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The Photodecomposition of Selected Organic Micropollutants in the Presence of Chlorides †

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Abstract: This paper determined the influence of selected inorganic substances on the UV-based decomposition of organic micropollutants from a group of pharmaceuticals, pesticides, industrial additives, hormones, and food additives, depending on the number of days in water. It was determined that the presence of NaCl and $CaCl_2$ did not significantly affect the photodecomposition of micropollutants. A marked decrease in compound decomposition compared to the solution without inorganic compounds was noted in suspensions with Al^{3+} and Fe^{3+} cations. The addition of NH_4^+ affected the increase in compound decomposition, which was especially noted for compounds belonging to the group of pesticides, industrial additives, and hormones.

Keywords: UV light; organic micropollutants; inorganic compounds

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1. Introduction

The presence of several types of organic pollutants in different water streams is a well-known problem in many branches of industry [1]. However, this problem is most acute in the development of drinking water treatment technologies. The presence of even small amounts of micropollutants in drinking water can have a negative impact on human health. One of the most popular techniques for the decomposition of micropollutants are UV-based advanced oxidation processes [2]. Their effectiveness strongly depends not only on the selected oxidation processes, the reagent doses, and the operation time, but also on the physicochemical composition of the treated water matrix. Therefore, it is necessary to determine the influence of individual organic and inorganic compounds on the course of the micropollutants decomposition process.

This paper presents a comparison of removal degrees of selected organic micropollutants in water solutions during the UV radiation process in the presence of NaCl, $AlCl_3$, $FeCl_3$, $CaCl_2$, or NH_4Cl.

2. Materials and Methods

Gas chromatography with mass detection (GC-MS) proceeded by solid-phase extraction (SPE) was used for the estimation of the tested micro-polutants in the initial and post-processed water samples. Details of both procedures were given in previous studies [3]. The research was conducted on deionized water solution spiked with a mixture of selected organic micropollutants: benzocaine, BE; diclofenac, DCL; ibuprofen, IBU; caffeine, CAF; carbamazepine, CBZ; triallat, TRI; triclosan, TCS; oxadiazon, ODZ; bisphenol, A BPA; 4-tert-octylphenol, OP; β-estradiol, E2; 17α-ethinylestradiol, EE2; mestranol, EEME; progesterone, P4; butylated hydroxytoluene, BHT; and acridine, ACR. The prepared solution was subjected to UV radiation, emitted by a medium-pressure mercury vapor UV lamp with a power of 150 W by Heraeus (Hanau, Germany), with and without the addition of 0.5 g/L of NaCl, $AlCl_3$, $FeCl_3$, $CaCl_2$, or NH_4Cl.

3. Results and Discussion

Liao et al. [4] indicated that the presence of both organic and inorganic substances affect the course of the micropollutant's decomposition process. The removal degrees of tested micropollutants exposed to 10 min of UV radiation in the presence of selected salts are summarized in Table 1.

Table 1. Micropollutant's removal degree after 10 min of UV process in the presence of selected inorganic compounds.

Compound	Removal Degree, %					
	Inorganic Compound					
	-	NaCl	$AlCl_3$	$FeCl_3$	$CaCl_2$	NH_4Cl
BE	15	15	10	8	15	16
DCF	55	55	45	40	54	57
IBU	23	23	20	17	23	25
CAF	3	0	0	0	0	0
CBZ	5	2	3	2	2	4
TRI	86	85	79	75	85	88
TCS	93	93	91	88	93	94
ODZ	86	86	78	77	86	87
BPA	60	60	54	51	59	62
OP	26	26	21	16	26	30
E2	60	60	58	56	59	65
EE2	75	75	70	67	75	77
EEME	72	72	70	66	71	75
P4	66	66	62	60	66	67
BHT	87	86	83	82	86	87
ACR	7	7	5	4	7	6

It was observed that the removal of individual micropollutants in the presence of NaCl and $CaCl_2$ was very similar to those observed in the process carried out in deionized water solutions. In the cases of CAF and CBZ only, it was observed that the presence of Cl^- and Na^+ ions decreased the degree of their removal. Sun et al. [5] showed that the presence of Cl^- ions in water solutions exposed to artificial UV light in combination with the chlorine action negatively affects the decomposition of CAF.

The introduction of Al^{3+} and Fe^{3+} ions into the solutions resulted in a decrease in the removal degrees of the tested organic micropollutants, and the removal degrees of individual pollutants in solutions containing Fe^{3+} ions were lower than those noted in solutions containing Al^{3+} ions. For example, the DCF removal degree was equal to 45% in the solution containing Fe^{3+}, and it did not exceed 40% in water solutions with the addition of Al^{3+}. The decrease in compound decomposition may be related to the appearance of light color and turbidity in solutions containing Al^{3+} and Fe^{3+}, which may cause the absorption of energy carried by UV radiation waves, leading to a disturbance in their proper penetration of the reaction mixture [6].

The presence of NH_4^+ ions in UV-irradiated water solutions increases the number of $HO^\bullet$ radicals [7]. This results in an increase in the removal degree of BE, DCF, and IBU, as well as compounds belonging to the group of pesticides, industrial admixtures, and hormones. On the other hand, the decomposition of CAF, CBZ, and ACR was at a lower level than in the solution without NH_4^+.

High concentrations of Cl^- ions may also negatively affect the decomposition of micropollutants during integrated oxidation processes [8]. Cl^- ions, competing with micropollutants, react with $HO^\bullet$ radicals according to Equations (1) and (2) [9], leading to a reduction in their number in the reaction mixture and the production of more selective and much weaker oxidants [10]. This is particularly important during the treatment of solutions with high salinity.

$$Cl^- + HO^\bullet \rightarrow HClO^{\bullet -} \quad (1)$$

$$HClO^{\bullet -} + H^+ \rightarrow Cl^\bullet + H_2O \quad (2)$$

4. Conclusions

The conducted research has shown that the presence of chloride salts influences the decomposition process of the tested micropollutants. The presence of $AlCl_3$ and $FeCl_3$ decreases the efficiency of the micropollutant decomposition process during UV irradiation, which may be related to the change in color and the turbidity of solutions containing these types of salts. Only the presence of NH_4^+ ions had a beneficial impact on the course of the organic pollutant decomposition.

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