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BIOCHEMICAL OXIDATION OF MIXTURE OF SULPHIDES AND SULPHITES BY ACTIVATED SLUDGE

The acclimated activated sludge is able to oxidize sulphides, sulphites, thiosulphates, tetrathionates, and elemental sulphur to sulphates and tetrathionates. A part of the sulphur substrate (9%) is accumulated in the cells of activated sludge organisms. Activated sludge process is inhibited at the concentration of sulphides and sulphites exceeding 75 g S/m^3 and 60 g S/m^3, respectively. Activated sludge removes also efficiently COD and TOC. A conventional aeration of wastewater containing sulphur compounds gives substantially lower treatment effects.

1. INTRODUCTION

Oxidation of sulphur compounds occurs in the presence of heterotrophic organisms growing in the activated sludge. The heterotrophs have the ability to transform elemental sulphur, sulphides, sulphites, thiosulphates, and tetrathionates into oxidized forms. The oxidation reactions conducted by heterotrophic bacteria are usually markedly slower and less effective than those conducted by autotrophs [3, 7]. However, because of the insufficient number of sulphur bacteria both in natural waters and in the activated sludge, heterotrophic organisms prevail in the oxidation of sulphur compounds dissolved in water.

Sulphides and sulphites present in the wastewater have a disadvantageous influence on the mixed populations of microorganisms conducting the processes. Two fundamental factors account for the toxicity of the reduced sulphur compounds — a very high dichromate COD (which affects the pollution level and deteriorates aerobic conditions in the activated sludge tank) and pH considerably different from 7.0 [8].

Another mechanism governing the action of reduced sulphur compounds results from the influence of mineral salts on the protoplasm and metabolism of cells. They are responsible for the structural changes that occur in the external layer of the protoplasm, thus contributing to the decrease of turgor or condensation of the cell. This leads to a loss of some metabolites or to an inhibition of their penetration into the cell. Such a distur-

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bance in metabolism may bring about the destruction of the cell [6]. Besides, hydrogen sulphide easily reacts with the prosthetic group of proteins (inter alia with oxidizing enzymes) decreasing the physiological activity of many enzymes [1].

Experiments performed under dynamic conditions have revealed what part of sulphur compounds present in the wastewater can be oxidized without disturbing the biological balance of the system [1, 5]. AULENBACH and HEUKELEKIAN [1] have reported that with a continuous dosing the efficiency of the wastewater treatment process is not affected by sulphides concentrations up to 25 g S/m³, and that at the concentration of 50 g S/m³ they may be tolerated no longer than during one week. Toleration of sulphites by the microorganisms was markedly better. The biomass was able to oxidize these compounds at concentrations between 50 and 100 g S/m³.

But as soon as the activated sludge process starts, the oxidation of sulphides and sulphites, the mixture of sulphides, sulphites, elemental sulphur, thiosulphates, tetrathionates, and sulphates is the product of the process. In the available literature there are scarce references on biochemical oxidation of this combination of sulphur compounds.

2. MATERIALS AND METHODS

The experimental works have been conducted for combined wastewaters which consisted of synthetic municipal sewage (the source of nutrients) and of synthetic sulphuric-phenolic wastewater imitating pyrometallurgical scrubbing wastewaters. The composition of the mixture is characterized in tab. 1.

Table 1

Composition of the synthetic wastewater applied in the experiments

Skład ścieków stosowanych w doświadczeniach

Synthetic municipal sewage, g/m^3		Synthetic industrial sulphuric-phenolic wastewater	
Peptone	320	Sodium sulphide	500 $g\ S/m^3$
Broth	200	Sodium sulphite	400 $g\ S/m^3$
NaCl	70	Sodium sulphate	334 $g\ S/m^3$
NH_4Cl	60	Phenol	500 g/m^3
KH_2PO_4	20		
K_2HPO_4	50		
$NaHCO_3$	10		
$MgSO_4$	2		

The aeration and biodegradation study was carried out under laboratory flow-through conditions. Wastewater was supplied to the aeration of the completely mixed tank whose effective volume was equal to 13 dm³ (fig. 1).

2.1. AERATION

To determine the effect of chemical oxidation on the transformation of sulphur compounds during aeration, the experimental runs were conducted using the mixture of synthetic sewage containing 5%, 10%, 15%, and 20% of synthetic sulphuric-phenolic wastewater and applying the aeration at the same parameters as in the biodegradation study (see below). To prevent bacterial growth, the aeration tank was washed with 5% formalin solution, every time before experiment started. The aeration process was conducted for 12 hrs, and the experiments were repeated 3 times.

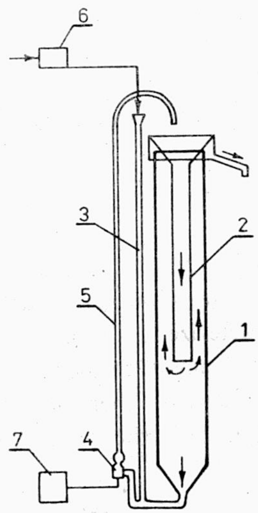

Fig. 1. Laboratory completely mixed activated sludge unit

1 – cylindrical vessel, *2* – central pipe, *3* – wastewater inflow, *4* – ejector, *5* – delivery pipe, *6* – peristaltic pump, *7* – air compressor

Rys. 1. Urządzenie strumienicowe do ciągłego napowietrzania osadu czynnego

1 – zbiornik cylindryczny, *2* – rura centralna, *3* – dopływ ścieków, *4* – strumienica, *5* – rurka doprowadzająca ścieki, *6* – pompka perystaltyczna, *7* – sprężarka

2.2. BIODEGRADATION

The biomass employed in the biodegradation study was taken from the municipal sewage treatment plant in which mixture of municipal and industrial sewage had been treated.

The acclimation of activated sludge to the synthetic municipal sewage was carried out by continuous feeding of the reactor over a period of 10 days. The acclimation of the biomass to the synthetic industrial wastewater containing sulphides, sulphites, and sulphates at concentrations of 5.0 g S/m^3, 4 g S/m^3, and 3.34 g S/m^3, respectively, took also 10 days. The activated sludge acclimated to the biodegradation of sulphuric and phenolic compounds was fed successively with 5%, 10%, 15%, and 20% mixtures of the model wastewaters. That means that the respective doses of sulphides, sulphites, and sulphates increased from 25 to 100 g S/m^3, from 20 to 80 g S/m^3, and from 16.7 to 66.8 g S/m^3 in the consecutive runs. The process parameters were the following: sludge loading of 0.3 (g O_2 BOD_5)/(g MLSS), flow rate of 0.12 dm^3/h, aeration time of 10 hrs, the biomass content in the tank of 3.0 g MLSS/dm^3, pH from 7.0 to 7.4, dissolved oxygen of 2.0 g O_2/m^3, and temperature of 20°C. The experimental run for every separate concentration lasted 2 weeks.

To avoid some analytical problems encountered in the determination of the mixture of inorganic sulphur compounds, each of them was determined separately applying methods described in [4].

3. RESULTS AND DISCUSSION

3.1. AERATION

The effluent from the aeration tank was turbid and contained sulphides, sulphites, thiosulphates, elemental sulphur, tetrathionates, and sulphates. The average composition of the aerated liquor is characterized in tab. 2.

Tab. 3 gives the data on the efficiency of the aeration process with no activated sludge. In this case the BOD_5 after aeration was higher than that in the inflow, probably due to the increased concentration of sulphites in the effluent, which continued to exert the oxygen demand.

As can be seen from tabs. 2 and 3, the percentage of oxidized sulphides and sulphites decreases with the increasing concentrations of sulphur compounds. The degree of oxidation of the reaction products also decreases as well as the percentage of sulphates in the oxidation product; the concentrations of thiosulphates, elemental sulphur, and tetrathionates increase.

Table 2

Variations in the composition of the model wastewater during aeration with no activated sludge

Zmiany w składzie ścieków modelowych podczas napowietrzania bez użycia osadu czynnego

Industrial wastewater ratio in model wastewater %	Average effluent concentrations g S/m^3					
	S^{2-}	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$	S°	$S_4O_6^{2-}$
5	5.2	12.6	19.2	18.0	4.8	2.2
10	30.0	37.5	50.2	11.3	1.9	3.3
15	39.8	55.7	57.5	18.6	2.9	3.3
20	53.3	78.3	69.2	24.9	7.8	11.8

Table 3

Efficiency of the aeration process with no activated sludge

Wydajność napowietrzania bez użycia osadu czynnego

Industrial wastewater ratio in model wastewater %	Removal %		Concentration in the oxidation product	Variation in comparison with the inflow values %		
	S^{2-}	SO_3^{2-}	% SO_4^{2-}	Permanganate COD	Dichromate COD	BOD_5
5	78.5	37.2	5.5	−10.1	−5.7	+7.0
10	40.0	5.8	18.7	−9.1	−4.8	+7.1
15	46.7	6.2	5.5	−8.3	−4.1	+7.3
20	46.7	2.7	1.3	−8.0	−4.0	+7.0

3.2. BIODEGRADATION

After 4 days of aeration, the biodegradation of 5% model wastewater reached a certain point (fig. 2) beyond which the effluent was no longer turbid, sulphides and elemental sulphur concentrations approached 0, whereas the content of sulphites, thiosulphates and tetrathionates continued to decrease. On the contrary, the concentration of sulphates (the main reaction product) increased rapidly. At that stage of biodegradation, bio-

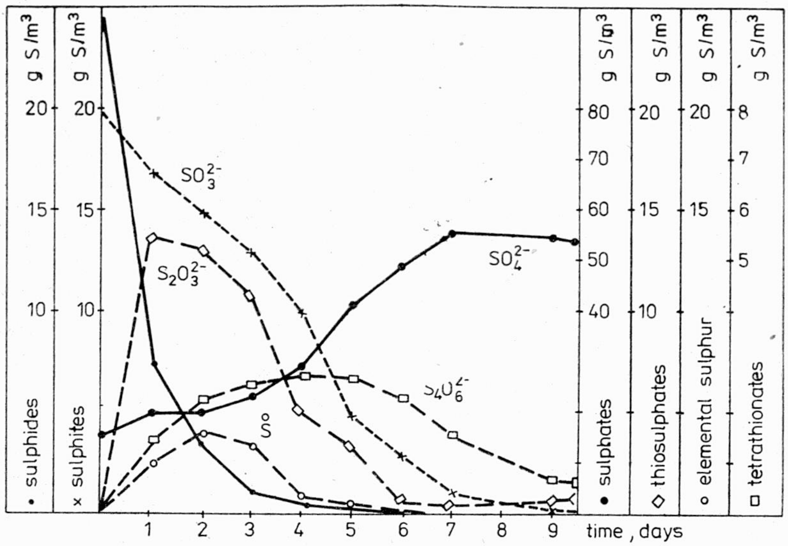

Fig. 2. Transformation of sulphur compounds during biochemical oxidation in activated sludge process (model wastewater containing 5% of industrial sulphuric-phenolic wastewater)

Rys. 2. Przemiany związków siarki w wyniku biochemicznego utleniania w osadzie czynnym (ścieki modelowe o stężeniu 5%)

chemical oxidation of sulphides and sulphites followed a different dynamics. Concentration of sulphides in the effluent was close to 0, whereas that of sulphites decreased gradually, these compounds being completely removed on the 7-th day of aeration. The persistency of this compound over such a long period of time can be due to the extended acclimation time of microorganisms [1, 5]. It may also be attributed to the nature of the chemical reactions that occur in the solution. At the initial stage of the process, sulphides are oxidized to sulphites, but the oxidation of sulphites to sulphates being inhibited by phenol, sulphides, and sulphates [2, 4] yields poor removal of sulphites (tab. 3).

From the comparison of sulphites concentrations in the effluents from the aeration process and the activated sludge process (tabs. 2 and 4), it follows that the biochemical oxidation of these compounds was not inhibited.

The dynamics of sulphur conversion in the dosing process for 10% and 15% model wastewaters did not differ from that for 5% model wastewater (fig. 2).

Tab. 4 gives the average concentrations of sulphur compounds resulting from the increasing concentration of sulphur substrates in the inflow.

Table 4

Biodegradation of sulphur compounds in the activated sludge process

Biodegradacja związków siarki w procesie osadu czynnego

Industrial wastewater ratio in model wastewater %	Average effluent concentrations, g S/m³					
	S^{2-}	SO_3^{2-}	SO_4^{2-}	$S_2O_4^{2-}$	S°	$S_4O_6^{2-}$
5	0.6	8.1	39.6	4.9	1.3	2.1
10	0.1	1.9	104.3	1.4	0.1	1.3
15	0.2	1.1	153.5	4.2	0.4	1.8
20	0.8	5.4	166.0	27.6	1.8	8.0

Table 5

Efficiency of the activated sludge process

Efektywność procesu osadu czynnego

Industrial wastewater ratio in model wastewater %	Average removal, %				Percentage of sulphate in the oxidation product
	Permanganate COD	Dichromate COD	BOD_5	TOC	
5	77.0	74.5	81.3	80.6	51.0
10	89.1	84.8	90.2	98.9	78.8
15	88.4	84.1	95.3	78,9	76.6
20	61.3	57.6	76.3	60.4	55.1

From tabs. 4 and 5 it follows that the highest removals of sulphides and sulphites and the best treatment effects were obtained for 10% and 15% model wastewaters. At these concentrations the percentage of sulphates in the effluent was the highest, whereas that of thiosulphates, elemental sulphur, and tetrathionates was the lowest.

As shown in fig. 3, the biooxidation of sulphides and sulphites in the activated sludge process was almost complete for 10% and 15% model wastewaters at the retention time of 3 days. The concentration of sulphates (which are the main product) increased proportionally to the aeration time to reach an almost constant value after several days.

Biodegradation proceded in a different way when 20% model wastewater was trea-

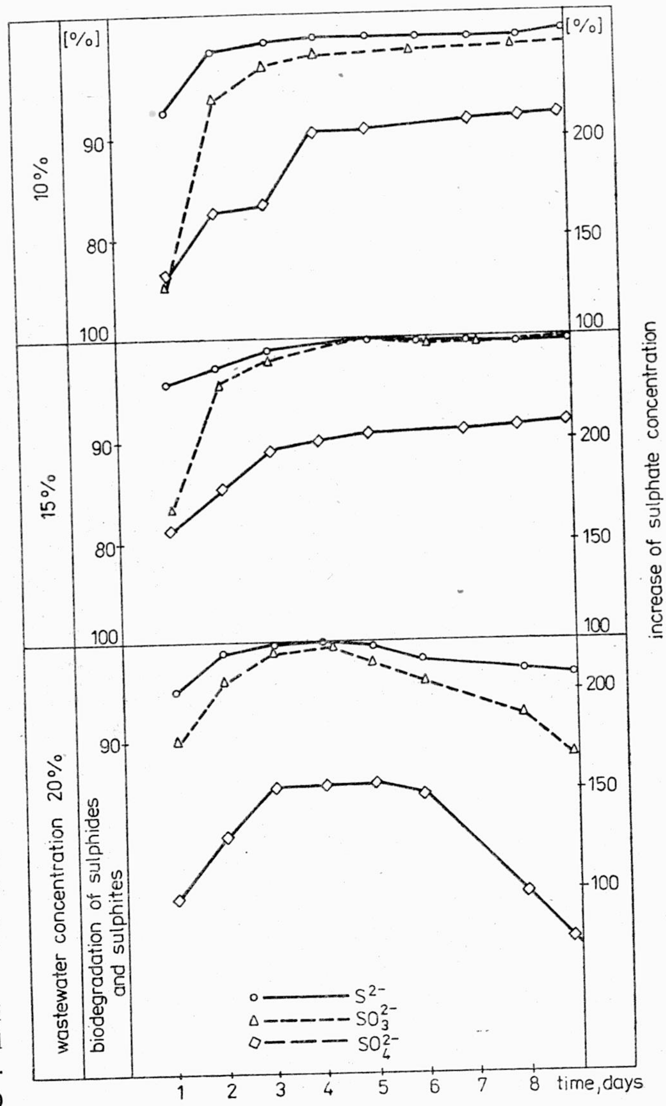

Fig. 3. Concentration of sulphur compounds in the activated sludge process vs. time of aeration (10%, 15% and 20% mixed model wastewaters)

Rys. 3. Stężenie związków siarki w osadzie czynnym zależnie od czasu napowietrzania (ścieki modelowe o stężeniu 10%, 15% i 20%)

ted. Sulphides and sulphites at concentrations exceeding 75 g S/m^3 and 60 g S/m^3, respectively, inhibited biomass growth, this inhibition being generally attributed to the toxic action of sulphides [5]. The activated sludge after 4 days of the process duration was deteriorated and finally destroyed. Thus, the concentrations of sulphites, thiosulphates, elemental sulphur, and tetrathionates in the effluent increased rapidly and the concentration of sulphates decreased (fig. 4). The average removals of permanganate and dichromate COD, TOC, and BOD_5 after 10 days were the poorest (tab. 5). Relatively high removals of sulphites and sulphides, even at the biomass destruction point may be attributed to the simultaneous chemical oxidation (tab. 2).

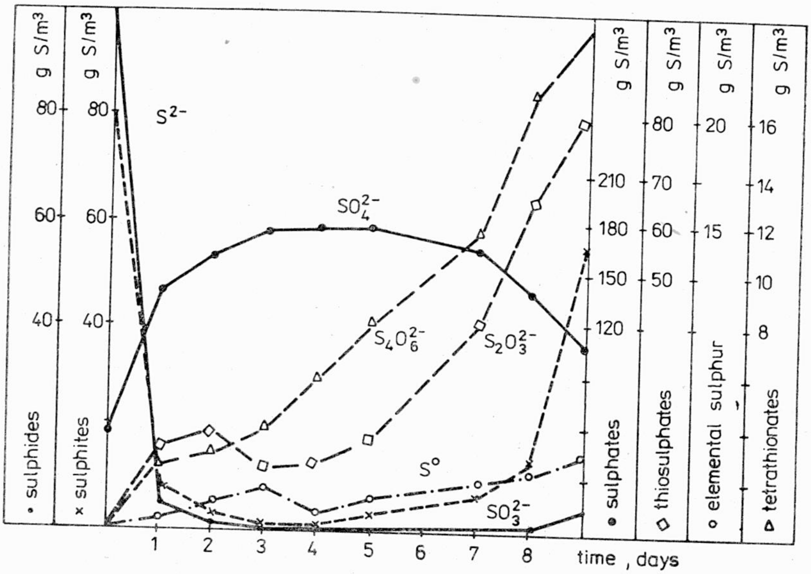

Fig. 4. Transformation of sulphur compounds during biochemical oxidation in activated sludge process (20% mixed model wastewaters)

Rys. 4. Przemiany związków siarki w wyniku biochemicznego utleniania w osadzie czynnym (ścieki modelowe o stężeniu 20%)

On the 5-th day the settling characteristics of the sludge deteriorated (tab. 6) in such a degree that the rate of sludge losses in the effluent exceeded its reproductibility.

Amount of sulphur accumulated by the microorganisms was established basing on sulphur balance and difference in ULSS and MLVSS. It has been found that the accumulation of sulphur did not depend on the concentrations of the reduced sulphur compounds and was equal to about 9% of the influent sulphur.

There was a strong relationship between raw wastewater chemical characteristics and the resulting changes in the biocoenosis of the activated sludge. Introduction of sulphur brings a rapid growth of filamentous bacteria (including sulphur bacteria). On the

Table 6

Sludge volume index at the increasing concentrations of sulphur substrates

Wskaźnik objętościowy osadu przy zwiększonych stężeniach substratów siarkowych

Industrial wastewater ratio in model wastewater %	Sludge volume index (avg.) cm^3/g MLSS
5	103.2
10	203.0
15	196.8
20	365.3

5-th day of the acclimation, i.e. as soon as the number of filamentous bacteria, *Beggiatoa* sp., in the activated sludge increased rapidly, the effluent from the aeration tank lost its turbidity. The activated sludge consisted of lumpy aggregates and its colour varied from dark to light brown. In the course of the process the flocks have lost their form and turned into a filamentous mass in which *Beggiatoa* sp., *Zoophagus insidians* and *Lemonrena agatica* prevailed.

4. CONCLUSIONS

Activated sludge can be acclimatized to moderately high concentrations of sulphides and sulphites, provided that their concentrations do not act on a shock basis.

An intensive mix combined with an effective aeration method give good removals of reduced sulphur compounds contained in the wastewater under treatment.

From authors' experiments if follows the survival of the activated sludge microorganisms was twice as long as that reported by other authors [1, 5], despite higher sulphides concentrations.

The microorganisms present in the acclimated activated sludge are able to oxidize sulphides, sulphites, thiosulphates, tetrathionates, and elemental sulphur. The acclimatization of the activated sludge biomass is accompanied by an intensive growth of filamentous sulphur bacteria.

Biochemical oxidation of the reduced sulphur substrates by activated sludge yields sulphates (51%–79%) and tetrathionates (about 3%). Some part of the substrates (sulphides and sulphites) is not completely oxidized. On the average 9% of the sulphur substrates are accumulated in a colloidal form by sulphur bacteria in or outside the cells.

Concentrations of sulphides and sulphites exceeding 75 g S/m^3 and 60 g S/m^3, respectively, exert an adverse effect on the biocoenosis of the activated sludge. They result in the destruction of many species of *Bacteriophyta*, *Protozoa*, *Rhizopoda*, and *Ciliata* and stimulate filamentous growth of sulphur bacteria and fungi. Consequently, sludge volume index increases rapidly and the biomass is washed out from the activated sludge system.

The treatment of wastewaters containing reduced sulphur compounds by the biooxidation method is more efficient than by aeration process carried out under the same conditions.

Chemical oxidation provides the removal of 53% of sulphides and 78% of sulphites; activated sludge process yields the removal efficiencies exceeding 95%. Sulphates which are a desirable product of aeration and the activated sludge processes reaction accounted for about 19% and about 79% of totals sulphur present in the effluent, respectively.

The compounds exerting an inhibitory effect on the chemical oxidation process (phenols) have no influence on the course of biooxidation process.

Permanganate and dichromate COD removal efficiencies of the aeration process are very low; they amount to 10% and 5%, respectively. Activated sludge process yields 89% removal of permanganate COD, 85% that of dichromate COD, 95% of BOD_5, and 99% of TOC.

Aeration may be applied as a pretreatment unit operation to decrease the concentrations of sulphides and sulphites to the levels below 75 g S/m^3 and 60 g S/m^3, respectively, and thus to enable their further biochemical oxidation by activated sludge.

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BIOCHEMICZNE UTLENIANIE OSADEM CZYNNYM MIESZANINY SIARCZKÓW I SIARCZYNÓW

Adaptowany osad czynny utlenia siarczki, siarczyny, tiosiarczany i tetrioniany. Część związków siarki (~9%) jest akumulowana w komórkach organizmów osadu. Przy stężeniach siarczków i siarczynów powyżej 75 i 60 g S/m^3 proces osadu czynnego ulega załamaniu. Osad czynny obniża również skutecznie ChZT i TOC ścieków. Zwykłe chemiczne utlenianie (przy napowietrzaniu ścieków bez udziału osadu czynnego) daje znacznie gorsze wyniki.

OXIDATION VON SULFIDEN UND SULFITEN IM BELEBTSCHLAMMVERFAHREN

Ein entsprechend eingefahrener Belebtschlamm oxidiert Sulfide, Sulfite, Thiosulfate und Tetrathionate. Die Mikroorganismen bauen einen Teil des oxidierten Schwefels (etwa 9%) in den Zellen ein. Kommen Konzentrationen von mehr als 75 g S/m³ in Form von Sulfiden und mehr als 60 g S/m³ in Form von Sulfiten vor, kommt es zu einem Abbruch des Reinigungsprozesses.

Im Belebtschlammverfahren baut sich auch der CSB und der TOC gut ab. Chemische Oxidation durch einfache Belüftung (d.h. ohne Belebtschlamm) ergibt wesentlich geringere Effekte.

БИОЛОГИЧЕСКОЕ ОКИСЛЕНИЕ АКТИВНЫМ ИЛОМ СМЕСИ СУЛЬФИДОВ И СУЛЬФИТОВ

Алаптированный активный ил окисляет сульфиды, сульфиты, тиосульфаты и тетратионаты. Часть соединений серы (~9%) аккумулируется в клетках организмов ила. При концентрациях сульфидов и сульфитов выше 75 и 60 г S/м³ соответственно процесс активного ила падает.

Активный ил успешно снижает также ХПК и ТОС сточных вод. Обычное химическое окисление (при аэрации сточных вод без участия активного ила) даёт значительно низшие эффекты.