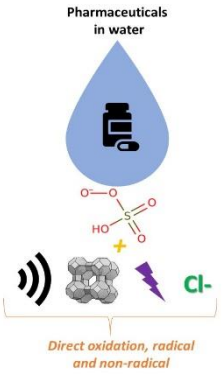
Taking advantage of peroxymonosulfate in diverse oxidation processes for the degradation of pharmaceuticals in water

ORAL
Ph.D. Student: N
Journal: YES

E. Serna-Galvis[1], *J Paniagua-Macias*[1], *Y. Martínez-Mena*[1], *M. Paredes-Laverde, D. Hoyos-Ayala, J. Arboleda-Echavarría, A. Echavarría-Isaza*[1], *R. Torres-Palma*[1]. *(1) Universidad de Antioquia UdeA, Calle 70 # 52–21, Medellín, Colombia, efrain.serna@udea.edu.co.*



Currently, pharmaceuticals are recognized as water pollutants, and PMS-based oxidation processes can be useful to degrade them. This work shows the treatment of 4 representative pharmaceuticals (acetaminophen, cefalexin, ciprofloxacin, and oxacillin), exploring the versatility of PMS alone and activated by several modes to produce radical and non-radical oxidizing species. The activation of PMS with a zeolite, a cobalt-based structures, a pyrogenic carbonaceous material (this last assisted with low-frequency ultrasound), UVC light, or chloride anion was evaluated. For cefalexin and oxacillin, PMS alone was enough to oxidize them. Meanwhile, acetaminophen and ciprofloxacin required the action of radicals or non-radical species coming from the PMS activation to achieve a successful degradation. In addition to the degradation efficiency, the primary transformation products were elucidated, finding that PMS-based processes can decrease the biological activity of the treated pharmaceuticals.

Introduction

Pharmaceuticals save millions of lives but they have emerged as pollutants of the aquatic environment and induce chronic and acute harmful effects on natural flora and fauna [1]. Also, it is recognized that one of the primary sources is the release of pharmaceuticals via urine after consumption [2]. Hence, efficient processes to deal with them in aqueous samples are needed. On the other hand, peroxymonosulfate (PMS) is an inorganic peroxide and it acts as an oxidant. There is a plethora of PMS activation ways to produce reactive radical and non-radical species. PMS can be activated by heterogeneous (metal oxides of transition metals, zeolites, carbonaceous materials) or homogeneous systems involving UVC light or chloride anions [3].

This work aims to present the versatility of PMS alone and in photochemical (using UV light), catalytic (utilizing a zeolite or a cobalt-based material), and ultrasound-assisted (carbocatalysis) processes for the production of radical and non-radical oxidizing species to degrade pharmaceuticals in aqueous samples. Herein, acetaminophen (analgesic), ciprofloxacin (fluoroquinolone antibiotic), cefalexin (β-lactam antibiotic), and oxacillin (β-lactam antibiotic) were used as representative pharmaceuticals. The degradation efficiency, action routes of the processes, primary transformations, and treatment extent were assessed.

Material and Methods

OXONE was used as the PMS source. The zeolite 4A (Z4A) and the Co-based material were synthesized using hydrothermal methods as detailed in references [4,5]. The carbocatalyst (p-CM) was prepared from rice husk via pyrolisis, as detailed in reference [6]. The pharmaceuticals were utilized in the 10-70 µmol/L range. PMS was used at 500 µmol/L. The dose of catalysts was 0.2 g/L. For the photochemical system, UVC lamps (60 W, 254 nm) were employed; whereas the ultrasound-assisted carbocatalysis was carried out in a low-frequency sonicator (40kHz). To elucidate the action routes, scavengers (e.g., methanol) were used.

The degradation efficiency was determined utilizing an HPLC apparatus equipped with an RP-column and a DAD. The primary transformations were established using LC-MS techniques. The analyses of biological activity were carried out with PASS software (free online version), which is based on analyses of structure-activity relationships [5,6]. In the case of antimicrobial activity for antibiotics, the Kirby-Bauer method was applied.

Results and Discussion

Firstly, the direct action of PMS alone on the pharmaceuticals was tested (Table 1). Oxacillin and cefalexin were fastly degraded (<5 min of treatment), which was associated with the high reactivity of the thioether moiety on those antibiotics toward the peroxymonosulfate [7]. For those pharmaceuticals that were recalcitrant to the direct PMS attacks, other oxidation strategies were applied (Fig. 1). Thus, peroxymonosulfate was combined with Z4A. This system promoted the degradation of ciprofloxacin but did not remove acetaminophen. The PMS/Z4A process produced a non-radical pathway [4], which slowly removed ciprofloxacin (~90% in 30 min). Then, PMS was heterolytically cleavaged by the Co-based material (PMS/Co-M), which promoted the formation of radical species [5], inducing the degradation of the fluoroquinolone antibiotic more effectively than that obtained by the PMS/Z4A system.

On the other hand, acetaminophen was treated by the carbocatalytic process (PMS/p-CM). The PMS/p-CM produced high quantities of singlet oxygen from the PMS activation [6], thus degrading acetaminophen. Additionally, the degrading action of the carbocatalytic process was enhanced by the addition of low-frequency ultrasound waves. The degradation improvement was linked to a particle size of the carbonaceous material decreasing plus a mass transfer increasing by the ultrasound waves [8]. The acetaminophen was also treated by a photochemical process (i.e., PMS/UVC). Moreover, the degradation of acetaminophen by the PMS in the chloride anion presence (at 0.1-0.5 mol/L) was assessed. Degradation of the pharmaceutical by the photochemical process (which produces radicals from the homolytic cleavage of the peroxymonosulfate) was found. Also, the PMS/Cl^- system induced the degradation of acetaminophen due to the formation of active chlorine species (e.g., HClO) from the chloride ions oxidation by PMS. The formed chlorine species are also strong oxidizing species capable of reacting with pharmaceuticals [4,6].

During the diverse treatments using PMS, it is required to go beyond the degradation efficiency and the identification of reactive species. Hence, for the systems that showed high degrading capability, the primary transformations were studied and the treatment extent was determined. For instance, the degradation of ciprofloxacin by the PMS/Co-M process (which involved radical species) induced the opening of the piperazyl ring and hydroxylation of the quinolone nucleus; and decreased the antimicrobial activity. In turn, the carbocatalytic process that involved a non-radical pathway promoted the hydroxylation of the phenolic ring on the acetaminophen structure and the decrease in the biological activity associated with this pharmaceutical. Finally, it is worth mentioning that the PMS-based process has high feasibility to be applied to degrade pharmaceuticals in matrices having high chloride anion concentration (e.g., fresh urine). However, the risk of generating organo-chlorinated by-products must be considered.

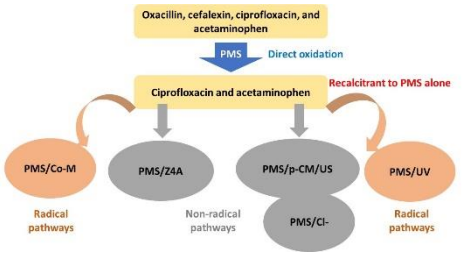


Figure 1. The sequence of treatments by the processes.

Table 1. Direct degradation of the target pharmaceuticals by PMS alone.

Pharmaceutical	Oxacillin	Cefalexin	Ciprofloxacin	Acetaminophen
Degradation	100% (fast)	100% (fast)	<20% (slow)	<10% (very slow)

Conclusions

Direct degradation of pharmaceuticals by PMS was dependent on functional groups of the pollutants. PMS can be activated using diverse strategies to form radical and non-radical species, which were used to degrade pharmaceuticals in water. Transformations decreased the biological activity of the treated pollutants.

Acknowledgments

The authors thank CODI-UdeA for the financial support to this work through the projects 2022-53586 and 2020-32251.

References

[1] M. Patel, R. Kumar, K. Kishor, T. Mlsna, C.U. Pittman, D. Mohan, Chem. Rev., 119 (2019) 3510.

[2] E.A. Serna-Galvis, Y.L. Martínez-Mena, P. Jazmín, R.A. Torres-Palma, Ing. Y Compet., 24 (2022) 1.

[3] Y. Ding, X. Wang, L. Fu, X. Peng, C. Pan, Q. Mao, C. Wang, J. Yan, , Sci. Total Environ., 765 (2021) 142794.

[4] E.A. Serna-Galvis, Y.L. Martínez-Mena, J. Arboleda-Echavarría, D.A. Hoyos-Ayala, A. Echavarría-Isaza, R.A. Torres-Palma, Chem. Eng. Res. Des., 193 (2023) 121.

[5] E.A. Serna-Galvis, C. Mendoza-Merlano, R.A. Torres-Palma, A. Echavarría-Isaza, D.A. Hoyos-Ayala, Molecules, 28 (2023) 28114536.

[6] M. Paredes-Laverde, J. Porras, N. Acelas, J.J. Romero-Hernández, S.D. Jojoa-Sierra, L. Huerta, E.A. Serna-Galvis, R.A. Torres-Palma, Environ. Sci. Pollut. Res., 30 (2023) 123616.

[7] C.M. Grisales-Cifuentes, E.A. Serna-Galvis, N. Acelas, J. Porras, E. Flórez, R.A. Torres-Palma, J. Environ. Manage., 323 (2022) 116148.

[8] S.E. Estrada-Flórez, E.A. Serna-Galvis, J. Lee, R.A. Torres-Palma, J. Environ. Manage., 350 (2024).