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STUDYING THE PHOTOCATALYTIC OXIDATION OF HYDROXYBENZENE IN AQUATIC MEDIUM ON THE PHOTOCATALIZERS SNO_2, ZNO, TIO_2

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Наведено результати дослідження фотокаталітичної активності оксидів SnO_2, ZnO, TiO_2 в процесі окиснення гідроксибензолу у водному середовищі, окремо розглянуто властивості алотропних модифікацій оксиду титану (IV): анатазу та рутилу. Обґрунтовано взаємозв'язок зменшення значення ширини забороненої зони та збільшення фотокаталітичної активності розглянутих оксидів. Встановлено вплив організації перемішування на зростання ступеня деградації гідроксибензолу у водному середовищі, яке становить в середньому 10–15 %. Досліджено вплив співвідношення вмісту анатазу до рутилу у фотокаталізаторі на ефективність деградації гідроксибензолу. Показано, що отримані при цьому результати досліджень узгоджуються з літературними даними, але відкриваються додаткові можливості збільшення ступеня окиснення гідроксибензолу прі сумісном використанні анатазу та рутилу. Встановлено, що найбільший ступінь окиснення з перемішуванням та без нього при часі опромінювання 60 хвилин досягається при співвідношенні кількості анатазу до рутилу 75/25 % мас. та складає 23 % і 37 %, відповідно. Використання такого складу дозволяє збільшити ступінь окиснення гідроксибензолу у водному середовищі на 11–18 %, що в 1,5–1,9 разів більше порівняно з чистим рутилом та анатазом. Показано, що при використанні фотокаталізатора із суміші анатазу та рутилу характер впливу перемішування на ступінь окиснення гідроксибензолу має іншу закономірність, ніж при використанні чистого анатазу або рутилу. Одержані результати дозволили зробити висновок, що для скорочення часу досягнення максимальних показників процесу деградації гідроксибензолу необхідно збільшувати відношення поверхні опромінювання до висоти самого апарату та збільшувати число Re процесу перемішування. На основі отриманих експериментальних даних встановлено оптимальний склад фотокаталізатору, який дозволяє досягти максимальний ступінь вилучення гідроксибензолу із розчину

Ключові слова: очищення стічних вод, гідроксибензол, фотокаталітична активність, оксид титану, анатаз, рутил

1. Introduction

There is a problem of pollution and purification of water resources in the modern world. A huge amount of different allogenic chemical substances penetrates water bodies. Such substances deteriorate water quality. The main sources of pollution of the environment are industrial enterprises, thermal power stations and transport. The transition to new technologies will reduce an impact of emissions into the environment.

The problem of environmental pollution with organic compounds is very important and relevant at present. It requires resolution at the stage of production, which is a source of pollution, or at the further utilization of discharges of this production. One of very harmful organic substances emitted to the environment, in particular to water basins, is hydroxybenzene. Its exposure to the environment leads to significant changes in the ecosystem itself.

Hydroxybenzene and its various derivatives belong to the most widespread and important substances in the world. Sources of the inflow of hydroxybenzene to the environment are enterprises of the chemical industry, which produce pesticides and plastics, production of oil refining, wood chemistry, coke, aniline, pharmaceutical industry. Hydroxybenzene appears during a variety of processes in natural conditions. Such processes are biochemical decomposition and transformation of organic substances, metabolism of aquatic organisms, which leads to formation of so-called low molecular weight and natural phenols.

The total content of hydroxybenzene and its derivatives can exceed 10 20 g/dm^3 in sewage water. And this is an indicator of pollution of water bodies [1, 2].

The presence of hydroxybenzenes in water leads to formation of chlorine-substituted and nitro-substituted hydroxybenzenes, which are even more dangerous for human health. Chlorhydroxybenzenes form by chlorination of water to disinfect it. They also get to sewage water and drinking water as a result of decomposition of pesticides, with waste of pulp-and-paper production. The smallest traces of chlorhydroxybenzenes (0.1 μg/dm^3) give water a characteristic smack and smell. Rather "hard" boundary permissible concentrations (BPC) for individual chlorhydroxybenzenes are connected with mutagenic influence on microorganisms, which suggests presence of carcinogenic properties. Appearance of nitrohydroxybenzene in water is a consequence of pollution of petrochemical production by sewage water and degradation of certain types of organophosphorus pesticides. BPC are 60 μg/dm^3 for o-, m-nitrohydroxybenzene and 20 μg/dm^3 for p-nitrohydroxybenzene [3,4].

Water purification is necessary almost always, especially in modern conditions, along with control and decontamination of food. Currently, people widely use chlorination, ozonation, bactericidal lamps and other methods for decontamination of water and air. But all methods have a number of disadvantages: either high cost, or impossibility of application near people, or low specification, that is, an action on one class of microorganisms only.

One of the promising directions is photocatalytic purification of water and aqueous media contaminated with organic compounds. The main advantages of the photocatalytic method of water purification are as follows:

1) ability to oxidize almost any organic substances and a number of inorganic compounds such as CO, H_2S, HCN, NH_3, NO_x and others;

2) the method works at room temperature and atmospheric pressure;

3) ability to oxidize even small concentrations of pollutants; purification of them with methods is economically inappropriate;

4) no additional reagents are necessary except for the oxidizing agent – oxygen air for implementation of the photocatalytic purification method.

We can conclude from all the above that the study of the process of photocatalytic oxidation of hydroxybenzene and its derivatives in the aquatic environment is an important scientific and technical task. The expediency of the study consists in development of a new optimal composition of a photocatalyst, which will increase a degree of oxidation of hydroxybenzene in an aqueous medium.

2. Literature review and problem statement

Researchers give great attention to the photocatalytic oxidation in recent years. It makes possible effective destruction of organic compounds in water. Also, there is great attention paid to combination of electrochemical, photocatalytic and membrane methods of water purification of organic compounds. Authors of paper [5] propose to carry out the oxidation of hydroxybenzene in an alkaline solution with a use of a glass-carbon electrode. They show that hydroxybenzene adsorbed on a surface of the electrode is oxidized to hydroquinone. But they do not consider the process of further oxidation of intermediate products to products of complete destruction of hydroxybenzene, which will cause certain difficulties at complete purification of sewage water. In addition, the presence of alkaline environment causes some difficulties for creation of this environment in practice with significant amounts for processing.

Work [6] studies the process of oxidation of hydroxybenzene on platinum-titanium anodes in an acidic medium. It considers two types of electrocatalysts. They are platinum on titanium and platinum on titanium modified with cerium. But the question remains whether it is possible to use these anodes in mediums, where pH varies in a wide range. In addition, a use of such metal as platinum will increase specific costs for servicing of such anodes, which will increase cost of water purification.

Authors of paper [7] propose a use of the method of electrochemical destruction of toxic and heavy oxidizing organic compounds under the high pressure of inert gas. But the use of high pressure in the technology of purified water will not make possible to provide high efficiency of purification facilities and will create certain difficulties for design of the main equipment.

Work [8] proposes to use a bacterial electrode for the oxidation of hydroxybenzene. The electrode was made of graphite, natural phosphate and modified bacteria. Experimental studies showed that we can use the electrode for degradation of various compounds of hydroxybenzene, but there is no data on efficiency of a use of such electrode over time and there is no justification of expediency of a use of such electrode on the industrial scale.

A use of membrane technologies for water purification of organic compounds is another way to overcome the problem. Membrane filtration processes are rationally coupled with photocatalytic oxidation in photocatalytic membrane reactors with ultrafiltration membranes [9] and membranes based on polyester anide and polyurethane [10]. The use of membranes can significantly improve a degree of removal of organic pollutants and products of decomposition from aqueous solutions, as well as to solve the problem of removal of a catalyst from purified water. But there is no indication of periodicity of membranes operation and feasibility of a use for removal of hydroxybenzene from sewage water.

Application of adsorption methods with a use of modified clay minerals [11], interlayer modified titanium nanotubes [12] also give a possibility to remove hydroxybenzene from an aqueous medium. However, there is no data on adsorbent regeneration technology in a paper [11], and there is no data on lifetime of these adsorbents and possibility of a use in the industry in work [12].

Photocatalytic decomposition of hydroxybenzene compounds belongs to destructive methods of sewage water purification. Application of the catalytic method in conjunction with the physical influence of UV irradiation can significantly intensify processes of oxidative destruction of organic pollutants and bring it to full mineralization in some cases. Photocatalysts should have the following properties: photoactivity, biological and chemical inertia, stability to photo corrosion, ability to use in the field of visible or near ultraviolet light, low cost and absence of toxicity. Titanium, iron, and zinc oxides and hydroxides play a role of catalysts in the process of photocatalytic decomposition of hydroxybenzene usually. Then they are removed from purified water.

We know that TiO_2 has excellent pigmentary properties, a high degree of ultraviolet absorption and high stability. Its characteristics give possibility to use it in various industries such as electro ceramics, glass production and photocatalytic destruction of organic and inorganic substances in water and air. Titanium dioxide is available, non-toxic and relatively cheap type of a photocatalyst.

Authors of paper [13] propose to use as a highly effective catalyst for decomposition of hydroxybenzene nanocrystalline TiO_2 film with an organic D35 dye. But the disadvantage of the catalyst is a long time needed for destruction of hydroxybenzene and possibility of its use for micro-pollutants of sewage water only.

Authors of a work [14] developed a highly active photocatalyst based on mesoporous TiO_2 modified by Al_2O_3. They established regularities of regulation of the synthesis conditions (temperature, pH, chemical composition of a reagent, concentration) for the directed change of characteristics of a photocatalyst. However, there are no experimental data on usability of application of this photocatalyst in processes of water purification.

Paper [15] suggests a use of a composition based on TiO_2 on the carbon carrier of promoted Cu for the decomposition of hydroxybenzene. As a result, we obtain a photocatalyst with a developed nanoporous structure, which gives possibility to reach a high degree of degradation of hydroxybenzene. Authors of work [16] investigated $CuO/WO_3/TiO_2$ photocatalyst composition obtained by sol gel technology. They established dependences of a photocatalyst activity change on Ph and an amount of H_2O_2 additionally introduced into the solution. However, the works do not provide data on stability of photocatalysts data on effects of various sulfur compounds, which are present in industrial sewage, and they will affect Cu negatively.

Paper [17] investigated photocatalytic activity of a catalyst made based on TiO_2 and phenol formaldehyde resin by the method of the sol gel technology with the use of tetrabutyl-titanate. The results showed that TiO_2 is in anatase form in a synthesized product. The degree of decomposition of hydroxybenzene was 62.8 % at irradiation at a temperature of 200 ^{o}C for 2 hours. However, there are no data on possibility of a use of such catalyst at room temperature, which limits the scope of its use. There is no data on possibility of a use of rutile form of TiO_2 in this process.

Duration of UV irradiation and introduction of oxidants (Fenton reagent, H_2O_2, O_2, O_3) into the system influences a degree of purification significantly. Authors of paper [18] investigated catalytic activity of B–N–Fe and Si–N–Fe compositions under conditions of ozonation and ultraviolet irradiation for the oxidation of hydroxybenzene compounds in an aqueous medium. They showed that we can achieve the highest degree of degradation by ozonation with the presence of boron nitride based composite. But a use of O_3 on an industrial scale will affect the economy of the process of sewage purification negatively. In addition, there is no data on an effect of duration of ozonation on the degree of oxidation of hydroxybenzene.

Work [19] proposes a photocatalyst based on iron-containing silica Fe-HMS-50 material with a use of hexadecylamine at room temperature. The authors investigated an influence of pH and H_2O_2 concentration on the oxidation process. At the use of H_2O_2, there is a series of problems with stability of this compound during storage, pH of a medium and with a cost. Decomposition of H_2O_2 in an alkaline medium limits the range of pH at which we can use it.

According to the results of the analysis of literature on the study subject, a choice of a photocatalyst, which should provide a high degree of oxidation and work in a wide range of pH, which should be stable in an operation environment, remains an unsolved problem.

A cost of electrodes and electricity is important for application of electrochemical methods. There is no information on time of use of various membranes and their efficiency on the industrial scale. There are no data on ways of further regeneration of adsorbents and there is a limited range of use of separate photocatalysts under conditions of industrial sewage water.

We should note that there is no investigation of an influence of the type of allotropic TiO_2 modification on the process of oxidation of hydroxybenzene in the reviewed and discussed publications of periodical scientific publishings. There is no information on the combined use of anatase and rutile at degradation of organic compounds. There is no data on possibility of a use of zinc oxide (II) and tin (IV) as photocatalysts for the oxidation of hydroxybenzene.

3. The aim and objectives of the study

The objective of the study was to examine the process of oxidation of hydroxybenzene on photocatalysts in an aqueous medium. We used zinc oxide (II), tin oxide (IV), titanium oxide (anatase), titanium oxide (rutile), and a mixture of rutile and anatase in various ratios. This will enable further determination of the optimal composition of a photocatalyst, which we can use in water purification technology.

We set the following tasks to achieve the objective:

– establishment of the dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation on the proposed photocatalysts;

– investigation of the influence of changes in the ratio of anatase/rutile on the degree of oxidation of hydroxybenzene and determination of the optimal composition of a photocatalyst.

4. Methodology for studying the photocatalytic oxidation of hydroxybenzene in an aqueous medium

The wavelength of ultraviolet radiation should be less than 380 nm for effective photocatalytic decomposition of organic contaminants in water. Fig. 1 shows the decomposition spectrum of organic substances, which corresponds to the wavelength in the range of 200–280 nm.

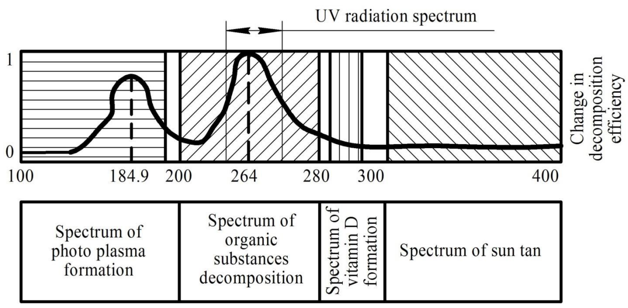

Fig. 1. Spectrum of decomposition of organic substances

We used the "UFOBACT" ultraviolet bactericidal lamp of 034 (2) modification with the UFBOT-40-01 timer (Ukraine) as a source of ultraviolet radiation in the study. The quartz LKB-40-02 lamp (Ukraine) had a special coating and self-restorable electrodes. The wavelength of radiation was 220–280 nm, the maximum radiation range was 255–260 nm. The power of irradiation in the range of 220–280 nm at the distance of 1 m behind the optical axis of the irradiator was not less than 1.8 W/m^2.

As a photocatalyst, we used zinc oxide of chemically pure grade, tin oxide of chemically pure grade and two allotropic modifications of titanium oxide: the anatase form of titanium oxide of PRETIOX AV-01-FG grade manufactured by Presheza a.s. (Czech Republic); and the rutile form of pigment titanium oxide of "SUMTITAN R-206" grade manufactured by PJSC "Sumykhimprom" (Ukraine). Table 1 gives some of their technical characteristics.

We carried out the investigation of the oxidation of hydroxybenzene in an aqueous solution in a laboratory glass of chemically resistant glass of 100 ml volume with the internal diameter of 50 mm. Firstly, we weighed 1 g of the photocatalyst and transferred it to the glass to cover the entire surface of the bottom of the glass with titanium oxide. After that, we added an aqueous solution of hydroxybenzene. We dissolved phenol in distilled water in the amount of 0.5 g per 1 dm^3 of water for preparation of the aqueous solution, and irradiated it with ultraviolet light for one hour.

We used a stirring device, which consisted of a cylindrical vessel with a stirrer of 25 mm diameter, to study an influence of stirring intensity. We used the following formula [20] to determine the Reynold's number of the stirring process for this type of a stirrer:

$$\mathrm{Re}=\frac{\rho\cdot n\cdot d^2}{\mu}=\frac{998{,}2\cdot 38\cdot 0{,}025^2}{1004\cdot 10^{-6}}=24000, \tag{1}$$

where μ_c is the dynamic viscosity, Pa×s; ρ is the density of mixed liquid, kg/m^3; d is the diameter of the stirrer, m; n is the rotational speed of the stirrer, s^{-1}.

The photocatalyst was in a fine-dispersed state and formed suspension with the solution. The presence of suspended particles was not permissible for further determination of residual content of hydroxybenzene in the aqueous solution by the titrimetric method. Therefore, we decided to remove the photocatalyst not by the filtration method, which does not give possibility to remove titanium oxide (IV) completely, but by centrifugation. After that, we separated the irradiated part of the solution by the decantation method. We used MLW T23D centrifuge with rotation speed of 6,000 min^{-1} for centrifugation.

We carried out determination of the content of hydroxybenzene according to the standard method [22, 23] based on the bromate-bromide method.

5. Results of studying the activity of photocatalysts in the process of liquid phase oxidation of hydroxybenzene

5. 1. Determination of SnO$_2$ and ZnO activity

Quantitative methods of analysis of analytical chemistry, namely the titration method used in this study to determine the initial concentration and the final concentration of hydroxybenzene in water, are very sensitive to various admixtures that may be present in the analyzed solution.

We used a solution with possible presence of admixtures of the photocatalyst for titration. Combined application of the centrifugation method and the decantation method to extract the photocatalyst from such solution does not make possible to ensure its high purity. Therefore, firstly, it was necessary to establish possibility of application of the titration method to determine adequate values of hydroxybenzene concentrations. To do this, we conducted studies with proposed catalysts without irradiation with ultraviolet light for one hour; all other operations of the mentioned earlier methodology remained unchanged.

We performed seven parallel experiments with the photocatalyst based on anatase mass of 0.5 g according to the methodology described above. Table 2 gives results of mathematical processing (absolute error Δ, absolute error δ and relative error E) of the obtained data on calculated concentration of hydroxybenzene in C solution at the given reliability P=0.95, Student coefficient $t_{0,95}$=2.447 and equipment error δ_n=0.1 mg/l.2. We calculated the absolute error from equation:

$$\delta=\sqrt{\left(t_{0,95}\cdot S_{n}\right)^2+\left(t_{0,95}\cdot\delta\ \ /3\right)^2}. \tag{2}$$

Table 1

Technical characteristics of grades of titanium oxide (IV)

Grade of titanium oxide	Mass fraction of TiO$_2$, % not less	TiO$_2$ rutile form, %, not less	TiO$_2$ anatase form, %, not less	Volatile particles, %, not larger	Water soluble substances, %, not larger	Size of particles, μm	Whiteness, %
PRETIOX AV-01-FG	99	–	99	0.5	0.25	0.3	97
SUMTITAN R-206	94	97	–	0.5	0.2	0.4	97

Table 2

Results of mathematical processing of data obtained as a result of titration of solutions

No.	C, mg/l	$\Delta = C - C$	Δ^2	Dispersion $S_i = \pm\sqrt{\frac{\Sigma\Delta_i^2}{(i-1)}}$	Absolute error, δ	Relative error $E = \frac{\delta}{C}\cdot 100\,\%$
1	501.68	1.68	2.8224	1.158627	1.075	0.215
2	498.54	1.46	2.1316			
3	500.06	0.06	0.0036			
4	501.24	1.24	1.5376			
5	499.68	0.32	0.1024			
6	501.12	1.12	1.2544			
7	500.45	0.45	0.2025			
Initial concentration C=500 mg/l			$\Sigma\Delta^2$=8.0545		500±1.075	

Thus, we can see in Table 2 that the proposed method of extraction of the photocatalyst from the solution and the subsequent use of the titrimetric determination method for the final content of hydroxybenzene have a very high accuracy and make up a relative error of no more than 1 %, which makes possible to use it in further research.

Fig. 2 shows results of the study of photocatalytic activity of oxides of tin (IV) (curve 1) and zinc (II) (curve 2) in the process of liquid phase oxidation of hydroxybenzene. As we can see in Fig. 2, zinc oxide (II) has a greater activity than tin oxide (IV) and makes possible to achieve the twice higher degree of oxidation over time. However, the degree of oxidation achieved during such period of time is not sufficient for a use of such photocatalyst for purification of sewage water of organic contaminants, in particular from hydroxybenzene.

In order to increase efficiency of the use of photocatalysts considered in the study, we arranged stirring of the solution during its irradiation to distribute the catalyst through the volume of the solution evenly. As a result, the specific surface of the photocatalyst, which takes an active part in the process of oxidation directly, increased, and consequently, its productivity increased. Fig. 2 shows this (curves 3 and 4). In both cases, an increase in the oxidation of hydroxybenzene was 8–10 % on average.

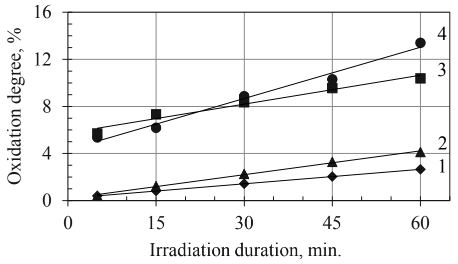

Fig. 2. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet radiation: 1 — SnO_2; 2 — ZnO; 3 — SnO_2 (Re=24,000); 4 — ZnO (Re=24,000)

The nature of the dependence of the degree of oxidation on irradiation time for these photocatalysts is linear. It is necessary to increase irradiation time for the solution with stirring and without it in order to achieve the most complete decomposition of hydroxybenzene in the solution. We should note that the degree of oxidation achieved over time remains not high enough for industrial application even with arrangement of stirring.

A photocatalyst, which will effectively oxidize various organic compounds in industrial and domestic sewage water in a short period of time, would find effective application in solution of the ecological problem.

5. 2. Determination of anatase activity and rutile activity

As noted in the literature review [13–16] above, there is another oxide effectively used to oxidize organic compounds in an aqueous medium. This is titanium oxide (IV). All three allotropic modifications found a widespread use: anatase, brookite and rutile, but brookite is practically not used due to complexity of its receipt.

Fig. 3 shows the results of the research on the oxidation of hydroxybenzene with a use of anatase and rutile. As in previous experiments, we analyzed a change in the degree of oxidation of hydroxybenzene in dependence on duration of ultraviolet irradiation, both with and without stirring, separately for anatase and rutile.

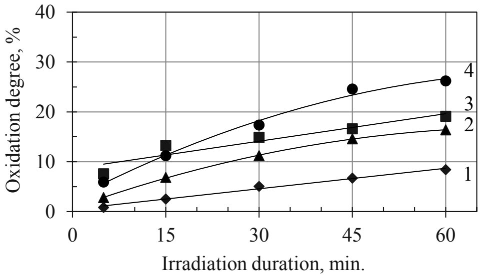

Fig. 3. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet radiation: 1 — anatase; 2 — rutile; 3 — anatase (with stirring, Re=24,000); 4 — rutile (with stirring, Re=24,000)

Comparing the results of previous experiments with tin oxides (IV) and zinc oxides (II), the oxidation of hydroxybenzene on rutile and anatase reaches 26.2 % and 19.1 % during the stirring time, and without stirring – 17.6 % and 8.4 %, respectively.

Thus, the photocatalytic activity of rutile and anatase is significantly higher than the activity of photocatalyst used in previous experiments. Comparing the degree of oxidation achieved during stirring over time on rutile and zinc oxide (II), as a more efficient photocatalyst of previous studies, this indicator is almost twice higher. The use of anatase, in comparison with the previous photocatalysts, gives a slight increase in the degree of oxidation at stirring after an hour of radiation, which is only 6 %.

Stirring (curves 3 and 4) helps to improve the process in both cases. We should note that the nature of an increase in the degree of oxidation at stirring over time relatively to the index of oxidation without stirring has an uneven character when using rutile as a photocatalyst. An increase in the oxidation during irradiation time is not proportional to other photocatalysts. For example, for anatase, this indicator is approximately the same at 5 and 60 minutes of irradiation and makes up 8–9 %, but for rutile at 5 minutes, it is only 3 %, while at the same time, at 60 minutes, it is 10 % already.

5. 3. Determination of the optimal ratio of anatase/rutile

The results presented in paper [24] show that, in some photocatalytic processes, we achieve the greatest activity of a photocatalyst based on titanium oxide (IV) not using pure anatase and rutile alone, but in the given ratio. Therefore, we carried out studies on the effect of the ratio of anatase and rutile in the photocatalyst on the degree of oxidation of hydroxybenzene in an aqueous medium and establishment of an optimal ratio to achieve a minimum final hydroxybenzene concentration in water.

For the study, we prepared photocatalysts with the following ratios of anatase to rutile, % mass: 40/60, 60/40, 75/25 and 80/20. The total mass of the photocatalyst remained the same as in previous studies and made up 1 g. Fig. 4, 5 show the results of the conducted studies.

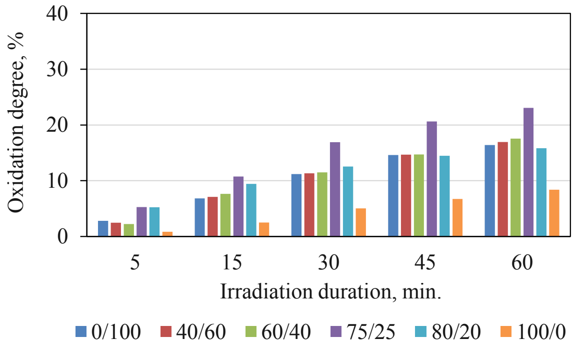

Fig. 4. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation and the ratio of anatase/rutile (without stirring)

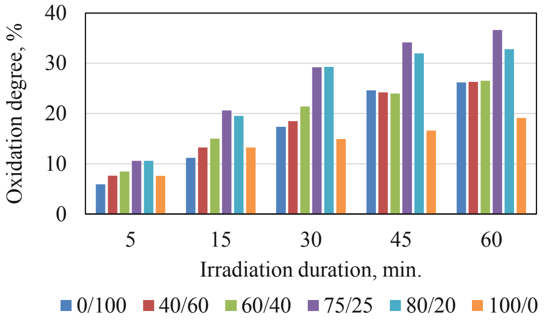

Fig. 5. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation and the ratio of rutile/anatase (with stirring, Re=24,000)

We can see in Fig. 4 and 5 that we achieved the highest degree of oxidation with and without stirring at an irradiation time of 60 minutes with the ratio of anatase and rutile of 75/25 % by weight. And this is 23 % and 37 %, respectively. The use of such composition makes possible to increase the oxidation of hydroxybenzene in an aqueous medium by 11–18 %. That is, such a photocatalyst, in comparison with pure rutile and anatase, has an activity of 1.5 times greater without stirring and 1.9 times greater with stirring, respectively.

The arrangement of stirring for the photocatalyst of this composition (Fig. 5) is even more significant for increasing of the oxidation of hydroxybenzene, as it is almost 1.5 times greater than at the use of pure anatase or rutile. The change in the ratio of anatase to rutile from 40/60 to 60/40 in comparison with pure anatase at arrangement of the process without stirring (Fig. 4) does not significantly affect the oxidation efficiency of hydroxybenzene for 60 minutes of irradiation. When arranging the stirring (Fig. 5), until the irradiation time of 30 minutes, the degree of oxidation increases with increased anatase content in the photocatalyst. After irradiation time of 30 minutes, this change is not very significant.

It is evident from the dependences of the degree of oxidation on time of irradiation (Fig. 6–8) for different ratios of anatase to rutile, that the more content of anatase in the photocatalyst is, the greater is an increase in the degree of oxidation at arrangement of stirring. Thus, at 60-minute irradiation for the photocatalyst with anatase/rutile ratio of 60/40, the difference is 9 % (Fig. 6), 75/25 – 14 % (Fig. 7), and (Fig. 8) it is 17 % already for the ratio 80/20.

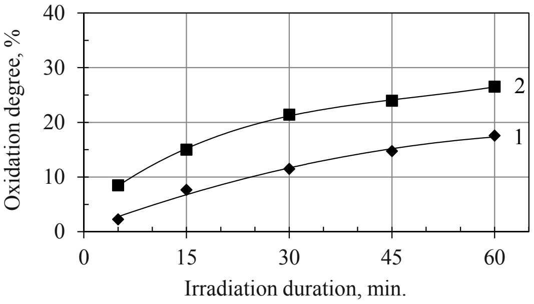

Fig. 6. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation on anatase/rutile catalyst (60/40): 1 — without stirring; 2 — with stirring (Re=24,000)

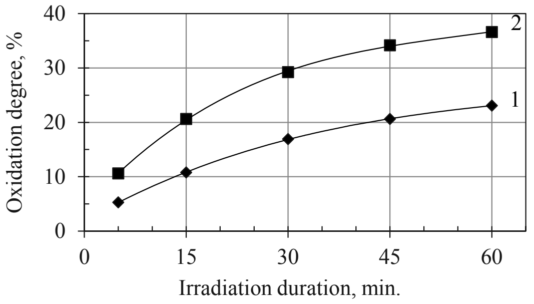

Fig. 7. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation on anatase/rutile catalyst (75/25): 1 — without stirring; 2 — with stirring (Re=24,000)

An increase in the degree of oxidation during the first 30 minutes of irradiation is more significant for photocatalysts with higher anatase content. For example, the oxidation degree for the photocatalyst with the ratio of anatase to routine of 60/40 (Fig. 6) is only 13 %, and for the photocatalyst with a ratio of 80/20 (Fig. 8), it is almost 20 %.

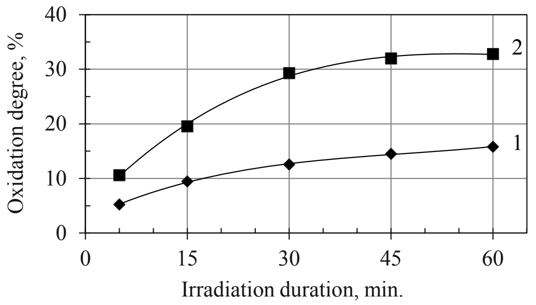

Fig. 8. Dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation on anatase/rutile catalyst (80/20): 1 — without stirring; 2 — with stirring (Re=24,000)

We should also note that the nature of the curve after 30 minutes of irradiation with an increase in the content of anatase in the photocatalyst becomes gradually almost linear, both with and without stirring, and it slightly increases during subsequent irradiation time.

6. Discussion of results obtained in the study of photocatalytic activity of metal oxides

Presence of valent zone of conductivity in any semiconducting metal oxide determines its photocatalytic properties, due to peculiarities of the electronic structure. Electrons in a semiconductor receive additional energy to overcome a bandgap width due to light energy. The magnitude of the bandgap width will determine the photocatalytic activity of one or another semiconductor. At its reduction, the photo absorption limit will be blended toward the long wavelength visible range.

Values of the bandgap of metal oxides used in the studies carried out were, respectively: SnO_2 – 3.54 eV; ZnO – 3.37 eV; anatase – 3.2 eV and rutile – 3 eV. The analysis of the correspondence of an increase in values of the bandgap width completely corresponds to an increase in activity (the degree of oxidation of hydroxybenzene) of these oxides in our process and are, respectively: SnO_2 – 10 %; ZnO – 13 %; anatase – 19 % and rutile – 26 %.

Dispersibility of the catalyst plays an important role in heterogeneous catalytic processes. Increasing of a specific surface of the photocatalyst enables to increase a number of active centers, which participate in the act of chemical photocatalysis, that is, as in our case, to accelerate the process of oxidation of organic compounds. In this aspect, the arrangement of stirring of a solution with the photocatalyst takes not the last position among factors that contribute to the increase in the degree of oxidation over a short period of time.

The effect of stirring may be different in dependence on dispersibility and physical-and-chemical properties of a photocatalyst itself. For two allotropic modifications of titanium oxide (IV) – anatase and rutile, the nature of the increase in the oxidation of hydroxybenzene due to stirring for some time is not the same (Fig. 3).

We can explain the difference by the fact that a part of anatase in the solution is initially mainly suspended. It forms a suspension of a photocatalyst with an aqueous solution of hydroxybenzene. Thus, a larger surface of the photocatalyst works from the first minutes of irradiation, and the stirring itself, due to turbulence, leads to a constant increase in the oxidation degree by 8–9 %. In the case with rutile, we observe another situation: rutile particles in the solution settle down initially into the lower part of the glass, that is, only a small surface of the photocatalyst that covers the bottom of the glass operates at the beginning of irradiation. During time, due to stirring, all particles of rutile pass into a suspended state. Due to this, the percentage of the photocatalyst surface that is working in the process of hydroxybenzene photooxidation increases and the oxidation degree reaches its maximum.

When we use a photocatalyst of a mixture of anatase and rutile, the effect of stirring on the degree of oxidation of hydroxybenzene has a different pattern (Fig. 5). Also, as for pure anatase and rutile, there is an intense increase in the oxidation of hydroxybenzene during stirring in the first 30 minutes of irradiation. However, the increase in the content of anatase in the photocatalyst does not lead to a decrease in this effect, but rather to its growth, although, as noted above, for rutile, the arrangement of stirring is more influential. We can explain this by the fact that anatase, being mainly in a weighted state, plays a double role in the first minutes of irradiation: on the one hand, it takes an active part in the process of oxidation of hydroxybenzene, and on the other, it shields particles of rutile from ultraviolet irradiation as a more active component of the catalyst. With increasing of content of anatase to more than 75 %, contribution of rutile to the total activity of the photocatalyst becomes less and the degree of oxidation of hydroxybenzene decreases.

As a result of the mathematical analysis of the dependence of the degree of oxidation of hydroxybenzene on irradiation time for a photocatalyst, which contains 75 % of anatase and 25 % of rutile, we obtained the following parabolic regression equation:

– without stirring:

$$y=-4{,}5\cdot 10^{-3}\cdot x^2+0{,}615\cdot x+2{,}42, \qquad (3)$$

– with stirring:

$$y=-8{,}9\cdot 10^{-3}\cdot x^2+1{,}037\cdot x+6{,}17. \qquad (4)$$

Determination coefficient R was 0.999 and 0.997, respectively. Thus, the calculation parameters of the model explain the relationship between the parameters studied by 99 %.

Thus, when we use rutile or a mixture with it as a photocatalyst to achieve the highest degree of oxidation of hydroxybenzene, stirring is required. In order to reduce time to reach the maximum values, it is necessary to increase the ratio of an irradiation surface to the height of an apparatus, which will be used to disinfect water of organic admixtures. Also, we can reduce process time by an increase in a number of rotation of a stirrer, that is, an increase in the Reynolds number, or by a use of these engineering solutions together. Therefore, the task of further research will be to study an influence of the Reynolds criterion and dispersion of a photocatalyst on the degree of oxidation and establishment of optimal values of these parameters in terms of maximum disinfection of hydroxybenzene and minimum energy costs.

The degree of oxidation achieved in this study on the photocatalyst is not high enough, which is the main disadvantage of the research data. However, we established the optimal composition of the photocatalyst with the ratio of anatase and rutile, which gives possibility to increase the degree of degradation of hydroxybenzene. Therefore, the main task of further research is to find ways to increase the oxidation of hydroxybenzene in less time of ultraviolet irradiation and to study the obtained composition of the photocatalyst in other photocatalytic processes.

Authors of papers [25, 26] note that oxygen plays an important role in the oxidation of organic compounds, therefore, in order to increase the oxidation of hydroxybenzene, there is a plan to use additional sources of oxygen further. In some cases, oxygen is considered as inert gas, because it does not destroy harmful substances in water. But during photocatalytic activation of air oxygen, it is not necessary to add expensive chemicals for purification of sewage water, which is very promising in its use.

There is a plan to use hydrogen peroxide as a source of oxygen. It intensifies degradation of hydroxybenzene by additional formation of hydroxyl-radicals when introduced into the photocatalytic system [27]:

$$H_2O_2 \rightarrow 2OH^-; \quad (5)$$

$$H_2O_2 + OH^- \rightarrow H_2O + HO^{2-}; \quad (6)$$

$$H_2O_2 + HO^{2-} \rightarrow H_2O + O_2 + OH^-. \quad (7)$$

It is also necessary to provide additional air barbotage through the solution. This will provide additional stirring of the photocatalyst and saturation of the solution with oxygen.

7. Conclusions

1. We established the dependence of the degree of oxidation of hydroxybenzene on time of ultraviolet irradiation over time on oxides of semiconducting SnO_2, ZnO metals and on allotropic modifications of TiO_2 – anatase and rutile. We showed that an increase in irradiation time and arrangement of stirring leads to an increase in the degree of oxidation of hydroxybenzene in an aqueous medium for the selected oxides. We established the interconnection of activity of the photocatalyst with its electronic structure, namely, the width of the bandgap. And this showed efficiency of the use of titanium oxide (IV) in the process of liquid phase oxidation of hydroxybenzene in comparison with other oxides.

2. We carried out investigation of the dependence of the degree of oxidation of hydroxybenzene on the composition of the photocatalyst, namely the ratio of anatase and rutile. We showed that we can achieve 37 % of oxidation in the photocatalyst of the following composition: 75 % of anatase and 25 % of rutile. We can explain this by physical-and-chemical properties of allotropic TiO_2 modifications. The specified degree of oxidation is not sufficient for application in practice, but the task of further research is to find ways to increase it.

3. We determined an additional possibility of increasing of the degree of oxidation of hydroxybenzene due to arrangement of stirring, which makes possible to increase the efficiency of degradation by 10–15 %.

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