The analysis of toxic connections content in water by spectral methods

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Abstract. The current state of ecology means the strict observance of measures for the utilization of household and industrial wastes that is connected with very essential expenses of means and time. Thanks to spectroscopic devices usage the spectral methods allow to carry out the express quantitative and qualitative analysis in a workplace and field conditions. In a work the application of spectral methods by studying the degradation of toxic organic compounds after preliminary radiation of various sources is shown. Experimental data of optical density of water at various influences are given.

1. Introduction

The management and observation of modern processes requires reliable and exact information about the content of substances that serves as a guarantee of providing high quality production. Therefore the methodology of works on monitoring of chemicals and methods of their analysis in the environment are constantly improved [1, 2]. The pollution detection is the necessary, but insufficient action directed to the environment protection. Among the modern methods used for the fight against pollution the biological cleaning is widely adopted [3]. Resistant organic compounds influence self-cleaning of natural waters, quality of water resources, soil fertility, biological efficiency of ecosystems and human health in a negative way [4-5]. Often such ecological toxicants are found in the places that are extremely far from the areas of their production or application [6]. Cross-disciplinary character of a problem demands integrated approaches to its decision either. The combination combining biological and photochemical methods [7-9] is the most perspective one.

2. Methodology

The direct instrumental methods of optical spectroscopy are generally the physical relative methods. On condition of the correctly selected equipment the advantages of the spectral analytics consist, firstly, in an opportunity to register the very small concentration of organic substances and, secondly, in speed of carrying out the analysis and repeated use of the same test as the studied substance during the analysis doesn't undergo considerable changes. Due to the variety of application opportunities,
high precision of results and detection sensitivity, without mentioning the essential time reduction for carrying out the analyses, spectroscopic methods have reached the highest degree of economic efficiency.

The spectroscopy with its variety of methods has turned into the most important supportive application of modern analytics. The minimum concentration of definition of substance reach $10^{-9}$ mol/l.

2.1. Metabolism studying

Metabolism studying is one of rather new scientific directions. The concept "metabolism" in this case means the processes of structure change and disintegration of organic substances in the (in)animated nature. The analytical research of the pesticides used in the agriculture, fungicides and herbicides is considered very complex and heavy business. It is necessary by the assessment of potential risk from their application. For studying of transfer and movement of metabolites the long-term experiments covering a set of special aspects are required. So, for example, compatibility with the environment can't be provided only because the some substances can be insatnsoluble in water and, therefore, are the subject to decomposition under the influence of microorganisms as, on the other hand, high solubility causes danger of ground waters infection.

The characteristic of the organic substances which are contained in water in many cases is traditionally based on total parameters, and the majority of ingredients with identical or similar properties is covered by one way of definition. At the same time a set of total parameters stretches from hydrocarbons and phenolic number with a narrow range of substances to chemical consumption of the oxygen including the huge volume of substances (natural organic acids). The research of fixing of nanoparticles TiO$_2$ and SnO$_2$ on the multifunctional polypropylene material (MPM) can be conducted by the spectroscopy UF method.

To be convinced that particles of TiO$_2$ and SnO$_2$ are fixed on a surface of the studied PMP, samples of PMP are located in water and mixed up in an ultrasonic mixer of Heidolph Multi Reax during 2÷10 minutes [10, 11]. Then the spectrums of absorption of the received water solutions were removed. The existence of the weighed particles in solution leads to increase in the optical density of absorption in a visible area of a spectrum. From the analysis of electronic ranges of absorption it is possible to define the most suitable conditions of fixing of nanoparticles of TiO$_2$ and SnO$_2$ on PMP (Table 1).

Table 1. Change of optical density of water absorption on the wavelength of 500 nanometers ($D_{500}$) in the presence of PMP after the influence by ultrasound (US) within 2 min and UV radiation.

| No. | Sample of PMP | Influence US | Influence UV | $D_{500}$, $\pm 0.0005$ relative units |
|-----|---------------|--------------|--------------|--------------------------------------|
| 1   | TiO$_2$ No.1*| -            | -            | 0                                    |
| 2   | TiO$_2$ No.1 | +            | -            | 0.003                                |
| 3   | TiO$_2$ No.1 | +            | +            | 0                                    |
| 4   | TiO$_2$/SnO$_2$ No.1 | - | - | 0.002 |
| 5   | TiO$_2$/SnO$_2$ No.1 | + | - | 0.005 |
| 6   | TiO$_2$/SnO$_2$ No.1 | + | - | 0 |
| 7   | TiO$_2$/SnO$_2$ No.2 | - | - | 0.003 |
| 8   | TiO$_2$/SnO$_2$ No.2 | + | - | 0.007 |
| 9   | TiO$_2$/SnO$_2$ No.2 | + | + | 0 |
| 10  | TiO$_2$ No.2 | - | - | 0 |
| 11  | TiO$_2$ No.2 | + | - | 0.013 |
| 12  | TiO$_2$ No.3 | - | + | 0.001 |
| 13  | TiO$_2$ No.3 | + | - | 0.01 |

where * is a number corresponds to the various conditions of the putting of nanoparticles on PMP surface.
From the analysis of Table 1 it is clear that the smallest value $D_{50\%}=0$ corresponds to a sample of TiO$_2$ of No. 1 which nanoparticles were fixed on the PMP surface best of all.

2.2. Fluorometry
Fluorometry is a rather widespread method of analytical definition at which electronic excitement of substance from a radiation source with the subsequent measurement of intensity of emission fluorescence as a function of wavelength of excitement and emission radiation is provided. On the basis of fluorescent data it is possible to receive both qualitative, and quantitative results with high sensitivity. If the studied substance doesn't fluoresce, so it is possible to use fluorescent probes. For express a quantitative assessment of efficiency of a naphthalene decrease (Table 2) and phenol in water the relation of intensity in a maximum of phenol fluorescence strips before UV-influence has been defined.

Table 2. A naphthalene decrease in water after radiation of KrCl by the eksilamp ($\lambda_{\text{rad}} = 222$ nanometers) according to fluorescent spectroscopy

| No. | UV radiation time, min | Naphthalene concentration, M $\times 10^4$ |
|-----|-----------------------|------------------------------------------|
| 1   | 0                     | 2                                        |
| 2   | 5                     | 1.4                                      |
| 3   | 10                    | 0.75                                     |
| 4   | 15                    | 0.35                                     |
| 5   | 30                    | 0.17                                     |
| 6   | 60                    | 0.01                                     |

The maximum photodecomposition of phenol in water (Figure 1) after the radiation without additives of oxidizers is reached after 60 min radiation in the flowing reactor with KrCl eksilampy (at $\lambda_{\text{rad}} = 222$ nanometers).

Along with chemical analytics the value of biotests at control of sewage has increased that has allowed to define toxicity of the substance in those cases where it can't be made by a direct chemical method. As biotests live organisms are used. On the basis of their manifestations in the environment containing toxic substances it is possible to determine the biological activity by the microorganisms luminescence by means of luminometer. Suppression of a luminescence of such bacteria indicates the toxicity degree of the environment.

![Figure 1. Change of relative intensity in a phenol fluorescence strip maximum (on $\lambda_{\text{max}}$ wavelength = 298 nanometers) in water after radiation by various eksilamp in the photoreactor, where 1 is PPM+XeCl (at $\lambda_{\text{rad}}=308$ nm); 2 is KrCl (at $\lambda_{\text{rad}}=222$ nm); 3 is PPM+XeCl (at $\lambda_{\text{rad}}=308$ nm)+KrCl (at $\lambda_{\text{rad}}=222$ nm).](image-url)
For the assessment of toxicity of water solutions it is accepted to use biological tests (bacteria, seaweed, crustaceans, etc.). And perspective biotests on the basis of sea luminescent bacteria are the most suitable [10-14]. Bioluminescent measurements are carried out by a standard technique which detailed description is provided in this work [11]. The toxicity of solutions is estimated by the size of the bioluminescent index \( BI = \frac{I}{I_0} \) where \( I_0 \) means intensity of a bioluminescence of bacteria in water NaCl solution (3%), \( I \) means intensity of a bacteria bioluminescence in solution in the presence of a toxicant.

In the world practice the environment is considered to be nontoxic at \( BI=1 \div 1.3 \) (there are no suppressions or a weak buildup of a bioluminescence), low toxicity at \( BI>0.7 \), average toxicity at \( BI>0.5 \) and extremely toxic at \( BI<0.3 \). The results of a toxicity research of water solutions after high-energy influence are given in the Table 3.

**Table 3. Bioluminescent index and toxicity level of the water solutions containing phenol (From \( =10^{-3} \) M) and humic acids (\( C = 0.01 \, \text{g/l} \)) at the excitement by various sources [12].**

| № | Source          | Solution               | t influence, s | BI  | Toxicity level |
|---|----------------|------------------------|----------------|-----|----------------|
| 1 | No             | Water                  | -              | 1   | nontoxic       |
| 2 |                | Phenol in water        | -              | 0.88| medium         |
| 3 |                | Phenol in water + humic acids | -              | 1.23| nontoxic       |
| 4 |                | Humic acids            | -              | 1   | nontoxic       |
| 5 | Electron stream| Water                  | 120            | 0.45| medium         |
| 6 |                | Phenol in water        | 15             | 0.53| medium         |
| 7 |                |                        | 30             | 0.42| medium         |
| 8 |                |                        | 60             | 0.34| medium         |
| 9 |                |                        | 120            | 0.18| extreme        |
|10 |                | Phenol in water + humic acids | 15             | 0.93| low            |
|11 |                |                        | 30             | 0.78| low            |
|12 |                |                        | 60             | 0.81| low            |
|13 |                |                        | 120            | 0.63| low            |
|14 |                | Humic acids            | 15             | 0.77| low            |
|15 |                |                        | 30             | 0.77| low            |
|16 |                |                        | 60             | 0.8 | low            |
|17 |                |                        | 120            | 0.8 | low            |
|18 | Barrier discharge| Water                | 60             | 0.04| extreme        |
|19 |                | Phenol in water        | 15             | 0.1 | extreme        |
|20 |                |                        | 30             | 0.1 | extreme        |
|21 |                |                        | 60             | 0.01| extreme        |
|22 |                | Phenol in water + humic acids | 120            | 0.01| extreme        |
|23 |                |                        | 15             | 0.7 | low            |
|24 |                |                        | 30             | 0.45| medium         |
|25 |                | Humic acids            | 60             | 0.1 | low            |
|26 |                |                        | 120            | 0.17| extreme        |
|27 | Ozonization    | Water                  | 15             | 0.8 | low            |
|28 |                | Phenol in water        | 60             | 0.75| low            |
|29 |                | Phenol in water + humic acids | 60             | 0.7 | low            |
|30 |                | Humic acids            | 1.1            | nontoxic |
From the analyses of Table 3 it follows that the influence by the barrier discharge leads to the extreme toxicity both pure, and the water solutions containing phenol. Addition of natural connections (humic acids) allows to reduce the toxicity after the influence by an electron beam. The lowest toxicity of water solutions is recorded after the ozonization.

Effective decomposition of methylphenols in the neutral environment is revealed by means of fluorescent spectroscopy at the UV radiation by KrCl eksilamp ($\lambda_{rad} = 222$ nanometers) [13]. In sour and alkaline environments (Table 4) when molecules are in an ionic form, phototransformations are carried out with a bigger efficiency at XeBr radiation by eksilamp ($\lambda_{rad} = 283$ nanometers).

The smallest efficiency of phototransformation is recorded after radiation by a mercury lamp (Table 4, No. 9). Oxygen removal of methylphenols solutions leads to efficiency decrease of phototransformations according to a fluorometry. Phototransformations of methylphenols lead to the photoproducts formation which are fixed in a spectrum of fluorescence and indicate effective transformation of initial molecules. It indicates that the fluorescent analysis needs to be built in the registration block in systems of water purification and it is necessary to watch the level of substances utilization.

Table 4. Spectral and luminescent properties of o-methylphenol in water solutions after UV processing.

| №  | pH  | Radiation source | $\lambda_{rad}$ nm | $\lambda^1$, nm | $\lambda^2$, nm |
|----|-----|------------------|--------------------|----------------|----------------|
| 1  | 6.4 | KrCl             | 222                | 350            | –              |
| 2  |     | KrCl             | 222                | 350            | 410            |
| 3  |     | XeBr             | 283                | 350            | –              |
| 4  |     | Mercury lamp     | 240-600            | 350            | –              |
| 5  |     | XeCl             | 308                | 365            | 410            |
| 6  |     | XeCl             | 308                | 365            | 410            |
| 7  | 11.4| KrCl             | 222                | –              | 410            |
| 8  |     | XeBr             | 283                | –              | 410            |
| 9  |     | Mercury lamp     | 365                | –              | –              |
| 10 | 0.2 | KrCl             | 222                | –              | –              |
| 11 |     | XeBr             | 283                | –              | 410            |
| 12 |     | Mercury lamp     | 240-600            | –              | –              |

Where * is Fluorescence of photoproducts.

By the method of fluorescent spectroscopy it is shown that preliminary radiation of water solutions of methyl phenols leads to their further effective biodegradation [1]. The application of a combination of UV-radiation and a strain of Penicillium tardum H-2 for utilization of methyl phenols and their mix has led to the full decomposition of n-methyl phenol and partial degradation of o-methyl phenol. Studying of the qualitative structure of the metabolites which are formed during the n-methyl phenol biodegradation with the usage of spectral and the chromatographic methods has shown that the preparatory metabolism of this connection happens as through oxidation of methyl group to formation of 4-hydroxybenzole acid, so through a hydroxylation to formation of a 4-methylkatechol.

3. Summary
It is found on the example of phenols that the preliminary radiation of solutions of ecotoxicant the modern sources of incoherent radiation by eksilamps leads to the change of rates of initial toxicant degradation [9]. The spectral analysis of a photoliz when using these sources of radiation allows to make the forecast for their choice for removal of toxic connections out of the water environment.
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