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THE ABILITY OF NATURAL WATERS TO SELF-PURIFY, DEPENDING ON THE DEGREE OF CHEMICAL POLLUTION

Self-purification in surface waters involves many components of the aquatic ecosystem, among which aquatic microorganisms play an important role, which perform the function of primary oxidation or reduction of pollutants entering the reservoir. However, a number of chemicals that pollute lakes and rivers inhibit the activity of bacterioplankton. This leads to the fact that the ability of the reservoir to self-cleaning is sharply violated and its degradation occurs. The activity of the process of destruction of organic substances can be judged by the oxygen parameters in the water of rivers and lakes. The purpose of this work was to study the effect of general chemical pollution of substances in natural water bodies on the ability of self-purification due to microorganisms.

To assess the ability of water bodies to self-purify, the R/BOD ratio was used. The functional activity of microorganisms in the samples was assessed by their ability to reduce the ratio of dissolved oxygen on the first day R_1/BOD_1 and on the fifth day R_5/BOD_5 in the presence of test pollutants: gasoline, surfactant and antibiotic.

It was shown that the decrease in the self-cleaning ability of natural waters under the influence of various pollutants from bioorganic pollution both in the river and in the lake is of a general nature. In a comparative study of the degree of suppression of heterotrophic destruction in lake and river water for gasoline, Fairy detergent and antibiotic Ospamox 250 mg, the latter most sharply reduces the ability of water bodies to bioorganic destruction at a dilution of 1:999, and at a dilution of 1:99 completely destroys it.

The second most inhibiting natural water self-purification agent is Fairy detergent. When diluted 1:9 and 1:99 Fairy reduces self-cleaning ability to zero on the fifth day.

Gasoline is capable of suppressing self-purification only in relatively large quantities: 1:9 in relation to water.

Key words: self-purification, bacterioplankton, dissolved oxygen, BOD, surfactant.

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Химиялық ластану дәрежесіне байланысты табиғи сулардың өзін-өзі тазарту қабілеті

Жер үсті суларының өздігінен тазаруына су экожүйесінің көптеген компоненттері қатысады, оның ішінде су қоймасына түсетін ластаушы заттарды бастапқы тотықтыру немесе тотықсыздандыру қызметін атқаратын су микроағзалары үлкен роль атқарады. Алайда көлдер мен өзендерді ластайтын бірқатар химиялық заттар бактериопланктонның белсенділігін төмендетеді. Бұл су қоймасының өздігінен тазару қабілетін бұзады және оның деградациясының орын алуына әкеледі. Органикалық заттардың бұзылу процесінің белсенділігін өзендер мен көлдердің суындағы оттегі көрсеткіші арқылы бағалауға болады. Жұмыстың мақсаты табиғи су қоймаларындағы жалпы химиялық ластанудың микроағзалар есебінен судың өздігінен тазару қабілетіне әсерін зерттеу.

Су қоймасының өздігінен тазару қабілетін бағалау үшін R/ОБК қатынасын қолдандық. Сынамалардағы микроағзалардың функциональдық белсенділігін тестілік ластаушы заттар: жанармай, ББЗ және антибиотик қатысында бірінші күнгі R_1/ОБК$_1$ және бесінші күнгі R_5/ОБК$_5$ еріген оттегі қатынасын төмендету қабілетімен бағаладық.

Өзенде де, көлде де әртүрлі ластаушы заттардың әсерінен биоорганикалық ластанудан табиғи сулардың өзін-өзі тазарту қабілетінің төмендеуі жалпы сипатқа ие екендігі көрсетілген.

Жанармай, жуғыш зат Fairy және Оспамокс 250 антибиотигін қосып, өзен және көл суларындағы гетеротрофты деструкцияның төмендеу дәрежесін салыстырмалы анықтауда, соңғысы яғни антибиотик 1:999 сұйылту кезінде су қоймасының биоорганикалық деструкцияға қабілетін жылдам төмендетеді, ал 1:99 сұйылту кезінде оны толығымен жояды.

Табиғи сулардың өзін-өзі тазартуының ең тежегіш құралы Fairy жуғыш заты. 1:9 және 1:99 сұйылтылған кезде Fairy бесінші күні өзін-өзі тазарту қабілетін нөлге дейін төмендетеді.

Жанармай салыстырмалы түрде көп мөлшерде ғана өзін-өзі тазарту қабілетін басуға қабілетті: сумен 1:9 қатынасында.

Түйін сөздер: өзін-өзі тазарту, бактериопланктон, еріген оттегі, ОБҚ, ББЗ.

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Способность природных вод к самоочищению в зависимости от степени химического загрязнения

В самоочищении в поверхностных водах участвуют многие компоненты водной экосистемы, в числе которых большую роль играют водные микроорганизмы, которые выполняют функцию первичного окисления или восстановления поступающих в водоем загрязняющих веществ. Однако ряд химических веществ, загрязняющих озера и реки, подавляют активность бактериопланктона. Это приводит к тому, что способность водоема к самоочищению резко нарушается и происходит его деградация. Об активности процесса разрушения органических веществ можно судить по кислородным показателям в воде рек и озер. Целью данной работы являлось изучение влияния общего химического загрязнения веществ в природных водоемах на способность самоочищения за счет микроорганизмов.

Для оценки способности водоемов к самоочищению использовали соотношение R/БПК. Функциональную активность микроорганизмов в пробах оценивали по их способности снижать соотношение растворенного кислорода в первый день R_1/БПК$_1$ и на пятый день R_5/БПК$_5$ в присутствии тестовых загрязняющих веществ: бензина, ПАВ и антибиотика.

Было показано, что снижение самоочищающей способности природных вод под воздействием различных загрязнителей от биоорганических загрязнений как в реке так и в озере имеет общий характер. При сравнительном изучении степени подавления гетеротрофной деструкции в воде озера и реки для бензина, моющего средства Fairy и антибиотика Оспамокс 250 мг, последний наиболее резко снижает способность водоемов к биоорганической деструкции при разведении 1:999, а в разведении 1:99 полностью уничтожает его.

Второе наиболее ингибирующее средство самоочищения природных вод – моющее средство Fairy. При разбавлении 1:9 и 1:99 Fairy сводит способность к самоочищению к нулю на пятый день.

Бензин способен к подавлению самоочищения только при сравнительно больших его количествах: 1:9 в соотношении с водой.

Ключевые слова: самоочищение, бактериопланктон, растворенный кислород, БПК, ПАВ.

Introduction

The increase in water pollution by various chemicals is aggravated every year throughout the world and, in particular, in the Republic of Kazakhstan [1].

In the State program of water resources management of the Republic of Kazakhstan for 2014-2040 "The problem of water security in the conditions of limited and vulnerable water resources is considered as a threat to the national security of the state" [1].

The state of rivers and lakes is influenced by a number of factors, both natural-climatic and anthropogenic. A dangerous cause of degradation of water resources are chemical, biological and other types of pollution. Most chemical pollutants cause both a direct deterioration in water quality, the death of aquatic organisms, and are the cause of a decrease in the potential for self-purification of water bodies and watercourses [2,3].

Self-purification in surface waters is a complex process involving many components of the aquatic ecosystem, the main of which are microorganisms. They perform the function of primary oxidation or reduction of pollutants entering the reservoir [4].

However, a number of chemicals that pollute lakes and rivers inhibit the activity of bacterioplankton. This leads to the fact that the ability of the reservoir to self-cleaning is sharply violated and its degradation occurs.

The purpose of this work is to study the effect of general chemical pollution of substances in natural water bodies on the ability of self-purification due to bacterioplankton.

The goal set defines the following tasks:

- Determination of the class of pollution of water bodies by chemical indicators.
- Determination of the self-purification potential in the aquatic ecosystem of the Yesil River and Bolshoi Taldykol Lake by oxygen indicators.
- Study of the influence of a number of pollutants on the process of self-purification in natural water

Objects of research and methods

The object of study of the self-cleaning ability of bacterioplankton in surface water bodies is the Yesil River and Bolshoy Taldykol Lake near Astana. Accordingly, the sampling coordinates are: the Esil River -51°05’25.1”N 71°43’19.2”E and Bolshoi Taldykol Lake -51°07’27”N 71°20’20”E.

Sampling was carried out in September 2022 at an air temperature of 26°C, water temperature in the river 10°C, in Taldykol Lake 14°C. Native samples were studied on the same day in the laboratory.

Hydrochemical studies of natural waters were an analysis of the content of anions – carbonates, bicarbonates, sulfates, chlorides, nitrates, phosphates, nitrites; and cations – calcium, magnesium, as well as dry residue, fluorine, total iron, chromium, nickel, zinc, manganese, surfactants, petroleum products, dissolved oxygen and suspended solids.

The water quality in Lake Taldykol and the Yesil River as water bodies for fishery purposes was determined [5]. According to the approved standards, Lake Taldykol belongs to class 5 of purity of reservoirs, where there is an excess of permissible concentrations of substances such as chlorides 4839.0 mg/dm3 (MPC-350 mg/l), sulfates 3992.0 mg/dm3 (MPC 250), ammonium salt 5.4 mg/dm3 (MPC 1), BOD5 30.0 (MPC 6), COD 143.4 mg/dm3 (MPC 30), total iron 3.09 mg/dm3 (MPC 0.3). According to monitoring data from official sources, as of October 2022, the Yesil River belongs to class 3 of purity of reservoirs. The main pollutant in the Yesil River are magnesium. (magnesium 32.602 mg/dm3 (MPC 30) [6]. (Table 1).

Table 1 – Hydrochemical components in the surface waters of the Akmola region

Name of the defined indicator	Unit of measure ment	MPC	Actual value/ multiplicity of exceeding MPC	
			The name of the selection point	
			Lake Taldykol	Esil river
1	2	3	4	5
pH	-	6.5-8.5	7.14	7.993
Suspended substances	mg /dm3	-	380.0	4.695
Dry residue	mg /dm3	1000	19044.0	320
Chlorides	mg /dm3	350	4839.0	188.76
Sulfates	mg /dm3	250-1500	3992.0	157.415
Hydrocarbonates		-	-	171,571
Phosphates	mg /dm3	3.5	0.63	0.167
Total phosphorus	mg /dm3	-	0.1-1	0.359
Total hardness	mg /dm3	7.0	96.0	9.3
Ammonium saline	mg /dm3	0.5-2.6	5.64	0.211
Nitrites	mg /dm3	0.1-5	0.224	0.006
Nitrates	mg /dm3	40-45	6.64	0.355
COD	mg/dm3	5-35	143.4	22.229
BOD5	mg /dm3	3-6	30,0	1.603
APAV	mg /dm3	0.1-0.5	0.40	0,02
Chlorides Common iron	mg /dm3	0.2-0.3	3.09	0.014

Table continuation

Name of the defined indicator	Unit of measure ment	MPC	Actual value/ multiplicity of exceeding MPC	
			The name of the selection point	
			Lake Taldykol	Esil river
1	2	3	4	5
Fluorides	mg /dm3	0.75-2.1	1.50	0.290
Manganese	mg /dm3	0.01-0.1	0.040	0.002
Magnesium	mg /dm3	20-100	-	32.602
Calcium	mg /dm3	-	-	77.468
Chromium	mg /dm3	0.1-0.55	0.013	0.001
Zinc	mg /dm3	0.3-5	0.068	0.013
Nickel	mg /dm3	0,05-0,2	0,059	-
Copper	mg /dm3	0.05-1	-	0.002
Lead	mg /dm3	0.006-0.05	-	0.001
Oil Products	mg /dm3	0,05-0,3	0,259	0.02
Alkalinity	mg /dm3	-	4,90	-
Water quality classes			5 classes	3 classes

The activity of the process of destruction of organic substances can be judged by the oxygen parameters in the water of rivers and lakes [7,8]. The total amount of oxygen in water is formed from dissolved atmospheric oxygen, and also as a product of photosynthesis of aquatic vegetation.

If part of the oxygen goes to the respiration of hydrobionts, then the other part is involved in the processes of chemical decomposition of substances. In ecologically safe reservoirs, the content of total oxygen in water always exceeds BOD_1, and in some cases even BOD_5. In this regard, the ratio of dissolved oxygen to BOD_5 can be conditionally taken as a criterion for assessing the ability of a reservoir to self-cleanse: the more intense photosynthesis in a reservoir, the more oxygenated the water, and the processes of destruction of pollution occur faster.

To assess the ability of water bodies to self-purify, the R/BOD ratio was used, which to a greater extent reflects the functional ability of heterotrophic bacterioplankton to self-purify [9]. Here R is the content of dissolved oxygen in water, BOD is the biological oxygen demand.

The functional activity of bacterioplankton in the samples was assessed by its ability to reduce the ratio of dissolved oxygen on the first day R_1/BOD_1 in the presence of test pollutants: gasoline, surfactant and antibiotic for five days to R_5/BOD_5.

A-92 gasoline, surfactant – detergent "Fairy", and antibiotic "Ospamox" 250 mg were used in final dilutions 1:9, 1:99. And for the antibiotic "Ospamox" 250 mg, a dilution of 1:999 was also taken, since the antibiotic is the most aggressive biocide for microorganisms. No contaminants were added to the control sample.

If chemical pollution in a natural reservoir suppresses the vital activity of bacterioplankton, then with the addition of test substances, its functional activity will be further reduced, and the R_5/BOD_5 ratio should decrease sharply. And vice versa: in a favorable natural environment, the functional capacity of bacterioplankton will remain high and the values of R_5/BOD_5 after the addition of test substances after a temporary decrease will recover after some time.

The mass concentration of dissolved oxygen and biochemical oxygen demand (BOD_5) were determined by the Winkler method [10]. Guiding document RD 52.24.420-2006, «Biochemical oxygen demand in waters. Methodology for performing measurements by the bottle method».

The mass concentration of oxygen dissolved in water X, mg/dm^3, was found by the formula:

$$X = \frac{M \cdot C_m \cdot V_m \cdot V \cdot 1000}{50 \cdot (V - V_1)} \quad (1)$$

where M is the molar mass of KVE oxygen, equal to 8 mg / mol;

C_m-concentration of sodium thiosulfate solution, mol/dm^3 KVE;

v_m is the volume of sodium thiosulfate solution used for titration, cm^3;

V-capacity of the oxygen bottle, cm^3;

V_1 is the total volume of solutions of manganese chloride and potassium iodide added to the flask during the fixation of dissolved oxygen, cm^3.

BOD_5, mg/dm^3, for undiluted samples (or biochemical oxygen demand of dilution water (BOD_5R), mg/dm^3), was found by the formula:

$$BOD_5=X_n-X_k \text{ or } BOD_5^R= X_n-X_k \qquad (2),$$

where X_n is the mass concentration of dissolved oxygen in the sample of analyzed water (or diluting water) before incubation, mg/dm^3;

$X_к$ – mass concentration of dissolved oxygen in the sample of analyzed water (or diluting water) after 5 days of incubation, mg/dm^3;

Biochemical oxygen demand BOD_5, mg/dm^3, for diluted samples was found by the formula:

$$BOD_5=(X_n-X_k) \bullet R\text{-}BPK_5^R\ (R\text{-}1) \qquad (3),$$

where X_n is the mass concentration of dissolved oxygen in the sample of analyzed water (or diluting water) before incubation, mg/dm^3;

X_k – mass concentration of dissolved oxygen in the sample of analyzed water (or diluting water) after 5 days of incubation, mg/dm^3;

BOD_{5r} – biochemical oxygen demand in dilution water samples, mg/dm^3;

P is the degree of sample dilution, equal to 1000/V, where V is the volume of analyzed water in 1 dm^3 of the mixture after sample dilution.

Research results

The influence of a number of pollutants on the ability of bacterioplankton to self-purify the Yesil River and Taldykol Lake is shown in Table 2.

A comparative analysis of the degree of influence of three different pollutants on the self-cleaning capacity of the Yesil River and Taldykol Lake in terms of oxygen content showed the following results.

From the control sample in the Yesil River, where we did not add any pollutants, it can be seen that in the control river water on the first day the self-cleaning capacity was 1.096. Then, after five days, it did not decrease, but even slightly improved due to the fact that the bacterioplankton continued to develop, and thus the self-purifying ability of the water improved to 1.296.

In the control sample of Lake Taldykol, during natural self-purification, the ratio R_1/BOD_1 increased from 1.028 to 1.471 (R_5/BOD_5) after five days. Thus, it can be said that in both reservoirs, both in the river and in the lake, the processes of self-purification are not disturbed and the hydrochemical composition of the water in them does not suppress the activity of bacterioplankton.

Quite different results were obtained in other experimental samples.

In a water sample from the Yesil River diluted with gasoline to 1 part gasoline and 9 parts water, the biological oxygen consumption was still 1.036 during the first day. But then, five days later, the self-cleaning capacity of the reservoir dropped to zero. This suggests that in our sample with a high content of gasoline, the bacterioplankton completely died because the oxygen content in the water dropped critically, the ability to self-purify is zero.

With a small content of gasoline in water (dilution 1:99), on the first day the self-cleaning ability was equal to 1.106. Five days later, the oxygen content dropped to 0.271. The self-cleaning ability this time is not zero, but compared to pure water has decreased by 6 times.

Samples of water with gasoline in Taldykol Lake also showed that the content of gasoline in water 1:9 is detrimental to bacterioplankton. If on the first day the oxygen content decreased from 17.8 (in pure water) to 9.1, then on the fifth day all oxygen was completely wasted and the self-cleaning ability was equal to zero.

When gasoline 1:99 was added to the water sample, oxygen was preserved on the fifth day and the self-cleaning ability was at the level of 0.263, which is also almost six times lower than in the control sample.

The experiment with gasoline in the river and in the lake showed identical results: the lake and the river cannot cope with a large amount of gasoline, since the film formed completely blocks the access of oxygen and the bacterioplankton dies. With a low gasoline content of 1:99, the self-purifying potential of water bodies is preserved, probably due to the oil-degrading fraction in the composition of bacterioplankton, but is suppressed compared to control water.

In the third sample of water from the Yesil River, with the addition of the detergent “Fairy” at its high content in a dilution of 1:9, as well as with a low content in a dilution of 1:99, the self-cleaning ability still remains equal to 1.166 and 1.104 during the first day, but after five days the oxygen concentration dropped absolutely to zero in both cases. After five days, the ability to self-purify was absent. Heterotrophic bacterioplankton against the background of the hydrochemical composition in the Yesil River loses its activity and the addition of a surfactant completely suppresses the river’s ability to self-purify.

Table 2 – Indicators of water's ability to self-clean in 1 day and 5 days

Sample	River Yesil						Lake Taldykol					
	R_1	BOD_1	R_5	BOD_5	R_1/BOD_1	R_5/BOD_5	R_1	BOD_1	R_5	BOD_5	R_1/BOD_1	R_5/BOD_5
Water	13.6±1.08	12.4±1.09	7.0±0.79	5.4±0.61	1.096	1.296	17.8±1.18	17.3±1.13	10.3±1.06	7.0±0.78	1.028	1.471
Casoline A-92 (1:9)	8.6*±0.74	8.3*±0.91	0	8.3	1.036	0	9.1*±0.95	7.4**±0.71	0	7.4±0.79	1.229	0
Casoline A-92 (1:99)	8.3*±0.91	7.5*0.72	1.6**±0.48	5.9±0.73	1.106	0.271	12.3*±1.06	11.5±1.05	2.4**±0.15	9.1±1.01	1.069	0.263
Surfactant Fairy (1:9)	6.3**±0.54	5.4**±0.42	0	5.4±0.42	1.166	0	7.8**±0.75	6.6**±0.71	4.1*±0.36	2.5**±0.15	1.181	1.6
Surfactant Fairy (1:99)	7.4*±0.73	6.7*±0.55	0	6.7±0.53	1.104	0	12.4±1.06	7.8*±0.65	2.0**±0.12	5.8±0.46	1.589	0.344
Antibiotic Ospamox 250 mg (1:99)	0	0	0	0	0	0	0	0	0	0	0	0
Antibiotic Ospamox 250 mg (1:999)	6.2**±0.57	5.4**±0.48	2.9**±0.12	5.4±0.45	1.148	0.537	12.8±1.09	12.4±1.06	0	12.4±1.08	1.032	0

***p<0.05 **p<0.01**

Lake Taldykol in the experiment with detergent “Fairy” results are different. The addition of surfactants at both concentrations of 1:9 and 1:99, although it reduced the amount of oxygen, did not completely suppress the ability of the reservoir to self-purify.

In the fourth experiment, where we tested the action of the antibiotic Ospamox 250 mg. With a high content of the antibiotic in a dilution of 1:99, all indicators fell to zero already on the first day, both in the river and in the lake. The oxygen content could drop due to its toxicity to phytoplankton, which completely lost their viability. At the same time, bacterioplankton also died, and instantaneous biodegradation began, which also reduced the level of oxygen. And after five days, the ability to self-purify, respectively, fell to zero.

However, in the Yesil River, if the antibiotic was added in very small quantities at a dilution of 1:999, then on the first day the self-purification ability still remained close to normal, equal to 1.148, but after five days it still halved and became equal to 0.537.

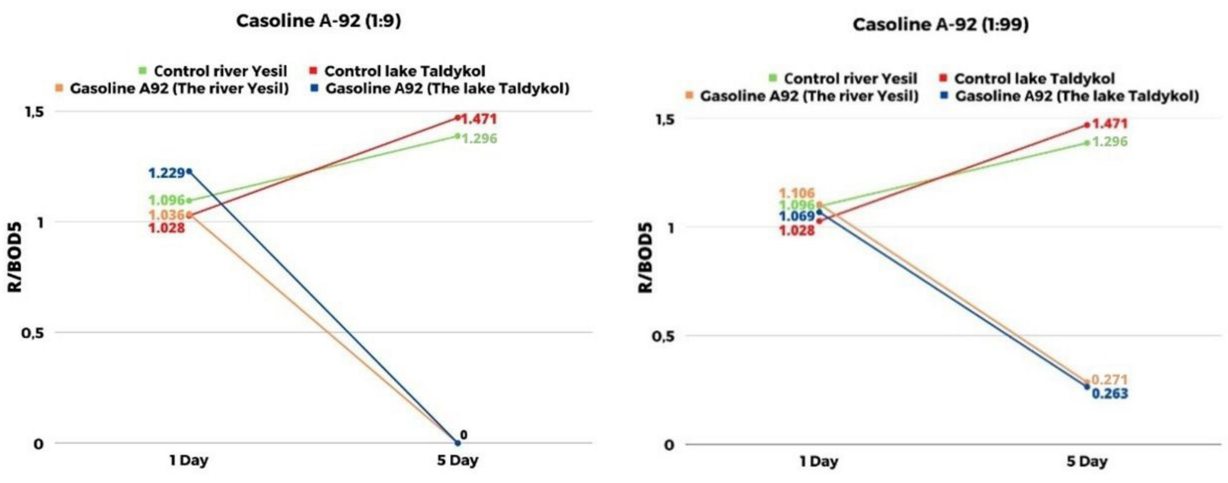
In the Taldykol lake, a high dose of the antibiotic caused the same effect as in the river, but at a dilution of 1:999, the self-cleaning ability remained only for 1 day, on the 5th day it was equal to zero.

Based on the results of the experiment, we can conclude that in terms of the degree of suppression of heterotrophic destruction, and hence the suppression of natural waters for self-purification, the studied antibiotic Ospamox 250 mg ranks first among the studied substances, since even at a dilution of 1:999 it sharply reduces the ability reservoirs to bioorganic destruction, and in a dilution of 1:99 it completely destroys it.

The second most inhibiting natural water self-purification agent is Fairy detergent. When diluted 1:9 and 1:99 Fairy reduces self-cleaning ability to zero on the fifth day. Since many detergent-type surfactants have a similar structure to “Fairy”, this conclusion is also true for them.

Gasoline is capable of suppressing self-purification only if it is used in large enough quantities: 1:9 in relation to water. Most likely, the mechanism of its action is not so much related to toxicity, but to its ability to block the access of oxygen to water.

The results obtained are presented in Figure 1.2.3.



a b

Figure 1 – Self-cleaning ability of surface waters with the addition of test substances:
A). Casoline-1:9, B).Casoline -1:99

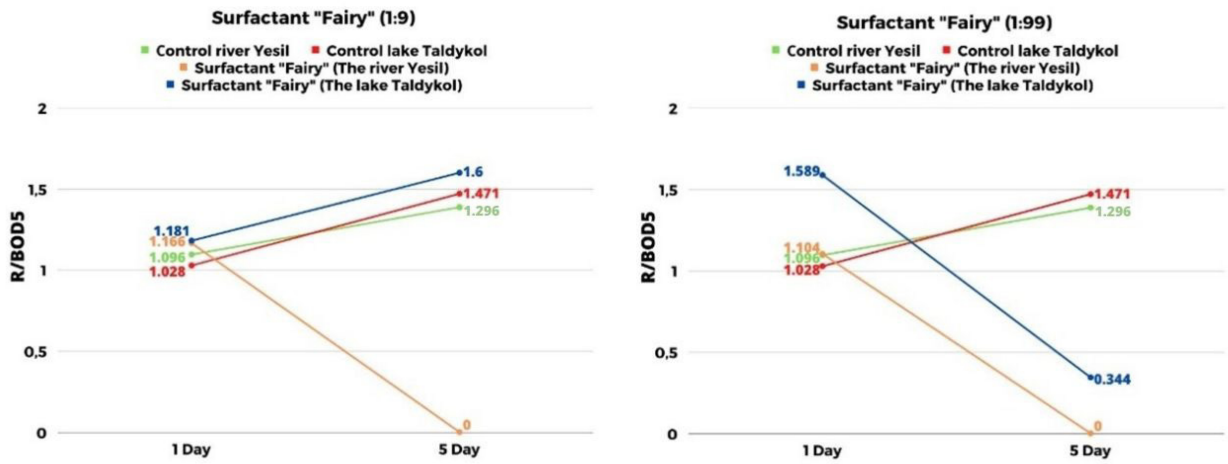


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Figure 2 – Self-cleaning ability of surface waters with the addition of test substances: A).Surfactant “Fairy” -1:9, B).Surfactant “Fairy” -1:99

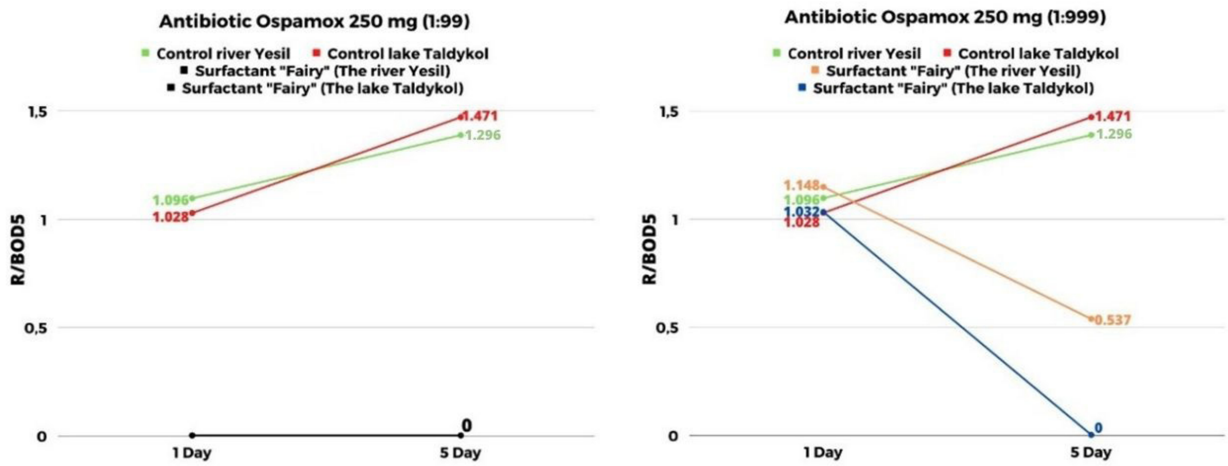

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Figure 3 – Self-cleaning ability of surface waters with the addition of test substances: A).Antibiotic Ospamox 250 mg-1:99, B).Antibiotic Ospamox 250 mg-1:999

The ability of water to self-purify is largely related to the processes of photosynthetic activity of aquatic plants and the destructive ability of heterotrophs, which use oxygen for this [9,11,12]. In this regard, to assess the ability of water bodies to self-purify, we can make an assumption: the more water is saturated with oxygen (R), and the less oxygen is required for the destruction of organic matter (BOD_1 or BOD_5), the higher the potential for self-purification of water bodies. In this case, the ratio of the amount of dissolved oxygen R and BOD_5 can be ued as an indicator of the self-cleaning potential: the higher the R/BOD_5 ratio, the higher the self-cleaning ability of the reservoir, and vice versa – the lower the ratio, the worse the self-cleaning ability of the reservoir [13].

Conclusion

1.The decrease in the self-cleaning ability of natural waters under the influence of various pollutants from bioorganic pollution both in the river and in the lake is of a general nature.

2.In a comparative study of the degree of suppression of heterotrophic destruction in lake and river water for gasoline, Fairy detergent and antibiotic

Ospamox 250 mg, the latter most sharply reduces the ability of water bodies to bioorganic destruction at a dilution of 1:999, and at a dilution of 1:99 completely destroys it.

3.The second most inhibiting natural water self-purification agent is Fairy detergent. When diluted 1:9 and 1:99 Fairy reduces self-cleaning ability to zero on the fifth day.

4.Gasoline is capable of suppressing self-purification only in sufficiently large quantities: 1:9 in relation to water.

Application of the research results: in assessing the impact of various types of pollutants from industrial, agricultural, municipal facilities, transport on the ecological state of lakes and rivers. And also for scientific purposes, where the characteristics of pollutants are required that affect the self-cleaning ability of surface waters.

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