SYNTHESIS OF TIO_2 BY SOLVOTHERMAL METHOD AND ITS PHOTOCATALYTIC ACTIVITY TOWARDS BISEPTOL AND CONGO RED

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The creation of ceramic membranes with additional functional properties, such as antibacterial and photocatalytic, is a popular and promising area of research in the field of water treatment. The article is devoted to the synthesis of titanium (IV) oxide powders by the solvothermal method for their further usage as a photocatalytic selective layer in ceramic membranes. The study of the peculiarities of the photocatalytic materials synthesis for the creation of photocatalytic and at the same time antimicrobial ceramic membranes on their basis is extremely relevant, because it will allow to develop a method of synthesis of photocatalysts active to various pollutants. Therefore, the aim of the work was the synthesis of TiO_2 powders by solvothermal method at different ratios of the starting reagents, the study of their physicochemical properties and the study of their photocatalytic properties in relation to different pollutant – antibiotics and dyes. The obtained powders were characterized by diffraction analysis, infrared spectroscopy, low-temperature nitrogen adsorption-desorption and scanning electron microscopy. It is established that the ratio of the initial components significantly affects the final properties and characteristics of TiO_2 powders. It was shown that the synthesis with a significant excess of the starting reagent (titanium isopropoxide) does not lead to the crystalline TiO_2 sample, which was confirmed by diffraction analysis and infrared spectroscopy. The revealed porous structure of all TiO_2 samples indicates a high specific surface area in them, which is also consistent with scanning electron microscopy studies. The highest photocatalytic activity is possessed by TiO_2 samples, which are nanocomposites of anatase and rutile modifications. Such nanocomposites showed quite high activity towards antibiotics (Biseptol) and anionic dyes (Congo red).

Keywords: *antibiotics, dyes, ceramic membranes, photocatalytic properties, solvothermal synthesis, titanium (IV) oxide*

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1. Introduction

Availability of clean water for daily consumption is one of the most important global problems of all countries. The most common and economical methods of water purification are baromembrane processes. Due to their versatility, they are highly efficient and competitive for filtering / separation / concentration of different pollutants from water of varying degrees of contamination. Usually, both polymeric and ceramic membranes are used to implement these processes (Serhiienko, 2020). Among the latter, ceramic membranes are of particular interest. At high temperatures, ceramic membranes are more stable in operation compared to polymeric membranes, which allows effective sterilization of technological equipment. In addition, they are usually quite resistant to microbial and biologically aggressive environment, which is a problem for organic membranes. Ceramic membranes are also more mechanically stable at high pressures. One of the main disadvantages of ceramic membranes is the high cost. However, the longer lifetime and reduced replacement costs of ceramic membranes compensate for this disadvantage to some extent (Erdem, 2017). In addition, modification of ceramic membranes can significantly change the properties of ceramic matrices.

Nanostructured materials based on TiO_2 as modifiers of ceramic membranes are of particular interest and have a wide range of practical applications in various fields of science and technology. It should be noted that titanium (IV) oxide has been used as a white pigment since ancient times, so TiO_2 is safe for humans and the environment (Hashimoto, 2005).

The bactericidal effect of nanoscale TiO_2 against various types of pathogenic bacteria has also been well studied (López de Dicastillo, 2020). TiO_2 is one of the widely used photocatalytic materials, which has high stability and low cost and is suitable for industrial use. In work (Lim, 2016), the photocatalytic properties of ceramic membranes were studied, which, due to their high permeability, good thermal, mechanical, chemical and biological stability, UV resistance and durability, are successfully used in hybrid photocatalytic membrane reactors. Improvement of the technical characteristics of ceramic membranes can also be carried out by adding TiO_2 directly to the membrane in the process of forming its matrix or by applying a selective top layer to the ceramic matrix. An example of adding TiO_2 as an active modifying component to the matrix is the production of ceramic membranes based on natural kaolinite (Fatimah, 2015). Ceramic membranes with different content of TiO_2 were evaluated for the ability to remove ferric ions, manganese, nitrate (NO^{3-}), suspended solids and reduce the number of bacteria in the reverse filtration process. It was found that the addition of TiO_2 affects the formation of porous structure, and even the filtering capacity of the membrane. The analysis of the membrane fouling mechanism showed that the distribution of pores in the membrane significantly affects the filtration efficiency, the ceramic membrane with TiO_2 content of 1.5% showed the best results in reducing the content of ferric ions, manganese, nitrates and bacteria in the treated water.

In work (Ajenifuja, 2016), it was shown that a mesoporous ceramic membrane with a matrix of local diatomaceous aluminosilicate materials was modified with Ag/TiO_2 and applied to remove some heavy metals and microbial contaminants from polluted local river wastewater. The prepared membrane has unique functional properties such as high thermal and mechanical strength, chemical stability and high ion exchange capacity. Studies on the filtration of polluted river water have shown a reduction in the concentration of certain cations such as Mg^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+} and K^+. The antimicrobial microfiltration process showed 100% removal of bacteria and 70% removal of fungi in most samples.

A significant improvement in the resolution, membrane activity and selectivity of ceramic membranes is also achieved by applying the top (selective) layer of the ceramic membrane on the matrix. Precipitation of TiO_2 photocatalytic layers on porous ceramic substrate involves different coating technologies: chemical vapor deposition, physical vapor deposition, molecular layer deposition from the vapor phase, immersion coating, spin coating, in situ hydro(solvo)thermal synthesis, spray pyrolysis, electrochemical deposition, etc (Song, 2016).

The synthesis of the selective layer can be carried out by various methods that provide the formation of nanostructured particles: sol-gel method, chemical deposition method, atomic layer deposition, anodic oxidation, hydrothermal method, CVD method, etc. In order to obtain an active layer of the membrane with the desired characteristics, the researchers propose to control various parameters: the method of application, the nature of the precursors, the pH of the medium, the temperature of heat treatment.

The hydrothermal method allows the synthesis of nanostructured TiO_2 particles and is one of the simplest methods for the synthesis of nanoparticles of the active layer of membranes (Zhang, 2017). The authors show the efficiency of a ceramic membrane with an active layer in the form of TiO_2 nanorods on Al_2O_3 substrate in the process of photodegradation of Methylene Blue (MB). The TiO_2 nanorods were synthesized by a two-stage hydrothermal method with varying the concentration of anions (Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and temperature in the reaction medium. It was found that the addition of anions with small radius (Cl^-, Br^-) to the reaction medium promotes the formation of TiO_2 nanorods, the addition of ions of larger radius (SO_4^{2-}, PO_4^{3-}) leads to the formation of TiO_2 nanospheres. The authors showed a 1.9–2.2 times higher photoactivity of TiO_2 nanorods compared to TiO_2 nanospheres in MB photodegradation process.

Thus, the preparation of a selective layer based on titanium (IV) oxide is widely used due to the special properties of TiO_2 and remains an urgent task. Sol-gel and hydro(solvo)thermal methods are the most attractive due to their simplicity and versatility. They allow to control the chemical and phase composition of different morphology of nanoparticles obtained at low temperatures.

The aim of this study was to obtain TiO_2 powders by solvothermal synthesis method at different ratios of the initial components and to investigate their photocatalytic properties towards dyes and antibiotics.

2. Materials and Methods

Reagents of analytical grade were used for the synthesis of titanium (IV) oxide powders: Titanium (IV) isopropoxide 98% (ACROS ORGANICS, China), isopropyl alcohol and ethylene glycol (Ukraine).

The synthesis of TiO_2 samples was carried out as follows. First, isopropyl alcohol and titanium isopropoxide were added to the reactor under stirring in the ratios given in Table 1. Then, with constant stirring, 1 cm^3 of distilled water was added dropwise to the reactor, as a result of which the reaction took place: $Ti\{OCH(CH_3)_2\}_4 + xH_2O \rightarrow TiO_2 \cdot xH_2O\downarrow + 4(CH_3)_2CHOH$.

After stirring for 15 minutes, the suspension was placed in a Teflon reactor and a steel reactor vessel. The reactor was placed in an oven for 12 hours at 170 °C to crystallize TiO_2. The obtained samples were dried at 80 °C for further characterization and study of photocatalytic activity.

Table 1. *Ratio of components in TiO_2 samples*

Sample	Volume of isopropyl alcohol, cm^3	Volume of titanium isopropoxide, cm^3
0.2/TiO_2	5.8	0.2
1/ TiO_2	5	1
2/ TiO_2	4	2
3/ TiO_2	3	3

To characterize TiO_2 samples, diffraction methods of analysis, infrared spectroscopy, low-temperature nitrogen adsorption-desorption method and scanning electron microscopy were used. The phase composition of TiO_2 samples was determined using X-ray diffractometer Rigaku Ultima IV (Japan). Infrared spectra were recorded on Shimadzu IRAffinity-1S FTIR spectrometer (Japan). Nitrogen adsorption-desorption was carried out on porous structure analyzer JWGB Meso 112 (China). Scanning electron microscopy (SEM) was used to determine the morphology of the obtained samples using Tescan VEGA3 SEM microscope (Czech Republic).

The photocatalytic properties of the synthesized samples of titanium (IV) oxide were investigated at different duration of the experiment for two pollutants – dye Congo Red and antibiotic Biseptol. The methodology of photocatalytic studies was the same for these pollutants and was as follows: solutions of the pollutants were prepared with concentration of 10 mg/dm^3; 40 cm^3 of the solution of the corresponding pollutant was transferred to the bubble and 0.03 g sample of TiO_2 was added; then the bubble was placed in an ultrasonic bath and kept for 200 sec; then the bunch was placed under UV radiation (λ = 365 нм) with constant stirring for an appropriate period of time (5 min, 10, 15 min, 20 min) for photodegradation of the pollutants; after the photocatalysis time expired, the suspension was filtered to separate the photocatalyst. Spectrophotometric studies of pollutant solutions before and after photocatalytic treatment were performed using Shimadzu UV/VIS spectrophotometer UV-2600i (Japan).

3. Results and Discussion

3.1. Characterization of TiO_2 samples

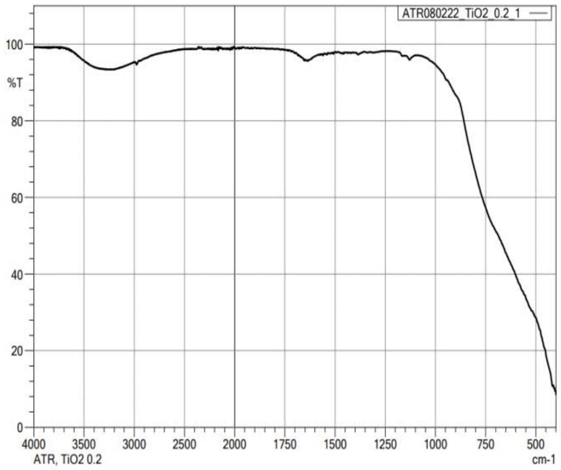
To identify the synthesized samples, User (COD) and ICDD (PDF-2/Release) databases were used and, according to the standard cards No. 9009086 (Anatase) and No. 00-021-1276 (Rutile), the X-ray diffraction patterns were decoded. The results of studies of the phase composition and crystallite size of the obtained samples of titanium (IV) oxide are given in Table 2.

Table 2. *Phase composition and crystallite size of titanium (IV) oxide samples*

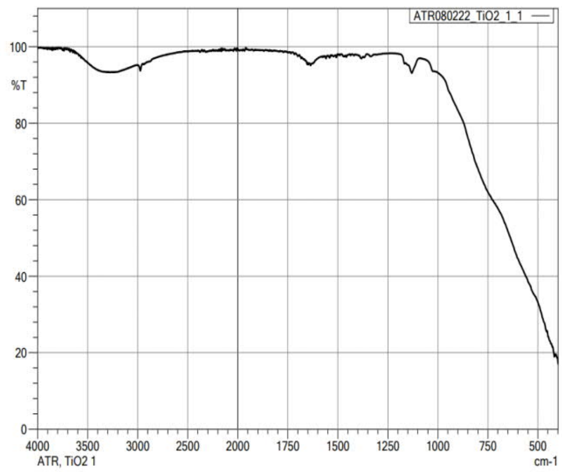
Sample	Phase composition, %	Crystallite size, nm
0.2/TiO_2	93 (A), 7 (R)	4.2 (A), 6.4 (R)
1/TiO_2	100 (A)	4.3 (A)
2/TiO_2	95 (A), 5 (R)	5.3 (A), 7.4 (R)
3/TiO_2	-	-

As can be seen from the results presented in Table 2, pure anatase phase is formed only in the case of 1/TiO_2 sample. In the cases of 0.2/TiO_2 and 2/TiO_2 samples, a mixture of anatase and rutile is formed, where the anatase modification with a small content of rutile (up to 7%) prevails. 3/TiO_2 sample had a corresponding halo on the diffractogram, which indicates its amorphous state. The size of crystallites in all cases is small and is in the range of 4.2–7.4 nm.

Fig. 1 shows the infrared transmission spectra of TiO_2 samples obtained using Fourier transform infrared spectrometer. Fig. 1 shows that in the range 3850–2600 $cm^{-1,}$ a broad intense absorption band is observed, which corresponds to the valence vibrations of ν(OH), indicating the presence of physically adsorbed water in the samples. The amount of water in all TiO_2 samples, except for sample 3/TiO_2, is approximately the same.



a



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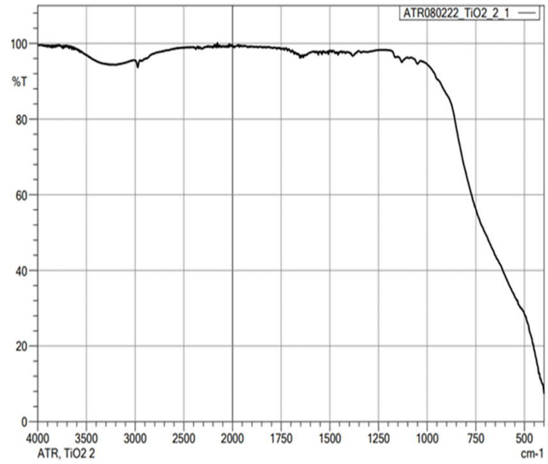

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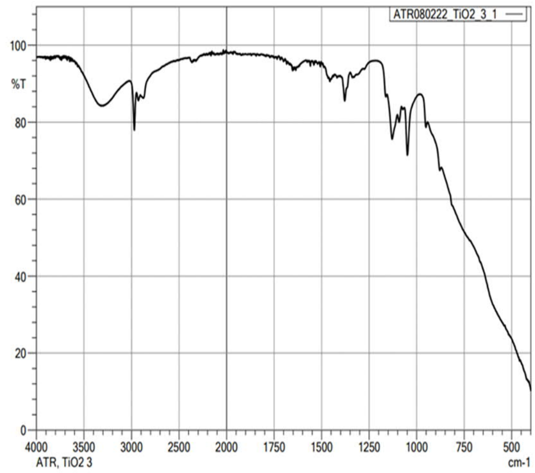


d

Fig. 1. *Spectrum of TiO_2 samples:*
a *– 0.2/TiO_2,* ***b*** *– 1/TiO_2,* ***c*** *– 2/TiO_2,*
d *– 3/TiO_2*

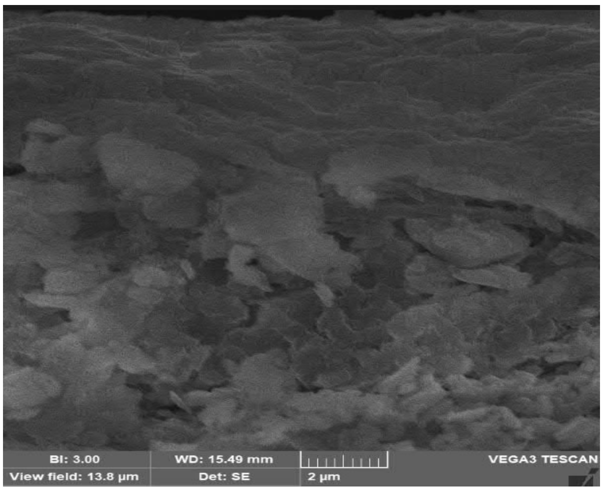
3/TiO_2 sample has a more intense absorption band in the valence vibration region ν(OH) (Fig. 1d), which is consistent with its diffractogram. 3/TiO_2 sample differs not only in this, but also in the presence of a large number of peaks in its spectrum belonging to organic compounds (interval 1250–1000 cm^{-1}). This indicates that with a significant excess of the starting reagent – titanium isopropoxide, crystallization of titanium (IV) oxide is not observed.

Studies of the specific surface area indicate a fairly developed surface in all samples of titanium (IV) oxide (Table 3). The highest value of specific surface area is characteristic of $3/TiO_2$ sample (694 m^2/g) and is explained by the previously obtained data on its amorphous structure. The average pore radius in the samples varies in the range of 3.1–5.5 nm.

Table 3. *Structural characteristics of synthesized TiO_2 samples*

Sample	Specific surface area (BET), m^2/g	Average pore radius (BJH), nm
$0.2/TiO_2$	361	4.5
$1/TiO_2$	409	3.7
$2/TiO_2$	290	5.5
$3/TiO_2$	694	3.1

The morphology of the samples was characterized by scanning electron microscopy. Fig. 2 shows SEM images of $0.2/TiO_2$ sample at different resolutions. Other samples had similar morphology, so their SEM images are not presented. The SEM image of the sample indicates the porous structure of the samples and confirms their high specific surface area.



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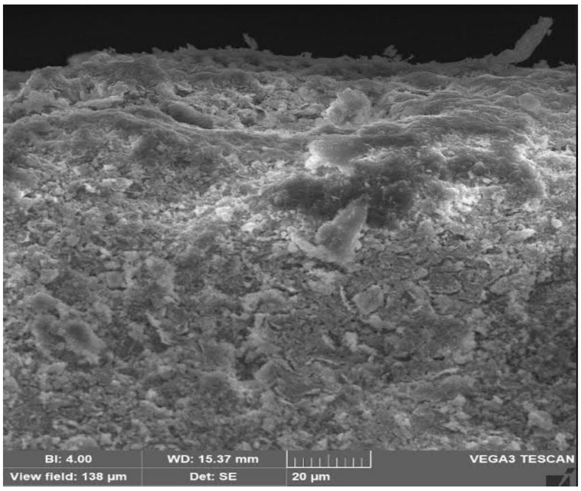

b

***Fig. 2**. SEM image of $0.2/TiO_2$ sample*
a – 2^x2 µm resolutions,
b – 20^x20 µm resolutions

3.2. Photocatalytic activity of TiO_2 samples

The photocatalytic activity of the synthesized TiO_2 samples was studied towards such pollutants as antibiotics (Biseptol) and dyes (anionic dye Congo Red).

Fig. 3 shows the obtained spectra of the initial solution of Biseptol (curve 1) and Biseptol solutions after the photocatalysis process with samples of $0.2/TiO_2$, $1/TiO_2$, $2/TiO_2$, $3/TiO_2$.

As can be seen from Fig. 3, the highest photocatalytic activity is exhibited by $0.2/TiO_2$ and $2/TiO_2$ samples (disappearance of peak in 4 curves in 260 nm region and decrease of peak in 200 nm region, Fig. 3a and c). This is due, in our opinion, to the fact that: 1) these samples are nanocrystalline composites consisting of two phases – Anatase and Rutile, 2) these samples have a slightly larger average pore diameter.

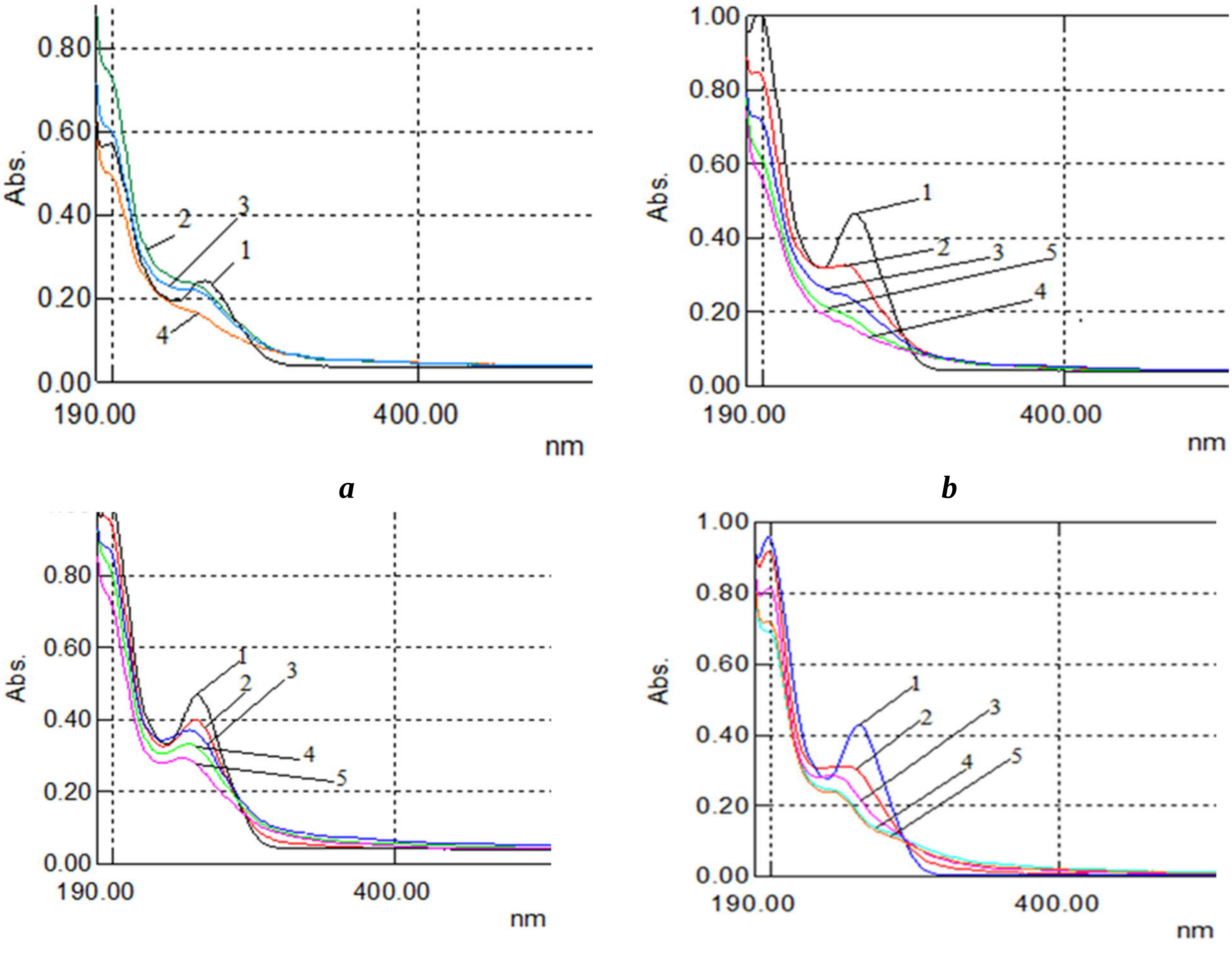

Fig. 3. *Photocatalytic degradation of biseptol solution by TiO_2 samples at different process duration: a – 0.2/TiO_2, b – 1/TiO_2, c – 2/TiO_2, d – 3/TiO_2; 1 – initial Biseptol solution; 2 – Biseptol solution after 5 min of photocatalysis; 3 – after 10 min; 4 – after 15 min*

The decrease in peak intensity in 260 nm region in the case of 1/TiO_2 and 3/TiO_2 samples can be explained by the adsorption processes of pollutants occurring on the developed surface of these samples.

Fig. 4 shows the spectra of dye solutions before and after 5–15 minutes of the photocatalysis process with 0.2/TiO_2, 1/TiO_2, 2/TiO_2, 3/TiO_2 samples.

As in the case of the antibiotic, the highest photocatalytic activity towards Congo Red was shown by 0.2/TiO_2 and 2/TiO_2 samples, which, as shown in Fig. 5, completely decolorize the dye solution in 5 min.

It should be noted that in the case of 1/TiO_2 sample, a gradual decrease in the intensity of all peaks is clearly observed, which also indicates the adsorption interaction of the dye with the surface of this sample. Sample 3/TiO_2 is practically inactive to the anionic dye, which is probably due to the surface chemistry of the sample.

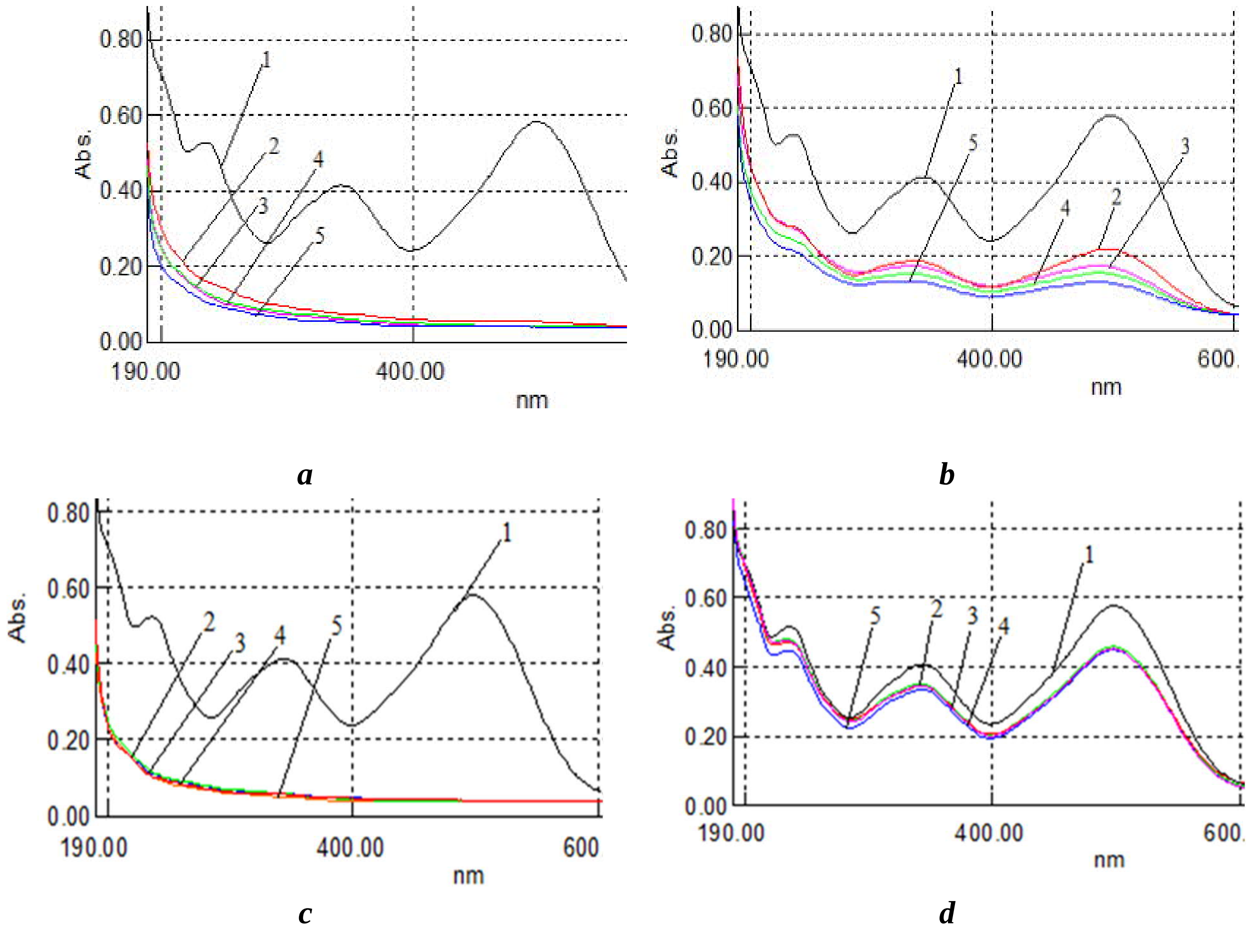

Fig. 4. *Photocatalytic degradation of Congo Red solution by* TiO_2 *samples at different process durations: a – 0.2/*TiO_2*,*
b – 1/TiO_2*, c – 2/*TiO_2*, d – 3/*TiO_2*;*
1 – initial Congo Red solution; 2 – Congo Red solution after 5 min of photocatalysis;
3 – after 10 min; 4 – after 15 min

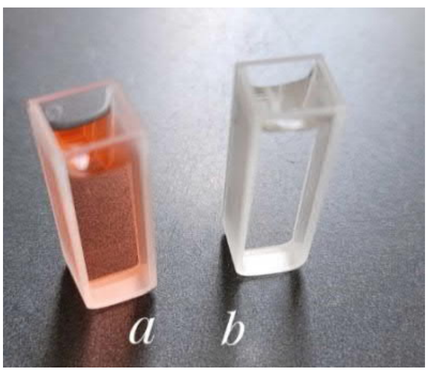

Fig. 5. *Congo Red solution before and after photocatalysis with 0.2/*TiO_2 *sample*
a – before photocatalysis, b – after photocatalysis for 5 min

4. Conclusions

The samples of titanium (IV) oxide at different ratios of the initial reagents were synthesized by the solvothermal method and their photocatalytic properties were studied. Characterization was carried out by diffraction analysis, infrared spectroscopy, low-temperature nitrogen adsorption-desorption method and scanning electron microscopy. It was established that with a significant excess of the starting reagent –

titanium isopropoxide, the crystallization of titanium (IV) oxide is not observed, as evidenced by the halo on the diffractogram and a large number of intense peaks inherent in organic molecules on IR spectrum of this sample. Studies of the porous structure of TiO_2 samples revealed a highly developed surface (290–694 m^2/g) with an average pore radius in the range of 3.1–5.5 nm. The obtained SEM images of the samples confirm their high porosity.

The results of photocatalytic studies have shown that the highest photocatalytic activity towards antibiotics (Biseptol) and anionic dyes (Congo Red) is observed for samples 0.2/TiO_2 and 2/TiO_2, which is explained by the fact that these samples are nanocomposites with a slightly larger average pore diameter compared to other samples.

Acknowledgments

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References

1. Serhiienko, A. O.; Dontsova, T. A.; Yanushevska, O. I.; Nahirniak, S. V. Hosseini-Bandegharaei A. Ceramic membranes: new trends and prospects (short review). *Water and water purification technologies. Scientific and technical news* **2020**, *27* (2), 4-31. https://doi.org/10.20535/2218-93002722020208817

2. Erdem İ. Sol-gel applications for ceramic membrane preparation. In *AIP Conference Proceedings*, **2017**, 1809, 020011, 9 pages. https://doi.org/10.1063/1.4975426

3. Hashimoto, K.; Irie, H.; Fujishima, A. TiO_2 Photocatalysis: A Historical Overview and Future Prospects. *JJAP* **2005**, *44* (12), 8269-8285. https://doi.org/10.1143/JJAP.44.8269

4. de Dicastillo, C. L.; Correa, M. G.; Martínez, F. B.; Streitt, C.; Galotto, M. J. Antimicrobial Effect of Titanium Dioxide Nanoparticles. In *Antimicrobial Resistance - A One Health Perspective*; Mares, M., Ed.; IntechOpen, 2020; p. 208. https://doi.org/10.5772/intechopen.90891

5. Lim, T-T.; Goei, R. Combined photocatalysis-separation processes for water treatment using hybrid photocatalytic membrane reactors. In *Photocatalysis: Applications*, 2016, 130-156. https://doi.org/10.1039/9781782627104-00130

6. Fatimah, I.; Sahroni, I.; Purnama Putra, H.; Nugraha, M. R.; Hasanah, U. A. Ceramic membrane based on TiO_2-modified kaolinite as a low cost material for water filtration. *Appl. Clay Sci*. **2015**, *118*, 207-211. https://doi.org/10.1016/j.clay.2015.09.005

7. Ajenifuja, E.; Ajao, J.; Alayande, S.; Bakare, M.; Taleatu, B.; Ajayi, E. Synthesis and Characterization of Pure and Ag-TiO2-Modified Diatomaceous Aluminosilicate Ceramic Membranes for Water Remediation. *Water Resour. Prot*. **2016**, *8*, 594-607. https://doi.org/10.4236/jwarp.2016.85049

8. Song, Z.; Fathizadeh, M.; Huang, Y.; Chu, K. H.; Yoon, Y.; Wang, L.; Xu W. L.; Yu M. TiO_2 nanofiltration membranes prepared by molecular layer deposition for Water Purification. *JMSR* **2016**, *510*, 72-78. https://doi.org/10.1016/j.memsci.2016.03.011

9. Zhang, S.; Du, Y.; Jiang, H.; Liu, Y.; Chen, R.; Controlled synthesis of TiO_2 nanorod arrays immobilized on ceramic membranes with enhanced photocatalytic performance. *Ceram. Int.* **2017**, *43*(9), 7261-7270. https://doi.org/10.1016/j.ceramint.2017.03.019

ФОТОКАТАЛІТИЧНА АКТИВНІСТЬ TIO_2, СИНТЕЗОВАНОГО СОЛЬВОТЕРМАЛЬНИМ МЕТОДОМ, ПО ВІДНОШЕННЮ ДО БІСЕПТОЛУ ТА КОНГО ЧЕРВОНОГО

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У статті розглядається синтез порошків титану (IV) оксиду сольвотермальним методом для майбутнього використання їх як фотокаталітичний селективний шар в керамічних мембранах. Вивчення особливостей синтезу фотокаталітичних матеріалів для водоочищення є вкрай актуальним через можливість створення антимікробних керамічних мембран за їх участі. Тому метою роботи було синтезувати порошки TiO_2 сольвотермальним методом за різних співвідношень вихідних реагентів, дослідження їх фізико-хімічних властивостей та вивчення фотокаталітичних властивостей по відношенню до Бісептолу та Конго червоного. Отримані порошки охарактеризовано дифракційними методами аналізу, ІЧ-спектроскопією, низкотемпературним методом адсорбції-десорбції азоту та скануючею електронною мікроскопією. Встановлено, що співвідношення вихідних компонентів суттєвим чином впливає на кінцеві властивості та характеристики порошків TiO_2. Показано, що синтез за суттєвого надлишку вихідного реагенту (титан ізопропоксиду) не приводить до отримання кристалічного зразку TiO_2, що підтверджується дифракційними методами аналізу та ІЧ-спектроскопією. Виявлена пориста структура усіх зразків TiO_2 свідчить про високу питому площу поверхні в них, що також узгоджується з дослідженнями скануючої електронної мікроскопії. Найбільшою фотокаталітичною активністю володіють зразки TiO_2, що являють собою нанокомпозити з анатазної та рутильної модифікацій. Такі нанокомпозити проявили досить високу активність до антибіотиків (Бісептол) та аніонних барвників (Конго червоний).

Ключові слова: *антибіотики, барвники, керамічні мембрани, титан (IV) оксид, сольвотермальний синтез, фотокаталітичні властивості*