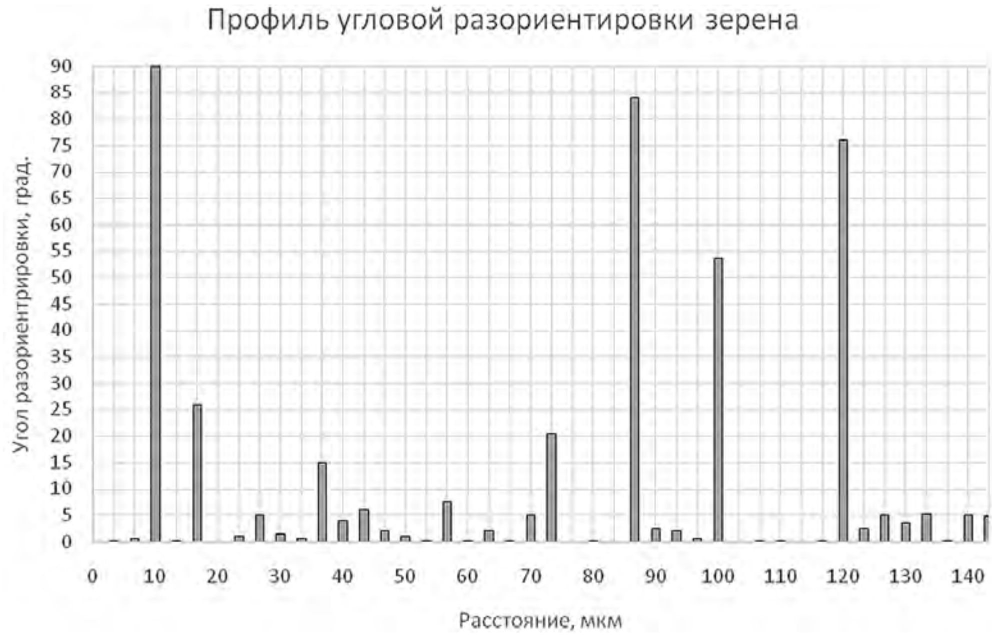

Рисунок 4 – Гистограмма угловой разориентировки зерен первого сплава фольги на поверхности А

Максимальный угол разориентировки достигает 90 градусов. Доля зерен с высокоугловыми границами вдоль сканируемой поверхности приходится на 18%. Легирование висмутом обеспечивает уменьшение размеров зерен. Предложен механизм формирования зеренной структуры, учитывающий влияние движения расплава на рост зерен.

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INFLUENCE OF PLASMA TREATMENT ON PHOTOCATALYTIC ACTIVITY OF ZnO DOPED WITH Ag

ВЛИЯНИЕ ПЛАЗМЕННОЙ ОБРАБОТКИ НА ФОТОКАТАЛИТИЧЕСКУЮ АКТИВНОСТЬ ZnO ДОПИРОВАННОГО Ag

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In this study, nanoparticals Ag (Ag-NPs) were impregnated onto the ZnO microparticles. Impregnated catalysts were prepared by a wet impregnation method followed by plasma treatment. For this purpose, dielectric barrier discharge (DBD) plasma was applied. The photocatalytic degradation of sodium caffeine-benzoate was investigated under ultraviolet (UV) light irradiation in the presence of aqueous suspension of Ag-NPs impregnated ZnO. The catalysts were characterized by UV-Vis spectroscopy and IR spectroscopy. A diminished catalytic activity was observed after impregnation with Ag-NPs. A subsequent treatment by DBD-plasma lead to the enhancement of catalysts' performance.

В этом исследовании наночастицы Ag были импрегнированы на микрочастицы ZnO. Пропитанные катализаторы готовили методом мокрой пропитки с последующей обработкой плазмой. Для этого была использована плазма диэлектрического барьерного разряда (ДБД). Фотокаталитическую деградацию кофеин-бензоат натрия исследовали под воздействием ультрафиолетового (УФ) света в присутствии водной суспензии ZnO, пропитанной наночастицами Ag. Катализаторы были охарактеризованы методами УФ-видимой и ИК-спектроскопии. Пониженная каталитическая активность наблюдалась после пропитки наночастицами Ag. Последующая обработка DBD-плазмой приводит к повышению эффективности катализаторов.

Keywords: ZnO-based photocatalyst, nanoparticle, plasma treatment, dielectric barrier discharge, zinc oxide, sodium caffeine-benzoate, photocatalytic activity, pharmaceutic waste, photodegradation.

Ключевые слова: фотокатализатор на основе ZnO, наночастицы, плазменная обработка, разряд диэлектрического барьера, оксид цинка, кофеин-бензоат натрия, фотокаталитическая активность, фармацевтические отходы, фотодеградация.

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Photocatalysis using semiconductor materials is one of the most effective ways of purifying water from organic waste enterprises. One of the main sources of entry into production is the waste of enterprises using organic dyes (textile, leather and other industries) and pharmacological waste in technological processes. This leads to the fact that some substances that enter the aquatic environment are subject to industrial and pharmacological consequences.

Currently, the most common photocatalysts are titanium dioxide (TiO2) and zinc oxide (ZnO) [1]. Moreover, ZnO is available as a less expensive catalyst. ZnO based catalysts are stable, inexpensive, nontoxic, and do not require reactivation. The attractiveness of photocatalysts based on semiconductor materials: water purification from water and water. Nevertheless, for the application of ZnO on an industrial scale, its activity as a photocatalyst should be increased. One of the methods for improving the characteristics of catalysts is the replacement of plasma heat treatment during their synthesis. Another method for increasing the efficiency of catalysts is their use as metal nanoparticles.

As a rule, in the materials available today, the probability of recombination of a photoinduced electron – hole pair is high, which leads to a decrease in the quantum yield of the reaction. Another significant drawback of photocatalysts is that their photochemical activity lies in the ultraviolet (UV) region. This significantly limits the use of photocatalysts based on zinc oxide (ZnO) or titanium dioxide (TiO2) on an industrial scale in real water treatment systems, since the fraction of UV radiation in the solar spectrum is relatively small.

The problem of disposal of medical waste and, in particular, pharmacological waste is currently considered as an important environmental component of the safety of the population of countries. Some medical waste is considered hazardous materials, which can be toxic, infectious or radioactive. Medical waste includes chemicals and pharmaceuticals.

The treatment and disposal of medical waste can create additional indirect health risks from the release of toxic pollutants into the environment.

Actively developing alternative methods for the disposal of medical waste, such as microwave treatment, chemical treatment and some others. The problem of purification of aqueous media from pharmaceutical industry waste is especially difficult, since it is impossible to determine what substances and in what quantities are contained in pharmaceutical wastewater [2]. This is primarily due to the rapidly changing demand for pharmaceutical products. A number of studies have shown the feasibility and advisability of using biological wastewater treatment methods in the pharmaceutical industry, in particular, the use of membrane bioreactors with ceramic membrane modules [2]. The membrane reactor includes conventional biological wastewater treatment and membrane separation. Biological treatment involves the use of microorganisms to remove organic pollutants and nutrients - phosphorus and nitrogen. Thanks to the installed membranes, the separation of suspended particles and microorganisms is achieved. However, traditional biological methods cannot provide selective waste disposal of drugs, and in many cases biological methods are not applicable for the removal of antibiotics, steroids, hormones [3].

Heterogeneous photocatalysis using nanocatalysts based on zinc oxide and titanium dioxide is considered as a promising method for purifying aqueous media from pharmaceutical industry wastes [3].

The main attention when choosing a model substance for optimizing the processes of photocatalytic decomposition of pharmaceutical industry waste should be given to non-steroidal anti-inflammatory drugs, analgesics, antibiotics, antiepileptic drugs [4]. As a model reaction, the following substances: chlorhexidine digluconate (chlorhexidine digluconate), phenazopyridine (phenazopyridine), acetaminophen (paracetamol), tetracycline (tetracycline), sulfamethoxazole (SMX), methyl-theobromine (benzoid) benzoid-benzobenzokislota, benzoefirbenzokislota, benzoefirbenzoefirbenzoefirbenzoefirbenzoefirbenzoefirbenzoefirbenzokislota (acetylsalicylic acid, aspirin) and some others.

Considering the possibilities of over-the-counter drug purchases in pharmacies of the Republic of Belarus, sodium caffeine-benzoate was chosen as model experiments.

As a catalyst, zinc oxide powder ZnO was used (Ch, ECOS-1, Russia). To carry out a model photodegradation reaction of organic impurities, caffeine, an alkaline purine series (C8H10N4O2, sodium caffeine benzoate), was chosen. The structural formula of sodium caffeine-benzoate is shown in Figure 1. Distilled water was used to prepare all the solutions.

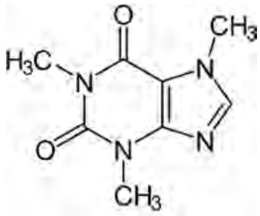

Figure 1 – The structural formula of sodium caffeine-benzoate

To prepare a photocatalyst based on zinc oxide (ZnO) doped with silver (Ag), we used a colloidal solution of silver nanoparticles prepared according to the procedure described in [5].

To prepare a colloid of silver nanoparticles in 50 ml of an aqueous solution of AgNO3 with a concentration of 10-3 mol heated to boiling, 1 ml of a 1% aqueous solution of C6H5O7Na3 was added. The mixture was boiled for 1 hour, then cooled to room temperature.

To obtain catalysts doped with silver nanoparticles, ZnO powder was impregnated with the prepared colloid. Preliminarily, the mixture of ZnO and Ag colloid was homogenized in an ultrasonic mixer for 15 minutes. Then the liquid was evaporated at room temperature. The amount of colloid for impregnation was selected so that the calculated concentration of Ag in the samples was 1.0 wt.% - approximately 91 ml of colloid was used for impregnation per 100 mg of ZnO). ZnO starting material was pretreated in a plasma dielectric barrier discharge.

The processing of the catalysts was carried out in a plasma dielectric barrier discharge. A dielectric barrier discharge is a discharge that occurs in a gas under the influence of an alternating voltage applied to the electrodes, and at least one of the electrodes must be coated with a dielectric. ZnO treatment in a plasma of a dielectric barrier discharge at the facility was carried out at a frequency of 1 kHz for 5 min.

Photocatalytic activity was investigated in the model reaction of decomposition of sodium caffeine-benzoate under the action of ultraviolet radiation in aqueous suspensions of the synthesized samples.

To prepare a suspension, 10 mg of the catalyst sample was mixed with 5 ml of an aqueous solution of sodium caffeine-benzoate at a concentration of 300 mg / L. All solutions were prepared using distilled water.

The selected concentration of caffeine sodium benzoate falls into the linear range of the calibration curve of the dependence of the optical density on the concentration of the absorbing substance.

The selected concentration of sodium caffeine-benzoate falls into the linear range of the calibration curve of the dependence of the optical density on the concentration of the absorbing substance. Catalyst suspensions in aqueous solutions of sodium caffeine-benzoate were exposed to UV radiation. The DRT-240 mercury-quartz lamp (power 240 W) was used as a source of ultraviolet radiation. Test samples were placed in Petri dishes at a distance of 10 cm from the radiation source. Samples were irradiated for 1 hour until complete discoloration with constant stirring of the suspension in a SCOLID IKAMAG WHITE magnetic stirrer (IKA, Germany) at a speed of 250 rpm. During the irradiation process, the change in the concentration of sodium caffeine-benzoate in the solution was monitored using a SOLAR PB 2201 spectrophotometer (SOLAR, Belarus). A small amount of sample was taken every five minutes to determine the dye concentration by the photometric method.

The IR absorption spectra (Figure 2) were recording using a Nicolet iS 10 FTIR-spectrometer (Thermo Fisher Scientific USA).

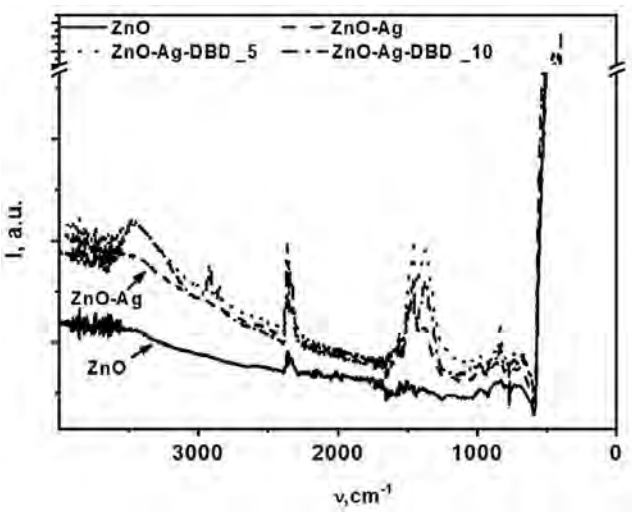

Figure 2 – IR absorption spectra ZnO, ZnO-Ag, ZnO-Ag DBD_5 min and ZnO-Ag DBD_10 min

The relative concentration of sodium caffeine-benzoate Cr was determined by measuring the optical density at the maximum absorption:

$$C_r = \frac{C(t)}{C_0}\cdot 100\% = \frac{A_t}{A_0}\cdot 100\%,$$

where C_0 is the initial concentration of sodium caffeine-benzoate, C (t) is the concentration of sodium caffeine-benzoate after irradiation with UV radiation at time t, A_0 and A_t are the optical density of the solution of sodium caffeine-benzoate at the absorption maximum before irradiation and at time t after the start of irradiation of the sample respectively.

The photodegradation reaction rate constant, determined from the slope of the graph of the C_r concentration versus time, was used as a quantitative characteristic of the photocatalytic activity of the samples.

In work (6) the Purcell coefficient, which determines the presence of an exciton-plasma interaction, was calculated for photocatalysts based on zinc oxide doped with silver nanoparticles and processed in a plasma dielectric barrier discharge. Doping with nanoparticles was carried out by the method of impregnation (deposition from a colloidal solution). A colloidal solution was prepared according to the procedure described in [5]. Processing was carried out for 5, 10, 15 and 25 minutes.

Figure 3 shows the dependence of the Purcell coefficient on the treatment time in a plasma of a dielectric barrier discharge.

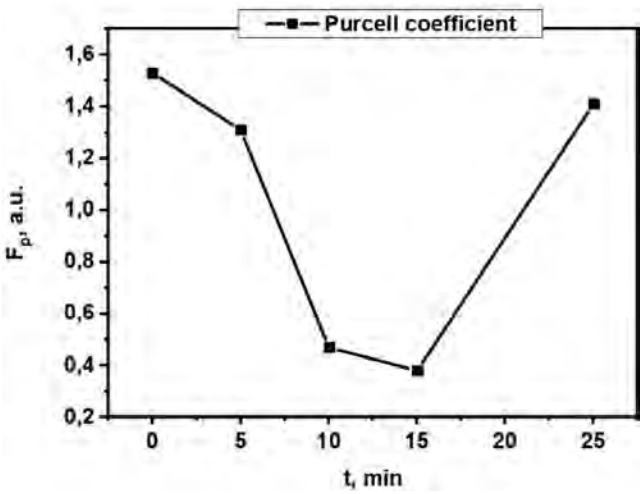

Figure 3 – The dependence of the values of the Purcell coefficient on the processing time

The Purcell coefficient for the treatment time t = 0 was calculated for a catalyst impregnated with nanoparticles, but not processed in plasma. The characteristic fluorescence decay time of unmodified ZnO was 5.02 ns. The fluorescence decay time for materials with an exciton-plasmon bond should be less than for untreated materials. Thus, the values of the Purcell coefficients in excess of 1 indicate the presence of an exciton-plasmon bond.

To conduct a study of the photocatalytic activity of catalysts in photodegradation reactions, an initial concentration of 300 mg / L.

The effect of the doping of microdispersed semiconductor materials (ZnO) with Ag nanoparticles on their photocatalytic properties in the photodegradation reactions of organic pollutants in aqueous media is compared using the model photodegradation reaction of pharmacological wastes as an example of the model sodium caffeine-benzoate photodegradation reaction (Figure 4).

According to the data presented in Figure 4, we can conclude that the photodegradation reactions of sodium caffeine-benzoate at initial concentration of 300 mg / L in the presence of a ZnO-based catalyst doped with silver nanoparticles are characterized by the constant reaction rate - $k = -4{,}2\ 10^{-3}\ s^{-1}$.

As a result of the study, a model of a substance simulating pharmaceutical industry wastes was selected. Sodium caffeine-benzoate was selected as model substances for studying the photocatalytic activity of materials for pharmaceutical industry waste disposal.

The absorption spectra of organic substances in model solutions were measured in the region of 190-700 nm sodium caffeine-benzoate.

It was found that the photodegradation reactions of sodium caffeine-benzoate in the initial concentration in the presence of a ZnO-based catalyst doped with silver nanoparticles are characterized by a reaction rate constant of $k = -4.2\ 10^{-3}\ s^{-1}$. For samples ZnO-Ag_DBD_10 min and ZnO-Ag_DBD_5 min, the reaction rate constants are $k = -1.0\ 10^{-2}\ s^{-1}$and $k = -0.64\ 10^{-2}\ s^{-1}$ respectively.

Thus, by the example of a model reaction of the decomposition of sodium olein-benzoate under the influence of ultraviolet radiation, it was shown that a ZnO-based catalyst doped with nanoparticles and treated with plasma for 10 minutes is effective in photodegradation reactions of pharmacological wastes.

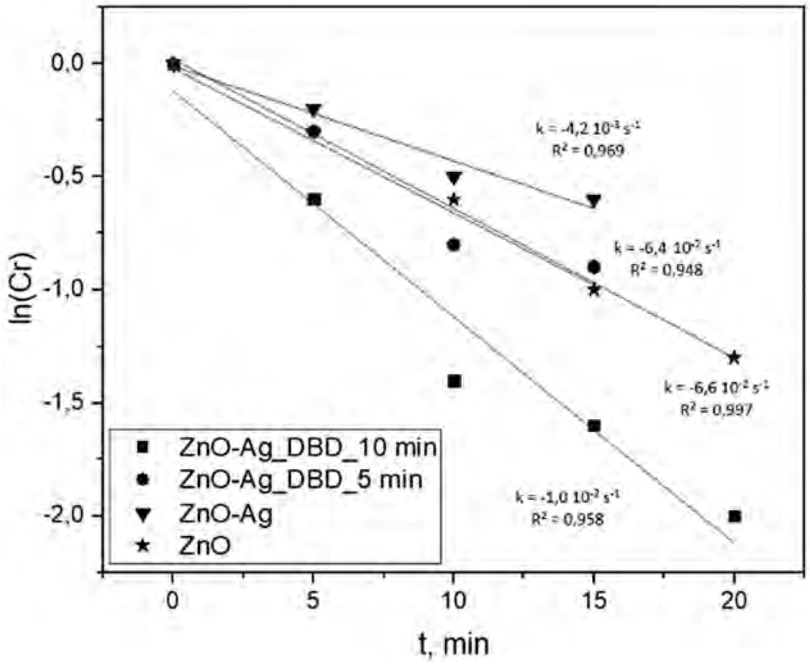

Figure 4 – The dependence of the optical density of sodium caffeine-benzoate solutions at the absorption peak (λ = 272 nm) on the concentration of sodium caffeine-benzoate

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ОЧИСТКА СТОЧНЫХ ВОД ОТ ХЛОРИД- И ФОСФАТ-ИОНОВ
WASTEWATER TREATMENT FROM CHLORIDE- AND PHOSPHATE-IONS

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Сточные воды предприятий являются источником загрязнений городских очистных сооружений, а также водных объектов. Качество сточных вод регламентируется законодательством и все категории предприятий обязуются выполнять эти требования. Наличие в технологическом процессе производства растворов