

# EPR spectroscopy in wastewater treatment technologies

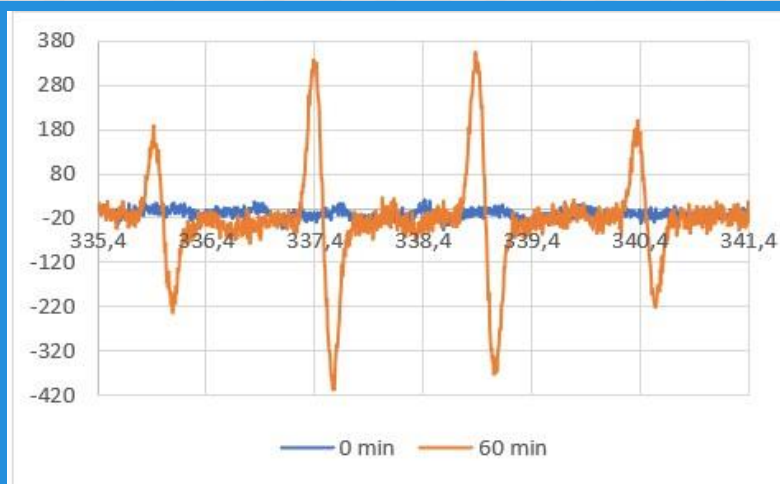


The volume of effluents released into the environment is steadily increasing due to the development of industry and the growth of the population. Wastewater treatment for their purification is an important practical problem. One of the approaches to solving this problem is based on the use of photocatalysts.



The most common photocatalyst in industry is titanium dioxide ( $\text{TiO}_2$ ). It is inexpensive and chemically stable, but  $\text{TiO}_2$  can only absorb radiation in the UV range. For this reason, intensive research is being carried out towards the development of catalytic systems activated by visible light. One of the promising photocatalysts are bismuth oxyhalides ( $\text{BiOHal}$ ,  $\text{Hal}=\text{Cl}, \text{Br}, \text{I}$ ). EPR spectroscopy has some benefits for studying photochemical processes occurring in various media because the activation process of photocatalysts causes the formation of free radicals in the system.

The EPR spectrum recorded on bench-top EPR spectrometer Spinscan X before and after irradiation of a suspension of bismuth oxobromide in water with UV radiation (365 nm) (fig.1).



**Figure 1 – BiOBr Photocatalytic activity**

Experiment parameters: center field, 338.4 mT; sweep width, 6 mT; modulation frequency, 109.375 kHz; modulation amplitude, 200  $\mu\text{T}$ ; attenuation, 10 dB, number of points 1000 and sweep time 200 c.

UV radiation leads to the activation of BiOBr, which causes the formation of free radicals in the system. Then EPR spectrum are recorded. The EPR spectroscopy with the spin trapping technique was used for monitoring the processes of photodegradation of pollutants in wastewater.

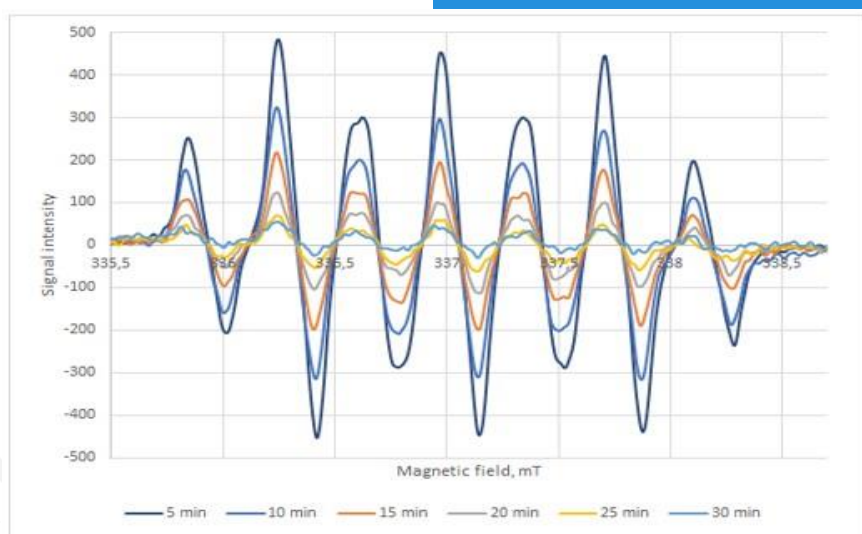
The photocatalytic activity of bismuth oxyhalides was studied in the processes of photodecomposition of rhodamine B and 2-chlorophenol [1], methylene blue [2, 3], nonylphenol, octylphenol, sodium pentachlorophenolate and bisphenol A [4], phenol [5], cyanotoxins [6] and in the disinfection treatment of liquids containing *Micrococcus lylae* [7]. The effect of bismuth oxyhalides can be enhanced by using the Fenton reaction by introducing into the system hydrogen peroxide or a peroxide-containing oxidant (for ex., oxon). Bismuth compounds catalyze the decomposition of oxidant molecules. It leads to forming "reactive oxygen species" - oxygen-centered radicals, singlet oxygen and other particles with high chemical activity. The impact of these active particles on pollutant molecules contributes to their decomposition. EPR spectra of catalytic reaction were obtained by adding oxone to a system containing BiOBr (fig.2).

The EPR method allows to detect the formation of unstable oxygen radicals. The EPR signal caused by them fades away during ~30 minutes.

Examples of experimental EPR study of photoinduced free radical processes occurring in the presence of bismuth oxyhalides demonstrate the wide possibilities of practical application of the method for the development of technologies for wastewater treatment from a wide range of pollutants.

## References

1. W. Li et al. / Molecular Catalysis 438 (2017) 19–29
2. Y.I. Choi, K.H. Jeon, H.S. Kim, J.H. Lee, S.J. Park, J.E. Roh, M.M. Khan, Y. Sohn, Sep. Purif. Technol. 160 (2016) 28–42.
3. D.T. Yue, T.Y. Zhang, M. Kan, X.F. Qian, Y.X. Zhao, Appl. Catal. B 183 (2016) 1–7.
4. Chang, X., Huang, J., Cheng, C., Sui, Q., Sha, W., Ji, G., Deng, S., Yu G., 2010. BiOX (X = Cl, Br, I) photocatalysts prepared using NaBiO<sub>3</sub> as the Bi source: Characterization and catalytic performance. Catal. Commun., 11, 460–464.
5. L. Zhang, X. F. Cao, X. T. Chen, Z. L. Xue, J., 2011. BiOBr hierarchical microspheres: Microwave-assisted solvothermal synthesis, strong adsorption and excellent photocatalytic properties. J. Colloid Interf. Sci. 354, 630–636.
6. Yanfen, F., Yingping, H., Jing, Y., Pan, W., Genwe C., 2011. Unique Ability of BiOBr To Decarboxylate D-Glu and D-MeAsp in the Photocatalytic Degradation of Microcystin-LR in Water. Environ. Sci. Technol., 45, 1593–1600.
7. Zhang, D., Wena, M., Jianga, B., Li, G., Yub, J., 2012. Ionothermal synthesis of hierarchical BiOBr microspheres for water treatment. J. Hazard. Mater., 210, 104–111.



**Figure 2 – BiOBr catalyzed decomposition of oxone**

Experiment parameters:  
 center field, 337 mT;  
 sweep width, 6 mT; modulation frequency, 109.375 kHz; modulation amplitude, 200 uT; attenuation, 10 dB, number of points 1000 and sweep time 200 c.

