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ПОЛУЧЕНИЕ В ТЛЕЮЩЕМ РАЗРЯДЕ НА ПОВЕРХНОСТИ ЦЕОЛИТОВ ОКСИДОВ ЦИНКА И МЕДИ ДЛЯ РАЗЛОЖЕНИЯ МЕТИЛЕНОВОГО СИНЕГО

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Представлен новый метод получения сложных оксидов меди и цинка на поверхности цеолита марки NaX. Цеолиты погружали в водный раствор нитратов меди, цинка и их смеси (50:50) на несколько часов, после чего сушили в течение 1 сут. Цеолиты, покрытые нитратами, обрабатывали тлеющим разрядом атмосферного давления воздуха в течение 10 мин. Во время плазменной обработки изменялся цвет поверхности цеолитов. Изменение морфологии поверхности исследовали с помощью сканирующей электронной микроскопии. Показано, что на поверхности образуются сложные наноразмерные структуры, которые по данным энергодисперсионной рентгеновской спектроскопии представляют собой оксиды меди и цинка. Определение удельной площади поверхности и распределения пор по размерам показало, что плазменная обработка цеолитов с нанесенными на них нитратами ведет к уменьшению площади микропор и уменьшению мезопор. Фотокаталитическая активность проверялась на примере разложения стандартного красителя метиленовый синий. Так облучение ультрафиолетовым светом раствора метиленового синего в течение 180 мин раствора без цеолита не показало никакого изменения оптической плотности растворов, как и исследования, проведенные в условиях отсутствия какого-либо светового излучения. Показано, что после 180 мин воздействия света на раствор метиленового синего разложилось 70,3% красителя на цеолите с оксидом меди и 83,8 на цеолите с оксидом цинка. Наилучшие результаты показали образцы с цеолитами, покрытыми комплексным оксидом меди и цинка, где фоторазложение составило 87,9% за 180 мин облучения ультрафиолетовым светом.

Ключевые слова: тлеющий разряд, сложные оксиды, фотодеградация, метиленовый синий

OBTAINING ZINC AND COPPER OXIDES IN A GLOW DISCHARGE ON THE SURFACE OF ZEOLITES FOR THE DECOMPOSITION OF METHYLENE BLUE

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A new method for producing complex copper and zinc oxides on the surface of NaX zeolite is presented. Zeolites were immersed in a solution of copper and zinc nitrates for several hours, after which they were dried for 24 h. Zeolites coated with nitrates were treated with atmospheric pressure glow discharge in air for 10 min. After plasma treatment, the zeolites changed their color. Changes in surface morphology were studied using scanning electron microscopy. It has been shown that complex nano-sized structures are formed on the surface, which, according to energy-dispersive X-ray spectroscopy, are copper and zinc oxides. Determination of the specific surface area (BET) and pore size distribution showed that plasma treatment of zeolites with nitrates depos-

ited on them leads to a decrease in the area of micropores and a decrease in mesopores. The photocatalytic activity was tested using the example of the decomposition of methylene blue dye. Thus, the irradiation of a solution of methylene blue with light for 180 min without zeolite did not show any change in the optical density of the solutions, as did shadow studies. After 180 min, 70.3% of the dye on zeolite with copper oxide and 83.8% on zeolite with zinc oxide decomposed. The best results were shown by samples with zeolites coated with complex copper and zinc oxide, where photodecomposition was 87.9% after 180 min of light irradiation.

Keywords: glow discharge, complex oxides, photodegradation, methylene blue

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INTRODUCTION

Transition metal oxides are strategically important in various types of production. In recent years, there has been increasing interest in the use of metal oxides to purify water from various types of contaminants [1-3]. In this case, oxides of one metal (TiO_2, Al_2O_3, ZnO) [4] are traditionally used. Single semiconductors have some disadvantages, including high electron-hole pair recombination rate, photocatalyst deactivation, poor selective adsorption, and high photocatalyst cost. To improve the photocatalytic activity of a semiconductor and use its advantageous properties, the use of multicomponent systems and oxides began. Thus, double oxide ZnO/CuO has proven itself as a catalyst and has been used for more than 30 years for the synthesis of methanol [5-6]. A new round of interest in ZnO/CuO research is associated with its use for the conversion of CO_2 into methane and methane into methanol in DBD reactors [7-9]. Recent studies have shown the possibility of using double oxide to purify wastewater from organic contaminants, such as Rhodamine blue, methylene orange [10], and methylene blue [11].

Methylene blue has many potential applications in the textile, pharmaceutical, paper, dyeing, printing, paint, medical, and food industries [12]. It is also used as a potential material in dye-sensitized solar cells [13], capacitors [14], sensors [15], microbial fuel cells [16], etc. Despite its widespread use in industry and medicine, methylene blue is toxic, carcinogenic, not biodegradable, can pose a severe threat to human health and aquatic organisms, and has a destructive environmental impact [17]. Therefore, using simple and complex approaches to decompose methylene blue in water is very important [18]. The use of semiconductor materials will make it possible to decompose MB into CO_2 and H_2O. The copper-zinc complex oxide was previously shown to be effective in dye decomposition, but the decomposition rate was over 5-8 h [19-20].

Existing methods for producing oxide nanoparticles on the surface of zeolites involve using a large number of reagents, complexity of execution, and high cost of equipment. The method based on the use of low-temperature gas-discharge air plasma is free of these disadvantages. Using nitrates to apply zeolite and air as a plasma-forming gas is a cheap and environmentally friendly replacement for existing methods. The products formed during plasma combustion and processing of nitrates are already an integral part of natural air. Moreover, the use of a simple structural and electrical circuit makes the process fast and scalable. As a result, we obtain oxides and complex oxides of transition metals, which have previously proven themselves as catalysts for the decomposition of organic dyes, such as methylene blue.

EXPERIMENTAL SECTION

Materials and methods

All the chemical reagents used in the experiments were of analytical grade without further purification. 2.95 grams copper nitrate hexahydrate $Cu(NO_3)_2 \cdot 6H_2O$ 100%, 2.97 grams zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$, as well as their mixture in a molar ratio of 1 to 1 were used as starting materials. NaX zeolite (Sorbis Group) with a 3-5 mm diameter was used. In 40 ml of solution prepared by dissolving nitrates in distilled water, 20 g of zeolites were placed for 2 h and then dried at 50 °C for 24 h.

Zeolites with nitrates deposited on them were processed in a particular cell, as shown in Fig. 1. A Spellman SL1200 was used as a power source. A voltage of 8 kV was applied to the titanium anode (sufficient for a breakdown of the interelectrode space); a steel plate with holes through which air was blown was used as a cathode. The airflow rate was 5 L/min. The cell was a cylinder 5 cm high with a conical narrowing at the base (up to 1.2 cm). The interelectrode distance was 7 mm. Discharge current was 50 mA – processing time was 10 min. The cell design and flow are selected so that the zeolites fall into the discharge generation zone, where the main processes of converting nitrates on the surface of the zeolites into oxides occur.

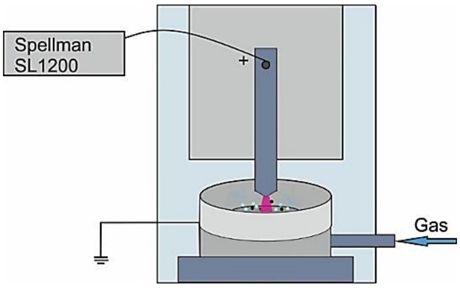

Fig. 1. Scheme of the experimental setup
Рис. 1. Схема экспериментальной установки

As a result, the following samples were obtained and used for morphological and catalytic studies:

- NaX (original zeolite without treatment)
- CuO@NaX (zeolite coated with copper nitrate and processed in a gas discharge)
- ZnO@NaX (zeolite coated with zinc nitrate and processed in a gas discharge)
- ZnOCuO@NaX (zeolite with a deposited mixture of copper-zinc nitrates processed in a gas discharge)

Characterization

A scanning electron microscope Tescan VEGA 3 SBH (Czech Republic) with an attachment for elemental analysis was used to study the morphology and composition of the surface.

XRD analysis was used to determine the composition, XRD analysis was used (DRON 3 M, Burevestnik, Russia) with Cu Ka radiation at 0.154 nm. The diffraction patterns were processed using QualX2 software [21] and the open crystallographic COD database [22].

Specific surface area determinations (BET) and pore size distributions were measured on a Microtrac Belsorp miniX apparatus (BELSORP-miniX, Microtrac BEL Corp., Japan).

Study of the decomposition of methylene blue

An SF-56 spectrophotometer (OKB Spektr, St. Petersburg) with an optical path length of 10 mm was used to study the kinetics of changes in optical density. Experiments were carried out at room temperature. To study the kinetics of changes in optical density, an aqueous solution of methylene blue (MB) with a concentration of $2.8 \cdot 10^{-8}$ mol/l was used. We used 5 g of zeolites and 100 ml of methylene blue solution. Zeolites and the solution were placed in 100 ml beakers. Next, experiments were carried out using ultraviolet light without stirring. An ultraviolet lamp with a wavelength of 254 nm and a power of 9 W was installed at a height of 30 cm from the glasses (power consumed from the network was 30 W). At regular intervals, 2.5 mL of sample was taken, and the spectral changes were recorded at 663 nm to determine the residual concentration of MB using a UV-Vis spectrometer, after which the sample was returned. The degree of decomposition of MB was calculated as follows:

$$D(\%) = \frac{C_0 - C_t}{C_0} \cdot 100\%, \tag{1}$$

where C_0 is the initial concentration of methylene blue; C_t – concentration of methylene blue after t minutes of interaction with light.

For the completeness of the experiment, we studied six samples, which were carried out in parallel. The first experiment and the first sample were 100 ml of a methylene blue (hereinafter MB) solution, which was irradiated with ultraviolet light for a long time. This was necessary to understand how quickly the dye decomposes in distilled water without additives.

The second experiment involved 5 g of the original zeolite in 100 ml of an aqueous solution of methylene blue, which was placed in a box without natural or lamp lighting (hereinafter NaX no UV). This experiment is necessary to understand the degree of adsorption of the dye inside the zeolite.

The third experiment involved 5 g of the original zeolite in 100 ml of a methylene blue (MB) solution, which was irradiated with ultraviolet light for a long time (hereinafter NaX UV). This experiment was carried out to evaluate the photocatalytic activity of the original NaX, which contains aluminum oxide, which exhibits catalytic activity [23]. The fourth experiment was 5 g of zeolite with copper oxide after plasma treatment in 100 ml of methylene blue (MB) solution, which was irradiated with ultraviolet for a long time (CuO@NaX). The fifth experiment was 5 g of zeolite with zinc oxide after plasma treatment in 100 ml of methylene blue (MB) solution, which was irradiated with ultraviolet for a long time (ZnO@NaX). In the sixth experiment, 5 g of zeolite with complex zinc and copper oxide after plasma treatment in 100 ml of methylene blue (MB) solution, which was irradiated with ultraviolet for a long time (CuOZnO@NaX).

RESULTS AND DISCUSSION

After plasma treatment, zeolites with nitrates applied to them uniformly change their color over the entire surface, in the case of nitrates containing copper cations, from blue to dark brown. However, no color change is observed on zeolites coated with zinc nitrates. After the zeolites were immersed in the solution, dried, and cut, we found that the nitrates were adsorbed by the surface layer of the zeolites no more than 1 mm thick. Further plasma treatment changes the zeolite granules' color; when cut, a color change is also clearly visible at a depth of no more than 1 mm (the entire depth of nitrate penetration). Based on the visual changes, one can judge the decomposition of nitrates to oxides. Therefore, plasma treatment of zeolites with nitrates deposited on them occurs evenly over the surface. Further studies using X-ray diffraction analysis and energy-dispersive X-ray spectroscopy confirmed that only a thin layer of zeolite was processed.

X-ray diffraction analysis of zeolites with deposited nitrates after plasma treatment in a glow discharge is shown in Fig. 2. The spectra correspond to NaX zeolite (00-150-5696). Since the ratio of the original zeolites and the oxides formed on them is not comparable, and most of the characteristic peaks of NaX can overlap the peaks of CuO and ZnO, it is difficult to judge from the X-ray spectra the successful formation of copper and zinc oxides on the surface of the zeolites.

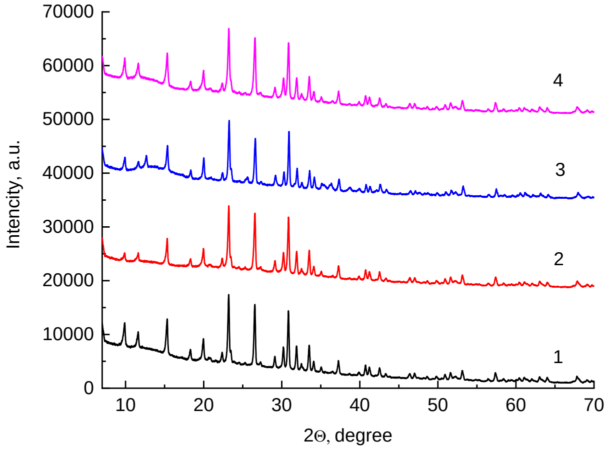

Fig. 2. X-ray diffraction analysis of the original zeolites, and zeolites with deposited oxides after plasma treatment. 1) NaX; 2) ZnO@NaX; 3) CuO@NaX; 4) ZnOCuO@NaX

Рис. 2. Рентгеноструктурный анализ исходных цеолитов, и цеолитов с нанесенными нитратами после плазменной обработки. 1) NaX; 2) ZnO@NaX; 3) CuO@NaX; 4) ZnOCuO@NaX

Due to the difficulty of identifying oxide peaks on the NaX surface, energy-dispersive X-ray spectroscopy was used. The results of elemental analysis are shown in Table 1.

Table 1

Result of energy dispersive X-ray spectroscopy

***Таблица 1.* Результат энергодисперсионной рентгеновской спектроскопии**

Elements	Content in atomic percent			
	NaX	ZnO@NaX	CuO@NaX	CuOZnO@NaX
O	63.33	57.16	56.42	57.50
Na	10.23	10.07	7.99	9.05
Al	10.72	9.43	10.09	10.68
Si	15.71	14.31	17.88	14.92
Cu			6.81	3.98
Zn		9.03		3.86

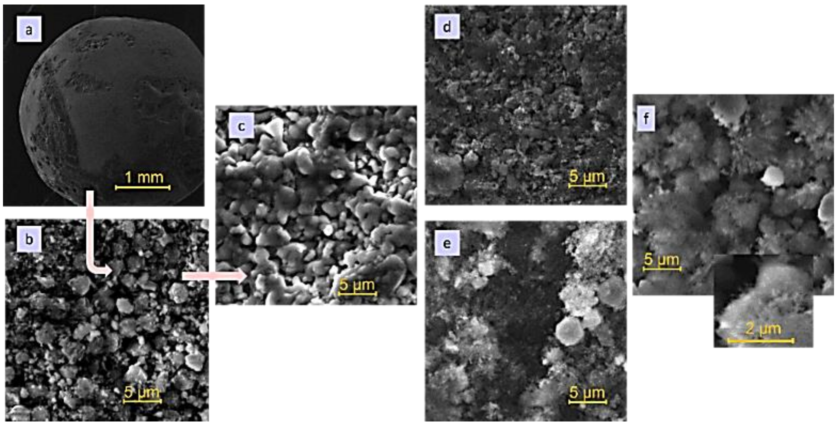

Fig. 3. Images obtained on a scanning electron microscope of the original zeolites; zeolites after plasma treatment; and zeolites with deposited oxides after plasma treatment. a) General appearance NaX; b) NaX; c) NaX after plasma treatment; d) CuO@NaX; e) ZnO@NaX; f) ZnOCuO@NaX

Рис. 3. Изображения, полученные на сканирующем электронном микроскопе, исходных цеолитов, после плазменной обработки, и цеолиты с нанесенными оксидами после плазменной обработки. a) Общий вид NaX; b) NaX; c) NaX после плазменной обработки; d) CuO@NaX; e) ZnO@NaX; f) ZnOCuO@NaX

Fig. 3 shows images obtained on a scanning electron microscope of the original zeolites after plasma treatment and zeolites with deposited nitrates after plasma treatment. Zeolites coated with copper nitrates and treated in a glow discharge are very similar in surface structure to the original samples. The main difference becomes noticeable on the surface of zeolites coated with zinc nitrates after plasma treatment; the surface is covered with villi. Zeolite samples, after wetting in a mixture of zinc and copper nitrates after plasma treatment, have a well-developed surface on which nanofilaments with inclusions of nanoballs are clearly visible.

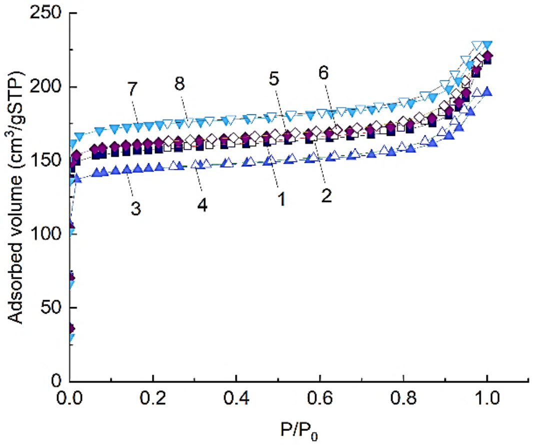

Fig. 4. Adsorption and desorption isotherms of NaX and NaX with deposited oxides after plasma treatment. CuO@NaX: 1 – Ads, 2 – Des; ZnO@NaX: 3 – Ads, 4 – Des;ZnOCuO@NaX: 5 – Ads, 6 – Des; NaX: 7 – Ads, 8 – Des

Рис. 4. Изотермы адсорбции и десорбции исходного цеолита и цеолитов с нанесенными нитратами после плазменной обработки. CuO@NaX: 1 – Ads, 2 – Des; ZnO@NaX: 3 – Ads, 4 – Des;ZnOCuO@NaX: 5 – Ads, 6 – Des; NaX: 7 – Ads, 8 – Des

N_2 adsorption/desorption isotherms at 77 K and pore sizes distribution of nano-NaX and micro-NaX are shown in Fig. 4. The isotherm of micro-NaX is type IV (defined by IUPAC) [24]. Pore distribution analyzed following the method in [25] are shown in Table 2 shows data on the analysis of porosity of all samples. Interestingly, the area of micropores and mesopores for all obtained samples is smaller than for the original NaX. The ZnO@NaX sample had the lowest values among the obtained samples, while the ZnOCuO@NaX sample was closest to the original one. This is most likely due to the thermal effects of gas-discharge plasma (discharge temperature 1000-2000 K). As a result, the surface may sinter, and the pore size may decrease.

Study of the decomposition of methylene blue

The study of catalytic activity was carried out using the example of the decomposition of the methylene blue dye using previously prepared samples; a UV lamp was used as a radiation source. Absorption spectra were examined at a wavelength of 664 nm, which is associated with the MB monomer. The shoulder of this peak at a wavelength of 612 nm belongs to the MB dimer, and two bands in the ultraviolet region with peaks around 292 and 245 nm are associated with substituted benzene rings [26]. Fig. 5 shows the change in the absorption spectra of the MB solution during the destruction process. As can be seen from Fig. 5-a there is no significant change in the intensity of absorbance light depending on the time of exposure to UV irradiation. Additional tests have shown that the UV radiation of this lamp does not have any effect on the aqueous solution of methylene blue, even over a long period of time (2-3 days). Approximately the same result was shown by the dark experiment with the original NaX (Fig. 5-b); in the absence of UV radiation, no change in optical density was observed. However, irradiation of the starting NaX leads to the decomposition of methylene blue (Fig. 5-c). Most likely this is due to the composition of this zeolite. There are known studies where titanium dioxide [27], $SiO_2@TiO_2$ [28], $ZrO@TiO_2$ – $Al_2O_3@TiO_2$ [29], $ZnO@Al_2O_3$ [30] were used for photodegradation.

Table 2

Results of studying samples using the BET method

***Таблица 2*. Результаты исследования образцов методом БЭТ**

Sample name	BET surface area	Micropore area	Mesopore area	Micropore volume	Mesopore volume
	$a_{s,BET}$ [m^2 g^{-1}]	a_2 [m^2 g^{-1}]	a_p [m^2 g^{-1}]	V_p [cm^3 g^{-1}]	V_p [cm^3 g^{-1}]
NaX	709.8	627.8	37.7	0.271	0.096
CuO@NaX	641.3	565.1	34.1	0.256	0.101
ZnO@NaX	587. 7	515.4	31.3	0.226	0.088
ZnOCuO@NaX	659.6	586.5	32.4	0.238	0.099

Quite expected and natural results were demonstrated by zeolites with nitrates deposited on them and treated in a gas discharge. For the CuO@NaX sample (Fig. 5-d), the change in intensity of absorbance light was almost the same as for the original NaX; ZnO@NaX showed a better result (Fig. 5-e). It is known that ZnO can be efficiently excited by ultraviolet light. However, the radiative recombination rate is high for photogenerated electrons and holes in pure ZnO, which limits its effectiveness as a photocatalyst. ZnOCuO@NaX showed the best efficiency (Fig. 5-f).

In Fig. 6 shows the change in the concentration of methylene blue over time of UV irradiation. The percentage of MB degradation is shown in the Table 3. The best degradation effect during exposure to UV light is observed for the ZnOCuO@NaX sample – 87.9%.

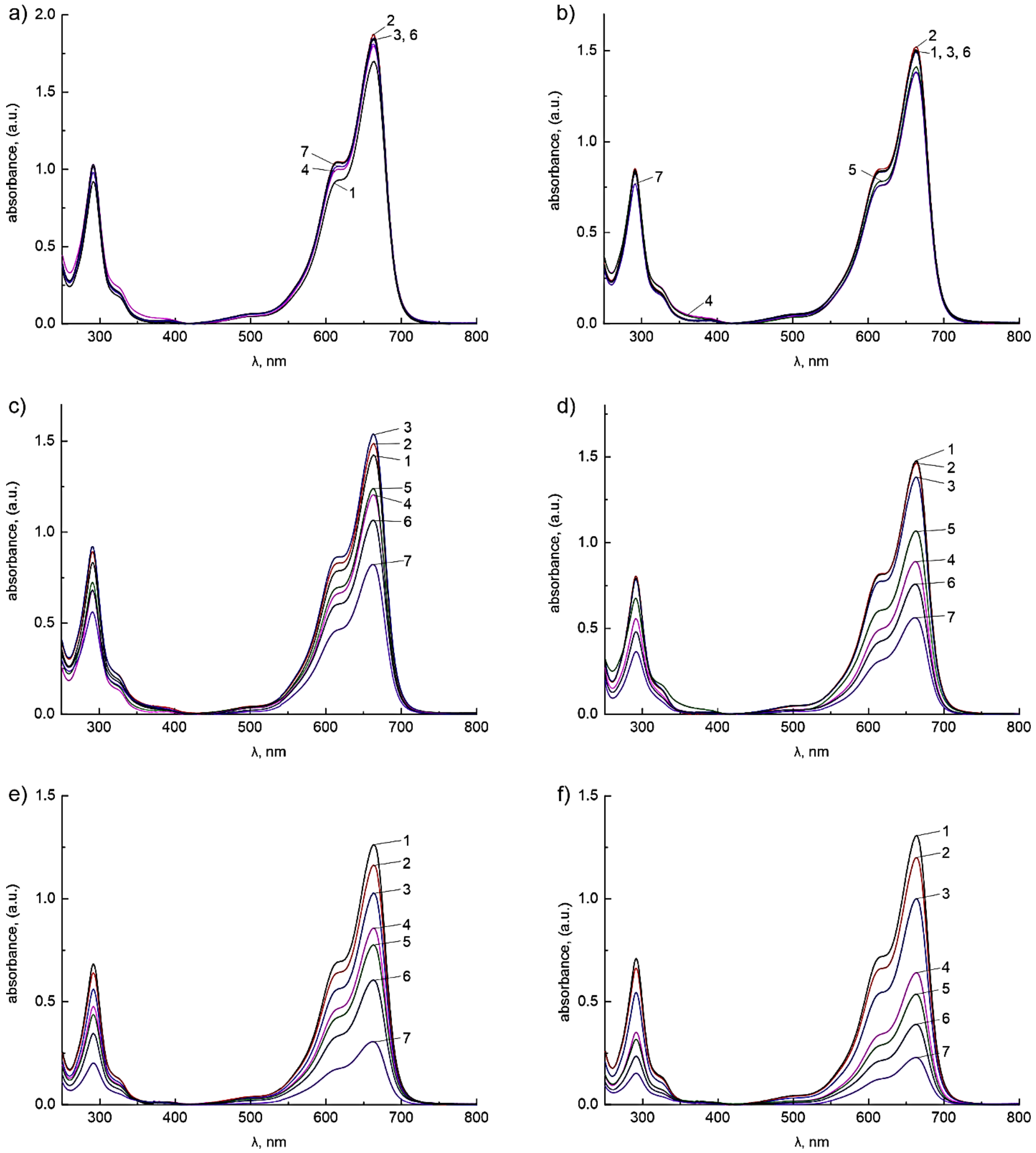

Fig. 5. Time-dependent UV-Vis absorption spectra for decolorization of methylene blue in the presence of samples: a) MB; b) NaXnoUV; c) NaX; d) CuO@NaX; e) ZnO@NaX; f) ZnOCuO@NaX. 1 – 10 min, 2 – 20 min, 3 – 30 min, 4 – 60 min, 5 – 90 min, 6 – 120 min, 7 – 180 min

Рис. 5. Спектры поглощения метиленового синего от времени взаимодействия с ультрафиолетовым излучением для образцов: a) MB; b) NaXnoUV; c) NaX; d) CuO@NaX; e) ZnO@NaX; f) ZnOCuO@NaX. 1 – 10 мин, 2 – 20 мин, 3 – 30 мин, 4 – 60 мин, 5 – 90 мин, 6 – 120 мин, 7 – 180 мин

Table 3

Percentage of MB degradation depending on the time of ultraviolet irradiation

***Таблица 3.* Процентное соотношения разложения метиленового синего от времени воздействия с ультрафиолетовым светом**

Irradiation time, min	D, %				
	NaXnoUV	NaXUV	CuO@NaX	ZnO@NaX	CuOZn@NaX
10	20.1	24.3	21.4	32.8	30.3
20	19.0	20.8	21.9	38.2	36.1
30	20.8	18.2	26.5	45.4	46.8
60	26.7	35.8	52.9	54.4	65.9
90	24.8	34.1	43.2	58.8	71.5
120	20.3	43.4	59.9	67.9	79.3
180	26.4	56.3	70.2	83.8	87.9

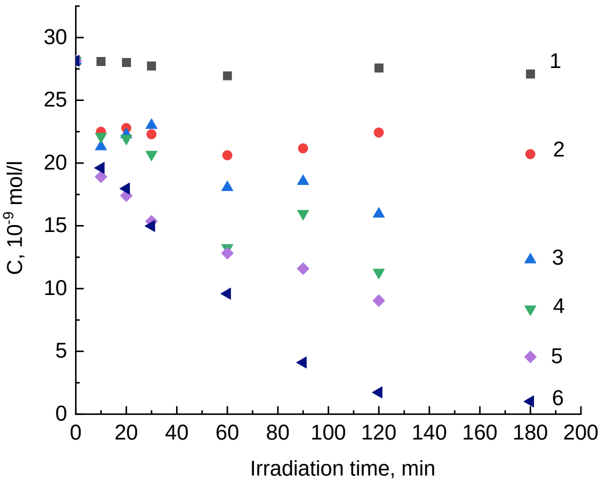

Fig. 6. Dependence of the concentration of methylene blue on the time of interaction with catalysts in the presence of UV light. 1) MB; 2) NaXnoUV; 3) NaX; 4) CuO@NaX; 5) ZnO@NaX; 6) ZnOCuO@NaX

Рис. 6. Зависимость концентрации метиленового синего от времени взаимодействия с катализаторами в присутствии УФ света. 1) MB; 2) NaXnoUV; 3) NaX; 4) CuO@NaX; 5) ZnO@NaX; 6) ZnOCuO@NaX

CONCLUSION

Thus, the work demonstrated a new method for the synthesis of complex oxides on the surface of zeolites from nitrates under the influence of low-temperature gas-discharge plasma. According to SEM data, the resulting oxides had a well-developed surface morphology. Using the example of the decomposition of methylene blue, the catalytic activity of the resulting substances was studied. Determined specific surface area (BET) and pore size distribution showed that plasma treatment of nitrate-loaded zeolites led to a decrease in micropore area and a decrease in mesopores. The maximum degree of purification was achieved when using zeolite coated with double oxide of copper and zinc 87.9% under the action of ultraviolet radiation. The use of zeolites with copper oxides deposited on them showed a result of 70.3%, and with zinc oxide – 83.8%. Additional study of the decomposition mechanisms is required, since zeolites themselves, when exposed to UV, are capable of decomposing methylene blue by 56.3%. Additional research into the processes of formation of oxides on the surface of zeolites from nitrates under the influence of a gas discharge at atmospheric pressure is also necessary.

БЛАГОДАРНОСТЬ И ФИНАНСИРОВАНИЕ

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Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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