Evidencing a dual synergistic effect of peroxymonosulfate as an activated substance and activating agent through non-radical pathways in sonocarbocatalytic processes

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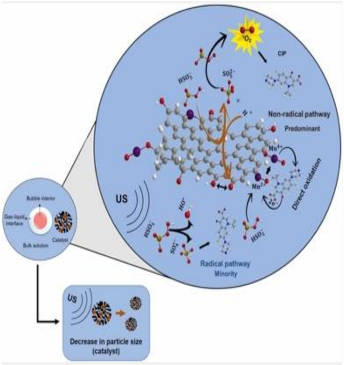

A carbonaceous material from agro-industrial (sawdust) wastes was prepared and modified with Mn (SW-Mn) to activate peroxymonosulfate (PMS) in the presence of ultrasound waves (US), for degrading a relevant contaminant (ciprofloxacin) in water. The combination of SW-Mn + PMS + US (at 40 kHz) induced synergistic effects (synergy index: 1.65). In the synergistic system, a dual role of PMS was evidenced. PMS was activated by SW-Mn to produce $^1O_2$, and PMS also modified the material favoring the direct pollutant oxidation involving Mn^{4+} species. Non-radical pathways dominated the ciprofloxacin degradation, leading to transformations on the piperazyl ring of the pollutant. Besides, the treatment of irrigation crop water spiked with ciprofloxacin induced an elimination faster than in distilled water.

Introduction

The activation of inorganic peroxides such as peroxymonosulfate (PMS), peroxydisulfate (PDS), or hydrogen peroxide by carbonaceous material to degrade organic pollutants in water is known as carbocatalysis. Recently carbocatalysis using wood sawdust (an abundant solid waste of the forestry industry, having the capability to cause serious health and environmental issues due to inadequate disposals, has been effectively used for the production of degrading species (e.g., free radicals). In addition, the positive effect of modifying the carbonaceous material with transition metals such as Mn is of increasing interest [1].

In this work, a carbonaceous material (SW-Mn), prepared from sawdust and modified with manganese carbonate, was tested as a carbocatalyst to activate PMS and to eliminate a relevant contaminant of emerging concern (the pharmaceutical ciprofloxacin, CIP). Initially, the synthesized SW-Mn was characterized. Then, the activating capability of SW-Mn toward PMS was assessed. Afterward, degradation of CIP by the carbocatalytic system in combination with ultrasonic waves at 40 kHz was assessed. For the combined system (i.e., the sonocarbocatalytic treatment), the matrix effects (using irrigation crop water) were evaluated. Moreover, both the ROS involved in the sonocarbocatalysis and the activation routes were determined using specific scavengers, and carrying out electrochemical and XPS analyses. The primary transformations of the model pollutant were established and the mechanism of PMS activation was proposed.

Material and Methods

The sawdust sample was carbonized (SW). Subsequently, SW was mixed with $MnCO_3$ and this mixture was heated at 800°C. The resultant carbonaceous material was washed and finally, it was dried, obtaining SW-Mn. The material was characterized using diverse techniques as detailed in [1].

Adsorption, carbocatalysis, and sonocarbocatalysis experiments to eliminate CIP were performed in a batch-type reactor. For the carbocatalytic process, 0.5 mM of inorganic peroxides concentration was used. In the sonocarbocatalytic system, the ultrasound frequency was set at 40 kHz. For the matrix effects, real irrigation water collected from river Cauca (Cali, Colombia) and spiked with CIP was used. CIP was followed using a UHPLC instrument equipped with a DAD detector.

Results and Discussion

After the preparation and characterization of the SW-Mn material, the degradation tests were assessed. The carbocatalytic degradation of the antibiotic resulted much higher than those obtained from the single adsorption or direct oxidation by PMS alone. Thus, denoting the synergy of the combination of PMS with SW-Mn. On the other hand, the combination of US with PMS improved the CIP removal (even increased the PMS consumption) concerning the individual US and PMS systems (due to the physical effects of ultrasound on the disaggregation of the carbocatalyst, doing sites on SW-Mn more suitable for the PMS activation). When benzoquinone was added to the sonocarbocatalytic system CIP degradation was similar to the obtained in the scavenger absence, indicating that anion radical superoxide did not participate significantly in the removal of the pollutant. Methanol inhibited CIP removal slightly, suggesting low participation of sulfate and/or hydroxyl radicals. Meanwhile, in the presence of NaN_3, the pollutant elimination was considerably decreased. Furthermore, a degradation by-product was predominantly detected and its chromatographic area decreased when adding sodium azide. The above results suggest that $^1O_2$ played a relevant degrading role in the sonocarbocatalytic treatment.

Even if $^1O_2$ played an important role during CIP degradation (25% of CIP reduction in the presence of sodium azide) and radicals had a low contribution, other oxidative species also participated in the process. Therefore, the role of manganese was evaluated. Interestingly, the sonocarbocatalytic system induced very low leaching of Mn (0.07% of Mn) into the solution, suggesting that homogenous catalysis can be neglected in this process. The deconvolution of orbital Mn $2p^{3/2}$ in XPS analysis indicated the presence of MnO and MnO_2 in SW-Mn after treatment. Such results suggest that the Mn^{2+} was directly oxidized to Mn^{4+}, without the formation of Mn^{3+}-based species.

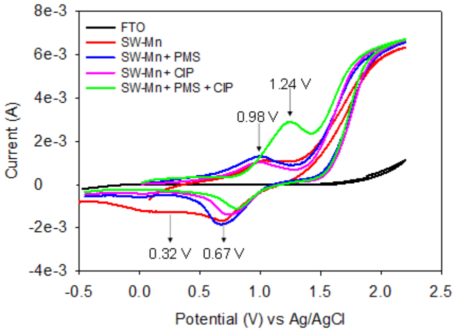

Figure 1. Cyclic voltammetry of SW-Mn. Scan: −0.5 and 2.2 V versus Ag/AgCl, rate:20 mV s^{-1} in 0.1 M $NaSO_4$.

The manganese oxide formed (MnO_2) can directly oxidize organic compounds by electron transfer pathways [2]. The comparison of CV for SW-Mn + CIP (pink line in Fig. 1) and SW-Mn + PMS + CIP (green line in Fig. 1) showed in the latter case a new peak at 1.24 V, which confirms the direct oxidation of CIP by MnO_2.

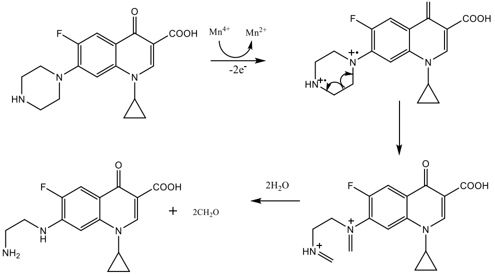

Figure 2. Proposal of direct oxidation of CIP by MnO2 for the formation of the pollutant byproduct.

It was proposed that the transfer of two electrons from CIP to MnO_2, produces MnO and an intermediate, which evolves toward a di-imine, having subsequently hydrolysis to produce the detected byproduct of CIP (Fig. 2). Hence, PMS had a dual role in the sonocarbocatalytic treatment of CIP, acting as the precursor of singlet oxygen being activated by SW-Mn, and as an activating agent via the oxidation of Mn on SW-Mn.

On the other hand, the degradation of CIP in a real complex matrix (an irrigation crop water spiked with CIP) was assessed. The real matrix contained organic matter and several ions such as bicarbonate and chloride. The CIP removal rate strongly increased (100% degradation after only 5 min of treatment) in the complex matrix when compared to the elimination in distilled water. The elimination improvement was ascribed to the formation of HOCl (from the reaction between chloride ions and PMS), which can react directly with CIP. Furthermore, HOCl can produce $^1O_2$ from both, self-decomposition and reaction with PMS. Then, the extra formation of degrading species (i.e., HOCl and $^1O_2$) enhanced the elimination of CIP in the irrigation crop water. The competition of other matrix components with CIP for the degrading species is low, owing to the considerable selectivity of the degrading species.

Conclusions

In the interaction of the SW-Mn with PMS for degrading ciprofloxacin, a dual role was observed. The SW-Mn material activated PMS toward ROS production, and PMS modified SW-Mn making Mn capable of oxidizing CIP. The coupling of the carbocatalytic system with low-frequency ultrasound (40 kHz) was synergistic for the CIP elimination due to the physical effects of ultrasound. $^1O_2$ was the predominant ROS from PMS in the degradation of the target pollutant. Furthermore, the changes in SW-Mn evidenced that MnO_2 species can also oxidize CIP directly. Finally, the sonocarbocatalysis led to a better degradation of CIP in actual irrigation crop water than in distilled water, which was associated with the production of hypochlorous acid and extra singlet oxygen that could selectively degrade CIP in this complex matrix.

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