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Preliminary studies of photolysis and TiO_2-montomorillonite-immobilised photocatalysis processes for the degradation of organic pollutants in water treatment

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Abstract: Organic compounds are the most diverse group of contaminants. The largest anthropogenic source of these contaminants in water is municipal and industrial wastewater. One of the indicators of surface water pollution is biological oxygen demand (BOD). Purifying water from organic micropollutants is a serious challenge and requires the development of newer and more effective methods. The removal of such contaminants is most effective only in advanced oxidation processes (AOP), which include UV photolysis and photocatalysis.

The presented results are from preliminary research to evaluate the effectiveness of water treatment by ultraviolet (UV) photolysis and photocatalysis. Treatment efficiency was evaluated on the basis of changes in the BOD index before and after the advanced oxidation process of raw water. The values of the BOD_5 index determined in accordance with PN-EN 25813:1997. The exposure time of the samples was a maximum of 60 minutes. The tested material was water samples taken from the Rudawa River, which is one of the drinking water sources for Krakow. The initial BOD_5 value (expressed as concentration of O_2) for all samples was about 8 mg/L but it has decreased to over 2 mg/L due to AOP processes. This means that after an hour, more than 75% of organic compounds present in the raw water were removed. For photocatalysis (TiO_2-MMT), the exposure time of the samples was a maximum of 35 minutes. Water samples taken from the Rudawa River were also used as test material. The initial BOD_5 value for all samples was about 9 mg/L but it has decreased to about 4 mg/L due to the photocatalysis process. This means that after 35 minutes, 55% of the organic compounds present in the raw water were removed.

Keywords: surface waters, water contamination, advanced oxidation processes, biological oxygen demand

INTRODUCTION

Water covers almost 75% of the Earth's surface, and more than 97% of water resources are seas and oceans. The remaining 3% is fresh water, more than 90% of which is trapped in glaciers and permanent snow cover. Less than 1% of the fresh surface and groundwater bodies are directly used

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by humans (Kindler 2013). This water is in constant circulation and is exchanged between surface, ground, and rainwater. Due to the circulation of water in the natural environment, and the fact that it is an excellent solvent for a large group of mineral and polar organic substances, it does not exist in nature as a chemically pure compound of oxygen and hydrogen. In fact, water is always a highly dilute solution of acids, salts, gases, and bases. Apart from the presence of dissolved substances in the water, there are also colloidal and suspended compounds (Oki & Kanae 2006). The composition of surface waters is shaped by their circulation in the hydrological cycle. The direct contact of anthropogenic pollutants with surface water determines its physical properties and chemical composition to a large extent (Taylor & Senac 2014).

Water resources are limited and therefore steps should be taken to ensure their quality. The main routes for pollutants to enter the aquatic environment are shown in Figure 1. Among the anthropogenic pollutants of surface waters there are polycyclic aromatic hydrocarbons, pesticides, petroleum substances, chlorine organic compounds, radionuclides, nitrogen compounds, pharmaceuticals, and many others (Gervais et al. 2008, von der Ohe et al. 2011, Taylor & Senac 2014). These compounds have toxic, pathogenic and even mutagenic properties, and therefore are dangerous to human health and life. Hence, it is extremely important to minimize their amounts in water (Franke et al. 2005, Styszko & Drobniak 2015).

One of the methods used for the removal of the aforementioned micropollutants from drinking water are advanced oxidation processes (AOP) (Martinez et al. 2016, Dong et al. 2022). Generally, AOPs use the generated hydroxyl radicals, which have a high oxidizing potential required for the degradation of compounds that are difficult to biodegrade. AOP processes involve photochemical or photocatalytic oxidation as well as the addition of an oxidant to the sample, which may be ozone, hydrogen peroxide, or Fenton's reagent. These methods are often combined with one another to improve the degradation efficiency of organic compounds (Andreozzi et al. 1999, Deng & Zhao 2015, Książek et al. 2015, Dong et al. 2022).

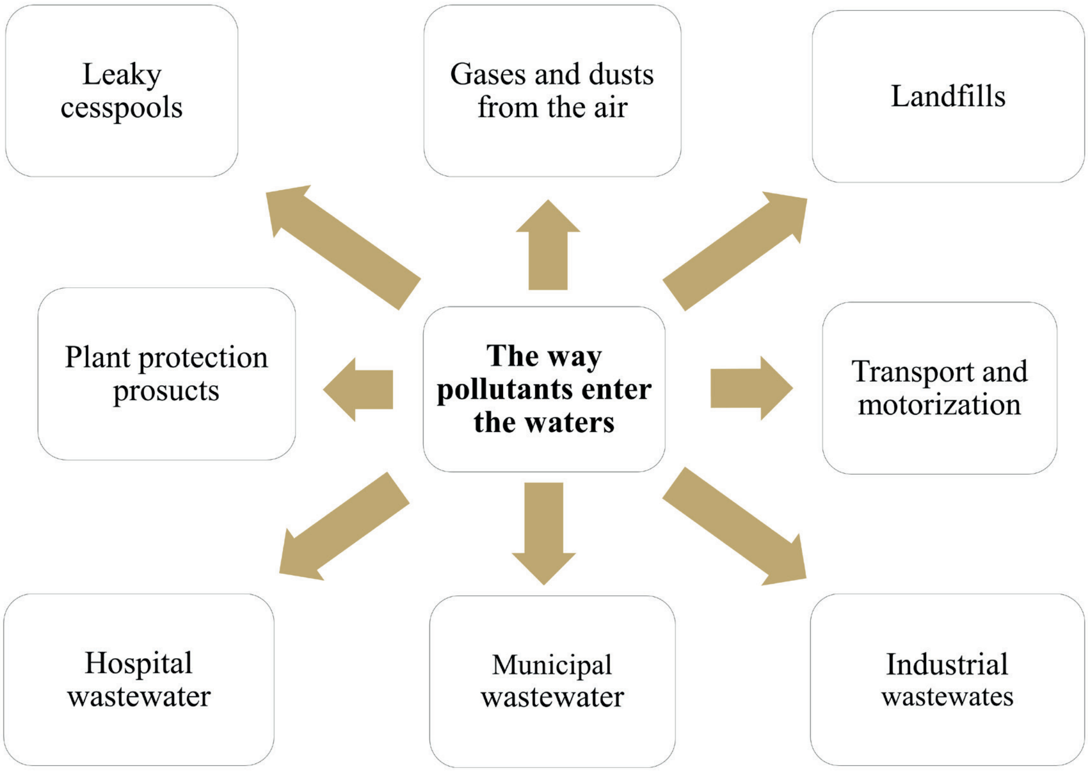

Fig. 1. *Sources of water pollution*

The aim of this research was to determine the biological oxygen demand (BOD_5) i.e., one of the indicators of surface water contamination. BOD_5 is the amount of oxygen needed for the proper oxidation of organic substances contained in a given volume of water by microorganisms under aerobic conditions at room temperature within 5 days. The value of this indicator increases in direct proportion to the amount of organic pollutants in the water. The effectiveness of water quality improvement due to the use of UV photolysis and photocatalysis was also assessed. This assessment was carried out by comparing the BOD_5 values.

EXPERIMENTAL PART

Acquisition of samples

The research material was water taken from the Rudawa River. The Rudawa is a left-bank tributary of the Vistula River, with a length of 75.4 km. The catchment area is 318 km^2. In the Rudawa, about 9 km from the mouth of the river, there is a water intake point of the "Rudawa" Water Treatment Plant (WTP), which is one of the five drinking water intakes for the inhabitants of the city of Krakow (Jagoda et al. 2015). This WTP satisfied 17% of the total water demand of Krakow's inhabitants in 2018 (UMK 2019).

The water for analyses was collected in October 2018 into dark glass bottles and transported to the laboratory under cool transport conditions. The collection point was located 2 km from the river mouth. The volume of water taken was 5 L.

Chemicals

The reagents used to determine the BOD_5 index were: sulfuric(VI) acid 95%, alkaline potassium iodide solution – potassium hydroxide and potassium iodide, manganese(II) sulphate solution – manganese(II) sulphate monohydrate, sodium thiosulphate 0.01 mol – sodium thiosulphate pentahydrate and sodium hydroxide, soluble starch. Additionally, the reagents used for the preparation of the catalyst were: montmorillonite, titanium oxide (98.5% anatase), hydrochloric acid (20%) and hydrogen peroxide (90%). All the above-mentioned materials came from POCH (Gliwice, Poland).

Catalyst preparation

The catalyst was applicated on clean slides with a diameter equal to the inner diameter of the reaction vessel. Cleaning the slides consisted of washing them and then keeping them for 24 hours in a development of 95% H_2SO_4 and 30% H_2O_2 in a 1:1 volume ratio. After that time had elapsed, the slides were removed from the solution, rinsed with deionized water and dried at a temperature of 100°C. The catalyst is a mixture of powdered titanium oxide (TiO_2) and montmorillonite (MMT) in a weight ratio of 1:1, treated with HCl, sequentially dried in open air and then calcined at a temperature of 450°C to activate the montmorillonite precursor. The application of such temperature allowed to obtain the desired anatase and prevent the formation of rutile (the form of TiO_2 photochemically inactive). 0.2 g of the catalyst was weighed successively and dissolved in 30 mL of deionized water. The suspension prepared in this way was applied to the cleaned glass slides. Preparation of glass plates consisted of drying them at room temperature for 24 h, and after drying, the excess sediment was rinsed off with a wash bottle containing deionized water. When slides were dry, the prepared catalysts were used for the photocatalysis process. The catalyst used for the tests contained 3.5 mg of catalytically active substance. The process of preparation of TiO_2-MMT catalysts was taken from the publications of Grabowska (2011) and Kasza (2016).

UV photolysis

The test stand consisted of three main elements, namely: a high-pressure mercury lamp, a motorless BMM 21 type magnetic stirrer and a reaction vessel. The power of the lamp is 125 W. About 90% of its radiation is converted into heat and UV radiation, the rest is converted into visible light. The source of UV radiation is mercury discharge in vapours under high pressure (approx. 1 MPa). This discharge takes place in an arc tube which contains mercury and argon. During the photolysis process, the test stand was covered with aluminium foil to protect the pattern during lamp operation.

Five exposure times were selected: 12, 24, 36, 48 and 60 min. Each time, the same volume of water sample (250 mL) was irradiated in the glass reactor. In order to ensure an even application of UV radiation, the water sample was subjected to a continuous stirring process during irradiation by means of a magnetic stirrer.

UV photocatalysis with the use of immobilised TiO_2-MMT

The process of photocatalysis was almost identical to that of photolysis. The only difference in the construction of the test stand is that the TiO_2-MMT catalyst was placed in the reaction vessel on a magnetic stirrer. This arrangement allowed for the mixing of the liquid during the experiment and, at the same time, the active layer of the catalyst was not mechanically damaged by the moving stirrer. Other exposure times were also used, namely: 7, 14, 21, 28 and 35 minutes. Otherwise, everything was as described in section UV photolysis.

BOD_5 designation

The determination of the content of organic compounds in water samples using the BOD_5 method was carried out in accordance with PN-EN 25813:1997. This standard describes the iodometric method for determining the content of oxygen dissolved in water (PN-EN 25813:1997). BOD_5 was determined at time 0, just before starting UV photolysis and photocatalysis and after each exposure time.

Determining the effectiveness of water treatment

The water treatment efficiency was assessed on the basis of the change in the BOD_5 value before and after the advanced oxidation process for raw water collected from the Rudawa River. The percentage of efficiency was calculated according to the following formula:

$$\frac{x_i}{x_0} \cdot 100\% \qquad (1)$$

where:

x_i – BOD_5 value after AOP [mg/L],
x_0 – BOD_5 value before AOP [mg/L].

RESULTS AND DISCUSSION

Determination of the BOD_5 value

Biological oxygen demand is one of the most important indicators of water quality. It shows that water is contaminated by biodegradable organic matter (Basant et al. 2010, Šiljić et al. 2015). The discharge of wastewater and agricultural runoff cause the increase in BOD_5 in surface watercourses (Floury et al. 2012).

For the raw water taken from the Rudawa River, the BOD_5 value was on avg. 8.97 ±0.17 mg/L. Importantly, the obtained result coincides with the results of research carried out by the Provincial Inspectorate for Environmental Protection in Krakow. In 2016–2020, the Małopolska State Environmental Monitoring program was carried out in Małopolska, which placed the emphasis, among others, on monitoring the quality of surface waters. WIOŚ (The Provincial Inspectorate for Environmental Protection) controlled the water quality indicators for the Rudawa River at the mouth of the Vistula River in 2017 and 2020. BOD_5 of 9.0 mg/L was obtained each time (Żuk et al. 2017). The BOD_5 value determined in our research coincides with the maximum average values measured on the Cetynia River (in Poland) in the winter period, which amounted to 9.20 mg/L in the autumn and winter period (Bus & Mosiej 2018). The publication by Šiljić et al. (2015) summarizes the BOD_5 values which European countries reported to the European Statistical Office and World Bankin the years 2000–2008. In this comparison, the highest value was achieved by waters in Romania, where the average BOD_5 is 4.69 mg/L. Compared to the results obtained in our research, it is almost two times less. Poland is in the second place in the above-mentioned ranking, with a biological oxygen demand of 4 mg/L (Šiljić et al. 2015). The European Environmental Agency (EEA) has been collecting data on BOD_5 for rivers over many years. According to data from 1992 to 2017, average BOD_5 in Europe decreased by 1.96 mg/L, in 2017 it was 1.86 mg/L. In 2017 the best countries in this ranking were: France (1.25 mg/L), Latvia (1.19 mg/L), Slovenia (0.81 mg/L), and Ireland (0.79 mg/L). At the other end of the list are Romania (3.22 mg/L), Bulgaria (3.24 mg/L), North Macedonia and Cyprus (3.31 mg/L), and Spain (3.98 mg/L). In the case of Poland, reports for the EEA were prepared in years 2000–2017. During this period, BOD_5 decreased by only 0.88 mg/L to the value of 2.74 mg/L (EEA 2022). In other Romanian studies, for the Danube River from January 2010 to December 2012, the mean BOD_5 was below 2 mg/L (Bărbulescu & Barbeş 2020). Similar values were obtained in studies carried out in France on the Loire River in the period from 1977 to 2008. The BOD_5 ranges from 1.4 to 5.1 mg/L (Floury et al. 2012). The Japanese rivers are also characterized by similar values. There, the BOD_5 ranges from 1.0 to 5.3 mg/L (Chee et al. 1999). Subsequently, in the USA, in the state of Minnesota, the biological oxygen demand index for five rivers was measured. Results ranged from 1.0 to 7.0 mg/L (Heiskary & Markus 2001).

The place where the water was collected for analyses is located in the city of Krakow. In its immediate vicinity, on the left bank of the Rudawa River, there are the Krakus Family Allotment Gardens, and on the right, small residential buildings, mainly in the form of single-family houses. The area has been heavily transformed and developed. The increase in the BOD_5 value in the waters of the Rudawa River can be explained by the inflow of waste from nearby buildings (Hachoł & Krzemińska 2008). Households may supply the river with a large amount of organic matter and dissolved substances such as nitrates, phosphates, detergents and other pollutants (Lewkiewicz-Małysa & Macuda 2008). The Allotment Gardens are areas where small plots are cultivated. Its surface runoff causes the supply of organic matter and mineral fertilizers to the river, which deteriorates the water quality (Malaj et al. 2014).

Polish legislation, namely the regulation of the Minister of the Environment on the requirements to be met by surface waters used to supply the population with drinking water, divides the water intended for human consumption into three categories: A1, A2 and A3, where A1 is the cleanest water. One of the water quality indicators is BOD_5 (*Rozporządzenie*… 2002). The limit values of BOD_5 [mg/L] for individual classes are given below:

- category A1 < 3,
- category A2 < 5,
- category A3 < 7.

Since water from the Rudawa River is intended for the inhabitants of Krakow, it is important that it meets the requirements contained in the above-mentioned regulation. The BOD_5 value obtained by us, amounting to an average of less than 9 mg/L, its value is greater than 7, which means that the tested water does not fall into any of the water purity categories – it is out of class water (*Rozporządzenie*… 2002). The Rudawa River is an organically polluted river. To comply with the requirements of the Regulation, it must be purified.

The efficiency of the AOP methods

The calculations of the efficiency of photolytic and photocatalysis removal of pollutants depending on the exposure time were carried out in accordance with the Formula (1). The results of the advanced oxidation processes are shown in Figure 2. The bars show the BOD_5 changes for individual exposure times. Error bars are also marked in the graph in the form of standard deviation.

The efficiency of the UV photolysis process for the water from the Rudawa River increased by about 10% every 12 minutes until 36 minutes. The greatest leap in efficiency occurred between 36 and 48 minutes of exposing the samples to UV rays. Efficiency was increased by over 25%. After 48 minutes of the photolysis process, more than 50% of the organic compounds present in the raw water were removed. In the case of photocatalysis, it can be seen that the BOD_5 index decreases during the first 14 minutes and then oscillates around one value until the end of the exposure time. The efficiency of pollutant removal amounted to 55% at the end of the exposure time. During the first 7 minutes of irradiation, the efficiency of removing biodegradable compounds was 34%. An additional 35 minutes were necessary to achieve this efficiency for the photolysis process. To obtain the same effects (55% of degradation) photolysis should be carried out for 48 minutes, whereas through catalysis it only takes 14 minutes. The final results are considered to be relatively satisfactory.

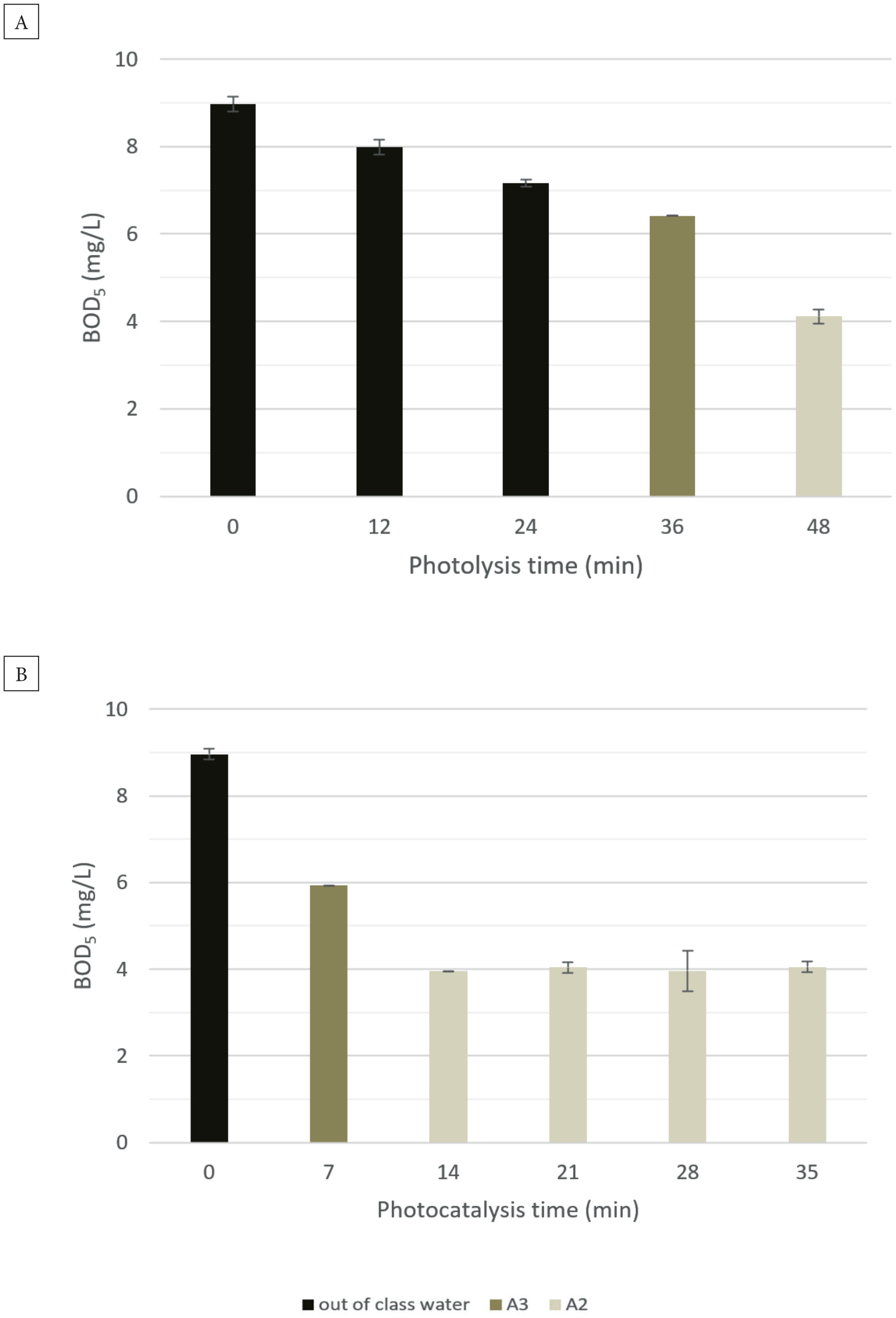

Fig. 2. *Variations of BOD over time during UV photolysis (A) and UV photocatalysis with* TiO_2*-MMT catalyst (B) with the assignment of water quality categories*

They show that the classic UV irradiation itself is able to improve the water quality, as proved by a significant decrease in the BOD_5 value. Nevertheless, the initial stage of irradiation did not bring any surprising results. The slow decrease in the BOD_5 value up to 36 minutes may be due to initially small amounts of hydroxyl radicals. However, photocatalysis not only gives better results, but also purifies water in a superior way through the AOP method. Less than a quarter of an hour is enough to reduce the number of organic compounds by more than half. Achieving satisfactory results in a shorter time span is a tremendous advantage.

Many studies conducted on the photolysis of organic compounds indicate that this process occurs slowly due to the fact that many organic pollutants being difficult to remove (Pereira et al. 2007, Vilhunen et al. 2010, Wang et al. 2020). One of the examples is the research conducted on the removal of perfluorinated organic compounds (POC), which was carried out using a mercury lamp with similar parameters to the lamp used in our study. The POC half-life for these conditions was 24 hours (Książek et al. 2015). Also, the research conducted on the decomposition of sodium dodecylbenzene sulphonate shows that this decomposition practically does not take place during the photolysis process itself (Perkowski et al. 2008). In the case of polycyclic aromatic hydrocarbons, irradiation with the use of a xenon lamp allowed for the degradation of these compounds only in 33%. The reactive oxygen content increased the degradation efficiency to 69% (Xia et al. 2009). Bisphenol compounds react in differently to direct UV photolysis. As a result of the experiment involving irradiation of water enriched with eighteen bisphenols, these compounds can be divided into three groups: highly removable (>94%), moderately removable (50–80%) and poorly removable (25–45%) (Kovačič et al. 2019). Other contaminants found in surface waters are pharmaceuticals. Among them, we can distinguish diclofenac and ibuprofen, which are the most popular non-steroidal anti-inflammatory drugs. As a result of irradiating water with the addition of the above-mentioned compounds, the following results were achieved. The irradiation removed 88% of ibuprofen in 30 minutes and over 82% of diclofenac in 60 minutes. Nevertheless, the photocatalytic degradation gave the same results in less than 10 minutes (Kocot & Dyrda 2015). Other organic compounds that are degraded from water by photocatalysts with TiO_2-MMT under UV light are dyes. Their removal from water is 97% for crystal violet, 93% for methylene blue and 80% for Rhodamine B (Djellabi et al. 2015). Subsequent studies on the removal of Rhodamine B from water show that the use of the same catalyst as in our experiment, but lamps with twice the power allow the pollution to degrade by as much as 92% after 100 minutes of exposure (Butman et al. 2020). The legitimacy of the use of TiO_2-MMT as a photocatalyst is confirmed by studies on phenol removal. The removal efficiency of this compound for TiO_2-MMT catalyst was 89%. It is not only better by 12% than MMT alone, but also 59% more effective than pure TiO_2 (Li et al. 2022).

According to the data presented in Figure 2, at the beginning of our experiment, the value of the BOD_5 index in the raw water taken from the Rudawa River was almost 9 mg/L, which, as already mentioned, puts it as out of class in terms of quality of water. Water quality improves only after 36 minutes of photolysis. Along with the subsequent intervals of the experiment, the water quality increased. After 48 minutes, BOD_5 was below 5 mg/L, and thus the water could be classified as the A2 class (*Rozporządzenie*… 2002). In the case of UV photocatalysis with the TiO_2-MMT catalyst, the improvement of the water quality takes place after 7 minutes of photocatalysis, allowing the water to be classified as class A3. As the experiment progressed, the water quality remained the same, with BOD_5 oscillating around a value of 4 mg/L, so the water was classified as A2 (*Rozporządzenie*… 2002). Our research shows that the simplest technique, which is UV photolysis, can influence the quality of drinking water. Nevertheless, the combination of AOP processes such as photocatalysis are more efficient. The use of the TiO_2-MMT photocatalyst and UV radiation seems to be a good pre-treatment process for water that can ultimately be used for human consumption. Less than a quarter of an hour is enough to significantly raise the water quality class in relation to BOD_5.

Reaction kinetics

During the photodegradation of organic compounds and also photocatalysis, only the AOP process should not be taken into account, because many complex reactions take place simultaneously, e.g. radical chain reactions. This makes it difficult to establish the exact course of the kinetics for the removal of biodegradable compounds. Therefore, the kinetics of the zero-order, first-order and second-order reactions as well as the BMG (Behnajady–Modirshahla–Ghanbery) kinetic model were analysed in order to best reflect the kinetic model of the AOP processes.

The kinetic equations of the individual reactions are as follows:

– the zero-order reaction (Bain et al. 2018):

$$c_t - c_0 = -k_0 t \tag{2}$$

– the first-order reaction (Doll & Frimmel 2003, Bubev et al. 2016, Baena-Nogueras et al. 2017):

$$\ln(c_t) = -k_1 t + \ln(c_0) \tag{3}$$

– the second-order reactions (Adak et al. 2005):

$$\frac{1}{c_t} = \frac{1}{c_0} + k_2 t \tag{4}$$

– the BMG kinetic model (Behnajady et al. 2007):

$$\frac{c_t}{c_0} = 1 - \frac{t}{m+b} \tag{5}$$

where:

c_t – concentration of organic compounds at time t,

t – AOP time [min],

k_0, k_1, k_2 – reaction rate constant [min^{-1}],

c_0 – initial concentration of organic compounds,

m, b – two characteristic constants relating to the reaction kinetics and oxidation capacities. Plotting $t/(1 - c_t/c_0)$ as a function of t, a straight line was obtained with the intersection of m and the slope of b.

As a measure of the concentration of organic substances, the value of the BOD_5 index was adopted, which determines the total concentration of organic compounds in water. The kinetic curves of the photolysis and photocatalysis process are shown in Figure 3.

The k-rate constants for the first order kinetic model for photocatalysis are higher than for photolysis. The reaction of photocatalytic degradation of biodegradable pollutants in the water from the Rudawa River is faster than in the photolysis. A similar relationship is observed in the second order kinetic model. The coefficient of determination (R^2) for both the first and second order reactions are relatively low, respectively 0.8773 and 0.8009 for photolysis and 0.6718 and 0.6844 for photocatalysis. The highest value of the coefficient of determination for photolysis was obtained for the zero-order reaction. The kinetic reaction rate constant k and the correlation coefficient R were calculated according to the Formula (2). They are equal $k = 0.094\ \text{min}^{-1}$ and $R^2 = 0.9408$. The half-life of BOD_5 was also calculated. Its value was obtained equal to 10 minutes. For photocatalysis the best correlation was obtained for the BMG kinetic model. According to Formula (5) $1/b = 0.5820$ and $R^2 = 0.9816$. The reciprocal of the constant b is the theoretical maximum removal of impurities, which is equal to the maximum oxidation capacity. Taking into account the value of $1/b$ and the calculated efficiency of the photocatalysis process presented in a decimal fraction and amounting to 0.56, we can assume that these values coincide. This would mean the compliance of the BMG kinetic model used in describing the kinetics of degradation of organic pollutants on the basis of changes in the BOD_5 index value in the photocatalysis process. According to literature reports, the BMG kinetic model for the degradation of pollutants by AOPs methods correlates best with the data. This is confirmed by the research of Ertugay & Acar (2017), who dealt with the degradation of the dye in the Fenton oxidation process. For their experiment, the BMG kinetic model provided the best correlation of the experimental data used compared to the pseudo-first and second-order kinetic models (Ertugay & Acar 2017). The same conclusions were obtained by Tunç et al. (2012), who dealt with the change in the amount of dyes in water as a result of degradation by the Fenton reaction.

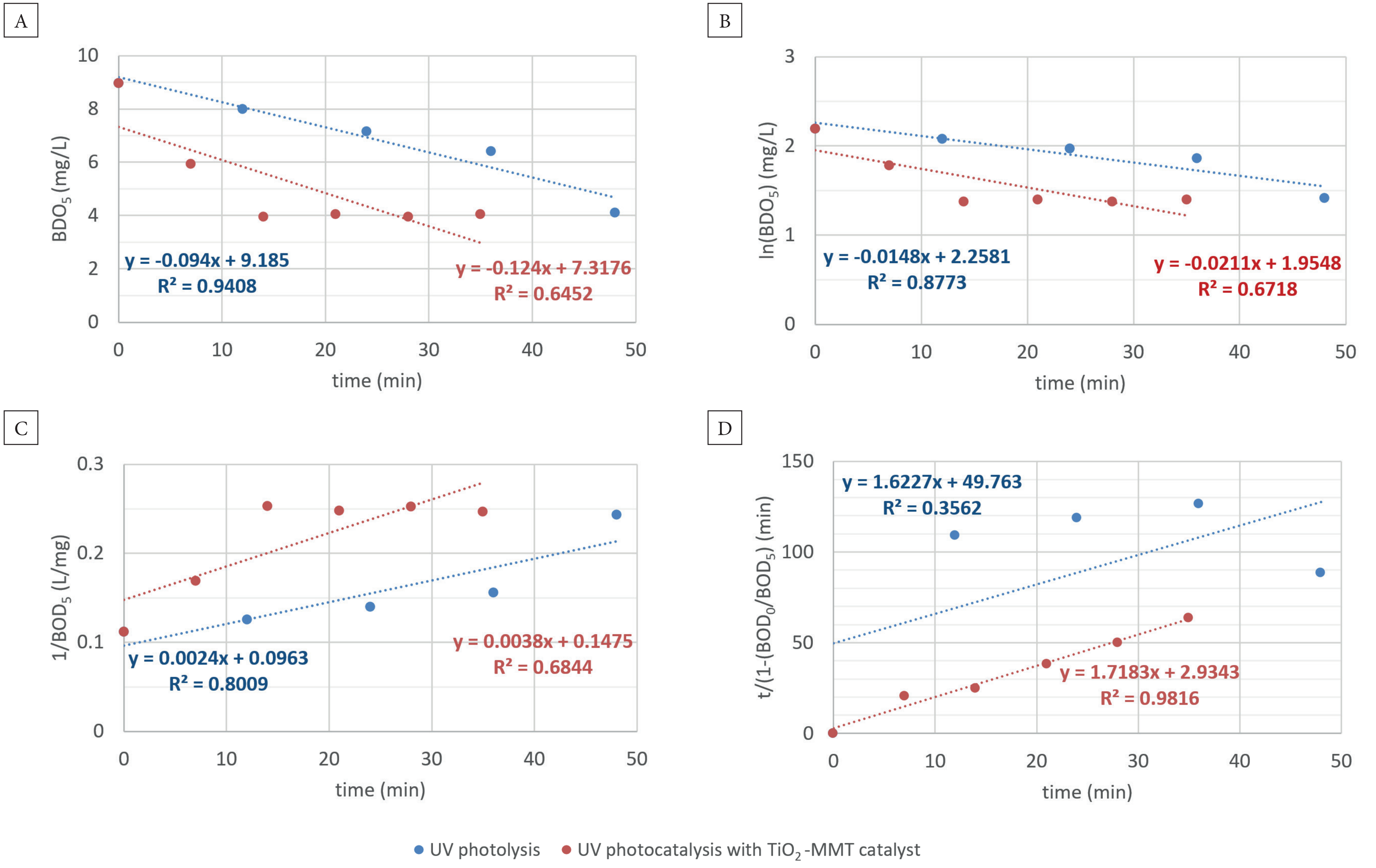

Fig. 3. *The kinetics of degradation of biodegradable pollutants based on changes in the BOD_5 index value of the photolysis and photocatalysis processes carried out zero-order reaction (A), first-order reaction (B), second-order reaction (C), and BMG kinetic model (D)*

CONCLUSION

The conducted research focused on the evaluation of the effectiveness of two AOP methods, i.e., UV photocatalysis and UV photocatalysis with use of immobilized TiO_2-MMT. The BOD_5 index was measured for the water taken from the Rudawa River, which was subsequently subjected to treatment using selected AOP techniques. Photolysis allowed the reduction of organic pollutants in over 50% within 48 minutes. The same effect for photocatalysis was obtained after 14 minutes. Continued photocatalysis for the next 21 minutes did not cause a significant drop in the BOD_5 index. The experimental kinetic data are represented well by Behnajady–Modirshahla–Ghanbery model that performs better than the zero-order, first-order and second-order kinetics reactions.

Taking into account the biological oxygen demand, water taken from the river can be classified as out of class water, in accordance with Polish legislation. The discussed AOP techniques allow for the partial treatment of water for human consumption. Photocatalysis gives better results, because after only 14 minutes the water increases its quality to class A2 (water requiring typical physical and chemical treatment, in particular pre-oxidation, coagulation, flocculation, decantation, filtration, disinfection (final chlorination)). These methods are believed to have the potential for use in water treatment plants. Not only do they give good results in a short time, but the simplicity and ease of handling is an additional advantage.

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