UDC 614.777:628.113:546.32:547.295.94 https://doi.org/10.26641/2307-0404.2022.2.260295

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SANITARY AND HYGIENIC CHARACTERISTICS OF POTASSIUM STEARATE AS A SOURCE OF ANTHROPOGENIC POLLUTION OF WATER RESERVOIRS

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***Цитування:** Медичні перспективи. 2022. Т. 27, № 2. С. 159-167*
***Cited:** Medicni perspektivi. 2022;27(2):159-167*

Key words: *water pollution, potassium stearate, sanitary and hygienic characteristics, hazard class*
Ключові слова: *забруднення води, стеарат калію, санітарно-гігієнічна характеристика, клас небезпеки*
Ключевые слова: *загрязнение воды, стеарат калия, санитарно-гигиеническая характеристика, класс опасности*

Abstract. Sanitary and hygienic characteristics of potassium stearate as a source of anthropogenic pollution of water reservoirs. Lototska O.V., Krytska H.A., Kucher S.V. *Monitoring of surface water quality indicates deterioration of its quality due to anthropogenic pollution. Among them, potassium stearate (PS) occupies a prominent place. The purpose of the study is to substantiate regulations of potassium stearate in the water of reservoirs on the basis of sanitary and hygienic assessment of potassium stearate, study its stability and transformation, the impact on the organoleptic properties of water, the sanitary condition, self-cleaning processes and the sanitary condition of reservoirs. Research methods – bibliographic, analytical, statistical, sanitary and hygienic. It was found that the average effective concentration of PS by taste for the threshold of sensation (1 point) was at the level of 6.43 mg/dm^3. The intensity of the taste of 1-2 points was maintained for 10 days. Potassium stearate is a hydrolyzing and non-chlorinating substance. As a result of assessing the impact of potassium stearate on the processes of self-purification of water from organic pollution by observing the dynamics of water oxidation, dissolved oxygen concentration and biochemical oxygen demand (BOD), the processes of ammonification, nitro- and nitrification, it was found that the limiting potassium stearate for reservoirs is BOD. On the basis of threshold and inactive concentrations by all limiting signs of harmfulness one allows recommending the maximum permissible concentration for potassium stearate at the level of 0.25 mg/dm^3. The limiting indicator of harm is sanitary. Comprehensive assessment of the obtained experimental and calculated data by the hygienic rationing of PS in general the water of open reservoirs allows classifing it as the 4th class of danger (practically non-toxic substances).*

Реферат. Санітарно-гігієнічна характеристика стеарату калію як джерела антропогенного забруднення води водойм. Лотоцька О.В., Крицька Г.А., Кучер С.В. *Моніторинг якості води поверхневих водойм свідчить про погіршення її якості внаслідок антропогенного забруднення. Серед них чільне місце посідає стеарат калію (СК). Метою дослідження було обґрунтування регламенту СК у воді водойм на підставі проведення санітарно-гігієнічної оцінки СК, вивчення його стабільності та трансформації, вплив на органолептичні властивості води, процеси самоочищення і санітарний стан водойм. Методи досліджень – бібліографічний, аналітичний, статистичний та санітарно-гігієнічні. Установлено, що середньоефективна концентрація СК за присмаком для порога відчуття (1 бал) була на рівні 6,43 мг/дм^3. Інтенсивність присмаку 1-2 бали зберігалася впродовж 10 діб. Було виявлено, що СК є гідролізуючою і нехлоруючою речовиною. У результаті оцінки впливу СК на процеси самоочищення води водоймищ від органічного забруднення шляхом спостереження за динамікою окиснюваності води, концентрацією розчиненого кисню та біохімічним споживанням кисню (БСК), за процесами амоніфікації, нітро- і нітрифікації було встановлено, що лімітуючою ознакою для нормування СК у воді водойм є БСК. Порогова концентрація БСК дорівнює 0,25 мг/дм^3. Максимально не діюча концентрація за токсикологічною ознакою шкідливості становить 4,0 мг/дм^3. На підставі порогових і недіючих концентрацій за всіма лімітуючими ознаками шкідливості можливо рекомендувати гранично допустиму концентрацію для стеарату калію на рівні 0,25 мг/дм^3. Лімітуючий показник шкідливості – зальносанітарний. Комплексна оцінка отриманих експериментальних і розрахункових даних за гігієнічним нормуванням СК у воді відкритих водоймищ дозволяє віднести його до 4-го класу небезпеки (практично нетоксичних речовин).*

It has been established that long-term use of substandard drinking water causes an increase of both non-infectious and infectious diseases in the population [1, 6, 10]. Monitoring of surface water quality indicates that despite the significant decline and the reduction in industrial production and discharges into wastewater reservoirs in recent years, there is deterioration in water quality of reservoirs [3]. Among the large list of factors that lead to the deterioration of drinking water quality are various anthropogenic pollutions that enter surface and groundwater sources through soluble compounds from the soil surface, such as pesticides or fertilizers, due to emissions from industrial enterprises or vehicles, etc. Existing water treatment plants provide virtually no barrier function to many chemicals and they enter drinking water [8].

For many years, synthetic surfactants (SS) have been one of the top-priority surface water pollutants. Among them is potassium stearate (PS), which is widely used in the manufacture of detergents, shampoos, hair dyes, hand creams, shaving foams, as an additive to toothpaste and cosmetic creams, and also are among the main components of solid and liquid soap. They are also used in the production of polyolefins, caoutchouc and rubber, in dry construction mixtures, as a thickener, stabilizer and lubricant in the formation of polyamides, as an antifoam in the food industry, in the processing of thermoplastics, as a lubricant in the paper industry [2].

The purpose of the study is to substante regulations of potassium stearate in the water of reservoirs on the basis of sanitary and hygienic assessment of potassium stearate, study its stability and transformation, the impact on the organoleptic properties of water, the sanitary condition, self-cleaning processes and the sanitary condition of reservoirs.

MATERIALS AND METHODS OF RESEARCH

Potassium Stearate (PS) – formula $CH_3(CH_2)_{16}COOK$, a white powder with a greasy odor, which is soluble in hot water or alcohol, insoluble in ether, gasoline, chloroform, has a melting point of 255-260°C. It is an anionic surfactant and is obtained by neutralizing an alcoholic solution of stearic acid with a solution of potassium hydroxide [2].

The effect of PS on the organoleptic properties of water was studied according to [5] the team-based approach by a group of trained volunteer-odorants, 30 people by setting threshold concentrations for the taste of water. The following concentrations were investigated: 250.0; 125.0; 62.5; 32.2; 15.6; 7.8 and 3.9 and 1.9 mg/dm^3.

The influence of PS on the processes of water self-clarification from organic pollution was studied according to [5] by observing the dynamics of biochemical oxygen consumption (BOC_{20}), processes of ammonification, nitro- and nitrification, dissolved oxygen concentration, water oxidation. The experiments were performed in experimental model reservoirs with initial concentrations of PS 0.05, 0.1, 0.2, 0.25, 1.5 and 15.0 mg/dm^3 and PS 0.015, 0.05, 0.15, 0, 25, 0.5, 1.0, 1.5 and 5.0 mg/dm^3

The stability and chlorooxidation of PS in the water medium were studied according to [5]. The stability of substances in the water medium was determined by an indirect method of changing the intensity of the taste in the dynamics after 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 days by a group of trained volunteer-odorants, 30 people. For this purpose, tap dechlorinated water containing the preparation in concentrations corresponding to the intensity of taste from 0 to 4 points was kept for 10 days in open vessels in diffused light at a temperature of 20-22^{o}C.

The property of substance to interact with active chlorine was detected by the method of experimental chlorination and subsequent determination of residual free chlorine in water containing the test substance. The aqueous solution of chlorinated lime with an active chlorine content of at least 25% was previously prepared. Chlorinated lime was added at the rate of 1 mg of active chlorine per 1 mg of substance. Residual free chlorine was determined 15, 30, 60 and 120 min after the addition of chlorinated lime.

Statistical processing of digital data was performed using Excel software ("Microsoft", USA) and STATISTICA 6.0 ("Statsoft", USA) [4]. Effective concentrations (EC) of PS on the effect on the taste of water were determined by the method of least squares for probit analysis by V.B. Prozorovsky [9] using StatPlus 2009 Professional 5.8.4 (AnalystSoft, USA, 2009), which gives the chance in the automated mode to receive schedules and the basic toxicometric indicators.

RESULTS AND DISCUSSION

Effect of stearates on the organoleptic properties of water was evaluated by taste. PS has been found to give the water an astringent soapy taste. The intensity of its taste at the level of 1-2 points was determined in a wide range of concentrations (Table 1). The intensity of taste in 1 point was observed in the range from 1.9 to 15.6 mg/dm^3, in 2 points – from 3.9 to 31.2 mg/dm^3.

Statistical processing of the obtained results established that the concentration corresponding to the threshold of taste sensation (1 point) is at the level of 4.96 mg/dm^3, the practical threshold (2 points) is at the level of 11.85 mg/dm^3 (Table 2).

Table 1

Distribution of indices of taste intensity of potassium stearate in distilled water (t°=20°C)

Concentration of sodium stearate, mg/dm^3	Intensity of taste, points					
	0	1	2	3	4	5
	Positive information, %					
250.0					10	30
125.0					31	6
62.5				25	21	
31.2			8	27		
15.6		6	26	2		
7.8	2	21	22			
3.9	14	24	5			
1.9	28	12				

To clarify the data obtained when establishing the threshold concentrations of PS by the on the taste of water, we conducted "closed" test experiments with concentrations of the substance, which gave the water a taste of 1-2 points (Fig. 1). It was found that the taste of water, established by a "closed experiment", was directly dependent on the concentration of PS. At a concentration of PS 1.9 mg/dm^3, it was experienced by only 16.1% of volunteer-odorants. 61.3% did not feel any taste even at a concentration twice as high. According to 90.3% of volunteer-odorants, it appeared at a concentration of 15.6 mg/dm^3.

Table 2

Determination of threshold concentrations (TC_{50}) of potassium stearate by the impact on taste of distilled water (t^{o}=20^{o}C)

Intensity of taste, points	Indicator of statistical processing						
	n	M	± m	± δ	P	V	M-2m
1	63	5.93	0.48	3.838	8.09	64.72	4.96
2	61	13.87	1.009	7.880	7.27	56.81	11.85

Effective concentrations of PS by the effect on the taste of water were calculated by probit analysis [9]. The following effective concentrations of the substance were calculated:

A_1 =0.30

A_0 =3.96

EC_{16} =0.247 mg/dm^3

EC_{84} =12.62 mg/dm^3

S_x =1.79 mg/dm^3

EC_{50} =6.43 (4.64±8.22) mg/dm^3

The average effective concentration (EC_{50}) of PS by taste for the sensation threshold (1 point) was at the level of 6.43 (4,64÷8,22) mg/dm^3. The approximate value of the practical threshold (2 points) by taste was found by multiplying the obtained value of EC_{50} by a factor of 1.5 and it was found that the PS will cause a taste of 2 points at a concentration of 9.45 mg/dm^3.

Chlorination of aqueous solutions of PS did not lead to strengthening or emergence of additional taste at the content of free residual chlorine from 0.3 to 0.5 mg/dm^3 neither at a temperature of 20°C, nor at its increase to 60°C.

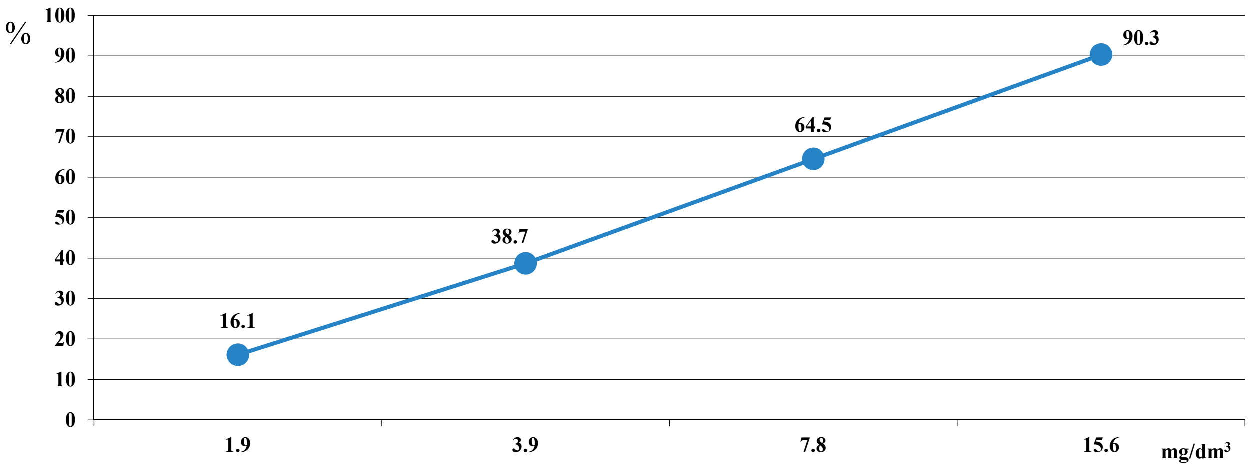

Fig. 1. Percentage of positive responses depending on the concentration of potassium stearate (number of observations 31)

It is established that the PS has foam ability. In distilled water at a temperature of 20°C, the threshold concentration was 250.0 mg/dm^3. The foaming ability of the PS was evaluated by the height of the foam column in graduated cylinders with a volume of 1000 ml. The threshold was taken to be the concentration at which there is no stable large-bubble foam, and the height of the small-bubble near the walls of the cylinder does not exceed 1 mm. With increasing temperature to 60°C there was an increase in foam ability by 2 times.

It is established that the substance forms a film on the water surface. To find out some features of the behavior of PS in the aquatic environment and the qualitative characteristics of its distribution on the water surface, 2 series of studies were conducted. During the first one in chemical beakers with the same surface area 20 ml of settled tap water was poured and a different amount of PS was added: 0.1, 0.5, 1 and 2 mg. As a result of the research, it was found that in all samples the particles floated on the water surface. In the first two vessels with the content of PS in doses of 0.1 and 0.5 mg on the surface of the water initially there were single particles, which gradually in the following days formed a film in the center. In vessels 3 and 4 with PS in the amounts of 1 and 2 mg, the particles accumulated in the center, forming a film with an area of 2-3 cm^2. No qualitative changes were observed when the samples were left for 10 days.

During the second study, 0.5, 1.0, 10 and 20 mg of PS were added to beakers filled with 500 ml of settled tap water, which corresponded to the following concentrations: 1.0; 2.0; 20; 40 mg/dm^3. In the first two beakers, with concentrations of 1.0 and 2.0 mg/dm^3, separate particles were observed on the surface of the water, which gradually formed films and after a few days they merged into large one floating on the surface. At the amount of the substance 20.0 and 40.0 mg/dm^3, PS on the surface of the water accumulated in the form of a film in the center of the vessels. After a few days, the size of the film increased, part of the substance was sorbed on the walls of the vessel. During 14 days no other qualitative changes with this water were observed.

The stability of the PS was studied by changing the intensity of the taste by the indirect method (Table 3). Distilled water was evaluated with a substance content of 250.0; 125.0; 62.5; 31.2; 15.6; 7.8 and 3.9 mg/dm^3 (flavor intensity from 0 to 5 points).

For 10 days the water was in open vessels at diffused light at a temperature of 20-22°C. The change in the intensity of the taste was observed on 1, 2, 3, 4, 5, 6, 8, 9 and 10 day by a group of volunteer – odorants. According to research results, the intensity of the taste of 1-2 points was maintained for 10 days. In high concentrations, the substance formed a precipitate, and a putrid odor appeared.

Chlorooxidation was evaluated using PS solutions with a concentration of 10 and 100 mg/dm^3 in distilled water. The interaction of the substance with active chlorine was detected by the method of experimental chlorination, followed by determination of residual free chlorine in water containing PS, after the addition of chlorinated lime at the rate of 1 mg of active chlorine per 1 mg of substance. Residual chlorine was determined immediately after the addition of chlorinated lime solution and after 15, 30, 60 and 120 minutes. At the maximum (2 h) contact time, the amount of free residual chlorine in the control and experimental samples was the same in all solutions, which indicates that the PS is a hydrolyzing and non-chlorinating substance.

Table 3

Stability of potassium stearate by taste

Concentration, mg/dm³	Taste in points on the days of observation								
	1	2	3	4	5	6	8	9	10
250,0	5	5	5	5	5	5-4	5-4	5-4	4-5
125,0	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4
62,5	4-3	4-3	4-3	4-3	3-4	3-4	3-4	3-4	3-4
31,3	3	3	3	3	3	3-2	3-2	3-2	3-2
15,6	2	2	2	2	2	2	2-1	2-1	2-1
7,8	2-1	2-1	2-1	2-1	2-1	2-1	1-2	1-2	1-2
3,9	1	1	1	1	1	1	1	1-0	1-0

The influence of PS on the processes of self-purification of water from organic pollution was studied by observing the dynamics of water oxidation, dissolved oxygen concentration and biochemical oxygen demand (BOD), the processes of ammonification, nitro- and nitrification. The experiments were performed in experimental model reservoirs with initial concentrations of PS 0.015; 0.05; 0.15; 0.25; 0.5; 1.0; 1.5; 5.0 mg/dm³. The substance had virtually no effect on the oxidation of water. The maximum increase in oxidation was in the groups with a concentration of 1.0, 1.5 and 5.0 mg/dm³ in all observation periods and exceeded the control values by a maximum of 20%. In other vessels with lower concentrations of PS, small fluctuations were observed. The study of the effect of PS on the oxygen regime in water was performed under anaerobic conditions. No special relationship between its content in water and the duration of the experiment was observed at different concentrations. The increase in the amount of PS in the water caused a slight decrease in dissolved oxygen (up to 13%). Doses of 0.015, 1.5 and 5.0 mg/dm³ caused the most pronounced changes compared to control values. With increasing observation time, the difference with control decreased.

Evaluation of changes in BOD was performed using Winkler glasses. The maximum values of BOD were observed on day 3, especially at a concentration of PS 1.0 and 5.0 mg/dm³ – by 80 and 151%, respectively (Fig. 2). On day 10 of the observation, the increase in oxygen consumption also increased in beakers with a concentration of PS 0.15, 0.25, 1.0 and 1.5 mg/dm³. Only at the two lowest oncentrations – 0.015 and 0.05 mg/dm³ during the entire observation period, BOD did not differ much from the control.

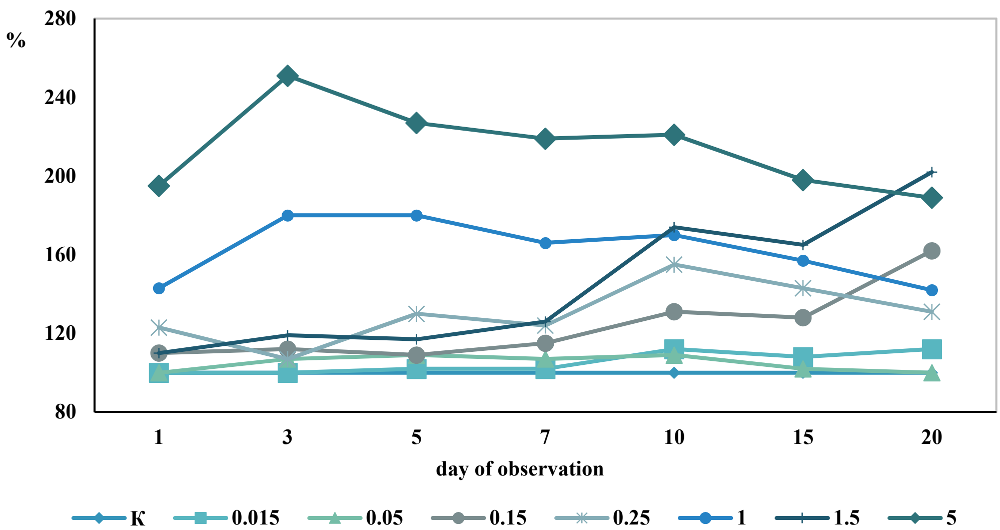

Fig. 2. Dynamics of biochemical oxygen demand depending on the concentration of potassium stearate in water (in % to control)

The processes of mineralization of organic substances play an important role in the self-purification of water. No significant changes in the ammonification process were detected in aquariums under conditions of diffused light with PS at concentrations of 0.015, 0.05, 0.15 and 0.25 mg/dm^3. Larger changes were observed in the content of PS in the amount of 1.0 and 1.5 mg/dm^3. The concentration of 5.0 mg/dm^3 had a significant effect on the ammonification processes (Fig. 3).

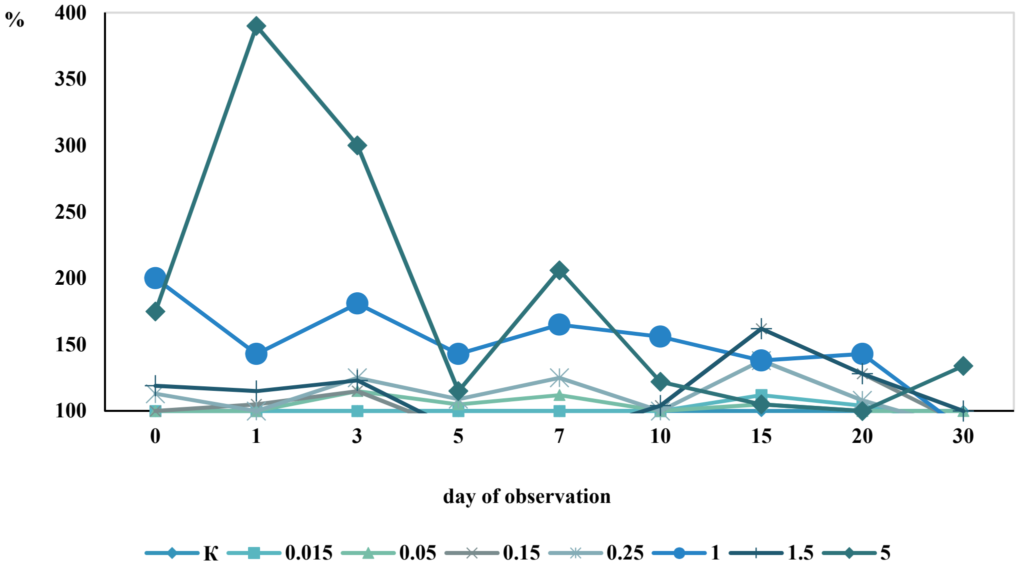

Fig. 3. Impact of potassium stearate on the dynamics of ammonia nitrogen in water (in % to control)

The effect of PS on nitrogen nitrates, as can be seen from Table 4, appeared in the water of experimental reservoirs only on day 15.

It caused the inhibition of nitrification processes in the water of all experimental concentrations, except the lowest, by 4-17%. On day 30, the decrease in nitrogen nitrate content was maintained in water with a concentration of 0.5, 1.5 and 5.0 by 34, 5 and 35%, respectively. The effect of PS on the content of nitrites in the water of experimental reservoirs was manifested from day 3 to day 30 at concentrations of 0.5 and 5.0 mg/dm^3. Nitrite nitrogen in the water of the experimental reservoirs decreased from 30 to 60% (Table 5).

Table 4

Impact of potassium stearate on the dynamics of nitrogen nitrates in water (in % to control)

Observation period, days	Potassium stearate concentration, mg/dm^3						
	control	0,015	0,05	0,15	0,5	1,5	5,0
7	100	100	113	100	113	100	106
10	100	100	97	112	95	112	94
15	100	96	93	83	93	83	87
20	100	98	100	84	83	70	87
30	100	100	95	100	66	95	65

Table 5

Impact of potassium stearate on the dynamics of nitrite nitrogen (in % to control)

Observation period, days	Potassium stearate concentration, mg/dm^3								
	control	0,015	0,05	0,15	0,25	0,5	1,0	1,5	5,0
immediately	100	-	100	-	100	-	100	-	-
1	100	-	96	-	96	66	96	-	-
3	100	-	96	-	96	66	96	-	40
5	100	100	93	100	93	66	91	100	40
7	100	100	94	100	91	70	91	100	58
10	100	100	100	100	84	72	79	111	48
15	100	91	102	91	100	52	91	100	40
20	100	100	104	93	95	66	99	66	41
30	100	105	100	105	100	70	100	131	35

Threshold concentrations of PS and the nature of their impact on the indicators of self-purification of water are given in Table 6.

Thus, BOD is a limiting feature for the rationing of PS in the water of reservoirs by the impact on the sanitary regime. To clarify the value of the threshold concentrations during stimulation of BOD the amount of oxygen per 1 mg of PS in the process of biochemical oxidation according to [5] was determined:

$$A = BOD_x - BOD_C / C, \quad (1)$$

where A – the amount of oxygen per 1 mg of potassium stearate,
BOD_x – BOD in the experiment, the last term of observation,
BOD_C – BOD in the control, the last term of observation,
C – the concentration of potassium stearate.

Table 6

Threshold concentrations of potassium stearate by the impact on the sanitary regime of water reservoirs

No	Indicators	Threshold concentrations, mg/dm^3	Magnitude of the deviation (in%) and the direction of deviation (↓ ↑) from the control							
			terms of determination (observation day)							
			1	3	5	7	10	15	20	30
1	Impact on BOD	0.05	2↑	7↑	9↑	15↑	13↑	2↑	3↑	-
2	Ammonification processes	0.05	-	18↑	5↑	12↑	-	11↑	8↑	11↑
3	Nitrification processes	0.25	4↓	4↓	7↓	9↓	16↓	-	4↓	9↓
4	Nitrofication processes	0.15	-	-	-	-	12↑	17↓	16↓	-
5	Oxidation	5.0	3↑	8↑	16↑	7↑	7↑	7↑	6↑	14↑

The difference between the experimental and control values determined the amount of oxygen used for the oxidation of each of the introduced concentrations of PS, as well as the amount of oxygen used for the oxidation of 1 mg of PS. The value of the latter is 3.4 mg O_2/mg of the substance.

According to the Rules of protection of surface waters from pollution by waste waters, [7] the water of reservoirs has to contain the dissolved oxygen of 4-6 mg/dm^3. Hence, in field conditions and with a favorable regime of the reservoir, it is possible to use not more than 1-2 mg/dm^3 of oxygen without harming the general sanitary regime of reservoirs. Dividing this value by the amount of oxygen consumed per 1 mg of PS, the concentration was calculated, which is the threshold by impact on BOD, it does not affect the processes of mineralization, water oxidation, dissolved oxygen content and pH of water – 0.25 mg/dm^3.

To substantiate the threshold level value of PS in the water reservoirs (Table 7), the threshold values by organoleptic and sanitary signs of harm and the No Observed Effect Concentration (NOEC) by the toxicological sign of harm were compared [4]. NOEC is calculated from the value of the No Observed Adverse Effect Level (NOAEL), taking into account the average human weight (60 kg) and daily water consumption, which includes water for drinking and cooking (3 liters), according to the formula:

$$\textbf{NOEC(mg/dm}^3\textbf{)=NOAEL x AAW/V = NOAEL x F,} \quad (2)$$

where AAW – average adult weight,
V – volume of daily water consumption,
F is the generalized conversion factor of NOEC to NOAEL.

F=60/3=20

Hence, **NOEC=NOAEL x 20.**

The smallest of them is taken as the maximum allowable with an indication of the relevant sign of harm.

Table 7

Basic hygienic parameters of potassium stearate

Limiting sign of harm	Sign of action	Potassium stearate concentration, mg/dm^3
Organoleptic	The threshold of perception of the sign	6,43
General sanitary	BOD control	0,25
Sanitary and toxicological	NOEC (NOAELx20)	4,0 (0,2x20)

CONCLUSIONS

On the basis of threshold and inactive concentrations by all limiting signs of harmfulness it is allowed to recommend the maximum concentration limit for potassium stearate at the level of 0.25 mg/dm^3. The limiting sign of harm is sanitary. Comprehensive assessment of the obtained experimental data and calculated data on the hygienic rationing of PS in the water of open reservoirs allows classifying it as the 4th class of danger (practically non-toxic substances) [5].

Contributors:

Lototska O.V. – conceptualization, methodology, validation, formal analysis, investigation, data curation, writing – original draft, visualization;

Krytska H.A. – conceptualization, methodology, validation, writing – review & editing;

Kucher S.V. – formal analysis, investigation, writing – original draft.

Funding. This research received no external funding.

Conflict of interests. The authors declare no conflict of interest.

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Стаття надійшла до редакції
22.06.2020