Methods for detection of antibiotics in urban wastewater

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Abstract. This review provides analysis of existing methods for detection of antibiotics in wastewater. Special attention is paid to the classification of methods for the detection of antibiotics and the possibility of these methods during antibiotics formation with separate components of wastewater complex compounds. According to the classification and a review of detection methods, preference was given to the analysis of the antibiotic content in dust on a solid-state polarograph, analyzing a sample of the solution using a KORIAN-3 analyzer, and differential spectroscopy.

1. Introduction
In most cities of the Russian Federation, sewage system is common and sewage treatment plants receive wastewater from residential buildings, industrial enterprises, public and administrative buildings, including hospitals [1-2]. At the same time, in Russia there are no strict standards for receiving effluents containing pharmaceutical preparations, especially antibiotics.

As a result of studies conducted in many countries of the world, it was proved that penetration of antibiotics into the waste water leads to the adverse effects that result in changes in water micro flora [3-13]. The presence of antibiotics in the environment affects the growth of toxicological risks for the ecosystem, which includes humans and other species [5, 7, 9].

It must be mentioned, that the uncontrolled spread and presence of antibiotics in the environment contributes to the development of pathogens resistant to them. Thus, the bacteria develop resistance and pharmaceuticals, including antibiotics, lose their effectiveness, and stop treating [3-5]. This process is practically impossible to control. We are talking more about resistance – the resistance of bacteria to antibiotics, which occurs due to constant mutations, and the emergence of new pathogens instead of old ones [6, 10, 11]. That’s why studying of methods for detection actual concentrations of antibiotics in wastewater is an urgent issue today.

2. Theoretical basis
Nowadays, about 14,000 antibiotics produced just by microorganisms have been described. Besides, at least 1800 antibiotic substances are produced by higher plants and animals. Consequently, the total number of known antibiotics is at least 15.8 thousand items, and there is a tendency of increasing the release of new antibiotics [14]. Penicillin and cephalosporin are the most commonly used antimicrobial drugs [15].

Over the past decades, aspects of the organic and biological chemistry of penicillin and cephalosporin have been studied well [14-15]. Inorganic chemistry of penicillin and cephalosporin has been less studied, that is, the interaction of these antibiotics with metal cations with the formation of...
complex compounds, as well as acid-base equilibrium in their solutions. This aspect is especially important because of the significant concentration of various metal cations in urban wastewater. According to published data, many antibiotics in molecular or ionic forms are able to form stable complexes with metal cations. Generation of metal complexes has a significant effect on antimicrobial activity, toxicity, pharmacokinetics, resistance to hydrolysis and other biological and chemical properties of antibiotics. There is also considerable theoretical and practical interest to the interaction of antibiotics with other substances polluting wastewater. There are few publications on this issue and they are systematized in the monograph by V.G.Alekseev [16].

In case of water pollution with antibiotics, several situations can be distinguished:

- long-term antibiotic discharges in sewage from a number of enterprises and hospitals [4, 10];
- discharge of antibiotics into sewage by agricultural enterprises [10-11];
- emergency discharges of antibiotics into the wastewater by enterprises within a certain short period [5-7, 9].

The first two situations allow us to estimate these discharges using water samples, both in wastewater and in water basins [13]. Emergency discharges can only be detected by real-time monitoring of wastewater, which imposes restrictions on the use of many well-known wastewater control methods [17].

The purpose of this article is to analyze the existing methods of antibiotic control in water, taking into account the time of environmental control.

3. Materials and methods

There are different detection methods of water pollution with antibiotics and complex compounds forming from the interaction of antibiotics with metal cations (figure 1).

![Figure 1. Qualitative and quantitative methods for detection of antibiotics in urban wastewater.](image-url)
Control is the main form of detection of antibiotics in water, species identification and concentrations. Control includes two steps: obtaining information of the actual antibiotics availability (about their qualitative and quantitative characteristics) and comparing received information with established standards (requirements) in order to determine their relevance, that is, obtaining secondary information [3, 12].

Control includes the determination of qualitative (when it is sufficient to determine the presence (appearance) of an antibiotic in wastewater) and (or) quantitative characteristics when it is necessary to determine the content of the antibiotic. In this case, the number of antibiotics is expressed in the so-called units of action. Control includes operations of measurement, analysis, testing. The measuring method for determining numerical values of quantified characteristics is based on information obtained using technical measuring instruments (measuring instruments, reagents, etc.) [3-6, 8, 12].

Antibiotics from urban and agricultural sources are stored in soil and water, and selective pressure from these compounds affects the microbial community, environmental functions and leads to antibiotic resistance. Thus, antibiotic migration is the key for understanding behavior and effects of antibiotics in the aquatic environment. There are lots of popular methods for the quantitative determination of antibiotics: microbiological, spectrophotometric, fluorimetric, chemiluminescent, various options for chromatographic methods, including high performance liquid chromatography (HPLC), chromatography and mass spectrometry, inversion voltammetry, electroanalytical determination with modified electrodes [7-11, 18-19].

Each method has advantages and disadvantages. The choice of method depends on the availability of equipment, availability of staff, who knows the equipment, the number of analysis and their frequency, accuracy and other factors [18].

When the qualitative and quantitative determination of antibiotics in urban wastewater following difficulties arise in Russia:

- no approved standards for permissible concentrations of antibiotics in the waters: surface water, wastewater, groundwater, which does not allow to assess the degree of contamination;
- no certified methods for detecting antibiotics in the aquatic environment – in the state register of methods for quantitative chemical analysis there are only methods for the photometric and spectrophotometric determination of a number of antibiotics in the air.

4. Results

Traditional analytical methods for the quantitative and qualitative determination of antibiotics mainly depend on chromatographic methods, which are expensive and time-consuming, which limits their use. Also, capillary electrophoresis, diode-matrix detection and enzyme-linked immunosorbent assay are also successfully used to detect antibiotics, but they still have disadvantages such as a complex process of pretreatment of samples and the presence of highly qualified technical staff. Therefore, a reliable and fast method for detecting antibiotics is very necessary for human health and safety [19].

Perspective methods for detecting antibiotics in urban wastewater are: analysis of antibiotics content in the duct using a solid state polarograph; analysis of a sample of a solution on a KORIAN-3 analyzer designed to determine organic additives in galvanic solutions by differential voltammetry; differential spectroscopy, which allows you to analyze complex organic compounds by the characteristic resonant frequency.

5. Conclusions

The proposed classification of methods for the determination of wastewater antibiotic contamination with the use of a systematic approach to the development of a hierarchical model allows to increase the effectiveness of antibiotics usage, and to ensure the uniformity of measurements and reproducible results. To solve the problem of monitoring the content of antibiotics in water in real time can be used spectroscopy in ultra-violet and visible light, infrared spectroscopy [20-22].
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