

PHOTOCATALYTIC OZONATION OF MONURON OVER SUSPENDED AND IMMOBILIZED TiO₂

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Abstract

Heterogeneous photocatalysis, using photocatalyst in suspensions and in immobilized form, ozonation, and their combination (photocatalytic ozonation) at various ozone (O₃) concentrations (0–20 mg dm⁻³ O₃ in gas phase) were investigated and compared in the transformation of the herbicide monuron (3-(p-chlorophenyl)-1,1-dimethylurea). Using the photocatalyst (Aeroxide[®] P25) in immobilized form, the rate of transformation of monuron was considerably lower compared to the case of suspension (1.0 g dm⁻³ TiO₂). O₃ increased the rate of transformation in each case, while the photocatalyst decreased the concentration of dissolved O₃. However, there was no synergistic effect during the combination of heterogeneous photocatalysis and ozonation. The economic feasibility of the treatments was also compared based on the obtained values of Electrical Energy per Order (*E*_{EO}). The *E*_{EO} value decreased with the increase of O₃ concentration in each case, and there was no significant difference between the energy requirement of ozonation and its combination with heterogeneous photocatalysis using TiO₂ in suspension at each O₃ concentration.

Introduction

Pesticides are indispensable for agricultural use however, their application can be detrimental due to their usually low biodegradability, resulting in their presence in the soil and waters, including drinking waters. Among them, the group of phenylurea pesticides have received attention due to their biotoxicity [1], while diuron and isoproturon are also listed priority hazardous substances [2]. Their removal from waters is an important task, that often cannot be achieved by regular water treatment methods, and therefore the application of advanced oxidation processes (AOPs), such as ozonation [3,4], or heterogeneous photocatalysis is required [4,5]. It is widely accepted that titanium dioxide (TiO₂) is the most adequate photocatalyst. After purification it is important to get rid of TiO₂ particles, which makes its industrial application a challenge. Therefore numerous attempts have been made to immobilize photocatalysts. While ozonation and heterogeneous photocatalysis are effective processes on their own, their combination – photocatalytic ozonation – under optimum conditions can have a synergistic effect both in oxidation and mineralization efficiency [6,7], and could be more cost effective.

The goal of this study is to investigate the degradation of the phenylurea herbicide monuron by ozonation, heterogeneous photocatalysis– in suspensions and using self-made immobilized catalyst sheets– and their combination (photocatalytic ozonation) at various

O₃ concentrations. The economic feasibility of treatments was compared based on the obtained values of Electrical Energy per Order (E_{EO}).

Experimental

Aeroxide P25[®] (75±5 % anatase and 25±5 % rutile, $a_{BET}^S=35-65 \text{ m}^2 \text{ g}^{-1}$, $d_{anatase}\sim 25 \text{ nm}$, $d_{rutile}\sim 40 \text{ nm}$, Evonik Industries) was used in suspension or immobilized onto a high-purity alumina ceramic paper (1.6 mm thickness, COTRONICS Co., cat. no.: 300-040-1). Ceramic paper sheets (34.0×14.0 cm, 476.0 cm²) were immersed in isopropyl alcohol, impregnated with Ti(OEt)₄ and then sprayed with ethanol based TiO₂ suspension ($c_{P25}=76.9 \text{ g dm}^{-3}$), as described by Veréb, et al. [8]. The surface loads of the immobilized TiO₂ correspond to the 1.0 g dm⁻³ suspension concentrations, when TiO₂ was used in aqueous suspension form in photocatalytic measurements. The model contaminant was monuron (> 99%, Sigma-Aldrich), dissolved in ultrapure Milli-Q water. Pure oxygen (99.5%, Messer) was used to saturate the aqueous solutions and to produce O₃.

Scanning Electron Microscopy (SEM) measurements were made using a Hitachi S-4700 Type II FE-SEM instrument. The X-ray diffractograms (XRD) were taken by a Rigaku Miniflex II diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), equipped with a graphite monochromator. AJASCO-V650 spectrophotometer with an integration sphere (ILV-724) was used for measuring the Diffuse Reflectance Spectroscopy (DRS) spectra of the samples ($\lambda = 300-800 \text{ nm}$).

Agilent 8435 UV-Vis spectrophotometer was used to measure the concentration of gaseous O₃ at 254 nm wavelength ($\epsilon_{254 \text{ nm}}=2950 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ [9]). The concentration of dissolved O₃ was determined spectrophotometrically by the indigo method [10,11]. The concentration of monuron was determined by high performance liquid chromatography (HPLC) equipped with a DAAD detector, using an Agilent 1100 modular HPLC system with a LiChroCART[®] C-18 column (250 mm×4 mm, 5 μm particle size) and methanol/water (60:40 V/V %) mixture (1.0 cm³ min⁻¹ flow rate) as eluent. The quantification wavelength was 244 nm.

The experiments were carried out in a recirculation reactor system described by Kovács, et al. [4]. The light source was a fluorescent UV lamp ($\lambda_{\text{max}}=365 \text{ nm}$, 15 W, GCL303T5/365 nm, LightTech) with a photon flux of $1.20(\pm 0.06)\times 10^{-5} \text{ mol}_{\text{photon}} \text{ s}^{-1}$ [4]. Ozoniser (Ozomatic Modular 4HC, max. 95 W) was used to produce 5, 10, 15, 20 mg dm⁻³ gaseous O₃.

The effectiveness of treatments were evaluated based on the E_{EO} values reflecting the electric energy in kilowatt hours [kWh] required to degrade the volume [e.g.: 1 m³] of contaminated water [12]. E_{EO} values [kWh m⁻³ order⁻¹] is calculated using the following formula in a batch system:

$$E_{EO} = \frac{P \times t \times 1000}{V \times \lg(c_i/c_f)} \quad (1)$$

where P is the rated power [kW] of the AOT the system, V is the volume [dm³] of water treated in the time t [h], c_i , c_f are the initial and final concentrations [mol dm⁻³], and \lg is the symbol for the decadic logarithm.

Results and discussion

SEM micrographs provide, that increasing the amount of the immobilized photocatalyst, larger aggregates of nanoparticles formed. XRD measurements were performed in order to determine the exact P25 loading of the ceramic sheet. The real loading and equivalent suspension concentrations of the samples are listed in Table 1. To verify the optical properties of the ceramic papers, DRS spectra were recorded. In case of the Ti(OEt)₄ impregnated sheet the band-gap value calculated was 3.9 eV (320 nm), which is close to the value registered for amorphous titanium oxide hydroxide. After the addition of P25, the registered dR/d λ curves and the evaluated band-gap values corresponded to P25.

Table 1 Nominal and measured loads and equivalent suspension concentrations for the prepared ceramic sheets with immobilized photocatalyst

Sample name	Nominal loading ($\times 10^{-3}$ mg cm $^{-2}$)	Nominal susp. c. (g dm $^{-3}$)	eq. Measured loading ($\times 10^{-3}$ mg cm $^{-2}$)	Measured eq. susp. c. (g dm $^{-3}$)
P25-1	1.55	1.0	1.51	0.97

Table 2 The initial transformation rates of monuron and the corresponding dissolved O₃ concentrations (determined in Milli-Q water without monuron)

		Initial rates of transformation ($r_0(\times 10^{-8}$ moldm $^{-3}$ s $^{-1}$) and dissolved O ₃ concentration (c_{O_3} (mg dm $^{-3}$))				
c _{O₃} in gas phase (mg dm $^{-3}$)		0	5	10	15	20
O ₃	r ₀	—	6.9±0.4	14.8±0.5	24.4±1.6	41.7±4.5
	c _{O₃}	—	2.0±0.1	3.8±0.1	5.1±0.1	10.3±0.0
susp. TiO ₂ /O ₃	r ₀	24.4±2.2	31.7±2.6	42.5±4.2	49.6±4.7	68.1±6.8
	c _{O₃}	—	1.3±0.0	2.0±0.1	4.1±0.1	7.8±0.3
im. TiO ₂ /O ₃	r ₀	8.1±1.0	16.1±1.5	24.8 ± 4.1	34.6±1.5	49.8±4.1
	c _{O₃}	—	1.2±0.0	2.21±0.1	4.1±0.3	8.9±0.2

O₃: ozonation; *susp. TiO₂/O₃*: combination of ozonation and heterogeneous photocatalysis when P25 was applied in suspension; *im. TiO₂/O₃*: combination of ozonation and heterogeneous photocatalysis when P25 was immobilized on ceramic paper

The increasing amount of O₃ enhanced the degradation rate of monuron ($c_0 = 5.0 \times 10^{-4}$ moldm $^{-3}$). The suspended catalysts proved to be more effective compared to the immobilized form in all processes. Addition of 20 mg dm $^{-3}$ O₃ increased the rate of transformation by up to ~6 times compared to photocatalysis using immobilized P25 without O₃ addition, whereas in the case of suspended P25 the increase is only ~3 times. Comparing the data determined at 20 mg dm $^{-3}$ O₃ concentrations, the effect of the photocatalyst on the monuron transformation rate and on dissolved O₃ concentration is found to be more significant in suspension than in immobilized form. TiO₂ decreased the concentration of dissolved O₃ in both cases, indicating that the improved reaction rates are probably due to the reactive radicals produced by the photocatalytic degradation of O₃. Moreover the O₃ can also enhance the efficiency of heterogeneous photocatalysis as a very effective electron scavenger inhibiting efficiently the recombination of photogenerated charges. However, there was no significant synergism in the case of photocatalytic ozonation under the experimental conditions applied in this work. To compare the economic efficiency of the applied AOPs the values of E_{EO} were calculated. The total E_{EO} values decreased with the increase of O₃ concentration in each case. At lower O₃ concentrations (0, 5, 10 mg dm $^{-3}$), the application of immobilized TiO₂ results in significantly higher values than ozonation or its combination with heterogeneous photocatalysis using TiO₂ suspensions (Fig. 4c). It has to be noted however, that the energy requirement of filtration was not taken into account, which would make the use of immobilized catalysts more preferable. At higher O₃ concentrations (15 and 20 mg dm $^{-3}$), there was no significant difference between the energy requirements. There is no significant difference between the energy requirement of ozonation and its combination with heterogeneous photocatalysis using TiO₂ in suspensions at each O₃ concentration, however the rate of transformation of monuron is enhanced in the case of the combined method.

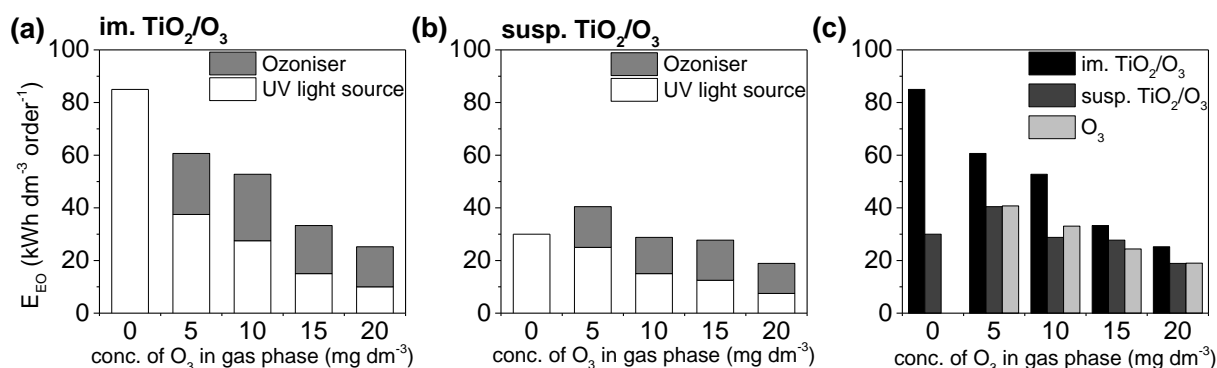


Figure 4 The E_{EO} values determined in the case of using immobilized TiO₂ (a), suspended TiO₂ (b) (white: the part of E_{EO} required by the UV light source; grey: the part of E_{EO} required by the ozoniser) and the total E_{EO} values determined in the case of investigated processes (c)

Conclusion

In this study photocatalytic ozonation of monuron over suspended and immobilized TiO₂ was investigated. O₃ increased the rate of transformation in each case, however there was no synergistic effect during the combination of heterogeneous photocatalysis and ozonation. The photocatalyst decreased the concentration of dissolved O₃. The E_{EO} value decreased with the increase of O₃ concentration in each case. At higher O₃ concentrations (15 and 20 mg dm⁻³) there was no significant difference observed between E_{EO} values of the methods.

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References

- [1] H. Mestankova, B. Escher, K. Schirmer, U. von Gunten, S. Canonica, *Aquat. Toxicol.*, 101 (2011) 466-473.
- [2] F.J. Benitez, C. Garcia, J.L. Acero, F.J. Real, *World Acad. Sci. Eng. Technol.*, 3 (2009) 648-656.
- [3] A.L. Tahmassebi, S. Nélieu, L. Kerhoas, J. Einhorn, *Sci. Total Environ.*, 291 (2002) 33-44.
- [4] K. Kovács, J. Farkas, G. Veréb, E. Arany, G. Simon, K. Schrantz, A. Dombi, K. Hernádi, T. Alapi, *J. Environ. Sci. Health, B.*, (2016) 1-10.
- [5] R.R. Solís, F.J. Rivas, A. Martínez-Piernas, A. Agüera, *Chem. Eng. J.*, 292 (2016) 72-81.
- [6] M.J. Farré, M.I. Franch, S. Malato, J.A. Ayllón, J. Peral, X. Doménech, *Chemosphere*, 58 (2005) 1127-1133.
- [7] F.J. Beltrán, F.J. Rivas, O. Gimeno, *J. Chem. Technol. Biotechnol.*, 80 (2005) 973-984.
- [8] G. Veréb, Z. Ambrus, Z. Pap, K. Mogyorósi, A. Dombi, K. Hernádi, *React. Kinet., Mech. Catal.*, 113 (2014) 293-303.
- [9] E.J. Hart, K. Sehested, J. Holman, *Anal. Chem.*, 55 (1983) 46-49.
- [10] H. Bader, J. Hoigné, *Water Res.*, 15 (1981) 449-456.
- [11] C.F. Chiou, B.J. Mariñas, J.Q. Adams, *Ozone Sci. Eng.*, 17 (1995) 329-344.
- [12] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, *Pure Appl. Chem.*, 73 (2001).