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## EFFECTIVENESS OF WATER TREATMENT BY MEANS OF INTEGRATED PHOTOCATALYSIS AND ULTRAFILTRATION PROCESSES

### EFEKTYWNOŚĆ OCZYSZCZANIA WÓD W ZINTEGROWANYM PROCESIE FOTOKATALIZA–ULTRAFILTRACJA

**Abstract:** In water treatment, photocatalysis is an advanced oxidation method which is becoming an alternative to classical processes. Its application results in the total degradation of contaminants present in water which are decomposed to carbon dioxide and water. The results of the study presenting the dependence of a catalyst dose, exposure time and feed water quality on the effectiveness of *natural organic matter* (NOM) photodegradation are discussed in this article. The research involved the treatment of surface water taken from a lake in Chelm Slaski area (southern Poland) and synthetic water which contained fulvic and humic acids. Photocatalysis was carried out using three catalyst ( $\text{TiO}_2$ ) doses of 0.25, 0.5, 0.75 g/dm<sup>3</sup> and an exposure time of 30–180 min. It has been found that it exhibited high effectiveness in removing NOM which increased with prolonged exposure time and depended on a catalyst dose and composition of treated waters. The choice of combined photocatalysis and ultrafiltration was fully justified, because ultrafiltration enabled the separation of catalyst particles from clean water.

**Keywords:** NOM, fulvic and humic acids, photocatalysis, ultrafiltration, water treatment

### Introduction

The increasing contamination of waters and shrinking resources of drinking water necessitate a search for and then implementation of new and more effective methods for treating waters. The conventional techniques (coagulation, sedimentation, filtration, adsorption on activated carbon) do not yield a complete removal of contaminants, but merely pass them to another phase, while the application of modern advanced oxidation techniques (photocatalysis) may lead to a complete degradation of contaminants in

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water, decomposing them to carbon dioxide and water. Photocatalytic oxidation using the  $\text{TiO}_2$  semiconductor is especially popular, because the anatase  $\text{TiO}_2$  catalyst has a lot of advantages. It displays a fast reaction time, high photochemical stability and reactivity, stability in a water system over a wide pH range, and low toxicity to the environment. Photocatalysis can be supplemented with microfiltration and ultrafiltration. During photocatalysis, which uses a suspended catalyst in a solution, a membrane can be an effective barrier for catalyst particles, enabling their recovery and return to the photoreactor [1, 2].

The study was aimed at assessing the effectiveness of combined photocatalysis (photooxidation process) and ultrafiltration (membrane process) to remove *natural organic matter* (NOM) from waters.

## Methods

The tests were carried out on a bench scale, using synthetic water which contained *fulvic acids* (FA) produced by Beijing Multigrass Formulation Co. Ltd., *humic acids* (HA) manufactured by Sigma-Aldrich and surface water collected from a lake near Chelm Slaski (southern Poland). The characteristics of the waters are given in Table 1.

Table 1

Characteristics of waters

Parameter	Synthetic water	Surface water
pH	5.52	5.50
Conductivity [mS/cm]	0.562	0.261
Turbidity [NTU]	2.49	1.60
Absorbance $\text{UV}_{254\text{ nm}}$ [l/m]	48.9	29.30
TOC [ $\text{gC}/\text{m}^3$ ]	12.45	13.46
DOC* [ $\text{gC}/\text{m}^3$ ]	10.01	12.70
Colour* [ $\text{gPt}/\text{m}^3$ ]	75	33
Alkalinity [ $\text{gCaCO}_3/\text{m}^3$ ]	10	10
$\text{NO}_3^-$ [ $\text{g}/\text{m}^3$ ]	—	18.63
$\text{SO}_4^{2-}$ [ $\text{g}/\text{m}^3$ ]	—	98.23
$\text{Cl}^-$ [ $\text{g}/\text{m}^3$ ]	—	309.1
SUVA** [ $\text{m}^3/\text{gC} \cdot \text{m}$ ]	4.88	2.31

\* Samples filtered through a 0.45- $\mu\text{m}$  filter; \*\* specific absorbance in ultraviolet radiation  $\text{UV}_{254}/\text{DOC}$ .

The integrated photocatalysis – ultrafiltration system (Fig. 1) covered sequential photocatalysis followed by ultrafiltration. NOM photodegradation was carried out at  $25 \pm 2$  °C in a Heraeus reactor with a 150 W multi-wave UV lamp. The P25 titanium dioxide  $\text{TiO}_2$  produced by Degussa was used as the photocatalyst. The photocatalytic oxidation of natural organic matter from the waters was conducted over a time range of

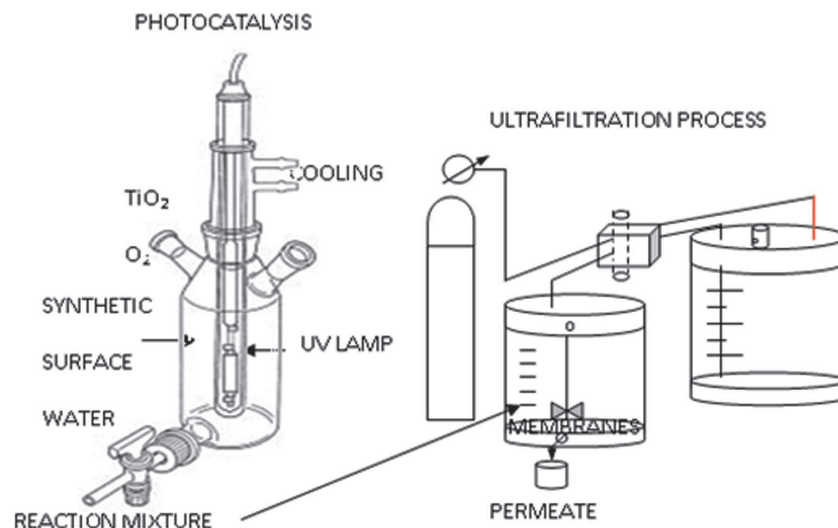


Fig. 1. Scheme integrated photocatalysis – ultrafiltration system

30–180 min with intervals after every 30 min. The ultrafiltration of the reaction mixture was carried out in the dead-end mode, using a polyethersulfone UF membrane (for synthetic water) and polyvinylidene fluoride (UF) membrane (for surface water), cut-off of 30 kDa. The membrane filtration was conducted at a transmembrane pressure of 0.1 MPa, using the Millipore CDS-10 System described in paper [3]. The tests examined the effect of  $\text{TiO}_2$  catalyst dose (0.25; 0.50; 0.75  $\text{g}/\text{dm}^3$ ) and exposure time (30–180 min) on the effectiveness of NOM photodegradation. The effectiveness of the processes was determined measuring *dissolved organic carbon* (DOC) with a HiperTOC analyzer produced by Thermo Electron Corporation, absorbance at a wavelength of 254 nm with a Cecil UV-VIS CE 1021 spectrophotometer and colour with a Merck Nova 400 photometer.

## Results and discussion

### Synthetic water

The effectiveness of photocatalytic oxidation is affected by a number of operational parameters [2, 4–6], the most important being a catalyst dose, exposure time, quality, temperature, pH and the concentration of dissolved oxygen in water. Table 2 shows the results of natural organic matter removal from synthetic water (humic and fulvic acids) by photocatalysis and the integrated system of photocatalysis – ultrafiltration. The tests examined the effect of a catalyst dose and exposure time on the photocatalytic oxidation of organic matter in water.

Table 2

The effectiveness of natural organic matter removal from water by photocatalysis and integrated photocatalysis-ultrafiltration system (*synthetic water*)

Exposure time [min]	Reduction in value [%]								
	Catalyst dose [gTiO <sub>2</sub> /dm <sup>3</sup> ]								
	0.25	0.5	0.75	0.25	0.5	0.75	0.25	0.5	0.75
	Colour			DOC			UV <sub>254</sub>		
30	87.5	—	92.9	50.8	62.1	76.8	83.6	93.3	98.1
60	93.8	—	92.9	70.5	86.8	95.4	97.3	99.1	99.2
UV 60 – UF*	—	—	—	72.5	93.6	95.2	97.7	98.8	98.7
90	100	—	92.9	92.2	89.6	100	99.8	99.5	99.4
120	100	—	100	94.1	93.1	100	99.3	99.8	100
UV 120 – UF*	—	—	—	95.1	95.5	100	99.1	99.5	100
150	100	—	100	97.2	91.2	100	99.8	98.8	100
180	100	—	100	97.8	95.3	100	100	99.8	100
UV 180 – UF*	—	—	—	98.4	96.1	100	100	100	100

\* UV exposure + ultrafiltration.

## Surface water

Like synthetic water in Table 2, Table 3 shows the results of natural organic matter removal from surface water by photocatalysis and integrated photocatalysis-ultrafiltration system.

Table 3

The effectiveness of natural organic matter removal from water by photocatalysis and integrated photocatalysis-ultrafiltration system (*surface water*)

Exposure time [min]	Reduction in value [%]								
	Catalyst dose [gTiO <sub>2</sub> /dm <sup>3</sup> ]								
	0.25	0.5	0.75	0.25	0.5	0.75	0.25	0.5	0.75
	Colour			DOC			UV <sub>254</sub>		
30	28.4	60.6	54.5	40.1	48.2	41.5	77.4	83.7	79.0
60	55.3	72.7	69.7	53.5	65.9	57.5	86.3	89.9	90.6
UV 60 – UF*	68.4	72.7	72.7	56.7	68.0	67.9	86.3	98.4	91.9
90	47.4	69.7	66.6	64.1	67.8	67.2	91.1	94.8	89.1
120	50.0	66.6	66.6	71.4	69.3	83.1	91.1	96.7	96.8
UV 120 – UF*	68.4	72.7	70.4	71.8	79.2	90.4	93.5	98.7	97.3
150	55.3	72.7	69.7	69.8	76.7	81.2	92.5	99.7	91.6
180	68.4	72.7	66.6	70.5	83.2	89.6	95.6	99.6	94.4
UV 180 – UF*	73.7	84.8	78.8	73.1	88.0	94.5	95.2	99.9	98.3

\* UV exposure + ultrafiltration.

The photocatalytic oxidation of natural organic matter carried out in the synthetic and surface water revealed an effect of water matrix (physical and chemical composition) on the effectiveness of photooxidation. In the synthetic water, a reduction in DOC at a level of 51–77 % and absorbance of 84–98 % (depending on a catalyst dose) were observed as early as 30 minutes after the photocatalysis had started. As to the surface water, DOC and absorbance reduction were lower and reached 40–48 % and 77–84 %, respectively. The complete removal of colour after a 90-minute exposure was obtained for the synthetic water while in the surface water, it was 70 % maximum and did not exceed the standard for drinking water of 15 mgPt/dm<sup>3</sup> [7]. That was probably connected with the quality of treated water. Water quality definitely affects the efficiency of advanced photocatalytic processes with TiO<sub>2</sub>. The tested waters had identical alkalinity but different SUVA parameter which is an indicator of the qualitative composition of water. Waters that contain considerable amounts of hydrophobic, aromatic, macromolecular humic organic matter exhibit a SUVA value of  $\geq 4$  m<sup>2</sup>/gC. On the other hand, the hydrophilic, low-molecular and non-humic matter exhibit  $SUVA \leq 2$  m<sup>2</sup>/gC. The  $SUVA_{254}$  values over a range of 2–4 m<sup>2</sup>/gC indicate the presence of a mixture of hydrophilic and hydrophobic matter in water [8]. SUVA for the synthetic water, which displayed higher photocatalysis effectiveness than the surface water, was 4.88. This proves that humic matter is considerably degraded during photocatalysis. The exposure to UV radiation in the presence of titanium dioxide results in the breaking of the aromatic rings of humic and fulvic acids and their partial mineralization.

The higher effectiveness of photocatalysis for the synthetic water than surface water is connected to the fact that natural water is composed of inorganic ions which can affect the efficiency of photocatalysis. The authors of paper [6] found that the use of a suspended catalyst in the presence of inorganic ions in water can cause the deactivation of the photocatalyst surface. At certain concentrations, some ions (Cu<sup>2+</sup>, Al<sup>3+</sup>, PO<sub>4</sub><sup>3-</sup>) reduce the effectiveness of the photocatalytic reaction, while others (Ca<sup>2+</sup>, Mg<sup>2+</sup>) do not affect its efficiency. The literature [6] also reports that the activity of a catalyst surface can be inhibited by the presence of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> ions in water. Such inhibition mechanisms normally involve competition in the adsorption on the surface of active places and photons on the surface of particles, “sweeping” of radicals and “electron holes”, and direct reaction with the photocatalyst. The composition of the tested surface water included nitrate, sulfate and chloride ions which probably decreased the effectiveness of photocatalysis compared with the process carried out in the synthetic water.

The increasing catalyst dose increased the effectiveness of photocatalysis, however, one should remember that if the dose is too high, it may cause screening *ie* preventing UV radiation from reaching the deeper layers of a solution. Thus, the rate of a photocatalytic reaction depends on a catalyst dose and exposure time to UV radiation. The course of photocatalytic oxidation of natural organic matter can be described calculating constant reaction rates ( $k$ , 1/min) from the following Langmuir-Hinshelwood equation [9–11]:

$$r = \frac{dC}{dt} k \left( \frac{KC}{1 + KC} \right) \quad (1)$$

Assuming that the degradation of organic matter by photocatalysis is a first-order reaction, then the constant of the reaction rate can be calculated as follows:

$$\ln \left( \frac{C_0}{C_1} \right) = kt \quad (2)$$

where:  $k$  – rate of organic matter oxidation following the “L-H” model  
[mg/dm<sup>3</sup> · min];

$K$  – equilibrium constant of organic matter adsorption;

$C_0/C_t$  – concentration of organic matter at time  $t = 0$  and after time  $t$ .

Table 4 shows the reaction rate constants ( $k$ ) and half-lives of the contaminants in the synthetic and surface waters. An analysis of the reaction rate constants proved that the oxidation of natural organic matter in the synthetic water was much faster than that in the surface water. The reaction rate constant correlated with the half-life of NOM. In the surface water, the half-life for organic matter was much longer than in the synthetic water.

Table 4

Rate constants of NOM photocatalytic degradation calculated  
for different catalyst doses

Catalyst dose [g/dm <sup>3</sup> ]	Reaction rate constants $k$ [min <sup>-1</sup> ]		Half-life [min]	
	Synthetic water	Surface water	Synthetic water	Surface water
0.25	0.023	0.009	30.1	77.0
0.50	0.022	0.010	31.5	69.3
0.75	0.050	0.013	13.9	53.3

### Effect of catalyst particles on ultrafiltration membrane fouling

The research into water treatment was carried out in the integrated system of photocatalysis and ultrafiltration. The latter was aimed at separating catalyst particles from clean water. The reaction mixture underwent ultrafiltration after 60, 120 and 180 minutes of exposure to UV radiation. Table 5 shows the relative permeabilities of UF membranes ( $\alpha$ ) which indicate the intensity of membrane fouling.

Table 5

Relative permeability ( $\alpha$ ) of membranes

Catalyst dose [gTiO <sub>2</sub> /dm <sup>3</sup> ]	Coefficient, $\alpha$					
	PES membrane Synthetic water			PVDF membrane Surface water		
	Exposure time [min]					
	60	120	180	60	120	180
0.25	0.97	0.97	0.91	0.90	0.91	0.94
0.50	0.80	0.86	0.86	0.73	0.85	0.89
0.75	0.84	0.85	0.91	0.80	0.86	0.94

The results proved that both the polyethersulfone and polyvinylidene fluoride membranes retained 100 % of the catalyst particles which resulted in clean and clear water. The intensity of membrane fouling increased with increasing concentration of the photocatalyst and reduction in exposure time. The relative permeabilities for the membranes were similar, which points to the similar intensity of fouling. Ultrafiltration after a 60-minute exposure produced the lowest  $\alpha$  coefficients. Probably, the reaction mixture after 60 minutes of exposure contained the highest load of undegraded contaminants which could have accumulated in the membrane pores causing its lower efficiency. The highest relative permeability was observed for the catalyst dose of 0.25 g/dm<sup>3</sup> over a range of 0.91–0.97 for the PES membrane and 0.90–0.94 for the PVDF one, while the lowest  $\alpha$  coefficients were found for higher catalyst doses ranging from 0.80 to 0.91 for PES and from 0.73 to 0.94 for PVDF membranes. The application of the higher catalyst doses resulted in the formation of a thick layer of filter cake, composed of catalyst particles, which covered the membrane surface thus increasing the resistance of the filter layer.

## Conclusions

The results revealed high effectiveness of NOM removal by photocatalysis, being higher for the synthetic (Table 2) than surface water (Table 3). This was also confirmed by the higher reaction rate constants and shorter half-lives for the synthetic water than the surface water (Table 4). That is connected with the diversified composition of natural waters in which some contaminants may inhibit photocatalysis. The application of ultrafiltration enabled a 100 % retention (recovery) of the catalyst and increase in the effectiveness of water treatment.

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## References

- [1] Mozia S. Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review. *Sep Purif Technol.* 2010;73:71-91.
- [2] Bodzek M, Rajca M. Fotokataliza w oczyszczaniu i dezynfekcji wody. Część I. Podstawy teoretyczne. *Technol Wody.* 2011;4:18-33.
- [3] Rajca M, Bodzek M. Usuwanie kwasów fulwowych z wody metodami fotokatalitycznymi wspomaganymi ultrafiltracją. *Inż Ochr Środow.* 2011;14(2):101-110.
- [4] Erdim E, Soyer E, Tasiyici S, Koyuncu I. Hybrid photocatalysis/submerged microfiltration membrane system for drinking water treatment. *Desal Water Treatm.* 2009;9:165-174.
- [5] Choo KH, Tao R, Kim MJ. Use of a photocatalytic membrane reactor for the removal of natural organic matter in water: Effect of photoinduced desorption and ferrihydrite adsorption. *J Membr Sci.* 2008;322:368-374.
- [6] Chong MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* 2010;44:2997-3027.
- [7] Rozporządzenie Ministra Zdrowia z dnia 20 kwietnia 2010 roku zmieniające rozporządzenie w sprawie jakości wody przeznaczonej do spożycia przez ludzi z dnia 29 marca 2007 r (DzU Nr 61, poz 417).
- [8] Mołczan M, Szlachta M, Karpińska A, Biłyk A. Zastosowanie absorpcji właściwej w nadfiolecie (SUVA) w ocenie jakości wody. *Ochr Środow.* 2006;28:11-16.
- [9] Fu J, Ji M, Wang Z, Jin L, An D. A New submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst. *J Hazard Mater.* 2006;B131:238-242.
- [10] Fu J, Ji M, Zhao Y, Wang L. Kinetics of aqueous photocatalytic oxidation of fulvic acids in a photocatalysis – ultrafiltration reactor (PUR). *Sep Purif Techn.* 2006;50:107-113.
- [11] Rajca M, Bodzek M, Cichy J. Kinetyka degradacji kwasów fulwowych w zintegrowanym procesie fotoutlenianie-ultrafiltracja. *Ochr Środow.* 2011;33:63-66.

### EFEKTYWNOŚĆ OCZYSZCZANIA WÓD W ZINTEGROWANYM PROCESIE FOTOKATALIZA-ULTRAFILTRACJA

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**Abstract:** Alternatywną metodą uzdatniania wody w stosunku do metod klasycznych jest zaawansowana technika utleniania – fotokataliza, w której dochodzi do degradacji zanieczyszczeń, w efekcie otrzymuje się ditlenek węgla i wodę. W pracy omówiono wyniki badań wpływu dawki katalizatora, czasu ekspozycji oraz jakości wody na efektywność fotodegradacji *naturalnych substancji organicznych* (NOM). W badaniach oczyszczano wodę modelową zawierającą kwasy fulwowe i humusowe oraz wodę powierzchniową z jeziora na terenie Chełmu Śląskiego. W procesie fotokatalizy zastosowano trzy dawki katalizatora ( $\text{TiO}_2$ ) 0,25; 0,5 i 0,75 g/dm<sup>3</sup> oraz czas naświetlania 30–180 minut. Stwierdzono wysoką efektywność usuwania NOM w procesie fotokatalizy, która rosła z wydłużaniem czasu naświetlania oraz zależała od dawki katalizatora i składu oczyszczanych wód. Połączenie procesu fotokatalizy z ultrafiltracją było w pełni uzasadnione, ponieważ ultrafiltracja pozwoliła oddzielić cząstki katalizatora od czystej wody.

**Słowa kluczowe:** NOM, kwasy fulwowe i humusowe, fotokataliza, ultrafiltracja, oczyszczanie wód