absorbance measured at λ=400 nm (without unit)

**The influent concentration was calculated as average number from organic and inorganic WW concentrations than 100 mg of COD/L. Measurement of absorbance confirmed improved quality of permeate compared to effluent from real WWTP Duslo Šal'a a.s. The colour of influent wastewater was moderate brown and contains soft and dispersed suspended solids (SS). Permeate from pilot plant was yellow or light brown and was pure. The efficiency of MBR nitrification process (77%) was higher than nitrification process in the real WWTP (negative), because of ammonium nitrogen (NH_4-N) decrease and nitrite nitrogen (NO_2^-N) increase in permeate. Also inorganic nitrogen removal process was more effective (53.5%) in the pilot plant than in the real plant (21.2%).

According to laboratory results from also this study confirmed positive influence of membrane filtration on nitrification process stability in real condition of industrial WWTP Duslo Šal'a [15]. The higher sludge age, higher sludge concentration in MBR, high sludge separation efficiency on membrane creates optimal technological conditions for reduction of inhibitors influence on nitrification process. On the other hand, the classic activated sludge system with sedimentation tanks showed high nitrification sensitivity on tested wastewater from chemical industry. 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.

4. Conclusions

Presented pilot tests proved good possibilities of industrial wastewater treatment by using MBR technology with submerged hollow fibre membranes. During 2 years long operation, the various operation status were recorded, which had direct or indirect impact on filtration process. For a long term operation, optimalization of filtration capacity (enlarging of filtration area) was performed.

The chemical regeneration process was optimised and it was investigated, that important and integral part of chemical regeneration was acidous step. By using acidous step, undissolved inorganic compounds on membrane surface and also in membrane pores were dissolved. Chemical regeneration was done every 3 months (both oxidizing and acidous steps). Presented tests pointed at significant quality improvement of treated wastewaters, above all values of organic compounds (COD). After application of membrane separation also nitrogen removal was more effective, especially nitrification. Next testing will be focused on optimisation of these processes.

Pilot tests were performed directly in area of WWTP Duslo a.s., and was operated by employees of Duslo Inc. and supervised by supplier Envi-pur, Ltd. Testing of new technology and research works have been realised by team of Duslo Inc., Envi-pur Ltd., VUCHT Inc., and IChEE FChFT SUT.

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