

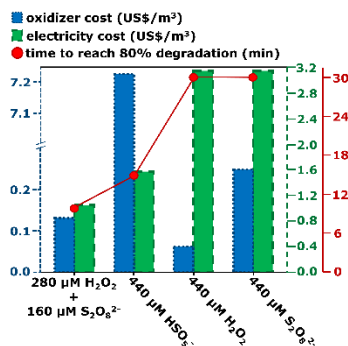
Intensification of UVC Treatment for Micropollutant Removal by Combined Use of the Oxidants H_2O_2 and $\text{S}_2\text{O}_8^{2-}$

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The combined use of oxidants under UVC_{254 nm} radiation has been assessed by multivariate optimization tools aiming to reach high degradation percentages of a mixture of microcontaminants (colchicine, nitazoxanide and sulfamethoxazole, 325 nM each) in short times and to reduce costs (electricity and reagent). Several combinations between hydrogen peroxide (H_2O_2), persulfate ($\text{S}_2\text{O}_8^{2-}$) and hypochlorite (OCl^-) at different concentrations (0-400 μM) were evaluated for municipal tertiary wastewater at pH 6.4 ± 0.2 . Best results ($\geq 95\%$ degradation in 20 min) were reached using the mixture of H_2O_2 (280 μM) and $\text{S}_2\text{O}_8^{2-}$ (160 μM) compared to 72-75% in the presence of 440 μM of $\text{S}_2\text{O}_8^{2-}$ or H_2O_2 . In addition, treatment capacity improved by 25% and reagent and electricity costs reduced by 98% and 34%, respectively, compared to HSO_5^- ($\geq 95\%$ degradation in 25 min). These results demonstrate that the combination of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ is the best alternative for scale-up in future studies.

Introduction

The diversity of contaminants generated by anthropogenic action results in complex wastewaters, posing risks to the environment and human health. With their distinct molecular characteristics, the degradation efficiency of these contaminants by advanced oxidation processes is closely linked to the preferential reactions of each oxidative radical [1]. The use of peroxymonosulfate (HSO_5^-), a commercial oxidant that generates both hydroxyl and sulfate radicals has demonstrated better efficiency of micropollutants degradation when compared to the isolated use of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ under UVC radiation [2]. On the other hand, HSO_5^- has a high cost as its main disadvantage [1]. Therefore, the chemometric tools Mixture Design and Rotatable Central Composite Design were used to optimize a mixture of oxidants (between hydrogen peroxide (H_2O_2), persulfate ($\text{S}_2\text{O}_8^{2-}$) and hypochlorite (OCl^-)) to reach the maximum simultaneous degradation of the target compounds colchicine (COL), nitazoxanide (NTZ) and sulfamethoxazole (SMX) in municipal tertiary wastewater and at a lower cost when compared to HSO_5^- .

Material and Methods

At first, a Simplex-centroid Mixture Design (STATISTICA® software - version 8.0) was used to investigate the simultaneous influence of the concentrations of H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ and OCl^- (ranged from 0 to 400 μM), with the response factor being the average degradation (%) of the target compounds after 20 min of irradiation. Residual concentrations of the target compounds were measured by HPLC-DAD and the respectively average degradation was calculated considering the initial concentration of each target compound. Next, based on the results of the Mixture Design, a two-factor Rotatable Central

Composite Design (STATISTICA® software - version 8.0) was applied to optimize the concentrations of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, also using the average degradation of the target compounds as the response factor.

Experiments were performed at lab-scale in a dark glass vessel (5.5 cm depth, 15.5 cm diameter and 4.3 cm optical path) under magnetic stirring. 500 mL of the effluent at pH 6.4 ± 0.2 (natural of the matrix) were spiked with a solution containing the mixture of target compounds to reach the desired concentration (325 nM of each compound). Then, the solution was exposed to irradiation provided by two 8 W UVC mercury vapor lamps ($\lambda_{\text{max}} = 254 \text{ nm}$) separated from each other by 3.5 cm and positioned 1 cm above the reactor. The matrix used in the experiments was sampled in a municipal wastewater treatment plant after the steps of bar screens and desanders, upflow anaerobic sludge blanket and coagulation-flocculation (FeCl_3) and kept under refrigeration at 4 °C until experiments were performed.

Results and Discussion

Applying special cubic modeling in a Simplex-centroid Mixture Design, the best degradation was obtained by combining H_2O_2 (200-320 μM) and $\text{S}_2\text{O}_8^{2-}$ (80-200 μM). The concentration of OCl^- can be neglected, as it had no significant effect on the response. Once the interaction between the variables and the concentration range that generates the best degradation of the target compounds had been determined, a Rotatable Central Composite Design was applied to optimize experimental conditions, and maximum degradation was observed in the presence of 280 μM of H_2O_2 and 160 μM of $\text{S}_2\text{O}_8^{2-}$.

Kinetic experiments were performed under 30 min of irradiation and these conditions (Figure 1). The

degradation performance was also compared to kinetic experiments in the presence of isolated oxidants (440 μM H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ or HSO_5^-) and with control experiments (photolysis or oxidant action in the dark). Under the optimized mixture of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, the concentrations of target compounds reached the quantification limit (QL < 16 μM), resulting in $\geq 95\%$ degradation after 20 min of irradiation while $77 \pm 3\%$ and $80 \pm 1\%$ of degradation were obtained for $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 , respectively, after 30 min of irradiation (Figure 1). These results highlight the improvement on the degradation of target compounds by the combination of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, as a consequence of simultaneous generation of hydroxyl and sulfate radicals. The effect of these reactive radicals is confirmed by control experiments since degradations of $21 \pm 3\%$ (oxidants actions in the dark) and $55 \pm 3\%$ (photolysis) were obtained after 30 min (Figure 1). In addition, a faster degradation occurred when the mixture of oxidants was used (20 min), compared to 440 μM HSO_5^- alone, which demanded 25 min to reach the QL (< 16 μM) (Figure 1), thus enhancing treatment capacity by 25 %. The best result obtained in the presence of the mixture of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ compared to HSO_5^- can be explained by the higher energy required to cleave the O-O bond in the HSO_5^- molecule (377 kJ/mol) compared to H_2O_2 (213 kJ/mol) and $\text{S}_2\text{O}_8^{2-}$ (92 kJ/mol) [3]. In parallel, electricity (energy tariff: US\$ 0.20 per kW/h) and reagents costs to treat 1 m^3 of effluent were estimated (Graphical abstract), considering the time needed to achieve 80 % degradation [4] of the mixture of target compounds (Figure 1). In addition to improving treatment capacity by reducing

irradiation time, the combined use of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ provided significant reductions of 34 % in electricity costs and 98 % in reagent costs (Graphical abstract) compared to HSO_5^- . These results reinforce that the mixture of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ is the best option for large-scale studies, since the treatment capacity was improved with significant reductions in electricity and reagent costs. However, it is worth noting that this estimate is based on a laboratory scale, and full-scale studies are needed to obtain greater precision in terms of operational costs.

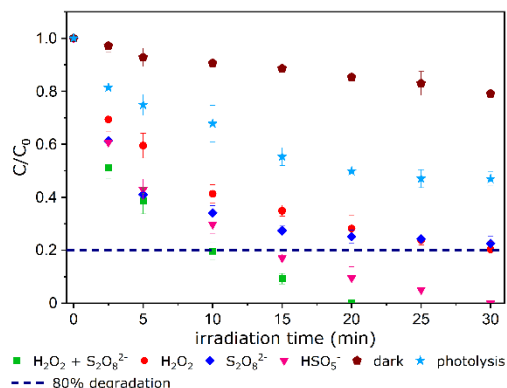


Figure 1. Comparison of the isolated and combined use of oxidants under optimized conditions in the degradation of the mixture of COL, NTZ and SMX (325 nM each compound) under UVC radiation. Initial conditions: (■) 280 μM H_2O_2 and 160 μM $\text{S}_2\text{O}_8^{2-}$, (●) 440 μM H_2O_2 , (◆) 440 μM $\text{S}_2\text{O}_8^{2-}$, (▼) 440 μM HSO_5^- , (●) dark and (★) photolysis; pH= 6.4 \pm 0.2.

Conclusions

The performance of a mixture of oxidants has been evaluated for degradation of microcontaminants in a municipal tertiary wastewater, and results were compared to those obtained in the presence of isolated oxidants (H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ or HSO_5^-). An improvement of degradation efficiency with an expressive reduction on reagent and electrical energy costs (Graphical abstract) were reached using a mixture of 280 μM H_2O_2 and 160 μM $\text{S}_2\text{O}_8^{2-}$ compared to experiments using 440 μM of the oxidants alone. These results suggest that the combination of these oxidants is the best alternative for future studies in continuous flow mode.

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