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IMPACT OF THE WATER COMPOSITION
ON THE DEGRADATION KINETICS OF NATURAL ORGANIC
MATTER IN PHOTOCATALYTIC MEMBRANE REACTORS

Decomposition kinetics of natural organic substances during the photocatalytic process with a semi-conductor TiO_2 has been investigated. In the study, a laboratory reactor Heraeus and in a photocatalytic membrane reactor were used. Simulated solutions of deionized water, surface water and fulvic acids, differing in composition, were tested in the experiment. In order to determine reaction rate constants, the Langmuir–Hinshelwood kinetic model based on the first order reaction was applied. It was found that photocatalytic process enabled effective degradation of natural organic substances although its run was affected by inorganic ions, mainly those producing water hardness, present in water.

1. INTRODUCTION

Sufficient and highly effective removal of natural organic matter (NOM) from water during its treatment is a very important topic in water technology. Basic NOM components are humic substances, including fulvic and humin acids. The presence of NOM in purified water directed to disinfection results in formation of harmful halogenated organic disinfection byproducts (DBPs) [1]. A promising method of NOM removal from water is photocatalysis which has recently become a subject of interest of many researchers. It was mainly due to its high effectiveness and no side streams formation. The mechanism of the process is based on transient in-situ generation of highly reactive $OH^\bullet$ radicals responsible for the mineralization of organic compounds, water pathogens and disinfection byproducts [2]. The combination of photocatalytic process with membrane filtration in so-called hybrid system has also

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become a popular water treatment method [3–7]. One of the most interesting devices, in which both processes are performed, is photocatalytic membrane reactor (PhMR). In such a device a photocatalyst can be present in the form of suspension being easily separated from the purified stream with a membrane immersed in the reaction chamber [2, 8].

In many studies on the degradation of natural organic compounds with the use of photocatalysis, negative or the positive impact of inorganic ions, e.g. Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- on the process is the subject of the interest [9]. Very interesting conclusions, however, often differ from each other, depending on the type of contaminants present in water as well as on their interactions. The results of the studies performed by many researchers indicate that at certain conditions the presence of positive ions may improve the degradation of organic compounds during photocatalysis, however those ions may become process inhibitors as well [10, 11]. Negative ions generally cause the decrease of the photocatalytic decomposition rate of organic compounds [9]. The knowledge on the impact of inorganic ions but also of other factors on the effectiveness of photocatalysis is very important for proper configuration of photocatalytic reactors operation.

The aim of the presented study was to determine the effect of the chemical composition of water on the kinetics of decomposition of natural organic substances during photocatalysis in various photocatalytic reactors.

2. EXPERIMENTAL

Waters. Simulated solutions of fulvic acids in deionized water and tap water as well as in surface waters were used in the study. The characteristics of investigated organic substances and waters is shown in Tables 1 and 2.

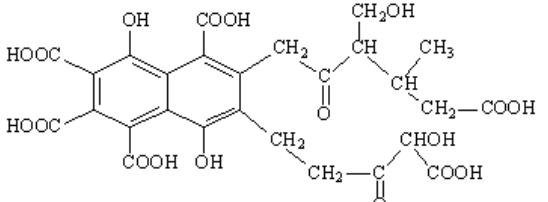Table 1

Characteristics of fulvic acid

Chemical formula	Properties
	Powdered fulvic acid by Beijing Multigrass Formulation Co., Ltd. (China) The content of dry salts of fulvic acids ≥70%. pH range 5.5–6.5 Solubility in water ≥99% Moistness ≤10%

Characteristics of investigated waters

Indicator, unit	Simulated solution with FA				Surface water	
	Deionized water + FA		Tap water + FA		I	II
Dissolved organic carbon DOC, mg/dm^3	5.08	10.1	8.85	12.8	13.5	5.48
Absorbance, UV_{254}	15.9[b]	32.8[b]	18.6[b]	35.5[b]	27.0[b]	10.5[b]
SUVA[a], m^3/(g C·m)	3.12	3.23	2.10	2.78	2.00	2.22
Color, mg pt/dm^3	21[b]	44[b]	23[b]	48[b]	22[b]	9.0[b]
Turbitity, NTU	0.44	1.23	0.78	1.96	6.42	4.40
Temperature, °C	22		21		23	22
pH	7.40		7.40		7.95	7.08
Coductivity, µS/cm	16		769		328	187
Total hardness, mg CaCO$_3$/dm^3	0.00		440		140	82.0
Calcium, mg/dm^3	0.00		–		32.0	30.4
Chlorides, mg/dm^3	0.00		–		35.0	21.8

[a]Specific absorbance in UV, UV254/DOC.
[b]Prefiltered sample (0.45 µm).

Reactors. The photocatalytic processes were carried out in a laboratory reactor Heraeus of the volume of 0.7 dm^3 equipped with one UV lamp and in a photocatalytic membrane reactor (PhRM) of of the volume of 20 dm^3 equipped with two UV lamps (Fig. 1).
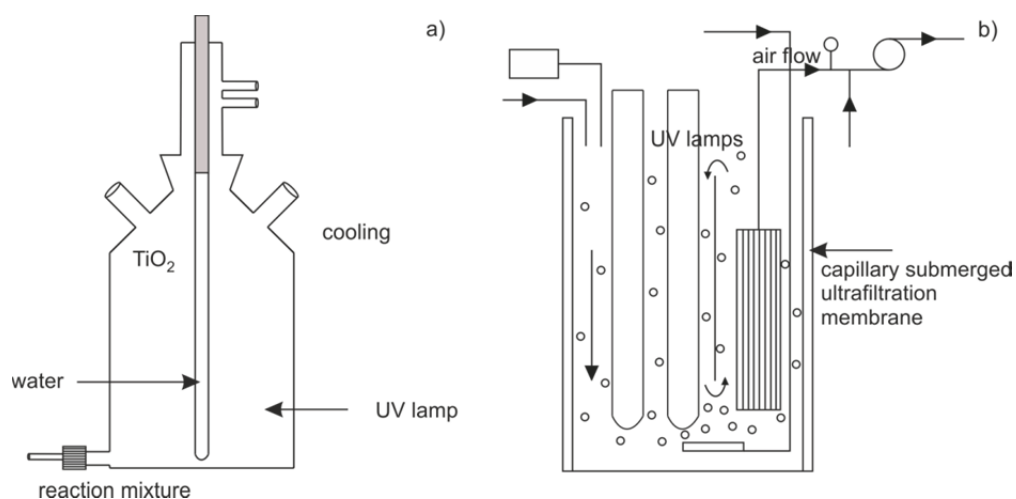

Fig. 1. Schemes of the reactors: a) laboratory photocatalytic reactor Heraeus,
b) a photocatalytic membrane reactor (PhRM)

A low pressure monochromatic UV lamp TNN15 (15 W) emitting UV radiation of the wavelength of 254 nm was mounted inside the reactors. The lamp was cooled with water to keep its temperature constant at the level of 23±2 °C. In order to mix the reactors content and provide the oxygen essential for the photocatalysis run, air was constantly supplied to reactor chambers. To minimize loses and improve effectiveness of UV radiation, external walls of the reactors were covered with aluminum foil.

Catalyst. Titanium dioxide (Degussa, Germany) of the trade mark P25, specific surface area of 50±15 m^2/g and mean particle size of 21 nm was used as a catalyst. TiO_2, being the most active photocatalyst with the photon energy in the range of 300–390 nm, possesses high mechanical, thermal and chemical resistances, what guarantees its successful, wide range of application to water and wastewater treatment systems [12–15]. The catalyst dose of 0.1 g/dm^3 was used for the simulated water, while 0.2 and 0.3 g/dm^3 for surface waters and in both cases the radiation time was equal 120 min.

Measurements. The effectiveness of the processes was determined based on the results obtained by analyses of dissolved organic carbon content (DOC) using HiPerTOC analyzer by Thermo Elektron Corporation, absorbance (UV_{254}) with the spectrophotometer UV-Vis Cecil 1000 by Analytical, color with the photometer NOVA 400 by Merck taken for raw water and water after photocatalysis.

3. RESULTS AND DISCUSSION

The rate of reaction of degradation (r) has been determined based on the Langmuir–Hinshelwood (L–H) model. It is directly proportional to the rate of surface cover with organic substrate (Θ_x) [2, 16, 17] according to the equation:

$$r = -\frac{dC}{dt} = k\Theta_x = \frac{kKC}{1 + KC} \tag{1}$$

where: r – rate degradation, $1/(m^2 \cdot min)$, k – reaction rate constant, 1/min, t – time, min, C – concentration of organic substance, mg/dm^3, K – Langmuir's adsorption constant.

For the interpretation of the decomposition rate, the first order reaction kinetics was used. Thus, the reaction rate constants were calculated using Eq. (2), while the linear dependence of $\ln(C_t/C_0)$ on time was used to calculate the reaction rate constants and half-lives of natural organic substances

$$\ln C_t = \ln C_0 - kt \tag{2}$$

3.1. IMPACT OF WATER HARDNESS ON THE KINETICS OF DECOMPOSITION OF FULVIC ACIDS DURING PHOTOCATALYSIS

The studies on the impact of the water hardness on the rate of decomposition of natural organic substances were made in photocatalytic membrane reactor (PhMR). Simulated water solutions containing fulvic acid were used. The solutions differed in the fulvic acid concentration and in the total hardness content. In Table 3, the values of reaction rate constants, determination coefficients and half-lives of fulvic acid (at 0.1 g TiO_2/dm^3 dose) at the presence and the absence of ions responsible for water hardness are presented. In Figure 2, exemplary linear time dependence of $\ln(DOC_t/DOC_0)$ is shown.

Table 3

Reaction rate constants and FA decomposition half-lives during photocatalysis (PhMR)

Matrix	Reaction rate constant k, min^{-1}			Determination coefficient, R^2			Half-life $t_{1/2}$, min		
	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color
Deionized water + FA (5.08 mg C/dm^3) 0 mg CaCO$_3$/dm^3	6.8×10^{-3}	32×10^{-3}	30×10^{-3}	0.83	0.92	0.94	101	21.6	22.6
Tap water + FA (8.85 mg C/dm^3) 440 mg CaCO$_3$/dm^3	1.5×10^{-3}	8.7×10^{-3}	12×10^{-3}	0.92	0.98	0.98	362	79.7	56.3
Deionized water + FA (10.1 mg C/dm^3) 0 mg CaCO$_3$/dm^3	3.4×10^{-3}	9.8×10^{-3}	14×10^{-3}	0.80	0.97	0.95	203	70.7	49.5
Tap water + FA (12.8 mg C/dm^3) 440 mg CaCO$_3$/dm^3	2.8×10^{-3}	4.5×10^{-3}	5.5×10^{-3}	0.87	0.91	0.92	247	154	126

The obtained results indicate negative impact of ions responsible for total water hardness, i.e. Ca^{2+}, Mg^{2+} on degradation of fulvic acid during photocatalysis. The rate of photocatalytic degradation of fulvic acid determined for simulated solution prepared on tap water matrix characterized with a significant total hardness content (440 mg CaCO$_2$/dm^3), was two times lower than the one determined for the solution prepared on the deionized water matrix. It also resulted in longer half-lives of fulvic acid obtained for tap water. Those observations hold for both concentrations of fulvic acid used in experiments (Table 3). Higher reaction rate constants (k) and shorter half-lives ($t_{1/2}$) for measured parameters (DOC, UV254 and color) revealed that aromatic structures of fulvic acid were effectively decomposed. However, the byproducts formed during the photodegradation of fulvic acids, determined as DOC, characterized with lower k and $t_{1/2}$ values. It indicated, that the pathway of fulvic acid degradation

depended on the susceptibility to photodegradation of the formed byproducts, which conditioned the complete mineralization of contaminants in water.
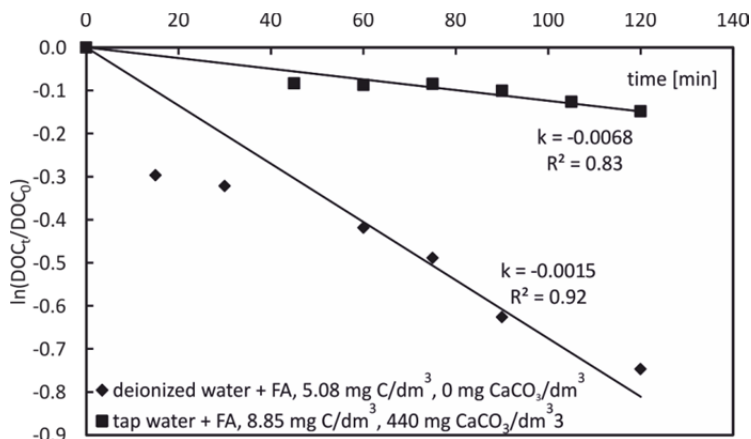

Fig. 2. Kinetics of FA decomposition at various water hardness

Considering the inhibition of photocatalytic reaction by ions responsible for water hardness, it must be noted, that on the one hand Ca^{2+} and Mg^{2+} ions in tap water are able to form complexes with humic substances (FA) what decreases their solubility and favors the adsorption on TiO_2 surface. On the other hand, Mg^{2+} ions may react with organic substances responsible for water color and generate hardly degradable compounds, which affect photocatalytic reaction rate [9–11]. Precipitation of carbonates on the glass UV lamp cover was also observed during experiments, what surely affected the effective UV radiation in water solution and, the same, decreased the degradation rate of organic compounds. It also caused the need of periodical cleaning of UV lamp covers during the photocatalysis of waters of increased hardness.

3.2. IMPACT OF THE CHEMICAL COMPOSITION OF WATER ON THE KINETICS OF DECOMPOSITION OF NATURAL ORGANIC SUBSTANCES DURING THE PHOTOCATALYSIS

Similar experiments as those performed for simulated solutions were also run for natural surface waters. The rate of NOM decomposition in surface waters was determined with the use of Heraeus reactor and with the photocatalytic membrane reactor. The investigated surface waters differed in concentrations of the NOM and inorganic compounds (Table 1). In Tables 4–7, the values of reaction rate constants, determination coefficients and half-lives assigned for NOM during photocatalysis (doses 0.2 and 0.3 g TiO_2/dm^3) of investigated surface water I (Tables 4 and 6) and surface water II (Tables 5 and 7) are presented. In Figure 3, an exemplary linear time dependence of $ln(DOC_t/DOC_0)$ for the Heraeus reactor is shown.

Table 4

Reaction rate constants and half-lives of NOM obtained during photocatalysis of surface water I
(Heraeus reactor, DOC concentration 13.7 mg/dm^3)

Catalyst dose [g/dm^3]	Reaction rate constant k, min^{-1}			Determination coefficient, R^2			Half-life $t_{1/2}$, min		
	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color
0.2	7.0×10^{-3}	24×10^{-3}	35×10^{-3}	0.92	0.86	0.98	99.0	28.5	19.3
0.3	9.5×10^{-3}	28×10^{-3}	36×10^{-3}	0.84	0.89	0.92	72.9	24.3	16.3

Table 5

Reaction rate constants and half-lives of NOM obtained during photocatalysis of surface water II
(Heraeus reactor, DOC concentration 5.48 mg/dm^3)

Catalyst dose [g/dm^3]	Reaction rate constant k, min^{-1}			Determination coefficient, R^2			Half-life $t_{1/2}$, min		
	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color
0.2	3.2×10^{-3}	19×10^{-3}	–	0.83	0.82	–	217	36.3	–
0.3	3.9×10^{-3}	26×10^{-3}	–	0.78	0.72	–	177	26.1	–

Table 6

Reaction rate constants and half-lives of NOM obtained during photocatalysis of surface water I
(PhMR reactor, DOC concentration 13.7 mg/dm^3

Catalyst dose [g/dm^3]	Reaction rate constant k, min^{-1}			Determination coefficient, R^2			Half-life $t_{1/2}$, min		
	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color
0.2	2.4×10^{-3}	11×10^{-3}	13×10^{-3}	0.98	0.95	0.93	288	61.9	52.1
0.3	4.8×10^{-3}	13×10^{-3}	14×10^{-3}	0.85	0.96	0.96	144	50.6	50.6

Table 7

Reaction rate constants and half-lives of NOM obtained during photocatalysis of surface water II
(PhMR reactor, DOC concentration 5.48 mg/dm^3

Catalyst dose [g/dm^3]	Reaction rate constant k, min^{-1}			Determination coefficient, R^2			Half-life $t_{1/2}$, min		
	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color	DOC	UV$_{254}$	Color
0.2	3.0×10^{-3}	18×10^{-3}	–	0.96	0.91	–	231	37.1	–
0.3	1.9×10^{-3}	17×10^{-3}	–	0.85	0.91	–	365	40.5	–

Firstly, it was found that the catalyst dose had a significant impact on the degradation of NOM in surface water I. For the higher catalyst dose (0.3 g/dm^3) the reaction rate constants were higher, while half-lives shorter. In the case of surface water II the impact of the dose of the catalyst on the reaction rate was weaker, while during the

experiment performed in PhMR (Table 7) results obtained for the higher catalyst dose
were worse, i.e. lower reaction rate constants and longer half-lives. It might be due to
both, recombination phenomenon and screening effect. The recombination causes the
decrease of so called electron gaps as a result of the electron come back from the con-
duction band to the valence band of the catalyst. The screening effect affects the UV
radiation to deeper parts of the solution, thus the decrease of photoactive catalyst sur-
face takes place [2].
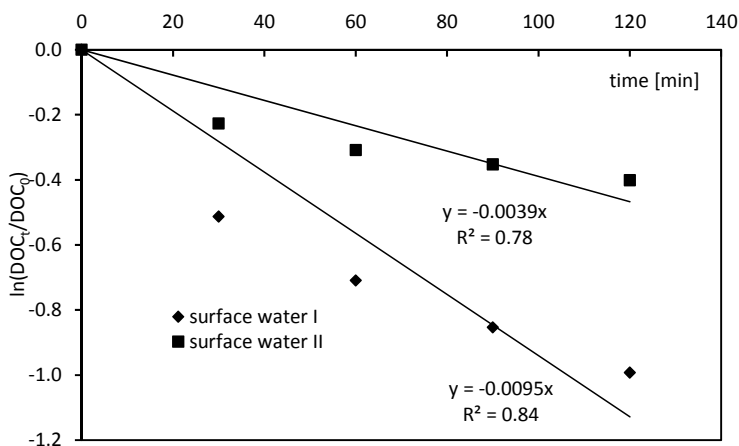
Fig. 3. Kinetics of NOM decomposition in function of time
in surface waters (DOC measurement, TiO_2 0.3 g/dm^3, Heraeus reactor)

The influence of the reactor type on the NOM degradation rate for surface water I
was also observed. The results obtained for PhMR were worse than ones for Heraeus,
that was probably caused by the amount of water in the reactor. In the case of surface
water II, the type of the reactor did not affect the process performance and the ob-
tained results of calculations were comparable.

The photocatalytic reaction in surface water I run faster than in surface water II
during experiments performed in Heraeus reactor, while NOM degradation rate con-
stants determined for PhMR experiments were similar. It is an important observation
as surface water I characterized with higher DOC concentration (13.7 mg/dm^3) than
surface water II (5.48 mg/dm^3) and the NOM decomposition rates were comparable in
PhMR reactor and higher in Heraeus reactor. It was surely caused by the presence of
inorganic ions in waters, especially anions Cl^- and by the character of NOM. Proba-
bly, the lower rate of the photocatalytic reaction observed in surface water II was the
result of a negative impact of anions on the TiO_2 catalyst action. Anions are very
strong sweepers of hydroxyl radicals $OH^\bullet$ and electron gaps, what weakens the ad-
sorption of humic substance on TiO_2 surface [2, 9]. Moreover, the inhibition of the
photocatalytic reaction cause by anions is also caused by the adsorption affinity to OH

ions bonded with the catalyst surface. It decreases the number of active sites on the surface of TiO_2, and the substituted anions, e.g. Cl^- increase the recombination of electron-electron gap pairs [2, 12].

3.3. TREATMENT OF SURFACE WATER IN THE PHOTOCATALYTIC MEMBRANE REACTOR (PHMR) WITH IMMERSED MEMBRANE

The experiments on the kinetics of degradation of NOM in various waters enabled the determination of the conditions of surface water treatment in the photocatalytic membrane reactor. Surface water I was used in the experiment. The water treatment was carried out for 7 days in the flowing system based on the inflow of the raw water to the reactor (volume of water in the reactor – 17 dm^3) to complement the volume of the collected permeate (purified water) after ultrafiltration. The capillary immersed ultrafiltration membrane (cut-off 25 kDa) was used. The reactor was operated in the sequential mode based on the following processes, i.e. photocatalysis process, which lasted for 30 min (the retention of water and the catalyst in the reactor) and ultrafiltration process which run for 60 min. Such repetition of cycles was carried out for 7 days. In Figure 4, the average results of the effectiveness of the water treatment after a week of studies are shown.
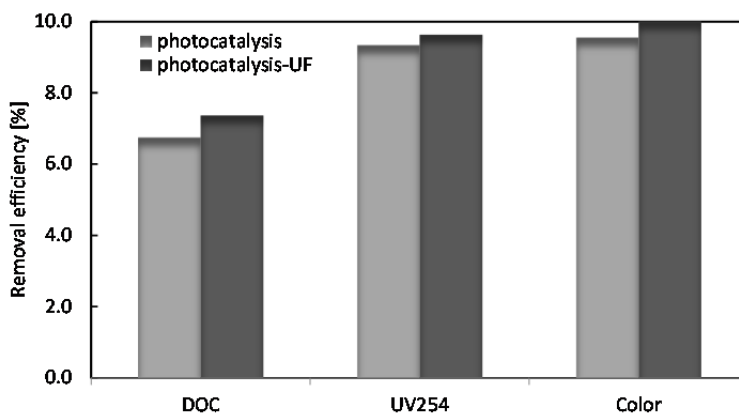

Fig. 4. The effectiveness of the surface water I treatment
in the photocatalytic membrane reactor PhMR
(dose TiO_2 0.3 g/dm^3, 7 days of the reactor operation)

The combination of photocatalysis with ultrafiltration in a single device (PhMR) enabled the retention of the catalyst in the reaction environment and its constant usage (the regeneration took place as a result of the mineralization of impurities on the catalyst surface at the presence of hydroxyl radicals) due to the ultrafiltration membrane, which acted as a barrier for catalyst particles (separating them from the purified water)

and eventually polished the water. The photocatalyst introduced to the water in the first day of the treatment (dose 0.3 g TiO_2/dm^3) worked effectively for 7 days of the process run, what was confirmed by the results presented in Fig. 4.

4. CONCLUSIONS

Natural organic substances are effectively decomposed in photocatalytic reactors with the use of TiO_2 in a suspended phase but the organic compounds of aromatic structure (humic substances of hydrophobic character) undergo faster photodegradation.

The chemical composition of treated water is important. Inorganic ions responsible for total water hardness (Ca^{2+}, Mg^{2+}) act as inhibitors of the photocatalysis with the use of TiO_2. The decomposition of natural organic compounds at the presence of inorganic compounds runs slower.

The rate of the photocatalytic reaction and half-lives of organic compounds depend on the radiation rate on the unit surface and the proper distribution of UV in the reactor.

The increase of the dose of the catalyst causes the increase of the decomposition rate of organic compounds, however the exceeding the critical dose results in the decresing of the photocatalytic reaction rate.

The Langmuir–Hinshelwood model properly describes the degradation of natural organic compounds and can be used for the prediction of organic substances contents in water at various conditions of the photocatalysis process performance; it can also be used in performance of photocatalytic reactors.

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