Taping the Presence of Acidic Pollutants in Photocatalytic Degradation Processes
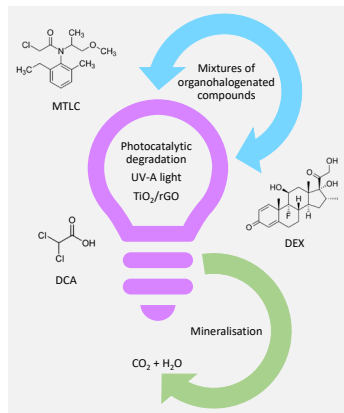
M.J. Rivero[i], C. Barquín[1], I. Ortiz[1]. (1) Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Avda. Los Castros s/n, 39005, Santander, Spain, riveromj@unican.es

This work reports the analysis of the photocatalytic degradation of aqueous mixtures of the organohalogenated compounds dexamethasone (DEX), S-metolachlor (MTLC) and dichloroacetic acid (DCA) with TiO_2/rGO. Experiments of single components, binary and tertiary mixtures are performed and compared in terms of degradation kinetics of the primary components and of the mixture mineralisation. In single solutions, MTLC is adsorbed to ≈50% on the photocatalyst, but this adsorption capacity is reduced in the presence of the other compounds. Comparing mineralisation rates, the binary mixture DEX+MTLC, requires 1.3 longer times than the single component solutions to remove 90% of the total organic carbon, due to the higher carbon load in the binary solution. However, the addition of DCA to the mixture surprisingly increased the mineralisation rate. This was later shown to be due to the decrease of the pH of the solution.

Introduction

The presence of organohalogenated compounds in aqueous media deserves special attention due to their toxicity. The stability of C-halogen bonds is responsible for their recalcitrant character [1,2]. TiO_2 is the most widely used photocatalyst in water treatment, producing mainly hydroxyl radicals [3]. To prevent the fast e^-/h^+ recombination and enhance the efficiency of photocatalysis, efforts are focused on the synthesis of composite semiconductors. Here, TiO_2/rGO with 5% of reduced graphene oxide (rGO) is synthesised [4]. The rGO promotes the formation of superoxide radicals and improves the photonic efficiency [3,5]. A challenge in up-scaling photocatalysis for water remediation is understanding the degradation of complex mixtures, as unfortunately the behaviour of individual compounds cannot be extrapolated to more complex mixtures. Previously, we investigated the degradation and mineralisation of single fluorinated dexamethasone (DEX), chlorinated metolachlor (MTLC) and double-chlorinated dichloroacetic acid (DCA) [1,6]. This work aims to clarify and compare the degradation and mineralisation kinetics of solutions with one, two and three organohalogenated pollutants.

Material and Methods

The photocatalytic activity of single DEX and MTLC, binary mixture DEX+MTLC, and tertiary mixture DEX+MTLC+DCA is evaluated. Experiments are performed in a 1 L photoreactor surrounded by UV-A LED lamps of 200 W m^{-2} irradiance with 0.11 mM of each pollutant and 0.5 g L^{-1} of TiO_2/rGO; the pH corresponds to the natural values of synthetic solutions. DEX and MTLC are quantified in a high-performance liquid chromatograph. DCA is measured by ion chromatography. Total organic carbon (TOC) is assessed in a TOC-V-CPH analyser.

Results and Discussion

Figure 1 represents the degradation of pollutants in solutions of 1, 2 and 3 components over time.
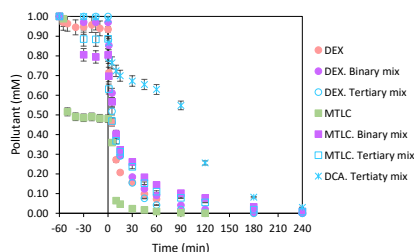

Figure 1. Photodegradation of DEX, MTLC and DCA, individual and complex mixtures, after 240 min of irradiation.

After 60 min in the dark, there is no evidence of DEX adsorption on either single component experiments or the mixtures. The measured adsorption of MTLC is ≈50%, ≈20% and ≈10% on TiO_2/rGO from solutions with one, two and three components, respectively. These results evidence competition between pollutants for the catalyst active centres. In the tertiary mixture, DCA is not adsorbed on the catalyst. In terms of photocatalysis, the degradation rate of MTLC is slightly

higher in the single component solution than in the mixtures; this could be related to the adsorbed concentration, since the MTLC concentration in solution after the adsorption period is reduced by half when it is the only component in solution. Degradation kinetics of DEX and MTLC in single component solutions follows a pseudo-first order model, with kinetic constants of 12.8×10^{-2} and 16.4×10^{-2} min^{-1}, respectively [6]. However, this difference is less notable in binary and tertiary mixtures, where the kinetic trend fits perfectly to a second order model with kinetic constants of 1.20 and 1.59 mM^{-1} min^{-1} for binary and tertiary mixtures, respectively. DCA individual degradation follows a pseudo-first order kinetic model as well [1], but its degradation in the tertiary mixture is influenced by the presence of the other compounds, showing an S-shaped trend with 2 kinetic zones and inflection point at 60 min. To evaluate the change in TOC of the solutions, experiments are conducted for 480 min, Figure 2. The mineralisation rate of DEX and MTLC single solutions is quite similar and follows the same trend, ≈90% of mineralisation is achieved after 360 min. For the binary mixture, two distinct kinetic trends are observed in the curve. A first zone up to 240 min and the second zone from 240 to 480 min. The change in slope can be attributed to the initial degradation of the parent compounds and the formation of intermediates, that mineralise faster once DEX and MTLC are fully degraded. However, mineralisation in the tertiary mixture occurs at a higher rate compared to the binary mixture, and follows the same trend as the mineralisation in the single component solutions.
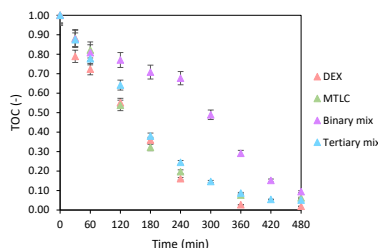

Figure 2. Mineralisation of single component, binary and tertiary mixtures after 480 min of irradiation.

The binary mixture takes 1.3 longer time to reach 90% mineralisation than the tertiary mixture or the single component solutions. This phenomenon can be explained by the difference in the initial pH values of the synthetic solutions, which after the adsorption period are: 4.3 for DEX, 4.2 for MTLC, 4.8 in the binary mixture and 4.0 in the tertiary mixture. The isoelectric point of TiO$_2$/rGO is ≈5.8 [4], therefore, the catalyst is positively charged in all experiments, but during degradation of the organohalogenated compounds Cl$^-$ and F$^-$ anions are released into the solution, that may be attracted by existing protons. Therefore, lower pH values accelerate the release of halides and may explain, the faster mineralisation in single component and tertiary solutions compared to binary solutions.

Conclusions

The rate of degradation and mineralisation of solutions containing one, two and three organohalogenated compounds is studied using TiO$_2$/rGO as photocatalyst. In the single solutions, all pollutants follow a pseudo-first order kinetic model, whereas in the binary and tertiary mixtures, the degradation curves of DEX and MTLC are fitted to a second order kinetic model, indicating that the photocatalytic sites on the catalyst are shared between the pollutants. DCA degradation is also altered by the presence of the other organic pollutants, showing an S-shaped curve with two different kinetic trends in the tertiary mixture. Regarding the rate of mineralisation, DEX+MTLC binary mixtures evidence lower rate than single component solution, fact that is easily attributable to the higher carbon load. However, surprisingly, the mineralisation rate of the tertiary mixture after addition of DCA is higher than in the binary solution, fact that can be associated to the effect of DCA in lowering the pH of the solution. Collectively, the presence of acidic compounds favours the rate of photocatalytic mineralisation in more complex mixtures.

References

[1] M.J. Rivero, P. Ribao, B. Gomez-Ruiz, A. Urtiaga, I. Ortiz, *Separation and Purification Technology*, 240 (2020) 116637.
[2] R. Yin, L. Ling, S. Lu, H. Li, C. Li, C. Shang, *Chemosphere*, 260 (2020) 127644.
[3] E. Brillas, S. Garcia-Segura, *Journal of Environmental Chemical Engineering*, 11 (2023) 109635.
[4] C. Barquín, M.J. Rivero, I. Ortiz, *Chemosphere*, 307 (2022) 135991.
[5] A. Joseph, A. Vijayanandan, *Sustainable Materials and Technologies*, 38 (2023) e00703.
[6] C. Barquín, M.J. Rivero, I. Ortiz, *Chemopshere*, 349 (2024) 140806.