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CALCULATION AND 3D MODEL OF THE PHOTOCATALYTIC PANEL REACTOR FOR DYES AND PHENOL DEGRADATION

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The article is devoted to the calculation and 3D modeling of the photocatalytic panel reactor for the degradation of dyes and phenol. To do this, the photocatalytic reactors of various types for the photodegradation of organic pollutants in aqueous solutions were theoretically examined. In our opinion the panel type photoreactors are the most rational. The prospect of photocatalytic treatment of wastewater from organic pollutants by the so-called methods of Advanced Oxidation Processes, among which the heterogeneous photocatalysis with the participation of such a catalyst as titanium (IV) oxide is most effective, is also noted. In order to determine the optimal design of such equipment various available in the literature types of photoreactors are considered. It is shown that the separation of powdered photo-catalysts can be successfully implemented using membrane modules. Based on theoretical analysis, the choice of the panel type photoreactor was substantiated and its calculation was carried out. It has been shown that for the uniform molar concentration of such pollutants as phenol and dyes (Congo red and Methylene blue), the different number of lamps and sections of the photoreactor are required. As a result, the more versatile design, the panel photoreactor is developed. The number of sections in it can be increased if necessary, and such reactor is capable of providing highly effective photo-destruction of pollutants of different genesis in sewage of various origins. According to the developed design of the photoreactor, its 3D modeling is carried out, which allows to visualize all the structural elements of such unusual type of special equipment.
***Keywords**: AOPs processes, Photocatalysis, Reactors, Panel reactor design, Water treatment from organic compounds*

Introduction

To date, the development or modernization of special equipment for water treatment of such type such as photocatalytic reactors is relevant in connection with the rapid development of photocatalysis for the purification of water bodies from organic matter. Despite intensive scientific research on the subject of the possibility of organic substances degradation in water, the commercialization of this purification method and scaling of the photocatalytic process is still very limited. At the same time, various types of reactors such as microreactors[1], advanced LED-driven flow reactors[2], water-bell photoreactors[3], FluHelik reactors[4,5], panel photoreactors[6], etc. are considered in the literature.

The design of microreactors is optimized by researchers to achieve greater efficiency both in terms of quality and quantity in accordance with the application. Considerable attention is paid to capital and operating expenses. The disadvantages of such reactors are small amounts of water systems, which can be cleaned with their help.

The advanced LED-driven flow reactors are energy-efficient, but their hydrodynamic regimes have not yet been worked out, so their overall effectiveness for the profound destruction of organic matter is still in doubt.

The water-bell photoreactors are an interesting and fairly simple photoreactors by design solution. Photocatalytic decomposition in this type of reactor takes place in a thin film of water, which ensures maximum sunlight penetration and does not require continuous saturation with oxygen. Advantages

of this type of reactors are effective mixing and avoiding dead zones in the photoreactors, and the drawbacks are the dependence of the cleaning efficiency on the quality of the inlet water.
FluHelik reactors are considered to be innovative modern reactors to reduce the toxicity of actual effluents, but they are aimed at destroying essentially pharmaceutical preparations.
Panel photoreactors have a diverse design and are capable of cleaning large volumes of aqueous solutions and, in our view, is the most optimal design for the deep destruction of organic matter in aqueous solutions, which is flexible, simple and allows for the processing of large water volumes. But this type of reactor requires a more detailed calculation of the main structural elements depending on the pollutant type and their optimization for the effective purification of water from organic matter.
The purpose of this work is the theoretical choice of photoreactor's design, its calculation and optimization of the main structural elements for the effective cleaning of water from dyes (Congo red and Methylene blue) or phenol and the design of its 3D model in Blender software.

Mechanisms of organic substances photodegradation with the participation of photocatalyst

Recently, processes known as Advanced Oxidation Processes (AOPs) are becoming popular in wastewater treatment technology. AOPs include the number of methods: oxidation using H_2O_2 in the presence of UV; usage the Fenton reagent in the presence of UV light; ozone oxidation in the presence of UV; oxidation on TiO_2 surface in the presence of UV; combinations of the above methods[7].The basis of these methods for liquids purification is oxidation of pollutants, mainly organic, to non-toxic substances or to their full mineralization. The possibility of full mineralization of organic pollutants is based on the formation of OH● radicals, whose oxide potential is 2.80 eV and which exceeds the potentials of other oxidants (O_2, Cl_2, H_2O_2, O_3, etc.). Thus, the main mechanism of AOPs action is the generation of radicals that have the extremely high oxidation potential. The main advantage of the use of these radicals is the high and non-selective reactivity. AOPs have the following advantages[7,8]: fast kinetics; high potential for full mineralization of highly toxic organic impurities; no secondary solid or liquid waste. At the same time, AOPs also have certain disadvantages. These methods require tuning for specific sewage, that is, they have low level of the unification, and almost all of them are energy-intensive. In our opinion, among the available AOPs methods the heterogeneous photocatalysis has the greatest prospects, as it characterized by the number of advantages, namely: the prospect of switching from UV light to visible light, which allows significantly to reduce energy costs, and it is characterized by the absence of cooling and energy consumption for ozone generation.
The photodestruction process of the pollutants with the photocatalyst participation is by creating the electron-hole pairs generated by the action of the light quanta. In such reactions, the photocatalyst plays the role of the initiator, resulting in the formation of active particles $\bullet O_2^-$, $\bullet HO_2$, OH●, H^+, and others that participate in the oxidation processes. The mechanism of the process is as follows. Under the action of light with sufficient energy, that is, more than the width of the semiconductor bandgap, the electron valence band is excited and transferred to the conduction band. This creates the separation of charges and the presence of two particles with opposite charges: electrons and holes. When particles reach the surface of the semiconductor, they participate in chemical transformations[9]. Oxygen molecule O_2 dissolved in water captures the electron and forms the superoxide radical $\bullet O_2^-$. After that, it interacts with the proton and forms the over-perooxide radical $\bullet HO_2$. Interactions of radicals $\bullet O_2^-/\bullet HO_2$/OH● with organic molecules lead to the final mineralization of the latter[10]. Titanium (IV) oxide (TiO_2)[11] is the most promising and widespread photocatalyst for the generation of photoexcited electrons.

Comparison of photoreactors types and their application

In the literature, the processes of photodegradation of various pollutants in the aqueous medium have been thoroughly investigated, mechanisms have been established and kinetics has been studied. In this case, there are no real photocatalytic reactors for the destruction of pollutants in aqueous solutions, and there is only single information in literary sources about the types of photoreactors in which the process of photodegradation of pollutants in aqueous media can be carried out. So, nowadays there are several types of reactors which are considered for the implementation of photocatalytic oxidation in aqueous solutions. The most popular are photoreactors[12–16], shown in Figures 1 and 2.

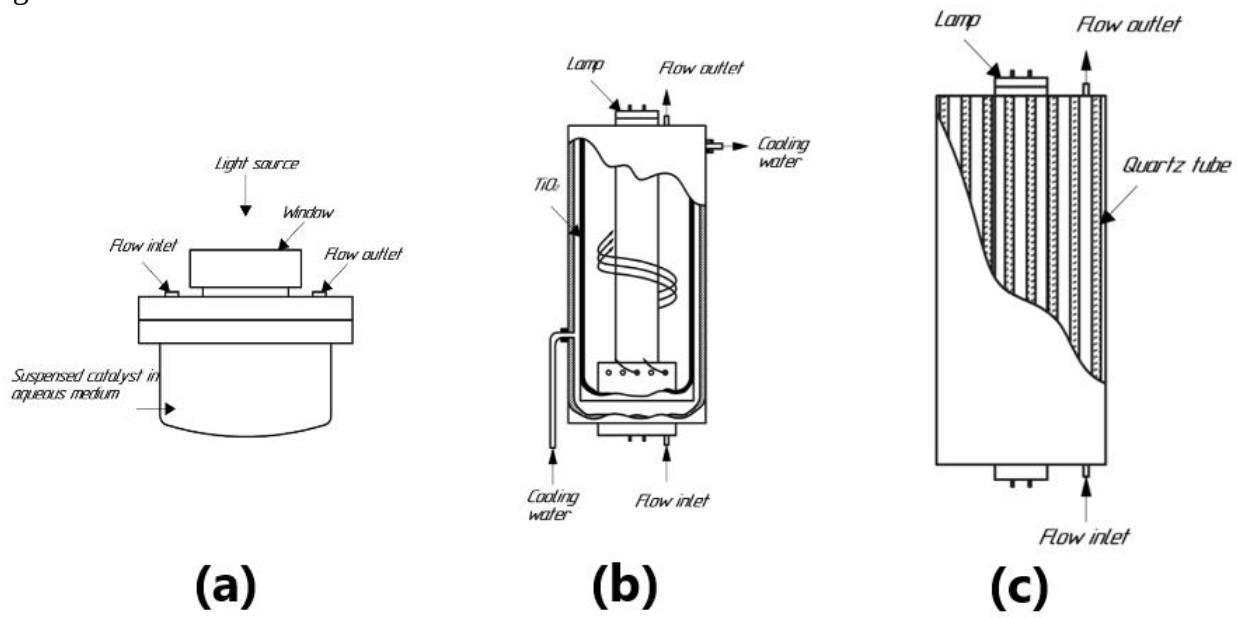

Fig. 1. Photoreactors for oxidizing of pollutants in aqueous media: (a) – photoreactor with the external radiation source, (b) and (c) – with the internal source of radiation

In the photoreactor shown in Fig. 1 (a), the oxidation of the pollutants is realized by the powder-like photocatalyst and there is possibility of using both artificial and natural radiation. For the photooxidation in cylindrical photoreactors (Fig. 1 (b) and (c)) with the internally installed lamp, the difference in photoreactors consist in the place of the photocatalyst application. In the case of the photoreactor shown in Fig. 1 (b), it is applied on the walls of the reactor, and in the case of the photoreactor in Fig. 1(c) – on quartz tubes located inside the reactor. The feature of photoreactors with the applied photocatalyst is that it is not necessary to separate the latter after the oxidation process, but the degree of its use in this case is less than in the case of the powder-like photocatalyst. All reactors presented in Fig.1 are designed for low consumption and therefore can be used in local water purification systems.

U-shaped multi-tube photoreactors have other design and can be manufactured either in closed (Fig. 2 (a)) or opened systems (Fig. 2 (b)). The first type is intended for artificial radiation, the second one is for natural radiation. Such reactors are designed for purifications of the large volumes of contaminated wastewater. In both cases, the powder-like photocatalyst is used.

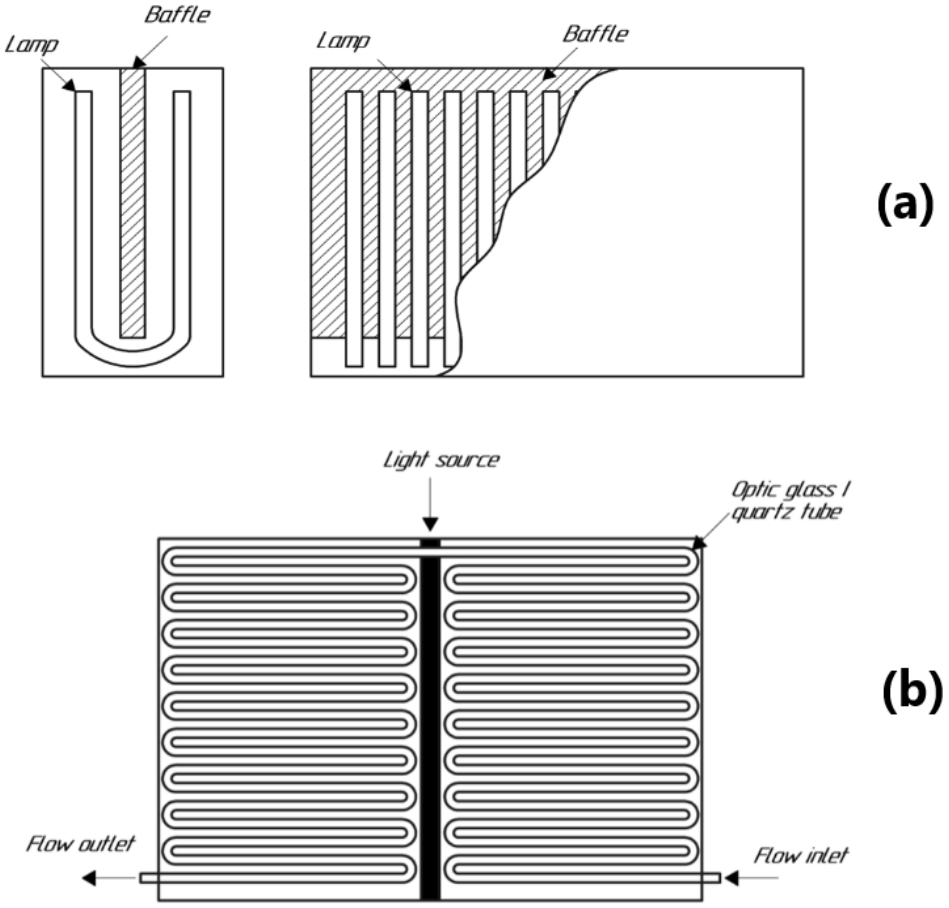

Fig. 2. U-shaped multi-tube photoreactors for oxidizing pollutants in aqueous media:
(a) – photoreactor with the external source of radiation, (b) and (c) – with the internal radiation source

The main problem with the use of the powder-like photocatalyst is its separation. For solving this problem either centrifugation or ultrafiltration (membrane methods) can be used. The first way is inappropriate, since it is too energy-consuming. The second approach is more promising, because it will allow to separate the fine dispersed photocatalyst fully, economically and quickly enough. Generally, membrane methods can be implemented in several ways[17]: the first is the irradiation of the additional reservoir for the photocatalyst activating (Fig. 3 (a)), which is located between the mixer and the membrane module; the second is irradiation directly in the mixer (Fig. 3 (b)); the third is the irradiation of the membrane at the catalyst separation (Fig. 3 (c)). All methods have perspectives and should be studied in more detail.

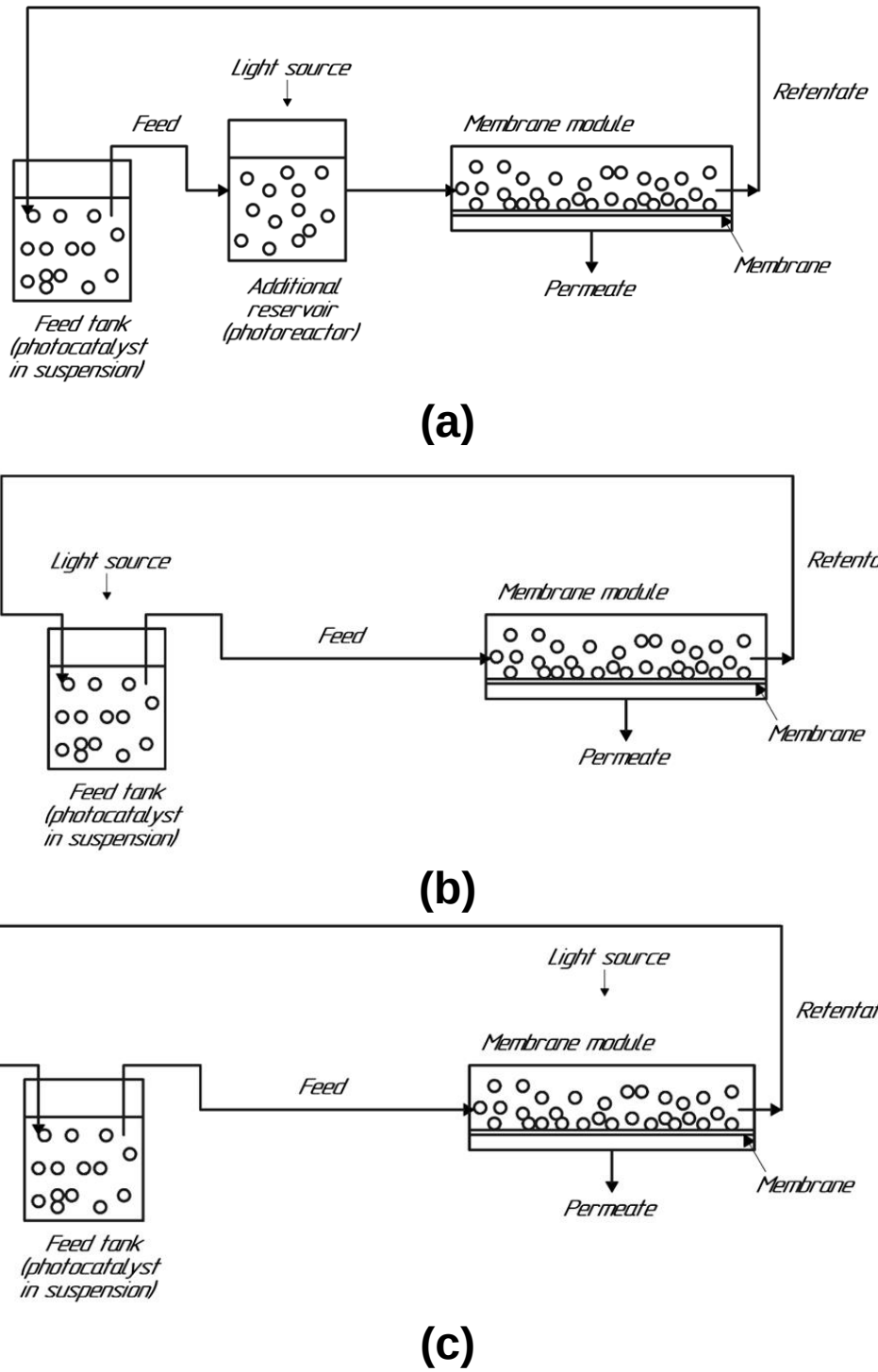

Fig. 3. Methods of separating the fine dispersed photocatalyst from aqueous solutions: (a) – irradiation after mixing and before separation, (b) – irradiation in the mixer, (c) – irradiation in the membrane module

Therefore, based on the above mentioned literature data and its analysis, it can be concluded that the development of photoreactors for the destruction of pollutants only acquires "turns", but, in our view, the implementation of photodegradation "irradiation after mixing and before the separation" is more promising. In this case, the block for radiation implementation should consist of panels the number of which can be increased if necessary. So, further the panel photoreactor has been calculated.

Calculation of the panel photoreactor

Data presented in the Table 1 were used to calculate the panel photoreactor.

Table 1. Output data for the panel photoreactor calculation

Parameter	*Value*	*Symbol*
Contact time (sec)	1200	τ
Consumption (m^3/sec)	0.0028	Q
The level of the concentration reduction (%)	98	P
Molar concentration of the pollutant (mole/m^3)	0.15	C_M
Absorption coefficient of lighted water (sm^{-1})	0.5	α
Flow rate	0.9	η_n
Power flow of the lamp (W)	25	E_{uv}
Photon energy (J)	$5.44 \cdot 10^{-19}$	$E_{h\vartheta}$
Quantum yield	0.1	φ

The calculation of the panel reactor for the phenol oxidation was carried out using the following algorithm.

The intensity of the photons emission by the lamp:

$$\vartheta_{uv} = \frac{E_{uv}}{E_{h\vartheta}},$$

where E_{uv} – power flow of the lamp, W; $E_{h\vartheta}$ – photon energy, J.

$$\vartheta_{uv} = \frac{25}{5.44 \cdot 10^{-19}} = 4.596 \cdot 10^{19}\ \text{sec}^{-1}.$$

The number of dye molecules decomposable per unit of time is determined by the formula:

$$\text{Nph} = \vartheta_{uv} \cdot \varphi,$$

where φ – quantum yield.

$$\text{Nph} = 4.596^{19} \cdot 0.1 = 4.596 \cdot 10^{18}.$$

The number of pollutant molecules oxidized over time τ = 1200 sec:

$$\text{N}_{\text{ph(t)}} = \text{N}_{\text{ph}} \cdot \tau = 4.596 \cdot 10^{18} \cdot 1200 = 5.515 \cdot 10^{21}.$$

The number of matter moles decomposed over time τ:

$$\text{N}_{\text{ph(m)}} = \frac{\text{N}_{\text{ph}}}{\text{N}_{\text{a}}} = \frac{5.515 \cdot 10^{21}}{6{,}02 \cdot 10^{23}} = 9.1576 \cdot 10^{-3}\ \text{mole}.$$

The amount of degradable substance during time τ in volume V:

$$\text{N}_{\text{destr(t)}} = Q \cdot \tau \cdot P \cdot \frac{C_M}{100},$$

where Q – consumption, m^3/sec; P – the level of the concentration reduction, %; C_M – the molar concentration of the pollutant, mole/m^3.

$$\text{N}_{\text{destr(t)}} = 0.0028 \cdot 1200 \cdot 98 \cdot \frac{0.1493}{100} = 0.4915\ \text{mole}.$$

The number of lamps required for photocatalytic oxidation:

$$N_{lamps} = \frac{\mathrm{N_{destr(t)}}}{\mathrm{N_{ph(m)}}} = \frac{0.4915}{9.1576 \cdot 10^{-3}} = 54 \text{ lamps.}$$

The height of the water layer:

$$n = — \frac{[lg(1 — \eta_n)]}{\alpha lge},$$

where η_n – flow rate; α – absorption coefficient of lighted water, sm^{-1}:

$$n = — \frac{[lg(1 — 0.9)]}{0.5\ lge} = 4.6 \text{ sm.}$$

Basic parameters, design and 3D model of the panel photoreactor

As a result of the above calculation, we obtain the following parameters of photocatalytic reactor:

1) lamp dimensions: length l_{lamps} = 1,7 m; diameter d_1 = 0,04 m;
2) number of sections n_s = 10, 6 lamps each (one backup section attached to the case of lamps replacement) which are located in sections at the distance l_1 = 2n/100=0.09 m one from another, as well as sections; distance between panels l_2 = 0.05 m;
3) The length, width and height of the reactor (internal) are defined as l_r = 20n; $b_r = l_{lamps}$ + 0,1; h_r = 12n.

Thus, L = 1.7 m, H = 1.36 m, W = 0.82 m; reactor volume – Vr =1.98 m^3. All obtained data is summarized in the Table 3

Table 2. Parameters of the panel photocatalytic reactor for the phenol oxidation

	Number of lamps	54
	Number of sections	10
Lamp dimensions	Length (m)	1.7
	Diameter (m)	0.04
	Distance between panels (m)	0.09
	Distance from reactor walls (m)	0.05
Reactor dimensions	Length (m)	1.7
	Width(m)	1.36
	Height (m)	0.82
	Reactor volume (m^3)	1.98

Based on the data presented in Table 3, the design of the photoreactor is developed, which is shown in Figure 4. This design has the following advantages: it consists of panels that can be expanded, what allows to clean sewages of various composition with different power. In addition, the 3D photoreactor model (Fig. 5) was constructed for the more visual representation, which allows visualizing all structural elements of this non-typical equipment.

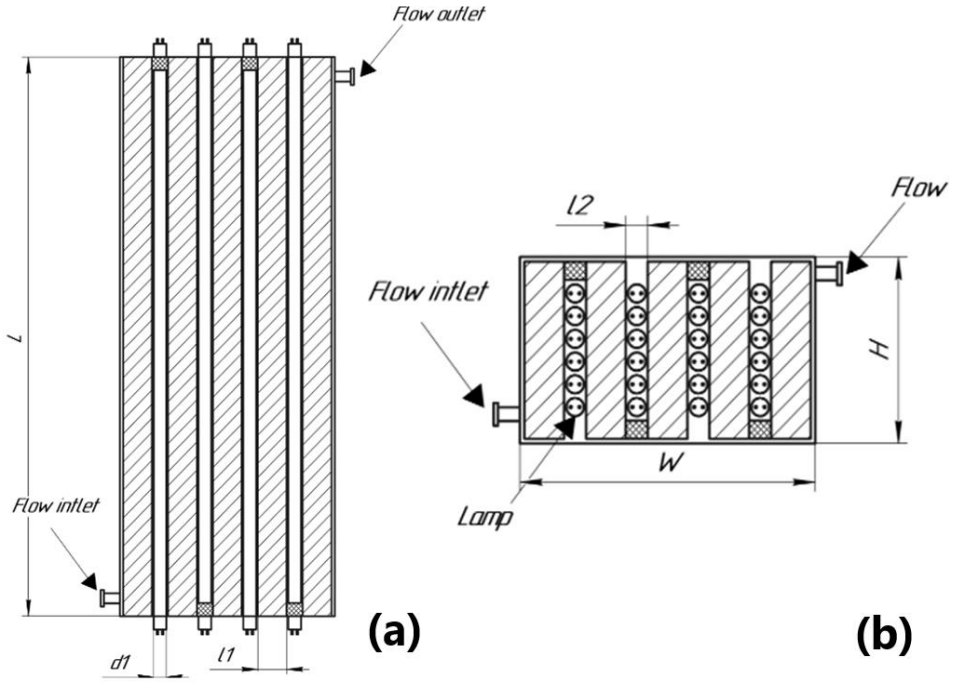

Fig. 4. Photoreactor designed on the basis of calculation: (a) – top view, (b) – side view

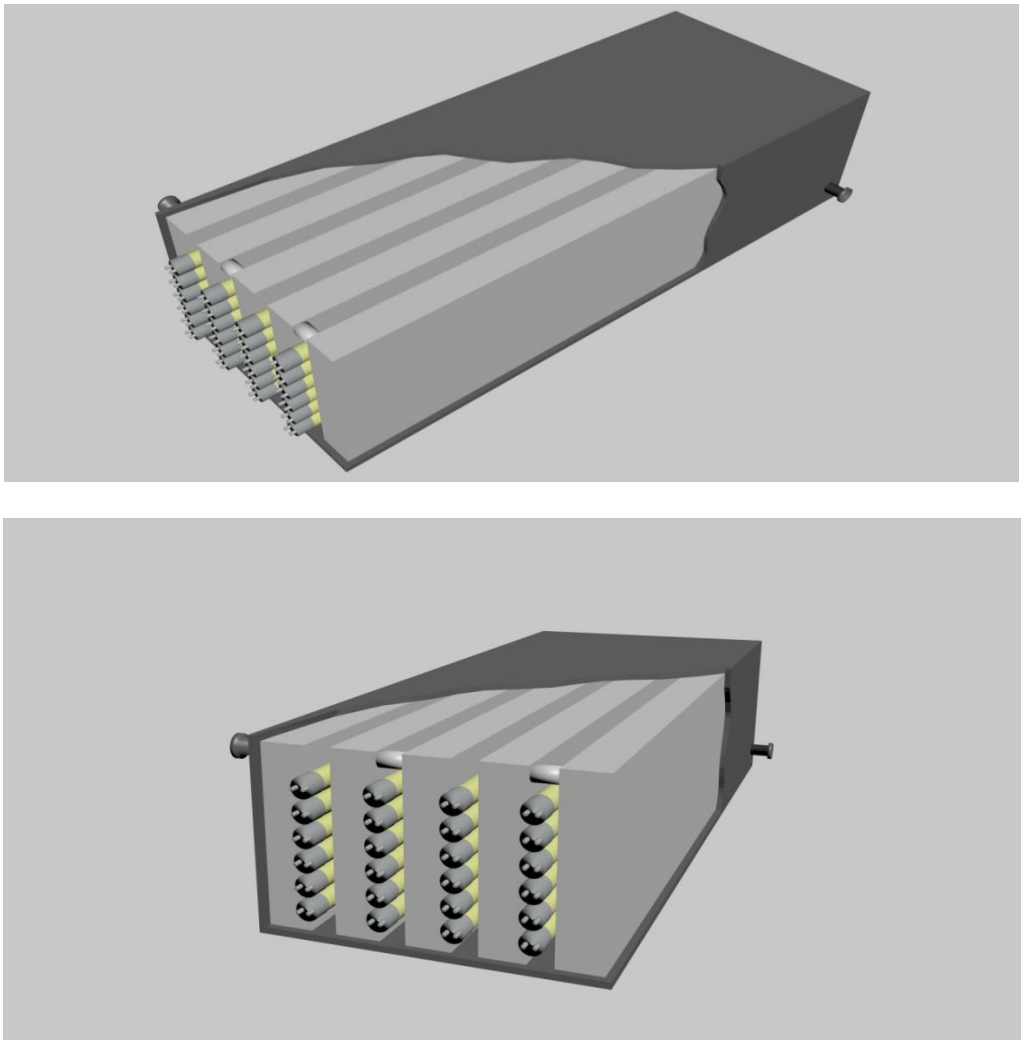
Fig. 5. 3D photoreactor model

Also, based on the presented algorithm, the parameters of the panel photoreactor for the dyes destruction (Congo red and methylene blue) with the same power and molar concentration as in the case of phenol, were calculated. The results are presented in Table 3.

Table 3. Parameters of the photocatalytic reactor for dyes oxidation (Congo red and methylene blue)

Congo Red		
	Number of lamps	5
	Number of sections	2
Lamp dimensions	Length (m)	1.7
	Diameter (m)	0.04
	Distance between panels (m)	0.09
	Distance from reactor walls (m)	0.05
Reactor dimensions	Length (m)	1.7
	Width(m)	0.25
	Height (m)	0.82
	Reactor volume (m^3)	0,37
Methylene blue		
	Number of lamps	11
	Number of sections	3
Lamp dimensions	Length (m)	1.7
	Diameter (m)	0.04
	Distance between panels (m)	0.09
	Distance from reactor walls (m)	0.05
Reactor dimensions	Length (m)	1.7
	Width(m)	0.39
	Height (m)	0.82
	Reactor volume (m^3)	0,57

As one can see from the data shown in Table 3 for the destruction of dyes, much less lamps and panels are needed. This is due to the influence of the molar mass of the pollutant that must be oxidized.

Conclusions

Based on theoretical analysis, the choice of the panel type photoreactor was substantiated. A simple design of the panel reactor was proposed, which was calculated for such popular pollutants as dyes (Congo red and methylene blue) and phenol. It has been shown that for the equal molar concentration of such pollutants as phenol and dyes (Congo red and methylene blue), the different number of lamps and sections of the photoreactor are required. More lamps require substances with higher molar mass: 54 lamps are required for the destruction of phenol, for the destruction of methyl blue – 11 lamps, for destruction of the Congo red – 5 lamps with the power of 25 W.

It was found that the received number of lamps is inversely proportional to the molecular mass of the pollutants. This fact may be associated with the higher stability of molecules having smaller molecular masses of substances. Accordingly, the reaction volume will also change, namely, for the destruction of phenol in an aqueous solution at a concentration of 0.15 mole/m^3, the reaction volume is 2 m^3, while for Congo red with the same concentration is 0.4 m^3.

As a result of the calculations, the more versatile design of the panel photoreactor was developed. The number of sections and lamps in it can be increased or reduced if necessary and such reactor is capable to provide highly effective photodegradation of pollutants of different genesis in sewage of various origins. According to the developed photoreactor design, its 3D modeling is carried out, which allows to visualize all the structural elements of such unique type of special equipment. The

3D photoreactor model was implemented in a free and available Blender software, which can be recommended for designing equipment and process circuits.

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РОЗРАХУНОК ТА 3D МОДЕЛЬ ФОТОКАТАЛІТИЧНОГО ПАНЕЛЬНОГО РЕАКТОРУ ДЛЯ ДЕГРАДАЦІЇ БАРВНИКІВ І ФЕНОЛУ

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Стаття присвячена розрахунку та 3D моделюванню фотокаталітичного панельного реактору для деградації барвників та фенолу. Для цього було теоретично розглянуто фотокаталітичні реактори різних типів для фотодеструкції органічних полютантів у водних розчинах. Серед наведених фотореактори панельного типу, на наш погляд, є найбільш раціональними. Також зазначена перспективність фотокаталітичного очищення стічних вод від органічних полютантів так званими методами Advanced Oxidation Processes, серед яких гетерогенний фотокаталіз за участі такого фотокаталізатору як титану (IV) оксид є найбільш ефективним. Для проведення фотодеструкції забруднюючих речовин у водних розчинах розглянуто різні типи фотореакторів, що розглядаються у сучасних літературних джерелах, з метою визначення найбільш оптимальної його конструкції. Показано, що відділення порошкоподібного фотокаталізатору від водного розчину після завершення фотокаталітичного процесу успішно можна реалізовувати як за допомогою ультрафільтрації, так й мембранних модулів. На підставі проведеного теоретичного аналізу обґрунтовано вибір фотореактору панельного типу та проведено розрахунок його конструкційних параметрів. Показано, що для однакової молярної концентрації таких полютантів як фенол та катіонний й аніонний барвники (конго червоний та метиленовий голубий) необхідна різна кількість ламп та панелів у фотореактору, а отже й різний об’єм фотореактору. В результаті розроблено більш універсальну конструкцію – панельний фотокаталітичний реактор, який можна у разі необхідності нарощувати з метою збільшення як об’єму фотореактору, так й для досягнення необхідного ступеня очищення від полютантів, і який здатний забезпечити високоефективну фотодеструкцію полютантів різного генезису у стічних водах різноманітного походження. Згідно розробленої конструкції фотокаталітичного реактору проведено його 3D моделювання, що дозволяє наочно уявити всі конструкційні елементи такого нетипового спеціального обладнання.
Ключові слова: Процеси АОП, фотокаталіз, реактори, проектування панельних реакторів, очищення води від органічних сполук

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