

JAN SIKORA*

SULPHITE WASTES TREATMENT WITH ACTIVATED SLUDGE AERATED WITH PURE OXYGEN

This paper presents results of the investigations on organics removal kinetics in an aeration basin at high concentrations of dissolved oxygen. The research was carried out in two laboratory systems. In the first system high-purity oxygen was used for aeration, whereas air was used in the second. The comparison of obtained results has shown that the improvement of aerobic conditions during the purification of sulphite wastes caused an increase in the biochemical conversion rate. In these improved aerobic conditions oxidation of some contaminant groups resistant to biodegradation at low concentration of dissolved oxygen in the aeration basin was more complete.

1. INTRODUCTION

Optimum conditions for an activated sludge process are among other created by adequate supply of oxygen for biodegradation of carbonaceous and nitrogenous compounds and for endogeneous respiration [3]. Oxygen diffusion into the bacterial floc depends on the concentration of dissolved oxygen (DO) and its rate of solution in the wastewaters.

For the single microorganism the required concentration of the oxygen fully dissolved should be minimum $0.1 \text{ mg O}_2/\text{dm}^3$ [10]. Since microorganisms form zoogical clusters (flocs) the concentration of the DO has to exceed this value in order to assure aerobic conditions inside the floc. Research proves that the minimum oxygen concentration indispensable for proper functioning of activated sludge is over $2 \text{ mg O}_2/\text{dm}^3$ (for conventional systems) [7]. For completely mixed systems this quantity is equal to $0.5 \text{ mg}/\text{dm}^3$ [13]. It is feasible that the greater oxygen concentrations, the higher are the process rates. It may partly be due to the total eradication of tiny activated flocs in anaerobic chambers, and partly to the domination of other microbial species having a greater activity than the species dominant at lower oxygen concentrations. Thus, oxygen conditions influence directly the efficiency of oxidation process. In the conventional sewage treatment of the activated sludge, DO concentrations higher than $2 \text{ mg O}_2/\text{dm}^3$ are not used for economical reasons, since greater oxygen concentrations require larger oxygen inputs at lower efficiencies [9]. In the activated sewage treatment better oxygen conditions can be achieved by applying

* Institute of Environment Protection Engineering, Silesian Technical University, Gliwice, Poland

pure oxygen. The concentration of the oxygen dissolved in the aerated chamber ranges normally from 6 to 10 mg O_2/dm^3 [1]. The possibility that these conditions may increase biochemical changes was verified for sulphite wastewater containing considerable amounts of poorly biodegradable substances. In such wastewater the sludge activity and treatment rate are lower. The eventual process efficiency improvement for these wastes would be of considerable importance. The purpose of the paper was to investigate the rates of sulphite wastewater treatment by the activated sludge at higher concentrations of DO in the aeration tank.

2. METHODS

The experimental part of the work consisted of comparative studies on sulphite wastes treatment in two independent model systems. The activated sludge air system consisted of two aeration tanks combined with secondary settling tank [12]. The working volume of each tank is 12.5 dm^3 , and that of secondary settling tank — 5.5 dm^3 . The air was introduced by means of the surface rotor.

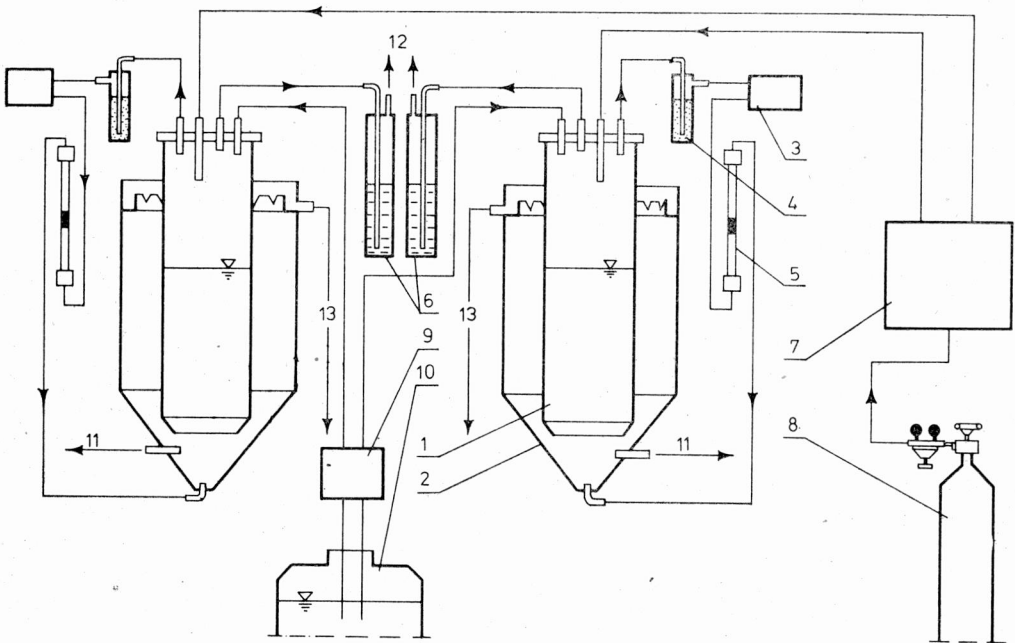


Fig. 1. The model system for investigation of sulphite wastes treatment by the oxygen activated sludge
 1 — aeration tank, 2 — secondary settling tank, 3 — suction-force pump, 4 — glass-wool washer, 5 — rotameter, 6 — overpressure control, 7 — oxygen flow governor, 8 — oxygen cylinder, 9 — raw wastes pump, 10 — raw wastes tank, 11 — sludge evacuation, 12 — release, 13 — treated effluent

Rys. 1. Układ modelowy do badań procesu oczyszczania ścieków metodą osadu czynnego z zastosowaniem tlenu

1 — komora napowietrzania, 2 — osadnik wtórny, 3 — pompka ssąco-tłocząca, 4 — płuczka wypełniona watą szklaną, 5 — rotometr, 6 — regulacja naciśnieniowa, 7 — regulator przepływu tlenu, 8 — butla z tlenem sprężonym, 9 — pompa ścieków surowych, 10 — zbiornik ścieków surowych, 11 — odprowadzenie osadu, 12 — wyjście, 13 — ścieki oczyszczone

The pure oxygen system consisted of two aeration tanks in form of cylinders air tight, each of 2.5 dm³ volume (fig. 1). The space around the aerated chamber and the outer walls of the installation formed the secondary settling tank of 5 dm³ volume with an overflow weir at the tank perimeter. Such a construction and the great volume of the secondary settling tank, in proportion to the aerated chamber volume, assured a proper operation even at considerable hydraulic loads. The activated sludge recirculation was performed over the perimeter clearance between the cone ending of the aerated chamber and the secondary settling tank walls. The suction-force pump in the closed cycle was supplying oxygen into the sludge. Considering the great humidity of the sucked gas, the laboratory washer filled with glass-wool was installed on the suction conduit. The measurements of the gas flow rate were performed by means of a rotameter installed at the pressure outlet. From the gas cylinder oxygen was fed to the top part of aerated chamber, and its flow was controlled by means of the governor T-101. In the aerated chamber a constant overpressure of 0.1 m H₂O was maintained. The oxygen concentration in the waste gas and tonnage oxygen purity were controlled by automatic oxygen analyser Permolit 2. The model systems worked continuously and were fed with sulphite wastes with COD and BOD concentrations of about 1 500 mg O₂/dm³ and 400 mg O₂/dm³, respectively. The raw wastes were prepared from waste sulphite liquor from a paper-mill (table). The pH value was then corrected to 7.5-8.5. The lacking nutrients in form of NH₄Cl and Na₂HPO₄ were added in the proportion BOD:N:P as 100:5:1 [11].

Table

Characteristics of pulp and paper industry sulphite wastes
 Charakterystyki siarczynowych ścieków pocelulozowych

Determination	Unit	Value
Specific gravity	g/dm ³	1083
Solids residue	g/dm ³	217.0
Volatile solids residue	g/dm ³	152.0
SO ₂ -bound	g/dm ³	6.10
SO ₂ -free	g/dm ³	4.01
Reducing sugars	g/dm ³	32.60
Resinous acids	g/dm ³	1.58
Lignin compounds	g/dm ³	98.40
COD	g/dm ³	359.10

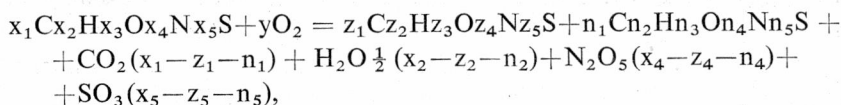
Technological investigations were aimed at evaluating the treatment efficiency at the sludge loading (food to microorganisms — F/M) of 0.2-0.8 g BOD/g MLVSS·day for air and 0.2-1.4 g bod/g MLVSS·day for oxygen. The change of F/M was attained by changing gradually the sludge age in aerated chambers at constant average concentration of activated sludge suspension amounting to 6.3 g/dm³ for air system and to 3.4 g/dm³

for oxygen system. During the investigations of COD, BOD, lignosulphonic acids [8], pH, DO, MLVSS (mixed liquor volatile suspended solids) and SVI (the sludge volume index) have been determined in raw and treated wastewaters.

To determine the kinetics of organic compounds removal, the multiple regression equation was used with constants determined by the least squares method [4].

3. DISCUSSION

The stoichiometric equation describes in a simplified manner the aerobic degradation of organics [2]:



where:

- $x_1C_{x_2}H_{x_3}O_{x_4}N_{x_5}S$ — the generalized organics formula,
- yO_2 — the oxygen requirement for biooxidation of organics,
- $z_1C_{z_2}H_{z_3}O_{z_4}N_{z_5}S$ — excess sludge,
- $n_1C_{n_2}H_{n_3}O_{n_4}N_{n_5}S$ — the intermediate oxidation products,
- CO_2, H_2O, N_2O_5, SO_3 — the final mineral products,
- x, y, z, n — the molar numbers of components.

According to this equation, the removed organic compounds are partly assimilated as the excess sludge: the remaining part undergoes direct biooxidation to intermediate oxidation products and final mineral products. The organics are usually expressed in BOD or COD where COD represents total organic compounds contents $x_1C_{x_2}H_{x_3}O_{x_4}N_{x_5}S$, and BOD represents biodegradable part $x_1C_{x_2}H_{x_3}O_{x_4}N_{x_5}S - n_1C_{n_2}H_{n_3}O_{n_4}N_{n_5}S$. Thus biodegradability may be defined as COD to BOD ratio. For waste treated biologically the same value may be used as intermediate index of pollutants removal. The results of experiments confirm these conclusions.

The mean value of the COD/BOD ratio calculated for raw wastes amounting to 3.90 when compared with that for municipal wastes (1.5) proves that the amount of non-biodegradable substances in the investigated sulphite wastes is still considerable. With the increasing removal efficiencies the ratio of COD to BOD increased exponentially (fig. 2). The values of this ratio for oxygen system being also higher indicate that the biochemical changes are deeper than in the air system.

The sulphite removals during biological wastes treatment may be described by kinetic equations. The kinetics of the waste sulphite sewage treatment was interpreted by using the ECKENFELDER equation [5]. The preconditions of this equation (fully mixed system, raw wastes BOD < 500 mg O₂/dm³) were fulfilled during the experiments. The calculated reaction rate coefficients k show a considerable difference in BOD removal velocity in both

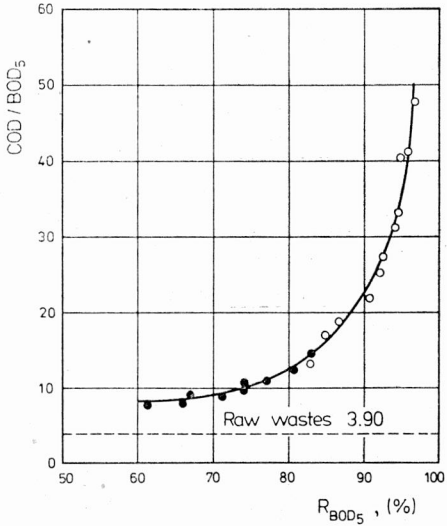


Fig. 2. COD/BOD ratio versus efficiency of sulphite wastes treatment

Rys. 2. Zależność ilorazu ChZT do BZT₅ od stopnia oczyszczenia ścieków posiarzynowych

technological systems. For air system the constant k is 0.00594 (fig. 3), that is four times less than in oxygen system where $k = 0.0254$ (fig. 4). Some differences may be observed also in theoretical limit of organics removal characterized by the amount of residual refractory organics, expressed in BOD which for air is 19.5 mg O₂/dm³ and 3.4 mg O₂/dm³ for oxygen systems.

The same interpretation was used for evaluating the COD removal kinetics. Also in case of oxygen system higher DO concentrations were accompanied by removal rates

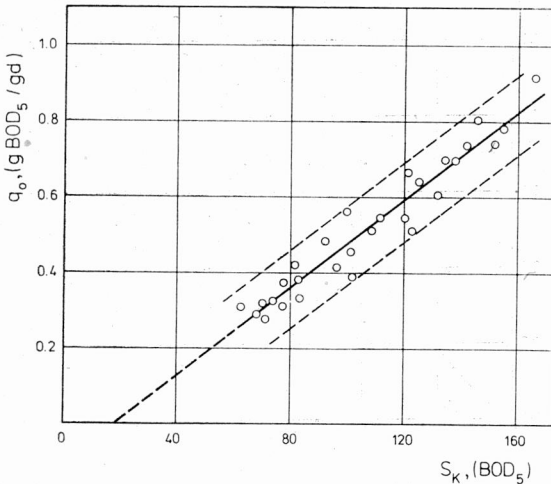


Fig. 3. BOD removal from sulphite wastes in the air system

Rys. 3. Przebieg procesu usuwania zanieczyszczeń wyrażonych jako BZT₅ ze ścieków posiarzynowych w układzie powietrznym

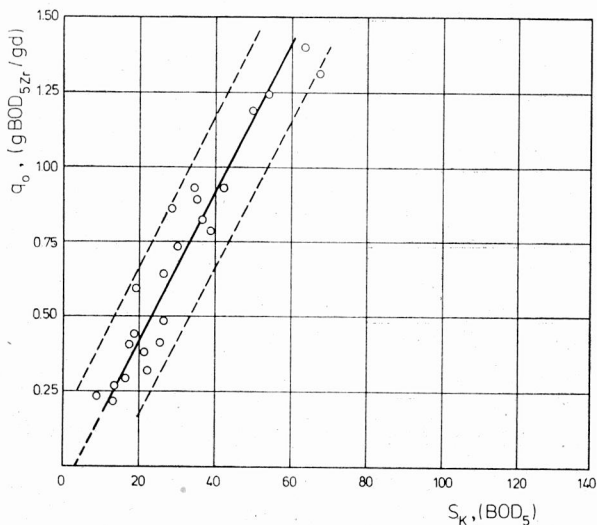


Fig. 4. BOD removal from sulphite wastes in the oxygen system

Rys. 4. Przebieg procesu usuwania zanieczyszczeń wyrażonych jako BZT₅ ze ścieków posiarczykowych w układzie tlenowym

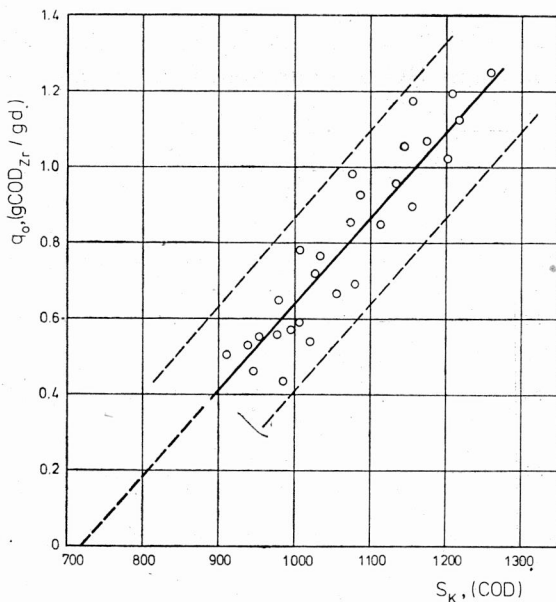


Fig. 5. COD removal from sulphite wastes in the air system

Rys. 5. Przebieg procesu usuwania zanieczyszczeń wyrażonych jako ChZT ze ścieków posiarczykowych w układzie powietrznym

greater than in air system. In these conditions the reaction rates k are 0.00227 for air (fig. 5) and 0.00511 for oxygen (fig. 6). It can be observed that the calculated velocity reactions for COD are much lower than for BOD. It means, the treated waste contains considerable amount of non-biodegradable (or only partly biodegradable) compounds. For COD the amount of these compounds is 589 mg O₂/dm³ in the oxygen system and 722 mg O₂/dm³

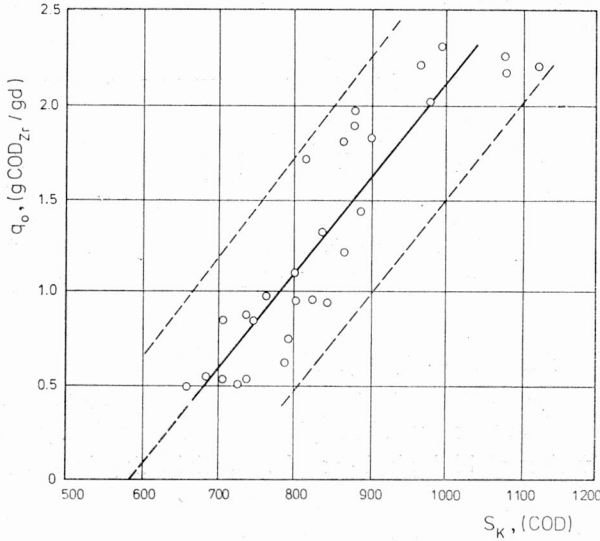


Fig. 6. COD removal from sulphite wastes in the oxygen system

Rys. 6. Przebieg procesu usuwania zanieczyszczeń wyrażonych jako ChZT ze ścieków posiarzynowych w układzie tlenowym

in the air system. Taking the mean COD value in raw wastes to be 1 546 mg O₂/dm³, the fraction of non-biodegradable substances is 38.1% of the initial quantity for oxygen and 46.7% for air systems. In sulphite wastes lignosulphonic acids constitute the prevailing part of non-biodegradable organics. From the relationship between the lignosulphonic acids removal and the activated sludge load it follows that the removal of the former compounds was not very efficient as it amounted to about 13% for air system and to 28% for the oxygen system (fig. 7). From this figure it follows also that sorption on the activated sludge flocs is the most important factor in removal of lignosulphonic acids. The mean concentration of the dissolved oxygen in the aeration tanks during the experiments was 1.5-3.7 mg O₂/dm³ — for the air system and 6.9-8.6 mg O₂/dm³ — for the oxygen system. The microscopic observations of activated sludge showed that the floc sizes in both technological systems were 150-400 μ, being less numerous and more fuzzed in the air system. It has been also confirmed by lower values of the sludge volume index stated in the oxygen system, though many observations indicate that for greater oxygen input the sludge sedi-

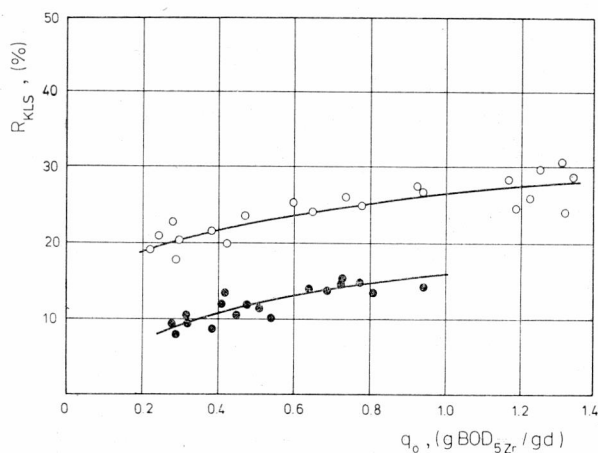


Fig. 7. Removal of lignosulphonic acids versus the activated sludge load

Rys. 7. Zależność pomiędzy stopniem usunięcia kwasów lignosulfonowych a obciążeniem osadu czynnego

mentation properties deteriorate [6, 14]. Thus, high DO concentrations in the aeration tank result in considerable advantages, manifesting in increasing rate of organics degradation, and extent of pollutant removal. This phenomenon is probably due to oxygen supply allowing a full activation of biological complex participating in the waste treatment.

4. CONCLUSIONS

1. It has been confirmed that the increasing concentrations of oxygen dissolved in aeration tank during the treatment of sulphite wastes increase the oxidation of some pollutants resistant to biodegradation in conventional conditions.

2. The improvement in oxygen supply increases the removal of lignosulphonic acids. The removal of these compounds — apart from biological changes — is substantially attributed to sorption process.

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ROZKŁAD ZANIECZYSZCZEŃ W CZASIE OCZYSZCZANIA ŚCIEKÓW POSIARCZYNOWYCH METODĄ OSADU CZYNNEGO Z ZASTOSOWANIEM TLENU

Spośród wielu czynników wpływających na kinetykę zachodzących przemian w czasie oczyszczania ścieków metodą osadu czynnego duże znaczenie mają warunki tlenowe. Z przeprowadzonych badań wynika, że najniższe stężenie tlenu niezbędne dla funkcjonowania osadu czynnego wynosi od 0,5 do 2,0 mg O_2/dm^3 w zależności od stosowanego systemu napowietrzającego. Nie można jednak wykluczyć możliwości zwiększenia szybkości przemian biochemicznych przy wyższych stężeniach tlenu, a szczególnie w przypadku zastosowania czystego tlenu do natleniania osadu czynnego. Celem przeprowadzonej pracy była ocena zdolności oraz szybkości rozkładu zanieczyszczeń w czasie oczyszczania ścieków posiarczynowych metodą osadu czynnego w warunkach dużej zawartości tlenu rozpuszczonego w komorze napowietrzania.

Doświadczalna część pracy obejmowała badania porównawcze procesu oczyszczania ścieków posiarczynowych w dwóch niezależnych układach modelowych, w których do napowietrzania osadu czynnego stosowano powietrze i czysty tlen. Uzyskano w ten sposób znaczne zróżnicowanie warunków tlenowych procesu przy stałej turbulencji zawartości komór osadu czynnego. Otrzymane wyniki badań wskazują, że zwiększenie zawartości rozpuszczonego tlenu z 2,6 mg O_2/dm^3 (średnie stężenie tlenu w układzie powietrznym) do 7,7 mg O_2/dm^3 (średnie stężenie tlenu w układzie tlenowym) powoduje prawie 4-krotny wzrost szybkości usuwania zanieczyszczeń oznaczanych jako BZT₅ oraz około 2-krotny wzrost szybkości w przypadku zanieczyszczeń oznaczanych jako ChZT. Równocześnie przy wyższym stężeniu tlenu zmniejsza się ilość teoretycznie nierozkładalnych związków organicznych. Podstawową część nierozkładalnych biochemicznie związków organicznych (w warunkach stosowanej metody oczyszczania) zawartych w ściekach posiarczynowych stanowią kwasy ligninosulfonowe. Usunięcie tych związków, wynoszące 13% w układzie powietrznym, zwiększyło się do 28% w układzie tlenowym. Stwierdzono również, że znaczną rolę w usuwaniu kwasów ligninosulfonowych odgrywają procesy sorpcji na osadzie czynnym.

ДИЕ РЕИНІГУНГ ВОН СУЛФИТАВВÄССЕРН МІТТЕЛС МІТ САУЕРСТОФ БАГАСТЕМ БЕЛЕБТСХЛАММ

Віельсеіт сінд діе Фактoren, діе аүф діе Аbbаукінетік ім Белебтсхламмверфahрен еінвіркен. Ін ерстер Лініе сінд діе Сауерстoфверhälтніссе ім Белебунгсбеккен зү неннен. Еіне Мінедст-Концентратіон вон $0,5 - 2,0 \text{ mg O}_2/\text{dm}^3$ Беккенінхалт вірд стетс — је нaч Белüфтунгсарт — ін дер Фaчлітeратур аңгeфöhрт. Еіне Аbbауеschleunіgunг дер Верунрeінуңен бeі höheren O_2 -Концентратіонен кaнн мaн дaher нічт аusschlіessen, діес умsomehr бeі еінем міт тechnіschen Сауерстoф бeгастem Бeлeбтсхламм.

Діе vorліeңдe Аrбeіт сетзтe сісh зүм Зіel, ден Аbbау вон Сулфітаввässерн саmт Аbbаукінетік бeі höheren Сауерстoфконцентратіонен ім Бeлeбунгсбеккен зү üбeрпрüfen.

Während der Versuche wurden zwei Modellbecken parallel gefahren — das eine mit der konventionellen Luftbelüftung, das andere mit einer Sauerstoffbegasung. Bei identischen Turbulenz- und Strömungsverhältnissen in beiden Becken, waren die O_2 -Konzentrationen grundverschieden. Sie betrug entsprechend 2,6 und 7,7, $\text{mg O}_2/\text{dm}^3$. Der BSB₅- Abbau im Sauerstoffbecken ging demzufolge etwa viermal so schnell vonstatten, der CSB-Abbau nur zweimal so schnell im Vergleich zum Luftbecken. Zu gleicher Zeit sind im Sauerstoffbecken weniger theoretisch nicht abbaubare organische Stoffe nachgewiesen worden. Von den nicht abbaubaren Inhaltsstoffen dieser Abwässer sind die Ligninsulfonsäuren zu nennen. Im Luftbecken wurden diese bis zu 13%, im Sauerstoffbecken bis zu 28% abgebaut. Eine große Rolle scheint hier die Sorption auf den Schlammflocken mitzuspielen.

РАСПРЕДЕЛЕНИЕ ЗАГРЯЗНЕНИЙ ВО ВРЕМЯ ОЧИСТКИ ПОСЛЕСУЛЬФИТНЫХ СТОЧНЫХ ВОД МЕТОДОМ АКТИВНОГО ИЛА С ПРИМЕНЕНИЕМ КИСЛОРОДА

Среди многих факторов, влияющих на кинетику происходящих изменений во время очистки сточных вод методом активного ила большое значение имеют кислородные условия. Из проведенных исследований следует, что самая низкая концентрация кислорода, необходимая для функционирования активного ила, составляет от $0,5$ до $2,0 \text{ mg O}_2/\text{dm}^3$ в зависимости от применяемой аэрирующей системы. Однако нельзя исключить возможности повышения скорости биохимических превращений при более высоких концентрациях кислорода, а в частности, в случае применения чистого кислорода для насыщения активного ила.

Целью проведенной работы была оценка способности, а также скорости распределения загрязнений во время очистки послесульфитных сточных вод методом активного ила при условиях большого содержания растворенного кислорода в аэротенке.

Экспериментальная часть работы охватывала сопоставительные исследования процесса очистки послесульфитных сточных вод в двух независимых модельных системах, в которых для аэрации активного ила применялся воздух и чистый кислород. Таким образом была получена значительная дифференциация кислородных условий процесса при постоянной турбулентности содержания камер активного ила. Полученные результаты исследований показывают, что увеличение содержания растворенного кислорода с $2,6 \text{ mg O}_2/\text{dm}^3$ (средняя концентрация кислорода в воздушной системе) до $7,7 \text{ mg O}_2/\text{dm}^3$ (средняя концентрация кислорода в кислородной системе) вызывает почти четырехкратное повышение скорости удаления загрязнений, обозначаемых как БПК₅, а также приблизительно двукратное повышение скорости в случае загрязнений, обозначаемых как ХПК. Одновременно при более высокой концентрации кислорода уменьшается количество теоретически нерастворяемых органических соединений.

Основную часть биохимически неразлагаемых органических соединений (в условиях применяемого метода очистки), содержащихся в послесульфитных сточных водах, представляют собой лигнисульфоновые кислоты. Удаление этих соединений, составляющее 13% в воздушной системе, увеличилось до 28% в кислородной системе. Отмечено также, что значительную роль в удалении лигнисульфоновых кислот выполняют процессы сорбции на активном иле.