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# BIODEGRADATION OF ORGANIC AND INORGANIC CONTAMINANTS ARISING FROM MANUFACTURING OF BIPOLAR-ORIENTED FILMS FROM POLYETHYLENETEREPHTALATE

A proposal of biodegradation of waste components formed during manufacturing of films of biopolar orientation from polyethyleneterephtalate (PETP) is described. In the paper, utilisation of such wastes as resorcinol and nitrates is presented. The principle of elimination of these compounds is based on the utilisation of resorcinol as a donor of carbon in the suspension undergoing denitrification. The conditions necessary for wastewater treatment in a production plant are described.

# 1. INTRODUCTION

One of the important technologies applied in plastics industry is manufacturing of very thin films of bipolar orientation from polyethyleneterephtalate (PETP). The films are utilised in the electroengineering and foodstuff industries and also for other purposes. Generally, this technology is considered to be very clean; this viewpoint is one-sided because on the one hand the production itself does not present any hazard for environment, but on the other hand is connected with production of wastes. The main contaminant in exhalates and, consequently, in aquatic medium (gases scrubbed in diluted sodium hydroxide) is resorcinol (1, 3-dihydroxybenzene) used in the manufacturing process for etching the surface of the films prior to their being printed. Another significant contaminant is sodium nitrate, which is a waste from the cleaning of filtres used for filtering the PETP polymer melt (filters are cleaned by means of nitric acid and sodium hydroxide).

Phenolic substances occur relatively often in industrial wastewaters. Numerous papers dealing with their biological decomposition are to be found in technical

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literature: according to the data reported by PITTER [1] resorcinol ranks as one of the substances which can be easily decomposed under aerobic conditions, provided that:  $COD = 1810 \text{ mg } O_2 \cdot dm^{-3}$ , COD/TOD = 96.4%, and the specific rates of substrate removal are 10 mg  $\cdot g^{-1}h^{-1}$  and 38 mg  $\cdot g^{-1}h^{-1}$  for the respective non-adapted and adapted cultures of municipal activated sludge. Relatively high residual values of COD were observed during decomposition. The biodegradation of resorcinol was also successful under anaerobic conditions. TSCHENK and SCHINK [2] describe its very rapid decomposition by bacteria isolated from sea and river sediments which break it down into usual metabolite as follows: acetate  $\rightarrow$  methane  $\rightarrow$  carbon dioxide. Resorcinol also decomposes well in anoxic reactor [3] in the presence of nitrates as electron acceptors.

According to the data obtained by manufacturers, the annual consumption of resorcinol was presumed to be approximately 1.5 tons (6 kg/day for a period of 250 working days), while the cleaning of filters by means of nitric acid and sodium hydroxide would produce 5.34 tons of NaNO<sub>3</sub>/year. The indispensable condition for a successful waste decomposition is to reduce the concentration of resorcinol in the effluent waters below 0.1 mg  $\cdot$  dm<sup>-3</sup> and that of nitrates below the permissible limit, i.e. 50 mg  $\cdot$  dm<sup>-3</sup>. The optimal solution seems to be the development of cleaning biotechnology (denitrification) with the resorcinol as the dominant external donor of carbon. Such a biotechnology allows degradation of a substantial amount of contaminants during a single technological step. The modification of a technological cycle in this case was limited because of the need to utilise fully the existing equipment in the wastewater treatment plant (non-utilised rectangular tanks of 500  $m^3$  approximate volume). On the other hand, such a procedure was advantageous since it gave the possibility of improving the cleaning efficiency of the denitrified effulent in the tank with activated sludge (loaded mainly by dimethylformamide from the manufacturing of poromeric hygienic leather).

The aim of this paper was to propose the treatment system which could be applied in the plant. Utmost attention was devoted to the suspension single-sludge system; denitrification column and plastic rings covered with heterogeneous biological culture were tested, more or less, just as a "reference" variant. Biological degradablity under conditions of existing activation was simultaneously verified.

## 2. EXPERIMENTAL

## 2.1. BIOLOGICAL MATERIAL, CHEMICALS AND SOLUTIONS

Biological material. Biomass from the biological treatment plant, i.e. Technoplast Company Chropyně, was used. It was adapted primarily to dimethylformamide as the main contaminant. The return activated sludge was decanted using drinking water, filtered and used in the proper fermenters and model tanks. The denitrifying biomass was obtained from the same sludge which was utilized for a long time in the presence of nitrate ions and methyl alcohol.

Model wastewater. Actual wastewater was not available (the solution was sought prior to a start-up of production). Model wastewater (MWW) and synthetic wastewater (SWW) were prepared using stored solutions (in distilled water) of resorcinol, dimethylformamide, sodium nitrate + potassium nitrate + hydrogen ammonium phosphate (constant composition), and resorcinol + methyl alcohol (variable composition, methyl alcohol as a donor of electrons was progressively replaced by resorcinol) + phosphate buffer (pH = 7.2). The relevant stored solutions (according to the type of test) were diluted, at least  $100 \times$ , with drinking water to the desired concentration. The phosphate buffer was always added, except for the denitrification column. The initial and actual concentrations of the components examined (resorcinol, nitrates, nitrites, etc.) were determined in the relevant tests. In continuous denitrification experiments, the solutions of nitrate + nitrite and donors of carbon (resorcinol+methyl alcohol) were dosed separately and mixed at the entry to the model set-up in a ratio of 1:1. The dosing was done using a standard peristaltic pump. Chemicals used were of standard laboratory purity (class – clean, p.a.); they were supplied by the Lachema Company, Brno, being either their manufacturer or supplier.

## 2.2. APPARATUSES AND MODEL EQUIPMENT

Biochemical analyzer BSK-meter, SL-01, manufacturer – DAK Slušovice, Czech Republic.

Laboratory glass fermenters of approximate volume of  $2.5 \text{ dm}^3$  made in the facilities of the Faculty of Technology according to [4].

Denitrification column – a cast-iron cylinder, 0.21 m internal diameter and 0.40 m length. The column was filled with plastic rings ( $20 \times 20$  mm) covered with biomass; the rings were supported by a perforated PVC element. Inlet located at the bottom (5 ports located symmetrically), outlet – cap at the centre. A gas-holder of volume of 2.4 dm<sup>3</sup> was located at the outlet. The solution was delivered by the peristaltic pump. Total volume of the column – 13.2 dm<sup>3</sup>, volume of the biomass support – approximately 1.5 dm<sup>3</sup>, specific surface of the support – approximately 360 m<sup>2</sup> m<sup>-3</sup>.

Model of activated sludge – the rectangular tank of 1 m length, 0.2 m width and 0.18 m depth, filled to 0.1 m level, approximate volume of 20 dm<sup>3</sup>. The tank was made on a scale of 1 to 30 compared the tanks in the wastewater treatment plant (available for processing the "resorcinol-type" wastewaters) which were out of use at that time. The sludge suspension was mixed and aerated by pressurized air, pumped through a U-tube at the bottom of the tank. The model solution and recirculated activated

sludge were delivered by a peristaltic pump. Sedimentation of the sludge was carried out in a conical sedimentation tank (of approximate volume of  $1.6 \text{ dm}^3$ ). Samples for analyses were taken off at the inlet of the aeration tank and sedimentation tank.

Model of denitrification. Denitrification is brought about by the suspended culture in the tank of the same dimensions as that in the case of activated sludge model. The content of the denitrifying section was stirred by slow-running mixers. The last 1/8 section of the tank was separated from the anaerobic zone by a partition wall and mixed both by air admission and mechanically. In order to ensure anaerobic conditions in the course of the experiment, the surface of the denitrification section was covered with floating plates of foamed polystyrene (from 45th day till the end of the experiment). The samples for analyses were taken off at the inlet of the denitrification zone, in the aerobic section and in the sedimentation tank.

### 2.3. ANALYTICAL PROCEDURES

Determination of nitrogenous components was done using standard procedures [5]: nitrites – spectrophotometrically (reaction with NED dihydrochloride), nitrates – measurement using the ionic selective electrode. Resorcinol was determined by a modified procedure intended for determination of phenols in drinking water, i.e. photometrically after reaction with p-nitroaniline [6].

# 3. RESULTS AND DISCUSSION

The biodegradability of resorcinol is sufficiently documented in literature, e.g. [1]–[3], and the possibilities of treating the wastewater containing considerable amount of oxidized nitrogen salts (nitrates and nitrites) by biological denitrification are known and documented in numerous publications. However, the case in question represents a specific matter: the simultaneous occurrence of both types of contaminants, the need for single-stage processing based on the existing technological equipment (predetermining the "suspension-type" cycle of denitrification), eventual re-treatment in the existing biological treatment plant of the factory, where waters containing mainly dimethyloformamide are processed. Attention was devoted to all of these aspects.

Complementary experiments involving manometric measurements of BOD in laboratory fermenters and in an activated sludge tank proved that resorcinol under aerobic conditions can be efficiently degraded [7]. Practically immediate decomposition of resorcinol by non-adapted sludge is proved by the relations of BOD (without the lag phase); the maximal values of BOD were obtained after 30–60 hours of experiments (at initial resorcinol concentration ranging from 0.02 to  $0.20 \text{ g} \cdot \text{dm}^{-3}$ ). The dependence of  $\text{BOD}_5^{25}$  on the resorcinol concentration was linear, and the coefficient of correlation r = 0.99915. The ratio  $\text{BOD}_5^{25}/\text{TOD} = 0.498$ ,  $\text{BOD}_5^{25}/\text{COD} = 0.52$  (COD according to [1]); the value of BOD/TOD = 0.5 is always presented as the limit to characteristics of the substances readily biodegradable [8]. With the increase of the sludge loading (F/M, food/microorganisms) from 0.17 to 1.7 the average specific rate of resorcinol degradation in the solution shifted within the limits from 3.3 to 33 mg  $O_2 \cdot g^{-1} \cdot h^{-1}$ . This concurs with the data gathered during inoculation with municipal activated sludge.

Analogous results were obtained in experiments in laboratory fermenters. They concerned an open system, where the balance of degradation was made on the basis of a resorcinol decline in the system tested (solution). The most important results of these tests are given in table 1. Apparently, in the course of the repeated tests (tests no. 2 versus tests no. 1 in table 1) partial adaptation of the sludge occurred, which was manifested by an almost 15 fold increase in the biodegradation rate of resorcinol in the solution (to the values ranging from 3 to 12 mg  $\cdot$  g<sup>-1</sup>  $\cdot$  h<sup>-1</sup>). The results obtained confirmed both the data in literature [1] and the data mentioned above.

Table 1

	Fermenter Design. Exp.		Initial Dry m conc. con . [g·dm		c.	Specific rate of degradation	Residual conc.	Degradation of resorcinol	
	Design.	No.	[mg·dm <sup>-3</sup> ]	Initial	Final	$[mg \cdot g^{-1} \cdot h^{-1}]$	[mg·dm <sup>-3</sup> ]	[%]	
		1	25	2.2	2.0	0.3	$\approx 0$	≈100	
	D	2	100	2.3	2.0	3.1	$\approx 0$	$\approx 100$	
		1	100	2.6	1.6	0.8	3.1	96.9	
	E	2	500	2.1	2.0	11.7	9.6	98.1	
		1	500	3.1	2.8	2.1	12.7	97.5	
	F	2	2000	2.7	2.6	7.5	127.7	93.6	

Decomposition of resorcinol under discontinuous conditions in fermenters

On the basis of the specific rates stated it can be presumed that the whole volume of waste resorcinol could be, especially after longer adaptation of sludge, degraded without any problems based on the existing technology (processing the wastewaters containing dimethylflormamide); in a 500 m<sup>3</sup> tank of sludge (a dry matter content of approx. 1 g  $\cdot$  dm<sup>-3</sup>) it would be possible to degrade up to 5 kg of resorcinol per hour (the expected daily consumption of resorcinol was approx. 6 kg). However, the actual input quantities of resorcinol will be incomparably smaller due to the fact that a decisive part of this compound will be decomposed in the predetermined denitrification; activated sludge will eliminate its eventual excess.

The possibility of aerobic "re-treatment" was tested in a 4-month continuous operation of activated sludge, in which model wastewater containing resorcinol (in concentration of 100, and then 200 mg  $\cdot$  dm<sup>-3</sup>), dimethylformamide (200 mg  $\cdot$  dm<sup>-3</sup>) and basic biogenic elements were processed. The dry matter content of activated sludge ranged from 1.5 to 2.5 g  $\cdot$  dm<sup>-3</sup>, while the flow of model water was 0.3 dm<sup>3</sup>  $\cdot$  h<sup>-1</sup>. The values of these parameters were continuously measured except for

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the dimethylformamide content, whose degradability was sufficiently proved by the increase in the nitrification products  $(NO_2^-, NO_3^-)$ . After stabilisation of the activation process, a high degree of resorcinol degradation was achieved (higher than 99.8%), its outlet concentration being about 0.5 mg  $\cdot$  dm<sup>-3</sup>. On loading the activated sludge by dosed resorcinol (from denitrification), at the most in mg  $\cdot$  dm<sup>-3</sup>, it can be assumed that the effluent concentration will be smaller than 0.1 mg  $\cdot$  dm<sup>-3</sup>. The excellent nitrification efficiency of this activated sludge was manifested by the outgoing concentrations of nitrates ranging from 150 to 270 mg  $\cdot$  dm<sup>-3</sup>. These values exceeded the permitted limit (50 mg  $\cdot$  dm<sup>-3</sup>); a part of the effluent will have to be denitrified (recycled) repeatedly.

Utmost attention was paid to a denitrification procedure brought about by a suspensed culture, utilising resorcinol as a source of carbon. Denitrification was preceded by processing with methanol as the standard donor of electrons. This part of investigation was designed in detail, bearing in mind its desired exploitation on a technological scale.

The denitrification model was operated for a period of seven months using synthetic wastewater (SWW). The dosing of nitrogen components (SWW-A) was constant over the entire period of operation; the actual input concentrations (after mixing the solution of nitrates and nitrites and solution of carbon donor in the ratio of 1:1) were the following:  $625 \text{ mg} \cdot \text{dm}^{-3} \text{ NO}_3^-$ ,  $445 \text{ mg} \cdot \text{dm}^{-3} \text{ NO}_2^-$ ,  $1.8 \text{ mg} \cdot \text{dm}^{-3}$  N-NH<sup>+</sup><sub>4</sub>, 2 mg  $\cdot \text{dm}^{-3}$  P-PO<sup>3-</sup><sub>4</sub>. The dosage of carbon donors (SWW-B) varied: step-by-step methyl alcohol was replaced by resorcinol; altogether 131–280% of donors were dosed stoichiometrically. The actual concentrations of donors at the input were calculated by means of the following equations (all concentrations are in mg  $\cdot \text{dm}^{-3}$ ):

Methyl alcohol =  $(0.43 \text{ NO}_3^- + 0.35 \text{ NO}_2^-) + 0.67 \text{ O}_2 + \text{assimilation}$ 

=  $(0.097 \text{ N}-\text{NO}_3^- + 0.107 \text{ NO}_2^-) \cdot (\text{dose in } \%)/100$ .

Resorcinol =  $(0.34 \text{ NO}_3^- + 0.28 \text{ NO}_2^-) + 0.53 \text{ O}_2 + \text{assimilation}$ 

 $= (0.077 \text{ N}-\text{NO}_3^- + 0.084 \text{ NO}_2^-) \cdot (\text{dose in \%})/100.$ 

The total flow of SWW was approximately  $0.36 \text{ dm}^3 \cdot \text{h}^{-1}$ , thus the lag time was 33 hours. The initial concentration of biological sludge (2.4 g  $\cdot$  dm<sup>-3</sup>) dropped progressively in the course of the entire experiment to the approximate value of  $1.5 \text{ g} \cdot \text{dm}^{-3}$ . A chronological survey of experimental conditions and some of the results (serving only as an illustration) are given in table 2.

The model denitrification tank was filled with activated sludge, which was "run in" step-by-step. It was operated as an open system approximately for the first 6 weeks. The suspension in the denitrification zone was stirred by slow-moving mixers, and thus a more or less undefined transfer of oxygen occurred from the air to water. This transfer was significant: the concentrations of dissolved oxygen measured in the "denitrification" section of the model tank and in the aerated section were of about 2.5 and 5.5 mg  $\cdot$  dm<sup>-3</sup>, respectively. It was evident that the greater part of the donor of carbon (140% of the stoichiometric quantity of methyl alcohol was dosed) was competitively oxidized by the present oxygen and that denitrification slowed

down noticeably (table 2, 30th and 35th days); denitrification was significantly reduced or did not occur at all. This unfavourable effect could not be prevented even by doubling the added volume of methyl alcohol (280% of stoichiometric quantity in table 2, 40th and 44th days). In this phase, the sludge manifested poor sedimentation characteristics, obviously a consequence of flotation of nitrogen microbubbles which were formed in the sediment tank (denitrification in this primary stage).

## Table 2

Results of progressive laboratory suspension-type denitrification with carbon substrates – methyl alcohol and resorcinol. Input concentration 623 mg·dm<sup>-3</sup> NO<sub>3</sub><sup>-</sup> (140.7 mg·dm<sup>-3</sup> N-NO<sub>3</sub><sup>-</sup>)+445 mg·dm<sup>-3</sup> NO<sub>2</sub><sup>-</sup> (135.4 mg·dm<sup>-3</sup> N-NO<sub>2</sub><sup>-</sup>), donor doses and their presumed concentrations at the input stated directly in table. All concentrations are in mg·dm<sup>-3</sup>

		· · · ·			Removed		
Day	Section	N-NO <sub>2</sub>	N-NO <sub>3</sub>	Resorcinol	N-total Resord		
1	2	3	4	5	6	7	
1.	Donor: 14	40% methy	l alcohol	$(590 \text{ mg} \cdot \text{dm}^{-3})$			
30.	D A S	3.5 1.5 0.9	214 112 99.4		21.2 63.7		
35.	D A S	3.9 2.6 0.2	203 203 201		25.1 27.1		
40.	Donor: 28 D A S	80% methy 2.0 1.5 0.2	1 alcohol 214 191 169	(1180 mg·dm <sup>-3</sup>	21.8 38.7		
44.	D A S	3.0 2.6 0.1	203 214 108		25.4 60.8		
45.	D* A S	2.0 0.4 0.1	<0.2 <0.2 2.9	Note: denitrification zone	99.2 98.9		
47.	D* A S	0.3 0.2 0.06	<0.2 <0.2 <0.2	covered by polystyrene plates	99.8 99.9		
49.				$(420 \text{ mg} \cdot \text{dm}^{-3})$ mg $\cdot \text{dm}^{-3}$ )	)		
52.	D* A S	9.4 21.3 8.5	18.1 24.8 13.5	26 25 23	90.0 92.0	75.2 76.2 78.1	

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	1	2	3	4	5	6	7
_	56.	D*	0.7	45.2	36	83.4	· · · · ·
		Α	0.2	42.9	36		
		S	0.06	40.6	36	85.3	65.7
	59.	Donor:			(840 mg·dm 0 mg·dm <sup>-3</sup> )	<sup>-3</sup> )	
	75.	D*	0.08	< 0.2	57	99.9	72.9
		A	< 0.02	< 0.2	51	00.0	75.7
		S	< 0.02	< 0.2	50	99.0	76.2
	87.	D*	< 0.02	< 0.2	34	99.9	83.8
		Α	< 0.02	< 0.2	26		87.6
		S	< 0.02	< 0.2	24	99.9	88.6
	89.	Donor:			(340 mg · dm <sup>-</sup> 30 mg · dm <sup>-3</sup>		
	01	D <b>*</b>		< 0.2	96	99.9	81.9
	91.	D*	< 0.02 < 0.02	< 0.2	90 94	77.7	82.3
		A S	< 0.02	<0.2 <0.2	100	99.9	81.1
							01.1
	97.	Donor:	40% methy + 100% re	yl alcohol sorcinol (3	$(170 \text{ mg} \cdot \text{dm}^{-3})$ 36 mg \cdot dm^{-3})	)	
	110.	D*	12.1	33.9	0.3	83.3	99.9
		А	12.5	31.6	0.2		99.9
		S	15.8	30.1	0.1	83.4	99.9
	119.	D*	0.11	< 0.2	0.7	99.9	99.8
	117.	Ā	0.07	< 0.2	0.3		99.9
		S	0.03	< 0.2	0.2	99.9	99.9
	140.	D*	4.4	49.7	0.8	80.4	99.8
	140.	A	3.3	51.9	0.8		99.8
		S	2.5	49.7	0.6	81.1	99.8
	160.	D*	7.6	33.4	1.1	85.1	99.7
	100.	A	7.1	38.4	1.1	05.1	99.7
		S	5.6	42.9	0.7	82.4	99.8
	165				(170 mg · dm		
	165.	Donor:			$170 \text{ mg} \cdot \text{dm}^{-3}$		
	167.	D*	< 0.02	< 0.2	1.5	99.9	99.7
		Α	< 0.02	< 0.2	1.5		99.7
		S	< 0.02	< 0.2	1.3	99.9	99.7
	182.	D*	< 0.02	0.6	1.7	99.8	99.6
	102.	A	< 0.02	0.7	1.5		99.7
		S	< 0.02	0.8	1.2	99.7	99.7
	190.	D*	< 0.02	0.5	1.8	99.8	99.6
	190.	A D	< 0.02	1.6	1.3	22.0	99.7
		S	< 0.02	1.0	1.4	99.6	99.7
		3	< 0.02	1.1	1.2	79.0	//./

#### Biodegradation of organic and inorganic contaminants

1	2	3	4	5	6	7
196.	D*	< 0.02	0.9	1.8	99.7	99.6
	Α	< 0.02	1.1	1.6		99.7
	S	< 0.02	1.2	1.3	99.6	99.7
217.	D*	< 0.02	< 0.2	1.6	99.9	99.7
	Α	0.03	0.4	1.4		99.7
	S	< 0.02	0.4	1.2	99.8	99.7

Notes: D – denitrification section, A – aerobic section, S – sedimentation tank,  $D^*$  – denitrification zone covered with polystyrene plates.

Poor denitrifying effect in the first phase of the experiment (after 45 days of operation) was not, most probably, caused by insufficient representation of denitrifying bacteria in the biomass, but rather by competing oxygen respiration with the nitrate respiration. For this reason, in the next phase (from 45th day till the end), the surface in the denitrifying section was "sealed off" by floating polystyrene plates. This caused a significant decline in the concentration of denitrifying efficiency (more than 99%, table 2, 45th and 47th days).

When denitrification was found to be satisfactory, the dose of carbon donor was again reduced and part of the methyl alcohol was replaced by resorcinol in the following ratio: 100% methyl alcohol + 31% resorcinol according to stoichiometry (49th day). It is evident (see table 2, 52nd and 56th days) that denitrification efficiency progressively worsened to ca. 85%. Besides the nitrates and nitrites, ca. 30% of the input volume of resorcinol was found on the output side. Thus in this phase, resorcinol proved to be a carbon donor of poor utility. Again, doubling of the dosages of both substances (59th day, 200% methyl alcohol + 62% resorcinol) caused during one month an outstanding denitrifying effect (table 2, 75th and 87th days) and degradation of resorcinol approaching 76–88% (outgoing approximate concentration 25–50 mg  $\cdot$  dm<sup>-3</sup>).

High efficiency of denitrification and rough degradation of resorcinol were maintained even on changing the ratio of dosing of both carbon substrates (89th day, 80% methyl alcohol + 160% resorcinol). It is true that the concentration of resorcinol in the effluent increased (table 2, 91st day), nevertheless, with respect to its high overdosing, the values found confirmed its effective degradation. This concerned a short phase, an intermediate step. Further experiments were carried out in order to confirm this trend.

The aim of the project was to verify the usage of resorcinol by the denitrifying bacteria as a carbon donor. It was for this reason that the adaptation of the actually present denitrifying mass to this substance was continued. The dosing of both components was changed in the subsequent long-term operation in the following manner: 97th-164th days - 40% methyl alcohol + 100% resorcinol,

165th-217th days - 40% methyl alcohol + 140% resorcinol.

The results confirmed the evidence that the use of the total dosage of carbon donors (40% methyl alcohol + 100% resorcinol) was questionable and unreliable if the efficiency of denitrification was taken into account. The concentrations of nitrates and nitrites at the outlet varied greatly and were often unacceptably high (see the results in table 2, 110th, 119th, 140th and 160th days). The doses of donors proved to be insufficient, at best of limit value, not ensuring the required "safety" of operation ( taking account of the efficiency of denitrification). Apparently, a strong reason was inaccuracy of dosing and especially the questionable assertion of competing oxygen respiration at the suspension cycle during denitrification. In the circumstances, it will be necessary to calculate the does with greater variability. Resorcinol was degraded efficiently, its outlet concentrations being always lower than 1 mg  $\cdot$  dm<sup>-3</sup>.

For the last two-month stage, the 1.4 times addition of stoichiometric requirement of donor was increased (a coefficient of 1.4 is recommended in literature as standard for column denitrification) to a value of 1.8; 40% methyl alcohol + 140% resorcinol were dosed (beginning with the 165th day). The results according to the analysis presented in table 2 (167–217th days) were very good. The outflow concentrations of nitrites were below the level of determination (0.05 mg  $\cdot$  dm<sup>-3</sup>), the outlet concentrations of nitrates were of the order of mg  $\cdot$  dm<sup>-3</sup> (up to a maximum of 7 mg  $\cdot$  dm<sup>-3</sup> NO<sub>3</sub><sup>-</sup>) and the resorcinol content ranged from 1.2 to 1.3 mg  $\cdot$  dm<sup>-3</sup>. Denitrification with a suspension culture and resorcinol as the main donor of carbon has shown to be a realistic possibility.

Simultaneously with the suspension denitrification, the denitrification in a column was tested. The latter involved the attached biomass in an arrangement which proved its significance in the processing of wastewater with a high content of nitrites and nitrates from the manufacturing rubber profiles [9]. The column was operated after a six-week "revival" period (prior to the experiment it had been out of operation for half a year) under conditions roughly comparable to the conditions of "suspension" experiment. Only two variants of the test were selected:

46-97th days - dosage of 100% methyl alcohol - 31% resorcinol,

97-119th days - dosage of 40% methyl alcohol + 100% resorcinol.

Operation of the column was distinguished, to a certain extent, by better "stability" if the cleaning effect was taken into account. During this experiment it was shown that addition of the mixed donor, amounting to 131% stoichiometry, is insufficient, while addition of 140% stoichiometry reaches the "limit" of sufficiency. The outlet concentrations of pollutants in the denitrification column confirmed the following statement: the concentrations of nitrites ranged from 1.1 to 3.9 mg  $\cdot$  dm<sup>-3</sup>, these of nitrates were below 1.0 mg  $\cdot$  dm<sup>-3</sup> (detectable limit of determination) and these of resorcinol were in the range of 2.7–7.0 mg  $\cdot$  dm<sup>-3</sup>.

## 4. CONCLUSIONS

The results of this study have confirmed unambiguously that resorcinol is a biodegradable substrate under aerobic conditions as well as under anaerobic conditions of biological denitrification. It is apparent that effective denitrification with resorcinol as the electron donor requires a relatively longer period of adaptation allowing the reproduction of the present bacterial culture resulting in its desired structure. After this period (approximately 2 months in this experiment) it will be, most probably, possible to use solely resorcinol as a carbon substrate in the doses of, at least, 180% of stoichiometric requirement; any excess of resorcinol will be degraded in the following aerobic stage.

The arrangement of suspension culture during denitrification proved itself fully on a laboratory scale taking account of long-term operation and effective degradation of nitrogenous salts and resorcinol. The results obtained were fully comparable; moreover, they were better than those in column denitrification with an anchored culture. A necessary precondition for the attainment of analogous results on a technological scale will be the maintenance of anaerobic conditions which will not be simple in a suspension arrangement. A feasible method proposed (and verified on a long-term basis in the laboratory) consists in covering the surface of the denitrifying zone with plates of foamed polystyrene. The latter very significantly limits the passage of oxygen from the air.

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## BIOLOGICZNE UNIESZKODLIWIANIE ZANIECZYSZCZEŃ Z ZAKŁADU PRODUKCJI BIPOLARNYCH MEMBRAN Z POLIETYLENOTEREFTALANU

Przedstawiono propozycję biodegradacji składników ścieków pochodzących z produkcji bipolarnych membran z polietylenotereftalanu. Zasada usuwania takich substancji jak dwuhydroksybenzen i azotany polega na wykorzystaniu rezorcyny jako źródła węgla w procesie denitryfikacji. Omówiono warunki niezbędne do oczyszczania ścieków pochodzących z wymienionego zakładu produkcyjnego, do czego wykorzystano istniejące urządzenia.

## БИОЛОГИЧЕСКОЕ ОБЕЗВРЕЖИВАНИЕ ЗАГРЯЗНЕНИЙ ИЗ ЗАВОДА, ПРОИЗВОДЯЩЕГО БИПОЛЯРНЫЕ МЕМБРАНЫ ИЗ ПОЛИЭТИЛЕНТЕРЕФТАЛАТА

Представлено предложение биодеградации компонентов сточных вод, происходящих из производства мембран из полиэтилентерефталата. Принцип удаления таких веществ, как дигидроксибензен и нитраты состоит в использовании резорцина как источника углерода в процессе денитрификации. Обсуждены условия, необходимые для очистки сточных вод, происходящих из вышеуказанного завода, для чего были использованы существующие установки.