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Photocatalytic self-cleaning lime coatings

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Abstract. The article presents the results of assessing the self-cleaning properties of lime coatings. The use of zinc oxide immobilized on synthesized aluminosilicates as a photocatalyst is considered. The technology of synthesis and properties of aluminosilicates are described. The photocatalytic activity of zinc oxide is analyzed depending on the technology of obtaining the photocatalyst. It was found that the band gap width of the photocatalyst obtained by immobilizing zinc oxide on synthetic zeolite decreased from 3.37 eV to 2.7 eV. Comparison of the self-cleaning ability of lime coating samples, in the formulation of which the photocatalyst was introduced, is carried out using the methods specified in the regulatory documentation- according to the test method in accordance with GOST R 57255-2016, according to the method of the Italian standard UNI 11259. The results of tests according to the methods established in regulatory documents indicate the high photocatalytic activity of the lime coating. It has been established that the lime coating with the use of zinc oxide photocatalyst immobilized on synthetic zeolite exhibits high photocatalytic activity. In accordance with the requirements of the Italian standard UNI 11259, the photocatalytic activity of the surface after 4 hours is R=21.94-55.42%, and after 26 hours – 51.96 - 98.2% depending on the specific surface of zinc oxide.
Keywords: photocatalyst, self-cleaning ability of surface, decomposition of organic pollutant, lime coating, zinc oxide, synthetic aluminosilicates

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1. INTRODUCTION

During operation, protective and decorative coatings of external enclosing structures of buildings are exposed to moisture due to the action of rain, high relative humidity, and also due to the diffusion of water vapor through the enclosing structure from the inner surface to the outer surface during the cold period of the year [1-4]. Air pollution has stimulated the development and implementation of self-

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cleaning coatings in the construction industry. Photocatalytic coatings are especially effective, which decompose pollutants and dust deposited on their surface under the influence of ultraviolet radiation [5, 6].

There are many semiconductors that can be used as photocatalysts, such as TiO_2, ZnO, WO_3, and Fe_2O_3. The transparency of titanium dioxide (TiO_2) in the visible and near-infrared regions of the spectrum can be significantly increased, and light reflection can be reduced by alloying with 5% nickel [7, 8].

One of the common photocatalytic materials is zinc oxide ZnO [9-11]. ZnO nanoparticles have a large surface area and a large number of active centers. To increase its photocatalytic activity, zinc oxide ZnO is modified by organic materials, mono- and co-alloying methods, and interaction with other semiconductors. Nickel Ni is widely used among the sources of transition metals for alloying Zn. The doping of nickel Ni in ZnO makes it possible to shift the optical band gap towards red wavelengths.

In recent years, the technology of increasing the activity of the photocatalyst has been widely used, which consists in immobilizing the photocatalyst on inert media. Silicon dioxide, activated carbon, mordenite, and zeolite are used as inert substrates [12].

To increase the photocatalytic activity of zinc oxide, a technology for immobilizing the photocatalyst on substrates has been proposed [13-15].

In the work [16] it is proposed to use synthetic aluminosilicates as a substrate. The method of zeolite synthesis developed by us includes the dispersion of a micro-sized aluminum powder in a solution of sodium silicate (liquid glass). The reaction proceeds in the temperature range of 60-90 ° C for a period of half an hour to two hours [17,18].

The synthesized additive has a bulk density of 0.55 ± 0.05 g/cm^3, the specific surface area measured by the low-temperature nitrogen sorption method is 101.28 m^2/g The composition of the additive is mainly represented by aluminum oxides, which make up 51.03%.

The active interaction of the aluminosilicate additive with the photocatalyst, due to its high content of SiO_2 and Al_2O_3, as well as its acid-base properties, allows it to be considered as an effective carrier. The results obtained confirm the prospects of using the synthesized additive as a carrier for photocatalytic materials.

2. METHODS AND MATERIALS

The developed surface of the photocatalyst was obtained by mechanical grinding of zinc oxide (ZnO) in a planetary mill [19]. The specific surface area was determined on a PSKh-10a device. Two approaches were used to immobilize zinc oxide on zeolite:

- mechanical mixing: zinc oxide powder was simply mixed with the already synthesized zeolite;
-Joint synthesis: zinc oxide was added to the reaction mixture during the synthesis of zeolite in a ratio of 1:8:14:2.

Methylene blue ($C_{16}H_{18}ClN_3S$), analytical grade, produced by Loba Chemie (India), oleic acid (GOST R 57255–2016), and Rhodamine B were used as organic pollutants.

The assessment of the efficiency of the self-cleaning capacity of coating samples, in the formulation of which a photocatalyst was introduced, was carried out in two ways:

– according to the method of assessing the photocatalytic decomposition of the organic dye rhodamine B (Rhodamine B, $C_{28}H_{31}ClN_2O_3$) (according to the method of the Italian standard UNI 11259 "Determination of the photocatalytic activity of hydraulic binders – rhodamine test") by the change in the color of the samples after ultraviolet irradiation;

– according to the test method in accordance with GOST R 57255-2016.

The method for assessing the photocatalytic decomposition of the organic dye rhodamine B, in accordance with the Italian standard UNI 11259 "Determination of the photocatalytic activity of hydraulic binders – rhodamine test" consisted of monitoring the measurement of the surface color (by visual observation and photography) according to the CIELAB system using color coordinates L* a* b*, where L* is the luminosity, a* and b* are the colorimetric coordinates, which represent the measurement of the color tone in a two-dimensional plane.

The digital image data were analyzed using ImageJ software. The photocatalytic activity was calculated based on the obtained coordinates.

The measurement procedure according to GOST R57255-2016 was as follows. To remove organic contaminants, the sample was previously irradiated with ultraviolet light for 24 hours. A UV lamp with a wavelength of 350 nm and an intensity of 85 m^3/h was used (Fig. 1). Then, oleic acid was applied to the surface, which served as a model pollutant. To determine the effect of ultraviolet radiation on the wetting angle, measurements were carried out for five samples at five different points. Based on the data obtained, the coefficient of variation was calculated. The measurements were completed when the values of the variation coefficients became less than 10%. In addition, for a comparative assessment of the photocatalytic activity of the lime composition in the presence of a photocatalyst, coating samples were prepared using a methylene blue solution as an organic pollutant. In order to determine the effect of UV radiation on the wetting angle, measurements were carried out for at least five samples at five different points. Based on the data obtained, a coefficient was calculated reflecting the degree of change in the wetting angle. of variation.

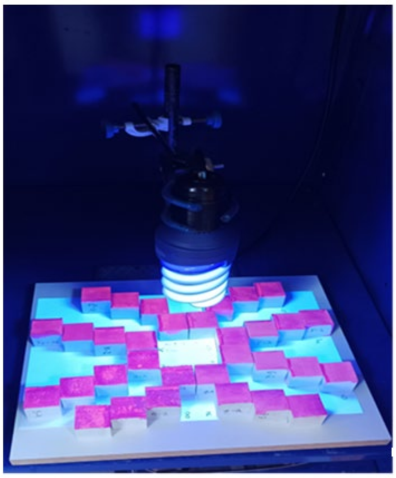

Fig. 1. A pilot plant for ultraviolet irradiation of coating samples.

3. RESULTS AND DISCUSSION

The degree of degradation of methylene blue was preliminarily determined depending on the degree of ZnO grinding. The kinetics of dye absorption was determined using a KFK-3KM photocolorimeter at a wavelength of 664 nm. The research results are shown in Fig. 2-4.

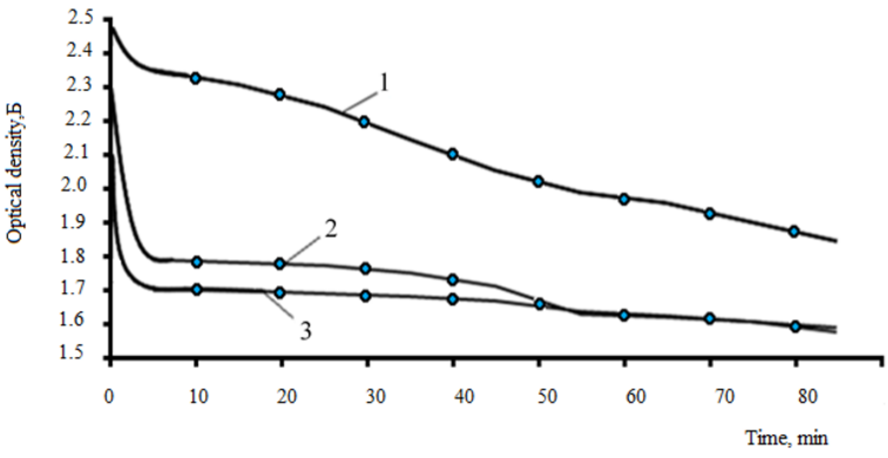

Fig. 2. Change in optical density of methylene blue solution (specific surface area of zinc oxide S= 5.9 m^2/g), zinc oxide content: 1-1,5 %; 2-1 %; 3-0,5 %.

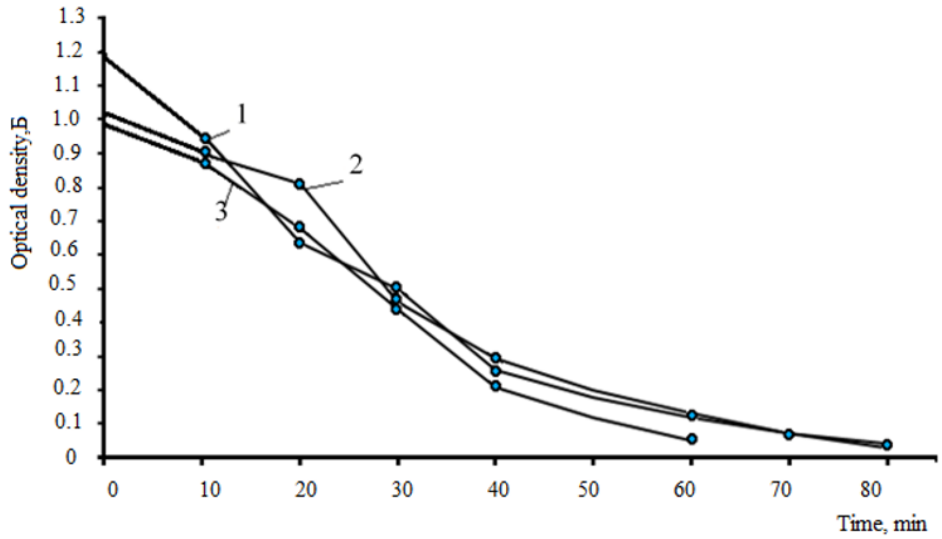

Fig. 3. Change in optical density of methylene blue solution (specific surface area of zinc oxide S= 6.2 m^2/g), zinc oxide content: 1 – 1,5 %; 2 – 1 %; 3 – 0,5 %.

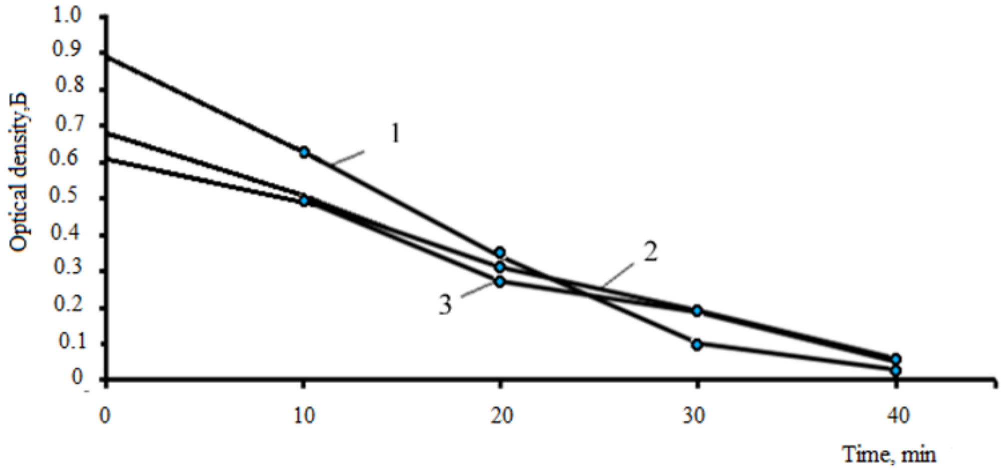

Fig. 4. Change in optical density of methylene blue solution (specific surface area of zinc oxide S= 8.5 m^2/g), zinc oxide content: 1-1.5%; 2-0.5%; 3-1.0%.

Experiments have shown that the rate of discoloration of the solution increases with an increase in the concentration of zinc oxide and an increase in its specific surface area. Zinc oxide with a specific surface area of 8.5 m^2/g demonstrated the best photocatalytic activity. The maximum rate of decolorization of the methylene blue dye solution is observed when using a photocatalyst immobilized on the surface of the synthesized synthetic zeolite (Fig. 5).

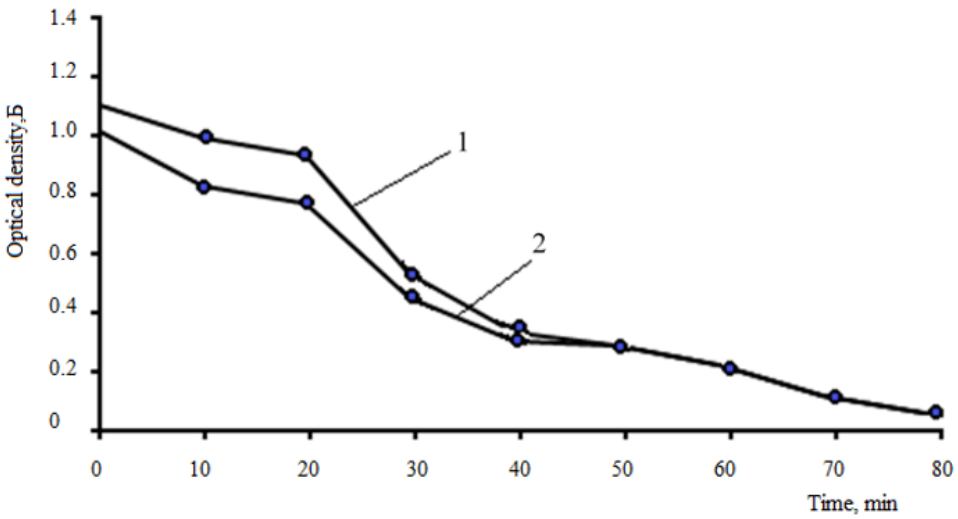

Fig. 5. Change in optical density of methylene blue solution (specific surface area of zinc oxide S= 6.2 m^2/g): 1-1,0 %; 2-1% zinc oxide immobilized on the surface of synthetic zeolite.

The data presented in Fig. 6 confirm the photocatalytic activity of zinc oxide immobilized on an aluminosilicate carrier (the configuration described in row 3 of Fig. 7), using the example of methylene blue degradation.

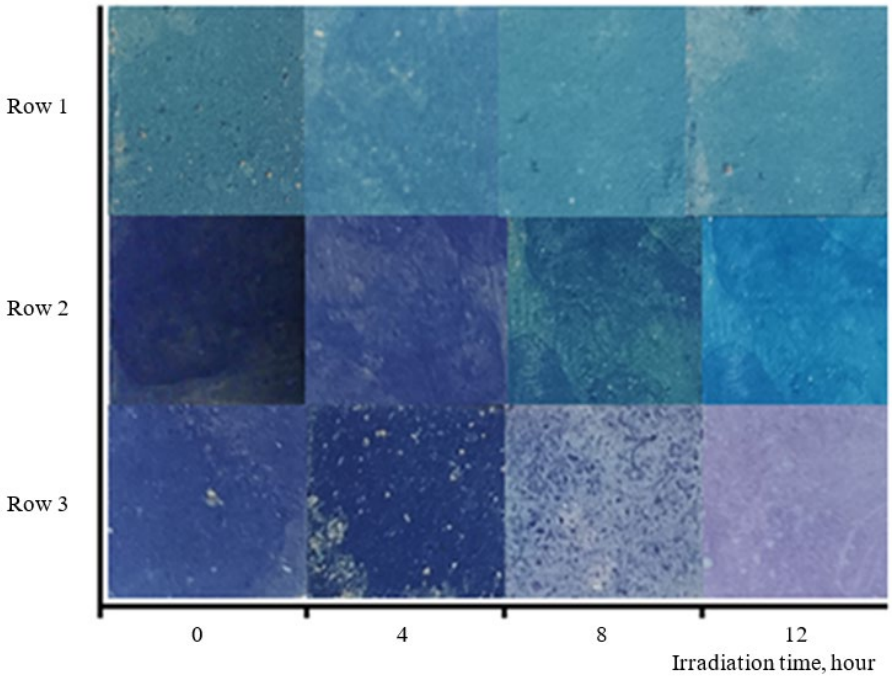

Fig. 6. Color change of methylene blue on the surface of lime coating. The composition contains: row 1-5% ZnO (S = 6.2 m^2/g); row 2-10% ZnO (S = 6.2 m^2/g); row 3-10% synthetic zeolite + 10% ZnO (S = 6.2 m^2/g).

To understand the mechanism of decomposition of methylene blue in the presence of zinc oxide and aluminosilicate additives, the IR transmission spectra of the samples were analyzed (shown in Fig. 7). Spectrophotometric measurements of the samples were carried out using a SF-56 spectrophotometer (OKB Spektr, Russia).

The key feature of the analyzed IR spectra is the presence of absorption bands and peaks corresponding not only to the aluminosilicate additive, but also to the ultrafine ZnO powder. Several characteristic absorption bands and peaks directly correspond to the qualitative composition of the aluminosilicate additive, for example, a wide intense absorption band near 1010 cm^{-1} corresponds to symmetric and asymmetric stretching vibrations of the Si-O-Si bonds.

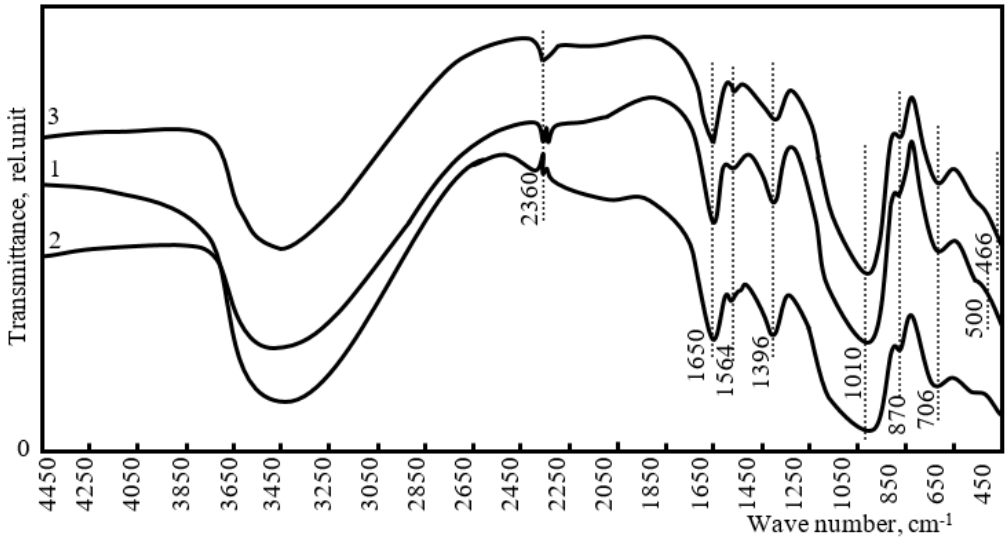

Fig. 7. IR transmission spectra of the samples under study: 1 – aluminosilicate additive, 2 – mixing ultrafine ZnO powder and aluminosilicate additive; 3 – aluminosilicate additive with ultrafine ZnO powder introduced during the synthesis process.

To determine the band gap (Eg) of zinc oxide (ZnO), the Tauck method based on equation (1) was applied [20, 21]. The optical properties of the samples were previously studied, including the analysis of transmission spectra in the visible and ultraviolet ranges (Fig. 9). These spectra showed high transparency of the samples at wavelengths over 300 nm, which allowed the use of the Tauka method.

$$(ahv)^n = A(hv - E_g) \quad (1)$$

where α, is the absorption coefficient;

A is the photon energy; h is Planck's constant;

υ is the oscillation frequency;

Eg is the optical width of the forbidden zone.

The optical band gap (Eg) was estimated by analyzing the absorption spectra using the Tauck method. Dependence $(ahv)^2$ of the photon energy (hv) was approximated by a linear function in the region of strong absorption.Extrapolation of this linear dependence to $(ahv)^2 = 0$ allowed us to determine the value of Eg.The calculation used the value n = 2, corresponding to a semiconductor with a straight gap, which is consistent with the generally accepted concept of ZnO. Fig. 10 illustrates the results of using the Taucka method to determine Eg in the zinc oxide samples under study.

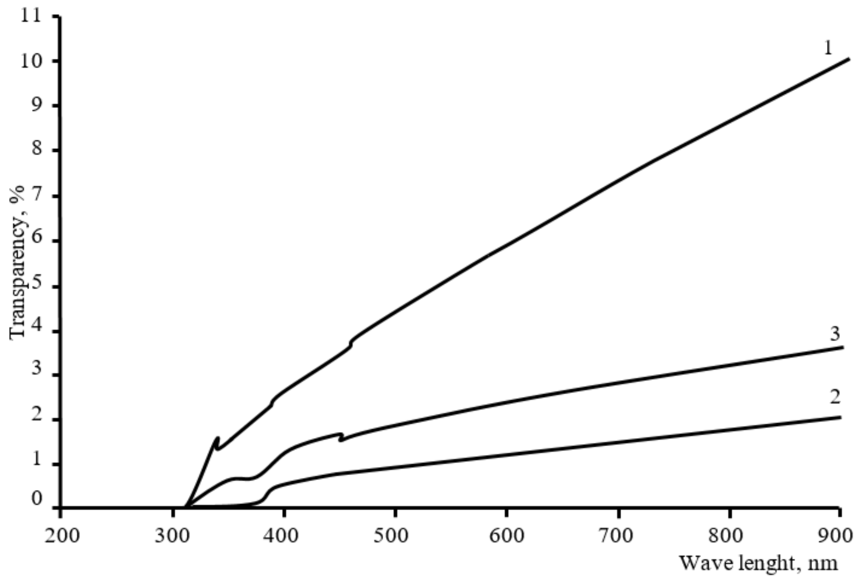

Fig. 8. Optical transmission spectra of the samples under study: 1 – synthetic zeolite; 2 – mixing ultrafine ZnO powder and synthetic zeolite; 3 – synthetic zeolite with ultrafine ZnO powder introduced during the synthesis process.

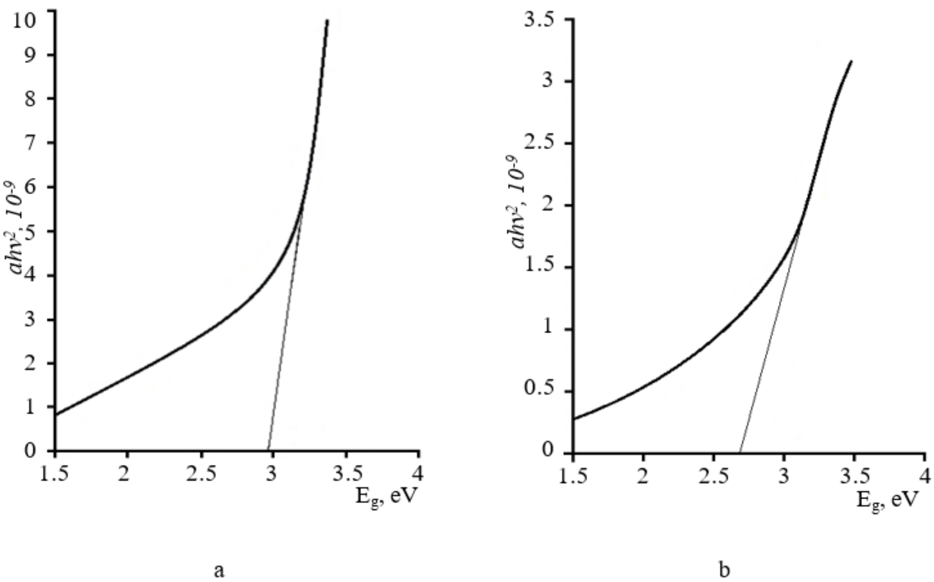

Fig. 9. Optical band gap of ZnO by the Tauck method: a) mixing of ultrafine ZnO powder and synthetic zeolite; b) addition of synthetic zeolite with ultrafine ZnO powder introduced during synthesis.

It was found that the optical width of the forbidden band of zinc oxide is 2.96 eV and 2.70 eV depending on the technology of photocatalyst synthesis, which is obviously associated with doping of highly defective ultrafine ZnO powder with aluminum or silicon ions. The data obtained are consistent with the results of infrared spectroscopy.

Fig. 10 shows photographs of samples immediately after application of the organic pollutant Rhodamine B to the prepared surface of lime coatings before and after UV irradiation.

The photocatalytic activity was calculated after 4, 8, 12, 26 hours using the formulas:

$$R = \frac{a_o - a_t}{a_o}$$

where a_0 is the value of the color coordinate at the zero moment of time;

a_t is the value of the color coordinate after t hours of UV radiation.

Table 1 shows the results of the evaluation of the photocatalytic activity of zinc oxide. According to the Italian standard UNI 11259, the R values must be greater than 20% after 4 hours and greater than 50% after 26 hours of exposure to ultraviolet radiation. The photocatalytic activity of the surface after 4 hours is R = 21.94-55.42%, and after 26 hours - 51.96 - 98.2% depending on the specific surface of zinc oxide.

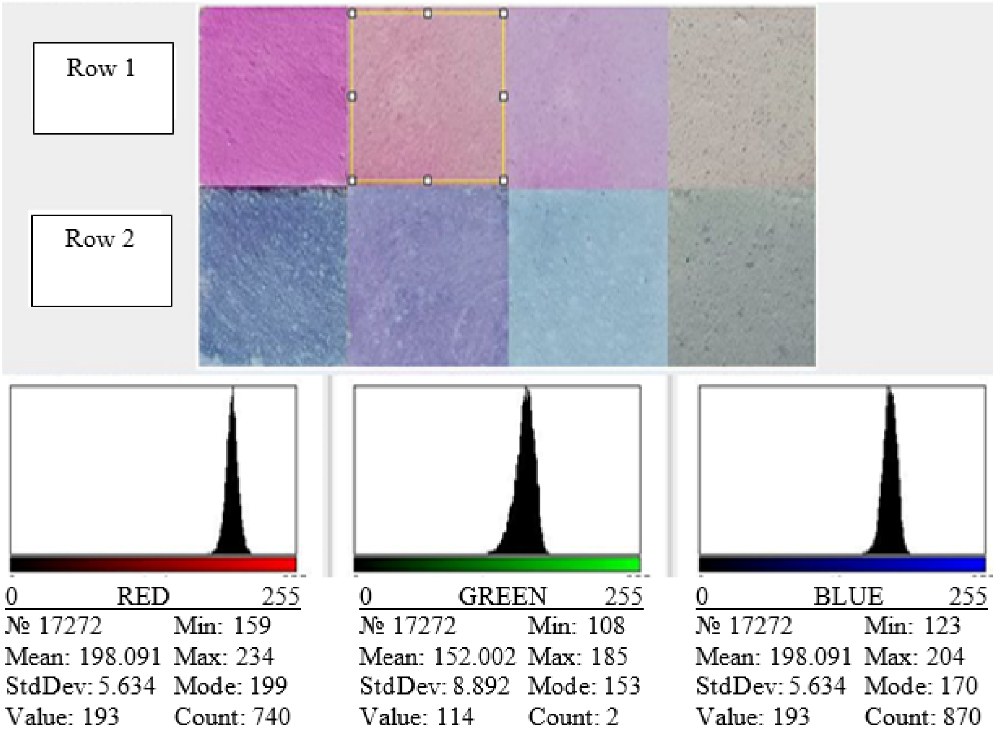

Fig. 10. Photo of the surface of lime coating samples with applied organic pollutant: 1 row – specific surface area of zinc oxide during photocatalyst synthesis 8.5 m^2/g; 2 row – specific surface area of zinc oxide during photocatalyst synthesis 6.2 m^2/g.

The use of zinc oxide with a higher specific surface area in the process of photocatalyst synthesis together with the addition of synthetic zeolite contributes to an increase in photocatalytic activity, however, a photocatalyst using zinc oxide with a specific surface area of Ssp = 6.2 m^2/g also provides high self-cleaning properties of lime coatings. In this regard, we recommend that the synthesis of the photocatalyst be carried out using zinc oxide with a specific surface area of Ssp = 6.2 m^2/g.

In addition, the self-cleaning ability of the coating based on the developed composition was investigated in accordance with the testing method of GOST R57255-2016 (Fig. 11).

Table 1. The activity of zinc oxide immobilized on synthetic zeolite.

Photocatalytic activity of the surface after, hour	R value,%
	Specific surface area of zinc oxide in the synthesis of aluminosilicates Ssp = 8.5 m^2/g
4	55.42060279
8	67.11650922
12	97.12100765
26	98.20062978
Specific surface area of zinc oxide in the synthesis of aluminosilicates Ssp = 6.2 m^2/g	
4	21.94600374
8	40.76450147
12	48.35605453
26	51.96471532

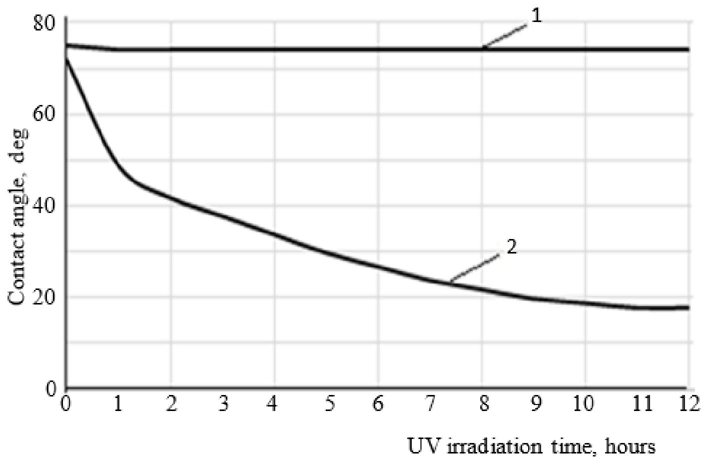

Fig. 11. Changing the wetting edge angle on the surface of the lime coating during ultraviolet irradiation: 1 – coating without a photocatalyst; 2 – coating based on a composition with a zinc oxide photocatalyst immobilized on synthetic zeolite.

The initial contact angle was 75° for the coating based on the composition without a photocatalyst, and 72° for the coating surface with a photocatalyst. For coatings based on a lime composition without the introduction of a photocatalyst, the initial contact angle is stable and does not change as a result of UV irradiation. In the coating based on the formulation with a photocatalyst, as the UV irradiation time increases, the contact angle gradually decreases to 26° in 5 hours, and to 18° after 10 hours. This indicates that the hydrophobic layer of oleic acid disappears from the surface during this period.

The decrease in the initial contact angle after UV irradiation of the surface confirms the photocatalytic properties of the surface.

4. CONCLUSIONS

A technology for synthesizing a photocatalyst has been developed, which consists of immobilizing zinc oxide with a specific surface area of 6.2-8.5 m^2/g on a synthetic zeolite. An increase in the optical width of the forbidden zone of zinc oxide immobilized on a synthetic zeolite to 2.96 eV and 2.70 eV has been established, depending on the specific surface area of zinc oxide.

The data obtained by the two methods for determining the self-cleaning ability of the surface of lime coatings are consistent with each other. The revealed pattern of increasing photocatalytic activity with ZnO in the composition of the aluminosilicate additive is traced both when determining the contact angle of wetting and when measuring the color intensity of the organic dye. Lime coating with the use of zinc oxide photocatalyst immobilized on synthetic zeolite exhibits high photocatalytic activity. According to the requirements of the Italian standard UNI 11259, the photocatalytic activity of the surface after 4 hours is R = 21.94-55.42%, and after 26 hours - 51.96 - 98.2% depending on the specific surface of zinc oxide. In accordance with the GOST R57255-2016 methodology, in the coating based on the composition with the photocatalyst, as the UV irradiation time increases, the wetting angle gradually decreases to 26° after 5 hours and to 18° after 10 hours. This indicates the manifestation of photocatalytic properties of the surface.

5. ACKNOWLEDGMENTS

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