ELIMINATION OF ANTIBIOTICS BY PHOTOCATALYTIC METHODS

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DOI: https://doi.org/10.20535/2218-930012021235229

Antibiotics have been found in water bodies of different origin around the world, including natural waters. The presence of antibiotics in natural waters is already an important environmental problem, as they pose a potential threat to the environment. Analysis of the literature shows that photocatalytic methods are considered to be more promising than biological methods and adsorption processes for the treatment of water bodies contaminated with antibiotics and other pharmaceuticals. The aim of this study was to determine the efficiency of antibiotics removal (ciprofloxacin, sulfamethoxazole and trimethoprim) by photocatalytic methods over TiO_2 *photocatalyst modified with yttrium oxide. For this purpose, a commercial sample of* TiO_2 *P25 (Evonik) was modified, which was further characterized by X-ray diffraction and X-ray fluorescence analysis methods. The obtained data indicate the presence of yttrium in commercial P25 sample after modification. Studies on the removal of antibiotics from aqueous solutions by photocatalytic methods were carried out in three ways: employing modified photocatalyst; combination of photocatalyst and hydrogen peroxide, and the combination of photocatalyst with hydrogen peroxide and ozone. The results of research demonstrate high efficiency of photocatalytic methods in the oxidation of antibiotics in aqueous solutions, among which the greatest oxidation is achieved using the combination of heterogeneous photocatalyst, hydrogen peroxide and ozone.*

Keywords: *antibiotics, AOPs methods, photocatalysis,* TiO_2*, yttrium modification*

Received: 23 June 2021 Revised: 6 July 2021 Accepted: 6 July 2021

1. Introduction

The presence of antibiotics in the environment has become an important environmental problem, as these pharmaceuticals pose a potential threat to human health and the existence of biota [1]. A wide range of antibiotics, including ciprofloxacin (CIP), sulfamethoxazole (SMX) and trimethoprim (TMP), have already been identified in effluents of wastewater treatment plants, as well as in surface water, groundwater and drinking water in Europe and the United States because of their wide use, high resistance to oxidation and metabolism, etc. [2, 3].

Table 1 presents data on the concentration levels of these antibiotics in some countries. As can be seen from the table, concentration levels of these antibiotics in natural waters are quite high, and tend to increase from year to year. Unfortunately, due to the lack of legal and analytical bases in Ukraine, the content of pharmaceutical substances in water bodies is not monitored. However, this fact does not mean that antibiotics are absent in the natural water bodies of Ukraine; because of the obsolete wastewater treatment technologies, their content might be much higher.

Antibiotics are usually removed from aqueous solutions by such processes as biological treatment or adsorption [4-7].

However, other methods of antibiotics removal are widely studied in modern literature: electrocoagulation, membrane processes and photocatalytic methods or so-called AOPs [8-10]. Among the listed methods, photocatalytic methods using TiO_2-photocatalysts are the most promising, as the employment of solid catalysts based on TiO_2 allows not only oxidation of antibiotics, but also their mineralization [11]. Commercial TiO_2-based photocatalysts, which have high photocatalytic efficiency, include photocatalysts of the brands Evonik P25 and Hombikat UV-100.

Table 1. *Average concentrations of TMP, CIP and SMX in wastewater[3]*

Antibiotic	**Country**	**Average concentration of antibiotics in wastewater (ng/dm^3)**
CIP	Europe	20-95
SMX	Spain	438
	Switzerland	280
	Sweden	70-233
TMP	France	128-271
	Switzerland	200

Despite the undeniable advantages of TiO_2 photocatalysts, there are significant disadvantages, such as low quantum efficiency and low photocatalytic activity under visible light. The improvement of these properties is achieved by doping TiO_2 with metal nanoparticles (Pt, Au, Ni, Mo, W, Nb, Mn, Pd, Fe, Ce, Co, etc.) or non-metals (S, C, N, etc.) [12-17]. In addition, a promising way to increase photoactivity of the TiO_2-photocatalysts is to create composites on its base [18-23]. In the scientific literature, modification of titanium (IV) oxide with rare earth metals has recently become very popular, among which yttrium is relatively cheap.

Thus, the aim of this work was to study the removal of antibiotics such as ciprofloxacin, sulfamethoxazole and trimethoprim by photocatalytic methods employing TiO_2 photocatalyst modified with yttrium oxide.

2. Materials and Methods

The following reagents and materials were used in the work: hydrogen peroxide (H_2O_2), antibiotics (ciprofloxacin $C_{17}H_{18}FN_3O_3$, trimethoprim $C_{14}H_{18}N_4O_3$, sulfamethoxazole $C_{10}H_{11}N_3O_3S$) and a commercial photocatalyst P25 Evonik, the characteristics of which are shown in **Table 2**.

Table 2. *Characteristics of titanium (IV) oxide* [24]

Characteristics	**Value**
TiO_2 content (%)	94
pH	6.5-8.0
Nanoparticle size (nm)	5-21

Modification of commercial titanium (IV) oxide with yttrium oxide (Y_2O_3) was performed as follows. Yttrium nitrate ($Y(NO_3)_3·6H_2O$) of analytical qualification was chosen as a precursor. The calculated amount of yttrium nitrate (to obtain 1 wt.% of yttrium oxide) was mixed with 1 g of TiO_2, and a certain amount of water was added. The obtained suspension was transferred to a stainless steel reactor with a Teflon liner, and heated to 160 °C for 12 hours. The reactor was then cooled and modified TiO_2 was washed and separated in a centrifuge.

The washed sample (Y_2O_3-TiO_2) was dried at 60 °C for 12 hours.

Modified samples of P25 were studied by X-ray fluorescence and X-ray diffraction methods of analysis. Chemical composition of the samples was determined using a precision analyzer EXPERT 3L (Ukraine). Diffraction analysis of the powder was performed using an X-ray diffractometer Rigaku Ultima IV (Japan) with CuKα radiation (40 kW, 30 mA). The phase composition and size of the crystallites were determined and calculated using relevant software.

Studies of the antibiotics removal by photocatalytic methods were carried out using setup shown in **Fig. 1**. This experimental setup allows to study the influence of ozone, hydrogen peroxide, UV radiation and photocatalyst both separately and simultaneously.

As can be seen from **Fig. 1**, the setup consists of a tank for model water, a pump, a chamber with a UV lamp inside and an ozonator that supplies O_3 to the ozone chamber. The system is looped and connected by tubes for water circulation in it.

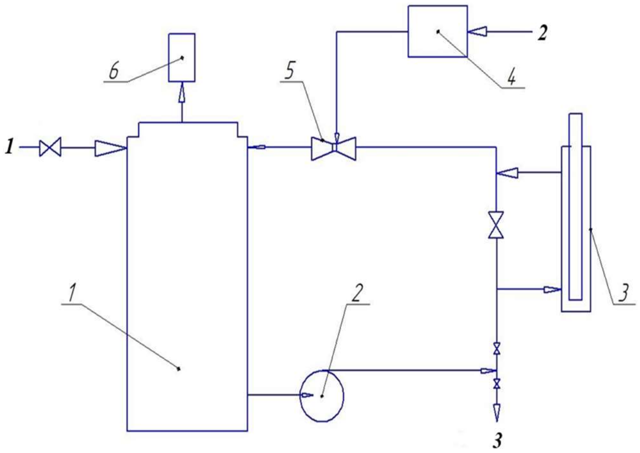

Fig. 1. *Photocatalytic setup. Positions: 1 – tank, 2 – pump, 3 – UV lamp (257 nm), 4 – ozonator, 5 – faucet, 6 – gas collector; flows: 1 – model water with catalyst and hydrogen peroxide, 2 – air, 3 – treated water*

The spectra of antibiotic solutions both before and after photocatalytic process were recorded on a UV/VIS Spectrophotometer (220V/50Hz) in the wavelength range of 190-800 nm.

The degree of removal was determined by the formula [25]:

$$X = \frac{A_0 - A_k}{A_0} * 100\%,$$

where A_0 and A_k – are initial and resulting optical densities of the antibiotic solution by characteristic wavelength.

3. Results and Discussion

The results of the characterization of titanium (IV) oxide modified with yttrium oxide (sample Y_2O_3-TiO_2) and unmodified P25 (for comparison) are presented in **Fig. 2** and in **Table 3.**

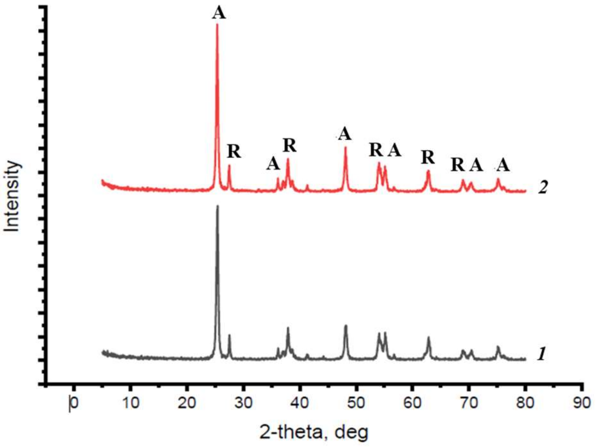

Fig. 2. *XRD patterns of the samples: 1 – P25, 2 – Y_2O_3-TiO_2*

As can be seen from Fig. 2, XRD patterns are identical, and only the peaks associated with P25 (90% anatase and 10% rutile; standard cards № 00-021-1276 for rutile, № 00-021-1272 for anatase) are clearly observed. Yttrium oxide phase was not detected.

Even though Y_2O_3 phase has not been detected, the chemical composition (**Table 3**) indicates the presence of yttrium in modified sample of TiO_2. In terms of oxide, it is 0.92 wt.% that is very close to theoretically calculated.

Table 3. *Chemical composition of the sample*

Sample	**Ti, %**	**Y, %**
P25	100	-
Y_2O_3-TiO_2	1.2	98.8

Studies of the antibiotics removal: CIP and co-trimoxazole (SMX + TMP) from model aqueous solutions by photocatalytic methods were carried out in three ways: employing Y_2O_3-TiO_2 photocatalyst only; employing Y_2O_3-TiO_2 photocatalyst in the presence of hydrogen peroxide; employing Y_2O_3-TiO_2 photocatalyst in the presence of hydrogen peroxide with the addition of ozone.

Fig. 3 shows the spectra of CIP solution before and after the photocatalytic process over Y_2O_3-TiO_2 photocatalyst in the absence of hydrogen peroxide (spectrum 2, **Fig. 3**) and in its presence (spectrum 3, **Fig. 3**). It can be seen that intensities of the antibiotic peaks become much lower after the photocatalytic process both in the case of Y_2O_3-TiO_2 usage and usage of photocatalyst combination with hydrogen peroxide. The greater degree of oxidation is observed for the employment of combination of Y_2O_3-TiO_2 and oxidant (**Table 4**). This is explained by the formation of more $OH^•$ radicals in this case [10].

Fig. 4 illustrates the spectra of the initial co-trimoxazole solution (spectrum 1, Fig. 4) and of the solution after the photocatalytic process using a combination of the catalyst with hydrogen peroxide (spectrum 2, Fig. 4).

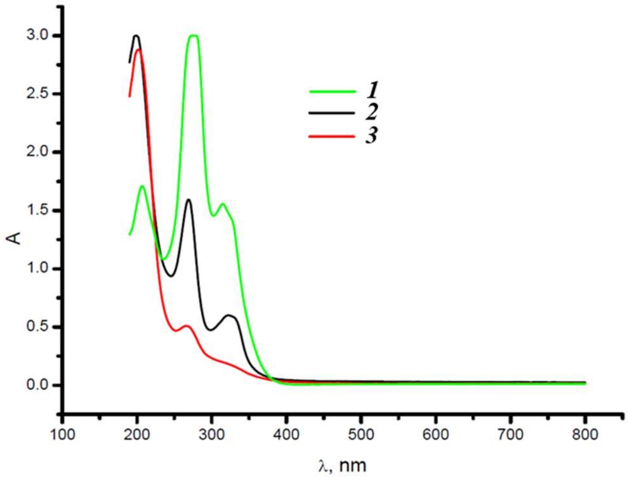

Fig. 3. *Spectra of CIP solution before photocatalytic process (1) and after (2, 3): 1 – initial CIP solution (50 mg/dm^3), 2 – solution spectrum after photocatalytic process over Y_2O_3-TiO_2, 3 – solution spectrum after photocatalytic process over Y_2O_3-TiO_2 in the presence of hydrogen peroxide*

Table 4. *Degrees of antibiotics oxidation in aqueous solutions by photocatalytic methods*

Antibiotic	**Oxidation degrees, %**		
	Y_2O_3-TiO_2	**Y_2O_3-TiO_2 + H_2O_2**	**Y_2O_3-TiO_2 + H_2O_2 + O_3**
CIP	52	87	100
Co-trimoxazole (SMX + TMP)	56	92	100

As in the case of CIP removal, there is a significant reduction in the intensity of the antibiotic peaks and according to the data in **Table 4**, a greater degree of oxidation is also observed for the combination of the catalyst with hydrogen peroxide.

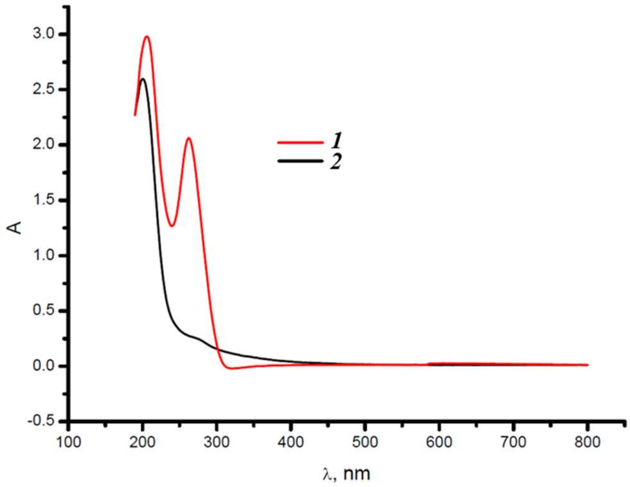

Fig. 4. *Spectra of SMX+TMP (co-trimoxazole) solution before photocatalytic process (1) and after (2): 1 – initial co-trimoxazole solution (50 mg/dm^3), 2 – solution spectrum after photocatalytic process over Y_2O_3-TiO_2 in the presence of hydrogen peroxide*

In **Table 4**, degrees of oxidation of antibiotics (CIP and co-trimoxazole) are given: using Y_2O_3-TiO_2 photocatalyst; combination of Y_2O_3-TiO_2 photocatalyst and hydrogen peroxide; combination of Y_2O_3-TiO_2 photocatalyst and hydrogen peroxide with the addition of ozone.

Analysis of the obtained data (Table 4) indicates complete degradation of antibiotics with a concentration of 50 mg/L using Y_2O_3-TiO_2 photocatalyst in the presence of hydrogen peroxide and the addition of ozone.

4. Conclusions

Studies have shown the effectiveness of antibiotics removal (ciprofloxacin, sulfamethoxazole and trimethoprim) by various combinations of photocatalytic methods using TiO_2 photocatalyst modified with yttrium oxide.

Characterization of modified and unmodified commercial sample of TiO_2 – P25 (Evonik) by X-ray diffraction and X-ray fluorescence methods of analysis revealed that after modification with yttrium oxide, the latter is present in the sample.

It was shown that the most effective photocatalytic system is the combination of heterogeneous photocatalyst, hydrogen peroxide and ozone, which oxidizes antibiotics in aqueous solutions by 100% at their initial concentration of 50 mg/L.

It was confirmed that the use of photocatalytic methods is a promising solution for the treatment of water bodies containing antibiotics.

Acknowledgments

We are grateful to the National Research Foundation of Ukraine "Support for research of leading and young scientists" for funding the project (project registration number 2020.02/0024).

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ВИЛУЧЕННЯ АНТИБІОТИКІВ ФОТОКАТАЛІТИЧНИМИ МЕТОДАМИ

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Антибіотики знайдені у водних об'єктах різного генезису по усьому світу, серед яких й природні води. Присутність антибіотиків у природних водах на сьогоднішній день вже є важливою екологічною проблемою, оскільки вони становлять потенційну загрозу навколишньому середовищу. Аналіз літературних даних свідчить, що фотокаталітичні методи вважаються більш перспективними у порівнянні з біологічними методами очищенням та процесами адсорбції для знешкодження водних об'єктів, що містять антибіотики та інші фармацевтичні препарати. Метою даного наукового дослідження було встановлення ефективності вилучення антибіотиків (ципрофлоксацину, сульфаметоксазолу та триметоприму) фотокаталітичними методами за участі модифікованого оксидом ітрію TiO_2*. Для цього було проведено модифікацію комерційного зразку* TiO_2 *P25 (Evonik), який далі охарактеризовано дифракційним та рентгенофлуоресцентним методами аналізу. Одержані дані, вказують на присутність ітрію в комерційному зразку P25 після модифікації. Дослідження щодо вилучення антибіотиків з водних розчинів фотокаталітичними методами реалізовано трьома шляхами, а саме, за участі модифікованого фотокаталізатору, комбінації фотокаталізатору з одночасним використанням пероксиду водню та комбінації фотокаталізу із застосуванням пероксиду водню та озону. Результати досліджень свідчать про високу ефективність фотокаталітичних методів для окиснення антибіотиків з водних розчинів, серед яких найбільш глибоке окиснення досягається використання комбінації гетерогенного фотокаталізатору, пероксиду водню та озону.*

Ключові слова: *антибіотики, нетрадиційні методи очищення, фотокаталіз,* TiO_2*, модифікація ітрієм*