The role of pH in the decomposition of organic micropollutants during the heterogeneous photocatalysis process

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Abstract. The study investigated that the change in the pH ranged from 5 to 7 affects the adsorption degree of selected organic micropollutants such as: polycyclic aromatic hydrocarbons (anthracene, benzo[a]pyrene), pharmaceutical compounds (diclofenac) and industrial additives (octylphenol and pentachlorophenol) on the photocatalyst surface (100 mg TiO_2/dm^3). For example, in suspension of pH 5 a 12% reduction in the concentration of octylphenol was noted, while in the suspension of pH 7 the concentration of this compound was reduced by 64%. In the case of anthracene an inverse relationship was observed. The concentration of this micropollutant decreased by 94% for pH 5 and only by 61% for pH 7 suspension. With the commencement of UV irradiation of reaction mixtures a gradual increase in the concentration of micropollutants reduction in aqueous solutions was observed. This indicates the decomposition of compounds as a result of their reaction with highly reactive OH• radicals or other reactive oxygen species generated during the process. For reaction mixtures of pH 7, already in the first 15 minutes, higher degrees of removal of micropollutants ware observed compared to suspension of pH 6. The obtained micropollutants removal degrees exceeded 91% for diclofenac, octylphenol, pentachlorophenol and amounted to 100% for anthracene and benzo(a)pyrene.

1. Introduction

Literature data indicate a continuous increase in the number of organic micropollutants in the water environment. These compounds belong to different chemical groups and have a differentiated impact on the water quality and also pose a serious threat to aquatic ecosystems [1–3]. The Water Frame European Directives (2000/60/EC) [4] listed some micropollutants including PAHs, EDCs, phenolic compounds and pharmaceuticals as "priority hazardous substances". It is therefore necessary to take any action to reduce their concentrations in the environment through the implementation of effective methods of their removal from aqueous streams. Advanced oxidations process, which include also the process of heterogeneous photocatalysis gives an opportunity to obtain satisfactory

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effects of micropollutant decomposition [5]. The oxidation and reduction of compounds by means of highly reactive free hydroxyl radicals $OH^{\bullet}$ formed during the process depends on different operating parameters of the process, which include the wavelength emitted by the applied UV irradiation source [6], oxygen concentration in the irradiated water solution [7], catalyst dose and type [8] and also the physicochemical composition of the treated water [9, 10].
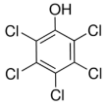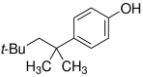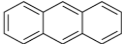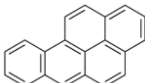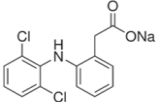
The paper presents the influence of the pH of water solution on the decomposition efficiency of chosen organic micropolutants from the group of polycyclic aromatic hydrocarbon – anthracene (ANT), benzo(a)pyrene (BaP), industrial admixtures – pentachlorophenol (PCP), octylphenol (OP) and pharmaceutical compounds – diclofenac (DCL) during heterogeneous photocatalysis. The photochemical process was conducted in the presence of TiO_2 as a catalyst. The kinetics of the process was described by means of Langmuir-Hisherwood equation. The concentrations of all compounds in water solution before and after their treatment were estimated by HPLC chromatography preceded by Solid Phase Extraction.

2 Materials and methods

2.1 Chemicals

All investigated organic micropollutants (octylophenol, pentachlorophenol, anthracene, benzo(a)pyrene, diclofenac,) were purchased from Sigma Aldrich (Poland). Their properties are shown in table 1.

Table 1. The structural and chemical properties of the studied micropollutants.

Structural formula	Chemical properties	
Pentachlorophenol (PCP)		
	Molecular weight, g/mol	266.34
	Solubility in water, mg/L	80
	log K_{ow}	5.12
4-tert-octylphenol (OP)		
	Molecular weight, g/mol	206.32
	Solubility in water, mg/L	7.0
	log K_{ow}	4.80
Anthracene (ANT)		
	Molecular weight, g/mol	178.23
	Solubility in water, mg/L	0.044
	log K_{ow}	4.45
Benzo[a]pyrene (BaP)		
	Molecular weight, g/mol	252.31
	Solubility in water, mg/L	0.00147
	log K_{ow}	5.97
Diclofenak sodium salt (DCL)		
	Molecular weight, g/mol	318.13
	Solubility in water, mg/L	50
	log K_{ow}	4.51

Due to the poor water solubility of the compounds from the group of polycyclic aromatic hydrocarbon (anthracene and benzo(a)pyrene) the stock solutions of all micropollutants were prepared with methanol (analytical standard), Avantor Performance Materials Poland S.A. (Poland). The study subjects, with a micropollutant concentration of 0.5 mg/L, were prepared by diluting the stock solution with deionized water. The pH of the water solutions were adjusted subsequently to 5.0, 6.0 or 7.0 using 0.1 mol/L HCl and 0.1 mol/L NaOH purchased from Avantor Performance Materials Poland S.A. (Poland).

TiO_2 applied as a catalyst into the process of heterogeneous photocatalysis was purchased from Evonik Degussa GmbH (Hanau, Germany) and labelled by the manufacturer with the symbol of P25.

2.2 Photocatalysis process

The process of heterogenic photocatalysis was conducted in a laboratory batch reactor with a volume of 700 mL by Heraeus (Germany) equipped with a medium-pressure mercury vapour UV lamp (150 W) placed in a cooling jacket. The temperature of the process did not exceed 20 ± 1 °C. The radiation emitted by the UV lamp have wavelength λ_{exc} equal to 313, 365, 405, 436, 546 and 578 nm. The scheme of the reactor was shown in figure 1.
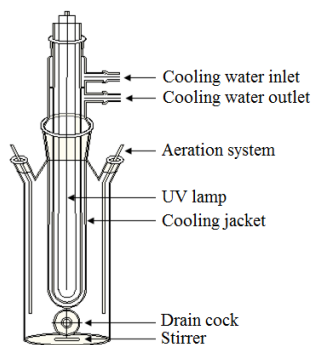
Figure 1. Scheme of the photocatalytic batch reactor [11].

The dose of catalyst was estimated during the preliminary stage of the research and was equal to 100 mg/L, whereas the contact time of the catalyst with the water solutions before UV irradiation process was set to 15 min. This dark mixing step ensured the adsorption of micropollutants on the surface of the catalyst. The reaction mixture was aerated by the use of an aeration pump of capacity of 4 L air per minute. Microfiltration membrane filters of 0.45 membrane pore sizes by Merck Milipore (Germany), were use for the separation of catalyst from the post-reaction mixture.

2.3 Kinetic of heterogeneous photocatalysis

Based on the Langmuir-Hinsherwood equation the kinetics of the photocatalysis process was calculated, as a correlation between the concentration of the micropollutant in the water solutions (C, mg/L) and the duration of the UV irradiation (t, min), according to the equation (1), where (K) is an equilibrium constant of the compound adsorption on the catalyst surface

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

(1)

With the assumption, that the degradation process of micropollutants becomes a pseudo-first order reaction, the reaction rate constant (k, min^{-1}) may be established as a linear regression slope (Equation 2), where (C_0) and (C_t) are the compound concentrations in the water solutions before the commencement of the UV irradiation process ($t = 0$) and after a given time indicated as (t).

$$\ln\left(\frac{C_t}{C_0}\right) = -kt$$

(2)

The determined reaction rate constant (k) enables to calculate the half life ($t_{1/2}$) on the basis of the Equation (3):

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

(3)

2.4 Analytical procedure

The analytical procedure of investigated micropollutants was performed by the use of high performance liquid chromatography HPLC-UV by Varian (Poland) equipped with a Hypersil GOLD column by Thermo Scientific of length 25 cm, diameter 4.6 mm and graining 5 μm. The mobile phase was a mixture of acetonitrile and water in the volume ratio of 85:15 (v/v). The chromatographic analysis was preceded by solid phase extraction (SPE) of analyzed water samples.

For the SPE Supelclean™ ENVI-18 columns of a volume of 6 mL (1.0 g) by Supelco (Poland) filled with octadecylsilane C18 bed were use. For compounds from the group of polycyclic aromatic hydrocarbons – anthracene and benzo[a]pyrene and industrial admixtures - pentachlorophenol, octylphenol, together with pharmaceutical compounds – diclofenac separate extraction procedure were applied. The column bed before the extraction of PAH was conditioned with methanol and washed with deionized water. After the samples with the addition of an aqueous solution of hyamine reagent had completely passed, the SPE bed was dried under vacuum. Then the column bed was wetted with methanol and the analytes were eluted with dichloromethane. The extraction of pentachlorophenol, octylphenol and diclofenac was preceded by conditioning of the columns bed with acetonitrile and methanol. Afterwards, the column bad was rinsed with deionized water. The isolated compounds were eluted with acetonitrile/methanol mixture (60/40, v/v).

Obtained eluates were dried under high purity nitrogen flux and then the residues were re-dissolved in 50 μL of methanol and analyzed chromatographically. Details of the method are presented in the reference [12].

3 Results and Discussion

The first stage of the study was devoted to assess the adsorption process of the investigated organic micropollutants on the surface and/or inside of the photocatalyst particles. The absorption of compounds in the active centers of the semiconductor, constitutes the basis for a proper run of their photocatalytic oxidation and/or reduction. The adsorption degrees of the micropollutants were estimated on the basis of the changes in their concentration in water solution subjected to 15 minute contact time with the catalyst.

Figure 2 presents the rates of concentration decrease of OP, PCP, ANT, BaP and DCL present in deionized water solutions.

(a)

(b)

(c)

(d)

(e)
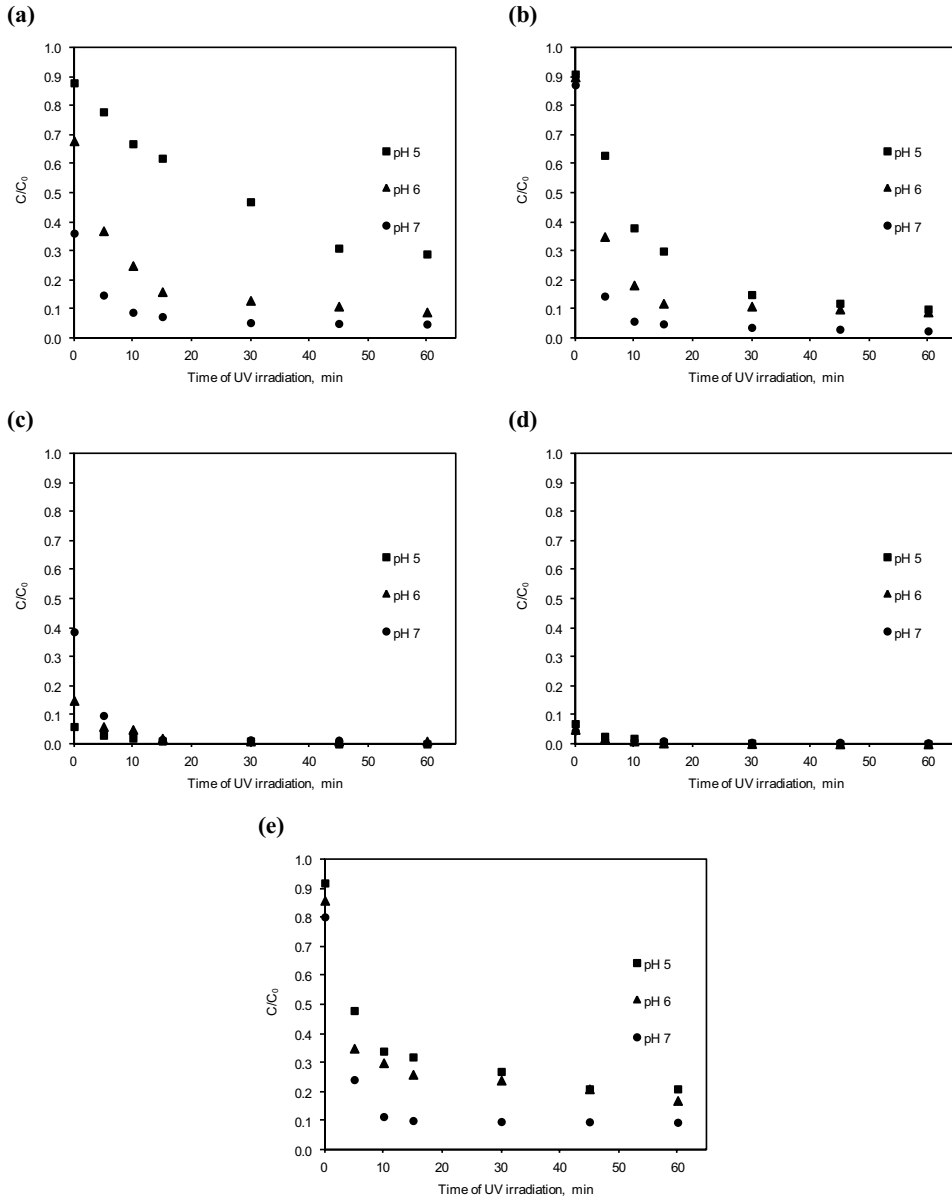
Fig. 2. Influence of solution pH on the degradation of **(a)** OP, **(b)** PCP, **(c)** ANT, **(d)** BaP and **(e)** DCL during the photocatalysis process.

It was observed that the adsorption degrees of OP and PCP increases with the increase of the pH of water solutions (Time of UV iradiation = 0). The 12% decrease of OP concentration, 9% PCP, 8% DCL was observed for pH 5. Whereas for solutions of pH 7 the concentration of micropollutants consecutively decreased by 64% for OP, 13% for PCP and about 20% for DCL. The adsorption degree of BaP was, regardless of the pH, at a constant

level of 95%. Different correlation was observed in case of ANT. The adsorption degree of this compound decreased with the increase of pH from 94% obtained for water solutions of pH 5 to 61% for pH 7 solutions. It should be highlighted that for pH values above pH_{zpc} (the value at which the total charge of the catalyst surface shall be zero), the surface of the semiconductor assumes a negative charge and repel anionic compounds. Whereas for pH below pH_{zpc}, the surface assumes a positive charge, resulting in repulsion of cationic donors and electron acceptors [13].

The obtained results indicated that the absorption of micropollutants on the photocatalyst surface depends on the chemical structure of the compound and the change of the charge of semiconductor surface in different pH values of micropollutant water solutions.

The implementation of UV irradiation on the reaction mixtures initiates the photochemical decomposition of organic compounds adsorbed on the catalyst surface and located directly in the water solutions (photolysis process). The reaction of compounds with $OH^{\bullet}$ radicals, which are generated in accordance with reactions from (4) to (6), resulted in the decrease of the micropollutant removal.

$$Ti^{IV} + H_2O \rightarrow Ti^{IV} - H_2O \tag{4}$$

$$Ti^{IV} - OH^- + h^+ \rightarrow Ti^{IV} - OH^{\bullet} \tag{5}$$

$$Ti^{IV} - H_2O + h^+ \rightarrow Ti^{IV} - OH^{\bullet} + H^+ \tag{6}$$

The decomposition of compounds occur most intensively in the first 15 minutes of the process regardless of the pH of the water solutions. For example, the concentration of PCP decreased after the 15th minute of UV radiation by 70% for solutions of pH 5, 88% for pH 6 and 95% for pH 7. The removal degree of ANT and BaP obtained in the considered irradiation time of 15 min in all mixture independent of the pH value was very similar and exceed 98%.

After 60 min of UV irradiation a complete removal of ANT and BaP was obtained. In the case of water solutions containing OP, PCP and DCL a clearly effect of pH on the efficiency of the compound decomposition was observed. The concentration of OP decreases by 71% for pH 5, 91% for pH 6 and 95% for pH 7. The removal degree of PCP reached the highest value exceeding 98% in water solutions of pH 7. While the concentration of DCL in the solution of pH 5 after 60 minutes of UV exposure was reduced by more than 79% and in water solutions of pH 7 the removal degree exceeded 91%. This phenomenon may be a result of the increasing degree of adsorption of micropollutants on the surface of the catalyst, which was shown during the first stage of the study, or results from the increase in the amount of OH^- ions, which are reactants by the production of $OH^{\bullet}$ radicals.

The kinetics assessment revealed a significant difference between the rapidity of micropollutant decomposition, expressed on the basis of the value of the reaction rate constant (*k*), appointed during the first period of the process (up to 15 min) and the rapidity observed after the 15th minute of UV irradiation (Table 2). These differences may result from a competitive adsorption of by-products of micropollutants decomposition on the surface of catalyst, which can inhibit the oxidation and/or reduction of parent compounds. An inverse relationship was observed only in the case of ANT decomposition in water solution of pH 5, where the reaction rate constant was higher after the 15 minute of the process.

Table 2. Half-life of investigated organic micropollutants during photocatalysis.

Compound	pH	Reaction time, min	Reaction rate constant k, min^{-1}	R^2	Half-life $t_{\frac{1}{2}}$, min
OP	5	0 - 15	0.0241	0.98	34.29
		15 - 30	0.0180	0.94	51.65
	6	0 - 15	0.1053	0.99	17.95
		15 - 30	0.0126	0.99	185.86
	7	0 - 15	0.0947	0.92	11.96
		15 - 30	0.0089	0.79	364.80
PCP	5	0 - 15	0.0767	0.98	10.43
		15 - 30	0.0235	0.89	72.10
	6	0 - 15	0.1339	0.97	6.97
		15 - 30	0.0065	0.99	417.39
	7	0 - 15	0.1911	0.87	6.50
		15 - 30	0.0148	0.99	237.28
ANT	5	0 - 15	0.1156	0.99	30.58
		15 - 30	0.2103	0.92	4.94
	6	0 - 15	0.1245	0.95	19.31
		15 - 30	0.1213	0.96	21.39
	7	0 - 15	0,2117	0.99	8.41
		15 - 30	0.0333	0.87	124.66
BaP	5	0 - 15	0.1827	0.95	20.00
		15 - 30	0.1442	0.94	21.86
	6	0 - 15	0.1622	0.99	20.67
		15 - 30	0.1336	0.96	31.79
	7	0 - 15	0.0905	0.78	45.13
		15 - 30	0.0200	0.86	252.40
DCL	5	0 - 15	0.0749	0.88	14.28
		15 - 30	0.0101	0.90	169.00
	6	0 - 15	0.0703	0.80	13.16
		15 - 30	0.0094	0.96	198.71
	7	0 - 15	0.1395	0.89	8.40
		15 - 30	0.0013	0.93	2288.81

An interesting relationship was observed for the appointed compound half-lifes. The value of this parameter in the first 15 minutes of the process gradually decreases with the increasing pH of the water solutions. For example, the half-life of OP determined at pH 5 amounted 34 minutes, whereas at pH 7 the compound half-life was shorter than 12 minutes. Only in the case of BaP decomposition the half-live increased with the increasing pH of water solution and subsequently received values from 20 min in solutions of pH 5 to over 45 min in water solutions of pH 7. The half-live values of all investigated compounds estimated after the 15th minute of UV irradiation also increased with the increasing solution pH. An exception was only the half-live appointed for PCP in solutions of pH 7, with a value of 237 minutes, compared to solutions of pH 6, which half-live was longer than 417 minutes.

4 Conclusions

On the basis of the conducted investigations it can be observed that the absorption of micropollutants on the photocatalyst surface depends on the type of the compound and their chemical structure. The pH values of micropollutant water solutions influences the charge

of the surface of the semiconductor, which alters the degree of adsorption of compounds. The adsorption degree of investigated micropollutants on the surface of the semiconductor reflected on the removal degrees observed during photocatalysis. It was noted that the concentration of micropollutants decreased with the increase in the pH of the water solution. Moreover the data analysis from the kinetics assessment of the photocatalysis process proved a significant difference between the rapidity of micropollutant decomposition observed during the first 15 min of the process and the rapidity of the process observed between the 15th and the 30th minute of UV irradiation.

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