Application of concrete modified with TiO₂ to reduce anthracene concentration

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Abstract. In this study, samples of fine-grained concrete with the additive TiO₂ microparticles were made. The photocatalytic properties of TiO₂ for the decomposition of anthracene in solutions under UV irradiation were studied. To evaluate the efficiency of photodegradation, the method of luminescence analysis was used. For improving the quality of the analyzed solutions, model surfaces were made based on chitosan with the addition of TiO₂. According to the results of the experiments, it was found that the degree of photodegradation of anthracene in solutions using solid chitosan-TiO₂ matrices reaches 74% after 60 minutes under UV irradiation. The conducted studies confirm the feasibility of using chitosan-TiO₂ matrices as model surfaces for studying the photocatalytic properties of TiO₂ for the oxidation of anthracene.

1. Introduction

Anthracene belongs to the group of polycyclic aromatic hydrocarbons (PAHs). PAHs are organic compounds that are among the most common environmental pollutants [1]. Many representatives of PAHs have bioaccumulative properties and are dangerous to human health, even in small amounts. It is known that when the maximum concentrations of substances of the PAH group in the environment are exceeded, the risk of developing cancer significantly increases [2]. Thus, a prospective direction of modern research is the development of methods for the oxidation of PAHs. One of the most effective methods of PAHs oxidation is the use of photocatalytic reactions under light radiation [3].

TiO₂ was used as a photocatalyst in this work. This substance has high photocatalytic activity, chemical and thermal stability, and low cost [4-5]. It is also known that TiO₂ significantly accelerates the decomposition of PAHs under UV irradiation [6]. The use of TiO₂ in various materials contributes to the active purification of the environment. For example, the authors [7] developed concrete road surfaces with the addition of TiO₂ for the decomposition of pollutants. Also effective for improving the environment is the application of photocatalytic coatings on the enclosing structures of buildings and structures [8].

A prospective direction in the construction industry is the use of photocatalytic concrete (PhC), which also reduces the concentration of pollutants in the air and has the property of self-cleaning the surface. The production technology of PhC does not differ from standard concrete and does not require additional equipment. As a rule, the photocatalyst is added to the dry mix in the ratio of 0.25-5 wt.%. [9] This type of concrete has been used for several decades in construction in the United States, Japan, Belgium, Italy and France. Due to the prospects for the use and development of PhC manufacturing...
Due to the relevance of PhC in modern environmental conditions, the efficiency of degradation of an individual representative of PAHs in the presence of a TiO\textsubscript{2} photocatalyst was investigated in this work. At the same time, anthracene was chosen as a representative compound from the substances of the PAH group, and the photodegradation process was studied under various experimental parameters.

2. Backgrounds

TiO\textsubscript{2} has three main types of crystal structure: anatase, rutile and brookite. It is known that anatase phase of TiO\textsubscript{2} with a band gap of 3.2 eV exhibits good photocatalytic properties. If there is an absorption of a photon with an energy equal to or exceeding the band gap in TiO\textsubscript{2}, an electron transition from the valence band to the conduction band can occur. Then the formation of electron-hole pairs occurs due to the formed free vacancies in the valence band. These electron-hole pairs have a sufficient lifetime in the nanosecond range to transfer charge to adsorbed PAHs on the semiconductor surface [10]. Then, excited electrons in the conduction band and holes in the valence band recombine, followed by dispersion of energy in the form of heat. If suitable absorbers are available for trapping an electron or a hole, redox reactions can occur [11]. Figure 1 shows a scheme of the described photocatalytic processes.

Recently, the process of decomposition of PAHs in aqueous media using a TiO\textsubscript{2} photocatalyst has been actively studied. The authors [12] have studied the process of photocatalytic decomposition of a mixture of 16 PAHs under UV radiation in aqueous media with the addition of TiO\textsubscript{2}, whose particles have a large surface area. In [13] it has noted that TiO\textsubscript{2} can effectively oxidize PAHs, for example, anthracene, fluorene, and naphthalene, when irradiated with artificial light or sunlight. Also in the study [14], it has proved that pyrene photodegrades in the presence of TiO\textsubscript{2} with the formation of some intermediate reaction products. These products are not as dangerous as PAHs and ultimately pyrene can completely mineralize to H\textsubscript{2}O and CO\textsubscript{2}.

Previously, the authors of [15] have proved the efficiency of the method of luminescent analysis of solutions for the determination of PAHs. This method is highly sensitive, reliable and does not require
long sample preparation. Luminescence analysis allows us to assess the degree of photodegradation of substances from the PAH group in aqueous media. Then, based on the obtained results, it is possible to draw conclusions about the effectiveness of the use of various photocatalytic additives.

However, when analyzing the necessary condition is sufficient optical transparency of the test samples. This condition often cannot be met due to the peculiarities of the analyzed media [15]. For example, during the study of the process of photodegradation of PAHs on PhC in aqueous media, the optical transparency can significantly decrease. This process occurs due to the formation of a suspension of solid particles from the PhC samples in the volume of the PAH solution. The error of the luminescence analysis increases significantly with a decrease in the optical transparency of the studied solutions. For solving this problem in practice, a method of evaluating the efficiency of photocatalytic additives is required. At the same time, sufficient optical transparency of the studied samples must be maintained.

One of the ways to solve these problems is to use model surfaces for the study of photocatalytic activity. Such surfaces can be made of various materials. In recent years, the possibilities of using biopolymers as the bases of solid matrices for various practical applications have been actively studied. One of the most prospective biopolymers for formation of model surfaces is chitosan, a product of chitin deacetylation [16]. Chitosan has a high ability for chemical modification, which allows to select different characteristics of the manufactured matrices, depending on the tasks set [17].

In this study, model surfaces were developed from chitosan with the addition of TiO$_2$ (Figure 2). They have a similar character of the surface distribution of the photocatalyst particles, but at the same time the optical transparency remains high. In this case, the chitosan-TiO$_2$ matrices are model surfaces for studying the photocatalytic oxidation of PAHs in the presence of TiO$_2$.

3. Materials and methods

Chitosan (Diam LLC, 95% deacetylation degree) was used for the manufacture of model surfaces. A solution of chitosan at a concentration of 25 g/l was prepared in a 2% solution of acetic acid. TiO$_2$ particles (Puriss. spec., Promchim, Russia) were added to the resulting solution in three different concentrations, which calculation is given below. The solution was poured into Petri dishes and dried at room temperature for 72 hours. After drying, the chitosan-based films were kept in a 5% KOH aqueous solution to convert the biopolymer to the hydrophobic form. Then the samples were washed in distilled water pH = 7 and dried at a temperature $t=20^\circ$C and a relative humidity $\varphi=60\%$ for further studies.

Figure 2. Chitosan-TiO$_2$ matrix.  
Figure 3. Sample of PhC concrete with TiO$_2$ additive.
To study the effect of the TiO$_2$ additive on the photocatalytic degradation of anthracene, samples were made of fine-grained concrete with dimensions of 20 x 20 x 20 mm (Figure 3). The samples were solidified at a temperature of 20±2 °C and a relative humidity of 90-95 %. As a binder, Portland cement "Eurocem 500 Plus", CEM I 42.5 H produced by LLC "Peterburgcement" was used. The sand was used with a fineness modulus of 2.0-2.5 according to Russian GOST 8736-2014.

The concrete composition was calculated according to Russian GOST 26633-2015 using the Recommendations for the Selection of Heavy and Fine-grained Concrete Compositions (Russian GOST 27006-86). For the production of the mixture, components were used in the following ratios: cement/sand = 1/3, water/cement = 1/2. The content of the TiO$_2$ additive in the mixture was 0.5, 2 and 5% respectively by weight of the cement.

TiO$_2$ particles were investigated under the ZEISS SteREO Discovery V20 optical microscope (Figure 4). The particle size was determined (ImageJ program) and a histogram of the size distribution was constructed (Figure 5). As can be seen from Figure 5, the average diameter of the microparticles is 21 ± 4 μm.

![Figure 4. TiO$_2$ particles under the microscope.](image)

![Figure 5. Histogram of the size distribution of TiO$_2$ microparticles.](image)
For creating the same experimental conditions, the amount of TiO$_2$ was recalculated by the area of the particles irradiated with UV, for further addition of the photocatalyst to the model surfaces. In the approximation of the same size and spherical shape of all particles, it was calculated from the value of the average diameter at a concentration of 0.5 wt. cement % on one face of a cube measuring 20×20 mm, the mass of TiO$_2$ is $m_{\text{ave}}=1.46\times10^{-5}$ g. Then the mass per 1 cm$^2$ of the surface area of the concrete sample is equal to $m_{\text{rel}}=3.65\times10^{-6}$ g cm$^{-2}$. In this case, the mass of TiO$_2$ is $m_{0.5\%}=7.31\times10^{-6}$ g in recalculation of the area of the matrix sample of chitosan with dimensions of 20×20 mm. Similarly, the TiO$_2$ masses are respectively 2 and 5 wt. cement % were calculated, which were $m_{2\%}=29.22\times10^{-6}$ g and $m_{5\%}=73.06\times10^{-6}$ g.

Anthracene was used as a model PAH. Anthracene has an electron-vibrational structure of the fluorescence spectra, which is characterized by four well-resolved main vibronic bands [18]. This representative of PAHs does not have a high toxicity, which makes its use in laboratory studies relatively safe [2].

Anthracene solutions (Fluka, Germany) were prepared in a 20% dimethylsulfoxide (DMSO) solution. The concentration of anthracene in the prepared solutions was $10^{-5}$ M. Distilled water pH=7 was used. The pH value was monitored on a pH meter (F20-Standard, Mettler Toledo, USA).

For the research, previously made samples of PhC and samples of solid matrices made of chitosan with a size of 20×20 mm were used. All samples were kept in anthracene solutions from 15 to 60 minutes at a temperature of $t=20^\circ$C under the influence of UV radiation (Camerion lamp 26 W, 365-395 nm). At intervals of 15 minutes, the luminescent analysis of anthracene solutions was performed on the HORIBA Fluorolog-3 TCSPC modular system. The error of the measured parameters consisted of the error of the emission monochromator and the error of measuring the luminescence intensity. The manufacturer HORIBA indicated the value of the error of the monochromator radiation of 0.5 nm [19].

4. Results and discussion
In the course of studying the processes of photocatalytic decomposition of anthracene on PhC, it was found out that the optical transparency was significantly decreased when PhC samples were kept in anthracene solutions. This can be explained by the contamination of the studied solutions with concrete particles. This fact negatively affects the quality and accuracy of the results of the luminescent analysis of solutions. The obtained luminescence spectra were indistinct and with a low luminescence intensity due to light scattering on concrete particles in the solutions. Also, a decrease in optical transparency negatively affects the reproducibility of the experiment results.

In the present study, solid matrices made of chitosan with the addition of TiO$_2$ were used as model surfaces to solve this problem. The main advantage of the manufactured matrices is that their use does not reduce the optical transparency of the anthracene solutions under study. Also, these matrices are easy to manufacture and convenient to use for research.

In the experiment, luminescence spectra were obtained (Figure 6) of anthracene solutions ($\lambda_{\text{ex}}=340$ nm) after keeping in them chitosan-TiO$_2$ matrices under UV ($t=60$ min) and control samples without TiO$_2$.

According to the results of the luminescence analysis, it can be concluded that the luminescence intensity of anthracene solutions after holding chitosan-TiO$_2$ matrices in them under UV irradiation decreases by 63% compared to the intensity after holding the control matrices under UV irradiation. Thus, it can be concluded that TiO$_2$ accelerates the photodegradation of anthracene. The graphs also show that the efficiency of using chitosan-TiO$_2$ matrices for PAH oxidation depends on the amount of photocatalyst added. The highest degree of photodegradation of PAH at $t=60$ min under UV irradiation is observed in solutions in samples with a content of TiO$_2$ $m_{5\%}=73.06\times10^{-6}$ g.
Figure 6. Luminescence spectra of anthracene solutions: A - $m_{5\%} = 73.06 \times 10^{-6}$ g; B - $m_{2\%} = 29.22 \times 10^{-6}$ g; C - $m_{0.5\%} = 7.31 \times 10^{-6}$ g; D - control sample without TiO$_2$.

To evaluate the efficiency of anthracene oxidation in the process of photocatalytic reactions on chitosan-TiO$_2$ matrices, depending on the mass of TiO$_2$, photodegradation graphs were plotted (Figure 7). The graphs show the ratio of the luminescence intensity $I_t$ of anthracene solutions after exposure of chitosan-TiO$_2$ matrices under UV irradiation time $t$ to the initial luminescence intensity of anthracene solutions $I_0$ before UV irradiation ($t_0=0$ min). The graphs show that the efficiency of photodegradation of anthracene in solutions after keeping the chitosan-TiO$_2$ matrices ($m_{5\%} = 73.06 \times 10^{-6}$ g) reaches 74% and only 15% for the control sample without adding TiO$_2$ after $t=60$ min under UV irradiation.

Figure 7. Graphs of degradation of anthracene anthracene solutions after aging of chitosan-TiO2 matrices: A - $m_{5\%} = 73.06 \times 10^{-6}$ g; B - $m_{2\%} = 29.22 \times 10^{-6}$ g; C - $m_{0.5\%} = 7.31 \times 10^{-6}$ g; D - control sample without TiO$_2$. 

In general, the results of kinetic studies confirm that the TiO$_2$ photocatalyst is effective for the decomposition of anthracene. The values obtained as a result of the experiment are comparable with the data of other authors. For example, in [20], the photodegradation of anthracene was investigated under various experimental conditions with an initial concentration of $C_{\text{anthracene}}=1\times10^{-6}$ M. The authors obtained the values of the photodegradation efficiency of anthracene of 60% after 60 minutes under UV irradiation.

In addition to studying the photocatalytic properties of TiO$_2$ on chitosan-TiO$_2$ matrices, the luminescence spectra of anthracene solutions after exposure PhC under UV irradiation were previously studied. Despite the low clarity of the obtained spectra, the change in the luminescence intensity depending on the amount of TiO$_2$ added in PhC is comparable to the change in the luminescence intensity of anthracene solutions after exposure chitosan matrices with a similar amount of TiO$_2$ in them. This confirms the feasibility of using chitosan-TiO$_2$ matrices as model surfaces for studying the photocatalytic properties of TiO$_2$ for anthracene oxidation.

5. Conclusion
A series of experiments demonstrates the efficiency of the decomposition of anthracene in solutions under UV irradiation due to the photocatalytic properties of TiO$_2$. Up to 74% of anthracene was oxidized in 60 minutes under UV irradiation with chitosan-TiO$_2$ matrices ($m_{TiO_2}=73.06\times10^{-6}$ g). Thus, the developed model surfaces of chitosan-TiO$_2$ can be used in luminescence analysis to study the photocatalytic properties of TiO$_2$ used as an additive for concrete. The developed matrices do not decrease the optical transparency of solutions, which makes it possible to carry out fast and accurate studies of photocatalytic additives.

The photocatalytic properties of the PhC samples were also studied and similar values of the photodegradation efficiency of anthracene in solutions were obtained. Based on the results of the experiments, it can be concluded that the photocatalyst significantly accelerates the process of oxidation of PAHs on the surface of the PhC. After that, the relatively harmless products of the photocatalytic reaction are released into the environment without causing harmful effects. In general, the obtained results prove the feasibility of using TiO$_2$ as an additive in PhC for the oxidation of PAHs.

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