

On the issue of sanitary and hygienic condition of the river network of the Pokutsko-Bukovynian Carpathians

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Abstract

The sanitary-hygienic and microbiological condition of surface waters of the river network of the Pokutsko-Bukovynian Carpathians is analyzed. As a benchmark for comparing the impact of anthropogenic activities on the state of mountain ecosystems, we have chosen the protected areas of the Vyzhnytskyi National Nature Park (hereinafter NNP), where for more than two decades a specific ecosystem has been formed related to environmental protection.

The main risks to the ecological safety of the hydrosphere of the studied region have been identified. Two types of ecological threats have been identified: microbiological pollution of streams and watercourses by domestic effluents and washes of polonyn farms and pollution of the hydrosphere by effluents of processing enterprises. Contamination of surface waters with organic residues is accompanied by a change in their hydrochemical composition and the level of contamination of indicative forms of bacteria. Based on the monitoring studies of the hydrosphere, the main threats were identified and engineering and technical and management solutions were developed to minimize the level of ecological danger of the mountain ecosystem.

In order to improve the quality of surface waters of the river network, the use of special structures "ViKa", mounted on the basis of wooden structures of pulp and fibrous carrier "Via", as well as the use of a modified method of obtaining pellets and wood waste from adjacent loggers based on lignin soap. To reduce the inflow of discharges into the river network of alcohol enterprises, in the absence of centralized treatment facilities in the region, the method of waste treatment using a reagent method based on sodium hypochlorite was quite effective.

It is shown that one of the ways to reduce the loss of the river network by wood waste may be the creation of facilities for the production of fuel pellets and briquettes in traditional economic landscapes.

Keywords: surface waters, river network, organic pollution, water quality, protected areas, engineering and technical solutions, Pokutsko-Bukovynian Carpathians

1. Introduction

A lot of research has been done to determine the quality of surface water, which proves the urgency of this issue in connection with the exacerbation of the problem of drinking water on the planet. Assessing surface and groundwater quality remains a major public interest in the developed world fecal contamination of water and thus to assess health hazards (Ince et al., 2011; Rylskkyi and Masikevych, 2012; Pall et al., 2013). Identification of pathogenic bacteria in water, according to a number of researchers, is one of the main problems in assessing the safety of the environment for human health and the ecosystem in general. Microbiological contamination of *E. coli* is one of the specific indicators of fecal contamination in tropical and temperate regions. The study of bacterial water density can provide an approach to assessing the reliability of monitoring data. Fecal indicator bacteria, such as total coliform forms, fecal coliforms (thermotolerant coliform forms), *Escherichia coli* and intestinal enterococci (fecal streptococci), are released by humans and warm-blooded animals into wastewater in large quantities, and these bacteria retain longevity and longevity (Megan et al., 2020; Srivastava, 2020). In order to study the differential detection and quantification of the viability of *Escherichia coli* cells in recent years, in addition to traditional methods of culture on nutrient media, use quantitative polymerase chain reaction (Deshmukh et al., 2021), flow cytometry, inclusion and sequencing of the 16S rRNA gene (Kirschner et al., 2021).

Pathogens themselves are normal components of natural ecosystems, but the growth of fecal bacteria due to anthropogenic activity is a very important problem of the river network of the Carpathians and in particular the Danube basin (Kirschner et al., 2021; Mayr et al., 2021; Pekarova et al., 2021). Studies conducted by the authors have shown that the Danube Delta, where the biosphere reserve is located, has become one of the most vulnerable ecosystems. The Danube is one of the most important rivers in Europe and the world. To preserve its ecosystem in 1991 in the river delta created a biosphere reserve. Despite this, the water areas of the Danube are subject to severe physical, chemical and biological pollution. The river network of the Pokutsko-Bukovynian Carpathians is a component of the Danube basin (its upper part), where intensive anthropogenic activity is developing. Bacteria turned out to be ideal markers of microbial contamination of surface waters due to their rapid response to environmental changes.

Fecal coliforms and intestinal enterococci are good indicators for assessing fecal emissions and the potential presence of pathogens, which are mainly due to untreated wastewater from agricultural lands and pastures. However, the low

concentration of bacteria in surface waters, high costs and long-term detection technologies create certain methodological limitations in this way.

Therefore, the search for simple and affordable technologies for detecting minor amounts of pathogens remains relevant today. It should be noted that the use of sanitary-microbiological indicators to assess the condition of protected areas is now episodic and does not apply to specific functional areas of these areas (Mudrak, 2012; Patyka and Symochko, 2013).

2. Materials and Methods

2.1. Object and concept of research

The object of the study was the sanitary-hygienic and microbiological indicators of surface waters in the region of Pokutsko-Bukovynian Carpathians. The aim of the research was to investigate the ecological condition and to develop a system of engineering measures to minimize the ecological danger to the river network. The defining point of the research was the monitoring of pollution in the Pokutsko-Bukovynian Carpathians. The hydrological grid of the research region is presented in Fig.1.

As a benchmark for comparing the impact of anthropogenic activities on the state of the river network of mountain ecosystems, we chose protected areas located in the Pokutsko-Bukovynian Carpathians, in particular the Vyzhnytskyi National Nature Park (hereinafter NNP). To prevent microbiological contamination of streams and watercourses, we used a fibrous carrier type "Vija" (TU 995990), made of textured plait thread (TU 6-06-C116-87, tex 350). Earlier, a number of authors (Hvozdiak, 2003) found that the fibrous carrier "Vija" can be successfully used for the construction of "bioreactors" for surface degree of purification. The reliability of the results is ensured by laboratory control of errors in the composition of the samples and mathematical verification of data for a statistically significant relationship using rank correlation coefficients. The validity and reliability of the conclusions and recommendations are confirmed by the close connection of theoretical and experimental data. water treatment. Invertebrates, where they are able to accumulate, which is the basis of water treatment. In addition, some bacteria become part of the food chain and serve as food for invertebrates trophic chains on the second. To minimize the environmental risk of pollution of the hydrosphere by effluents of processing industries used a reagent method of contamination (use of sodium hypochlorite solution), which is effective, reliable, allows to provide the required.

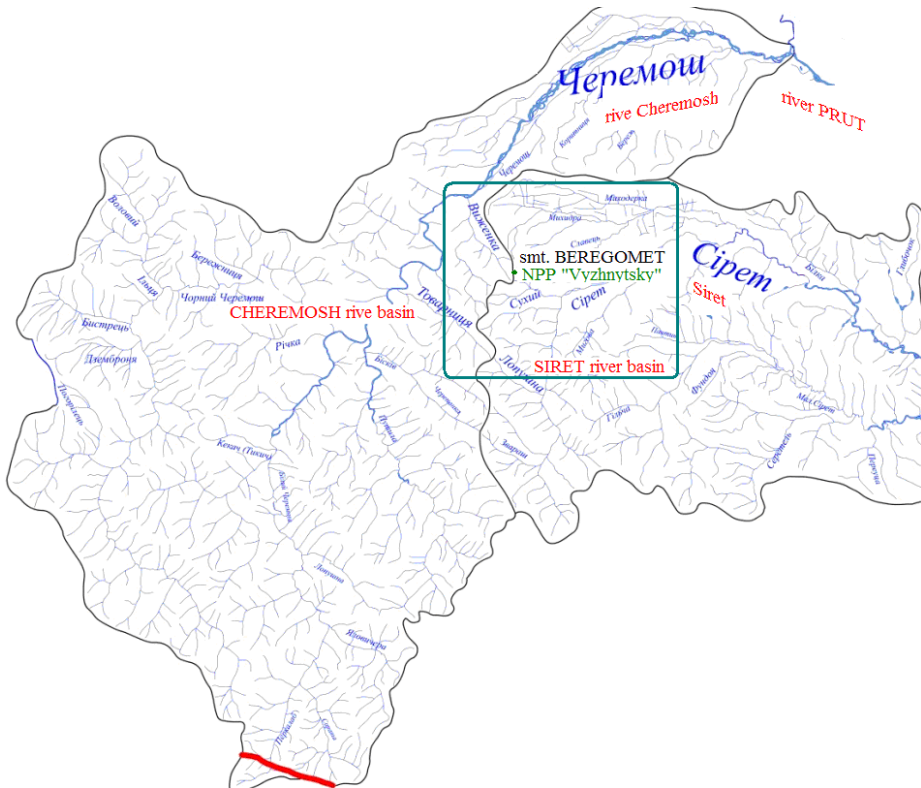


Fig.1. Hydrological network of the Pokutsko-Bukovynian Carpathians

2.2. Methods for determining the sanitary and hygienic indicators, chemical composition and pH of the aquatic environment

Determination of chemical oxygen consumption (COC) determined by the dichromate method according to the method in the presence of phenylanthranilic acid as a redox indicator of orange green (MVV 081/12-0019-01). The value of chemical oxygen consumption (COC, $\text{mg O}_2/\text{dm}^3$).

The biochemical oxygen consumption (BOC-5) index was determined by the method (MVV 081/12-0014-01).

Determination of the pH of the aqueous medium. The pH of the aqueous medium was determined by electrometric method, according to DSTU 4077–2001. "Water quality. Determination of pH" and instructions for the device Ionomer laboratory I-160 MI.

Water sampling was carried out in the Chyremosh and Siret river basins, which flow into the Pokutsko-Bukovynian Carpathians and are part of the Ukrainian part

of the Danube basin. The research was conducted during the summer season of 2013–2020. Water sampling (23–25°C) was carried out by watercourses of various functional zones of the protected object of national importance (Vyzhnytskyi National Nature Park) and territories of landscapes with intensive economic activity. Coli-index, total microbial count was determined by generally accepted methods in accordance with methodological guidelines (Nakaz MOZ Ukrainy 284, 2007).

To confirm the morphological and other properties of the culture of microorganisms used the method of microscopy with subsequent identification according to the determinant of Bergi (Khoult et al., 1997).

3. Results and discussion

3.1. Sanitary and microbiological condition of surface waters

The obtained results show that downstream of the studied watercourses in the territories of the NNP (at the transition from the protected to the economic zone), the nitrate content increases in the water, the BOC indicator increases and the dissolved oxygen decreases. It is established / that there is an increase in pollution of the river network with organic residues, in particular they may be fecal compounds of the economic zone, where there are no active treatment facilities. Studies of sanitary and hygienic indicators of the part of the river network adjacent to the Vyzhnytskyi National Park and not part of it, showed a significant increase in the content of suspended solids in water (mainly sawdust – wood processing waste), compared with the reference "protected" area of the NPP (Table 1). The increase in the content of suspended solids is accompanied by a decrease in free oxygen in the water and an increase in the value of BOC, COC, total oxidation. At the same time, the content of chlorides and nitrites (salts of hydrochloric and nitric acids) in water increases, which leads to acidification of the river network (pH = 5.8, below the norms (San PiN 4360-88; Surface Water Directive). It also turned out that the river network of territories with traditional management in terms of sanitary and hygienic indicators is inferior to the quality of water samples taken from the watercourses of the "economic zone" of the NNP (Fig. 2).

In addition, we conducted a study of the microbiological state of water of all these objects. Indicators include coli index, coli titer, and microbial count. In most cases, there is a direct correlation ($r = 0.95$) between the indicators of biological BOC, COC and the value of microbiological indicators. Studies have shown that the values of sanitary-microbiological indicators increase downstream in all these watercourses. This was especially true of the increase in the number of lactose-positive *Escherichia coli* (*E. coli*) per 1 liter of water (coli-index). It should be noted that *Escherichia coli* is a sanitary indicator and indicates fecal contamination in this case of water bodies.

Comparing the coli-index in the river water samples of the protected area and the selected water samples in the economic zone, we found an increase in the coli-index on average by 2 times (Table 1).

The total microbial count (CFO/dm³) was 2–4 times higher than the normative indicators adopted in the EEC countries (Surface Water Directive: 75/440 EEC) and was 1500–1700 (for the protected area), 2300–3500 (for the stationary recreation area) and more than 5000 (for the economic zone).

A comparative analysis of microbiological indicators of surface water bodies of the NNP economic zone and traditional management areas adjacent to the protected object is shown in table 1, which shows that there is a significant difference in water quality in the river network between these areas.

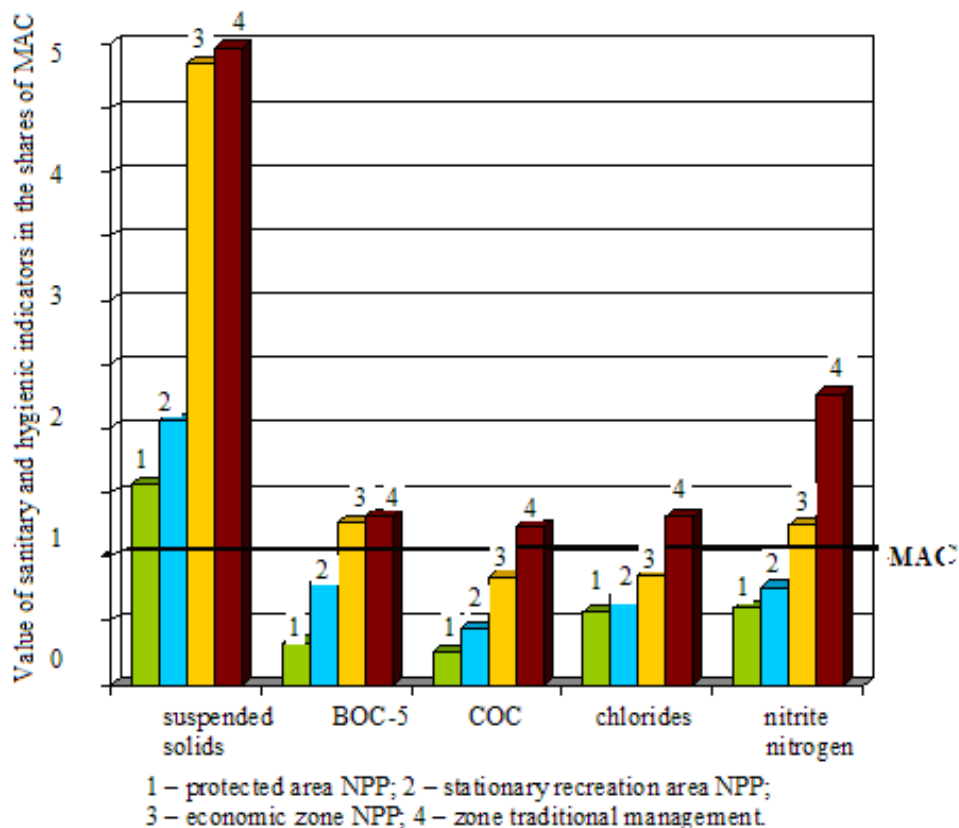


Fig. 2. Sanitary and hygienic indicators of surface waters of Pokutsko-Bukovynian Carpathians in shares of maximum allowable concentration (MAC)

Table 1. Comparative analysis of sanitary-microbiological indicators of surface waters of the economic zone of NPP "Vyzhnytskyi" and adjacent to the NPP areas of traditional management

N	Sanitary-microbiological indicators	economic zone	adjacent areas NPP	(±), B %	San PiN 4630-88	EEC Water Directive
1	Coli Index (CFO/dm ³)	107.5 ±13.5	122 ±10.2	+13.5		
2	Total microbial count (CFO/dm ³)	5350 ±270	6500 ±310	+21.5	<5000	<5000

- CFO – colonies forming organisms

Figures 3 show the dynamics of the main microbiological indicators of the aquatic environment of different functional load and conservation status of the Pokutsko-Bukovynian Carpathians over the past 10 years.

Based on monitoring observations, it can be stated that there is a progressive trend of pollution of the river network in the territories of traditional economic landscapes, which are outside the protected areas and where there is active anthropogenic activity. At the same time, the relative stability of the studied indicators of the hydrosphere is preserved within the protected areas, despite the existing some annual fluctuations.

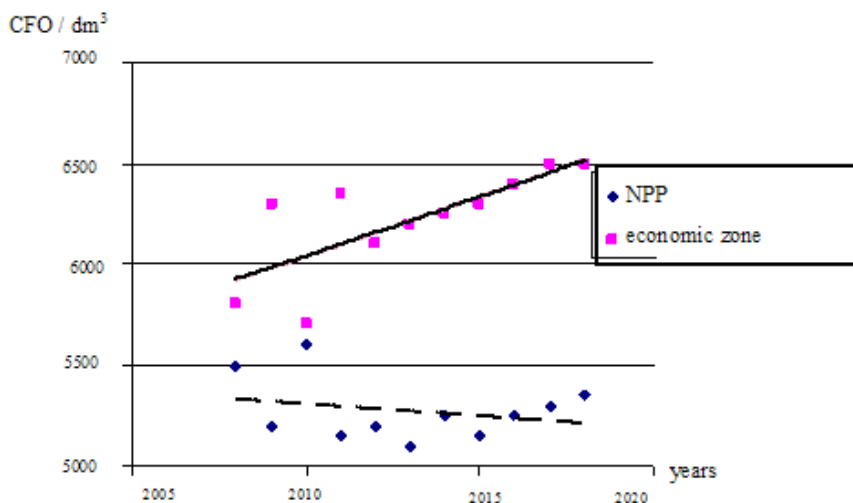


Fig. 3. Dynamics of the total microbial number of surface waters of the river network of the Pokutsko-Bukovynian Carpathians; CFO – colonies forming an organism/dm³; the difference is significant at $p < 0.05$

3.2. Technical measures are aimed at improving surface water quality

Research to reduce the level of organic and microbiological pollution of watercourses. In order to improve the quality of surface waters of watercourses, we used a fibrous carrier type "Via" (TU (995990), made of textured plait thread (TU 6-06-C116-87, tex 350). Previously, a number of authors (Hvozdiak, 2003; Rylskyi and Masikevych, 2012) established that the fibrous carrier "ViKa" can be successfully used for the construction of "bioreactors" for surface water treatment, for saturation of streams with oxygen. This design is presented in Fig. 4.

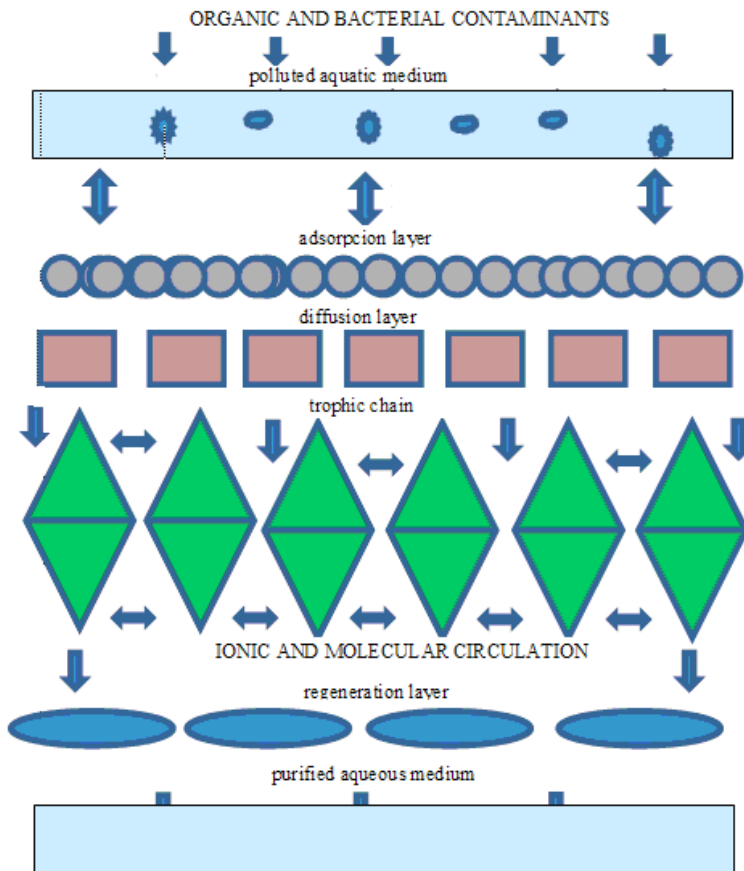


Fig. 4. Schematic representation of the processes occurring in the "bioreactor - ViKa"

During the season, "Vija" is overgrown with invertebrates (the so-called periphyton is created). Bacteria and algae also accumulate on the eyelashes. As can be seen from Figure 5, "Vija" is capable of almost 15-fold accumulation of bacteria and aquatic organisms.

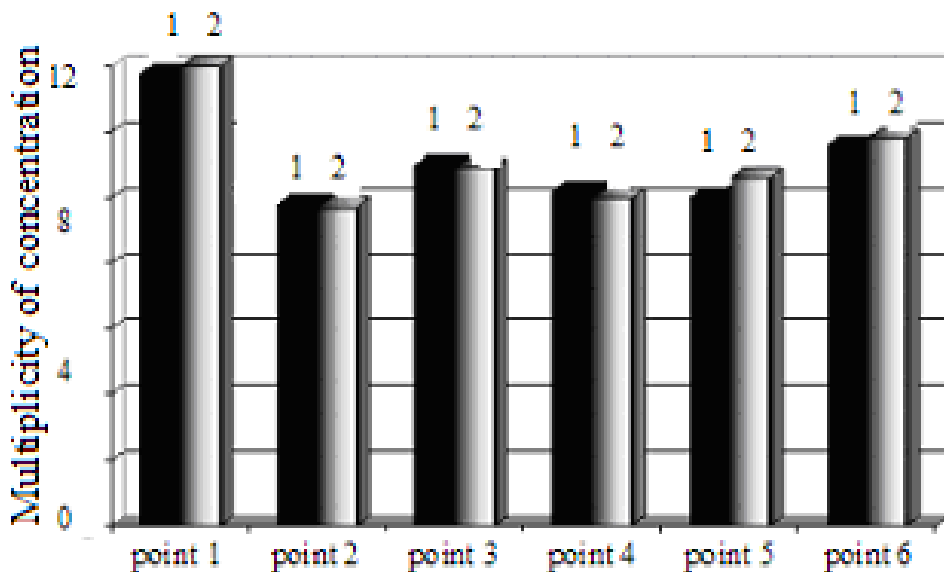


Fig.5. Accumulation of bacteria and aquatic organisms on a fibrous carrier type "Vija":
1 – temperature 23°C, 2 – temperature 6°C

A specific "biofilter" is formed on fibrous media in the form of an artificially created microecosystem. In it, such a carrier serves as a kind of "home" for microorganisms, plant and invertebrates, where they are able to accumulate, which is the basis for water treatment. In addition, some bacteria become part of the food chain and, consequently, food for invertebrates. Thus, the purification of reservoirs is observed in two stages: due to adsorption on a synthetic carrier on the first and a trophic chain on the second. The mounted cleaning device "ViKa" ("Vija" + "Kashytsia") works on the principle of a bioconveyor, which was once described by P. I. Hvozdyak (Hvozdiak, 2003). In fact, the proposals and arguments presented by the author became both a theoretical and methodological basis for the creation of the treatment plant "ViKa". The "ViKa" bioconveyor accumulates a significant amount of BECG (*Escherichia coli* bacteria), forming a spatial succession of microorganisms, as well as a trophic chain of aquatic organisms, which includes representatives of eight systematic groups: see section 3). In terms of numbers, the studied microperiphyton was dominated by ciliates (510 specimens/100 cm²), rotifers accounted for 33% of the total number of fouling biocenosis. Both prokaryotes (aerobic and anaerobic microorganisms) and eukaryotes (filters and predators of different trophic levels)

take part in the water purification process. The advantages of the proposed scheme of natural water treatment are that the biomass accumulated on "Via" is consumed and mineralized in the trophic chain, as evidenced by the indicators of BOC, COC, the amount of suspended solids in the water. For comparison, we note that during the treatment of wastewater with activated sludge involved in the process only protozoa and bacteria (others can not survive in the toxic fluid of collectors), while in the case of treatment plant "ViKa" also involved more complex aquatic organisms (consumers II tv. III order), forming a more complete trophic chain. In nature, a priori, there is no organism that could dispose of all types of pollution and even yourself. On the contrary, there are many organisms in the biosphere that form complex hydrobiocenoses and that are able to work on the principle of "bioconveyor". There are many examples when treatment plants based on synthetic fiber "Via", arranged for direct-flow biotechnology, have become very efficient, easy to maintain, environmentally friendly, low-cost facilities that have been operating for decades. Thus, we can assume that the fibrous carrier "Via" (which is similar in structure to man-made fibers) not only serves as a substrate where BGKP and a number of aquatic organisms accumulate, but also is a hiding place from predators and a source of food because it retains particles gross detritus. The results obtained by us fully confirm the opinion (Hvozdiak, 2003) that "the future of biotechnology to protect the environment, in particular water, from chemical and biological pollution – in the use of as much diversity as possible in these technological processes."

Wastewater treatment of an alcohol enterprise by the reagent method.

Pollution of the hydroecosystem of the Pokutsko-Bukovynian Carpathians and Precarpathians by effluents of small processing enterprises, which contain mostly organic pollutants, can be minimized, in our opinion, by an effective reagent method that allows for effective treatment. The most available, safe, and cheapest reagent that can be used to oxidize organic compounds is sodium hypochlorite, a multi-ton production waste.

Indicators such as COC and dry residue were used as criteria for cleaning efficiency. The protocol of sewage tests of Vashkivtsi distillery showed an increase in wastewater, the concentration of nitrates, sulfates, suspended solids and indicators of COC and BOC, which suggests the presence in the discharges of proteins, fats and carbohydrates and the process of biodegradation of organic pollutants. The results of experimental studies are presented in Fig. 6.

As can be seen from Figure 6, it is optimal to use hypochlorite for sewage treatment in the ratio of 0.5 L/m³ of the effluent to be treated. This ratio is recommended for the introduction of industrial wastewater treatment technology at the Vashkivtsi distillery.

Improving the technology of wood waste disposal. We studied the technology of utilization of wood processing waste by creating fuel pellets and briquettes using as a binder waste pulp – paper production – sulfate soap, the main component of which is lignin. This approach allows to significantly reduce the working pressure in the equipment where the pellets are formed, and to involve in the production of low-grade wood waste. In the process of extrusion method of obtaining granules, to improve their quality, we used a lignin binder. In Fig. 7 shows the results of experiments to determine the static strength of the briquette with the addition of different concentrations of binder.

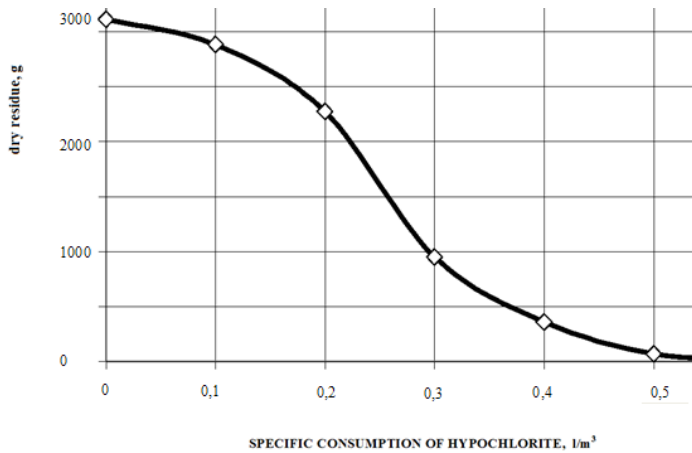


Fig. 6. The dependence of the mass of the dry residue on the specific consumption of hypochlorite

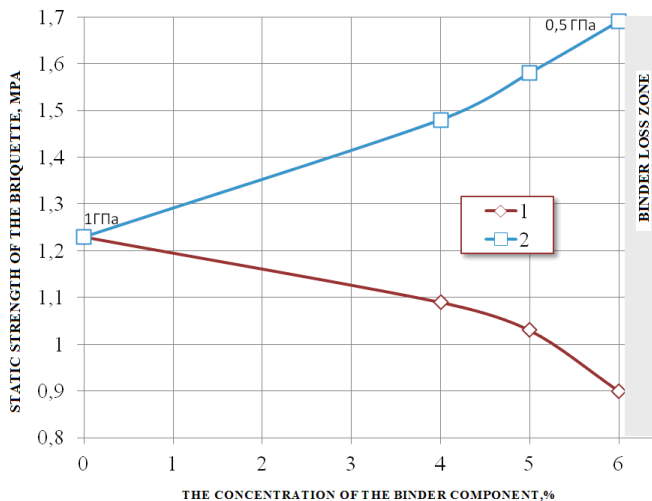


Fig. 7. Change in the static strength of the briquette with different concentrations of binder depending on the pressure: 1 – supply of the binder component in the center of the mixture, 2 – mixing of the binder component with wood waste

From fig. 7 shows that the static strength increases in those briquettes in which the binder was mixed with wood waste. This is due to the better distribution of the binder within the volume of the briquette with the formation of a reinforcing frame of wood, and the binder did not allow it to disintegrate.

4. Summary and Conclusions

As a result of research, 2 types of environmental threats to surface waters of the region were identified: microbiological pollution of streams and watercourses and pollution of the hydrosphere by effluents of processing enterprises, which are a common industry in the study region. The prospects of the method of biological purification from organic and microbiological pollution of watercourses of the hydroecosystem of the Pokutsko-Bukovynian Carpathians and minimization of ecological danger from their negative impact on the hydrosphere by using a fibrous carrier type "Via" are proved. A method of wastewater treatment of processing enterprises from organic pollutants by oxidation of them with sodium hypochlorite has been developed. The proposed method does not require a radical restructuring of existing treatment facilities and significant material costs to create new ones based on our proposed technology. Failure to comply with the requirements for the formation of protected areas on the watershed principle leads to significant contamination of soils and river network with sawdust, bark and other wood waste requires the introduction of urgent measures for the disposal of this type of waste. Grinding of wood waste and their preparation do not require large costs, and lignin-binding substance requires proper disposal.

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