

THE ANALYSIS OF THE THREAT OF REUSING PET BOTTLES FOR THE STORAGE OF DRINKING WATER

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Introduction

Up to present-2017-year in Ukraine existing an ambiguous situation. Known, that 450 cities (100%), 783 (88%) of urban-type villages and 6490 (23%) of villages being ensured by tap-water, what covering more than 70% of the all country population (according to the World Bank the total population of Ukraine for 2016 was more than 45 million people). But the quality of tap water isn't satisfy over than 88% of the respondents from Kharkiv, Ukraine. The same situation can exist in some other cities and villages. The taste of chlorinated water which transported by old, rusty water-pipes are being characterized by the majority of respondents as "unsatisfactory". That's why the population of Kharkiv usually buys, as a drinking-water, the water from artesian wells (46% of pollees) or independently takes the water from certified sources (34% of pollees). At the same time, for storing and transporting the drinking-water, the population of Kharkov mostly (68.8% of pollees) uses PET bottles. In the case of reuse it's can pose a serious threat to health.

The idea of reusing PET bottles for a water storing isn't new. Research of the possibility of reusing PET bottles for a water storing was conducted by scientists from the United States [1] and Canada [2]. The results of research clearly indicate the impossibility of using disposable PET bottles without disinfection.

Known, that in countries with high ecological literacy the used PET bottles are sorted and completely remanufactured [3], so the necessity of their sanitary treatment isn't considered. In addition, existing disinfectants for polymers are based on acids or alkalis can't be used for PET disinfection. Such substances can destroy the polymer or/and provoke the migration of monomers from it. It should be mark, that some of monomers, like phthalates or alkylphenols, can be very harmful for a human health [4].

If PET bottles of small volume have an alternative in the form of bottles of individual use made of a special polymer, then PET bottles of a large volume (in volume of 5 - 19.5 liters) for the storage of drinking water don't have an alternative. For many years, Ukrainians have used disposable PET bottles as water tanks, and since there is no

alternative, they will still use it even if they understand that PET bottles are disposable. About 55% of respondents from Kharkiv, realizing that PET bottles are disposable, still use them without replacement more than a one month.

PET has been used in the food industry for more than forty years. The first PET bottles appeared in 1973 and are used today. The question of the chemical hazards of PET has risen more than once. Today there is a clear position shared by such organizations as International Life Science Institute, Pediatric Environmental Health Specialty Units, Plastics Europe, European Federation of Bottled Waters and some others. This position is that when using PET bottles, the release of hazardous chemicals into the water, in particular BPA [4], in concentrations that can harm a person is impossible. Migration of monomers from PET to water almost does not exist; the amount of such substances in water cannot exceed the MPC.

Thus, it is possible to use PET bottles in terms of chemical safety for humans. However, this only applies PET, HDPE, LDPE and PP. All other types of plastic that are used to store food are undesirable.

Among the risks that can be caused by the repeated use of PET packaging, microbiological - the most dangerous. In the report for EPA Advisory Committee in 1993, Dr. Robert Tardiff identified by objective criteria that microbiological contaminants are much (1000 to 100000 times) more dangerous than chemical. Under the chemical contaminants should be understood as so-called "Disinfection By-Products (DPB)". Dr. Tardiff's report talked about the by-products of chlorination of water. Many studies, including those conducted on request U.S. Environmental Protection Agency [5], American Chemistry Council [6] and others are identified as potential carcinogens. The negative impact of such substances on human health has been investigated by WHO [8]. Therefore, even chlorinated water that contains potential carcinogens is safer than water contaminated with microorganisms.

Materials & Methods

The sociological survey method

In a sociological survey, 584 respondents from Kharkiv, Ukraine aged 18 to 75 years took part. The form of the survey was a questionnaire. The questionnaire composed of 15 questions. All of respondents independently answered the questions. The answers for some questions was a simple (Yes/No/No answer) and for some questions the respondents wrote extended answers. The original questionnaire was in Ukrainian, so we translated it to English. The English questionnaire is in Figure 1.

Date	Place	Time	Age	Sex	Do You have kids?
Does the tap water for drinking satisfy you (why)?		What kind of drinking water do you use?		Do you always (even in the summer) boil the drinking water before you use it?	
<input type="text"/>		<input type="text"/>		<input type="text"/>	
Do you have a plastic bottle for water storage of volume 3 liters or more (how many)?		Do you know that some polymeric bottles are only one-time use?		How often do you change a bottle of water (which forces you to throw a bottle)?	
<input type="text"/>		<input type="text"/>		<input type="text"/>	
Do you know what type of plastic your bottle is made of (specify type)?		Do you disinfecting your own water bottle before using it (how)?		Do you think is using of your water bottle puts your health at risk (why)?	
<input type="text"/>		<input type="text"/>		<input type="text"/>	
If the city municipality offer a plastic water bottle sanitation tool for you, will you use it (why)?		Would you like to sanitation your plastic water bottles?		Would you like to receive information about the threats contained in plastic bottles? (enter your email address, please)	
<input type="text"/>		<input type="text"/>		<input type="text"/>	

Questions are optional to answer. If you don't want to answer a question, put "-" or a text or a sign of a refusal at your discretion.

Hello! You will very much help us if you fill out and send this form to email: plastic.bottles.disinfection@gmail.com

Figure 1. The questionnaire in English

Characteristics of the tested apparatus

The tested device is an electrical device consisting of a block with electrodes, an electronic control, a water pump and a sprinkler for spraying the disinfectant. The

electrode was made of 925° silver (sterling silver). Water for the preparation of a disinfectant was tap water and wasn't treated additionally. The schematic draft of the tested apparatus is in Figure 2.

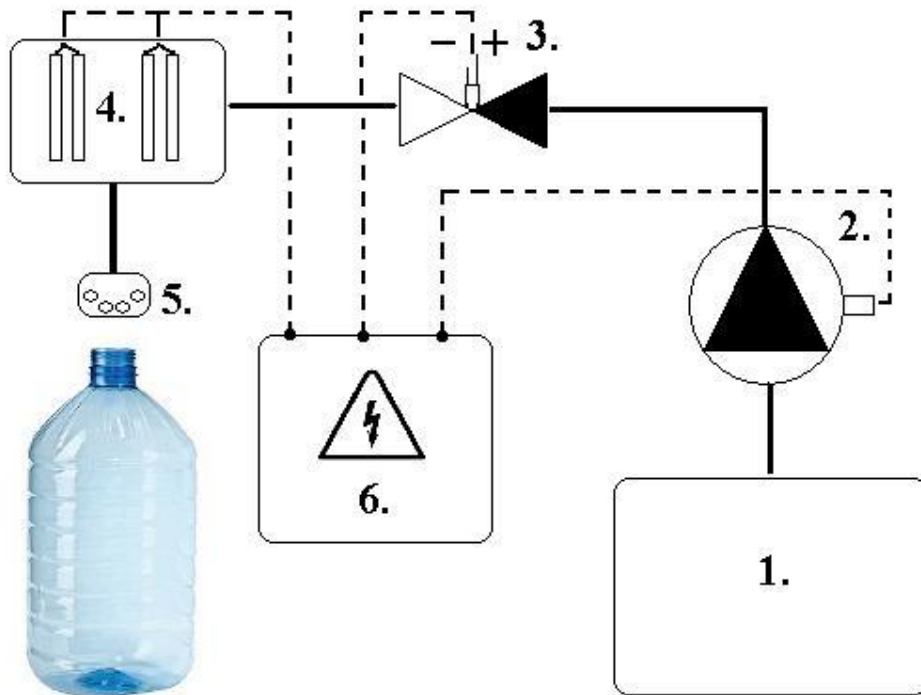


Figure 2. Schematic draft of the tested apparatus

Note: 1. – Tank for water for preparation of disinfectant; 2. – water pump; 3. – electric valve; 4. – block with silver electrodes; 5. – sprinkler for spraying the disinfectant; 6. – an electronic control block.

Bottle sanitation method

The sprinkler for spraying the disinfectant (Fig. 1, 5) was placed in the neck of the infected bottle. Disinfectant solution was sprayed inside the bottle for 4 seconds. The water pressure was about 1.5 atmospheres. After that, the sprinkler was removed and the disinfectant was drained.

A smear for microbiological composition was taken from three parts of the bottle - the neck, the middle part and the bottom according [9,10].

Results & Discussion

Identification of the mechanism of infection of the surface of PET bottles

In cooperation with the Mechnikov institute of microbiology and immunology (further - Mechnikov Institute) studied the possibility of contamination of the surface of PET-capacity and determined the level of danger with such infecration. The conditions of study 1-a are below.

Terms of the research 1-a

The capacity of PET with a useful volume of 6 dm³ with a life span of 8 weeks was filled with water from

urban water supply and left in a room with an open lid. The exposure time is 14 days, the average water temperature is +26 °C. Samples for microbiological analysis were chosen in the zone of water-air contact with the container wall at a depth of ½ height and from the bottom of the bottom. Results are in Table 1.

Table 1 Contamination of the inner surface of the container by study 1-a

Microflora	Place of research		
	The bottle neck	Middle part of the bottle	The bottle bottom
Total microbial number, TMN, CFU/mL	260	320	380
The number of coliform bacteria, index, NCB, CFU/L	80	60	30
The amount of sulfate-reducing clostridia, CFU/100 mL	70	30	30
Number of thermostable intestinal sticks, index NTIS, CFU/100 mL	–	–	–
Number of pathogenic microorganisms, CFU/L	70	30	30

Note: "-" - the growth of microorganisms is not observed.

Here and further in the text - microbiological analyzes were conducted by the Mechnikov institute of microbiology and immunology, Certificate No. 100-081 / 2015 of June 30, 2015y.

Specialists of the Mechnikov Institute give the following characteristics of infection in Study 1-a: after filling the bottle with tap water after 14 days, a biological film developed. The water in the bottle doesn't correspond to the microbiological characteristics of drinking water. After draining contaminated water from the vessel, it was filled with fresh tap water, after which microbiological

parameters were violated after 2.5 hours (the water temperature was +26 °C).

Thus, it becomes obvious that the internal surface of PET bottles for long-term storage of water, like PET of individual use [2], [9] can be a source of water pollution that is stored in such containers.

We consider the most likely and widespread - air way of contamination of internal surfaces of PET bottles for long-term storage of water. So, it does not exclude other types, such as contact, with contaminated water, etc. Scheme of airborne contamination of polymer bottles are in Figure 3.

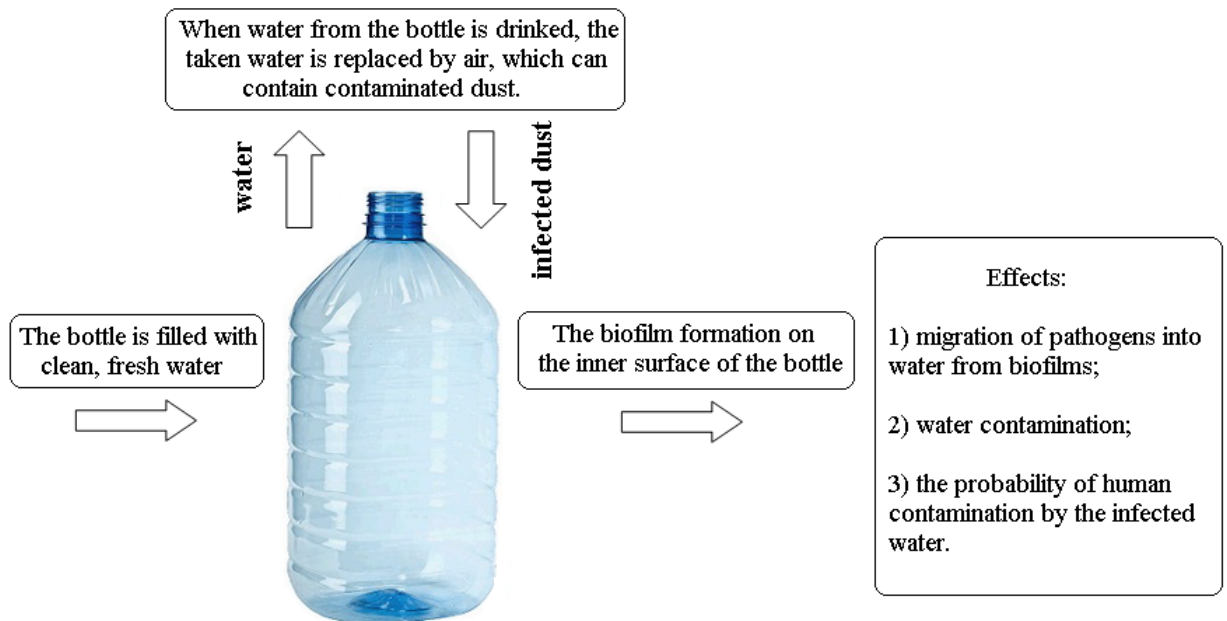


Figure 3. Scheme of contamination of PET bottle by air

The risk of drinking microorganisms from the drinking water that can cause harm to health rises to a

rather probable temperature in the summer, when the temperature of the water in the container can be above 20 °C. In addition, the risk will be increased by the following factors:

- Defects on the container - dents, cracks, etc. ;
 - Capacity left open for a long time;
 - Touch your hands to the bottle cap and throat;
- Prolonged use without replacement or disinfection;
- Do not rinse the container before the water set;
 - Prolonged storage of water in a warm place;
 - Water storage in a bright, sunny place.

A biological film that has already been formed cannot be destroyed by rinsing. Primitive agents such as soda, vinegar or soap solution, etc., are ineffective at low temperatures and in combination with the high resistance of modern strains of microorganisms cannot destroy the biological film. Increasing the processing temperature can spoil PET or cause the migration of monomers from plastic to water. Industrial and specialized PET detergents are dangerous for storage, since they contain concentrated alkali and acids, they are still difficult to obtain and they are relatively expensive.

Therefore, the question arises of how to abandon the use of PET bottles to store water and find funds for their sanitation. We see the prospect of decontamination, since a complete refusal is almost impossible because of the lack

of an alternative to PET bottles. At the same time, a method and device for decontamination has been developed and tested, which inactivates the biological film and has a lasting effect.

Testing the method and apparatus for a PET bottles sanitation

The proposed method of decontamination has more than a hundred-year history of research. It consists in the destruction of microorganisms that come into contact with silver ions. Disinfection with an agent such as silver is common in the United States [10]; Center for Research into Environment and Health in its 2014 report “Silver: water disinfection and toxicity” [11]; the organization highlights the antiseptic properties of silver. The University of Arizona conducted research on the use of silver in drinking water supply systems [12]. Legislation – the State sanitary norms and rules of Ukraine also provides for the use of silver for the conservation of drinking water (SSNR of Ukraine 2.2.4-171-10) [13].

Our proposed method consists in spraying water droplets saturated with silver ions up to 50 microns inside the container (Fig. 4). The amount of the sprayed solution of concentrated silver does not exceed 0.85% of the clean capacity.

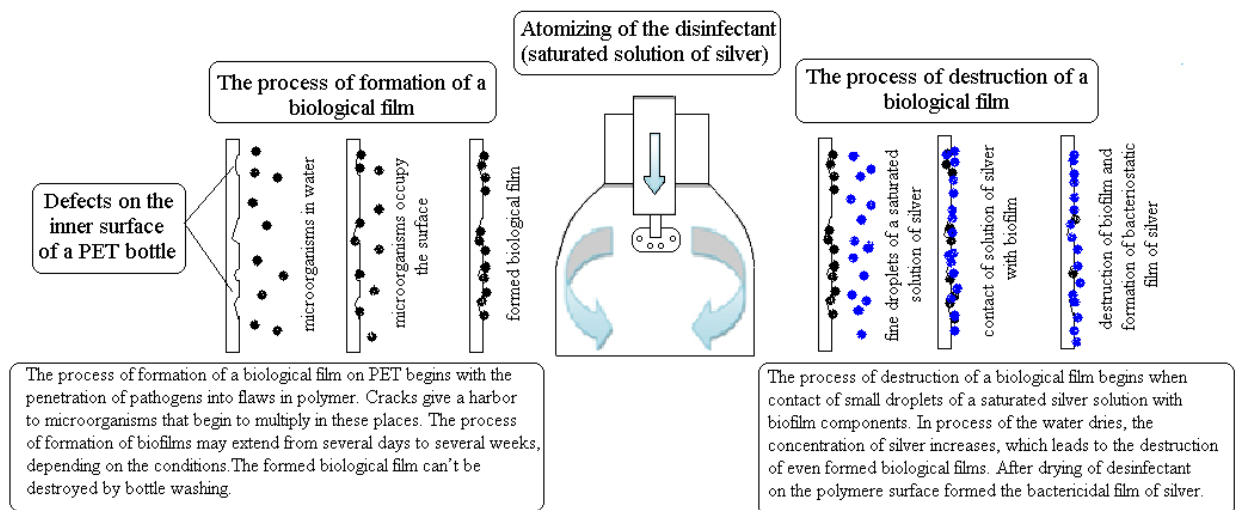


Figure 4. Mechanism of inactivation of biological film on PET

The concentration of silver in a concentrate that is sprayed - in the range of 2.5 to 3 mg/dm³, the maximum achievable concentration of silver in the container after full bay capacity of water - in the range from 0.024 mg/dm³ (volume of the bottle of 5 liters) to 0.006 mg/dm³ (the volume of the bottle is 10 liters). The MPC, set by the legislation of Ukraine, is 0.025 mg/dm³ according with SSNR of Ukraine 2.2.4-171-10 [13].

Non-mandatory US standards (NSDWRs) [14], and Canadian standards [15] provide a safe silver content in drinking water, and MPC is 0.1 and 0.05 mg/dm³ (ppm) for the United States and Canada, respectively.

EU and WHO standards do not regulate silver content in drinking water.

Maximum achievable concentration of silver in drinking water after dilution represent in Table 2.

Table 2 Estimated concentrations of silver in drinking water after treatment

Capacity Volume	Concentration of silver, mg/dm ³ (ppm)				
	In concentrate	After Dilution	MPC (Ukraine)	Non-mandatory MPC (USA)	MPC (Canada)
5 L / 1.3 Gal.	2.5 – 3	0.020 – 0.024	0.025	0.1	0.05
6 L / 1.6 Gal.		0.016 – 0.020			
7 L / 1.9 Gal.		0.014 – 0.017			
10 L / 2.6 Gal.		0.010 – 0.012			

12 L / 3.2 Gal.		0.008 – 0.010			
19 L / 5.0 Gal.		0.005 – 0.006			

From the data of Table 1.2 it's can be seen that when the concentrate is diluted with drinking water, an excess of MPC for silver in drinking water is not possible. The method corresponds to both Ukrainian, American and Canadian standards.

Risks to human health associated with the content of silver in food, researched by specialists WHO [16], Centre for Research into Environmental and Health [11], etc., are considered insignificant.

Chronic silver poisoning can lead to arginia - the accumulation of silver sulphide in the skin and in some other tissues of the body. The side effects of argyria are showed only by changes in skin color, mucous membranes and eyes [11].

To reduce the probability of such coloring to zero, it is sufficient to drain the concentrate from the bottle and wash it after treatment. Such simple measures can reduce the maximum silver concentration by 60 - 80% to 0.015 – 0.003 mg/dm³, which is 8 times less than the maximum permissible concentration foreseen by the legislation of

Ukraine and 30 times less than the MPC, that recommended by the EPA in the United States.

Efficiency of the prototype of the apparatus against the formed biological film on PET

For the evaluation of the effectiveness of the method, 2-a and 2-b studies were conducted. In the study of 2 - a prototype of the apparatus was tested on PET containers with the formed biological film (Table 1.1).

Terms of research 2-a

Using a prototype of device inside the infected container (Table 1.1), sprayed in the form of fine droplets, 40 cm³ of a concentrated aqueous solution of silver. According to visual observations, the solution wets the entire inner surface of the container. After 60 seconds and 28 minutes after treatment, a smear was made from the three points inside the container and a microbiological analysis was accomplished. The obtained data were compared with the results of the study 1-a. The results are in Table 3.

Table 3. Efficiency of a prototype of a device against a formed biological film on PET

Microflora	Place of research								
	The bottle neck			Middle part of the bottle			The bottle bottom		
	1	2	3	1	2	3	1	2	3
Total microbial number, TMN, CFU/ml	260	50	10	320	20	10	380	30	10
The number of coliform bacteria, index, NCB, CFU/L	80	10	–	60	20	–	30	10	–
The amount of sulfate-reducing clostridia, CFU/100 mL	70	–	–	30	–	–	30	–	–
Number of pathogenic microorganisms, CFU/L	70	–	–	30	–	–	30	–	–

Note: 1 - microbiological parameters for processing (research 1-a), 2. - microbiological indicators in 60 seconds after sanitation, 3 - microbiological parameters in 28 minutes after sanitation, "-" - the growth of microorganisms is not observed.

According to the data, it is established that the device is capable for reducing the concentration of microorganisms to a safe state. Even such a significant infection, which is represented in columns 1 of Table 1.3, can be eliminated by the device.

In the framework of testing the effectiveness of the prototype apparatus, a study 2-b was conducted to determine the effect of treatment of the inner surface of the PET container for the period of maintaining the microbiological parameters of the drinking water in accordance with SSNR of Ukraine 2.2.4-171-10 [13].

Terms of the research 2-b

To determine the period of microbiological water storage in PET containers, three tanks with a volume of 6

dm³ were taken. In the bottles No. 1 and No. 3 water was poured from the city water main in Kharkov. In the bottle No. 2 water of the producer was left. Bottle No. 1 was used in the study of 1-a and 2-a, it was treated with a prototype device. Bottle No. 2 was bought in a supermarket together with water and bottle No. 3 was examined for less than 2 weeks (water changed 4 times).

All three containers were placed in a place protected from sunlight with an open lid at room temperature. The temperature graph is shown in Figure 5. The study was conducted for 19 days, water samples were taken once a day. The results in Table 4

Table 4. Determination of the time of violation of microbiological indicators of drinking water when stored in PET bottles.

Exposure time, days	Bottle 1	Bottle 2	Bottle 3
1	+	+	+
2	+	+	+
3	+	+	-
4	+	+	-

5	+	+	-
6	+	+	-
7	+	+	-
8	+	+	-
9	+	-	-
10	+	-	-
12	+	-	-
14	+	-	-
16	+	-	-
18	+	-	-
19	+	-	-

Note: "+" - microbiological indicators of water correspond to [13],
 "-" - microbiological indicators of water do not correspond [13]

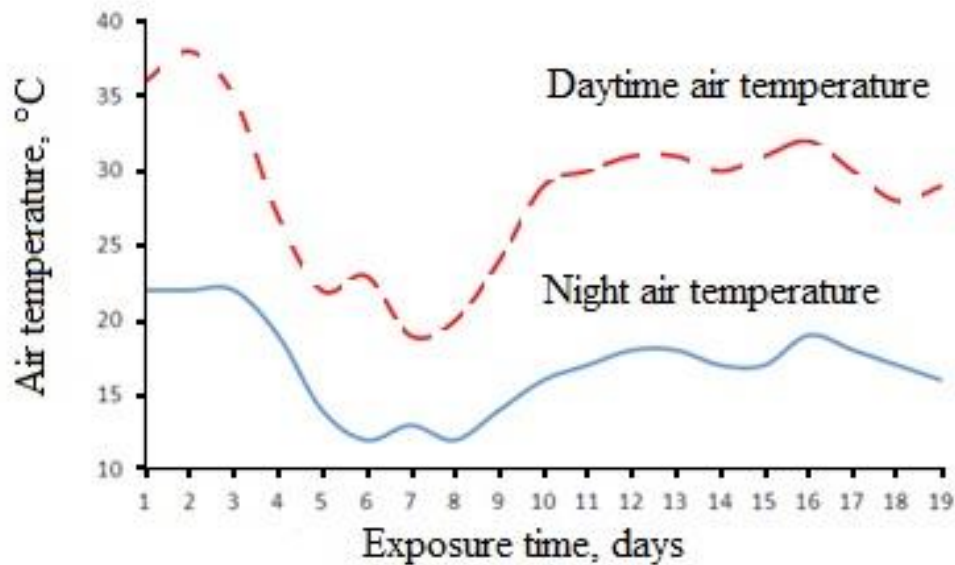


Figure 5. Thermal Study Schedule 2-b

The temperature schedule is compiled according to the web-site [17].

From Table 1.4 it can be seen that the water in bottle No. 1 (which was processed by the prototype of the device) allows to maintain microbiological indicators of drinking water almost ten times longer than water in bottle No. 3 and more than twice as large as bottled water in the bottle No. 2.

Conclusions

As a conclusion, the following key points can be distinguished:

1. Potable water storage containers made of PET contain threats, the most serious of which is microbiological.
2. Without conducting regular disinfection or inactivation treatment of PET containers may be potential spreaders of human diseases.
3. The formed biological film cannot be destroyed or inactivated by means and substances that are at home. Potentially dangerous is the use of special, concentrated disinfectants at home.
4. Ions of silver are acknowledged in the world of practice antiseptic.
5. The use of silver ions to inactivate the biological film, while complying with state standards and methods of treatment, is safe and effective, which has been proved by research.

6. The developed method and apparatus are effective against the formed biological film and comply with the current legislation of Ukraine and some other countries, in particular the USA and Canada.

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THE ANALYSIS OF THE THREAT OF REUSING PET BOTTLES FOR THE STORAGE OF DRINKING WATER

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Introduction. According to a sociological survey of about 86% of Kharkiv (Ukraine) residents reuse PET bottles for a drinking water storing. This type of reuse of PET bottles isn't safe and the results of numerous research unequivocally confirm this assertion. The largest hazard of plastic bottles reuse for drinking water storage is biological film on the internally surface of bottle. This biofilm may contain pathogenic microorganisms which can migrate from biofilm to fresh water. Human, who drinking contaminated water, may drink microorganisms in common with this water. It's very dangerous, because

the numerous strains of pathogens may migration in water and infect from gastric-bowel tract to the humans. Scientists from National technical university "Kharkiv polytechnic institute" in common with experts from Mechnikov institute of microbiology and immunology explored this problem and devised the apparatus, which can destroy a biofilm on polymer or another surface. **Materials & Methods.** The tested apparatus was the electrical device consisting of a block with electrodes, an electronic control, a water pump and a sprinkler for spraying the disinfectant. The electrode was made of 925° silver (sterling silver). Water for the preparation of a disinfectant was tap water and wasn't treated additionally. The sprinkler for spraying the disinfectant was placed in the neck of the infected bottle. Disinfectant solution was sprayed inside the bottle for 4 seconds. The water pressure was about 1.5 atmospheres. After that, the sprinkler was removed and the disinfectant was drained. A smear for microbiological composition was taken from three parts of the bottle - the neck, the middle part and the bottom. Growth of microorganisms and their detections was fixed by classic microbiological methods. **Results & Discussion.** In the article the scheme of the most probable and widespread way of infection of PET-bottles by pathogens and the way of minimization of this danger is given. Investigation of the contamination of the inner surface of the bottle by infected dust was carried out. It is determined that contaminated dust can cause a very serious infection contamination of inner surfaces of PET bottles and, subsequently, of water. In laboratory conditions and on the real object, a device for sanitizing surfaces was tested. It is established that the prototype of the device generates a disinfectant that destroys the most of known strains of microorganisms. This disinfectant is not toxic and is not dangerous to humans, the only product of evaporation of this product is water. With this disinfectant, the infection contamination on the inside of the PET bottle was completely eliminated. Thus, the use of a prototype device to minimize the threat of contamination of water consumers from recycled PET bottles is possible and very effective. **Conclusions.** 1.

Potable water storage containers made of PET contain threats, the most serious of which is microbiological. 2. Without conducting regular disinfection or inactivation treatment of PET containers may be potential spreaders of human diseases. 3. The formed biological film cannot be destroyed or inactivated by means and substances that are at home. Potentially dangerous is the use of special, concentrated disinfectants at home. 4. Ions of silver are acknowledged in the world of practice antiseptic. 5. The use of silver ions to inactivate the biological film, while complying with state standards and methods of treatment, is safe and effective, which has been proved by research. 6. The developed method and apparatus are effective against the formed biological film and comply with the current legislation of Ukraine and some other countries, in particular the USA and Canada.

Keywords: threat, reusing pet bottles, drinking water