INFLUENCE OF YTTRIUM AND NIOBIUM OXIDES MODIFIERS ON PHYSICOCHEMICAL AND PHOTOCATALYTIC PROPERTIES OF TITANIUM (IV) OXIDE

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1. Introduction

The high level of negative impact on the aquatic environment, which is widely contaminated with organic pollutants, causes considerable interest in finding new methods and materials for their removal. Promising materials include the titanium (IV) oxide (TiO₂) photocatalyst, which has already shown good efficiency in the destruction of toxic organic compounds in water treatment processes [1]. Its prospects are due to such advantages as high chemical stability, commercial availability, low cost, and high photocatalytic activity [2]. In addition, its usage in environmental heterogeneous photocatalysis is promising due to the short process duration, the absence of additional use of chemical reagents, and the possibility of their repeated use. However, TiO₂ has certain disadvantages, namely the low quantum efficiency of the process due to weak separation of the electron-hole pair and the limited absorption spectrum in the ultraviolet region [3].

To increase the TiO₂ quantum efficiency and, as a consequence, photocatalytic activity, different approaches are used: doping, modification, and creation of nanocomposites [4]. It is very promising to modify titanium (IV) oxide by transition metals ions [5]. Nanoparticles of metals, non-metals, and transition metal oxides, including rare-earth metal oxides, are used as modifiers [6]. At the same time, the latter has received more attention due to less research and the fact that titanium (IV) oxide modified by rare-earth metals has a high efficiency [7]. In this work, rare (Nb) and rare-earth (Y) elements were selected as modifiers, which also contribute to the near-UV light absorption [8].

Thus, the study of the effect of modifiers from among rare and rare-earth elements on the photocatalytic activity of semiconductor materials is highly relevant, the results of which will increase the efficiency of photocatalytic extraction of organic pollutants from water bodies of different origins.

2. Literature review and problem statement

It has been shown that traditional methods for the extraction of organic substances such as adsorption [9] and coagulation [10] can significantly reduce their content in water. However, these methods are not effective at low pollutant concentrations. In [11], it was found that magnetically controlled sorbents are more promising in this sense, showing a high adsorption capacity in relation to organ-
ic pollutants, particularly dyes. However, heterogeneous photocatalysis [12] is the most promising and rational for extracting organic pollutants at low concentrations, i.e., advanced treatment. This is due to the high efficiency of the photocatalytic process and the ability to oxidize organic matter to CO\(_2\) and H\(_2\)O. This fact is confirmed in the study of discoloration of colored waters, where the methylene blue extraction degree is more than 90 % at a pollutant concentration of 10 mg/l [13]. This is especially confirmed during the removal of antibiotics [14], where heterogeneous photocatalysis had the best result compared to biological purification and adsorption by several parameters simultaneously.

An unresolved issue is a method of using heterogeneous catalysts, which also significantly affects the photocatalytic process efficiency as a whole [15]. Using them in the powder form is the most effective [16]. However, there is a problem of their removal after the photocatalytic process. The use of photocatalysts in the form of granules [17] or electrodes [18] eliminates these disadvantages, but the efficiency of the photocatalytic process is lower.

The paper [19] shows that nanosized titanium (IV) oxide particles (<50 nm) have high photocatalytic activity, which necessitates TiO\(_2\) production with particle sizes at the nanoscale. The photocatalytic activity in nanoparticles is primarily achieved by reducing recombination and increasing the active surface area of the oxide. And due to the variation of phase composition and crystal size [20].

The most used methods for obtaining TiO\(_2\) nanoparticles are hydrothermal and sol-gel methods [21]. Their application allows controlling both the size of TiO\(_2\) particles at the nanoscale and their morphology [22]. Among these two methods, the hydrothermal synthesis method is probably more promising due to the possibility of obtaining monodisperse titanium (IV) oxide particles. This method is also promising for modifying the TiO\(_2\) photocatalyst.

The results of research [23] on the effect of modifiers on the photocatalytic activity, particularly TiO\(_2\), indicate a significant interest of scientists in rare-earth elements (REE). This is associated with experimental results after modification of titanium (IV) oxide by REE. It has been shown that the acetone extraction from the air by lanthanum, yttrium, and cerium-modified TiO\(_2\) was much more efficient than by non-modified titanium (IV) oxide [24]. The best results on the phenol degradation from aqueous solutions with cerium-modified titanium (IV) oxide were also obtained [25]. In addition, when using rare-earth element-modified TiO\(_2\), results on the improvement of the photocatalytic process in the visible light region were obtained [26]. Significant progress in this sense has been made using TiO\(_2\) nanotubes modified with such REE as Ho, Er, Nd, Y, Ce, Tm [27]. The authors in [28] achieved high phenol and toluene decomposition efficiency even by irradiating a low-power light source, such as LEDs with \(\lambda=465\) nm. Similar results were obtained using REE-modified TiO\(_2\) nanocrystals.

Analysis of the results on the degradation of organic dyes with REE-modified titanium (IV) oxide, obtained by other scientists, indicates the relevance of research in this area. In [29], the authors achieved almost complete degradation of the organic dye using the TiO\(_2\) photocatalyst modified by elements such as Ce, Eu, La, Nb, W, Y. In [30], almost complete degradation of an organic pollutant under visible light using erbium and ytterbium-modified TiO\(_2\) was obtained. A critical review of recent achievements in modifying TiO\(_2\) nanotubes for dye degradation indicates a significant increase in photocatalytic activity against dyes by modifying with REE [31]. In addition, the initiated studies on the REE modification of the zinc (II) oxide photocatalyst also indicate an increase in its photocatalytic efficiency, which is manifested by an increase in the degradation degree of methylene blue by almost 1.5 times [32]. Thus, most studies have confirmed that surface modification by rare-earth metals increases the efficiency of photocatalysts, in particular TiO\(_2\) [33].

However, the issues related to the REE choice for modification remain unresolved. An option to overcome these difficulties may be to focus on essential criteria: improving the photocatalytic process, photocatalyst efficiency, and availability. Some scientists claim that in terms of improving the photocatalytic process as a whole, almost all REEs increase the dye degradation efficiency due to the appearance of luminescent properties [34]. The appearance of luminescent properties and, as a consequence, an increase in the TiO\(_2\) photoactivity (efficiency) after modification by yttrium, erbium, and ytterbium are confirmed in [35]. These properties are associated with the appearance of a significant shift to the visible region through modifications by REE, for example, europium [36] or praseodymium [37]. This approach was used in [38], where the titanium (IV) oxide modification by europium resulted in a significant improvement in photocatalytic activity (degradation occurs under sunlight in natural conditions). Other researchers [39] found an increase in the dye degradation rate (at least 3 times) during the photocatalytic process of erbium-modified titanium (IV) oxide.

The above gives grounds to claim that it is advisable to conduct a study on the modification of titanium (IV) oxide by rare-earth elements. However, despite the high popularity of REE as modifiers, the most rational rare-earth element for modification has not been found. Thus, yttrium is selected as the REE modifier as being more available. Concerning niobium, although rare metals have been extensively studied in the literature, the effect of niobium on titanium (IV) oxide photoactivity has not been generally considered.

### 3. The aim and objectives of the study

The study aims to determine the effect of modifiers (oxides of rare-earth elements) on the photocatalytic-sorption and physicochemical properties of commercial and laboratory-synthesized titanium (IV) oxides, which will help increase the TiO\(_2\) photoactivity.

To achieve the aim, the following objectives were set:
- to modify commercial and laboratory-synthesized titanium (IV) oxide samples and characterize them;
- to investigate the structural, surface, and optical properties of modified and non-modified photocatalysts based on TiO\(_2\);
- to determine photocatalytic and sorption properties of modified and non-modified TiO\(_2\)-based photocatalysts to find the effect of modification by yttrium (Y\(_2\)O\(_3\)) and niobium (Nb\(_2\)O\(_5\)) oxides.

### 4. Materials, modification method, and research methods for the obtained TiO\(_2\)-based samples

Chemically pure reagents were used for synthesis and research. Titanium isopropoxide (C\(_{12}\)H\(_{26}\)O\(_3\)Ti, Acros Or-
The synthesis of titanium (IV) oxide was carried out by the hydrothermal method according to the following procedure. Isopropyl alcohol in a volume of 10 ml was added to the Teflon reactor, to which nitric acid was added dropwise to pH 1.5. Then 5 ml of titanium (IV) isopropoxide solution was added and stirred for 5 minutes. The solution obtained had a pH of 2–3. The Teflon reactor was then placed in an autoclave and subjected to hydrothermal treatment at 453–473 K for 12 hours. The resulting suspension was cooled, washed to pH 5, and centrifuged (5000 rpm, MPW-310 centrifuge, Poland). The washed samples were dried for 12 hours at 353 K and ground.

Modification of titanium (IV) oxide was also performed by the hydrothermal method. For this purpose, the commercial TiO$_2$ P25 and laboratory-synthesized samples were used. 1 g of the corresponding TiO$_2$ 7 ml of isopropyl alcohol with pH 1.5, and the calculated volumes of yttrium and niobium nitrate solutions (concentration 0.05 mol/l) were added to the Teflon reactor. After mixing all the reagents in the Teflon reactor, the resulting solutions had a pH of 2–3. Next, the Teflon reactor was placed in the autoclave for hydrothermal treatment of the suspension at a temperature of 453–473 K for 12 hours. The resulting samples were washed, washed to pH 5, and centrifuged. The washed samples were dried for 12 hours at 353 K and ground in an agate mortar. Thus, the TiO$_2$ sample was synthesized, and yttrium and niobium-modified titanium (IV) oxide samples were obtained based on commercial TiO$_2$ and laboratory-synthesized TiO$_2$ (Table 1). In addition, Table 1 presents a commercial TiO$_2$ sample, which was also investigated in this work for comparison.

Characterization of the modified and non-modified TiO$_2$ samples was performed by X-ray research methods (X-ray phase, X-ray diffraction, and X-ray fluorescence research methods).

The size of the crystallites was determined using Scherrer’s formula. A study of the phase composition of the samples was performed on a Rigaku Ultima IV X-ray diffractometer (Japan) with CuKα radiation (40 kV, 30 mA). The phase composition was calculated automatically using standard cards: No. 00-021-1276 (Rutile), No. 00-021-1272 (Anatase), No. 00-041-1445 (Cassiterite), No. 00-020-1412 (Y$_2$O$_3$), JCPDS card No. 30-0873 (Nb$_2$O$_5$).

The elemental composition of the modified TiO$_2$ samples was investigated using an EXPERT 3L IHAM analyzer (Ukraine).

Structural characteristics were studied by the nitrogen adsorption-desorption isotherms obtained on a Quantachrome® Nova 4200e sorptometer (USA). The mass of adsorbed and desorbed nitrogen of the studied samples was determined by an algorithm built into the device’s software based on the Brunauer-Emmett-Teller (BET) isothermal equations. The porous structure of the samples was determined by the Barrett-Joyner-Halenda (BJH) method.

Optical properties were determined by the band gap. The band gap was determined by absorption spectra (λ from 190 nm to 800 nm) of aqueous suspensions of the studied samples with a concentration of 0.1 g/l, which were obtained on a Specord 210 spectrophotometer (Germany). The obtained optical dependences were converted into Tauc coordinates according to the equation:

\[
(\alpha h\nu)^2 = f(\nu),
\]

where \(\alpha\) – suspension absorption coefficient; \(\nu\) – frequency; \(h\) – Planck constant.

Using the tangent on the constructed graphical dependencies, the optical band gap was determined.

To determine the surface properties, the acidity of the sample surface was measured. To do this, 1 wt. % suspensions were prepared, and their pH was measured for 2 hours using a Portlab 102 pH-meter (Russia). An isionic point characterizing the surface acidity was thus determined.

Photocatalytic properties were evaluated by the discoloration degree of dyes of different nature using UV irradiation of the suspension (368 nm). For this, a particular sample of photocatalyst weighing 0.05 g was added to 50 ml of the corresponding dye solution and mixed in an ultrasonic dispersant (40 kHz, 100 W, ultrasonic bath UZM-004-1, Ukraine). After that, the resulting suspension was stirred for 20 minutes in a magnetic stirrer under UV irradiation, and then the spent photocatalyst was separated from the solution by centrifugation. The dye concentration in the solutions before and after sorption was determined using a UV-5800PC spectrophotometer (Shanghai Metash Instruments, China).

Studies of the sorption properties of the photocatalyst samples were carried out similarly to the determination of photocatalytic properties without UV radiation.

The discoloration degree of the dye solution in both cases was determined by the relative change in the optical density of the dye solutions (methylene blue dye solution was investigated with a wavelength of 664 nm; Congo red solution – 505 nm):

\[
X = \frac{A_0 - A_t}{A_0} \times 100,
\]

where \(A_0\) – optical density of the initial dye solution; \(A_t\) – optical density of the solution after the photocatalytic or sorption process.

The dyes destruction was investigated by the absorption of CO$_2$ gas released during photocatalysis by an alkali solution, followed by its conversion into organic carbon content. The method is described in more detail in the paper [8].

| Sample     | Characterization                                      |
|------------|-------------------------------------------------------|
| P25        | Commercial TiO$_2$ P25 sample                         |
| YP25       | Commercial TiO$_2$ P25, modified by yttrium (III) oxide|
| NbP25      | Commercial TiO$_2$ P25, modified by niobium (V) oxide  |
| TiO$_2$    | Synthesized TiO$_2$                                   |
| YTiO$_2$   | Synthesized TiO$_2$, modified by yttrium (III) oxide   |
| NbTiO$_2$  | Synthesized TiO$_2$, modified by niobium (V) oxide     |


5. Results of characterization and physicochemical properties of the obtained TiO₂-based samples

5.1. Modification and characterization of TiO₂ samples

Four samples of photocatalysts were modified by the hydrothermal method according to the titanium (IV) oxide modification method, which is given in Section 4: YP25, NbP25, YTiO₂ NbTiO₂. Fig. 1 shows the XRD patterns of all the studied samples, which were automatically analyzed with PDXL software using the built-in ICDD/PDF-2 and COD databases. The XRD patterns of the modified samples almost do not differ from those of the individual TiO₂ phases. This is due to the low content of yttrium and niobium oxides (Table 2), which is confirmed by elemental analysis (Table 3).

The elemental analysis of the studied samples confirms the low content of rare-earth metal oxides (Table 3).

Table 3

| Element | YP25 | YTiO₂ | NbP25 | NbTiO₂ |
|---------|------|-------|-------|--------|
| Ti      | 96   | 97.1  | 96.8  | 97.4   |
| Y       | 4    | 2.9   | –     | –      |
| Nb      | –    | –     | 3.2   | 2.6    |

According to Table 3, the content of yttrium and niobium is at the level of 2.6–4 wt. %. This data almost coincides in terms of oxides with the content automatically determined by the built-in program in the diffractometer software.

5.2. Structural, optical, and surface properties of modified and non-modified TiO₂ samples

The results of structural characteristics (specific surface area and average pore radius), determined by the Brunauer-Emmett-Teller equation and the Barrett-Joyner-Halenda method, are presented in Table 4.

Table 4

| Sample | S, m²/g | Average pore diameter, nm | Band gap |
|--------|---------|---------------------------|----------|
| P25    | 61      | –                         | 3.25     |
| YP25   | 70      | 3.1                       | 3.2      |
| NbP25  | 66      | 3.8                       | 3.3      |
| TiO₂   | 172     | 3.8                       | 3.4      |
| YTiO₂  | 184     | 3.5                       | 3.2      |
| NbTiO₂ | 181     | 3.6                       | 3.15     |

The results of structural characteristics (specific surface area and average pore radius), determined by the Brunauer-Emmett-Teller equation and the Barrett-Joyner-Halenda method, are presented in Table 4.

Analysis of the obtained experimental data on the porous structure of the modified samples (Table 4) indicates that the obtained samples differ slightly from the individual titanium (IV) oxide phase in structural and porous properties. A similar relationship is also observed for optical characteristics (Fig. 2). The optical band gap determined by converting the optical absorption spectra in the Tauc equation (for direct electronic transitions) indicates slight changes in the band gap. For the modified commercial TiO₂ P25 sample, the band gap varies from 3.2 eV to 3.3 eV, and for the laboratory synthesized TiO₂ – in the range of 3.15–3.4 eV (Table 4).

Table 5 presents the results of studying the surface properties, namely the surface acidity of modified and non-modified samples.

Table 5

| Sample | Isoionic point |
|--------|----------------|
| P25    | 4.15           |
| TiO₂   | 5.78           |
| YP25   | 4.38           |
| YTiO₂  | 5.80           |
| NbP25  | 3.38           |
| NbTiO₂ | 3.55           |

Table 2, in addition to the phase composition, shows the crystallite size of the obtained modified and non-modified samples. X-ray diffraction analysis revealed that the values of the crystallite sizes practically do not change and are in the range of 4–13 nm.

Table 2

| Sample | Phase   | Crystallite size, nm | Content, % |
|--------|---------|----------------------|------------|
| P25    | Anatase | 4.4                  | 92         |
|        | Rutile  | 4.0                  | 8          |
| YP25   | Anatase | 4.5                  | 89.1       |
|        | Rutile  | 4.3                  | 10.0       |
|        | Y₂O₃   | 7.5                  | 0.9        |
| NbP25  | Anatase | 16.5                 | 89.6       |
|        | Rutile  | 22.5                 | 10         |
|        | Nb₂O₃  | 13.1                 | 0.4        |
| TiO₂   | Anatase | 7.1                  | 100        |
| YTiO₂  | Anatase | 7.4                  | 99.3       |
|        | Y₂O₃   | 7.2                  | 0.7        |
| NbTiO₂ | Anatase | 6.7                  | 99.7       |
|        | Nb₂O₃  | 4.4                  | 0.3        |

Fig. 1. Diffraction patterns of TiO₂-based samples
The results in Table 5 show that, in general, modification by yttrium (III) oxide slightly increases the acidity, and by niobium (V) oxide significantly reduces it.

5.3. Photocatalytic and sorption properties of modified and non-modified TiO$_2$ samples

Fig. 3 shows data of photocatalytic and adsorption studies. As shown from Fig. 3, modification of the commercial sample increases the photocatalytic properties with respect to both methylene blue and Congo red. A slightly different pattern is observed for the adsorption properties of TiO$_2$ samples, where the sorption activity for MB decreases, and for CR increases. The destruction results indicate oxidation processes that agree with the data obtained in the photocatalysis and adsorption processes.

6. Discussion of physicochemical and photocatalytic properties of titanium (IV) oxide samples modified by yttrium and niobium oxides

Modification of titanium (IV) oxide samples by yttrium and niobium oxides was performed by the hydrothermal method. The method used to modify titanium (IV) oxide powders is characterized by mild process conditions, unlike the commonly used heat treatment. During hydrothermal treatment, yttrium and niobium salts are first sorbed on the titanium (IV) oxide surface, then the decomposition of the corresponding salts takes place, resulting in yttrium and niobium oxides. Thus, yttrium and niobium oxides are deposited on the titanium (IV) oxide particles' surface.
Only individual phases for titanium (IV) oxide are found in the given XRD patterns of all the studied samples (Fig. 1). However, automatic analysis of the phase composition results of the modified TiO$_2$ samples indicates the production of the Y$_2$O$_3$ phase in the modification by yttrium nitrate and Nb$_2$O$_5$ in the modification by niobium nitrate (Table 2). Table 3 presents the yttrium and niobium content by X-ray fluorescence analysis. In terms of oxides for commercial and synthesized samples, it is 0.9 wt. % and 0.7 wt. % for Y$_2$O$_3$; 0.4 wt. % and 0.3 wt. % for Nb$_2$O$_5$, respectively. The obtained data are in good agreement with the phase composition results. The slightly lower oxides content compared to the theoretically planned one (1 wt. %) is associated with losses during hydrothermal synthesis of modified TiO$_2$-based samples. The size of crystallites practically does not change during the modification process (Table 2) and is explained by the mild conditions of the hydrothermal synthesis method.

Some structural, optical, and surface properties also undergo minor changes. This fact can be explained by the low modifier content and mild synthesis conditions. Due to the modification of the commercial TiO$_2$ P25 sample, the non-porous powder is transformed into a mesoporous one due to the slight particle coalescence during modification. At the same time, the specific surface area (S) increases from 61 m$^2$/g to 70 m$^2$/g. A similar increase in S (from 172 m$^2$/g to 180 m$^2$/g) is observed in the modification of the laboratory-synthesized TiO$_2$ due to the particles’ soft coalescence.

The optical band gap does not change in the modification of the commercial TiO$_2$ P25 sample, but for the laboratory-synthesized sample, it decreases from 3.4 eV to 3.15–3.25 eV. The effect of modifiers on surface properties (surface acidity) is more ambiguous. In the modification by yttrium oxide, the TiO$_2$ acidity decreases, and by niobium oxide – increases. The obtained regularities testify to the provision of alkaline properties in TiO$_2$ modification by yttrium oxide and acid properties in TiO$_2$ modification by niobium oxide.

Analysis of photocatalytic properties leads to the conclusion that in all cases, modification helps to increase the photocatalytic properties from 1.3 to 2 times. The effect of modifiers on the photocactivity of commercial and laboratory-synthesized titanium (IV) oxide samples is different. In the case of the commercial TiO$_2$ P25 sample, modification by yttrium leads to an increase in photocactivity against MB, niobium – against CR. This is due to the change in the acidity of the modified samples compared to the individual phase of titanium (IV) oxide and, consequently, the change in the electrostatic interaction of photocatalysts with cationic and anionic dyes.

A slightly different situation is observed for modified samples based on the laboratory-synthesized TiO$_2$, which can be explained by the greater influence of structural characteristics on the interaction with dyes of different nature. The results of the sorption interaction indicate a better interaction of all the studied photocatalysts with the anionic dye CR than with cationic MB, which is consistent with the surface acidity of the modified and non-modified samples.

The obtained data on destruction (determined by the released CO$_2$) indicate the possibility of oxidation to complete “mineralization”. The destruction of dyes is well consistent with photocatalytic and sorption experiments. However, despite the generally positive results obtained for the photocatalytic removal of dyes by modified photocatalysts, their usage still does not allow to completely “mineralize” dyes. This may be due to the low power of UV radiation during the photocatalytic process. More detailed research for determining the rational amount of modifier, type of modifier, type of precursor, and modification method will increase the percentage of “mineralization”.

7. Conclusions

1. Modification and characterization of commercial P25 and laboratory-synthesized titanium (IV) oxide samples were carried out. Rare-earth and rare elements are chosen as modifiers, namely in the form of yttrium and niobium oxides. Diffraction and X-ray fluorescence analysis methods showed that the Y$_2$O$_3$ and Nb$_2$O$_5$ phases were obtained at the level of 0.7–0.9 wt. %, and 0.3–0.4 wt. %, entirely consistent with each other.

2. The structural, surface, and optical properties of modified and non-modified photocatalysts based on TiO$_2$ have been determined. A slight increase in the specific surface area is shown (from 61 m$^2$/g to 70 m$^2$/g for the commercial sample and from 172 m$^2$/g to 180 m$^2$/g for the laboratory-synthesized one) due to the modification by yttrium and niobium oxides. The optical band gap was determined, which changes slightly for the commercial sample in the range of 3.2–3.3 eV and the laboratory-synthesized TiO$_2$ in the range of 3.15–3.4 eV due to modification. The surface properties (in terms of surface acidity) of modified and non-modified photocatalysts have been determined: in the modification by yttrium oxide, the TiO$_2$ acidity decreases, and in the case of niobium oxide, increases.

3. Studies of photocatalytic activity against dyes of various nature indicate its growth after modification by yttrium (Y$_2$O$_3$) and niobium (Nb$_2$O$_5$) oxides up to 2 times. The sorption capacity of the modified TiO$_2$ samples with respect to the cationic dye decreases, to the anionic one, increases. The destruction of the dye was found to take place, which is consistent with the photocatalytic and sorption properties. The obtained data indicate the prospects of modifying the titanium (IV) oxide photocatalyst by rare and rare-earth elements.

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