Creation and research of new bioindifferent photocatalysts that use the energy of solar radiation to purify wastewater from pollutants

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Abstract. This work is devoted to the study of new bioindifferent photocatalysts that use the energy of solar radiation to purify water from organic pollutants. Photocatalytic materials were obtained by a previously developed low-temperature pyrolytic synthesis. Varying the bismuth content in the precursor mixture within 15–30 %, allows controlling the phase formation of the bismuth and strontium silicate phases. The samples obtained at 25 % bismuth in the precursor mixture (in terms of Bi2O3, wt.) show the highest photocatalytic activity with Bi12SiO2, BiSiO12 formed in the catalyst composition. Photocatalytic activity of coatings with the predominance of bismuth silicates is inferior to coatings with the predominance of strontium bismuthates, but their greater hydrolytic stability is observed.

1. Introduction

The intensification of economic activity and increasing volumes of industrial wastewater every year increase the technogenic load on various natural water bodies. In recent decades, an increased interest of researchers has been aroused to the photocatalytic method of water treatment, the essence of which is the destruction of organic pollutants under the influence of solar radiation on semiconductor photocatalysts [1]. The choice of bismuth photocatalysts to study their effectiveness is justified by the fact that bismuth is non-toxic to living organisms. This is due to the absence of bismuth mobile ionic forms at the pH of biological media. In addition, its compounds are able to absorb light of the visible part of the solar spectrum. Accordingly, such photocatalyst is biologically indifferent and is characterized by high ecological safety for purification of water from organic pollutants.

Previously, the authors have shown that strontium bismuthates have promising photocatalytic properties in heterostructured compositions [2]. Recently, there has been information in the literature
about the high photocatalytic activity of compositions containing bismuth silicates of different stoichiometry [5], thus, the choice of silicate carrier to obtain the catalytic material seems promising. This will allow creating a prototype of an effective photocatalytic material for industrial use.

It is well known that the creation of photocatalytic material is a complex task, and both the choice of carrier and the technology of creating a catalytic coating play an important role in this case. The authors developed a method for creating a material that produces a photocatalytically active coating on the surface of the carrier as a result of chemical interaction at one stage. This method was implemented using strontium bismuthate and silicate ceramic carrier [4]. A coating [3] with high photocatalytic activity due to the presence of strontium bismuthate phase with Sr : Bi = 1 : 4 ratio was obtained. It can be expected that the coatings containing bismuth silicate phases will have significant stability in the aqueous medium. This will solve the problem of strontium leaching. Thus, the aim of this work was to obtain bioindifferent photocatalysts with high hydrolytic stability.

2. Experiment

The photocatalytic materials used in this work were obtained by a previously developed method based on a low-temperature pyrolytic synthesis [4]. Strontium nitrate Sr(NO$_3$)$_2$, bismuth (III) nitrate pentahydrate Bi(NO$_3$)$_3$ · 5H$_2$O and sorbitol C$_6$H$_{14}$O$_6$ were rubbed to form a transparent viscous solution. This solution was brought to the required concentration, after which the silicate glass-ceramic carrier was impregnated with it. Photocatalytically active coatings were obtained by isothermal annealing at 500°C. The parameters of the photocatalytic efficiency study were described in our work [4]. The purification efficiency from the model pollutant, methylene blue (MB), was calculated as follows: \((C_0 - C_t)/C_0\), where: \(C_0\) and \(C_t\) are the initial and current concentration of MS in the treated water, respectively.

3. Research results

By varying the composition of the precursor mixture, the possibility of controlling the composition of the photocatalytic active phases of the coating was investigated. Figure 1 shows the X-ray powder diffraction (XRD) analysis results of the materials obtained with different bismuth content in the precursor mixture. As the bismuth content increases, the bismuth silicate reflections of the corresponding Bi$_{12}$SiO$_{20}$ (ICDB 29-235); Bi$_3$Si$_3$O$_{12}$ (ICDB 33-215) also increase. The formation of strontium silicate phases Sr$_2$SiO$_4$ (ICDB 18-1281) is also observed with an increase in the bismuth content of more than 25 %.

![Figure 1](image-url)
The data of the X-ray phase analysis confirm the results of the element-by-element mapping of the microstructure of strontium bismuthate and bismuth silicate-based coatings formed on the surface of the glass-ceramic carrier (Figure 2). Examining of the sample chipping surface demonstrates the following distributions of the main phases of the coating and the carrier. The crystalline SiO$_2$-quartz included in the carrier is represented by dark, fairly well-faceted crystalline inclusions. They are clearly identified by elemental mapping as the areas richest in silicon and bismuth-free. The glass included in the carrier can be identified as areas with gray coloring and containing needle-shaped crystallites. According to the mapping results, this region is also rich in silicon, but contains some bismuth content. The highest bismuth content is registered in the coating containing phases: SrBi$_x$O$_y$ where x = 5.5–7.7, Bi$_4$Si$_3$O$_{12}$, Bi$_{12}$SiO$_{20}$ which is shown on microphotography as the lightest area with the minimum silicon content.

![Figure 2. Phase composition and morphology of photocatalytic coatings based on strontium bismuthate and bismuth silicates formed on the surface of glass-ceramic carrier](image)

The study of photocatalytic activity of the materials in the decomposition of organic pollutant methylene blue (MC) is shown in Figure 3. The sample obtained at 25 % bismuth content in the precursor mixture has the highest activity. Its composition has the highest content of bismuth silicates. At further increase in the bismuth content in the precursor mixture (up to 30 %), strontium silicates that do not have a pronounced photocatalytic activity begin dominating in the composition of the photocatalyst, and, as a result, the efficiency of water treatment decreases.

![Figure 3. Curves of catalytic activity of the coatings obtained at different bismuth content in the precursor mixture (in terms of Bi$_2$O$_3$ %, wt.)](image)
Based on the change in mass during cyclic tests, a comparative analysis of the hydrolytic stability of two groups of samples was carried out: (1) characterized by a predominance of strontium bismuthate and (2) by a predominance of silicate phases (Table 1). The photocatalysts of the second group show less mass loss and, accordingly, are characterized by greater hydrolytic stability. This is probably due to the absence of strontium leaching.

Table 1. Evaluation of the hydrolytic stability of samples with predominant strontium bismuthate (group-1) and samples with predominant silicate phases obtained at 25 % Bi₂O₃ (group-2) according to the results of mass loss in cyclic tests.

| Number of cyclic tests | group-1 (% wt.) | group-2 (% wt.) | Number of cyclic tests | group-1 (% wt.) | group-2 (% wt.) |
|------------------------|-----------------|-----------------|------------------------|-----------------|-----------------|
| 1                      | -1.017          | -0.432          | 6                      | -1.291          | -0.704          |
| 2                      | -1.219          | -0.688          | 7                      | -1.299          | -0.706          |
| 3                      | -1.273          | -0.691          | 8                      | -1.294          | -0.706          |
| 4                      | -1.294          | -0.701          | 9                      | -1.291          | -0.709          |
| 5                      | -1.286          | -0.698          | 10                     | -1.299          | -0.707          |

4. Conclusion

When varying the bismuth content in the precursor mixture within 15–30 %, the possibility of controlling the phase formation of silicate phases of bismuth and strontium appears. The greatest photocatalytic activity has the samples obtained at 25 % bismuth content in the precursor mixture (in terms of Bi₂O₃, wt.). The highest content of Bi₁₂SiO₂, Bi₄Si₃O₁₂ silicates in the material is registered. The photocatalytic activity of the coatings with a predominance of bismuth silicates is inferior to the coatings with a predominance of strontium bismuthates, but their greater hydrolytic stability is observed (group-2). This shows the promise of creating biologically indifferent photocatalysts based on bismuth silicates to purify water from pollutants, combining high catalytic activity and hydrolytic stability of the composition.

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