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(EXPLANATORY NOTE)

SPECIALTY 101 "ECOLOGY", EDUCATIONAL AND PROFESSIONAL PROGRAM: "ECOLOGY AND ENVIRONMENT PROTECTION"

Theme: <u>« Safety of modern phosphate-free detergents for aquatic</u>

<u>ecosystems</u>»

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МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ НАВЧАЛЬНО-НАУКОВИЙ ІНСТИТУТ ЕКОЛОГІЧНОЇ БЕЗПЕКИ КАФЕДРА ЕКОЛОГІЇ

> ДОПУСТИТИ ДО ЗАХИСТУ Завідувач випускової кафедри ______ Т.В. Дудар «_____» _____ 2022 р.

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Тема: «Безпечність сучасних безфосфатних мийних засобів для

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1. Theme: « Safety of modern phosphate-free detergents for aquatic ecosystems» approved by the Rector on April, 18, 2022, №388/ст.

2. Duration of work: <u>from 23.05.2022</u> to <u>19.06.2022</u>

3. Output data: scientific literature on safety without phosphate detergents for water systems, international and domestic data on the analysis and methods of phosphate-free detergents.

4. Contents of the explanatory note: analytical review of literature sources on the subject of the diploma. Consideration of materials on the safety of phosphate-free detergents. Introduction to quality assessment methods without phosphate detergents. Recommendations for improving environmental performance and increasing water safety.

5. List of compulsory graphic (illustrative) material: tables, figures, graphs

.6. Schedule of thesis fulfillment

№ з/п	Task	Term	Advisor's signature
1	Receive themes task, search the literature and legislation	08.04.2022	
2	Preparing the main part (Chapter I)	23.05-29.05.2022	
3	Preparing the main part (Chapter II)	30.06- 01.06.2022	
4	Preparing the main part (Chapter III)	02.06- 04.06.2022	
5	Formulating conclusions and recommendations of the thesis	05.06.2022	
6	Making and explanatory note to the previous presentation of the department, consultation with the norms controller	05.06- 07.06.2022	
7	Presentation of the work at the department	08.06.2022	
8	Tacing into account the comments and recommendations and training to protect	09.06- 13.06.2022	
9	Thessis defence at the department	14/15/16.06.2022	

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4. Зміст пояснювальної записки: аналітичний огляд літературних джерел з тематики диплому. Розгляд матеріалів щодо безпечності безфосфатних мийних засобів. Ознайомлення з методами оцінки якості без фосфатних мийних засобів. Рекомендації щодо покращення екологічних показників та збільшення безпеки води.

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2	Підготовка основної частини (Розділ І)	23.05-29.05.2022	
3	Підготовка основної частини (Розділ	30.06-	
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4	Підготовка основної частини (Розділ	02.06-	
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5	Формулювання висновків та рекомендацій дипломної роботи	05.06.2022	
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7	Презставлення роботи на кафедрі	08.06.2022	
8	Урахування зауважень, рекомендацій	09.06-	
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9	Захист дипломної роботи на кафедрі	14/15/16.06.2022	

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ABSTRACT

Explanatory note to the thesis on the topic " Environmental safety of Modern phosphate-free detergents for aquatic ecosystems ", pages-49, figures -6, tables -1, graphs -4 literary sources - 33.

The aim of the work: was to study the environmental safety of modern detergents on aquatic organisms, conducted under experimental conditions.

Object of research: the impact of detergents on aquatic ecosystems.

Subjects of research: is to determine the safety of the impact of Modern phosphatefree detergents on aquatic ecosystems by biotesting methods.

Purpose: was to study the environmental safety of Modern detergents on aquatic organisms, conducted under experimental conditions.

Research methods: analytical, chemical, toxicological, statistical methods of data processing.

Topicality. Among the various common contaminants, detergents pose significant risks to natural ecosystems. The most common are those that contain phosphates, the harmfulness of which there is much evidence. Once in water bodies, they affect aquatic fauna and flora. Eutrophication, foaming, changes in surface tension and pH of water, turbidity, reduction of biodiversity - these are the consequences that need to be controlled. Therefore, the production of modern detergents without phosphates is important and developed countries have long preferred them. However, their impact on aquatic ecosystems remains poorly understood and is currently a pressing challenge for researchers.

Scientific novelty: the analysis of influence of modern phosphate-free detergents on daphnia and two types of seaweed in experimental conditions is made.

WATER POLLUTION, PHOSPHATE-FREE DETERGENTS, BIOTESTING, DAFNIA, AQUATIC ECOSYSTEMS

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LIST OF SYMBOLS, ABBREVIATIONS AND NOTIONS

- D detergents;
- S-surfactants;
- LAS alkylbenzenesulfonate;
- SD Synthetic detergents;
- TPPs tripolyphosphate;
- PFD polyphosphate-based detergents;
- MPC maximum permissible concentrations;

INTRODUCTION

Relevance of the work. Among the various common contaminants, detergents pose significant risks to natural ecosystems. The most common are those that contain phosphates, the harmfulness of which there is much evidence. Gaining access aquatic ecosystems with domestic wastewater, they affect aquatic fauna and flora. Eutrophication, foaming, changes in surface tension and pH of water, turbidity, reduction of biodiversity - these are the consequences that need to be controlled. Therefore, the production of modern detergents without phosphates is important and developed countries have being preferred them for a long time. However, their impact on aquatic ecosystems remains poorly understood and is currently an important challenge for researchers.

Aim and tasks of the diploma work

Aim of the work – was to study the environmental safety of Modern detergents on aquatic organisms, conducted under experimental conditions.

Tasks of the work:

1. Analyze the impact of detergents on aquatic ecosystems

2. To study methods of research of influence of detergents on freshwater aquatic organisms

3. Apply the method of biotesting for Daphnia magna to determine the environmental safety of detergents

4. On the basis of the received data to define action of phosphate-free detergents on daphnia

Object of research is the impact of detergents on aquatic ecosystems.

Subject of research is to determine the safety of the impact of Modern phosphate-free detergents on aquatic ecosystems by biotesting methods.

Methods of research - analytical, chemical, toxicological, statistical methods of data processing.

Personal contribution of the graduate: analysis of scientific literature on the topic

of work, conducting experimental research on the basis of the Institute of Hydrobiology of the National Academy of Sciences of Ukraine, processing and analysis of results, preparation for implementation of research results.

WATER POLLUTION, PHOSPHATE-FREE DETERGENTS, BIOTESTING, DAFNIA, AQUATIC ECOSYSTEMS

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2. Бондаренко А.О, Гетьман А.О, Білик Т.І. Екологічна безпечність сучасних без фосфатних мийних засобів для водних екосистем // Матеріали науковопрактичної конференції Всеукраїнського конкурсу студентських наукових робіт зі спеціальності «Екологія» (17-19 березня 2021 року). – Полтава: Національний університет «Полтавська політехніка імені Юрія Кондратюка», 2021. – 14 с.

3. Білик Т.І., Бондаренко А.О., Гетьман А.О., Тирінова А. І. Перспективи удосконалення систем очищення стічних вод від фосфатів // Комплексне забезпечення якості технологічних процесів та систем (КЗЯТПС – 2020): матеріали тез доповідей X Міжнародної науково-практичної конференції (м. Чернігів , 29–30 квітня 2020 р.): у 2-х т. / Національний університет «Чернігівська політехніка». – Чернігів : ЧНТУ, 2020. – Т. 2. – С.145-147.

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CHAPTER 1.

IMPLEMENTATION OF ENVIRONMENTALLY SAFE DETERGENTS -PROSPECTS OF REDUCING POLLUTION OF AQUATIC ECOSYSTEMS

The usage of detergents (D) to maintain cleanliness of rooms, clothing and personal hygiene is an indisputable achievement of civilization. The rapid development of the chemical industry has led to the emergence of a huge variety of household chemicals, which have received widespread recognition. Household chemistry accompanies us everywhere: in the kitchen, in the bathroom, in the toilet, in offices, in cafes and restaurants. It is necessary to maintain cleanliness of rooms, to wash clothes, to remove dirt, to freshen the air, to wash dishes. The twenty-first century has brought a new meaning to cleaning: if before homework took a lot of effort and time, now with the help of modern D, the result is achieved with minimal cost. However, while maintaining cleanliness with detergents, we underestimate the harm they do. Most detergents contain polyphosphates that are dangerous not only to human health but also to the environment. Surfactants, chlorine, carbon dioxide, nitrogen oxides, phenol, formaldehyde, acetone, ammonia, enzymes, bleaches, abrasives, fragrances – there are not all structures to complete list of chemicals found in commonly used household chemicals. All these components are biologically aggressive. Once in the wastewater stream, detergents can have far-reaching consequences for the environment, especially aquatic ecosystems. [1] Excessive inflow of phosphorus into water objects due to anthropogenic pollution, namely, the use of phosphates in detergents, causes eutrophication, and, as a consequence, the accumulation of biotoxins, deterioration of water quality and death of aquatic organisms. By exhibiting diverse effects on physiological and biochemical processes in aquatic animals, phosphates can significantly affect metabolism and reproduction, modify adaptive responses caused by abiotic factors, thus complicating adaptation to a constantly changing environment [1,2]. This affects the ability of aquatic ecosystems to self-clean, the quality of drinking water and human as an end user.

Today, all developed countries are moving to replace phosphate detergents with

phosphate-free. At the same time, the urgent task is to determine their impact on aquatic ecosystems, which has not been studied yet enough to determine their ecological safety.

In this work is considered the problem of influence of modern phosphate-free detergents on aquatic ecosystems and determination of their ecological safety.

1.1 Modern detergents as sources of aquatic pollution

The development of technologies and the production of environmentally friendly detergents is an important task around the world, primarily due to significant pollution of aquatic ecosystems due to large volumes of insufficiently treated or untreated emissions of enterprises, car washes and domestic wastewater containing high concentrations of toxic substances.

Researchers who have studied the toxicological reactions of synthetic detergents to aquatic ecosystems, including neutralized alkylbenzenesulfonate, appear to be important [3]; contamination of the environment with biopermeable ingredients [4]. The influence of phosphates on natural reservoirs and aqueous solutions was studied by S. Kandu, S. Raindiren, P. Wuver, J. Koehler and others [5;6].

Foreign scientists pay special attention to eutrophication as the first consequence of excessive phosphorus consumption, while identifying three main anthropogenic sources of phosphate pollution: domestic wastewater with dissolved synthetic detergents and cleaning agents, agricultural effluents and industrial effluents with solutions.

fluorine-containing substances. Unfortunately, the increase in such emissions is growing. According to S. Kandu, "If the current level of man-made global impact on the environment continues, in the near future there is a probability of almost 2.4-2.7-fold increase in nitrogen and phosphorus eutrophication of terrestrial, fresh and marine ecosystems" [6]. The main reason for the intensification of these destructive factors is the intensification of urbanization and artificial stimulation of yields on agricultural lands.

Among the various contaminants, detergents pose serious risks to natural ecosystems, especially aquatic ones. They are part of human life and are consumed for various purposes, especially hygienic. Therefore, their components can get into the soil

and water from various sources. Detergents affect the fauna and flora, they have direct and indirect effects on ecosystems. In addition, they can reduce cleaning efficiency by being treated. Eutrophication, foaming and changes in water parameters such as temperature, salinity, turbidity, reduction of water surface tension and pH are important effects that need to be controlled.

One of the problems caused by the high concentration and incomplete degradation of detergents in the aquatic environment is the formation of a layer of foam on the water surface in streams and rivers near dams, which means reduced oxygen penetration from air into water, which reduces the adsorption of dissolved oxygen. aquatic organisms [7].

Most of the compounds in detergents can be broken down to some extent in aerobic destructive processes, but due to their toxicity and limited metabolic pathway, anaerobic degradation is less possible. It has been studied that surfactants can be completely decomposed only under certain conditions, for example, in the presence of special microorganisms for their degradation [8].

In addition to the general toxic effects on biota, there are two major problems associated with the entry of significant amounts of phosphates and surfactants into water bodies. Due to the addition of excessive doses of phosphates to detergents, when they enter water bodies, they cause eutrophication and, consequently, extraordinary growth of algae [9].

Finally, the increase in the mass of organic matter due to the death and degradation of algae leads to a decrease in dissolved oxygen, which causes mortality of aquatic organisms and reduced biodiversity in the ecosystem [10]. In addition to the above problems, water contaminated with phosphates and algal toxins is toxic to humans and aquatic organisms [4; 9].

Among industrial pollution, considerable attention is paid to environmental problems arising from the production and usage of detergents. The term "detergent" has been started to use to refer to synthetic soap substitutes, but today it is any ingredient that can be used as such. Detergents are widely used for industrial and domestic purposes. The problem of sedimentation of ordinary soap in hard water has led to the development of synthetic organic chemicals, the structural characteristics of which are similar to soap,

although their chemical characteristics are different and they have the ability to wash contaminants in water of varying hardness [11]

High concentrations of phosphates in wastewater and outdated technologies lead to insufficient treatment of water entering the wastewater channel. This situation leads to the deterioration of aquatic ecosystems, affects water quality and man as an end user.

In recent years, the amount of phosphates in the wastewater entering the Bortnytsia aeration station has increased sharply (according to PJSC AK Kyivvodokanal) (Fig. 1.1).

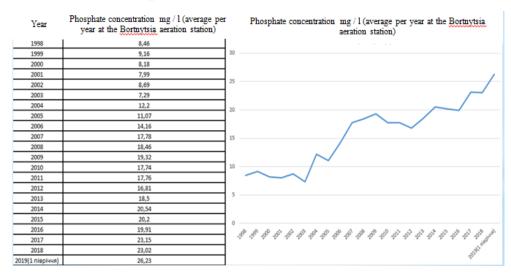


Fig. 1.1. Concentration of phosphates, mg / l (average per year) in wastewater entering the facilities of Bortnytsia aeration station for the period 1998-2019

The figure shows that the concentration of phosphates, mg / 1 (average per year) in wastewater entering the facilities of Bortnytsia aeration station for the period 1998-2019 shows nonlinear growth throughout the reporting period, except for some local extremum declines, which, however, never reached the norm.

Thus, there is now an acute environmental problem of control, and ideally a complete ban on phosphates as components of detergents in order to preserve the biota and ecosystem of water in general, which requires finding ways to reduce the negative impact on the environment due to the production and use of detergents.

If in the mid-90s of the last century the concentration of phosphates in wastewater entering the buildings was 6-8 mg / l, today it reaches almost 30 mg / l, with the standard discharge into the city sewerage network 8.0 mg / l. Phosphates in such significant

concentrations in wastewater significantly impair the quality of treatment, as they affect the biocenosis of activated sludge aeration tanks, reducing the amount of dissolved oxygen. Therefore, the only way to solve the problem right now is to reduce the amount of phosphates entering the aeration station.

Phosphates in such significant concentrations in wastewater significantly impair the quality of treatment, as they affect the biocenosis of activated sludge aeration tanks, reducing the amount of dissolved oxygen. Therefore, the only way to solve the problem right now is to reduce the amount of phosphates entering the aeration station.

A similar situation with changes in the composition of wastewater, accompanied by increasing concentrations of synthetic surfactants (SPAR) and phosphates, has recently developed at many sewage treatment plants in different cities of Ukraine (Kharkiv, Poltava, Lviv, Kramatorsk and others) [12; 13]. This indicates the universality of the problem under study. However, the technology of municipal wastewater treatment using aeration tanks is quite similar.

Ukraine uses a large number of detergents that contain phosphorus compounds, surfactants and other components. Given the global trend towards phosphate detergents, manufacturers are working to develop new phosphate-free formulations to reduce the negative impact on nature and humans. At the same time, there is a need to clarify the issue of their ecological safety for aquatic ecosystems, in particular, the study of toxicity to natural aquatic filters. At the same time, it is important to determine the results of biotesting detergents that have environmentally friendly characteristics.

Modern detergents as sources of aquatic pollution

Among industrial pollution, considerable attention is paid to environmental problems arising from the production and use of detergents. The term "detergent" has come to be used to refer to synthetic soap substitutes, but today it is any ingredient that can be used as such. Detergents are widely used for industrial and domestic purposes. The problem of sedimentation of ordinary soap in hard water has led to the development of synthetic organic chemicals, the structural characteristics of which are similar to soap, although their chemical characteristics are different and they have the ability to wash contaminants in water of different hardness [11].

Modern detergents are a huge range of different products that are currently produced by the chemical industry. The production of synthetic components for them is based on cheap raw materials, often on oil and gas products. They usually do not form sparingly water-soluble salts of calcium and magnesium. Synthetic detergents (SMD) are, first of all, sodium salts of acid esters of higher alcohols and sulfuric acid. Detergents work because they are amphiphilic: partly hydrophilic (polar) and partly hydrophobic (non-polar). Their dual nature makes it easier to mix hydrophobic compounds (such as oil and fat) with water. Because air is not hydrophilic, detergents are also foaming agents to varying degrees. The main component of MR is surfactants.

Other ingredients may include bleaching agents (releasing chlorine or oxygen), soda, liquid glass (silicic acid salts), fillers, foaming agents, stabilizers, water softeners (phosphates, zeolites and polycarboxylic acids), perfumery, perfumery. , dyes, optical brighteners, bactericidal substances (Quaternary ammonium compounds) and other materials [11-15], (Fig. 1.2).

Surfactants are molecules that have an amphiphilic nature with a hydrophobic hydrocarbon tail and a hydrophilic group - the head. The polar part, or hydrophilic component, contains functional groups: -OH, -COOH, -SO3H, -O-, etc., or, more often, their salts -ONa, -COONa. The hydrophil of the main group defines the detergent as anionic, cationic, nonionic or amphoteric; they can all be used in recipes. Most often, linear alkylbenzenesulfonate (LAS) is used as a surfactant - an anionic detergent that is toxic to aquatic organisms and humans [14-15].

Surfactants are used to enhance the wetting, foaming, dispersing and emulsifying properties of detergents. Phosphates are added to soften hard water. An important property of surfactants is surface activity, ie the ability of molecules to adsorb at the phase boundary and reduce the surface tension of the liquid to wet the contaminated surface. Molecules of solutes, wedged between water molecules, make the surface film less durable. Soap sharply - more than twice - reduces surface tension. This means that soapy water can penetrate into the most remote corners, into the smallest pores. The washing action of surfactants is also due to the fact that detergents form highly resistant foams, hydrophobic bubbles which float particles of contaminants. Entering with sewage into

rivers and reservoirs, these substances form on the surface of the water "mountains" of stable foam. In this case, all organisms in these reservoirs suffer

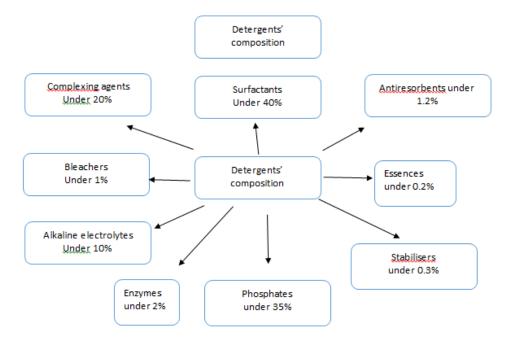


Fig. 1.2. Detergents' composition

For example, the Thames River killed all living things, and even made navigation difficult due to the foam that had accumulated within London. [14]

One of the main negative effects of surfactants in the environment is the reduction of surface tension. In reservoirs, the change in surface tension leads to a decrease in the content of CO2 and oxygen in the mass of water [15]. Since almost all surfactants have a positive adsorption on particles of earth, sand, clay, sediments, they can release heavy metal ions contained in these particles, thereby increasing the risk of these substances entering the biota. on aquatic organisms is associated with their effect on the permeability of cell membranes, as well as inhibition of enzymatic systems of microorganisms. Nonionic surfactants have virtually no such effect. The constant increase in the consumption of nonionic surfactants in recent years is due to the fact that they pollute less (decompose by 100%) and have a washing effect even in hard water [16,17].

The use of large amounts of phosphorus in detergents has become a major environmental problem. Modern detergents may contain up to 30-50% pentane sodium dior triphosphate (eg Na5P3O10 * 6H2O) and some polyphosphates. They firmly bind divalent and trivalent metal ions, which softens water and removes dirt, which consists of sparingly soluble compounds. In addition, polyphosphates enhance the action of surfactants [16-18]. Adsorbed on the fibers, polyphosphate molecules separate dirt particles from the fabric surface and due to electrostatic repulsion promote their distribution in the washing solution. However, they also have a significant disadvantage - they pollute the environment. Products of hydrolysis of polyphosphates accumulate in wastewater, enter natural reservoirs, and because phosphorus is a necessary component for plant nutrition, it creates an undesirable concentration of these nutrients, which causes such a great disaster as eutrophication of water bodies.

Phosphates act as fertilizers after washing together with sewage together with sewage. The "harvest" of algae in reservoirs begins to grow not by days, but by hours. Algae, decomposing, emit huge amounts of methane, ammonia, hydrogen sulfide, which destroy all living things in the water and disrupt the ecosystem of water bodies [19]. Many countries have banned the use of phosphate SMCs. Eutrophication leads to the mass development of not only microscopic algae, but also other microorganisms, bacteria that decompose organic matter. This consumes a significant amount of oxygen, and toxic decomposition products are released into the water, which leads to deterioration of living conditions of aquatic organisms. SMZ are also strong deoxygenators, ie substances that actively destroy dissolved oxygen in water. Therefore, they are dangerous to all living things in the water, even in very small concentrations. For example, it was found that the content of 1 mg of MH in 1 liter of water is toxic to fish [20].

Most developed countries have found safer alternatives to phosphates. The most popular replacement for tripolyphosphates (TPPs) are biologically and ecologically inert zeolites. From a chemical point of view, they are aluminosilicates. Zeolites have high ion exchange properties - they are able to selectively absorb and release various ions and molecules. They do not cause "sticking" of surfactants on the fabric, as a result of which it is easily polished. While when washing with standard phosphate powders surfactants are not completely washed away even after 10 rinses in hot water, remaining on some fabrics, such as wool, in potentially dangerous concentrations for up to four days. zeolites, along with increased environmental safety, have significant hygienic disadvantages: high silicate content, which causes degreasing of the skin; content of more than 7% of anionic surfactants, instead of the hygienic norm of 5%.

One of the main criteria of environmental safety is the ability to biodegradable surfactants that are part of the MoH. Most surfactants currently in use contain components that decompose quickly and efficiently. For example, alkyl sulfates and soaps are derived from fats because they contain unbranched hydrocarbon chains that "teeth" many bacteria. But alkylarylsulfonates, which are included in certain quantities in almost all SMZ, decompose worse, their branched chains of bacteria can not "digest" [19-21]. Contamination of water bodies with detergents is further complicated by the fact that even their biological destruction is not a solution to the problem, as the products of such destruction are in some cases toxic. Microorganisms, passing water through themselves and thus receiving nutrients, together with them receive a dose of contaminant. Contamination spreads along the food chain, the concentration of such a substance per unit weight of each subsequent consumer increases.

Chemical components: chlorine, bleaches, preservatives, disinfectants are practically not broken down. Once in wastewater, they destroy the life of water bodies. Generalized and the scheme of impact of detergents on the environment is presented in Fig.1.3.

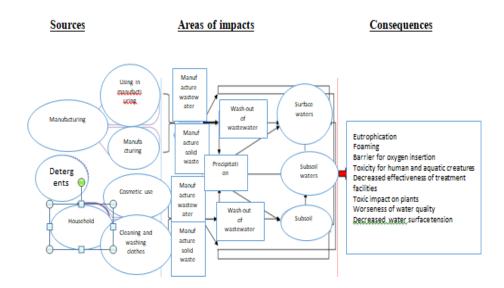


Fig. 1.3. Impact of detergents on the environment

1.2 Impact of detergents on the biota of aquatic ecosystems

The main negative impact of detergents on aquatic ecosystems today is associated with phosphates and surfactants. 1 gram of phosphate provokes the growth of 5 to 10 kilograms of blue-green algae.

The study of the process of hydrolysis of detergents based on polyphosphates (PF) showed that their half-life in wastewater is 7.3 h at 15 ° C and 3.0 h at 20 ° C [22]. Once in the water, phosphorus compounds are included in biochemical cycles of intra-reservoir processes of its cycle and practically do not leave it; the result is excessive production of autotrophs, especially algae and cyanobacteria. During reproduction, blue-green algae form a dense "coating" on the water surface that does not transmit sunlight and oxygen. This high productivity leads to an increase in the bacterial population and high respiration rates, which causes hypoxia or anoxia in poorly mixed bottom waters, as well as in surface waters at night in quiet, warm conditions. Low levels of dissolved oxygen cause the death of aquatic animals and the release of many substances, usually associated with bottom sediments, including various forms of R. This, in turn, enhances eutrophication [19,20]. Bacteria that oxidize organic compounds of algae actively consume oxygen, so the water begins to lack it. This leads to oxygen starvation and death of fish and other fauna in water bodies. Increased concentrations of phosphorus affect the activity of invertebrates. Thus, with increasing concentration of phosphorus in water, the mortality of daphnia, rotifers, diaptomuses increases sharply, which affects the ability of water bodies to self-clean due to the activity of filter organisms [19-23].

Since phosphorus, as one of the main elements of the phosphate buffer system, plays an important role in the mechanism of maintaining acid-base balance in the blood and other body fluids, its excess leads to physiological imbalance and death. With increasing concentrations of phosphates in water there is a risk of acidemia (increased acidity of biological fluids). This can disrupt the balance of acidic and alkaline elements in the blood, and consequently the acid-base balance in fish [19,24]. In addition, all detergents destroy the outer layers of mucus, which protect fish from bacteria and parasites. It has been shown that the accumulation of surfactants in water in a short time can impair the vision of fish, as well as damage the gills [25].

Therefore, in order to maintain the ecological balance in aquatic ecosystems, it is necessary to control the content of phosphates in water and not to exceed it.

3. Ways to solve the problem of environmental pollution with detergents in developed countries

Ways to solve the problem of environmental pollution with detergents in developed countries

Many European countries introduced legal restrictions on the use of phosphates two decades ago. Since then, they have achieved significant results, which has improved the ecological condition of water bodies.

Today, Germany, Italy, Austria, Norway, Switzerland and the Netherlands have legislation banning the use of phosphates in washing powders. In these countries, even car shampoo is produced on a phosphate-free basis. In Belgium, more than 80% of powders do not contain phosphates, in Finland and Sweden - 40%, in the UK and Spain -25%, in Denmark - 54%, France - 30%, Greece and Portugal - 15%. In Japan, as early as 1986, there was no phosphate in washing powders. Laws banning phosphates in detergents are in force in the Republic of Korea, Taiwan, Hong Kong, Thailand and South Africa. In the United States, such bans cover more than a third of the states.[26] In Germany, after the introduction of restrictions on the content of phosphates in detergents and changes in the technology of their manufacture, the concentration of phosphates in wastewater entering the aeration station decreased to 8-12.5 mg / 1. Phosphates are one of the most aggressive water pollutants. In view of this, the world community has set very strict requirements for the content of phosphates in wastewater, drinking water and food. In particular, in western countries, the content of phosphates in surface waters should not exceed 1 mg / dm3, and in drinking water - at the level of 0.03 mg / dm3 [27]. It should be noted that in Ukraine the maximum permissible concentrations (MPC) of phosphates in fishery water and drinking water is 3.5 mg PO4 / dm3, or 0.2 mg P / dm3 [15]. At the same

time, it is known that the action of strong anionic surfactants contributes to severe disorders of protein, fat and carbohydrate metabolism, immunity, damage to the brain, liver, lungs. These substances significantly reduce the barrier function of the skin [28]. Only these factors in Europe have identified all the harm of detergents and banned the use of anionic surfactants in the manufacture of washing powders. Penetrating into the microvessels of the skin, they are absorbed into the blood and spread throughout the body.

World Hygienic Science has identified three main areas for reducing the toxicity of washing powders. The first of them is the replacement of phosphates, softening of water with other substances. Well-known companies "Nenkel" (Germany) and "P & G" (USA) have developed a recipe based on zeolites, a patent issued in 1973. However, it took another nine years for mass production to begin in 1982. Currently, phosphate-free zeolitebased powders occupy a leading position in more than 50 developed countries [29-32]. Another direction to reduce the toxicity of washing powders is the introduction of legislative restrictions on the use of substances that are particularly hazardous to the environment in the Ministry of Health. The third direction is the complete replacement of phosphates and zeolites in the Ministry of Health, development of recipes and production of fundamentally new third-generation washing powders, which would be superior in consumer properties, hygienic and environmental performance washing powders based on zeolites, because zeolites are unfortunately not a panacea. The most hygienically and environmentally friendly washing powders should not contain the following chemical components: phosphates, zeolites, chlorine, sulfates, silicates, ammonia, boron. Strictly limited number of anionic surfactants - no more than 2%; nonionic surfactants of one species - not more than 3%; salts of toxic acids - not more than 1%; cationic surfactants not more than 2%; synthetic flavors - no more than 0.01%, or ideally - odorless; dust - not more than 0.5%. Standards for ensuring a high degree of polishing of D from tissues have also been established.

Today there is a positive trend of growth in the number of household chemicals with improved environmental performance, associated with the adoption in 2008 of the Technical Regulation of detergents, adapted to EU requirements (Regulation № 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents means),

which limits the content of phosphorus compounds at 0.05% since 2017 and sets requirements for the biodegradability of surfactants at 70% for 28 days (total organic carbon).

Thus, state-level control over the composition of modern MoHs, especially the amount of phosphates and surfactants used in them, is important for improving water quality, environmental protection and public health [32,33]. In Ukraine, a consistent government policy is needed to encourage detergent manufacturers to develop and offer environmentally friendly products, as well as to ban the sale of imported products that do not meet environmental and hygienic requirements.

1.4 Conclusion to Chapter I

It has been shown that the contamination of surface waters with phosphates is largely due to the inflow of domestic wastewater containing phosphates as components of synthetic detergents. Washing powders sold on the territory of Ukraine contain 5–35% of phosphate substances that are not removed by outdated cleaning technologies at the Bortnytsia aeration station. To solve this problem, it is necessary to impose restrictions on the use of phosphorus-containing detergents.

CHAPTER 2.

MATERIALS AND METHODS OF INVESTIGATION OF THE INFLUENCE OF DETERGENTS ON FRESHWATER HYDROBIONT FILTERS

The scientific work was performed on the basis of the Institute of Hydrobiology of the National Academy of Sciences of Ukraine on the basis of a cooperation agreement.

2.1. Characteristics of the composition and properties of detergents

Washing powders presented on the Ukrainian market, which are in great demand aDng different segments of the population, were selected for the study. To compare the impact on aquatic organisms, 4 types of washing powders were identified, 3 of which were phosphate-free and one contained phosphates. In order to prevent accusations of advertising or anti-advertising of certain brands, the names of the detergents used are not given here. The following Detergents were used:

D-1- phosphate-free, based on sodium gluconate, medium price category (Ukraine); composition: anionic and nonionic surfactants <5%, sodium gluconate, liquid soap, sodium bicarbonate and carbonate, electrolytes, antiresorbents, silicates, antiresorbent, optical brightener, flavoring;

D-2 - phosphate-free, based on sodium sesquicarbonate, medium price category (Ukraine); composition: anionic surfactants <4%, nonionic surfactants <1%, sesquicarbonate sodium and sodium bicarbonate <35%, electrolytes, antiresorbents, silicates, dye transfer inhibitor, tissue inlay inhibitor, enzymes, perfume composition;

D-3- phosphate-free, medium price category (Germany); composition: anionic and nonionic surfactants <5%, bleaching oxygen compounds, optical brighteners <5%, foam regulator, enzymes, flavoring.

D-4 - phosphate, low price category (Ukraine); composition: anionic surfactants - 5%, nonionic surfactants <5%, phosphates, phosphonates - 9.2% P, polycarboxylates,

enzymes, optical brighteners, flavors. (Fig. 2.1)



Fig. 2.1. Detergents that were selected for the experiment

Analysis of the composition of selected phosphate-free detergents, given by the information available to us from the manufacturers, allows us to determine their main differences:

D-1 contains sodium gluconate as a complexing agent for water softening (environmentally friendly substance), in the powder

D-2 includes sodium sesquicarbonate (an analogue of a natural mineral, "Egyptian salt") in order to soften the water; no specific substances were reported for D-3 powder, D-4 contains phosphorus compounds and slightly More surfactants, and all other components in the powders were similar.

It should be noted that the detailed quantitative composition of detergent formulations is not disclosed by the manufacturers, as this information is protected by the copyright of the developer. At the same time, it is known that in the development of phosphate-free detergents to replace phosphates as complexing agents used sodium gluconate, polycarboxylate, ethylenediaminetetraacetic acid derivatives, sodium sesquicarbonate, which reduce water hardness, binding metal cations and prevent repeating of settling dirt particles on clean surface. Optimization of the system of complexing agents increases the washing ability, reduces the deposition of minerals, stabilizes enzymes, reducing their proteolytic decomposition. The introduction of anionic and nonionic surfactants in a ratio of 1: 2 in the D allows to achieve a degree of detergency of 98%. Besides, fraction of excipients in all reciepes (dye, flavoring, optical brightener, preservative) should be less than 1% for presenting products like ecological – friendly.

Detergents were prepared for the study at concentrations with a concentration of 0.01 to 100 mg/l, in which pH measurements were performed (Table 2.1). As we can see from the measurement results, the pH corresponds to an alkaline environment, increases in the range of 0.2-0.7 units with increasing concentration and differs slightly for different D within the same concentration.

Table 2.1.

The name of the				
name of the powder	D -2	D-1	D -3	D -4
Concentr				
ation				
100	8.56	8.65	8.23	8.74
10	8.07	8.11	8.03	8.09
1	8.0	8.03	8.05	8.03
0.1	8.0	8.01	8.02	8.0
0.01	8.6	8.01	8.03	7.95
Control	7.95			

The results of pH measurement in D solutions

2.2. Representative of freshwater biota *Daphnia magna* as a test object of research

Environmental assessment of the safety of detergents was performed by biotesting solutions in concentrations ranging from 0.01 to 100 mg / 1 in experimental ecological and toxicological studies using as test objects branched invertebrate crustaceans *Daphnia magna*.

The choice of these aquatic organisms was due to the fact that they are characteristic for freshwater ecosystems and are used in standardized biotesting techniques to assess the toxicity of the aquatic environment.[19,31]

Daphnia magna - a species of small planktonic crustaceans ranging in size from 0.2 to 5 mm, permanent inhabitants of stagnant and low-flowing bodies of water. The peculiarity of this species of crustaceans is that in their life cycle alternate generations that reproduce sexually and by parthenogenesis. According to the way of eating *daphnia magna* are active filters. Daphnias' acclimatization to laboratory conditions was performed with maintenance of oxygen and temperature regime of the aqueous medium at a temperature of 25 \pm 1°C for 7 days. *Daphnia magna* was fed daily with chlorella, the concentration of microalgae was maintained in the range of 0.1-0.7 mg C/dm³ (mg of algae organic carbon) [22]. A synchronized, genetically homogeneous culture of *Daphnia magna* was used for the experiments. (Fig. 2.2)



Fig. 2.2. Daphnia magna

Daphnia magna has very interesting structural features. Their whole body is dressed in a leathery, bicuspid shell, which ends with two hooks of a specific horny type. One spherical eye has considerable mobility and consists of a large number of small eyes. Numerous photos taken during the observation of these living beings through a microscope, you can see all the features of such an eye.

Daphnia magna belongs to the species of typical planktonic crustaceans, which spend most of their lives in the water column. Ponds and puddles are home to the most common species of these crustaceans.

The genus *Daphnia magna* is worldwide. Despite the differences in the fauna of all continents, daphnia are found almost everywhere, and is particularly common in several continents.

Crustaceans are very voracious. The main food of *Daphnia magna* is represented by bacteria and unicellular algae. For species that survive the winter in a state of wakefulness, the place of nutrition is the bottom layers and deep freezing water. Under such conditions, the main food for water fleas is detritus.

The method of nutrition is filtration. The ability to create water currents with the help of rhythmic movements performed by the thoracic legs is important. For filtering food, special fans are used, located on the bristles of the filter type. This organ is located in the areas of the endopod from the third and fourth pairs of thoracic limbs.

When large particles get stuck in the filtration apparatus, a special organ, represented by the postabdomen and its claws, is triggered. Filtering fans serve as a transmitting link of food to the abdominal food groove, from which it moves to the maxilla and mandible. The final place for the assimilation of nutrients is the esophagus.

Daphnia magna body is compressed on the sides and everything is covered, except for the head, bivalve shell (carapace). Inside the sink, the body is placed freely, attached to it only by the front.

Between the walls of the shell and the dorsal surface of the animal in females is a brood (embryonic) chamber. The edge of the sink on the dorsal side will be pulled into a long spike. The head is bent to the abdominal side, the frontal part is extended in a downward and backward rostrum. The large middle eye, formed by the fusion of embryonic two complex eyes, is equipped with special muscles that determine its mobility inside the eye chamber. Some species of *Daphnia magna* also have a small odd eye. Short antennae, are the sense organs, articulated in females motionless with the head behind the rostrum; at the end they carry a bundle of sensitive bristles.

The antennae, which are the only organ of motion, are well developed, consisting of a large protodite and two branches, the outer, or exopodite, and the inner, or endopodite, armed with long feathered swimming bristles. Strong muscles are visible inside the antennas. Each antenna is driven by three abductors, three adductors and one levator; the first two abductors and the levator with their striking fan-shaped extended ends attached to the chitin of the dorsal part of the head. The rise of the antenna is due to the reduction of adductors and levator, abductors are their antagonists.

Mandibles, well visible in living organisms for their peculiar movements, devoid of tentacles, on the inside with a large chewing surface, consisting of chitinous plates, armed with spines. Maxillae are abbreviated. Maxill is completely absent. There are five pairs of thoracic legs, are turgor limbs.

Mandibles, well visible in living organisms for their peculiar movements, devoid of tentacles, on the inside with a large chewing surface, consisting of chitinous plates, armed with spines. Maxillae are abbreviated. Maxill is completely absent. There are five pairs of thoracic legs, are turgor limbs.

On the dorsal side of the abdomen (abdomen) there are several abdominal outgrowths that serve to close the back of the brood chamber; behind these outgrowths is a pair of feathered swimming or tail bristles. The posterior part of the abdomen behind the tail setae is called the postabdomen, or caudo. It is bent under the body of the body so that its upper, or dorsal, edge, which opens the anus and are the anal teeth, becomes as if the lower edge; at the end of the postabdomain is Furko, formed by two strong and slightly curved claws, called furcal, or caudal, claws.

The mouth, bounded on top by the upper lip, and on the sides by the mandibles, leads to a short esophagus, which passes into the long midgut, of the same diameter throughout; in the anterior part of the midgut are paired hepatic outgrowths, which have the appearance of short and curved blind appendages located in the head.

The heart looks like a round bag with one pair of side spines. Heart contractions occur at high speed, at room temperature, up to 200-290 beats per minute, which is the limit for animals. Blood from the heart enters the gaps of the body. Osmotic blood pressure at normal conditions are equal to two or four atmospheres. This situation is of great importance for maintaining body shape and elasticity of the limbs (turgor end).

The respiratory organs are the epipodes of the extremities, which are washed by streams of water that cause rhythmic movements of the legs.

How to arrange the provision of paired armor (shells that remain in the thickness of the shell sash, between the outer and inner layers), and well fixed after the separation of the sash from the body of daphnia.

Well the best brain consists of two merged halves. From its anterior part the nerves depart to a complex hole, and on the lower side is often an odd (nauplii) eye.

The reproductive organs of females extend from the sides of the intestine from the first pair of legs to the postabdomain; short berries open on the side of the body of the back of the brood chamber.

All embryonic development of young takes place in the brood chamber between the two links. *Daphnia magna* support parthenogenetic and latent eggs. The latter are enclosed by the inner strongly modified and dark upper part of the sash of the shell, which creates the so-called efippi (saddle).

Daphnia magna differ from the units of the available brood chamber, the ratio of large and mobile antennae and other weapons of the legs of the first pair.

After we learned what daphnia means, the environment of these members of the genus Plankton also remains known to us, because probably many of those who read this article are lovers of domestic fish and want to have such information. So, you can find these tiny crayfish in stagnant waters, such as lakes, ponds, as well as water pits, ditches and even puddles. used for self-procurement daphnia are excellent places for their mass accumulation. Such a place can be found quite easily: where daphnia lives, the water has a gray-green or reddish tinge. Food for them are ciliates, bacteria, plant plankton.

2.3. Plan of experimental research

To determine the impact of detergents on aquatic ecosystems, experimental ecological and toxicological studies were performed using *Daphnia magna* invertebrates.

The choice of these aquatic organisms was due to the fact that they are characteristic of freshwater ecosystems and are used in standardized biotesting techniques to assess the toxicity of the aquatic environment.

To determine the toxicity of daphnia was placed in glass beakers with detergent solutions of certain concentrations of 0.01, 0.1, 1.0, 10 and 100 m/l, respectively, 10 individuals; the control was pure water (Fig.2.3). [19].



Fig.2.3. Preparation of the experiment of biotesting the toxicity of detergents at the test facility *Daphnia magna*

For each concentration of the substance, the experiments were performed in 5 replicates. After 24, 48, 72 and 96 hours, the survival of *Daphnia magna* was calculated according to MOSTU 4166-2003, KND 211.1.4.054-97. Acute (24 hours) and chronic (96 hours) experiments were performed to assess the toxicity of detergents. Statistical processing of the obtained data was performed by the generally accepted methods [31].

2.4. Conclusions to chapter

Daphne is considered to be sensitive to the effects of MS and can be an information test facility to determine the toxicity and environmental safety of detergents.

Development and implementation of modern phosphate-free detergents designed to replace phosphates as complexing agents: trisodium salt of methylglycineacetic acid, sodium gluconate, sesquicarbonate sodium, polycarboxylate, which reduce water hardness - is a promising way to improve their safety for environmental performance.

CHAPTER 3.

ECOLOGICAL SAFETY OF MODERN PHOSPHOSPHATE DETERGENTS FOR AQUATIC ECOSYSTEMS

3.1.Determination of environmental safety of detergents by biotesting for *Daphnia magna*

For standard biological analyzes, there are standardized procedures and methodologies for assessing and monitoring the effects of substances on both one-off and multitasking tests, as well as on field experiments.

Acute toxicity tests are short-term tests that assess the effects of toxic substances on the body over a short period of their lives. He evaluates the impact of substances on the pricing of organisms after 24-96 hours

Initially, these tests were developed for aquatic ecotoxicology, but now for its acute toxicity, even when terrestrial organisms by modifying conventional acute aquatic toxicity tests depending on the nature and existence of habits [32].

We distinguish two main categories of toxic effects:

Acute toxicity - a large dose of short-acting poison, usually fatal, ie the toxic effect of a toxic substance is immediately manifested, directly affects the detected organism.

Chronic toxicity - a low dose of poison over a long period can be fatal or sublethal, the effect is not manifested until after a few days, months or years of activity and often accumulates toxins in organisms, symptoms of chronic intoxication are determined mainly for future generations [33].

The method is based on establishing the difference between the number of dead daphnia in the tested water (experiment) and the water in which the daphnia is kept (control). The criterion of acute toxicity is the death of 50% of *Daphnia magna* and more in the experiment compared to control

for 48 hours of biotesting. Biotesting was performed under standard conditions in a thermoluminescent temperature (25 \pm 2) ° C, illumination 400-600 lux, light period

duration 16 years, dark - 8 years. For control and cooking dilutions of water used drinking water, which previously dechlorinated by settling.

To determine the acute lethal toxicity of the water sample and its dilution, 15 cm3 is poured into vessels (experiment). Other vessels are filled with the same volume of control water. 6 daphnia are placed in each of the experimental and control vessels. *Daphnia magna* is not fed during biotesting. At the end of biotesting, live daphnia are visually counted. *Daphnia magna* are considered alive, which move freely in the water column or emerge from the bottom of the vessel after light shaking.

According to the results of the count of living daphnia calculate the number of dead ceriodaphnia in the experiment relative to control, obtaining the value. Acute lethal water toxicity is considered to be detected if $A \ge 50\%$. According to the results of calculations of dead daphnia (in percent) in each dilution compared to the control is a quantitative assessment (toxicity class) of each sample.

The results of biotesting for Daphnia magna are presented in Fig.3.1-3.12.

The main purpose of the experiment was to test the effect of phosphate-free detergents on aquatic organisms, comparation with the effects of phosphate, as well as establishing how improving the environmental performance of modern phosphate-free detergents affects the survival of daphnia, provided they enter the aquatic environment. .01 to 100 mg / 1. The experiment on acute toxicity (Fig. 3.1.) showed that the highest survival of daphnia was observed in solutions of phosphate-free D -1 at all concentrations studied, even at 100 mg / 1 - 90% of living individuals. The highest mortality was observed in phosphate detergent solutions in high demand.

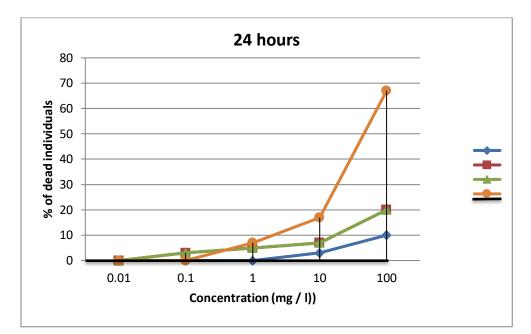


Fig.3.1. Effect of detergents on the survival of *Daphnia magna* after 24 hours of exposure (acute toxicity). Designation: 1- D-1; 2 - D-2; 3 - D-3; 4 –D-4

Phosphate-free powders produced in Germany and Ukraine D-3 and D-2 in this case showed the same good result - 80% of living individuals in the population at a concentration of 100 mg / 1. Studies have shown that this trend persisted after 48 and 78 hours of exposure (Fig. 3.2., 3.3).

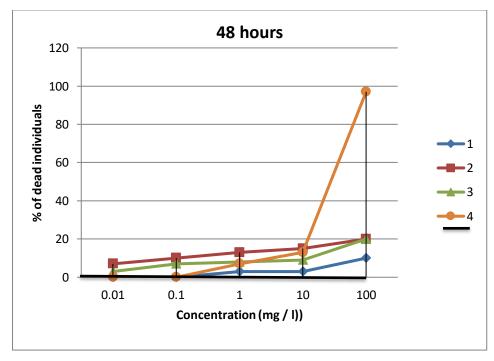


Fig.3.2. The effect of detergents on the survival of *Daphnia magna* after 48 hours of exposure. Designation: 1- D-1; 2 - D-2; 3 - D-3; 4 –D-4

At the same time, with prolonged exposure (96 hours), the Mortality of daphnia increased significantly for all DHs, except for phosphate-free detergent made in Germany. The explanation for this fact may be the presence of decomposition-resistant toxic components of prolonged action in the composition of funds in the case of high mortality and higher rate of their biodegradation in the case of low mortality (27%) *Daphnia magna* in D-3 solution at a concentration of 100 mg / 1.).

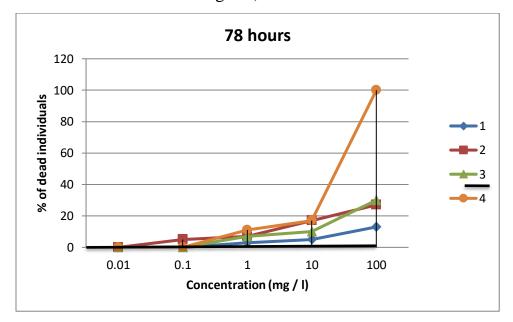


Fig.3.3. The effect of detergents on the survival of *Daphnia magna* after 78 hours of exposure. Designation: 1- D-1; 2 - D-2; 3 - D-3; 4 –D-4

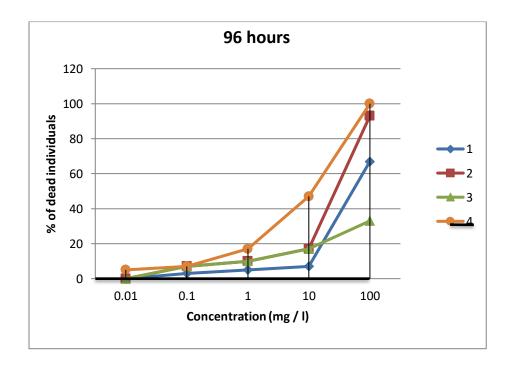


Fig.3.4. The effect of detergents on the survival of *Daphnia magna* after 96 hours of exposure. Designation: 1- D-1; 2 - D-2; 3 - D-3; 4 – D-4

The results of the study showed that concentrations of washing powders up to 10 mg / 1 were low-toxic to daphnia at exposure up to 78 hours, at the same time, with the continuation of the experiment up to 96 hours daphnia mortality increased in D-4 solution. The concentration of 100 m / 1 of phosphate detergent led to the death of almost 100% daphnia at 48 hours of exposure, and all studied without phosphate D showed low Mortality (up to 20%) up to 78 hours of exposure. Thus, we can conclude that the toxicity of phosphate-free washing powders is significantly lower than that of phosphate, and the best survival rates of Daphnia magna among them showed D-1.

3.2. Comparative characteristics of the impact of detergents on freshwater aquatic organisms and their environmental safety

It is well known that the role of filter organisms in the purification of water from a number of pollutants of both natural and anthropogenic origin, which is of great importance for the ability of natural aquatic ecosystems to self-purify. At the same time, the toxicity of xenobiotics may exceed the tolerance of organisms to them, which causes their death and will affect the ability of aquatic ecosystems to self-clean. Toxicity studies on Daphnia magna have shown significant safety of phosphate-free synthetic detergents, which used harmless substances instead of phosphates as complexing agents. The highest survival of daphnia was observed in solutions of phosphate-free D -1 based on sodium gluconate at all concentrations studied.

It should be noted that the author of the diploma took part in a number of events organized by the Kyiv City Administration and PJSC AK Kyivvodokanal to discuss the problem of phosphate surface water pollution and find ways to solve it, in particular, in the action STOP PHOSPHATES. (Appendix 2)

Photo information about this is presented in the Appendix.

3.3. Conclusions to chapter

The development and implementation of modern phosphate-free detergents to replace phosphates as complexing agents: trisodium salt of methylglycineacetic acid, sodium gluconate, sesquicarbonate sodium, polycarboxylate, which reduce water hardness - is a promising way to improve their environmental performance and improve their environmental performance

CONCLUSIONS

1. It is shown on the basis of the analysis of scientific sources that the pollution of surface waters with phosphates is largely due to the inflow of wastewater containing phosphates and other harmful substances as components of synthetic detergents. This causes eutrophication, release of toxins, death of aquatic organisms and degradation of aquatic ecosystems. Washing powders sold on the territory of Ukraine contain 5–40% of phosphate substances that are not removed by outdated cleaning technologies. To solve this problem, it is necessary to impose restrictions on the use of phosphorus-containing detergents at the state level, as did most developed countries.

2. Ecological and toxicological evaluation of detergents by biotesting for Daphnia magna showed significant safety of phosphate-free D: the highest survival of daphnia was observed in solutions of phosphate-free D -1 at all concentrations studied, even at 100 mg / 1 - 90% of living individuals. Phosphate-free powders produced in Ukraine and Germany D-2 and D-3 in this case showed the same good result - 80% of living individuals in the population at a concentration of 100 mg / 1. Studies have shown that this trend persisted for 78 hours of exposure. The highest mortality was observed in solutions of phosphate detergent of high demand D - 4 led to 100% death of branched crustacean filters in 48 hours.

3. Creation and implementation of modern Phosphate-free detergents, which contain sodium gluconate, polycarboxylate, ethylenediaminetetraacetic acid derivatives, sodium sesquicarbonate, which reduce water hardness, to replace phosphates as complexing agents, are a promising way to improve their environmental performance and increase water safety.

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APENDIXES

Appendix 1A.

PARTICIPATION OF THE AUTOR IN EXPERIMENTAL RESEARCH



Fig. A.1.

PARTICIPATION OF THE AUTOR OF THE WORK IN THE AII-UKRAINIAN ACTION "STOP PHOSPHATES"



Fig. A.2.1.



Fig.A.2.2.

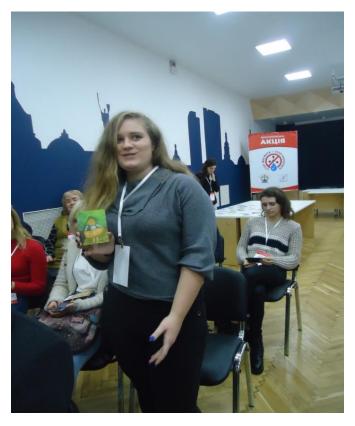


Fig. A.2.3.



Fig.A.2.4.



Fig.A.2.5.