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The effects of inorganic anions and organic matter on mesotrione (Callisto®) removal from environmental waters

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Abstract: The photocatalytic elimination of the herbicide mesotrione from the commercial formulation Callisto® in environmental and synthetic waters by means of heterogeneous advanced oxidation processes was investigated. The activities of the commercial photocatalyst TiO_2 Degussa P25 (TiO_2) and ZnO in the degradation of mesotrione under UVA and simulated sunlight in doubly distilled, ground and in river water was compared. Environmental waters as the matrix significantly lowered the removal rate (by about 4 and 1.5 times for TiO_2 and ZnO, respectively) under UVA irradiation. Besides, the organic additives from Callisto® also reduced the degradation rate of mesotrione. The effects of inorganic anions (Cl^-, SO_4^{2-} and HCO_3^-) and humic acid (HA), which were identified as major species in ground and river water, was evaluated. It was found that Cl^- (pH ≈4 and ≈8) and HCO_3^- (pH ≈8) using TiO_2 mainly accelerated the degradation rate of mesotrione, while SO_4^{2-} had the opposite effect at pH ≈4 and did not affect the degradation rate at pH ≈8. Furthermore, HA mainly did not significantly affect the degradation rate of mesotrione at pH ≈4 and ≈8. Moreover, almost all anions, and HA slightly inhibited the degradation rate of mesotrione in synthetic water using ZnO.

Keywords: herbicide; TiO_2 Degussa P25; ZnO; photocatalytic degradation; matrix effect.

INTRODUCTION

Herbicides are not only used in large amounts in agriculture, but also in urban and domestic applications, and represent potential pollutants that require further investigation. Mesotrione 2-[(4-methylsulfonyl)-2-nitrobenzoyl]cyclo-hexane-1,3-dione is a selective pre- and post-emergence herbicide, which con-

trols the growth of most broadleaf and some weed grass in maize crops. It was developed by Syngenta Agro and marketed under the commercial name Callisto®.[1] Safety data are available for Callisto[2] and describe two alcohol additives in the formulation, *i.e.*, poly(oxy-1,2-ethanediyl), alpha-isodecyl-omegahydroxy- and octan-1-ol, present respectively at 20–30 and 5–10 mass%.

Advanced oxidation techniques, including heterogeneous TiO_2-based photocatalysis, have proved to be efficient methods for the degradation of herbicides.[3] Heterogeneous photocatalysis is based on the production of highly reactive oxidizing agents, such as hydroxyl radicals ($^\bullet OH$). However, real water effluents usually contain a large number of substances, both inorganic and organic species that could affect the photocatalytic efficiency. In this sense, some studies suggested that inorganic ions and dissolved organic matter (DOM), commonly present in environmental water, may play an inhibition role on the photoefficiency in different ways: acting as competitive scavengers of $^\bullet OH/h^+$ or by competitive adsorption of other substrates onto the catalyst surface or by pH modifications.[4] Therefore, characterization of the TiO_2 photocatalytic oxidation of organics under experimental conditions that include realistic water compositions needs to be prioritized for the rational evaluation of the activity of TiO_2-based photocatalysis as a viable tertiary treatment option. Since ZnO has nearly the same band gap energy (3.2 eV) as TiO_2, its photocatalytic capacity is anticipated to be similar to that of TiO_2. However, ZnO nanoparticles may be able to absorb incident UVA irradiation more efficiently than TiO_2 and consequently have more active electronic transitions on its surface, resulting in a better photocatalytic activity.[5] Accordingly, ZnO is a potential substitute for TiO_2.[6]

The objective of this study was to investigate the matrix effect of environmental waters (ground and river waters) on the photocatalytic removal of mesotrione, the active ingredient of Callisto®, by means of heterogeneous photocatalysis. The effects of the most abundant ions (Cl^-, SO_4^{2-} and HCO_3^-) and humic acid (HA), as a surrogate for DOM, as well as the initial pH value of the reaction mixture were studied. An attempt was also made to investigate the influence of organic additives from Callisto® on the degradation rate of mesotrione. For this purpose, the activities of commercial catalysts, TiO_2 Degussa P25 and ZnO, under UVA irradiation and simulated sunlight were compared. Both photocatalysts have proven to be efficient in the degradation of mesotrione in doubly distilled water (DDW).[7]

EXPERIMENTAL

Chemicals, solutions, water samples and catalysts

All chemicals were of reagent grade and were used without further purification. Commercial formulation Callisto® 480–SC (90 % purity), containing 480±24 g dm^{-3} of mesotrione shown in Fig. 1, was supplied by Syngenta; 85 % H_3PO_4 was obtained from Lachema (Neratovice, Czech Republic); NaCl, $NaHCO_3$ and NaOH were from ZorkaPharm (Šabac, Serbia);

60 % $HClO_4$ from Kemika (Zagreb, Croatia); Na_2SO_4 from MP Hemija (Belgrade, Serbia); 99.8 % acetonitrile (ACN) from Sigma–Aldrich and technical humic acid, was the product of Fluka. All solutions were made using DDW. The initial pH of the reaction mixture was adjusted using a dilute aqueous solution of $HClO_4$ or NaOH. TiO_2 Degussa P25 (75 % anatase and 25 % rutile form, 50 m^2 g^{-1}, particle size of about 20 nm, non-porous, according to the producer's specification, hereafter TiO_2) and 99.96 % ZnO, Kemika were used as photocatalysts.
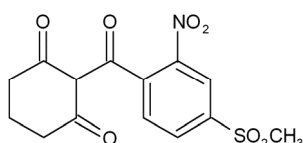

Fig. 1. Structure of the mesotrione molecule.

Physicochemical characteristics samples of ground water (Štrand, Novi Sad, Serbia) and river water, collected from Tisza (Szeged, Hungary) along with that of DDW are given in Table I.

TABLE I. The physicochemical characteristics of the analyzed water types; the concentrations are given in mg dm^{-3}

Parameter	Water type		
	DDW	Ground water	Tisza River
pH	6.50	7.20	7.75
Conductivity at 25 °C, µS cm^{-1}	2.9	1206	570
TOC^a, mg dm^{-3}	1.04	2.92	4.71
$c(HCO_3^-)$	8.07	768	249
c(fluoride)	$<DL^b$	$<DL^b$	0.31
c(chloride)	0.07	57.76	33.52
c(bromide)	$<DL^b$	$<DL^b$	0.06
c(nitrate)	0.09	$<DL^b$	1.94
c(nitrite)	$<DL^b$	$<DL^b$	$<DL^b$
c(sulphate)	$<DL^b$	131.64	63.17
c(lithium)	$<DL^b$	$<DL^b$	$<DL^b$
c(phosphate)	$<DL^b$	$<DL^b$	4.54
c(potassium)	0.03	3.41	5.39
c(sodium)	0.001	74.05	39.68
c(magnesium)	0.007	55.12	17.64
c(calcium)	0.03	115.7	64.5
c(ammonium)	$<DL^b$	$<DL^b$	0.10

[a]TOC: total organic carbon; [b]DL: detection limit

Photodegradation procedure

The photocatalytic degradation was realised in a cell using high-pressure mercury and halogen lamps, the characteristics of which were previously described in detail.[7,8]

The experiments were performed using 20 cm^3 of a 0.05 mmol dm^{-3} solution of meso-trione, as the active ingredient in Callisto®, containing 40 mg of catalyst (except for the study of direct photolysis). Experimental procedure of the degradation of TiO_2, *i.e.*, ZnO, suspen-

sion was described in a previous paper.[7] All experiments were performed at the natural pH (≈4 for TiO_2 and ≈8 for ZnO), except when studying the influence of the pH. In addition, in the experiments when HCO_3^- was added to the reaction mixture, the pH was adjusted to between 7 and 8, because of the instability of this ion at acid pH values, and to inhibit the appearance of carbonate ions above pH 8.3.[9]

Analytical procedure

Kinetics of the mesotrione photodegradation was monitored with UFLC Shimadzu Nexera[TM] with PDA detector at 225 nm (the wavelength of the maximum absorption of mesotrione).[8] *TOC* and pH measurements were performed in the conventional manner.[8]

RESULTS AND DISCUSSION

Effect of water type

The removal of mesotrione from different water types (DDW, ground and river) using two commercial catalysts and UVA or simulated sunlight irradiation was studied (Fig. 2). In DDW, the concentration of mesotrione decreased about 95 % within 20 min using both of catalysts under UVA irradiation. Besides, by comparing the efficiency of TiO_2 and ZnO, it could be noticed that the degradation rates of mesotrione were very similar (Fig. 2a). Namely, many authors in their studies of the removal of organics using different photocatalysts found that
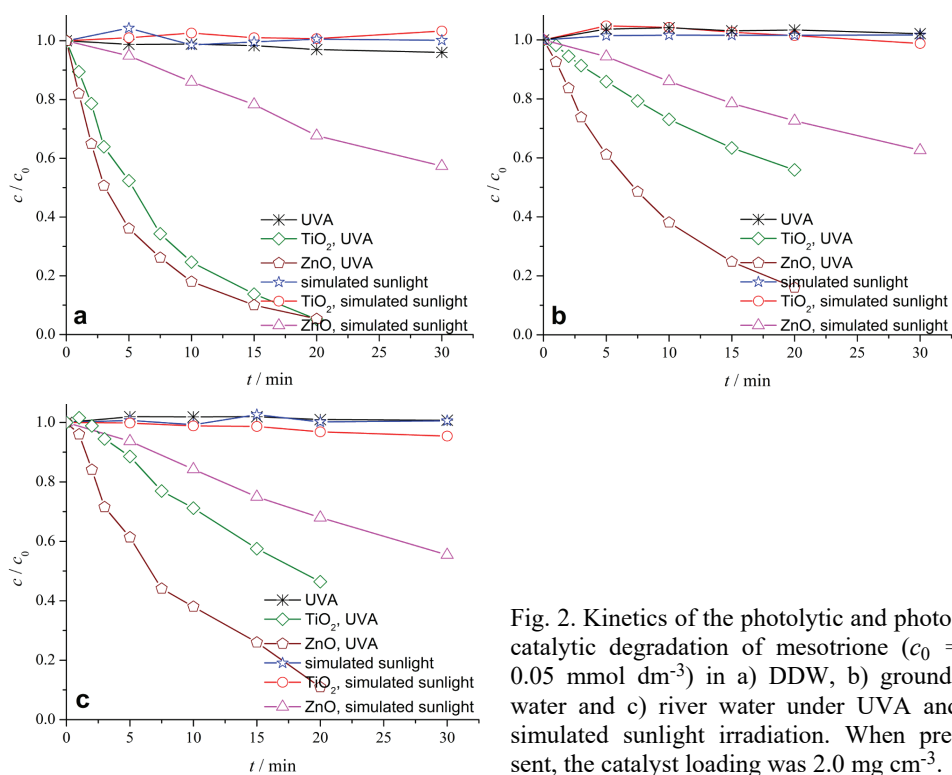

Fig. 2. Kinetics of the photolytic and photocatalytic degradation of mesotrione (c_0 = 0.05 mmol dm^{-3}) in a) DDW, b) groundwater and c) river water under UVA and simulated sunlight irradiation. When present, the catalyst loading was 2.0 mg cm^{-3}.

ZnO is a potential substitute for TiO_2 because of its similar or higher activities.[6,7,10,11] For simulation of sunlight irradiation, the degradation of mesotrione from Callisto® was performed using a halogen lamp, which, except the visible light irradiation, contains a smaller part of UVA irradiation. In this case, the concentration of mesotrione decreased by about 45 % using ZnO within 30 min of irradiation. On the contrary, practically no degradation was observed using TiO_2, as well as in the absence of catalysts for the same time of irradiation under simulated sunlight (Fig. 2a). This is understandable bearing in mind that the biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger fraction of the UV spectrum and the corresponding threshold of ZnO is 425 nm.[12]

Since Callisto® contains two alcohol additives, poly(oxy-1,2-ethanediyl), alpha-isodecyl-omegahydroxy- and octan-1-ol, an investigation was performed to clarify the effect of these species on the kinetics of mesotrione photodegradation. Namely, the degradation rate of mesotrione in Callisto® (Fig. 2a) was lower compared to the degradation rate of the mesotrione standard[7] using TiO_2 and ZnO under UVA and simulated sunlight irradiation. This difference could be attributed to the competitive reactions of the organic additives from Callisto® with oxidizing reagents, as a unique competitor, which results in a loss of the efficiency of the process. Namely, this formulated compound contains important amounts of the mentioned organic excipients, which are responsible for an important proportion of the organic matter and could interfere in the photo-oxidative process.[13] These results are in agreement with those obtained in study of the photocatalytic degradation of sulcotrione as standard and as the active ingredient in Tangenta®.[8]

Bearing in mind that the presence of inorganic ions in the water matrix has been shown to greatly influence the removal efficiency of target pollutants,[4] after investigations of mesotrione removal from Callisto® in DDW, its stability in ground, as well as in the river water was performed with/without catalyst and under UVA/simulated sunlight irradiation (Fig. 2b and c). Based on the kinetic curves ln c (substrate concentration) vs. t, the values of the pseudo-first order rate constant, k', can be calculated. It was found that the UVA/catalyst treatment was less efficient for the removal of mesotrione for both type of environmental water compared to DDW by about 4, and 1.5 times using TiO_2 and ZnO, respectively. Furthermore, the efficiency of mesotrione degradation in environmental waters using ZnO was about 2.7 times higher than using TiO_2. Moreover, practically no degradation was observed under simulated sunlight using TiO_2, as well as in the absence of both of catalysts for the same time of irradiation. However, the concentration of mesotrione decreased by about 40 % (for ground water) and 50 % (for river water), similar to in DDW, within 30 min of irradiation using ZnO under simulated sunlight (Fig. 2). Since the type of water did not significantly

affect the degradation efficiency of mesotrione under simulated sunlight, probably because of the lower degradation rate, all subsequent experiments were performed under UVA irradiation.

Effect of species in the solution matrix on mesotrione removal efficiency using TiO$_2$

An investigation of the effects of anions on the photodegradation performance is inevitable as these species are often associated with the complex matrices of ground and river waters or might evolve during the progress of the photocatalytic reaction. In this section, the effect of three inorganic anions (Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$), which were identified as major anions in ground and river water, were investigated during the photocatalytic oxidation of mesotrione from Callisto$^®$ using TiO$_2$ and UVA irradiation. In addition, it is expected that DOM in water could affect the decomposition rate of pollutants by a catalyst/UVA process. As with pollutants, organic compounds may react directly with $^•$OH or absorb UV light. Organic compounds may also react with organic radical intermediates formed during the treatment, thus decreasing the decomposition rate of the target pollutants.[14]

In order to investigate the effects of the mentioned inorganic anions and HA on the efficiency of mesotrione photodegradation, a series of experiments were conducted using TiO$_2$ under UVA irradiation at the natural and at pH ≈8. Namely, all the mentioned species were added in the initial suspension of Callisto$^®$ and catalyst at concentrations relevant to ground, *i.e.*, river water (Table I). In addition, the initial pH of the reaction mixture was adjusted to the pH of environmental waters after addition of the catalyst.

Effect of chloride. The effect of Cl$^-$ on the photodegradation of mesotrione under UVA light irradiation was investigated by adding NaCl to the reaction mixture. It is interesting to note that Cl$^-$ (1.6 mmol dm^{-3}, the concentration relevant to ground water) led to an obvious enhancement of the mesotrione removal at pH ≈4 (Fig. 3a). The obtained results are in agreement with literature data that in the lower concentration range of Cl$^-$ (0–50 mmol dm^{-3}), the degradation rate of the substrate increased.[15] This phenomenon was attributed to a surface chain-transfer mechanism involving chlorine radicals.[15] Namely, at pH ≈4, the TiO$_2$ surface is positively charged and mesotrione is in the anionic form. However, competition of Cl$^-$ with herbicide molecules for the limited active sites on TiO$_2$ was not significantly expressed because of the very low concentration of chloride ions (1.6 mmol dm^{-3}). Besides, the formed chloride radical with a high potential 2.47 V is capable of oxidizing organic compounds effectively.[16] Accordingly, the accumulation of Cl$^-$ on the TiO$_2$ surface promoted removal of mesotrione by Cl radical-initiated reactions. This result is in agreement with those obtained in the photocatalytic oxidation of Acid Orange 7.[15] The promotion effect of Cl$^-$ in this case declined with increasing addition of ions (50–

–200 mmol dm^{-3}), and a higher content of chloride ion (>200 mmol dm^{-3}) was found to reduce the dye bleaching rate. On the contrary, at pH ≈8 the degradation rate of mesotrione was not affected (Fig. 4a). Namely, the point of zero charge (pH$_{pzc}$) of TiO$_2$ is about 6,[17] and hence, the surface of the catalyst would be negatively charged at pH 8 and Cl$^-$ could not be adsorbed on the surface of the catalyst.
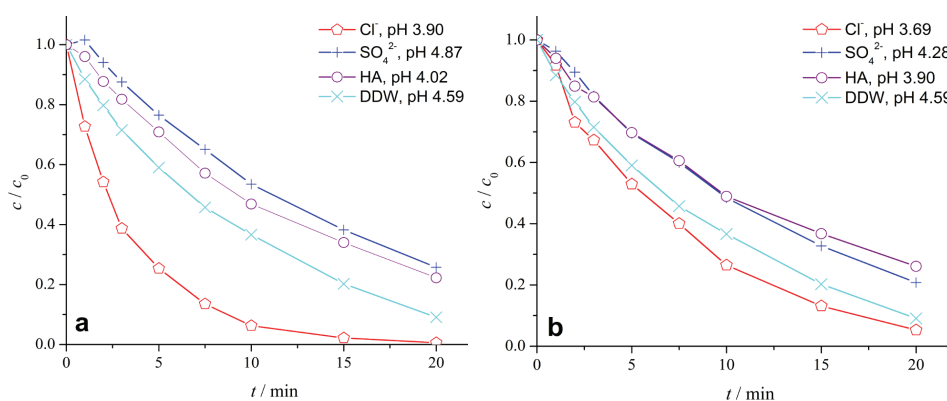

Fig. 3. Effect of different inorganic anions and HA in concentrations relevant to a) ground and b) river water on mesotrione (c_0 = 0.05 mmol dm^{-3}) removal by TiO$_2$ (2.0 mg cm^{-3}) under UVA irradiation.
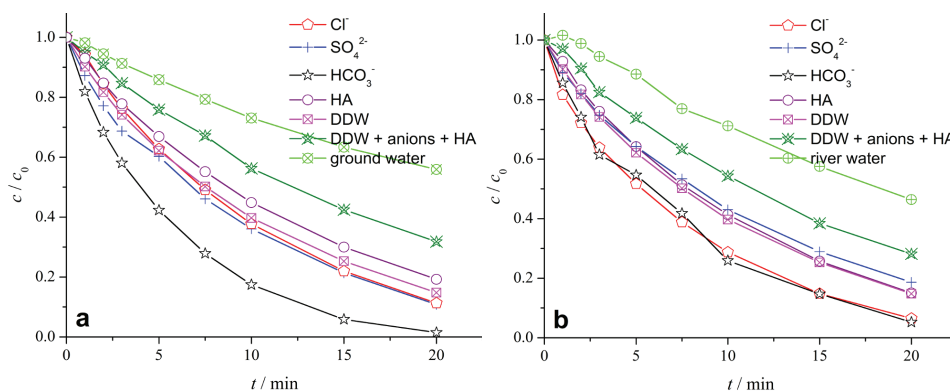

Fig. 4. Effect of different inorganic anions and HA in concentrations relevant to a) ground and b) river water on mesotrione (c_0 = 0.05 mmol dm^{-3}) removal by TiO$_2$ (2.0 mg cm^{-3}) under UVA irradiation, at pH from 7 to 8.

Furthermore, the presence of Cl$^-$ (0.94 mmol dm^{-3}, a concentration relevant to river water) at pH ≈4 showed slightly enhancement of the removal of mesotrione (Fig. 3b). The same was observed at pH ≈7 (Fig. 4b), probably because at this pH value, the TiO$_2$ surface is weakly negative compared to the case at pH ≈8

(Fig. 4a) and Cl⁻ accumulation on the TiO_2 surface was possible to a small extent.

Effect of sulphate. Single addition of SO_4^{2-} (1.4 and 0.66 mmol dm⁻³, concentrations relevant to ground and river water, respectively) inhibited the degradation rate of mesotrione (Fig. 3a and b). It was reported that SO_4^{2-} can adhere to the surface of TiO_2 *via* van der Waals forces and hydrogen bonds, and may displace some surface hydroxyl groups of TiO_2 *via* the ligand exchange mechanism.[18] According to the literature, the effect of decreasing the decomposition rate of the substrate in the presence of ions such as SO_4^{2-} is due to the fact that they act as scavengers of $^{\bullet}OH$.[19] It is well known that the reaction of the photocatalytic degradation of mesotrione proceeds mainly *via* OH radicals, and to a smaller extent *via* holes.[7] Besides, since SO_4^{2-} is doubly charged, it may display a higher adsorption ability on the surface of TiO_2 than HCO_3^-, Cl⁻ and other singly charged anions.[20] However, when the initial pH was set to ≈8, a value corresponding to the ground water, after the addition of catalyst and SO_4^{2-}, there was a no reduction in the rate of degradation (Fig. 4a and b) because the pH affects the surface charge of the catalyst and particle size diameter of the aggregates.[21] Namely, as was mentioned earlier, the pH_{pzc} of TiO_2 is about 6[17] and the surface of the catalyst would be negatively charged at pH 8 and SO_4^{2-} could not be adsorbed on the catalyst surface. Besides, at acidic pH, the adsorption of mesotrione on the TiO_2 surface and photon absorption would be reduced due to the agglomeration tendency of TiO_2.[22]

Effect of bicarbonate. Bicarbonate is one of the most abundant anions present in environmental waters. The effect of HCO_3^- (12.6 and 4.1 mmol dm⁻³, concentrations relevant to the investigated ground and river water, respectively) on the photocatalytic degradation of mesotrione was investigated by adjusting the solution pH to between 7 and 8. An enhancing effect on the removal of mesotrione using TiO_2 in DDW was found (Fig. 4a and b). Although both HCO_3^- and CO_3^{2-} are commonly used as scavengers to test whether the $^{\bullet}OH$ radical participates in a reaction solution[23] (reactions 1 and 2), it was also reported that, under certain concentrations, bicarbonate or carbonate may enhance the rates of pollutant degradation. Namely, in environmental waters (pH 6.5–8.5), HCO_3^- are present in higher amounts than CO_3^{2-} (pK_a HCO_3^-/CO_3^{2-} is 10.2), and their concentration rarely exceeds 0.05 mol dm⁻³. At this concentration, there is no noticeable effect of HCO_3^- on degradation.[24] Additionally, adding 3 mmol dm⁻³ bicarbonate to the suspension in the case of quinmerac[25] and 5 mmol dm⁻³ to the solution in the case of Methylene Blue[26] would greatly improve the degradation efficiency of the mentioned organics:

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \qquad (1)$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + OH^- \qquad (2)$$

Effect of humic acid. Humic substances are the major part of natural DOM and may accounts for up to 90 % of the total *TOC* content.[27] The effect of HA (9.0 mg dm^{-3}, which corresponds to a *TOC* value of 2.9 mg dm^{-3}, a concentration relevant to ground water) on the photocatalysis of mesotrione was investigated using TiO$_2$ (Figs. 3a and 4a). At pH $\approx$4 and $\approx$8, the addition of HA slightly affected the degradation rate of mesotrione. Namely, Wang *et al.*[28] investigated the effect of the concentration of HA in the range from 0–20 mg dm^{-3}. In their case, the photodegradation was impeded with increasing HA concentration in the range 5–20 mg dm^{-3}. Despotović *et al.*[25] also examined the effect of the concentration of HA in DDW in the range from 5 to 40 mg dm^{-3}. They found that, in the mentioned concentration range, increasing the HA concentration was accompanied by a decrease in the degradation rate of quinmerac.

The effect of HA (13.5 mg dm^{-3}, which corresponds to a *TOC* value of 4.5 mg dm^{-3}, concentration relevant to river water) on photocatalysis of mesotrione was also investigated using TiO$_2$ (Figs. 3b and 4b). The addition of HA at pH $\approx$4 influenced a decrease in the degradation rate of mesotrione. On the contrary, at pH $\approx$8, the presence of HA did not affect the degradation rate of mesotrione. This is in agreement with literature findings, stating that at pH $\approx$4 and in the presence of HA, the zeta potential of TiO$_2$ nanoparticles (NPs) is close to zero, and they reach an aggregation maximum. When the pH is greater than the pH$_{pzc}$, the zeta potential of TiO$_2$ NPs is high ($\approx$40 mV), and it barely changes with increasing HA concentration. Thus, TiO$_2$ NPs are notably stable, and their size does not grow at pH 8.[29]

Effect of typical natural water constituents in synthetic and environmental waters

To obtain further insight into the effect of constituents in water on photocatalytic degradation of mesotrione, ground and river water were employed in the photocatalysis to compare the results with those obtained using DDW. Namely, ground and river water were spiked with mesotrione and after the addition of TiO$_2$, irradiated as described earlier. In addition, the compositions of the environmental waters were simulated by the simultaneous addition of all the mentioned anions and HA, and by adjusting the initial pH in DDW (DDW+anions+HA, Fig. 4). The degradation rate in both of cases was lower than the degradation rate in DDW, but still higher than the degradation rate of mesotrione in environmental waters (Fig. 4a and b), probably because of some at this moment unexplored factors. Although single added anions and HA in DDW enhanced or did not affect the degradation rate of mesotrione, the simultaneous addition of all species decreased the degradation rate, probably due to increased adsorption of anions on the surface of TiO$_2$, which reduces the available catalytically active sites. In addition, catalyst deactivation found in environmental waters could be attributed to the combined effect of the presence of all species.

Effect of solution matrix species on mesotrione removal efficiency using ZnO

Ground and river waters were also spiked with mesotrione and subsequently ZnO was added. In both cases, the degradation rate was lower than in DDW (Fig. 5). In an attempt to clarify the role played by different ions (Cl^-, SO_4^{2-} and HCO_3^-), and HA, each of them has been separately investigated by adding at a concentration relevant to ground or river water. The obtained results indicated that the presence of the mentioned species mainly slightly inhibited the reaction and practically had no significant effect on the degradation rate of mesotrione. This could be explained by the fact that the ZnO surface is positively charged at pH 7.0 (pH_{pzc} of ZnO is ≈9.3[30]) and anions (Cl^-, SO_4^{2-} and HCO_3^-) were adsorbed onto the catalyst surface. Meanwhile, the ZnO surface charge becomes less positive (the positive site on the surface of ZnO), leading to decreased adsorption of mesotrione (which is present in the anionic form) onto ZnO. Furthermore, the adding of HA in these cases also did not significantly affect the degradation rate of mesotrione, as already mentioned, probably because of the relatively low concentration of HA.
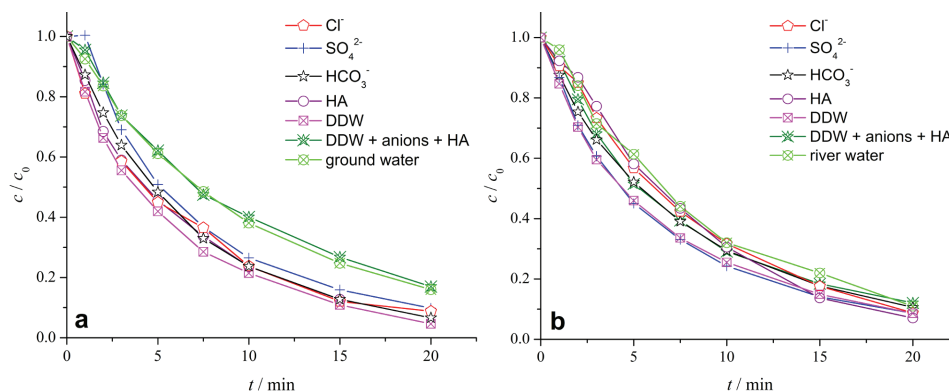

Fig. 5. Effect of separately and simultaneously addition of different inorganic anions and HA in concentrations relevant to a) ground and b) river water on mesotrione ($c_0 = 0.05$ mmol dm^{-3}) removal by ZnO (2.0 mg cm^{-3}) under UVA irradiation, at pH from 7 to 8.

Furthermore, the composition of environmental waters was simulated by adding all the mentioned anions, HA and by adjusting the initial pH in DDW after addition of ZnO (DDW+anions+HA, Fig. 5). The degradation rate in both of cases was lower than the degradation rate in DDW and very similar to the degradation rate in the case of ground, *i.e.*, river water.

CONCLUSIONS

The present study aimed at investigating the matrix effect of ground and river water on the photocatalytic removal of mesotrione, active ingredient of Callisto®, by means of heterogeneous photocatalysis. The obtained results

showed that efficiency for the degradation of mesotrione under UVA irradiation is higher with ZnO than with TiO_2 in ground and river water, while in DDW, the degradation efficiency was very similar. Moreover, practically no degradation was observed under simulated sunlight using TiO_2, as well as in the absence of both catalysts for the same time of irradiation. However, the concentration of mesotrione decreased by about 40, and 50 % using ZnO and simulated sunlight in the case of ground and river water, respectively. Besides, ground and river water as the matrix lowered significantly the removal rate (by about 4, and 1.5 times for TiO_2 and ZnO, respectively) during the photocatalytic oxidation of mesotrione under UVA irradiation. Inorganic anions and HA showed a significant water–matrix effect at acidic pH values compared to neutral/basic conditions, mainly due to the presence of anions adsorbed onto the TiO_2 surface. Using TiO_2, Cl^- (pH ≈4 and ≈8) and HCO_3^- (pH ≈8) accelerated the degradation rate of mesotrione, while SO_4^{2-} displayed a suppression effect on the degradation reaction at pH ≈4 but did not affect the degradation rate at pH ≈8. Moreover, HA mainly did not affect the degradation rate of mesotrione at pH ≈4 and ≈8. However, using ZnO, almost all anions, as well as HA slightly suppressed the degradation rate of mesotrione in synthetic waters. Finally, when anions and HA (at concentrations relevant to ground and river water) were simultaneously added to the reaction suspensions, the degradation rate of mesotrione was lower than in DDW, but still higher than the degradation rate in environmental waters using TiO_2, and very similar using ZnO. It was also found that the presence of organic additives from Callisto® inhibited the photodecomposition of mesotrione.

И З В О Д

УТИЦАЈ НЕОРГАНСКИХ АНЈОНА И ОРГАНСКИХ СУПСТАНЦИ НА УКЛАЊАЊЕ МЕЗОТРИОНА (CALLISTO®) ИЗ ПРИРОДНИХ ВОДА

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Испитана је ефикасност фотокаталитичког уклањања хербицида мезотриона из комерцијалне формулације Callisto® у природним и синтетичким водама применом хетерогене фотокатализе као вишег процеса оксидације. Упоређена је активност комерцијалних фотокатализатора TiO_2 Degussa P25 (TiO_2) и ZnO у случају разградње мезотриона применом UVA и симулираног сунчевог зрачења у дванут дестилованој води, подземној и речној води. Матрикс природних вода је значајно утицао на смањење брзине уклањања мезотриона (око 4 и 1,5 пута за TiO_2 и ZnO) под UVA зрачењем. Поред тога, органске супстанце присутне у Callisto® такође утичу на смањење брзине разградње мезотриона. Испитан је и утицај неорганских анјона (Cl^-, SO_4^{2-} и HCO_3^-) и ху-

минске киселине који су идентификовани као главне супстанце присутне у подземној и речној води. Нађено је да Cl⁻ (pH ≈4 и ≈8) и HCO₃⁻ (pH ≈8) у присуству TiO₂ углавном доводе до повећања брзине разградње мезотриона, док јони SO₄²⁻ имају супротан ефекат при pH ≈4, док при pH ≈8 не утичу на брзину разградње. Међутим, хуминска киселина углавном не утиче значајно на брзину уклањања мезотриона при pH ≈4 и ≈8. Поред тога, већина испитиваних ањона, као и хуминска киселина у малој мери утичу на смањење брзине разградње мезотриона у синтетичкој води у присуству ZnO.

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