PHOTODEGRADATION OF CONGO RED USING ZINC (II) OXIDE IN CIRCULATING CONDITIONS

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With the development of industry, a large amount of industrial wastewater appears, which can be discharged into reservoirs without proper treatment. Such wastewater contains toxic organic substances in various quantities and can cause great harm to human health and the environment. Among water pollutants, dyes have become an acute cause of environmental problems. The largest amount of wastewater with a wide range of pollutants is discharged by textile plants. Treatment of these wastewaters before their discharge is desirable and provided by law. Another problem is the small number of technologies for wastewater treatment from dyes at municipal treatment plants. One of the effective processes of removing organic matter from water is photocatalysis [1].

The most common and widely described photocatalysts are transition metal oxides and semiconductors: TiO_2, ZnO, SnO_2 та CeO_2, etc. [2-5]. Semiconductor metal oxide photocatalytic materials, such as zinc (II) oxide, are attractive materials due to their unique properties. These are high chemical stability, high coefficient of electrochemical bond, high refractive index, high thermal conductivity, antibacterial and UV-protective properties [6-7]. Due to these properties, ZnO is added to plastics, rubber, ceramics, paints, glass, cement, sealants, concrete, food, batteries, etc [8-10].

In the presented study, a comparison of the degradation efficiency of a common organic dye with zinc (II) oxide was performed. Two samples were used as a photocatalyst. The first ZnO sample was pre-synthesized by the method of precipitation from the precursor zinc (II) acetate, which is described in [7-8,11-12]. The second ZnO sample was a powder produced by industry. Congo red dye with an initial concentration of C_0=25.0 mg/L was used as a model pollutant. The degree of its photocatalytic degradation in the presence of the above-described samples of photocatalysts was studied in a model laboratory installation in circulating conditions.

A suspension of the photocatalyst in a small volume of the dye solution was first sonicated for 5 minutes. The resulting suspension was quantitatively transferred to a 5 dm3 vessel to a stock dye solution with a total volume of 3 dm3. After that, the pump was switched on to circulate the solution, and after 20 minutes, a 24-watt UV lamp was additionally turned on. Samples of the test solution were taken every 5 minutes for half an hour. Each suspension sample was filtered through a syringe membrane filter to separate the photocatalyst powder and the residual dye concentration was determined by the photometric method. Then calculated the degree of photocatalytic degradation (a,%). The results of this study are shown in Fig.1.

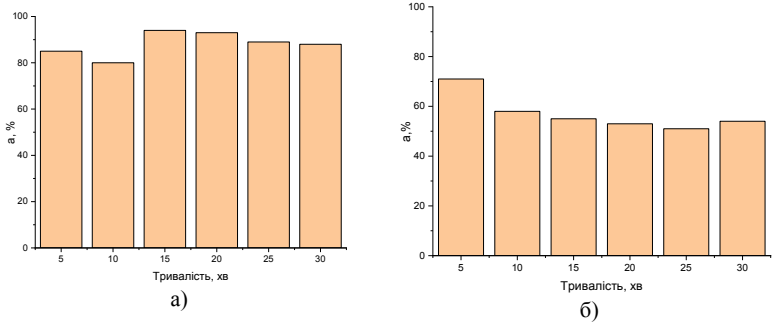

Figure 1 - The degree of photocatalytic decomposition of Congo red, in the presence of: a) synthesized ZnO, b) industrial ZnO.

As can be seen in Fig.1.a, a solution of Congo red dye with the initial concentration of 25 mg/L in the presence of synthesized zinc (II) oxide was subjected to discoloration by 95% after 15 minutes of ultraviolet irradiation under circulating conditions. The average degree of the dye photodegradation for 30 min of ultraviolet radiation consisted 93%. In the presence of an industrial sample of the photocatalyst, it was not possible to achieve similar high degrees of photodegradation, the highest of which did not exceed 70%.

To explain such difference in the catalytic activity of the same chemically identical samples and to find out the reasons for this, a study of the chemical composition of the surface of both photocatalysts was performed. In this experiment, we studied the distribution of surface centers by the degree of acidity by the method of Hammett using thirteen indicators with different pK_a values: in the range from +0.80 to +12.8.

Figure 2 shows the graphs of the distribution of surface centers by the degree of acidity for synthesized in the laboratory and industrial samples of zinc (II) oxide. With the help of these graphs, it is easy to compare the chemical composition of the surface of both applied photocatalysts.

For the synthesized sample of zinc (II) oxide, the surface properties were determined by the presence of intense peaks in the neutral (pK_a=6.4-7.15) and main (pK_a=8.80-9.45) areas of Brönsted. That is, it was characterized by electron-acceptor properties. But, due to the presence of peaks in the neutral region, it is possible to shift the established equilibrium towards the manifestation of the surface centers of proton-donor or proton-acceptor properties.

The surface centers at pK_a=7.15, which are present in the synthesized sample in the largest amount, are completely absent in the industrial sample of zinc (II) oxide. That is, its surface does not have multi-functional properties, and its surface centers cannot change the charge. This difference in the nature of the surfaces is the explanation for the different photocatalytic activity of the studied samples of photocatalysts, in our opinion.

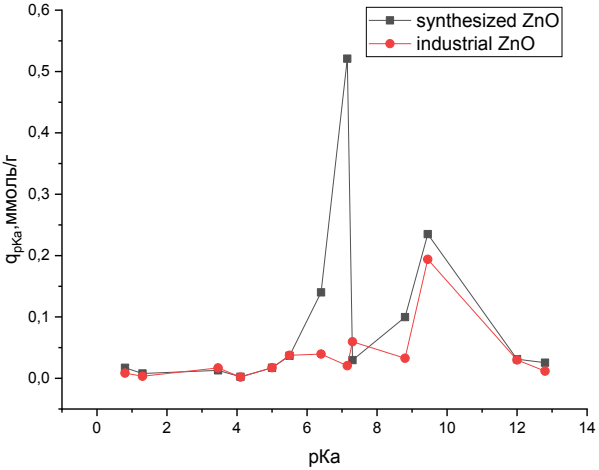

Figure 2 - Distribution of the surface centers by degree of acidity on:
a) synthesized ZnO, b) industrial ZnO.

Thus, the zinc (II) oxide synthesized by deposition in the laboratory experimentally confirmed its high activity in the process of photocatalytic decomposition of Congo red dye under circulating conditions, and its catalytic activity exceeds that of industrial zinc (II) oxide. It is due not only to their crystalline structure, but also surface chemistry, in particular due to the presence of acid-base centers of different strength, in our opinion.

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