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POSSIBILITIES OF WATER UTILIZATION FOR COOLING PURPOSES AFTER ITS RENOVATION PROCESS

The reclaimed water, when used for cooling purposes, very often makes the cooling process difficult causing, among others, the growth of microbial slimes. In order to inhibit this growth in the industrial cooling cycle, some investigations were performed.

The purposes of the investigations were:

— determination of the effects of 9 biocides on the complex of organisms forming microbial slimes, by the two methods (the TTC-test and manometric method in Warburg apparatus),

— investigation of the microbial slimes in the suitable testing apparatus to determine the variations of organisms at the continuous and batchwise way of biocide introduction,

— introduction of biocide into the industrial cooling cycle to check the eficiency of the latter.

Taking into account both the qualitative composition of the organisms forming the biological slimes and kind of the water used, the Hydrokryl AM was introduced into cooling cycle. From the experiments it followed that this biocide at its concentration equal to 1 mg/dm^3 inhibited the growth of microbes present in water.

1. INTRODUCTION

The direct use of water reclaimed from wastewater (not introduced into a natural water circulation) for municipal purposes is not advisable because of sanitary, hygienic and aesthetic reasons. There are, however, some possibilities for the application of the reclaimed water to industrial purposes, for instance to cooling processes. An example of such utilization are closed cooling cycles in one of the chemical plants in this country.

The plant has two separate, closed cooling systems of 2,000 m^3 and 1,000 m^3 each. The losses arising during refrigeration in fan cooling towers are made-up by industrial wastewaters treated in the biological treatment plant and additionally filled up with river water. The mixed water is subjected to coagulation, liming and filtration and directed to the so-called additional water tank. Due to inevitable perturbations in the wastewater treatment plants as well as to variations of the intaken river water com-

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position the quality of the additional water varies within a wide range. For instance the pH value varied from 5.8 to 7.8, the amounts of nitrogen present in nitrates, nitrites, ammonium, and organic compounds ranged from trace to 20 mg/dm^3, 0.01—0.70 mg/dm^3, 1.80–44.00 mg/dm^3, and 8.0–25.0 mg/dm^3, respectively.

Permanganate consumption and BOD ranged within 35.2 to 105.4 mg/dm^3 and from 8.0 to 76.0 mg 0_2/dm^3. It has been also found that phosphates, sulphates, iron and manganese occurred in amounts respectively ranging from traces to 8.0 mg/dm^3, 112.4 to 267.8 mg/dm^3, 0.2 to 2.0 mg/dm^3 and 0.1 to 1.8 mg/dm^3. The amount of total solids of that water was as high as 3280 to 10280 mg/dm^3, whereas volatile solids amounted from 240 to 3448 mg/dm^3. Phenols also present in water, ranged from 0.2 to 12.0 mg/dm^3. Presence of microbes (table 1) and biogenic substances (nutrients) in water and suitable temperature conditions create serious problems in the operation of cooling cycles.

Table 1

Amounts of microorganisms in additional cooling water
Ilość mikroorganizmów w wodzie chłodniczej dodatkowej

Amounts of microbes in 1 cm^3 of water					
Saprophytic			Aciduric		
min.	max.	average*	min.	max.	average*
1450000	3000000	1860000	200	21000	1800

* Average value calculated from 14 tests

Microbial slimes on the elements of the cooling and contamination of the total system by microbes decrease the efficiency of the cooling process.

The above difficulties in utilization of the purified industrial wastewater can be avoided by introducing biocides to inhibit the excessive growth of microbes. These biocides should be, however, studied before their introduction in order to establish their kind and quantity as well as the appropriate dosage method. These studies were the purpose of the paper presented.

2. PROGRAMME OF INVESTIGATIONS

In order to realize the above purpose of investigation the following programme has been accepted:

— determination of the effects of selected biocides on the complex of organisms forming microbial slimes by two biochemical methods: the TTC-test and manometric method,

— investigation of microbial slimes in suitable testing apparatus to determine the variations of biological slimes using two methods of dosing the selected biocide,

— introduction of biocide into the cooling cycle to check the efficiency of the latter.

3. EXPERIMENTAL

The attempts were made to determine toxic effect of nine selected reagents on a microbial slime grown in an industrial cooling tower. Dehydrogenase activity was measured by the TTC-test method on the microbial slime incubation with 1 dm^3 of the tested biocides for 17 hours. In the experiment different concentrations of reagents were used which were calculated for active substance (table 2). The methods of measurements were based on experiments made by LENHARD [4], WALLENS and ZAHN [8].

Table 2

Reagents used in toxicity examinations according to TTC-test
Preparaty zastosowane w badaniach toksyczności wg testu TTC

Name of reagent	Solution concentration (mg/dm^3)
N-phenylthiourea	5.0, 10.0, 25.0, 50.0
Ferrocid 591	20.0, 40.0, 80.0, 100.0
Hydrokryl AM	2.0, 5.0, 10.0, 25.0
Iodine	0.1, 0.5, 1.0, 2.0
Monuron	5.0, 10.0, 25.0, 50.0
Preventol AS	10.0, 25.0, 50.0, 100.0
Silenal ZB	0.1, 0.5, 1.0, 1.5
Simazyne 50	0.5, 1.0, 2.5, 5.0
Sterinol	0.5, 1.0, 2.0, 3.0

Measurements of respiration processes of organisms, constituting the microbial slimes were further carried-out by a manometric technique, in presence of Hydrokryl AM using the Warburg apparatus. Investigations were performed according to the compulsory principles [1], [7]. A six incubation of the tested biological material was carried out in presence of the six different quantities of biocide, so that its weight ratio to the mass of microbial slimes was equal to 110–22500 : 1,000,000.

Measurements performed in the apparatus for microbial slimes tests (fig. 1) were to determine the changes occurring in organisms forming the microbial slimes due to the striking and continuous action of the reagent. Suitability of the completed apparatus for testing has been checked, i.e. after water flow and the number of experimental culturing plates introduced into the apparatus were established and some comparative investigations on the changes in the activity of organisms in the apparatus and on an industrial cooling system have been performed. The biocide was introduced into the cooling water with which the microbial slimes were sprinkled. To show the changes in the organisms after introducing the Hydrokryl AM a dehydrogenase activity has been measured by the TTC-test [2].

To determine the amount of biocide required to inhibit the growth of microbes present in slimes and in water of the investigated cycle the tests of continuous batching of the reagent

were performed in four series. They consisted in a direct batching of the reagent in form of a solution, by a pumping it from the tank to the pipe of the heated circuit water. To check the amount of the biocide introduced, the measurements of its flow were taken. The separate series of investigations differed in the amount and batching period of the reagent and were carried out under various climatic conditions.

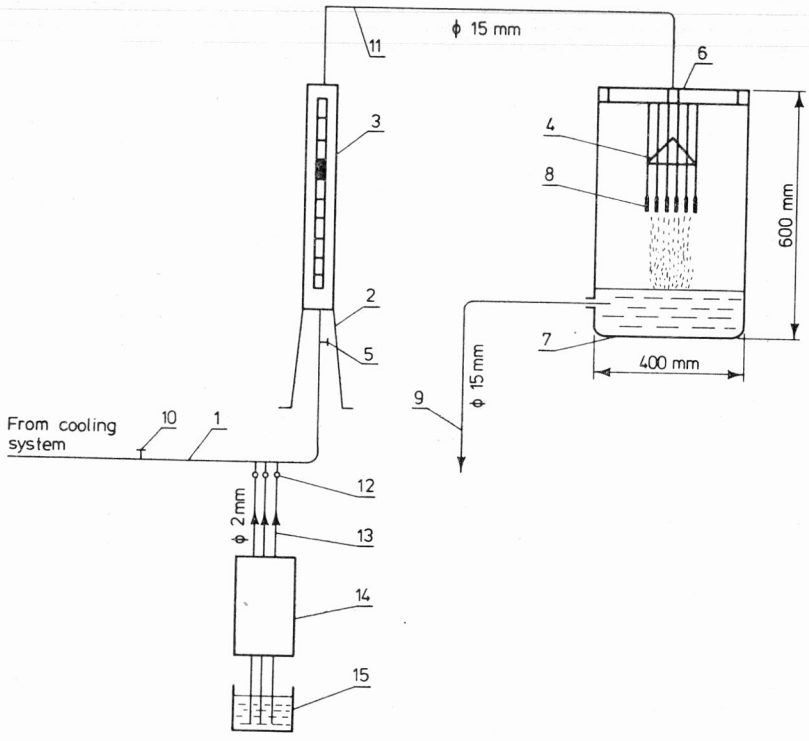

Fig. 1. Scheme of testing apparatus for biological slime

1 — colling water supplying pipe, *2* — tripod, *3* — rotameter, *4* — nickel, sprinkler, *5* — flow control valve, *6* — wooden cross, *7* — organic glass vessel, *8* — culture plates from eternit, *9* — outlet pipe, *10* — inflow control valve, *11* — pipe connecting rotameter with the system, *12* — injection needles, *13* — biocide supplying pipes, *14* — metering pump Elmed, type 304, *15* — vessel with biocide solution

Rys. 1. Schemat aparatury do testowania obrostów biologicznych

1 — przewód doprowadzający wodę chłodniczą, *2* — statyw, *3* — rotametr, *4* — zraszacz niklowy, *5* — zawór do regulacji przepływu, *6* — drewniany krzyżak, *7* — zbiornik ze szkła organicznego, *8* — hodowlane płytki eternitowe, *9* — przewód odprowadzający wodę do kanalizacji, *10* — zawór regulacji dopływu wody do układu, *11* — przewód łączący rotametr z układem, *12* — igły lekarskie, *13* — przewody doprowadzające biocyd, *14* — pompa dozująca Elmed typ 304, *15* — naczynie z roztworem biocydu

First series concerned the tests performed from September 29 to October 10; Hydrokryl AM being batched for seven days to obtain the concentration of 1.0 mg/dm^3.

In second series from November 24 to February 2 the reagent was batched for 38 days to obtain the concentration from 0.1 to 0.2 mg/dm^3 in cooling water. In this series there were 4 breaks in the batching of the biocide caused by difficulties with its pumping.

Third series was from February 16 to March 8; the preparation was batched for 15 days to obtain the concentration of 0.3 mg/dm^3.

In fourth series from April 7 to April 14 the biocide was dosed within 6 days to obtain the concentration of 3.7 mg/dm^3.

To show the toxic effect of Hydrokryl AM total number of saprophyte bacteria [5] was determined in water (before and after its cooling), and the hydrogenase activity of algae has been determined in slime taken from upper and lower parts of the cooling tower.

4. RESULTS OF INVESTIGATION

Nine reagents have been considered in the studies of the effect of biocide on the complex of organisms forming microbial slimes and taken from the cooling tower. Investigations by the TTC-test were performed for all the reagents in four basic concentrations which could be, in practice, used also in technical scale conditions (figs. 2 and 3). The investigations performed allowed to determine which of the tested substances showed the strongest activity. Iodine M has proved to be the strongest one, Sterinol, Hydrokryl AM, Preventol AS, Silenal ZB, Monuron, N-phenylthiourea, Simazyne 50 and Ferrocid 591 showed the decreasing activity.

In arranging this series a maximum toxic effect arisen for the lowest of the applied concentrations has been taken into account. The measuring method used for these tests

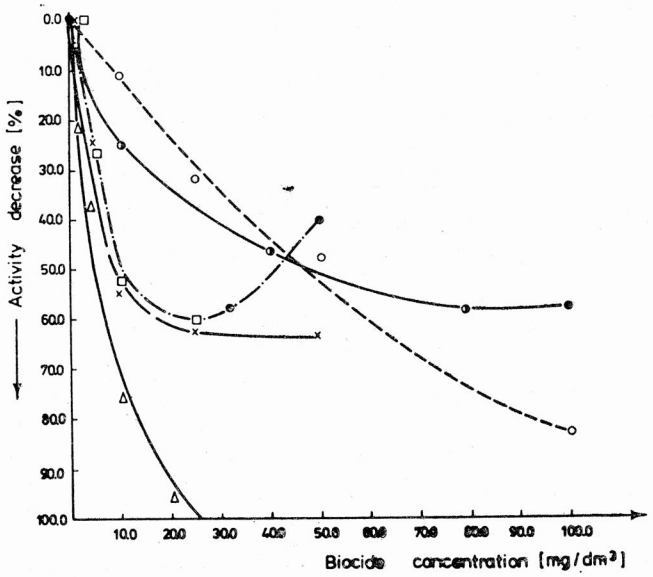

Fig. 2. Changes in enzymatic activity of slime due to the action of biocides
x – Manuran, ● – Creventol AS, □ – N-phenylthiourea, ◑ – Ferrocid 591, △ – Hydrokryl AM

Rys. 2. Zmiany w aktywności enzymatycznej obrostów pod wpływem działania biocydów
x – Manuran, ● – Creventol AS, □ – N-fenylotiomocznik, ◑ – Ferrocid 591, △ – Hydrokryl AM

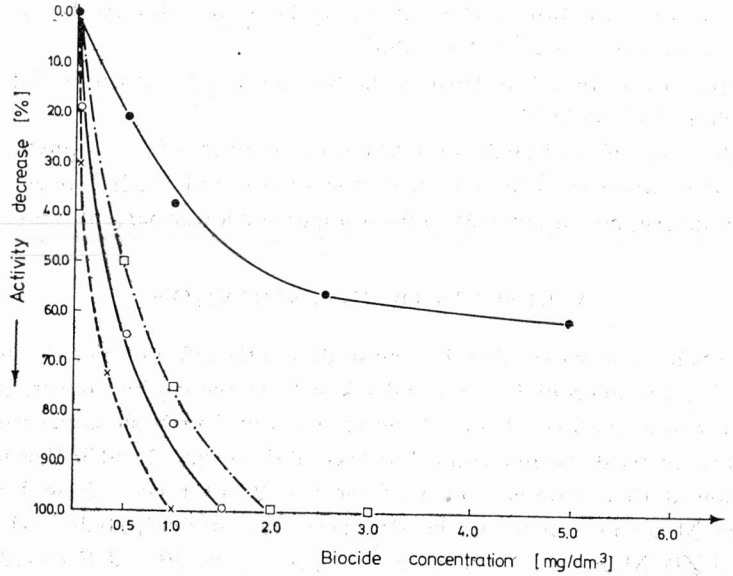

Fig. 3. Changes in enzymatic activity of slime due to the action of biocides
● – Simasine, x – Iodine, □ – Sterinol, ○ – Silenal 213

Rys. 3. Zmiany aktywności enzymatycznej obrostów pod wpływem działania biocydów
● – Simazina 50, x – Jod M, □ – Sterinol, ○ – Silenal

allowed to state only the maximum effect achieved during the 17 hour incubation, and did not permit to define which type of action occurring in each of the biocides was increasing or regressing.

To answer this question the toxicity tests have been performed by the manometric method. The reagent which could be applied to supress the microbial slimes in the tested cooling system was Hydrokryl AM (the selection has been made while taking into account the chemical properties of water and microbial slimes as well as the amount of the produced biocide and its price), therefore the respiration process of microbial slimes in the presence of the former has been measured in six hour series. It has been found that the effect of this reagent depends on the content of biocide in the sample [9]. Thus, at small quantities of Hydrokryl AM of the weight ratio of biocide and the mass of microbial slimes has been equal to 110 and 215 to 1,000,000; an increased intensity of respiration process occurred and amounted, after six hour incubation, 32 and 15% if compared with the experiment without biocide applied.

At the ratio of the reagent and slimes (900 : 1,000,000) a slightly toxic effect occurred, causing an approximately 9% inhibition of the respiration process which, however, after six hours of furthergrowing was reduced by approximately 50%. In subsequent tests, while successively increasing the quantities of reagent until the ratio of reagent and mass of microbial slimes amounted respectively 2750, 5625 and 22500 up to 1,000,000, it was

found that the inhibition of respiration process was approximately 10 up to 25% and was of increasing nature and in the final effect amounted from approx. 20 up to 50%.

Further tests performed in the apparatus for testing the microbial slimes enabled to determine the changes in hydrogenase activity of the organisms which formed microbial slimes during continuously and shock-wise way of reagent dosing. It has become evident that when the microbial slimes are continuously sprinkled with cooling water containing Hydrokryl AM 1 mg/dm^3 concentration the dehydrogenase activity of organisms is after 24 hours decreased by about 50%, while after 48 hours occurs only in traces.

Further tests performed with only one dosage of biocide lasting 1 hour and being applied in so-called shock doses (25.0, 50.0 and 90.0 mg/dm^3) shown that the effect (74–88% inhibition of the process) was a short lasting one and when dosing of reagent was stopped and further sprinkling only with cooling water continued, the activity was slowly increasing from 2 to 61% after 24 hours and from 6 to 31.0% after 48 hours due to biocide absence in the water and to nutrients inflow with water and air and to new populations of organisms capable to settle the plates. During further determination of the reagent influence on microbial slimes, a gradual growth of its effect could be observed with the biocide quantities increased up to 50 mg/dm^3, as shown in fig. 4. Further increase of Hydrokryl AM quantities up to 90 mg/dm^3 (i.e. by 40 mg/dm^3) resulted in the decrease of activity in 88.4%, so it changed only by 3.4%. It has to be emphasized that quantities of biocide applied in these series of tests were very large what may be justified only in such circumstances when within a short time a high efficiency is expected. It may occur e.g. at routine cleaning of cooling tower [3].

Investigations to determine the quantity of Hydrokryl AM to be introduced to an industrial cooling cycle under continuous dosing were performed in four series, which differed in the amount of introduced reagent (concentration 0.1 to 3.7 mg/dm^3) and time of dosing. It should be also mentioned that the quantity of water in this cooling cycle altered within a wide range.

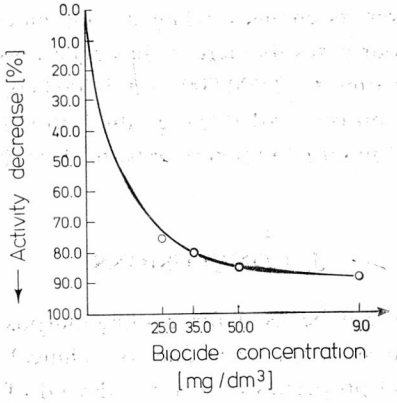

Fig. 4. Drop in the slime activity (in percent) at shock dosage of Hydrokryl AM

Rys. 4. Procentowy spadek aktywności obrostów przy uderzeniowym dozowaniu Hydrokrylu AM

Microscopic examination done before the reagent was dosed, indicated that the complexes of organisms which formed microbial slimes in the lower parts of cooling tower were thready forms of bacteria appearing in masses and blue-green algae of the *Oscillatoria* kind, occasionally *Zooglea ramigora*, diatoma of the *Navicula* and *Cyclotella*, non-identified *Rhisopoda*, *Infusoria*, *Rotifers* and *Nematoda*. Trypton was represented very numerously. Also in upper parts of cooling towers, non-identified thready bacteria forms appeared in masses and blue-green algae, as *Oscillatoria*, in large quantities. Occasionally appeared: *Eifflugia* sp., *Vorticella* sp., non-identified *Infusoria*, *Rotifers* and *Nematoda*. Trypton occurred very numerously as well. All the forms found were alive. All the biochemical investigations of microbial slimes performed at the same time indicated a very high dehydrogenase activity of the latter, equal to approx. 120 and 50 μ MTF/gb for microbial slimes of the lower and upper parts of the cooling tower, respectively. The average quantity of saprophytic bacteria in the cooling water amounted to 4045000/1 cm^3.

The changes in numbers of microbes detected during Hydrokryl AM dosing and their activity have been profitable in the first and fourth investigation runs, when biocide concentration has been 1.0 and 3.7 mg/dm^3 correspondingly. It has been stated that hydrogenase activity is then decreasing. At the end of a 5 days period of reagent dosing in the first investigation run the activity decreased 2 to 5 times correspondingly for the slimes taken from lower and upper parts of the cooling towers and the average number of bacteria in 1 cm^3 was 8000,000.

In the fourth investigation run, after a 5 days period of Hydrokryl AM dosing, the dehydrogenase acivity decreased 15 times, but average number of bacteria in 1 cm^3 was also approx. 800,000. While considering that the cooling cycle sterilization is not necessary, the biocide concentration of 1 mg/dm^3 could have been stated as admitted. The microscopic observations for this measuring run showed in addition that frequency of particular organisms does not change but 50% of the found floral forms were dead. It should be also indicated that in the remaining two runs (2nd and and 3rd) the dehydrogenase activity of slimes has been considerably lower due to non-favourable climatic conditions during the investigation run, however its changes, when dosing biocide have not been as clear as in runs I and IV and in four cases its increase has been observed. Numbers of bacteria in water amounted at some time to 2,000,000 and 5,500,000.

After the biocide dosing process ended the gradual growth of dehydrogenase activity of slimes and the increase of microbe numbers in water have been observed in all investigation runs.

5. CONCLUSIONS

1. Reclaimed wastewater can be used for cooling purposes even in the cases when large amounts of nutrients pass to the cycle due to technical failures.

2. Depending on chemical properties of water and kind of organisms forming slimes, the biocides ought to be introduced into water to prevent cooling system against the excessive growth of organisms forming the microbial slimes.

3. Separate investigations on the proper selection of biocide ought to be carried out for every cooling cycle.

4. Hydrokryl AM appeared to be the best biocide for the discussed cooling system. Dosed in suitable amounts to get its concentration in water of 1 mg/dm^3, it effectively inhibited the growth of the biological slimes as well as saprophytic microorganisms present in water.

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MOŻLIWOŚCI WYKORZYSTANIA DO CELÓW CHŁODNICZYCH WÓD PO PROCESIE ICH ODNOWY

Wykorzystywane — po procesie odnowy — wody do celów chłodniczych często utrudniają proces chłodzenia, powodując rozwój, między innymi, obrostów biologicznych. Dla zwalczania obrostów w przemysłowym obiegu chłodniczym wykonano badania, które obejmowały: określenie dwoma technikami (testu TTC i manometryczną w aparacie Warburga) wpływu 9-ciu biocydów na zespół organizmów tworzących obrosty; wykonanie badań w aparaturze do testowania obrostów, celem określenia zmian wśród organizmów przy ciągłym i okresowym sposobie dozowania wybranego biocydu; wprowadzenie biocydu do przemysłowego obiegu chłodniczego i sprawdzenie skuteczności jego działania. Biorąc pod uwagę skład jakościowy organizmów tworzących obrosty oraz charakter wody, do obiegu chłodniczego wprowadzano preparat krajowy o nazwie Hydrokryl AM. Przeprowadzone próby wykazały, że hamował on skutecznie rozwój niepożądanej w układzie wodnym mikroflory przy stężeniu 1 mg/dm^3.

RÜCKGEWONNENES WASSER DIENT FÜR KÜHLZWECKE

Wenn Wasser aus dem Abwasser rückgewonnen und für Kühlzwecke eingesetzt wird, ist mit einer starken Entwicklung des biologischen Rasens und demzufolge mit enormen Betriebsschwierigkeiten zu rechnen. Im Beitrag sind Maßnahmen besprochen worden, die gegen den Rasenwuchs im industriellen Kühlkreislauf ausgerichtet waren. Getestet wurden neun aus dem In- und Ausland stammende Biozide. Nachdem die Zusammensetzung des Rasens und des Wassers eingehend untersucht worden waren, wurde

für den Einsatz das Biozid Hydrokryl AM vorgeschlagen. Nach einer erfolgversprechenden Versuchsreihe im Labormaßstab, ging man auf eine Pilotanlage und letzten Endes auf eine technische Anlage über. Eine Dosis von 1 mg Hydrokryl AM auf 1 dm^3 Wasser, hemmte die Entwicklung der im Kühlkreislauf unerwünschten Mikroorganismen.

ВОЗМОЖНОСТЬ ИСПОЛЬЗОВАНИЯ ВОССТАНОВЛЕННОЙ ВОДЫ В ХОЛОДИЛЬНОЙ ТЕХНИКЕ

Вода, используемая после процесса восстановления для холодильных целей, часто затрудняет процесс охлаждения, вызывая развитие, между прочим, биологического оброста. Для борьбы с обростами в промышленном холодильном цикле проведены исследования, охватившие следующие работы: определение влияния 9 биоцидов на комплекс организмов, образующих обросты; испытания на специальной аппаратуре с целью определения изменений среди организмов при непрерывном и периодическом дозированиях избранного биоцида; введение биоцида в промышленный холодильный цикл и проверка результативности его действия. С учетом как качественного состава организмов, образующих обросты, так и характера воды для холодильного цикла введен отечественный препарат под названием Hydrokryl AM. Проведенные испытания показали, что он эффективно тормозил развитие нежелательной в водной системе микрофлоры при концентрации 1 мг/$дм^3$.