

## PHOTOCATALYTIC OZONATION OF MONURON - EFFECT OF REACTION PARAMETERS ON THE HYDROXYL RADICAL FORMATION AND MONURON TRANSFORMATION

**Máté Náfrádi<sup>1</sup>, Milán Molnár<sup>1</sup>, Krisztina Schrantz<sup>1</sup>, Klára Hernádi<sup>2</sup>, Tünde Alapi<sup>1</sup>**

<sup>1</sup>*Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary*

<sup>1</sup>*Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich Béla tér 1.*

*e-mail: nafradim@chem.u-szeged.hu*

### Abstract

The combination of ozonation and heterogeneous photocatalysis (photocatalytic ozonation) can enhance the efficiency of the transformation of target pollutant and sometime results in synergistic effect, which is generally explained by the higher rate of formation of hydroxyl radical due to the presence of ozone. The transformation of organic pollutants on the surface of the photocatalyst is very complex, mainly in the presence of ozone. In the case of the heterogeneous photocatalysis the efficiency highly depends on the chemical structure of the target pollutant which determines its rate of reaction with molecular ozone and/or hydroxyl radical, and the adsorbed amount of pollutants on the surface of the photocatalyst, which is crucial in the case of the transformation by direct charge transfer. Moreover the properties of the solutions such as pH and ionic strength, affect the way and efficiency of the transformation through the modification of the surface properties of the photocatalyst (surface charge and potential, adsorption properties).

In the present work, the ozonation, heterogeneous photocatalysis and photocatalytic ozonation of monuron and coumarin were investigated. Monuron, one of the phenyl urea pesticide and suspected endocrine disruptor was used as target substance, while the rate of formation of hydroxylated byproduct of coumarin (umbelliferone) was used to compare the formation rate of hydroxyl radical under various circumstances.

Both ozonation and photocatalysis were found to be effective in the transformation of coumarin and monuron. Efficiency was enhanced using photocatalytic ozonation, but synergism was not observed. pH had significant effect neither in the case of monuron nor coumarin. The formation rate of umbelliferone formed from coumarin due to its reaction with hydroxyl radical was much higher during photocatalysis compared to ozonation, verifying the importance of the HO•, which was confirmed by the negative effect of methanol as HO• scavenger. Addition of NaF proved the importance of catalyst surface properties during photocatalytic ozonation.

### Introduction

The advanced oxidation processes (AOPs) give us possibility to solve one of the most important problems of water treatment: elimination of those organic pollutants which can be treated hardly by conventional water treatment methods. Using AOPs the transformation of the contaminants takes place in reactions with different reactive radicals. The most important radical is HO• due to its high reactivity and low selectivity. The combination of AOPs can result in synergism, which is generally explained by the increased HO• formation rate. [1]

Addition of ozone to a photocatalytic system can have several positive effects. The ozone can react directly with the organic substrate. Moreover adsorption of ozone is preferred comparing to oxygen and behaves as an excellent electron scavenger, successfully inhibiting the recombination of photogenerated electron and hole pairs.



The adsorbed  $H_2O_2$  can react with photogenerated electron and hole and results in the formation of  $HO^{\bullet}$  and  $HO_2^{\bullet}$ :



While formation of one  $HO^{\bullet}$  from oxygen requires three electrons, that needs only one electron from adsorbed ozone. [2,3]



Planning efficient and economically feasible water purification systems based on photocatalytic ozonation, several parameters must be taken into account. The pH of the solution is critical, because it affects the aggregation of catalyst particles, surface properties and consequently the reactions taking place on the surface. The surface charge of  $TiO_2$  depends on the pH, which influences the absorption of substrates. pH also affects the concentration of dissolved ozone in the solution. [4,5]

In this work the effect of pH, methanol and NaF on the efficiency of ozonation, heterogeneous photocatalysis and photocatalytic ozonation was investigated. The model pollutant monuron was a phenyl-urea pesticide, which may generate several environmental and health problems due to its persistence, toxicity, and possible endocrine effects.

Methanol was used as  $HO^{\bullet}$  scavenger for investigation the role and importance of this radical in the transformation of monuron. NaF was used as surface modifying agent to study the effect of adsorption. Coumarine can be used in photocatalytic systems to measure the formation rate of  $HO^{\bullet}$ . The formation rate of umbelliferone, which is the hydroxylated byproduct of coumarin is directly proportional to the formation rate of  $HO^{\bullet}$ . [6]

### Experimental

500  $cm^3$  monuron solution ( $5.0 \times 10^{-4}$  mol  $dm^{-3}$ ) and coumarine solution ( $1.0 \times 10^{-4}$  mol  $dm^{-3}$ ) were irradiated in a reactor equipped with a fluorescent mercury-vapor lamp, which emits in the region 300 - 400 nm UV light. The solution was circulated using a peristaltic pump with 375  $cm^3$   $min^{-1}$  flow rate, thermostated at  $25 \pm 1^{\circ}C$  and saturated with oxygen. The oxygen/ozone mixture was generated using an ozonator based on silent electric discharge. The concentration range was adjustable between 5-20  $mg$   $dm^{-3}$ . The concentration of ozone in oxygen/ozone mixture, which was bubbled through the solution or suspension was 10  $mg$   $dm^{-3}$  in each case. The  $TiO_2$  photocatalyst (Aeroxide P25<sup>®</sup>) was added in 1.0  $g$   $dm^{-3}$  concentration, and the suspension was centrifuged and filtered before analysis. NaOH and HCl solutions (0.1

mol dm<sup>-3</sup>) were used to set the pH. Ionic strength was constant and adjusted with addition of NaCl (5.0×10<sup>-3</sup> mol dm<sup>-3</sup>). Concentration of methanol or NaF was 2.5×10<sup>-2</sup> mol dm<sup>-3</sup>.

The concentration of monuron was determined by high performance liquid chromatography equipped with DAD detector (Merck-Hitachi L-7100 pump, RP-18 column, water-methanol 40:60 eluent, L-4250 UV-Vis detector, wavelength of detection: 210 nm ). The degradation of coumarine was followed using spectrophotometry at 277 nm, while the formation of umbelliferone by fluorimetry at 456 nm, wavelength of the excitation light was 332 nm.

## Results and discussion

At first the effect of pH on the concentration of dissolved ozone was investigated. There was found no significant effect between pH 3 - 9, while above pH 10 it was significantly reduced because of the OH<sup>-</sup> initiated degradation of ozone. Consequently, the effect of pH was investigated between pH 3 and 9 in the further experiments.

Table I. Effect of pH, methanol and NaF on the initial transformation rate of monuron ( $r_0^{mon}$ )

pH		O <sub>3</sub>	TiO <sub>2</sub> /UV	TiO <sub>2</sub> /UV/O <sub>3</sub>
		$r_0^{mon} (\times 10^{-8} \text{ moldm}^{-3}\text{s}^{-1})$	$r_0^{mon} (\times 10^{-8} \text{ moldm}^{-3}\text{s}^{-1})$	$r_0^{mon} (\times 10^{-8} \text{ moldm}^{-3}\text{s}^{-1})$
3.0	-	8.67	8.92	12.9
	NaF	-	9.08	18.7
	Methanol	-	3.58	2.0
5.5	-	9.50	13.0	14.8
	NaF	-	19.8	29.3
	Methanol	4.75	2.70	3.33
9.0	-	9.42	13.0	12.9
	NaF	-	20.0	23.6
	Methanol	4.25	4.08	2.33

In the case of ozonation the pH has no significant effect on the transformation rate of monuron (Table I.) similar to the concentration of dissolved ozone. Consequently, the transformation of monuron is probably caused by the reaction with molecular ozone. However methanol decreased significantly the rate of transformation (Table I.), proving that the relative contribution of the HO• initiated transformation is not negligible. Using heterogeneous photocatalysis the rate of transformation at pH 3 was found to be significantly lower than that under neutral or basic pH. Methanol strongly inhibited the transformation at each adjusted pH, while the positive effect of NaF depended on pH. That was observed only at pH 5.5 and pH 9.0 and significantly enhanced the transformation rate of monuron (Table I.). The effect of NaF can be explained by the better hydrophobicity of the TiO<sub>2</sub> favoring the adsorption of monuron.

The negative effect of methanol as radical scavenger and positive effect of NaF suggest that, monuron does not adsorbed well on the surface of TiO<sub>2</sub> under neutral and basic pH and

mainly the formed HO• is responsible for the its transformation. At pH 3.0 NaF has no effect and the initial transformation rate decreased comparing that to the pH = 5.5 (Table I.). Regarding that, the point of zero charge (where the net surface charge is zero) of TiO<sub>2</sub> is at pH = 5.6 in the 5.0×10<sup>-3</sup> NaCl solution, the positive net surface charge is probably favors, while the zero or negative net surface charge hinders the adsorption of monuron and favours the formation of HO•.

Table II. Effect of pH on the initial transformation rate of coumarin ( $r_0^{kum}$ ), the slope ( $m_0^{umb}$ ) of the initial part of the curve fluorescent light intensity versus treatment time (linear fitting) and the maximum value of the fluorescence light, emitted by umbelliferon ( $I_{max}$ )

		$r_0^{kum}$ ( $\times 10^{-8}$ mol dm <sup>-3</sup> s <sup>-1</sup> )	$r_0^{kum}/r_0^{kum}(ref)$	$m_0^{umb}$	$m_0^{umb}/m_0^{umb}(ref)$	$I_{max}$
<b>O<sub>3</sub></b>	pH = 5.5 without NaCl	32.3	1.04	0.17	1.21	85
	pH = 3.0	30.9	0.99	0.18	1.30	83
	pH = 5.5	31.1	-	0.14	-	76
	pH = 9.0	31.6	0.78	0.15	1.07	74
<b>TiO<sub>2</sub>/UV</b>	pH = 5.5 without NaCl	60.1	1.31	8.95	0.91	3725
	pH = 3.0	33.8	0.74	6.42	0.65	2034
	pH = 5.5	45.7	-	9.85	-	4298
	pH = 9.0	51.7	1.13	9.64	0.98	3540
<b>TiO<sub>2</sub>/UV/O<sub>3</sub></b>	pH = 3.0	57.6	1.04	4.56	1.82	1224
	pH = 5.5	59.8	-	2.50	-	738
	pH = 9.0	66.1	1.10	0.46	0.184	192

Behavior of coumarin was found to be very similar to that of monuron. pH has no effect in the case of ozonation and the rate of transformation slightly increased with increase pH in the presence of TiO<sub>2</sub>. Using photocatalytic ozonation, the transformation of coumarin was faster than using ozonation or photocatalysis, but synergism was not observed. (Table II.)

Using ozonation the rate of formation of umbelliferone ( $m_0^{umb}$ ) and the maxima of its concentration was almost negligible (two order of magnitude lower) comparing that to the values determined in the case of heterogeneous photocatalysis (Table II.). This confirmed that during ozonation mainly the reaction with molecular ozone is responsible for the transformation of coumarin and this reaction does not results in the formation of umbelliferon. However the pH effect is not countable on the rate of transformation of coumarin, the formation rate of umbelliferon was two times higher at pH 5.5 and 9.0 than under acidic pH in the case of heterogeneous photocatalysis (Table II.). This result is in accordance with the observation of Tunesi and Anderson [7] and shows that, the formation rate of HO• on the surface of the TiO<sub>2</sub> is strongly depend on pH and favored under neutral and basic conditions.

The enhanced efficiency of the combination of ozonation with heterogeneous photocatalysis is generally explained by the higher rate of HO• formation. The effect of ozone

in on the formation rate of umbelliferon was out of accord with our expectation, since significantly decreased the formation rate of umbelliferon. This suggests that the addition of ozone not enhances but inhibits the formation of HO•. But the effect of methanol, as HO• scavenger is contradicts of this, since the inhibition effect is well magnifested and the transformation rated of monuron was decreased with more than 80% (Table I).

Comparing the reaction rate constants of the coumarin, ozone and oxygen with electron, each value is in the same order (Table III). Regarding that, the concentration of oxygen is much higher than that of coumarin or ozone, the photogenerated electrons reacts mainly with oxygen. But adsorption has to be taken into account, because affects importantly the concentration of the compounds on the surface of the TiO<sub>2</sub>. Thus there is a possibility for the competition between ozone and coumarin for the photogenerated electrons and both this competition and the direct reaction of coumarin and ozone in the solution can be responsible for the fact that, ozone decreased the formation rate of the hydroxylated byproduct of coumarin.

Table III. The concentration and reaction rate constants (data from the NIST Standard Reference Database 40) of the compounds with electron

	c (mol dm <sup>-3</sup> )	k(e <sup>-</sup> ) (mol dm <sup>-3</sup> s <sup>-1</sup> )	c×k(e <sup>-</sup> ) (s <sup>-1</sup> )	k(HO•) (mol dm <sup>-3</sup> s <sup>-1</sup> )	c×k(HO•) (s <sup>-1</sup> )
O <sub>3</sub>	6×10 <sup>-5</sup>	3.6×10 <sup>10</sup>	2.2×10 <sup>6</sup>	2×10 <sup>8</sup>	1.2×10 <sup>4</sup>
O <sub>2</sub>	1.25×10 <sup>-3</sup>	1.7×10 <sup>10</sup>	2.1×10 <sup>7</sup>	-	-
coumarin	1.0×10 <sup>-4</sup>	1.6×10 <sup>10</sup>	1.6×10 <sup>6</sup>	2×10 <sup>9</sup>	2.0×10 <sup>5</sup>

## Conclusion

- Combination of ozonation and heterogeneous photocatalysis enhances the efficiency of the transformation of monuron and coumarin, but synergism was not observed
- pH has no significant effect on the transformation rates
- methanol strongly decreased while NaF enhances the transformation rate of monuron. The degree of effect depends on pH.
- Ozone significantly inhibits the formation rate of umbelliferone, probably because of the competition for the photogenerated electrons.

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