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Wojciech Zmudziński, Tomasz Pawłowski

Poznań University of Economics and Business, Faculty of Commodity Science, Department of Food Commodity Science

Corresponding author: Tomasz Pawłowski, tomasz.pawlowski@ue.poznan.pl

PHOTOCATALYTIC PROCESSES IN ENVIRONMENTAL PROTECTION – DEGRADATION OF ANTHOCYANINS (E163 WS) ON ILLUMINATED TIO$_2$

Abstract: The research results on the possibility of anthocyanins' traces degradation – obtained from *Vitis vinifera* L. grapes peel (commercial colouring agent E163 WS) contained in water (sewage) are presented in this paper. Experiments were conducted in the model photocatalytic systems: UV/E163/H_2O/TiO_2 and UV/E163/H_2O. The level of the colour degradation was estimated on spectrophotometric measurements. The amount of mineralized colour in UV/E163/H_2O/TiO_2 system was inversely proportional to the initial concentrations in the examined solution. The E163 colourant loss expressed as absorbance decrease of tested solutions, which was a result of photocatalytic degradation ranged from 40% to 88%, depending on the initial concentration of colourant in the solution. On the basis of the conducted kinetics analysis it was found that in the range of the studied concentration of E163 WS colourant the photocatalytic process reveals substantial deviations from the generally accepted Langmuir-Hinshelwood model. This is among others due to the so-called a homogeneous photodegradation of substrate (in UV/E163/H_2O system) – 45–68% in relation to the process occurring in the heterogeneous system, UV/E163/H_2O/TiO_2. The examined conduction of variations in pH during illumination showed the formation of acid derivatives of anthocyanins photooxidation. The research results indicate that photocatalytic processes belonging to so-called advanced oxidation processes (AOP) may constitute an alternative to the traditional methods for sewage treatment of the food industry.

Keywords: water quality, photocatalysis, photolysis, TiO2, anthocyanins, E163 WS.

JEL classification: Q25, Q29, Q53, Q59.

PROCESY FOTOKATALITYCZNE W OCHRONIE ŚRODOWISKA – DEGRADACJA ANTOCYJANÓW (E163 WS) NA NAŚWIETLANYM TIO$_2$

Streszczenie: W prezentowanym artykule przedstawiono wyniki badań nad możliwością degradacji śladowych ilości antocyjanów – ze skórek winogron *Vitis vinifera* L. (barwnik handlowy E163 WS) zawartych w wodzie (ściekach). Eksperymenty prowadzono w modelowych układach fotokatalitycznych: UV/E163/H_2O/TiO_2 oraz UV/E163/H_2O. Stopień degradacji barwnika określano na podstawie pomiarów spektrofotometrycznych. Ilość zmineralizowanego barwnika w układzie UV/E163/H_2O/TiO_2 była odwrotnie proporcjonalna do jego początkowego stężenia w badanym roztworze. Ubytek barwnika E163, wyrażany spadkiem absorbancji badanych roztworów spowodowanej degradacją fotokatalityczną, wyniósł od 40% do 88%, w zależności od początkowego stężenia barwnika w roztworze. Na podstawie przeprowadzonych badań kinetycznych stwierdzono, że w badanym zakresie stężeń barwnika E163 WS proces fotokatalityczny wykazuje odstępstwa od ogólnie przyjętego modelu Langmuira-Hinshelwooda. Powodem tego zjawiska jest m.in. duży udział tzw. homogenicznej fotodegradacji substratu (w układzie UV/E163/H_2O) (45–68%) w stosunku do procesu zachodzącego w układzie heterogenicznym, UV/E163/H_2O/TiO_2. Zbadany przebieg zmian pH podczas naświetlania wykazał tworzenie się pochodnych kwasowych fotoutleniania antocyjanów. Wyniki przeprowadzonych badań wskazują, że procesy fotokatalityczne, należące do tzw. procesów zaawansowanego utleniania (AOP, Advanced Oxidation Processes) mogą stanowić alternatywę dla tradycyjnych metod oczyszczania ścieków przemysłu spożywczego.

Słowa kluczowe: jakość wody, fotokataliza, fotoliza, TiO_2, antocyjany, E163 WS.

Introduction

Food industry plants consume large amounts of water, thereby generating significant amounts of wastewater. Wastewater should be properly cleaned and contamination disposed of. Water consumption and the amount of wastewater generated by food plants in Poland in 2009–2013 are shown in Table 1.

Table 1. Water consumption and the amount of waste produced by the food industry in Poland

	2009	2010	2011	2012	2013
Water consumption [mln m^3]	97.6	98.2	102.0	105.6	104.5
Volume of generated wastewater [mln m^3]	80.5	83.4	82.2	85.3	84.7

Source: Based on: [GUS 2010, 2011, 2012, 2103, 2014].

Postproduction wastewater from the food industry is heavily polluted. It includes organic pollutants – proteins, fats, carbohydrates, and inorganic – chlorides, sulphates, phosphates, nitrogen and other elements [Konieczny and Szymański 2004, 2007; Kasztelan 2008]. The components of wastewater are also natural dyes, especially from sites where they are used as additives in food. Wastewater containing dyes is usually purified using biological processes, flocculation, coagulation, adsorption on activated carbon, as well as chemical oxidation. Wastewater treatment is carried out directly in the area of the industrial plant or, after proper pre-treatment, is directed to a dedicated sewage treatment plant [Konieczny and Szymański 2007, 2008].

For a long time, some hope in wastewater and water treatment associated with the so-called Advanced Oxidation Processes – AOP, which include chemical, photochemical and photocatalytic processes [Legrini, Oliveros, and Braun 1993; Sobczyński and Dobosz 2001; Kusic, Koprivanac, and Bozic 2006]. Most of the AOP reactions are carried out at ambient temperature [Gogate and Pandit 2004]. In the case of photocatalytic processes occurring in an aqueous medium, on the surface of the semiconductor induced by light radiation of suitable energy (in the case of TiO_2 > 3.2 eV) the hydroxyl radicals are formed ($^{\cdot}OH$). These radicals by direct contact with an organic compound cause its oxidation; often complete mineralization, i.e. to CO_2 and H_2O. Oxidation of organic compounds, leading to their total mineralization, is a multistep process consisting of a plurality of single-electron redox reactions [Bard 1979; Sobczyński, Duczmal, and Dobosz 1999; Gaya and Abdullah 2008]. The mechanism of the oxidation of organic compounds in the presence of a solid photocatalyst (TiO_2) can be summarized in five steps [Chong et al. 2010]:

- diffusion of the organic compound solution to the surface of the photocatalyst,
- its adsorption on the surface of TiO_2, activated with radiation energy,
- photocatalytic reactions in the adsorbed phase,
- desorption of the reaction products from the surface of TiO_2,
- diffusion of the reaction products from the semiconductor surface to a solution.

Currently, the best semiconductors (photocatalyst) used in the process of the mineralization of organic compounds is regarded to be titanium dioxide. Compared to other semiconductors used in photocatalysis, it is distinguished by low price, lack of toxicity, indifference to the environment, chemical and photochemical stability, stability in a wide pH range and high photocatalytic activity [Grzechulska-Damszel et al. 2006; Iino et al. 2006; Chang et al. 2009].

The processes taking place at the exposed surface of titanium dioxide, resulting in the final result to mineralization of organic compounds constituting contamination of water are shown schematically in Figure 1.

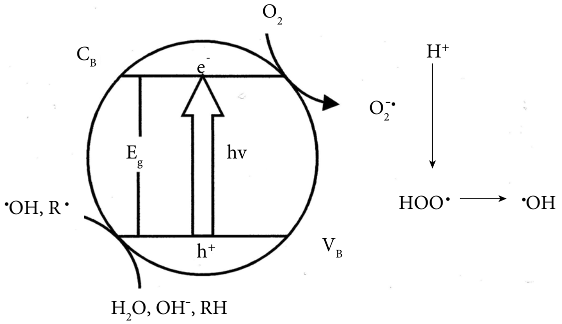

Figure 1. Diagram of the processes occurring during exposure of TiO_2

Source: Based on: [Sobczyński and Dobosz 2001; Robert and Malato 2002; Grzechulska-Damszel et al. 2006]

It is assumed that the photocatalytic oxidation of organic water pollutants takes place in accordance with the Langmuir-Hinshelwood model [Okamoto et al. 1985; Turchi and Ollis 1990]. According to this model, photooxidation process in liquid-solid system consists of the reaction between the molecules of substrate adsorbed on the surface of the photocatalyst and the hydroxyl radicals generated by the photochemical method. The speed of the process depends on the rate of the reaction radical – adsorbed molecule and is directly proportional to the concentration of the substrate adsorbed on the surface of the photocatalyst (which in turn is directly proportional to the concentration of the solution) – a I-row reaction. The linear form of Langmuir-Hinshelwood equation takes the following form [Zmudziński, Sobczyńska, and Sobczyński 2007]:

$$\frac{1}{r} = \frac{1}{k \cdot K_{ads}} \cdot \frac{1}{c_0} + \frac{1}{k},$$

where:

c_0 – the substrate concentration in water,
k – a rate constant,
K_{ads} – a constant of adsorption equilibrium.

A too high concentration of the oxidized substrate can, however, result in a strong decrease in the rate of photocatalytic oxidation reaction, or even completely inhibit the process. The reason may be, for example, strong adsorption of certain intermediates on the surface of the photocatalyst or the mutual organic reaction products of the forming organic radicals (*OH + organic molecule → organic radical) [Sobczyński, Gimenez, and Cervera-March 1997; Dobosz and Sobczyński 2003].

The aim of the research was to examine the applicability of the UV/TiO_2 and UV/H_2O processes to improve water quality in model systems containing commercial dye E163 WS (anthocyanins from grape skins *Vitis vinifera* L.). The research is a continuation of research work carried out in the Department of Food Commodity Science at Poznań University of Economics and Business, concerning the applicability of heterogeneous photocatalysis processes in the degradation of food industry waste.

1. Experimental

Photocatalytic tests carried out using aqueous solutions of the dye E163 WS containing 3% of active staining ingredient (manufacturer: Wytwórnia Aromatów Spożywczych „Hoffman"). In all photocatalytic experiments, 230 cm^3 of solution with proper concentration of the dye was mixed with 0.05 g TiO_2 (99.9%, Aldrich, anatase) and treated with ultrasonic waves for 10 minutes to obtain a homogeneous mixture. The mixture was placed in a glass reactor with periodic activity (Pyrex, volume of 250 cm^3), designed by Sobczyński and co-workers [Sobczyński, Gimenez, and Cervera-March 1997]. Such a reactor was used previously in studies of the photocatalytic degradation processes of pollutants of organic food industry waste [Zmudziński 2009, 2011, 2012]. Photocatalytic reactions were performed for 75 minutes. The mixture was stirred with an air stream, properly oriented, with a flow rate of 50 $cm^3 \cdot min^{-1}$. The reaction mixture was pre-aerated for 15 minutes. The reactor was illuminated from one side with two xenon lamps 300 W (Osram), located at a distance of 50 cm from the reactor. The distance between the lamps was 100 cm. The temperature of the reactor, cooled with an external air stream was 30 ± 1°C.

For the purpose of kinetic calculations, during the process of photodegradation, one taken from the reactor (every 15 minutes) a suitable amount of the reaction mixture to measure the absorbance by spectrophotometry was used. Before measuring absorbance, the sampled reaction mixture was filtered using a filter having a pore size 0.22 μm (PTFE, BGB Analytik AG). Measuring absorbance at a wavelength of 526 nm (maximum absorption of the dye

E163 WS defined experimentally) was performed using a spectrophotometer Genesys 6 (Thermo Spectronic).

In the case of studies performed in the system UV/H_2O (homogeneous photolysis) solutions were irradiated with the same concentrations as in the case of the photocatalytic experiments.

During all the tests, both the photocatalytic and photolytic, the degradation of the dye E163 WS, pH measurements were made for irradiated solutions every 15 minutes (Mettler Toledo MPC 227).

Each photocatalytic experiment was repeated at least twice, the absorbance of each sample was also conducted at least twice. In all of the experiments, double-distilled water in a quartz glass distiller was used. The photocatalyst titanium dioxide had a surface area equal to $11.9\ m^2 \cdot g^{-1}$, which was measured with the BET method on a Micromeritics ASAP 2010 apparatus.

2. Results and discussion

In the photocatalytic experiments E163 WS dye was used which consists of anthocyanins extracted from the skins of grapes *Vitis vinifera* L. It was necessary therefore, to appoint a light wavelength at which the dye is characterized by the highest absorbance. On the basis of the prepared spectrophotometric method absorption spectrum (in the range of 400 nm to 700 nm) it was stated that the VIS radiation wavelength which occurs at the maximum absorbance is 526 nm. All the spectrophotometric measurements made during tests were carried out for this wavelength.

As previously mentioned, the tests were carried out in a specially designed three-phase reactor, in which the contents were mixed with a properly directed air stream [Sobczyński, Gimenez, and Cervera-March 1996; Sobczyński, Duczmal, and Zmudziński 2004]. The possibility of using the reactor in kinetic experiments was examined in previous research [Zmudziński, Sobczyńska, and Sobczyński 2007]. Photocatalytic oxidation reactions of the dye E163 WS were performed at a substrate concentration of respectively: $2.46 \cdot 10^{-2}$; $2.82 \cdot 10^{-2}$; $3.24 \cdot 10^{-2}$; $3.81 \cdot 10^{-2}$ and $4.50 \cdot 10^{-2}\ g \cdot dm^{-3}$. Changes in substrate concentration depending on the time of exposure are shown in Figure 2.

The presented curves were used to determine the initial rate of reaction (r_0), by matching to each of them an ordinary exponential function $f(t) = Ae^{-kt}$ (for that purpose one used the Solver tool, being a part of Microsoft Excel) and calculations of the reaction rate for $t = 0$. The use of the initial reaction rate enables to omit the effect of forming during the photo-oxidation process

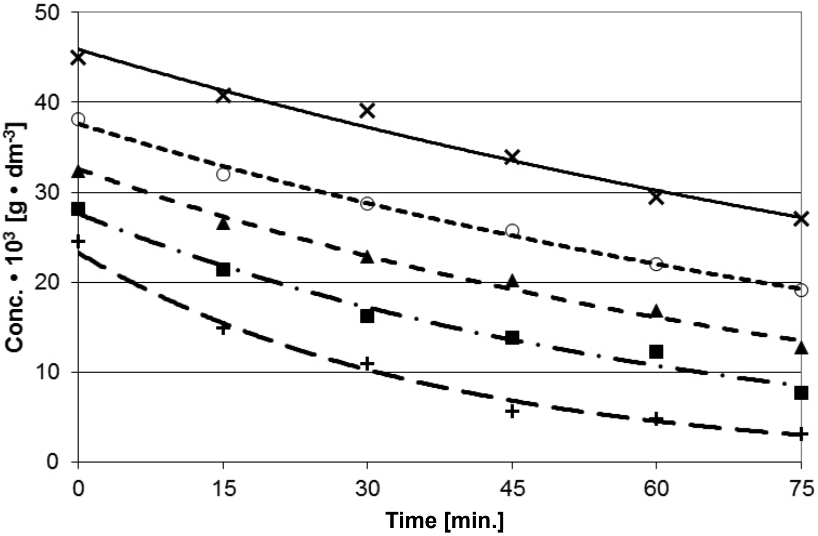

Figure 2. Kinetic curves of E163 WS delay *versus* time

intermediates on the reaction rate of the main substrate (anthocyanins included in the dye E163 WS). The values of the initial reaction rates with regard to the corresponding initial concentration of the photodegraded substrate are presented in Table 2.

Table 2. Initial reaction rates of E163 WS photodegradation

Substrate concn. $[g \cdot dm^{-3}]$	Initial reaction rate $r_0 [g \cdot dm^{-3} \cdot s^{-1}]$
2.46×10^{-2}	11.8×10^{-6}
2.82×10^{-2}	7.28×10^{-6}
3.24×10^{-2}	6.12×10^{-6}
3.81×10^{-2}	5.61×10^{-6}
4.50×10^{-2}	5.16×10^{-6}

Based on the calculated initial reaction rates (Table 2) one plotted the curve defining the relationship $1/r_0$ from $1/c_0$ for the reaction (dependence resulting from the Langmuir-Hinshelwood equation, see *Introduction*), which can be seen in Figure 2. According to this model, the relationship should be a straight-line for the I-row reaction. As already mentioned, the photocatalytic oxidation process of the vast majority of the organic compounds present in the water takes place in accordance with the kinetics of the I-row reactions [Okamoto et al. 1985; Turchi and Ollis 1990; Sobczyński and Dobosz 2001].

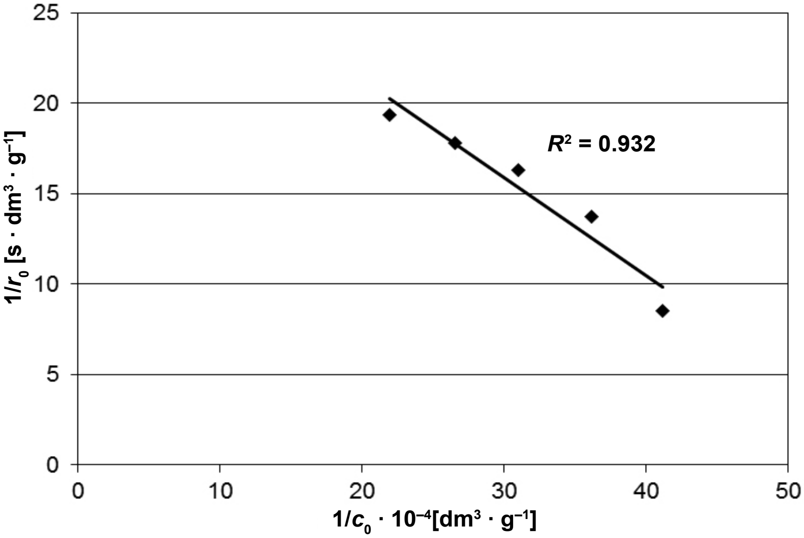

Figure 3. Plot $1/r_0$ *vs.* $1/c_0$ for E163 WS

As shown in Figure 3, the resulting relationship is rectilinear, with a high index of determination $R^2 = 0.932$, however, it shows an inverse relationship in relation to the assumptions of the Langmuir-Hinshelwood model: indicates the inhibition of the photocatalytic reaction rate with increasing substrate concentration in the solution. There may be several reasons for the observed phenomenon; two of them are mentioned in the *Introduction*.

Table 3 shows the results obtained by 75-minutes of irradiation of the aqueous solutions of the E163 WS dye in the presence of TiO_2 and in the system UV/H_2O (photolytic process). Experiments in the system UV/H_2O were conducted in order to determine the share of direct photolysis process in photocatalytic oxidation of the tested substrate.

From the data presented in Table 3 the results are that during the 75-minutes irradiation of aqueous solutions in the presence of the substrate TiO_2 both a photocatalytic reaction and a homogenous photocatalysis of E163 WS occur. In the presence of TiO_2 a decrease in absorbance is, depending on the concentration of the starting solution, from about 40% for the solution with the highest concentration to over 87% for the least concentrated solution, wherein the absolute amount of oxidized dye also decreases with the increase of its concentration in solution. The process of photodegradation of the substrate over the range of concentrations tested is inversely proportional to the initial content of the solution. During 75-minutes of exposure of the solution

Table 3. The degradation of E163 WS during 75-minutes of illumination of 230 cm^3 of the solution in the presence of TiO_2 and UV/H_2O

Concentration of E163 WS	Absorbance decrease [%]		Degradation of E163 WS [g]	
[g · dm^{-3}]	TiO_2	UV/H_2O	TiO_2	UV/H_2O
1	2	3	4	5
$2.46 \cdot 10^{-2}$	87.2 ± 1.0	28.8 ± 3.2	0.0214	0.0069
$2.82 \cdot 10^{-2}$	72.5 ± 1.0	26.1 ± 3.8	0.0204	0.0071
$3.24 \cdot 10^{-2}$	60.7 ± 1.1	26.5 ± 7.4	0.0197	0.0083
$3.81 \cdot 10^{-2}$	50.0 ± 6.5	22.2 ± 3.9	0.0191	0.0085
$4.50 \cdot 10^{-2}$	39.8 ± 0.9	21.9 ± 3.8	0.0179	0.0100

without suspension of TiO_2, E163 WS is also subjected to the process of oxidation, except that to a much lesser extent, from about 22% for the solution with the highest concentration to almost 29% for the least concentrated solution. However, unlike in the presence of titanium dioxide, the amount of oxidized dye increases with the increase of its concentration in the solution. The process of photo-oxidation of substrate over the range of concentrations tested is directly proportional to the initial content in the solution, indicating that the reaction in system UV/H_2O takes place in accordance with the kinetics of the first-order reaction. The dependence of the amount of dye photodegradated during 75-minutes exposure in the presence of TiO_2 and without the additive, from its initial concentration is shown in Figure 3.

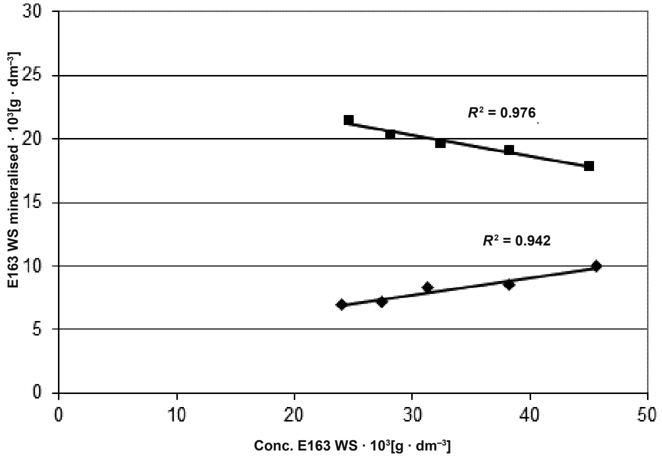

Figure 4. The dependence of the amount of E163 WS photodegradated in the presence of TiO_2 and without TiO_2 after 75-minutes illumination *vs.* initial concentration

The presented data indicates that inhibition of the photocatalytic reaction on the surface of titanium dioxide with increasing concentration of E163 WS in the solution is much higher than indicated by the results obtained for irradiation in the presence of TiO_2 (cf. figures in columns 4 and 5 of Table 3). However, the exact calculation is not feasible because the direct photolysis of the dye in the presence of titanium dioxide can be lower than the data shown in column 5 of Table 3. The reason is the shielding of the part of the solution by the suspended TiO_2, and the scattering of light by the photocatalyst.

As already mentioned in the *Experimental* part, during the experiments of photocatalytic degradation of the dye one measured the pH of irradiated solutions in 15-minute sequences. The results are shown in Figure 5. On the basis of the conducted measurements, it can be concluded that the photocatalytic degradation of anthocyanins contained in the dye E163 WS leads to the formation of acidic products – within 75-minutes exposure of solutions the pH decreases from values close to 3.6 ÷ 3.7 to a pH in the range 3.3 ÷ 3.6 (Figure 4).

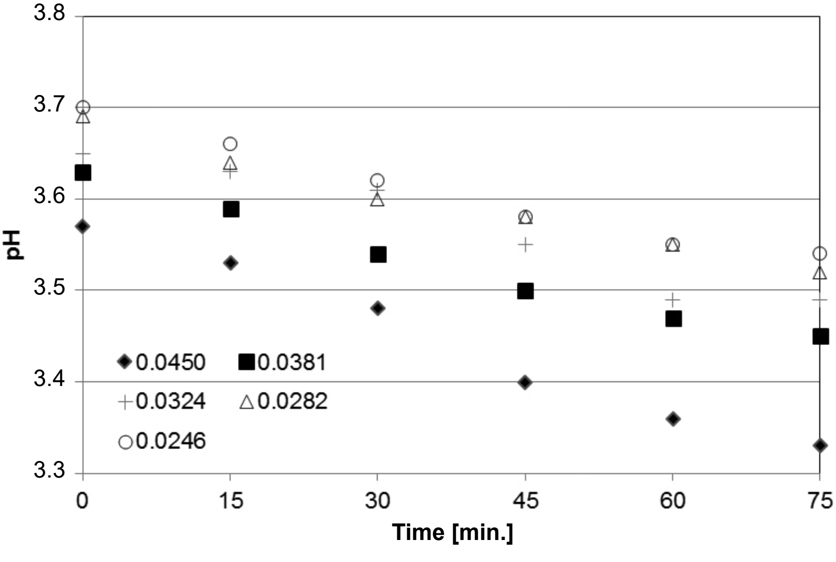

Figure 5. The changes of pH during 75-minutes of illumination of E163 WS solutions in the presence of TiO_2, substrate concentration 0.0246, 0.0282, 0.324, 0.0381, 0.0450 [$g \cdot dm^{-3}$]

In the case of studies conducted in the system UV/H_2O one also observed a decrease in the pH of the irradiated solution, while the rate of pH decline was lower than in the case of a UV/TiO_2 (see Figure 6).

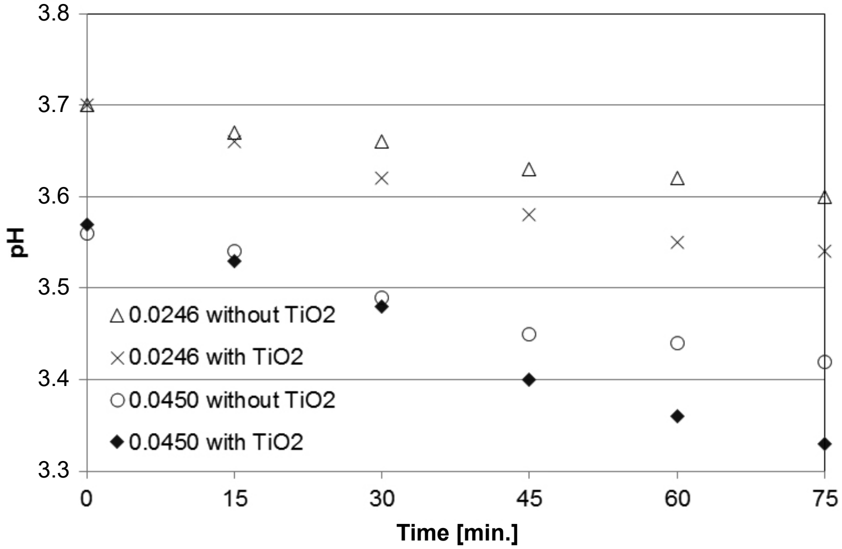

Figure 6. The changes of pH during 75-minutes of illumination of E163 WS solutions in the presence of TiO_2 and without TiO_2 for the selected substrate concentrations, 0.0246 and 0.0450 [g · dm^{-3}]

According to the literature, the oxidation of pollutants in the treated water in the presence of TiO_2 occurs predominantly by a reaction with forming hydroxyl radicals. The direct oxidation of organic compounds through the generated electron holes can occur only in the concentrated solutions and in the case of strong adsorption of the substrate on the surface of TiO_2 [Lawless, Serpone, and Meisel 1991; Stafford, Gray, and Kamat 1994]. In the case of very dilute solutions used in these experiments (the highest concentration of dye in the irradiated solution does not exceed 0.045 g · dm^{-3}) one should expect the participation of OH radicals in the occurring reactions. The study shows that during the process of photodegradation in the presence of a catalyst such as TiO_2, and without its addition, reactions occur which leads to the formation of intermediates that are acidic in nature. Formation of acidic intermediates during the processes of photodegradation of the tested dye in the presence of TiO_2, is due to the reaction between the dye and the hydroxyl radicals formed on the surface of the treated TiO_2. Very susceptible to oxidation reaction are hydroxyl groups (present in the structure of the flavin cation of anthocyanins), in which oxidation leads to the formation of the carbonyl group. Hydroxyl radicals attack the formed carbonyl group and this leads to the creation of a carboxyl group (–COOH). In the process of photodegradation without the presence of the photocatalyst TiO_2 (photolysis process) acidic intermediates are also formed, as shown by results of measurements of the pH of the irradiated solutions.

Conclusions

In the experiments on the possibility of using photocatalytic and photolytic processes to protect the environment, especially water, carried out in model systems containing dye E163 WS, it was found that anthocyanins present in the water are oxidized both in the presence of titanium dioxide and without the additive. In the concentration range of $2.46 \cdot 10^{-2}$ to $4.50 \cdot 10^{-2}$ $g \cdot dm^{-3}$ the efficiency of the process of photodegradation of anthocyanins contained in the product under the name E163 WS is inversely proportional to their concentration in the solution. The dye is oxidized in the process of direct photolysis, but its degradation is lower compared to the degradation that occurs in the photocatalytic process. On the basis of the conducted kinetic experiments, it was found that the process of photocatalytic degradation of dye E163 WS over a range of concentrations of the substrate has a derogation from the generally accepted Langmuir-Hinshelwood model. The observed changes in pH during the process of photodegradation of E163 WS indicate the formation of acid derivatives during the tested photooxidation processes.

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