

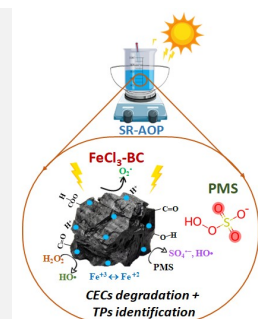
Activation of peroxymonosulfate by FeCl₃-modified biochar and sunlight for degradation of CECs: Transformation Products identification

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Sulfate radical-based advanced oxidation processes (SR-AOPs) have received great attention due to potential to degrade contaminants of emerging concern (CECs) from urban wastewater. In this study, FeCl₃-biochar was used to activate peroxymonosulfate under sunlight and applied for the degradation of CECs. Primary elimination of 90% was achieved and 19 TPs were generated during this process. FeCl₃-biochar was investigated under dark and sunlight. The use of FeCl₃-biochar/sunlight resulted 20% improvement compared to the system in dark, indicating positive effect of the sunlight in the process, under this conditions 2 TPs were identified. The identification of TPs strategy was based in the use of a purpose-built database and suspect screening analysis.

Introduction

Water pollution due to the presence of CECs is one of the main environmental issues we have nowadays. CECs are disposed of in the environment through wastewater discharges, as conventional treatments have low removal efficiency [1]. Therefore, several advanced treatments have been proposed as polishing step to promote their proper removal. Among them, Sulfate radical-based advanced oxidation processes (SR-AOPs) is receiving great attention due to its wide pH adaptability range, good selectivity, SO₄•⁻ stronger oxidative potential and longer life time compared to HO•, generated in other AOPs [2]. Peroxymonosulfate (PMS) is often used as oxidant, however, it requires activation to properly react and promote degradation of CECs. PMS activation by biochar (BC) could offer an environmental friendly and perhaps interesting economical approach. Additionally, BC can be easily modified (e.g. adding Fe) in order to improve PMS activation and CECs degradation [2]. As observed for other AOPs, one of the main drawbacks of BC/PMS system could be the generation of Transformation Products (TPs). Due to the potential to be more toxic and harmful than the parent compound, the identification of TPs generated during the process is of great interest. In this study, FeCl₃-BC/PMS process was investigated for the degradation of Carbamazepine (CBZ), Trimethoprim (TMP), Diclofenac (DCF) and Sulfamethoxazole (SMX) under sunlight. The TPs generated were identified using a purpose-built database and suspect screening analysis.

Material and Methods

All experiments were performed in batch mode in a 1L photoreactor under magnetic stirring at room temperature (blank experiments) or outdoors under sunlight. 1L of deionized water (DW) spiked with 100 µg/L of each CECs was added to the photoreactor prior to addition of BC. Pristine or modified BC were used. Modified BC (FeCl₃-BC) was prepared through precipitation method as reported by Adeel *et al* [3]. For this, pristine biochar was added in FeCl₃ solution and left overnight under stirring and room temperature. The

final step was activation by drying in a muffle furnace at 300° C for 3 h. The degradation of CECs was evaluated using FeCl₃-BC (0.25 g/L) under sunlight, and PMS (0.1 mM) was added at initial treatment time. Sampling was done throughout the experiments (0, 15, 30, 45, 60, 90, 120 min) and sodium thiosulfate (50 µL of 10 mM solution) was used to quench residual PMS and stop the degradation. PMS consumption was monitored during all the experiment. Samples were analyzed through UHPLC-DAD to monitor the degradation of CECs. The identification of TPs was accessed through LC-QTOF MS analysis and using a purpose-built database containing 107 TPs of the “parent” CECs that have already been published in the current literature. Additionally, the screening of suspect compounds approach was used and mass spectrum data information (exact masses of the molecular ion, characteristic fragments, isotopic pattern, and double-bond equivalency (DBE)). The experiments were performed under natural sunlight irradiation in clear sunny days at Plataforma Solar of Almería (Spain). UV-A irradiance of sunlight was monitored using pyranometer (Kipp & Zonen, CUV5, Netherlands). The data were obtained in terms of incident radiation (W/m²) in the range 280–400 nm and plotted as irradiation dose in kJ/m² at a given time.

Results and Discussion

The degradation of CECs was investigated using FeCl₃-BC and PMS concentrations selected from a previous study. Dark experiments done determined that FeCl₃-BC and FeCl₃-BC/PMS alone could eliminate 38% (by adsorption) and 50% (by adsorption and mild oxidation by PMS) of CECs in 180 min respectively. Obtained results (Fig. 1) showed that FeCl₃-BC/PMS/sunlight process achieved over 90% degradation of CECs within 10 min and 70% of PMS consumption. The same conditions were applied with pristine BC and 80% of CECs degradation was observed after 120 min and only 15% of PMS was consumed. Therefore, demonstrating improvement of modified BC. Pristine BC contains oxygenated functional groups (OFG) on its surface and it could

behave as a photocatalyst to activate PMS through electron transfer reactions generating both $SO_4^{\cdot-}$ and $HO\cdot$. The faster degradation of CECs in presence of $FeCl_3$ -BC could be attributed to the Fe particles in modified BC surface, which eventually fasten the removal of CECs by producing abundant ROS [2].

Additional blank experiments using only $FeCl_3$ -BC or PMS (under sunlight) were also performed (Fig. 1). The results showed similar behavior in both experiments and 80% degradation of CECs was observed after 150 min, with DCF and SMX being most sensitive compounds. However, in the system using only PMS/sunlight the concentration of PMS was constant during the experiment indicating that no $SO_4^{\cdot-}$ radicals were generated.

Concerning $FeCl_3$ -BC/sunlight process, higher removal rates were obtained, in comparison to the dark, indicating that not only adsorption of CECs took place but sunlight also had important role. Sunlight interaction with $FeCl_3$ -BC could be attributed to Fe particles attached on BC surface that might have triggered the Fenton (in small extension) and photo-Fenton like reactions under sunlight exposure, as BC contains abundant OFGs on its surface, which could generate superoxide radicals $O_2^{\cdot-}$ and under further reactions producing H_2O_2 and $HO\cdot$ (fasten by Fe^{2+})[2].

The identification of TPs was performed for the $FeCl_3$ -BC/PMS/sunlight process and also using only $FeCl_3$ -BC/sunlight, in order to have more details about CECs degradation. With PMS 19 TPs were identified, **Table 1**. TP from SMX was generated through oxidation of NH_2 group to NO_2 . While for TMP,

hydroxylation was the main mechanism involved. TPs from CBZ and DCF also involved hydroxylation, in addition to ring opening, with further oxidation and bond cleavage reactions. $FeCl_3$ -BC/sunlight (no PMS) resulted in the identification of only two TPs, CBZ (1) and DCF (1), both results of hydroxylation reactions. The generation of TPs corroborates the results obtained before, suggesting that adsorption is not the only process responsible for the removal of CECs in the system using only $FeCl_3$ -BC/sunlight. However, production of highly oxidizing species without PMS is not possible. Additionally, this demonstrates higher degradation capacity of $FeCl_3$ -BC/PMS/sunlight process, as $SO_4^{\cdot-}$ is being generated.

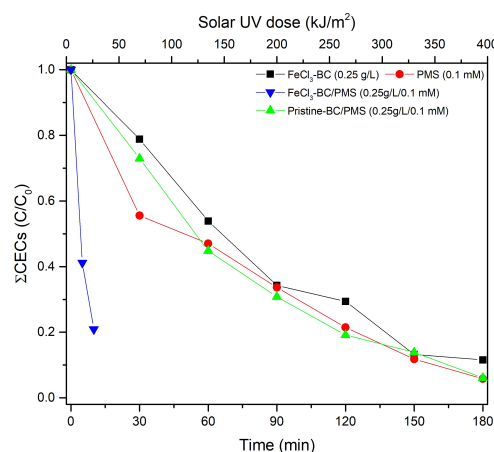


Figure 1. Degradation of CECs under different conditions.

Table 1. Accurate mass measurements of CECs and TPs found by LC-QTOFMS in positive ionization mode.

Compound	Rt/ min	Elem. Comp.	Ion Mass ^a / m/z	Error/ ppm	DBE	Compound	Rt/ min	Elem. Comp.	Ion Mass ^a / m/z	Error/ ppm	DBE
SMX	8	C ₁₀ H ₁₁ N ₃ O ₃ S	254.05939	-1.9	7	CBZ	11.4	C ₁₅ H ₁₂ N ₂ O	237.1022	-2.7	11
TP 284	10.5	C ₁₀ H ₉ N ₃ O ₃ S	284.0333	-1.3	8	TP 253 A	9.8	C ₁₅ H ₁₂ N ₂ O ₂	253.0971	-2.2	11
TMP	5	C ₁₄ H ₁₈ N ₄ O ₃	291.1452	-0.9	8	TP 253 B	10.3	C ₁₅ H ₁₂ N ₂ O ₂	253.0971	-6	11
TP 323 A	7	C ₁₄ H ₁₈ N ₄ O ₅	323.1350	0.3	8	TP 287	10	C ₁₅ H ₁₄ N ₂ O ₄	287.1026	-4.6	10
TP 323 B	6.5	C ₁₄ H ₁₈ N ₄ O ₅	323.1350	-2.2	8	TP 269	10.1	C ₁₅ H ₁₂ N ₂ O ₃	269.0921	-2.5	11
TP 323 C	5.5	C ₁₄ H ₁₈ N ₄ O ₅	323.1350	0.1	8	TP 256	10.7	C ₁₄ H ₁₁ NO ₄	258.0760	-2.4	10
TP 323 D	4.4	C ₁₄ H ₁₈ N ₄ O ₅	323.1350	-1.8	8	TP 251	10.6	C ₁₅ H ₁₀ N ₂ O ₂	251.0815	-2	12
TP 325	5.2	C ₁₄ H ₂₀ N ₄ O ₅	325.1506	1.7	7	TP 267	10.1	C ₁₅ H ₁₀ N ₂ O ₃	267.0764	0.4	12
TP 339	6.4	C ₁₄ H ₁₈ N ₄ O ₆	339.1299	1.4	8	DCF	13.5	C ₁₄ H ₁₁ Cl ₂ NO ₂	296.0240	-1.9	9
TP 307 A	6.3	C ₁₄ H ₁₈ N ₄ O ₄	307.1401	-1.6	8	TP 5	12.6	C ₁₄ H ₁₁ Cl ₂ NO ₃	312.0189	-4	9
TP 307 B	8.6	C ₁₄ H ₁₈ N ₄ O ₄	307.1401	0.4	8	TP 14	12.3	C ₁₃ H ₉ Cl ₂ NO ₂	282.0083	-4.8	9
						TP 18	12.1	C ₁₃ H ₉ Cl ₂ NO	266.0134	1	9

a: calculated m/z

Conclusions

Using $FeCl_3$ -BC/PMS/sunlight process was possible to achieve over 90% degradation of CECs after 10 min. In this way proving that BC modified with Fe particles has higher efficiency compared to the pristine BC. Additional experiments showed that the sunlight also had an important effect using only $FeCl_3$ -BC without any oxidant. The HRMS analysis allowed the identification of 19 TPs in the $FeCl_3$ -BC/PMS/sunlight process and only 2 TPs generated under $FeCl_3$ -BC/sunlight, indicating the importance of the production of oxidizing species from PMS.

Acknowledgments

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