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HOSPITALS SEWAGE TREATMENT BY METHOD OF ELECTROCHEMICAL OXIDATION

Introduction. Recently, the problem of wastewater containing residues of drugs and their derivatives, acquired a special urgency. More and more research have been performing and revealing the negative impact of pharmaceutical pollutants on the various components of the environment [1]. Adequately, scientists are trying to find a way of the effective disinfection wastewater, which would satisfy the requirements of virtually complete removal of the pollutants. The latter is because even an extremely small amount of medical contaminant causes a negative impact on the elements of the environment [2]. Analysis of the literature shows that the method for removing pharmaceutical contaminants has not been proposed and practically tested yet and couldn't satisfy these requirements [3]. Issues of wastewater treatment medical establishments are not paid attention at all. According to this, it is very relevant to choose and find implementation of hospitals sewage treatment method, specialized clinics and others medical establishments from pharmaceutical pollutants and their derivatives.

Goal and objective. The aim of this work is choosing and substantiation of the process for the wastewater purification from pharmaceutical pollutants to satisfy the growing environmental requirements for their release into the environment.

Objectives of the study are the following:

- to analyze the composition of the hospitals wastewater;
- to choice the purification method of wastewater and development of the fundamental principles of its implementation;
- to perform the experimental research of wastewater from pharmaceutical pollutants on model solutions;
- to analyze the obtained results for further using in studies for effective wastewater treatment from these pollutants.

Results of the research. Hospitals wastewater, contaminated by the drug substances may have the following features:

- they contain a lower concentration of contaminants in comparison with industrial wastewater from pharmaceutical companies. Consequently, the excretion of precipitates or solids, which generated during purification of these solutions for subsequent disposal, is economically and technically inappropriate;
- volumes of wastewater to be treated are determined by their origin (infection, surgery, etc. hospital departments or wastewater from the entire medical establishment and so on.). Their quantity may be comparatively small and could be 86 m^3 / h.
- wastewaters contain almost all groups of drugs, including priority pollutants and substances of biological effects on the activated sludge from municipal sewage treatment plants (MSTP);
- waters having a heterogeneous composition of contaminants can have negative effects of the summation on elements of the environment, as well as to form new compounds, the action of which has not been studied and could be also a dangerous for them;
- sewage from medical establishments can contain pathogens of infectious diseases, that's why it is impossible to discharge them into water bodies without an appropriate treatment [4, 5]. In addition, hospitals wastewater contain helminthic eggs, which also requires their disinfection.

Nowadays, almost all hospitals wastewaters without any pre-treatment are entering at MSTP. Thus, the difficult degradable substances are not removed finally and residual amounts are sending into natural waters with accumulating there. For example, the removal efficiency of diclofenac is only 17 - 69% [6]. The available data for disinfection of effluents from antibiotics, cholesterol, bisphenol A to 93-99% on MSTP

leads to the fact that the concentration of contaminants is reduced to 223 ng / l. However, it is not enough for the preventing of the negative impact of effluent on the environment [7].

Since most of pharmaceuticals are pollutants with organic compounds, the methods of wastewater treatment mostly correspond to the known methods for separation and destruction of organic matters. It is recommended well-known (membrane methods, electrocoagulation, etc.) and also a new developments. Latest still have certain drawbacks that limit their use (photocatalytic method Fenton, oxidation in supercritical water, etc.).

Known method of electrochemical oxidation has all the prerequisites for using it for purification of wastewater from pharmaceutical compounds. It is performed by using «active» (Pt, IrO_2 and RuO_2), or «inactive» (PbO_2, SnO and boron-doped diamond-BDD) anodes. During the anodic oxidation or direct oxidation, active hydroxyl radical, being the more active for oxidation of pollutants than oxygen, mineralizes the organic components (R) for the following reactions:

$$R+MO_x(\cdot OH)_z=CO_2+zH^++z\ e + MO_x \quad (1)$$

$$R + MO_{x+1}= RO + MO_x\ , \quad (2)$$

where the active hydroxyl radical oxygen is formed on MO_{x+1}.

The studies are presented in literature, the anodic oxidation method was used for destruction of diclofenac, ketoprofen, paracetamol and other pharmaceutical pollutants. However, these developments have several disadvantages, which are serious obstacles for their using in hospital wastewater treatment. They are including the following:

- the orientation for only one pollutant and development of cleaning mode based on decomposition just of this component [8];

- the lack of consideration of mutual influence pollutants from different groups of the drugs that are entering on the treatment, can be formed a new compounds;

- the low efficiency of the treatment of hard-degradable pollutants (for example, diclofenac is about 70-80%).

Currently, the groups of medicines include more than several hundred compounds. In particular, they are combined into groups: nonsteroidal anti-inflammatory drugs; hormonal methods; antibiotics; diuretics and others. From the viewpoint of chemical structure, these are large organic molecules that basically contain of aromatic functional group(s). For research would be appropriate to choose micro pollutants, which are most using and detecting in surface waters and sewage in Europe and Ukraine [9].

In experimental study, presented by authors in this article, is solving the initial problem of complex experiments for hospitals wastewater treatment, specifically:

- determination of electrode materials and development of the apparatus for electrochemical studies;

- selection of additives to enhance electrical conductivity of wastewater for further studies of the degradation of pharmaceutical pollutants.

- analytical study of model solutions for the presence of drugs contaminants.

The experiments were carried out in an open, not separated by membrane, in a cylindrical glass cell with volume of 250 ml, provided with two electrodes. As working electrodes were used graphite rod cathode, a platinum wire anode, grid titanium anode having a coating of RuO_2, cathode plate of alloy steel (working surface area of anodes was S= 1,72 $см^2$ and S=72 $см^2$ respectively). Constant current source was a laboratory device DC Power Supply model GPS-3030D. The temperature of the solution was roomed.

The authors conducted the research of efficiency degradation of pharmaceuticals in model solutions containing two types of conductive additives: chloride and sulfate sodium. In this case, the conditions were considered: the limitation concentration under the terms of water discharge into the sewer in Ukraine is for sulfate - 400 mg/l and chloride - 350 mg/l. It was taken into account that the concentration of Cl^- is more 400 mg/l violates the activity of microorganisms, activated sludge biological treatment of wastewater and becomes ineffective [10].

In the present study were used the powder pharmaceutical substance Diclofenac of company Sigma-Aldrich. As the electrolyte salt were used sodium chloride and sodium sulfate of company Merck KGaA.

For the selecting of the optimum electrolyte composition was tested destruction of Diclofenac with concentration in the solution from 0.5 to 3.5 mg/l. The initial concentration of chloride and sodium sulfate was 1,000 mg/l. Quantitative and qualitative analysis for identification the contaminant was performed using analytical equipment Shimadzu HPLC model LC-UV. Mode of process is shown in Table 1.

Table 1 - Conditions of HPLC with UV detector (LC-UV) for determination of drug Diclofenac.

Name of drug	Mobile phase		Wavelength, nm	Injection speed, ml / min	Time min
	A	B			
Diclofenac	1% HCOOH (30%)	100% CH3OH (70%)	270	0.7	7.4

The results of analysis of model solution after electrochemical destruction is shown in Fig. 1.

Concentration of NaCl – 500 mg/l, Na_2SO_4 – 500 mg/l. Concentration of Diclofenac is given in mg/l.

As shown in the diagram (Fig. 1), rate and efficiency of the degradation of the pollutant in the medium of sodium chloride is much higher than in sodium sulfate. 100% purification effect was also achieved with concentrations of Diclofenac 3 mg/l and sodium chloride - 300 mg / l.

Electrolysis of the pharmaceutical contaminated effluents containing sodium chloride, followed by electrochemical oxidation of pollutants directly at the anode, and the entire volume of treated water.

The adsorbed radical OCl^- is formed by using the anode RuO_x–TiO_x at presents of NaCl, having the form (RuO_x–TiO_x)(•OCl). Next, it is taking place the formation of a higher form of an oxide anode RuO_x–TiO_{x+1} with releasing of active oxygen and chlorine [11]. Under the influence of these substances, the decomposition of organic substances and an additional effect associated with the disinfection of the effluents occurs. Medium with such strong oxidants is detrimental for infectious agents and helminthes, located in hospital wastewaters [12]. This fact rules out additional operations of decontamination of such waters.

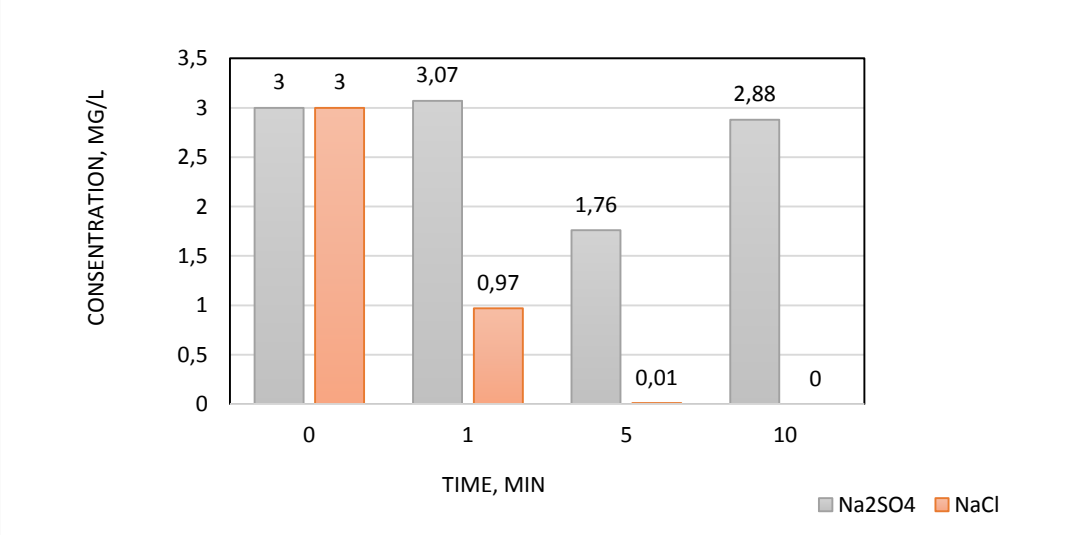

Fig. 1. Decomposition of Diclofenac in mediums of sulfate and chloride sodium.

Chlorinated organic compounds can be formed in the process of oxidation. However, their concentration would be negligible due to:

- mineralization of pharmaceutical contaminants and therefore reduce the amount of raw materials for their production;

- permanent degradation of chlorinated compounds in the electrochemical destruction.

Generally, the number of such compounds will be significantly less than in the case of the method is using for hospitals wastewater disinfection by chlorination, which is not included a preliminary cleaning them from the pharmaceutical pollutants.

Conclusions. Considering information in this paper is base for further research of electrochemical destruction, assuming of mix of hard biodegradable (of oxidized) pharmaceutical pollutants in sewage in the presence of chloride ions.

Wastewater treatment of hospitals from pharmaceutical pollutants by the proposed method can be recommended for the local wastewater treatment of medical institutions. It is appropriate the consideration of it in the projection and construction of sewer systems of the built environment.

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REFERENCES:

1. Kummerer K. Pharmaceuticals in the Environment/ Kummerer K. // Annual Review of Environment and Resources. – 2010. - №35. – с. 57–75.
2. Alistair B. A. Boxall. The environmental side effects of medication/ Alistair B. A. Boxall// EMBO reports. – 2004. - № 12. – с. 1110-1116.
3. Vystavna Y. Pharmaceuticals in rivers of two regions with contrasted socioeconomic conditions: occurrence, accumulation and comparison for Ukraine and France/ Vystavna Y., Huneau F., Grynenko V., Vergeles Y., Celle – Jeanton H., Tapie N., Budzinski H., Le Coustumer P.// Water, Air and Soil Pollution. – 2012.
4. ДБН В.2.5 - 75: 2013. Каналізація. Зовнішні мережі та споруди. Основні положення проектування. – Київ: Міністерство регіонального розвитку, будівництва та житлово-комунального господарства України. - 2013.
5. СНиП 2.04.01-85. Строительные нормы и правила. Внутренний водопровод и канализация зданий. – Москва: Госстрой СССР. - 1986.
6. Falås P. Occurrence and reduction of pharmaceuticals in the water phase at Swedish wastewater treatment plants / P. Falås, H.R. Andersen, A. Ledin, J. la Cour Jansen// Water Science and Technology. – 2012. - № 66. – с. 783-791.
7. Lapertot M. Photo-Fenton and bilogical integrated process for degradation of a mixture of pesticides / M. Lapertot, S. Ebrahimi, S. Dazio, A. Rubinelli, C. Pulgarin// Journal of Photochemistry and Photobiology. – 2007. - №186. - с. 34-40.
8. Feng L. Degradation of anti-inflammatory drug ketoprofen by electro-oxidation: comparison of electro-Fenton and anodic oxidation processes/ Feng L., Oturan N., van Hullebusch E.D., Esposito G. and Oturan M.A.// Environmental Science and Pollution Research. – 2014. – №21. – с. 8406-8416.
9. Ермакович И. А. Загрязнение муниципальных вод фармацевтическими препаратами и их производными/ Н.Н. Самойленко, И. А. Ермакович// Восточно-Европейский журнал передовых технологий. – 2013. - №64.- с. 8-11.
10. Skaisgirienė A. Modelling of chloride influence upon activated sludge community growth/ Skaisgirienė, A. Januteniene, J. Vaitiekūnas, P.// Journal of Environmental Engineering and Landscape Management. – 2009. - № 17. – с. 114-120.
11. Ignasi Sires. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review/ Ignasi Sires, Enric Brillas// Environment International. – 2012. - №40. – с. 212-229.
12. Ермакович И. А. Использование электрохимической деструкции для обезвреживания сточных вод лечебных учреждений / Н.Н. Самойленко, И. А. Ермакович // Восточно-Европейский журнал передовых технологий. – 2014. - №70.- с. 18 - 21.