# COMPARISON OF CONTRAST MEDIA ELIMINATION BY MEANS OF PHOTO CATALYSIS USING MODIFIED AND UNMODIFIED TITANIUM DIOXIDE

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**Abstract** - A lot of studies have revealed that unmetabolised drugs enter the sewage system and, later, appear in the wastewater treatment plants. The treatment process in the plant usually fails to completely eliminate the drugs from wastewater. In consequence, the drugs, together with treated wastewater, are released into surface waters. Iodinated contrast media (ICM) are substances used for imaging tissues, internal organs, etc., are commonly detected in aquatic environment in concentrations up to several milligrams (i.e. hospital wastewater). In this study, the investigation of the effectiveness of iohexol removal by means of solar irradiation with use TiO2 and TiO2+GO as catalysts was performed. The results showed that it was possible to achieve the significant iohexol elimination (above 90%) during photocatalysis process within 180 minutes. Moreover, the iohexol removal in the solar/TiO2+GO process was more efficient than solar/TiO2 alone and the time needed for its elimination was notably shortened with use of hybrid catalyst.

**Key Words** - Photocatalysis, contrast media, wastewater treatment

## I. INTRODUCTION

A lot of studies have revealed that unmetabolised drugs enter the sewage system and, later, appear in the wastewater treatment plants. The treatment process in the plant usually fails to completely eliminate the drugs from wastewater. In consequence, the drugs, together with treated wastewater, are released into surface waters. Iodinated contrast media (ICM), substances, which are used for imaging tissues, internal organs, etc., are commonly detected in aquatic environment in concentrations up to several milligrams, for example in hospital effluents. They are often discharged into sewage system which cause the decrease ICM concentration by diluting and then the sewage enter wastewater treatment plant. If the concentrations of pharmaceuticals in municipal wastewater are at the levels of ng/L and µg/L, in the hospital wastewater they can reach the level of tens of µg/L or even mg/L [1]. Iohexol is an example of contrast media, widely used in radiography. Its systematic name is 5- [N- (2,3-dihydroskypropyl) -acetamido] -N, N'-bis (2,3-dihydroxypropyl) -2,4,6-triiodoisophthalamide (Fig.1).

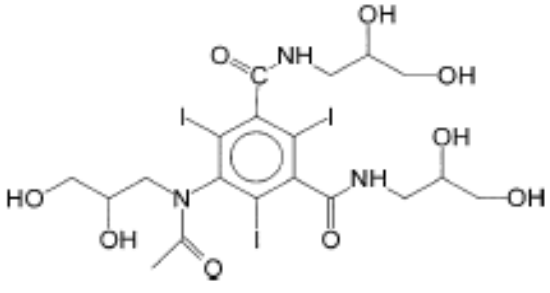



**Fig. 1. Contrast media iohexol structure [2].**

Iohexol belongs to the nonionic contrast agents having in their structure iodine. It is soluble in water and due to the low osmolality (from 411 to 862 mosm/kg $H_2O$) it has low toxicity. This substance is mainly used in the following studies: myelography, arthrography, nephroangiography, arteriography. It is most often used in the form of injections, but it can also be used orally interchangeably for barium sulphate in case of suspicion of intestinal perforation. It is mainly excreted by glomerular filtration along with urine. A small part, from 1 to 2%, is excreted into bile. From 80 - 90% of the dose is excreted within 24 hours of administration, and the highest concentration of the excreted dose occurs after 1 hour. Iohexol is available in the form of an Omnipaque pharmaceutical preparation with iodine density in $cm^3$ of preparation from 180 to 350 [2]. The toxicity tests of iohexol indicates that can cause high acute toxicity in Raphidocelis subcapitata and Daphnia magna, and the lack of acute toxicity was observed in such organisms as Thmanocephalus platyurus and Artemia salina [2, 3, 4]. However, the maximum measured environmental concentration of iohexol was 109.79 ng/L and such low concentration does not cause toxic effects on the test organisms. The lowest toxic dose in this case LC50 in Daphnia magna is 4.90 mg/L. In order to minimize the impact of ICM on the aquatic environment, new methods of their degradation are under investigation. Among these methods the photochemical processes become more and more popular.

Photocatalysis is defined as a change in the chemical reaction rate or its initiation occurring under the influence of ultraviolet, visible or infrared radiation in the presence of a photocatalyst absorbing light and

participating in the chemical transformation of reactants [5]. Photocatalysts are usually metal oxides ($SnO_2$, ZnO, $ZrO_2$, $TiO_2$) and sulphides, selenium and metal tellurides (ZnS, CdSe, CdTe). Photocatalysis belongs to advanced oxidation processes (AOP), and studies on its application for the distribution of organic pollutants contained in water have been going on for several decades [6].

The photocatalysis process itself involves the absorption of a quantum of radiation with an energy equal to or greater than the energy of the semiconductor transition, which causes the electron (e-) to pass from the valence band to the conduction band and simultaneously generate the electron hole (h +). In the water environment, electron holes generate free hydroxyl radicals with strong oxidizing properties, while free electrons together with oxygen form superoxide anion radicals (Fig.1). The most often and most frequently used catalyst is titanium dioxide ($TiO_2$). Since the mid-1970s, it has been used on an industrial scale to reduce nitrogen oxides in a selective catalysis process [7]. This inorganic chemical compound, due to its properties, is widely used not only in the process of photocatalysis, but also in other fields of science and industry. Research on the use of $TiO_2$ in the process of photocatalysis showed its suitability for the degradation of difficult biodegradable organic compounds, such as pharmaceuticals products. In order to improve the photocatalytic activity of $TiO_2$, its surface modification is made using metals, iron (III) chloride, silver cation, carbon derivatives, including graphene and graphene oxide. In addition, the literature also shows other advantages of using hybrids in elimination of organic compounds: better sorption properties, the possibility of using hybrids not only in the UV range, but also in the visible light and increasing the selectivity of the decomposition process [8, 9, 10].

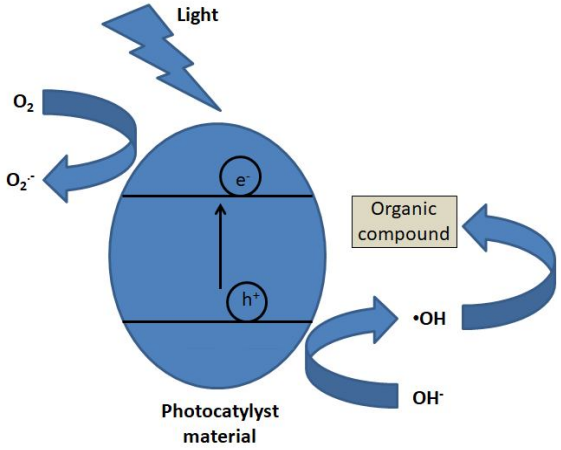



**Fig. 1. Scheme of photacatalyst process.**

The objective of this work was to evaluate the phtocatalysis process in elimination of iohexol from water samples using $TiO_2$ and hybrid $TiO_2$ – GO.

## II. MATERIAL AND METHODS

### A. Standards and reagents

Analytical standard of iohexol was purchased from Sigma Aldrich (Poland). Tetrabutylammonium bromide (TBAB) was purchased from Fluka. Titanium dioxide powder (CAS number 1317-70-0) was also purchased from Sigma Aldrich (Poland). Graphene oxide solution was obtained from Nano Carbon Sp. z o.o (Nano Carbon LLC).

For the preparation of the hybrid 1% graphene oxide solution (GO) was used and titanium dioxide powder. The ratio of GO to TiO2 in the hybrid to be prepared was 1:10. First, a solution of graphene oxide and titanium dioxide was prepared: 3 g of TiO2 and 30 ml of GO solution was added to 200 ml of bidistylated water. The mixture was subjected to an ultrasonication process for 1.5 h, and then stirred for 18 hours on a magnetic stirrer at 300 rpm. The homogeneous solution was dried until the liquid was completely evaporated at 90C. The above methodology with a few modifications is based on [10]. In the samples of the iohexol solution tested, the catalyst concentration was 500 mg/L.

### B. Test device

A SOLARBOX 1500e device was used to carry out the tests in a laboratory conditions and allows to simulate the natural weather conditions. The production of solar radiation is possible due to a xenon lamp. The location of this lamp in the focus and the special shape of the chamber guarantees identical distribution of radiation on the surface of the analyte under examination. Temperature was constantly measured in the chamber, controlled by B.S.T (Black Standard Thermometer), and irradiance, which is a measure of the amount directed on the surface of the UV radiation sample. Irradiance during the process of photocatalysis was a constant value of 500 $W/m^2$.

### C. Analytical methods

All measurements needed to perform analyses of iohexol were carried out with Dionex UltiMate 300 (Reverse Phase High Performance Liquid Chromatography) HPLC. The device consists of: HPLC pump, automatic sampler, precolumn LiChrospher 106 RP - 8 (5 µm), columns RP - 8 (5 µm), UVD 340U detector - allowing simultaneous observation of 4 wavelengths in the UV - VIS range.

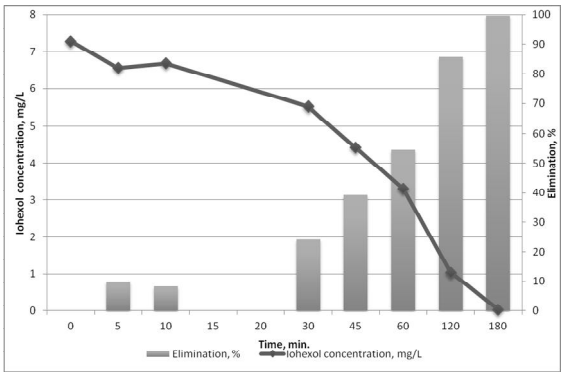
### D. Experiments performance

A catalysts were added to the test iohexol solution equal to 5 mg/L and placed on a magnetic stirrer located inside the SOLARBOX device. The experiment was carried out for a period of 180 minutes, and the time counted from the moment of adding the catalyst to the tested solution and placing it in the test apparatus. During the photocatalysis

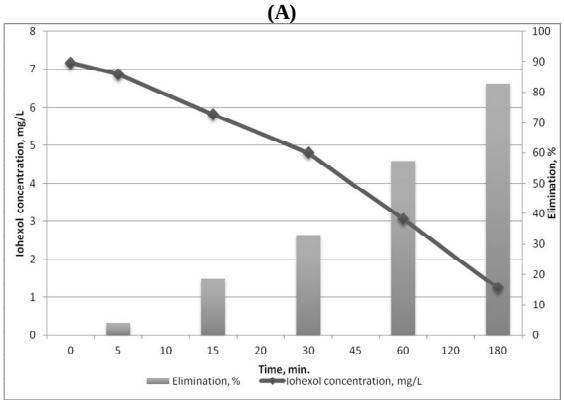
process, samples were grabbed for chromatographic analysis at the following time intervals: 0 min, 5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 120 min and 180 min. Each of the samples was filtered and accurately described for analysis. The tests were carried out in three series, maintaining the same working conditions for each repetition, and using the same reagents. At the beginning (0 min) and at the end (180 min) of the experiment, the temperature and pH of taken samples were measured.

## III. RESULTS AND DISCUSSION

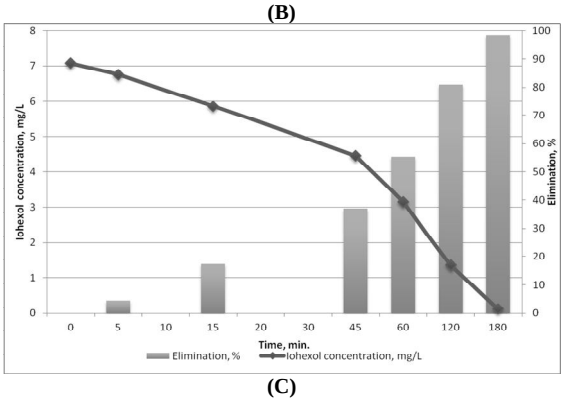
The tests with use of $TiO_2$ revealed that it is possible to eliminate iohexol at the significant level. In Fig.2. it can be seen the results of the three series of the experiments. It should be noticed, that start concentration of iohexol was higher than it was planned.




**(A)**



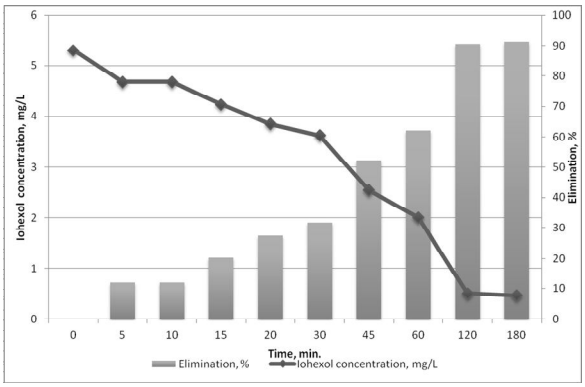

**(B)**



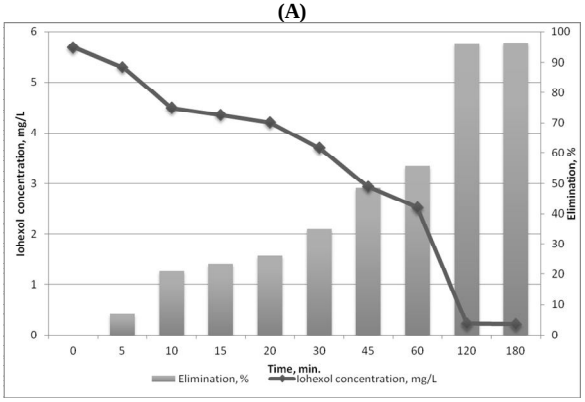

**(C)**

**Fig. 2. The results of the iohexol removal with use of $TiO_2$: (A) first series, (B) second series (C) third series.**

The elimination of iohexol after 60 minutes of the photocatalysis process in all series exceeded 50%. Next 60 min of irradiation in all samples caused the iohexol removal at the level above 80% of the initial concentration. The highest elimination was achieved in first series and it was equal to 99.6%. However, the second series showed removal at the level 82.6% and the final concentration of iohexol exceeded 1 mg/L.
In the case of tests using TiO2 + GO, the highest removal rate of iohexol was observed in the second series and it amounted to 96.3% (Fig. 3).




**(A)**




**(B)**

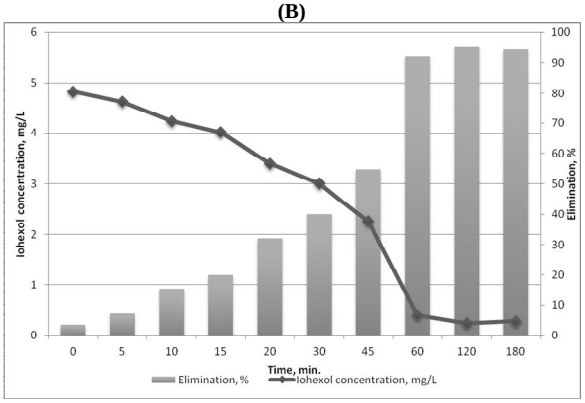



**Fig. 3. The results of the iohexol removal with use of $TiO_2$ + GO: (A) first series, (B) second series (C) third series.**

IV. In first and third series, the removal rate of the pharmaceutical was equally high and exceeded 90%. In the second and third series, a removal rate of more than 90% was achieved 120 minutes after the start of the photocatalysis process. In the first series of tests, after 60 min of the process, the concentration of iohexol dropped by as much as 92% in relation to the

initial concentration. Due to the small amount of data, however, it can not be unambiguously stated whether such a high removal of iohexol can be obtained after 60 minutes of the process, or only after 120 or 180 minutes. In all series with use of $TiO_2$ + GO, the differences in concentration of the contrast agent between 2 and 3 hours of the process were small (less than 0.05 mg/L). This fact may suggest the possibility of shortening the duration of the process from 180 to 120 minutes, without losing the high efficiency of removing the contrast agent. The main objective of this study was to compare the possibility of iohexol elimination in the process of photocatalysis using the $TiO_2$ and hybrid $TiO_2$ + GO as a catalyst. Based on the obtained results, it can be concluded that the hybrid used in the tests provides an efficient process of removing iohexol at the level 94%. However, the almost equally good results were be obtained by using $TiO_2$ as a catalyst – according to performed experiments the elimination of iohexol was equal to 93,6%. However, the duration of the photocatalysis process is more important. It can be noticed, that after 120 minutes of exposure was observed 93% removal of the pharmaceutical using the hybrid $TiO_2$ + GO, while in the case of $TiO_2$, the elimination rate was around 86%. Even after 5 minutes of irradiation the slightly advantage of elimination using hybrid can be observed. After 30 minutes the difference is equal to approximately 7%. The highest distinction (14%) was achieved after 60 minutes of the process duration (Fig. 3).

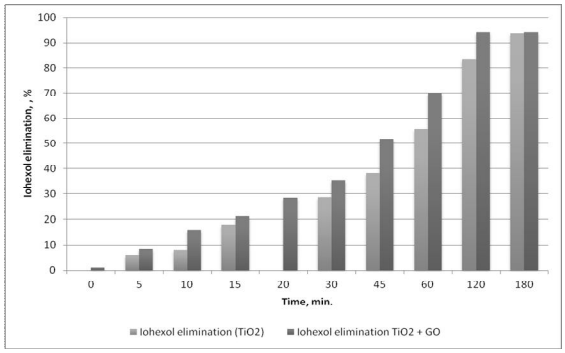



**Fig. 3. The average elimination of iohexol by means photocatalysis process with $TiO_2$ and hybrid $TiO_2$ and GO.**

## CONCLUSIONS

The presence of pharmaceutical products in environmental waters is an emerging issue in environmental engineering. Contrast media are persistent micropollutants and photocatalysis proved to be an efficient process in elimination of such compounds. The solar irradiation with use of two kinds of photocatalysts ($TiO_2$ and hybrid $TiO_2$ + GO) showed the high elimination of iohexol. However, the more important is the reduction of time of the elimination process using of the solar irradiation process with hybrid photocatalyst.

## ACKNOWLEDGMENTS

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