

INFLUENCE OF INORGANIC COMPOUNDS ON THE PROCESS OF PHOTOCATALYSIS OF BIOLOGICALLY ACTIVE COMPOUNDS

Edyta Kudlek¹, Mariusz Dudziak¹, Jolanta Bohdziewicz¹, Gabriela Kamińska¹

¹ Silesian University of Technology, Institute of Water and Wastewater Engineering, Konarskiego 18a, 44-100 Gliwice, Poland, e-mail: edyta.kudlek@polsl.pl

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ABSTRACT

Constant increase in concentration of organic micropollutants in the water environment influences the development of methods for their effective elimination from various matrices released into aquatic ecosystems. One of widely described in literature processes for the decomposition of hardly-biodegradable pollutants is the process of heterogeneous photocatalysis. The paper presents the influence of inorganic substances on the decomposition of polycyclic aromatic hydrocarbons (anthracene and benzo[a]pyrene), industrial admixtures – octylphenol and pharmaceutical compounds – diclofenac in the photocatalysis process conducted in the presence of TiO_2 . It has been shown that the presence of Cl^- ions did not affect the photochemical reaction of the micropollutant decomposition. Whereas, the presence of CO_3^{2-} , SO_4^{2-} and HPO_4^{2-} ions inhibited the decolonization of octylphenol and diclofenac, while the degradation efficiency of anthracene and benzo[a]pyrene was reduced only by the presence of CO_3^{2-} and HCO_3^- anions. The photooxidation of micropollutants in solutions containing Al^{3+} or Fe^{3+} cations proceeded with a much lower efficiency than that for solution without inorganic compounds. The analysis of the kinetics of the photocatalytic decomposition of selected micropollutants show a decrease in the reaction rate constant and an increase in their half-life due to the blocking of the active semiconductor centers by inorganic compounds. In addition, the toxicological analysis indicated the generation of micropollutant oxidation by-products, which aggravate the quality of treated aqueous solutions.

Keywords: water environment, organic micropollutants, photocatalysis, cations, anions

INTRODUCTION

Water is a valuable resource, whose physical and chemical composition depends strictly on human activity. Research undertaken in order to determine the degree of anthropogenic pollution of water environment indicates the presence of various micropollutant groups in surface water, groundwater and even drinking water sources [Li et al. 2015, Ternes et al. 2015]. The most of the municipal WWTPs are not designed to completely eliminate organic micropollutants, making the treated effluent a major source of that kind of pollution [Tijani et al. 2013, Morris et al. 2017].

Advanced oxidation processes (AOPs), such as photolysis or photocatalysis are conceptually based on the production of highly reactive oxidizing species (HO^\bullet , $\text{O}_2^{\bullet-}$, HO_2^\bullet) are able to oxidize unselectively organic pollutants and can be used as an effective post-treatment of a biological process [Giannakis et al. 2015, Moreira et al. 2016]. One of the most important features, deciding on the decomposition of compounds during the photocatalysis process, is the adsorption of micropollutants in active centres of the applied catalyst. The process of micropollutants adsorption may be hindered by the presence of inorganic compounds such as Cl^- , NO_3^- and SO_4^{2-} anions, that are

able to block active centres on the catalyst surface [Chládková et al. 2015]. On the other hand, composite catalysts formed from TiO₂ nanoparticles and some inorganic compounds may have a higher photocatalytic activity than conventional semiconductors [Zhang et al. 2016]. The effectiveness of the process depends therefore also on the physicochemical composition of the treated solution. It is necessary to determine which compounds support the micropollutant oxidation process and which act as decomposition inhibitors.

This paper describes the efficiency of removal of different micropollutants identified in the aquatic environment, i.e., diclofenac, octylphenol, anthracene and benzo[a]pyrene, from water suspensions in the process of heterogenic photocatalysis with the presence of selected inorganic compounds. The photochemical oxidation was conducted in the presence of titanium dioxide as a catalyst of this process. The Langmuir-Hisherwood equation allowed the description of the kinetics of the process. The efficiency of the process was assessed on the basis of the decrease in concentration of micropollutants measured by the use of high-performance liquid chromatography preceded by solid phase extraction.

MATERIALS AND METHODS

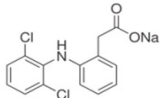
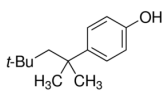
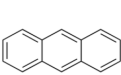
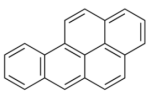
The research was carried out by using water solutions of selected micropollutants: diclofenac (DCF), octylphenol (OP), anthracene (ANT) and benzo[a]pyrene (BaP) purchased from Sigma-Aldrich (Poznań, Poland). The basic characteristic of micropollutants was shown in Table 1. The concentration of tested compounds in the prepared water solutions was established at 500 µg/L. The influence of inorganic ions on the efficiency of photocatalytic oxidation of micropollutants was

determined by the addition of 1 mol/L inorganic salts, i.e., NaCl, Na₂SO₄, NaHCO₃, Na₂HPO₄ and AlCl₃, FeCl₃ to the water solutions.

The process of heterogenic photocatalysis was conducted in a laboratory glass reactor with a volume of 700 mL by Heraeus (Hanau, Germany). The reactor was equipped with a medium-pressure mercury vapour UV lamp (150 W), which emanated radiation with a wavelength λ_{exc} range from 313 to 578 nm. The lamp was placed in a cooling jacket, which enabled to keep a constant temperature of the conducted process that did not exceed 20 ± 1 °C. The reactor was placed on a magnetic stirrer and connected to an aeration pump of capacity of 4 L air per minute to oxidate the system. TiO₂ was applied as a catalyst of the photocatalysis process and it was purchased from Evonik Degussa GmbH (Hanau, Germany) as a mixture of anatase and rutile in the ratio 75:25. The dose of catalyst applied to the reaction mixture reached the level of 100 mg/L. To ensure the adsorption of micropollutants on the surface of the catalyst the water solutions were mixing with the TiO₂ particles for 15 min before UV irradiation. The separation of catalyst from the post-reaction mixture was conducted by the use of a filtration set equipped with glass filters of 0.45 µm pore sizes by Merck Milipore (Darmstadt, Germany), with vacuum pump by AGA Labor (Warsaw, Poland).

The kinetics of the photochemical process was estimated with the Langmuir-Hinsherwood equation, as a correlation between the micropollutant concentration in the solutions and the time of UV irradiation Eq. (1). With the assumption, that the decomposition process of the investigated compound becomes a pseudo-first order reaction, the reaction rate constant k may be established as a linear regression slope Eq. (2), where K is an equilibrium constant of the micropollutant adsorption on the TiO₂ surface, whereas C_0 , C_t is

Table 1. Physicochemical characteristic of studied organic micropollutants

Compound group	Pharmaceutical compound	Industrial admixture	Polycyclic aromatic hydrocarbons	
Micropollutant	Diclofenac sodium salt	Octylphenol	Anthracene	Benzo[a]pyrene
Structural formula				
Molecular formula	C ₁₄ H ₁₀ Cl ₂ NNaO ₂	C ₁₄ H ₂₂ O	C ₁₄ H ₁₀	C ₂₀ H ₁₂
CAS No	15307-79-6	1806-26-4	120-12-7	50-32-8
Molecular weight, g/mol	318.13	206.32	178.23	252.31
Solubility in water, mg/L	50	7.0	0.044	0.00147
log K _{ow}	4.51	4.80	4.45	5.97

the compound concentration in the water solution before the irradiation process ($t = 0$) and after a given time t . The half life $t_{\frac{1}{2}}$ of the compound was identify on the basis of the Eq.(3).

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

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

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \quad (3)$$

The concentration of micropollutants before and after the oxidation process was measured by high-performance liquid chromatography HPLC equipped with UV-VIS detector by Varian (Warsaw, Poland). The analytes were separated from water samples with a volume of 20 mL (pH = 7) with solid phase extraction (SPE) in a single-use columns Supelclean™ ENVI-18 volume 6 mL (1.0 g) by Supelco (Poznań, Poland). Details of column bed preparation, analyte extraction and

elution were presented in Kudlek et al. (2017) and Bohdziewicz et al. (2016). The chromatographically identifications of the micropollutants were conducted by the use of Hypersil GOLD column by Thermo Scientific (Warsaw, Poland) of length equal to 25 cm, diameter of 4.6 mm and granulation of 5 μm . Detector wavelength λ necessary to obtain the required sensitivity was established for DFC and OP at 220 nm and at 254 nm for ANT and BaP.

RESULTS AND DISCUSSION

In the first stage of study the concentration decrease of organic micropollutant water solution with selected anions added as sodium salts was investigated. The obtained results were presented at Figure 1. The presence of inorganic compounds affect on the adsorption process of the investigated organic compounds on the photocatalyst particles. For example, the concentration of DCF decreased in water solution containing Cl^- at about 9% (Fig. 1a, reaction time 0 min) while in the presence of HCO_3^- and HPO_4^{2-} the

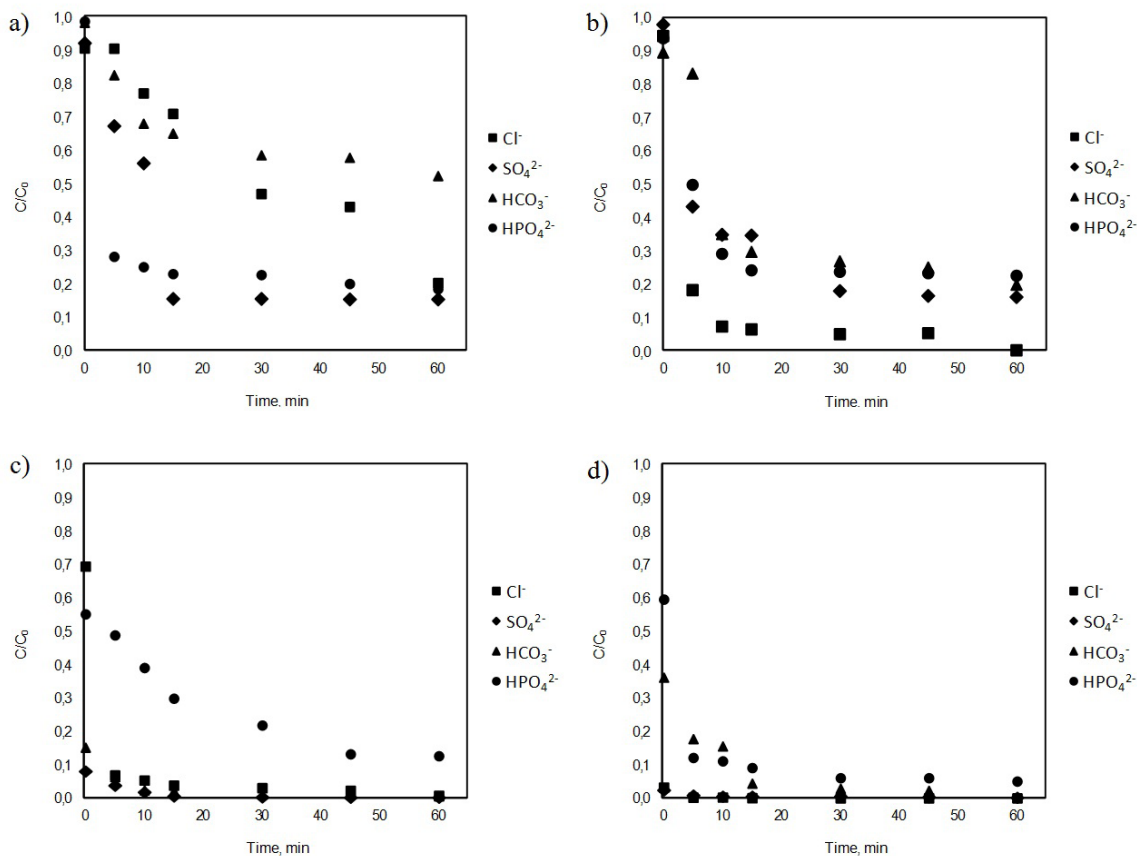


Figure 1. Influence of selected anions on the photocatalytic degradation of (a) DCF; (b) OP, (c) ANT and (d) BaP present in water solutions

adsorption on TiO_2 nanoparticles allowed only for a 2% decrease in the concentration of the compound. However, for solutions without inorganic compounds a 20% reduction in DCF concentration was observed (Fig. 2a). Also in OP and BaP solutions a negative influence of the tested ions on the degree of adsorption of micropollutants on the surface of the semiconductor was observed. The concentration of BaP in the presence of HCO_3^- and HPO_4^{2-} decreased only by 64 and 40% respectively, and for the solution without the addition of salt the removal degree reached more than 95%. Only in the case of ANT solution a beneficial effect of SO_4^{2-} and HCO_3^- ions on the adsorption degree of the compound on the TiO_2 surface was reported (Fig. 1c).

The start of UV irradiation of the reaction mixtures resulted in a gradual increase of the micropollutant removal. The removal degree of DCF after 60 min of irradiation of solutions containing Cl^- , SO_4^{2-} , HCO_3^- , and HPO_4^{2-} reached 80%, 85%, 45% and 82% respectively. For OP water solution the highest decrease in the compound concentration exceeding 99% was observed for reaction mixtures containing Cl^- ions (Fig. 1b). Conversely, the lowest reduction in the concentration of this compound, which did not exceed 77% was observed in solution, which consisted HPO_4^{2-} ions.

The concentration of ANT with the presence of such ions as Cl^- and HPO_4^{2-} after 15 min of photochemical oxidation decreased by 96% and 70% respectively (Fig. 1c). Only the presence of HCO_3^- and SO_4^{2-} did not affect on the decomposition mechanism of that compound and the micropollutant removal rate reached the same level of 98% as for solutions with no salt. Different correlations were observed in case of BaP (Fig. 1d). The addition of HCO_3^- as well as HPO_4^{2-} decreased the efficiency of the process and the obtained removal rates for this compound did not exceed 88% after 5 min of UV irradiation. In case of Cl^- and SO_4^{2-} ions did the removal rate for BaP reach 99%. The same compound removal degree was also obtained for the solution without the addition of salt (Fig. 2d).

The inhibition of the oxidation of the investigated micropollutants was caused mainly by the blocking of active centers on catalyst surfaces by competitive adsorbed Cl^- , SO_4^{2-} , HCO_3^- , and HPO_4^{2-} ions. It should be emphasized, that the mechanism of the heterogeneous photocatalysis assumes that the oxidation of micropollutants by

reaction with high reactive radicals occurs only when these compounds are adsorbed on the surface of the semiconductor, or are directly in close proximity [Augugliaro et al. 2012]. Therefore, if the presence of some ion group reduces the adsorption degree of organic compounds, it will also affect on the efficiency of the whole process of their photochemical decomposition.

The analysis of the kinetics of the heterogeneous photocatalysis occurring in the presence of Cl^- , SO_4^{2-} , HCO_3^- , and HPO_4^{2-} ions proved in some cases a significant difference between the rapidity of organic compounds' degradation observed during the first 15 min of the process and the rapidity of the decomposition reactions observed after the 15th min of UV radiation (Table 2). For example, the process of DCF decomposition in the solution containing SO_4^{2-} ions runs with a high reaction rate constant within the first 5 min of UV irradiation, and the half-life of the micropollutant reaching 5.4 min, but after the 15th min of the process the reaction rate constant significantly decreases and the DCF half-life exceeded 8513 min. Such large difference in the compound half-life was also observed in the case of OP decomposition in the presence of HPO_4^{2-} ions. The OP half-life up to 15 min of UV irradiation was equal to 9.3 min and then increases to 1395.4 min. A constant value of the reaction rate and the half-life during the whole 60 min of process running time was observed only for solutions containing DCF in the presence of Cl^- ions, ANT with HPO_4^{2-} ions and BaP with Cl^- or HCO_3^- ions.

These differences of the calculated compound half-life values may result from the formation of oxidation by-products, which were competitive adsorbed on the surface of catalyst or from the blocking of catalyst active centres by inorganic compounds, which leads to the inhibition of the oxidation of investigated parent compounds.

Figure 2 presented the influence of Al^{3+} and Fe^{3+} cations on the photochemical decomposition of investigated micropollutants. Both cations applied to the suspensions significantly influenced the adsorption rate of DCF and OP on the catalyst surface. The DCF decrease rate reaching 17% for Al^{3+} and 1% for Fe^{3+} (Fig. 2a), whereas the OP decrease rate reaching 44% and 22% correspondingly (Fig. 2b). In the case of polycyclic aromatic hydrocarbons ANT and BaP adsorption only the presence of Fe^{3+} inhibited the adsorption of the compound on TiO_2 nanoparticles. The concentration of ANT after the sorption process conducted

Table 2. Half-life of investigated compounds during heterogeneous photocatalysis in the presence of selected anions

Compound	Ions	Reaction Time. min	Reaction Rate Constant k . min ⁻¹	R^2	Half-Life $t_{1/2}$. min
DCF	Cl^-	0–60	0.0236	0.95	30.0
		0–15	0.1107	0.83	5.4
	SO_4^{2-}	15–60	0.0003	0.8	8513.8
		0–15	0.0286	0.95	25.7
	HCO_3^-	15–60	0.0044	0.93	242.5
		0–10	0.1373	0.81	6.5
HPO_4^{2-}	10–60	0.0044	0.93	242.5	
	OP	Cl^-	0–15	0.1804	0.87
15–60			0.0880	0.64	15.6
SO_4^{2-}		0–30	0.0489	0.85	21.4
		30–60	0.0036	0.89	644.6
HCO_3^-		0–15	0.0837	0.89	8.5
		15–60	0.0086	0.93	204.5
HPO_4^{2-}	0–15	0.0923	0.95	9.3	
	15–60	0.0015	0.98	1395.4	
ANT	Cl^-	0–15	0.1791	0.77	9.3
		15–60	0.0341	0.86	95.7
	SO_4^{2-}	0–15	0.1739	0.99	18.0
		15–60	0.0247	0.85	229.2
	HCO_3^-	0–15	0.1356	0.92	20.1
		15–60	0.0260	0.9	160.1
HPO_4^{2-}	0–60	0.0261	0.95	52.6	
BaP	Cl^-	0–15	0.2487	0.83	18.8
		0–15	0.1026	0.83	45.7
	SO_4^{2-}	15–60	0.0247	0.85	219.4
		0–60	0.0723	0.92	27.7
	HCO_3^-	0–15	0.1146	0.73	14.3
		15–60	0.0118	0.84	254.2

in the presence of Fe^{3+} cations decreased only by 34% (Fig. 2c) and the removal rate of BaP did not exceed 20% (Fig. 2d). Al^{3+} ions had no impact on the adsorption rate of BaP but they contributed to the increase in the adsorption rate of ANT, which reached 97%.

Additionally, it was determined that the presence of Fe^{3+} ions in the micropollutant solutions also decreases the efficiency of photochemical degradation of all investigated compounds. For example, the decomposition rate of DCF after 60 min of irradiation reached only 46% and for solutions without salts the removal degree of this compound exceeded 90% (Fig. 2a). Similar results indicating the inhibition of the process of decomposition of micropollutants by Fe^{3+} ions were obtained during the photocatalytically decomposition of pharmaceutical compounds such as carbamazepine and ibuprofen [Kudlek et al. 2016]. Also the presence of Al^{3+} lead to an decrease in the DCF and OP decomposition compared to salt-free solution. However, in the case of ANT oxidation, the Al^{3+} ions assisted the decomposition of the compound, especially in the initial time of UV exposure (Fig. 2c). The removal degree of ANT

after 5 min of irradiation reached above 98%, and for the solution without salt it only received 90%. On the other hand, Al^{3+} ions after the 15th min of UV irradiation of ANT and BaP solution did not have a significant influence on the reaction course. The removal degree of those compound equalled to 99% as in case of the process conducted with no inorganic compounds.

Table 3 summarizes the calculated reaction rate constants and half-lives of investigated compounds determined during the photocatalysis of solutions containing selected cations. The compounds half-lives estimated up to 15 min of UV irradiation and after the 15th min of the photocatalysis process demonstrate the same relationship as in the case of conducting the process in the presence of anions. Only for the decomposition of DCF in the presence of Al^{3+} and Fe^{3+} the half-lives in the first stage of the process were longer than these calculated after the 15th min of irradiation. For example, the half-live between the beginning of the process and the 15th min for the solution containing Al^{3+} was equal to 66 min and the half-live between the 15th and 60th min was not longer than 3.3 min.

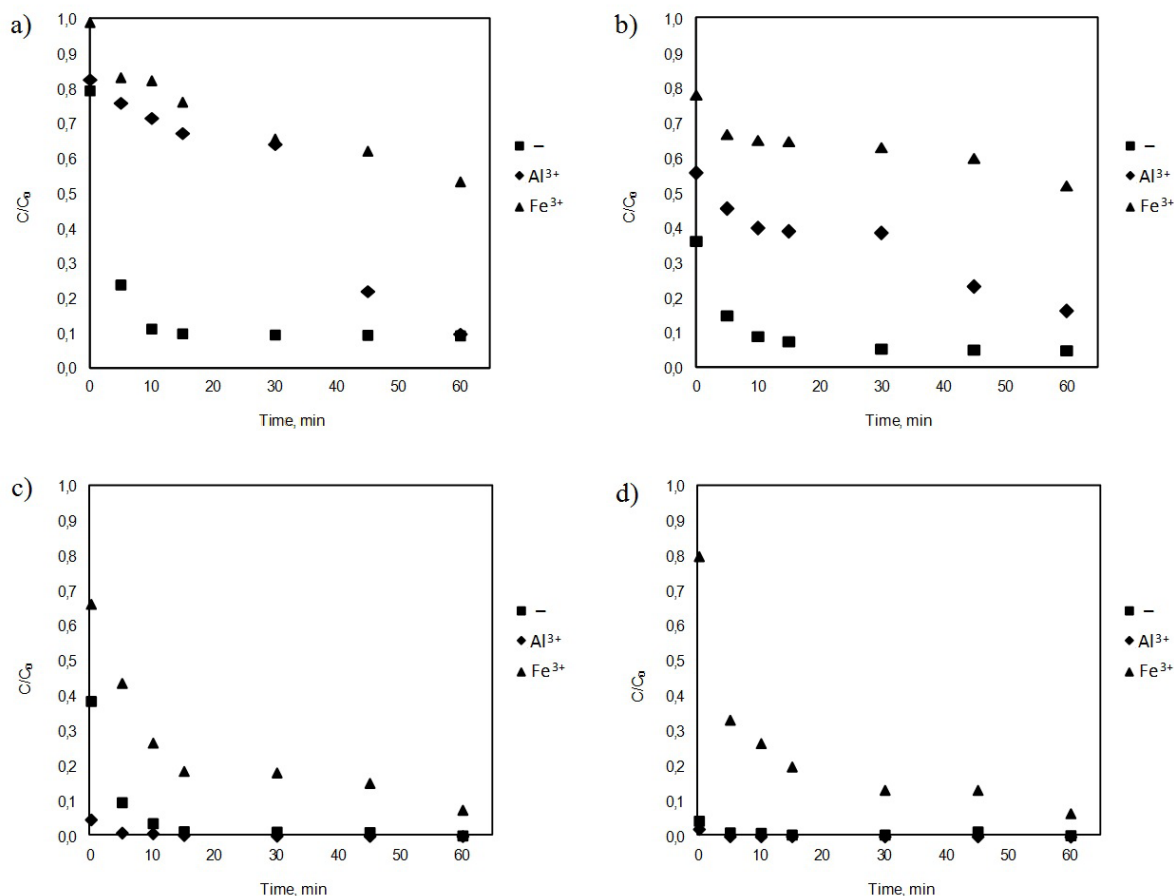


Figure 2. Influence of selected cations on the photocatalytic degradation of (a) DCF; (b) OP, (c) ANT and (d) BaP present in water solutions (■ – water solution without inorganic compounds)

Table 3. Half-life of investigated micropollutants during heterogeneous photocatalysis of water solutions in the presence of selected cations

Compound	Ions	Reaction Time. min	Reaction Rate Constant k . min^{-1}	R^2	Half-Life $t_{1/2}$. min
DCF	-	0–15	0.1395	0.89	8.4
		15–60	0.0013	0.93	2288.8
	Al^{2+}	0–15	0.0135	0.99	66.0
		15–60	0.0456	0.91	3.3
	Fe^{2+}	0–60	0.0091	0.94	86.8
		0–15	0.0118	0.73	83.4
OP	-	0–10	0.1403	0.98	12.6
		10–60	0.0117	0.83	266.0
	Al^{2+}	0–15	0.0240	0.9	55.0
		15–60	0.0209	0.91	57.5
	Fe^{2+}	15–60	0.0047	0.88	219.7
ANT	-	0–10	0.2313	0.99	7.4
		10–60	0.0373	0.80	103.1
	Al^{2+}	0–15	0.1477	0.9	26.9
		15–60	0.0235	0.95	249.1
	Fe^{2+}	0–15	0.0858	0.99	12.9
		15–60	0.0191	0.77	101.2
BaP	-	0–10	0.1338	0.87	29.5
		10–60	0.0215	0.91	231.4
	Al^{2+}	0–10	0.3091	0.75	16.3
		10–45	0.0231	0.84	319.3
	Fe^{2+}	0–15	0.0876	0.9	12.5
		15–60	0.0220	0.87	88.9

CONCLUSION

It was demonstrated that inorganic compound can influence the efficiency of micropollutants' decomposition. The oxidation process strictly depends on the type of compound as well as on the adsorption degree on semiconductor surface and the time of UV irradiation. The presence of Cl^- , SO_4^{2-} , HCO_3^- and HPO_4^{2-} ions in the tested micropollutants solution significantly decreased the adsorption degree of organic compounds on the TiO_2 surface. Only in the case of ANT solution a beneficial effect of SO_4^{2-} and HCO_3^- ions on the adsorption degree of the compound was reported.

The highest decrease in the compound concentration after 60 min of photocatalysis, which exceed 99%, was observed for ANT and BaP in solutions containing Cl^- , SO_4^{2-} and HCO_3^- ions. The lowest removal rate was observed for DCF in the presence of HCO_3^- anions. The presence of Fe^{3+} cations inhibited the reaction course of the compound decomposition in all tested micropollutant solutions. Al^{3+} affected the decrease of the process efficiency only for DCF and OP. In case of ANT the presence of Al^{3+} increased the decomposition of the compound, especially in the initial time of UV exposure.

The analysis of the kinetics of heterogeneous photocatalysis process showed a difference between the rapidity of organic compounds' decomposition during the first 15 min of the process and the and the rapidity of the decomposition reactions observed after 15 min of UV radiation. This fact indicates the generation of oxidation by-products of parent compounds, which were competitive decomposed during the photochemical process.

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