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ANALYSIS OF THE PHOTOCATALYTIC ACTIVITY OF TiO_2 COATING ON A GLASS AS A CRITERION OF ITS ABILITY TO SELF-CLEANING

Об'єктом дослідження є процес фотокаталітичної деградації метиленового синього на склі з покриттям з оксиду титану під дією ультрафіолетового випромінювання (УФ-випромінювання). Дослідження має на меті опосередковано оцінювати здатність стекол до самоочищення. Робиться аксіоматичне припущення про кореляцію між здатністю до самоочищення і фотокаталітичною активністю.

В ході дослідження використовувався фотокаталітичний реактор власної конструкції. Це циліндрична порожнина з кварцового скла у вигляді стакану, на внутрішню поверхню якого попередньо нанесене фотокаталітичне покриття з оксиду титану. Порожнина стакану заповнюється розчином метиленового синього. Ззовні стакан опромінюється ртутно-кварцовою лампою. УФ-випромінювання безперешкодно проходить крізь кварцове скло і з тильної сторони активує фотокаталітичне покриття. Для активації процесу потрібна участь атмосферного кисню. Для цього здійснюється барботаж розчину повітрям з перфорованого кільцевого трубчастого колектора, розташованого на дні стакану.

Розчин метиленового синього після різних термінів експозиції піддається спектральному аналізу. Кінетика деградації барвника оцінюється фотоколориметричним методом за зменшенням інтенсивності характеристичної смуги поглинання метиленового синього. Процес знебарвлення наочно демонструється на діаграмі колірності.

Новизна запропонованої схеми функціонування фотокаталітичного реактора полягає в тому, що УФ-випромінювання активує покриття, діючи на нього з боку внутрішньої поверхні поділу: кварцове скло-покриття. Електронно-діркові пари мігрують на поверхню і за умов контакту з киснем повітря здійснюють фотокаталіз модельного розчину. Така схема устрою фотокаталітичного реактору вигідно відрізняється від відомих через те, що УФ-випромінювання не проходить через досліджувану модельну рідину. Це виключає можливість їх взаємодії, що може внести похибку в кінцеві результати.

Ключові слова: *фотокаталітичний реактор, метиленовий синій, УФ-випромінювання, фотокаталіз, спектральний аналіз, знебарвлення, діаграма колірності.*

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1. Introduction

Recently, there has been a great demand for self-cleaning glass, which, under the influence of solar radiation, arbitrarily gets rid of pollution by atmospheric aerosols. Such bulky glass is produced by the float method, on which nanostructured titanium oxide coatings are applied by pyrolysis.

It is impossible to unambiguously establish criteria for evaluating the self-cleaning ability of glass. It depends on the operating conditions of light openings for the glazing of buildings, namely: their spatial orientation, meteorological conditions, presence of rainfall, insolation degree, and air pollution.

Currently, the need for the manufacture of self-cleaning glass is not limited to large-scale glazing of buildings and structures. There is a need to manufacture small-scale piece goods of complex configuration, including hollow ones. Known industrial coating methods may be incapable.

In the case may become a method of coating from aqueous solutions [1]. An indispensable sign of self-cleaning ability is the photocatalytic activity of such a coating. In this paper, an original technique of the corresponding tests is proposed. It can be axiomatically stated that self-cleaning ability correlates with the photocatalytic activity of the coating. And it can be traced to the kinetics of decomposition (degradation) of a certain substance in photocatalytic reactors. Their structure by each of the researchers is subject to the specific objectives of the research. Most often, this is an analysis of the effectiveness of this catalyst. In this case, the kinetics of the degradation of an aqueous solution of a substance is studied, the decrease of which can be traced by chemical or physico-chemical analysis. Organic dyes are most commonly used. Their discoloration is easily traced by photocolorimetry.

Sometimes research is purely utilitarian. For example, the neutralization of certain pollutants in wastewater. Then the reactors are adapted to solve the corresponding problem. Photocatalytic reactors can be batch and continuous (flow). The photocatalytic reaction is initiated by ultraviolet radiation (UV radiation), the source of which may be mercury-quartz lamps or UV LEDs.

In scientific research, photocatalytic processes are implemented in photocatalytic reactors. There are many options for their device. An essential sign of the functioning of reactors is the state of the photocatalyst. The photocatalyst can be in a dispersed state and located in the aqueous medium of the reactor in the form of Aquagel [2, 3]. The photocatalyst can be pre-applied to a specific surface and immobilized on it [4].

In the framework of this work, photocatalytic reactors with nanocoating deposited on glass are of particular interest [5, 6]. The original method is used in a reactor in which, unlike other methods, a photocatalytic coating is applied to quartz optical fibers, through which UV radiation from LEDs comes in [7]. This provides optimal conditions for the delivery of radiation to the photocatalytic reaction zone. Photocatalytic purification of water substances can be combined with filtration processes. In this case, the photocatalyst is applied to certain membranes [8]. The photocatalyst carrier can be molecular sieves, for example, zeolites [9, 10]. Thus, *the object of research* is the process of photocatalytic degradation of methylene blue on glass coated with titanium oxide under the influence of UV radiation. And *the aim of research* is indirectly assess of the ability of glasses to self-clean.

2. Methods of research

To test the proposed research methodology, a laboratory unit is assembled, the circuit diagram of which is shown in Fig. 1.

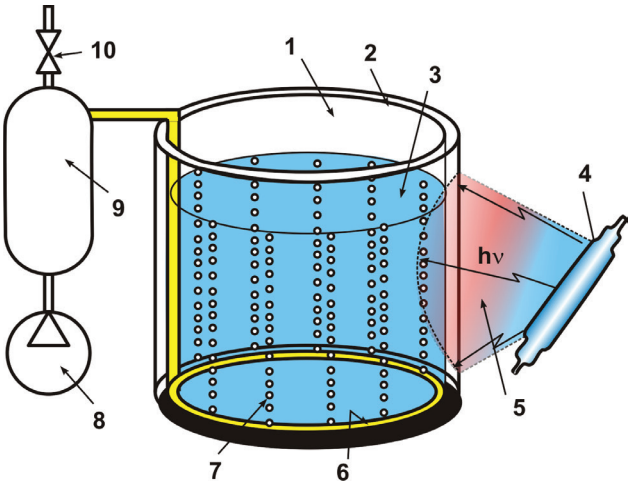

Fig. 1. Scheme of the photocatalytic reactor:
1 – glass of quartz glass; 2 – photocatalytic coating of the inner surface of the glass; 3 – an aqueous solution of methylene blue; 4 – source of ultraviolet radiation; 5 – radiation flux to the outer surface of the glass; 6 – perforated collector for sparging a solution of methylene blue with air; 7 – air bubbles; 8 – air pump; 9 – receiver; 10 – valve for relieving excess pressure

An indispensable condition for modeling this process is the following:

1. A prototype glass coated with titanium dioxide in the modification of nanostructured anatase.
2. Irradiation of the coating with photoactinic UV radiation.
3. Contact with water.
4. Contact with oxygen.
5. Contact with organic matter, analyzing the degradation (decomposition) of which it is possible to qualitatively state and quantitatively analyze the kinetics of the process.

The glass is a tube of quartz glass of optical quality. The diameter of the glass is 25 mm, the height is 50 mm. The need to use precisely quartz glass is dictated by the requirement of transparency of UV radiation in the range 200–400 nm. The lower section of the tube was plugged with latex plugs (bottom of the glass). Preliminary deposition of the photocatalytic coating on the inner surface of the glass is carried out according to the procedure [1].

3. Research results and discussion

The glass is filled with an aqueous solution (0.09 mmol) of methylene blue. A 350-watt mercury-quartz lamp is used as a radiation source. It is located horizontally at a distance of 20 mm from the glass. To avoid heating the glass with the solution, it is provided to blow it with a fan (not shown in the diagram). Spectral characteristic of a mercury-quartz lamp is given In Fig. 2.

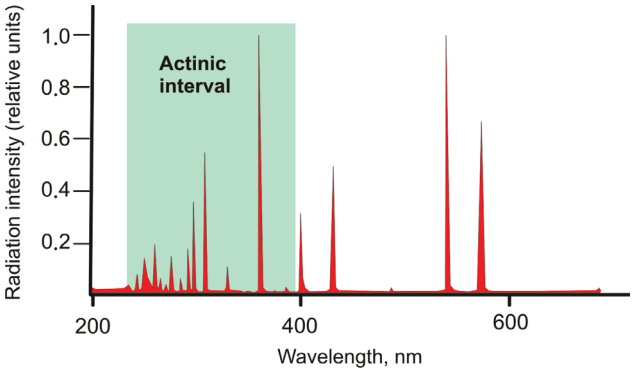

Fig. 2. Spectral characteristic of a mercury-quartz lamp

As follows from Fig. 2, in the actinic range of 200–400 nm, capable of provoking the photocatalytic properties of the coating, there are a large number of emission bands, including the most powerful of them.

For the course of photocatalytic processes, contact of the coating with water and oxygen is necessary. Water is a methylene blue solvent, and contact with air is carried out by sparging the solution with air. For this, an annular perforated collector with a plastic tube is installed at the bottom of the glass. Air bubbles rise up in close proximity to the inner surface of the glass, which ensures contact of the coating with air.

Air is pumped by a reciprocating compressor. A receiver is installed between it and the collector. The receiver is equipped with a valve to relieve excess pressure in order to avoid rapid bubbling of the solution. The methylene blue solution is irradiated for 3 and 6 hours.

The solutions are subjected to spectral analysis in the visible range of 400–800 nm. They fill rectangular glass cuvettes with an internal cavity of 1 cm in size. In order to avoid measurement error for loss of beam intensity on reflection at the interfaces: glass-air and glass-solution, as well as losses in absorption by water itself, a comparative measurement of the transmission of the cuvette with the solution is carried out and ditches with water. Due to this, it can be argued that the transmission value should characterize the methylene blue solution itself.

Transmission curves are shown in Fig. 3, and absorption of methylene blue solutions for three cases is shown

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in Fig. 4: the initial solution and the solutions with exposures of 3 and 6 hours.

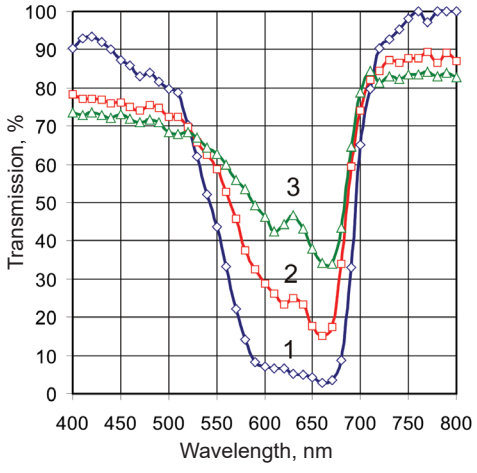

Fig. 3. Dependence on the transmission wavelength: 1 – initial solution; 2 – solution after exposure at 3 hours; 3 – solution after exposure at 6 hours

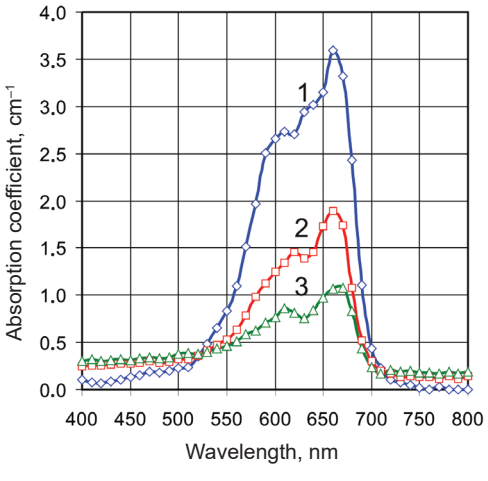

Fig. 4. Wavelength dependence of the absorption coefficient: 1 – initial solution; 2 – solution after exposure at 3 hours; 3 – solution after exposure at 6 hours

Analyzing the diagrams in Fig. 3, 4, it can be argued about the discoloration of the methylene blue solution. The characteristic absorption band at a wavelength of 663 nm, which is inherent precisely to methylene blue, is clearly traced. With an increase in the exposure time, the intensity of this band decreases, which indicates the degradation of the dye.

The initial concentration of methylene blue is C = =0.09 mmol. For a characteristic absorption band of 663 nm, the absorption coefficient is 3.6 cm^{-1}. The dye concentration is calculated by photocolorimetry after the exposure time of 3 and 6 hours (Table 1).

To determine the order of the reaction, functional scales are used for concentrations, respectively, for reactions: 0th, 1st, and 2nd order (Table 1).

Fig. 5–7 show the dependences of the corresponding concentration functions on the aging time and linearized by plotting the trend lines. The linear equations of the dependence of the corresponding concentration functions on the exposure time, as well as the value of the approximation reliability (R^2).

Table 1

Functional scales for concentration C

Exposure period, h	Absorption coefficient, cm^{-1}	Reaction order		
		0	1	2
		C, mmol	ln C	1/C
0	3.6	0.09	–2.41	11.11
3	1.89	0.047	–3.06	21.28
6	1.08	0.027	–3.61	37.04

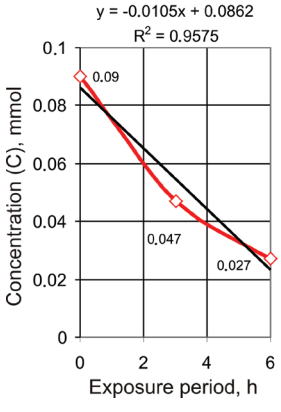

Fig. 5. Linearization of the dependence of the concentration function on the exposure time for the reaction of zero order

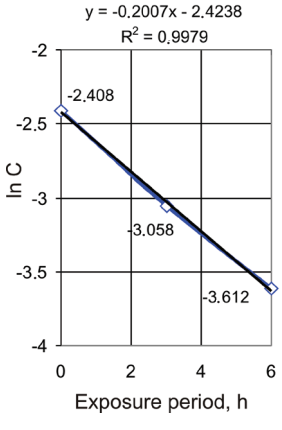

Fig. 6. Linearization of the dependence of the concentration function on the exposure time for the reaction of first order

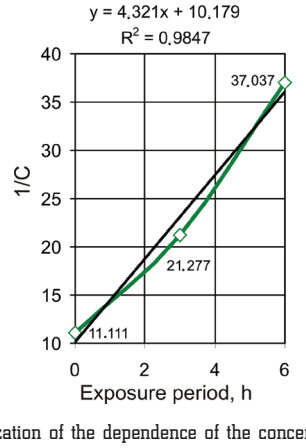

Fig. 7. Linearization of the dependence of the concentration function on the exposure time for the reaction of second order

As follows from the diagrams in Fig. 6, the process of heterogeneous photocatalysis corresponds to a first-order reaction.

According to the data of the spectral transmission curve (Fig. 3), the chromaticity coordinates of the solution are determined (Fig. 8).

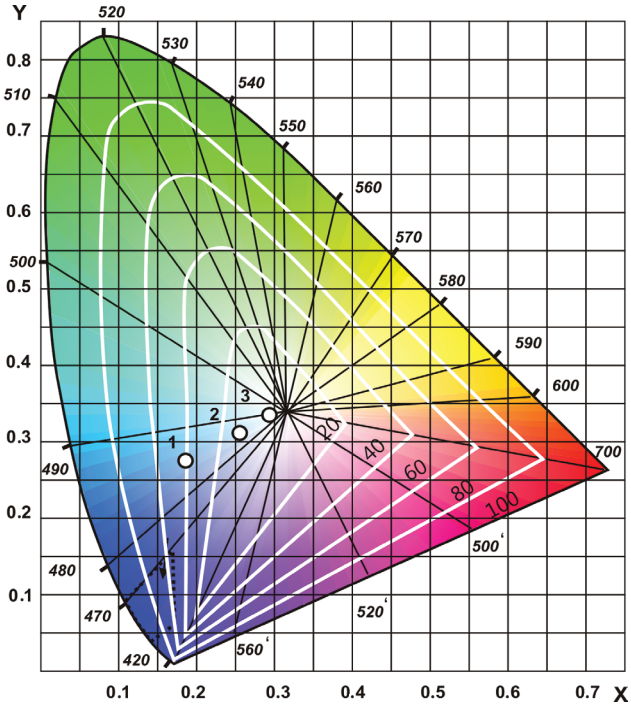

Fig. 8. Illustration of the discoloration process of methylene blue solution: 1 – color coordinate of the initial solution; 2 – color coordinate of the solution with an exposure time of 3 hours; 3 – color coordinate of the solution with an exposure time of 6 hours

As follows from the diagram in Fig. 8, the color tone for all cases is ~485 nm, which corresponds to a blue color. Depending on the duration of the exposure, the color coordinate shifts to an achromatic point, and the color purity decreases from 40 % to values less than 10 %. This clearly indicates the discoloration of the methylene blue solution.

4. Conclusions

There are no standard universal methods for determining the self-cleaning ability of photocatalytic coated glasses. This is due to the fact that glass products can have a diverse and complex configuration, operate in different atmospheric conditions, and be designed to self-clean from certain specific pollutants.

It can be axiomatically stated that the self-cleaning ability of glasses correlates with the photocatalytic activity of the coating. It is estimated by the kinetics of decomposition (degradation) of the model substance. By exploring this activity, one can indirectly evaluate self-cleaning ability.

Photocatalytic activity of the coating can be investigated in photocatalytic reactors. According to well-known schemes of their device, such a coating is applied to a specific surface and is irradiated from its side with UV radiation. In this case, this radiation must pass through a certain volume of the model substance and can change its intensity. A feature of the proposed scheme is that UV radiation acts on the coating layer from the back, after having previously overcome the quartz glass wall. The beam intensity should be constant.

A device for modeling the photocatalytic process occurring on the surface of coated glass is proposed. Such a photocatalytic reactor is a cylindrical cavity (glass) made of quartz glass. A coating layer according to the modification of TiO_2 (anatase) is deposited on its inner surface by the method of deposition from an aqueous solution. An aqueous solution of methylene blue is used as a model substance. By the method of spectrophotometry and photocolorimetry, its discoloration and the kinetics of degradation are established. This allows to determine the order of the reaction and its rate constant.

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