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Simultaneous elimination of multiple pharmaceuticals in real wastewater effluent using a commercial zeolite and peroxymonosulfate

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ABSTRACT

The combination of a commercial zeolite A (ZA, an affordable and highly available material) with peroxymonosulfate (PMS, at μmol L^{-1} levels) for treating several organic pollutants in water was explored herein. Firstly, the ability of the PMS/ZA combination to degrade three model compounds in distilled water, to understand the fundamental aspects of action routes, was tested. It was found the participation of adsorption on ZA, oxidation by PMS, plus the generation and action of $^1O_2$. After evaluating the model substances, the treatment of actual effluent from a municipal wastewater plant (EMWTP) was studied. The EMWTP contained eighteen relevant pharmaceuticals, whose environmental risk (employing the parameters of occurrence, bioaccumulation potential, and quotient risk for the mixture) was initially assessed. Afterward, the treatment of the EMWTP was studied, paying attention to the removal of target pharmaceuticals, color, and phytoxicity. The adsorption of the pharmaceuticals on the ZA alone led to a moderate removal due to its hydrophilic nature and low surface area. Also, PMS induced direct oxidation of some pharmaceuticals having highly reactive moieties (e.g., reduced forms of nitrogen and sulfur and activated benzene rings). In turn, the PMS/ZA system was very efficient for the elimination of most target pharmaceuticals. Also, this combined system led to the color removal and decreased phytotoxicity of the treated EMWTP. The results from this research revealed the high feasibility of the process based on accessible zeolites and PMS for the effective degradation of relevant organic pollutants and mitigation of environmental risks in actual wastewater effluents.

1. Introduction

Several organic pollutants arrive in municipal wastewater to the environment. Indeed, many compounds are recalcitrant to the conventional processes at municipal wastewater treatment plants (Patel et al., 2019). For instance, pharmaceuticals and dyes are refractory contaminants in water. Dyes can contribute to undesired aesthetic (such as color) and concern (toxicity) aspects of municipal wastewater (Periyasamy, 2024). In turn, pharmaceuticals are biologically active substances, and prolonged exposure to some of them can induce disruption of the endocrine system and produce toxic effects on microorganisms, flora, and fauna. Furthermore, the behavior of pharmaceutical mixtures is very complex and they can cause serious harm to the environment (Patel et al., 2019).

Research on alternative treatment systems to effectively eliminate recalcitrant pollutants before discharging them into the aquatic environment is a need (Patel et al., 2019; Verlicchi et al., 2023). As an alternative for dealing with refractory pollutants (as pharmaceutically active compounds and dyes) in EMWTPs, peroxymonosulfate-based advanced oxidation processes (PMS-AOPs) have been tested previously. The PMS-AOPs are attractive treatment systems due to the *in-situ* generation of species such as sulfate anion radical ($SO_4^{\bullet-}$), hydroxyl

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radical (HO•), and/or singlet oxygen ($^1O_2$); which are strong oxidizing species capable of degrading pollutants (e.g., pharmaceuticals) recalcitrant to the conventional treatments. For instance, the activation of PMS by Mn(III) has been utilized to degrade pharmaceutical hormones (17β-estradiol and 17α-ethinyl-estradiol) in real sewage treatment plant water (Jia et al., 2021).

Solar photo-Fenton using peroxymonosulfate has been applied to eliminate carbamazepine, diclofenac, and sulfamethoxazole in biologically treated domestic wastewater effluents (Ahmed et al., 2014). Also, ionizing radiation combined with peroxymonosulfate/H_2O_2 has been shown to degrade erythromycin, tetracycline, and sulfamethoxazole antibiotics in secondary effluents from a wastewater treatment plant (Chu et al., 2021). Furthermore, the combination of ultraviolet light (UVC) with PMS (UVC/PMS process) has been assessed for eliminating carbamazepine, gabapentin, metoprolol, and sulfamethoxazole in secondary-treated urban wastewater (Pesqueira et al., 2022).

The PMS-AOPs employing UVC lamps or ionizing radiation have high electric energy consumption. In contrast, the PMS-AOPs based on heterogeneous catalysts are less energy intensive. Zeolite-based materials can be used to activate PMS to produce useful species for degrading pollutants in water (Chi et al., 2020; Hu et al., 2023; Serna-Galvis et al., 2023; Xu et al., 2023). Zeolites are mainly used as catalytic supports, involving synthesis and/or modification steps that make the process costly. Recently, a non-modified zeolite has been used as a catalyst to activate PMS and degrade a representative antibiotic in water (Serna-Galvis et al., 2023). Despite the process based on zeolites and PMS has advantages such as easy reagents acquisition, low electric energy consumption, or high degrading efficiency, it can have some drawbacks, e.g., the need to recover the zeolites after the process, which increases operational costs, or the utilization of high PMS concentrations that can lead to excessive production of sulfate ions at the treated water.

The combination of PMS with zeolites is useful for eliminating diverse organic pollutants in aqueous samples (Chi et al., 2020; Hu et al., 2023; Serna-Galvis et al., 2023; Xu et al., 2023). Some fundamental aspects of the role of the pollutant type and the effects of chloride and ferrous ions on direct oxidation by PMS have not been explored in those previous works. Moreover, the simultaneous treatment of several pharmaceuticals (more than ten pollutants) in real-world EMWTPs has not been reported yet. Moreover, low-cost and commercially available zeolites have not been used for such purposes.

Considering the above-mentioned lacks in the literature, this work aims to provide an understanding of fundamental aspects of the PMS/ZA system (e.g., adsorption on the zeolite, direct oxidation by PMS, and the PMS-zeolite interaction), under controlled conditions initially. Then, our research work offers a primary approach to evaluate the combined action of a commercial zeolite with peroxymonosulfate to deal with pharmaceuticals in actual EMWTP. Thereby, in this work, the combination of ZA with PMS was applied to treat simultaneously five antibiotics, three antihypertensives, two analgesics, two antiparasitics, one antiulcer, one antiepileptic, one antiasthma, one antidepressant, one cholesterol-lowering, and one metabolite in an actual EMWTP.

Initially, to understand the fundamental aspects of the PMS/ZA system, experiments (e.g., adsorption on the zeolite, direct oxidation by PMS, and the interaction of PMS with the zeolite) using three different model pollutants (ciprofloxacin-CIP, diclofenac-DIC, and methyl orange-MO) in distilled water, were carried out. Afterward, the EMWTP was considered. The environmental risk associated with the pharmaceuticals in the EMWTP was determined. Then, the simultaneous degradation of the target pollutants in the actual EMWTP by the PMS/zeolite system was tested. Also, the EMWTP bleaching (i.e., color removal) by action of the PMS/ZA process was assessed. Furthermore, to test the potential reuse of the treated water for crop irrigation, the phytotoxicity and the environmental risk of the treated effluent were evaluated.

2. Experimental

2.1. Reagents and reaction system

In this work, atorvastatin, azithromycin, ciprofloxacin, clarithromycin, clindamycin, diclofenac, desmethyl venlafaxine, gabapentin, irbesartan, levamisole, losartan, metoprolol, metronidazole, pantoprazole, salbutamol, tramadol, trimethoprim, and venlafaxine were the target pharmaceuticals in MWTP. All the pharmaceutical reference standards were acquired from LGC Promochem (Bengaluru).

Ciprofloxacin (CIP), diclofenac (DIC), and methyl orange (MO), which were used as the model compounds for control experiments, were acquired from Laproff laboratories (Medellín), Sigma-Aldrich (St. Louis) and Merck (Darmstadt), respectively. OXONE, obtained from Sigma-Aldrich (St. Louis), was used as the PMS source. Acetonitrile, ammonium acetate, formic acid methanol, and sodium azide were purchased from Merk (Darmstadt). The commercial zeolite A (ZA) was provided by Supelco (Darmstadt). The EMWTP sample was taken from a local sewage treatment plant in Medellín-Colombia in the dry season (August moth). Table S1 (in the Supporting information) presents some water quality parameters of the used sample.

The treatments were performed using a beaker under magnetic stirring. A sample of model pollutant or EMWTP (50 mL) was considered, and PMS and ZA were added at 500 μmol L^{-1} and 0.2 g L^{-1}, respectively (see the justification in Text S1 (*TS.1.1*)).

2.2. Analyses

The structure of ZA was verified by the X-ray diffraction analysis (XRD). XRD was performed in a PANalytical Empyrean X-ray 2012 powder diffractometer, in reflection transmission spinner geometry mode with Cu-Kα radiation at 40 mA and 45 kV. The XRD pattern was recorded in the 3° and 50° (2θ angle) range. S_{BET} and V_{pore} were determined using a Quatachrome (NOVA 1200e) apparatus through the N_2-adsorption/desorption test at 77 K. The SiO_2/Al_3O_2 ratio was established using a Zetium Mineral Malvern-PANalytical X-ray fluorescence-XRF instrument (at 4 kW), for this analysis, the ZA sample was prepared by pearling and analyzed in the quantitative WROXI application. More details about the ZA characterization are shown in Text S1 (*TS.1.2*, Fig. S1, and Table S2).

The evolution of the model pharmaceutical compound (i.e., CIP), during the control treatments in distilled water, was followed using a Thermo Scientific Ultimate 3000 UHPLC. This apparatus had a DAD detector and an Acclaim™ 120 column (C18, 5 μm, 4.6 × 150 mm). For CIP analysis, a 15/85 mixture of acetonitrile/formic acid (10 mmol L^{-1}) at 1.0 mL min^{-1} was used as the mobile phase. A volume of 20 μL was injected, and the detection wavelength was 278 nm. For the DIC analysis, a 70/30 mixture of acetonitrile/formic acid (10 mmol L^{-1}) at 1.0 mL min^{-1} was used, injecting 20 μL and detecting the compound at 260 nm. In turn, the degradation of the model compound for color (i.e., MO) was determined by direct measurement of the absorbance at 465 nm, using a Mettler Toledo UV5 spectrophotometer and 1-cm quartz cuvettes.

It can be mentioned that evaluation of fundamental aspects such as the influence of the pollutant class (i.e., analgesic vs. antibiotic vs. dye, control experiments in distilled water) must be done at the same molar concentration of target substances (which is not possible to ensure in the actual complex matrix (i.e., EMWTP)). Also, the identification of degrading species participation in the degradation of pollutants (another fundamental aspect) is typically tested in control experiments. Indeed, the evaluation of these two fundamental aspects must be done at high analyte concentrations, which allows to properly follow the process (e.g., mg L^{-1} levels) (Serna-Galvis et al., 2019). Thus, as a proof of concept, control experiments with three model compounds of varied chemical structure (CIP, DIC, and MO) were carried out at 30 μmol L^{-1} (mg L^{-1} levels). In addition, the selected concentration allows the use of

conventional liquid chromatography with UV detection and/or directly by spectrophotometry to follow the pollutant concentration during the experiments and determine the catalytic ability of the material. Later, the process was applied to real-world water samples at the very low analyte concentrations present in those samples measuring the analyte concentrations by LC-MS/MS as indicated below.

Quantification of the target pharmaceuticals in the initial EMWTP sample and after treatments applied to this matrix was done by direct injection into the LC-MS/MS with a triple quadrupole (Waters Xevo TQS) mass spectrometer. Three MS/MS transitions were acquired for each compound, of which one (usually the most abundant) was used for quantification and the remaining ones (q1 and q2) for compound identification in the samples. Isotope-labelled internal standards (ILIS) were used for each analyte for an efficient matrix-effect correction, using relative peak areas analyte in sample/ILIS for the quantification (Botero-Coy et al., 2018; Nieto-Juárez et al., 2021). The chromatographic separation was performed using an Acquity UPLC BEH C18 analytical column, 1.7 μm, 100 mm × 2.1 mm (Waters), and the mobile phase consisted of a water/methanol gradient, both with 0.1 % formic acid and 2 mM ammonium acetate. Following the spirit of Good Laboratory Practices (GPL) in residue studies, quality control (QCs) samples were analyzed in every sample batch to support the reliability of the analytical procedure. The QCs consisted of the EMWTP sample to which the target pharmaceuticals were added at two levels, 0.1 and 1 μg L^{-1}. Several compounds under study were present in the "blank" samples used for QCs preparation; therefore, the concentrations found in the "blanks" were subtracted from those from spiked samples (i.e., QCs) for recovery calculation. Average QCs recoveries were between 60 and 140 % in all cases, and mostly between 70 and 120 %, which is the acceptability range for individual recoveries in routine analysis (EURL, 2021). Thus, data obtained for samples were considered satisfactory according to the GLP guidelines (EURL, 2023).

The bleaching of the treated EMWTP was determined through the absorption coefficients at specific wavelengths (α_λ). Such coefficients were calculated using the mathematical expression $\alpha_\lambda = A/b$, where A is the absorbance at the specific wavelength and b is the optical pathlength in m. Then, α_{254} was used to monitor the quality of samples regarding those compounds with aromatic rings or unsaturated carbon bonds (Prada-Vásquez et al., 2024). To quantify the yellow-brown coloration of samples was employed α_{410} (according to ISO standard 7887:2011). The sample absorbance at the specific wavelengths was measured in a 1-cm quartz cuvette by using the UV5 Mettler-Toledo spectrophotometer.

On the other hand, the environmental risk of the target pharmaceuticals in EMWTP was assessed using the scoring approach, considering occurrence, persistence, and bioaccumulation (Text S1 (*TS.1.3*)), based on the methodology proposed in the reference (Verlicchi et al., 2023). The occurrence is expressed in terms of the concentration of pharmaceuticals in the EMWTP. For the persistence parameter, it was employed the removal efficiency achieved by the sewage treatment plant, and Log K_{ow} was used as a surrogate for the bioaccumulation. After the acquisition of the values for the occurrence, persistence, and bioaccumulation criteria, proper scales were built using the assignment of a score between 1 (low environmental impact) and 5 (high environmental impact) (see Table S3).

In addition to the scoring approach, hazard quotients (HQ, indicator of potential toxicity) were determined under two scenarios (*i*-before discharge into the environment and *ii*-inlet at the environment). To establish the individual HQ values, the ratio between the measured concentrations (MEC) and predicted no-effect concentration (PNEC) was used. Meanwhile, HQ_{mix} was determined for the mixture of pharmaceuticals in EMWTP. More details for the HQs calculations can be found in Text S1 (*TS.1.4*).

To evaluate the possibility of reusing the treated EMWTP for crop irrigation, a phytotoxicity test was carried out, employing seeds of tomato (*Solanum lycopersicum,* purchased from Anasac Jardín®). Briefly, eight seeds were placed on a Petri dish containing 7 mL of sample, and then incubated for 120 h at 25 ± 2 °C. The analyses were carried out by duplicate. In such a test the germinate length and relative growth index (RGI) were determined. Phytotoxicity assessment was performed by measuring the germinate length (radicle plus hypocotyl). For comparative purposes, analyses of variances (ANOVAs) were carried out. More information is shown in Text S1 (*TS.1.5*).

3. Results and discussion

3.1. Treatment of model compounds by the PMS/ZA system

To evaluate the feasibility of the PMS/ZA system to deal with organic pollutants in water, the treatment of the three different model substances (CIP, DIC, and MO) was evaluated in the first part of our research. CIP is a representative compound of antibiotics in wastewater and environmental water (Nieto-Juárez et al., 2021; Oharisi et al., 2023; Patel et al., 2019). DIC is another representative pharmaceutical, which belongs to the analgesics class. This pharmaceutical was selected as a model compound due to its widely recognized ecological issues for aquatic animals, plants, and mammals (Sathishkumar et al., 2020). In turn, MO is a model of recalcitrant substances responsible for the color of wastewater (Sun et al., 2020)). This dye was considered because the target municipal wastewater also receives effluents from the textile industry. Therefore, the treatment of the model organic contaminants by adsorption on the ZA surface, direct oxidation by PMS, and the PMS/ZA combination were studied, as detailed in the following subsections.

3.1.1. Adsorption of model organic pollutants

Fig. 1A compares the adsorption of the model compounds on ZA in distilled water. It can be noted that after 20 min of interaction, the three model compounds were poorly adsorbed by ZA (<20 %). ZA is a material with a low SiO_2/Al_3O_2 ratio (1.5, Table S2). Consequently, it is very hydrophilic, which limits its ability to adsorb organic pollutants (Mijailović et al., 2022). Thus, the low adsorption of CIP, DIC, and MO on ZA is explained by the electrostatic interactions.

Distilled water after the ZA addition had a pH of 7.8. The zeolite has negative charges on its surface (pHpzc: 3.8, Table S2), and at this experimental pH, ZA is negatively charged. In turn, DIC and MO are anionic forms, while CIP is a zwitterion (Fig. S2A–C). Thus, CIP had more chances to be adsorbed on ZA (by electrostatic attractions through the positive moiety on CIP) than DIC or MO (which had electrostatic repulsions). To better support the role of negative charges on the ZA surface, another probe compound positively charged (methylene blue, Fig. S2D) was assessed. After 20 min more than 40 % of such probe compound was adsorbed (Fig. S2E). Therefore, the highest removal of the probe demonstrated the predominance of electrostatic interactions in the pollutant's adsorption on ZA.

3.1.2. Direct oxidation by PMS

The asymmetric structure of the peroxide-type bond on PMS makes it reactive toward certain functional groups on the organic compounds leading to their transformations (Ding et al., 2021). Thereby, the direct oxidation of the model pollutants in distilled water by PMS was tested. Fig. 1B presents the degradation of the model contaminants under interaction with PMS alone for 20 min. PMS degraded ~20 and ~80 % of CIP and MO, respectively. However, DIC was not degraded by PMS.

PMS can directly oxidize amine groups on CIP and MO (Nihemaiti et al., 2020; Serna-Galvis et al., 2023). Also, the azo moiety on MO can be modified in the PMS presence (Serna-Galvis et al., 2023); thus, explaining the higher degradation of MO than CIP. The reaction of PMS with amines in organic compounds produces N-oxide intermediates. This is the case of the fluoroquinolone antibiotics (e.g., ciprofloxacin) that have the secondary amine on their piperazine ring as the main reaction sites toward PMS. In turn, quinolone moiety is refractory to direct oxidation by PMS (He and Shea, 2020; Zhou et al., 2018).

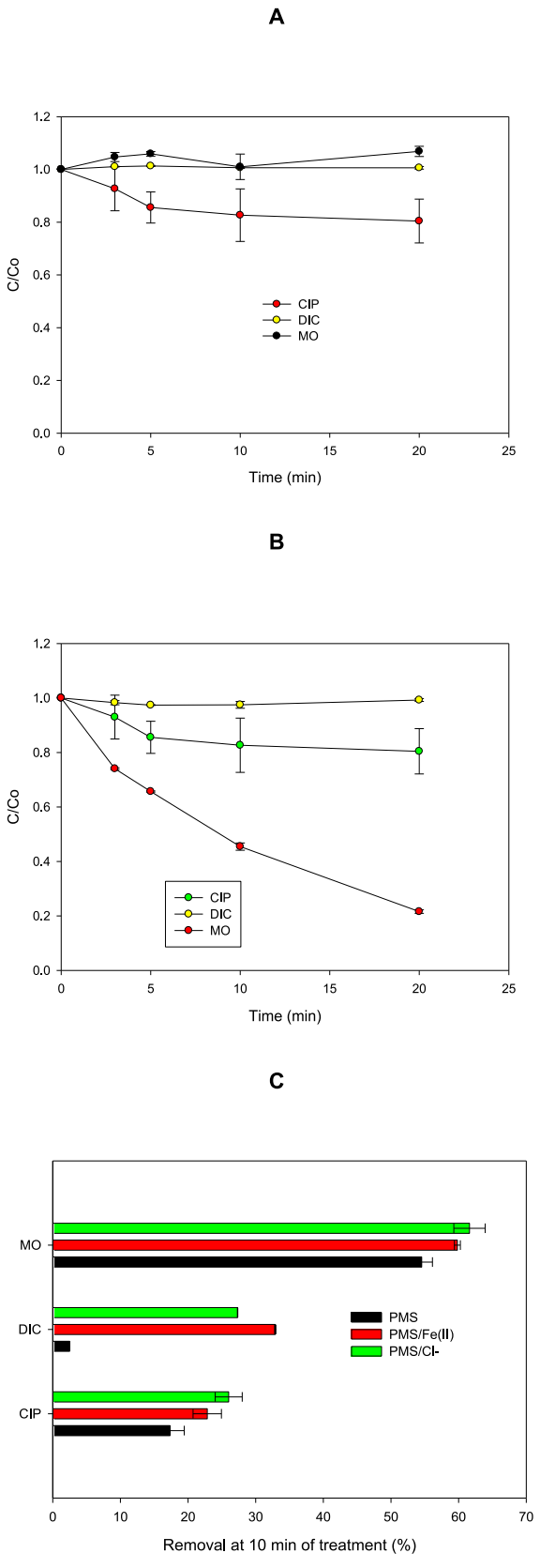

Fig. 1. Removal of the model pollutants in distilled water. **A.** Adsorption on ZA. **B.** Direct oxidation by PMS action. **C.** Effects of some matrix components on the direct action of PMS. Experimental conditions: [CIP] = [DIC] = [MO] = 30 μmol L^{-1}, [ZA] = 0.2 g L^{-1}, [PMS] = 500 μmol L^{-1}; and for matrix effects: [Cl^-] = 90.3 mg L^{-1}, [Fe(II)] = 0.3 mg L^{-1}.

In the case of DIC, despite it also having a secondary amine, such a moiety on the model pollutant seems to be little reactive toward PMS due to the influence of the dichlorophenol, which is an electron-withdrawing group, thus explaining the low degradation of this pharmaceutical by the inorganic peroxide. Our results were consistent with previous works that have also found, low direct degradation of DIC by PMS (Wu et al., 2025). Hence, the above results indicate that the direct oxidation by peroxymonosulfate is strongly dependent on the chemical structure of the organic compound.

In addition to the direct action of PMS, some degrading species could be produced by the reaction of PMS with matrix components such as iron or chloride ions (which are present in the EMWTP, Table S1). These matrix components react with the PMS, producing radicals or hypochlorous acid (Eqs. (1)–(3)). Then, to elucidate the participation of these two routes, control experiments (i.e., PMS/Fe(II) and PMS/Cl^-) in distilled water were carried out. Fig. 1C shows that the degradation of the model pollutants by PMS in the presence of iron or chloride ions is higher (especially for DIC) than using PMS alone. This suggests the participation of HO•, SO_4•-, and HClO in the elimination of such model compounds. It is important to mention that the involvement of HClO is more relevant when the matrix has high concentrations of chloride anions (e.g., 0.1 mol L^{-1} = 3550 mg L^{-1} (Serna-Galvis et al., 2023)).

$$HSO_5^- + Fe^{2+} \rightarrow HO\text{-} + SO_4\bullet\text{-} + Fe^{3+} \quad (1)$$

$$HSO_5^- + Fe^{2+} \rightarrow HO\bullet + SO_4^{2-} + Fe^{3+} \quad (2)$$

$$HSO_5^- + Cl^- \rightarrow HClO + SO_4^{2-} \quad (3)$$

3.1.3. *Degradation by the PMS/ZA combination and reactive oxygen species involved in this system*

The degrading action of the PMS/ZA toward the model compounds in distilled water was tested. Fig. 2A shows the evolution of such compounds. At 20 min of treatment, this process eliminated ~20, 70, and 95 % of DIC, CIP, and MO, respectively. We can note degradation of CIP, DIC, and MO by the PMS/ZA combination was more efficient than the individual systems (i.e., ZA or PMS acting independently, Fig. 1A and B).

The interaction of PMS with ZA can lead to the formation of reactive oxygen species (ROS) (Serna-Galvis et al., 2023). Then, to determine the participation of radical species (SO_4•- or HO•) in the degradation of CIP by the interaction of PMS with ZA, methanol (MeOH) was used, whereas sodium azide (NaN_3) was employed to trap singlet oxygen (Fig. 2B). In the MeOH presence there was no inhibition of the pharmaceutical degradation; thus, radical species such as hydroxyl radical or sulfate radical are not produced from the interaction between PMS and ZA. In contrast, the CIP degradation was strongly inhibited by the addition of NaN_3, indicating that the PMS/ZA system produces singlet oxygen ($^1O_2$). Zeolites having a low SiO_2/Al_3O_2 ratio (such as ZA) form $^1O_2$ via an initial acid-base reaction (Eq. (4)), with a subsequent decomposition of PMS (Eq. (5)) (Serna-Galvis et al., 2023). The singlet oxygen degrades CIP and MO, leading to a breakdown of the piperazyl ring on the model pharmaceutical and the chromophore azo group on the model dye inducing the water discoloration, as illustrated in Fig. S3. Meanwhile, DIC is degraded by $^1O_2$, promoting C-N cleavage, hydroxylation of the aromatic rings, or decarboxylation pathways (Chong et al., 2017; Yan et al., 2022).

$$\text{-Si-}O^-/\text{Al-}O^- + HSO_5^- \rightarrow \text{-Si-OH/Al-OH} + SO_5^{2-} \quad (4)$$

$$SO_5^{2-} + HSO_5^- \rightarrow SO_4^{2}\text{-} + HSO_4\text{-} + {}^1O_2 \quad (5)$$

The results from treating the model compounds (Figs. 1 and 2) evidenced the high potentiality of the combination of PMS with ZA to deal with the pharmaceuticals and color in an actual complex sample such as the EMWTP. These topics are developed in the following sections.

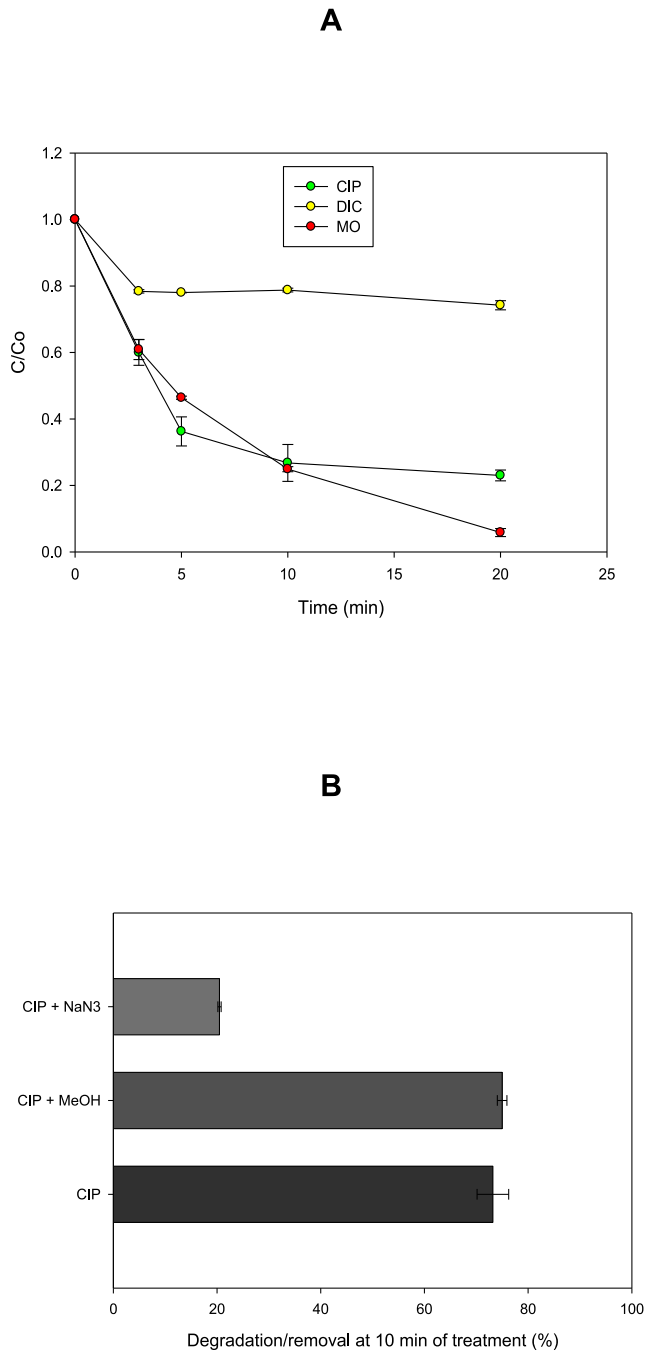

Fig. 2. Degradation of the model compounds in distilled by the PMS/ZA system, **A.** evolution of the model compounds. Experimental conditions: [CIP] = [DIC] = [MO] = 30 μmol L^{-1}, [ZA] = 0.2 g L^{-1}, [PMS] = 500 μmol L^{-1}. **B.** Determination of degradation routes using scavengers. Experimental conditions: [CIP] = 30 μmol L^{-1}, [NaN_3] = [MeOH] = 3.0 mmol L^{-1}, [ZA] = 0.2 g L^{-1}, [PMS] = 500 μmol L^{-1}.

3.2. Risk analysis and treatment of the EMWTP

3.2.1. Risks associated with pharmaceuticals in the EMWTP

Before applying any treatment, it is relevant to determine the environmental risks associated with the target pollutants contained in the EMWTP sample, which at the same time supports the need to eliminate such contaminants. In this context, the concentration of the target pollutants in the EMWTP was determined initially (Table S4a). The concentration levels (ng/L-μg/L) of the target pollutants were consistent with our previous work in the same municipal treatment plant (Botero-Coy et al., 2018), and similar to those reported for EMWTPs in other studies performed in Latin American and African countries (Nieto-Juárez et al., 2021; Oharisi et al., 2023).

According to the scoring method recently proposed in the reference (Verlicchi et al., 2023), we found that most pharmaceuticals had high occurrence values (i.e. score ≥4, Table S4b). The high occurrence of pharmaceuticals in EMWTP can be linked to aspects such as consumption/excretion (see Text S2 and Table S5) and removal inability of the processes used in the sewage treatment plants. Indeed, several target pharmaceuticals had high persistence scores (see Text S3 and Table S6), due to their recalcitrance to conventional treatments such as the biological processes (Botero-Coy et al., 2018).

In addition to acute toxic effects (denoted by HQ, see Table S4a), the bioaccumulation of the pharmaceuticals is also a parameter to take into account (Patel et al., 2019). As bioaccumulation refers to the potential of a compound to accumulate in the adipose tissue of aquatic organisms and this property may be expressed by the octanol-water partition coefficient (Kow) (Verlicchi et al., 2023), the risk of bioaccumulation of the target pharmaceuticals was determined (Table S7). Among the eighteen pharmaceuticals, atorvastatin, clarithromycin, diclofenac, irbesartan, and losartan had a high feasibility of being bioaccumulated (as denoted by their bioaccumulation score ≥4).

The risk items of occurrence, persistence, HQ, and potentiality to bioaccumulation confirm the necessity of proper treatments for degrading/removing the pharmaceuticals in the EMWTP sample before the discharge into the environment. Hence, the action of ZA and PMS acting individually, plus the PMS/ZA combination was used to deal with the target pollutants in the actual EMWTP.

3.2.2. Removal of pharmaceuticals in EMWTP via adsorption on the zeolite

The capability of the ZA to adsorb the target pollutants from the EMWTP is presented in Fig. 3. The removal of pharmaceuticals after 60 min was determined. It was observed a high removal (>80 %) of atorvastatin, azithromycin, pantoprazole, and salbutamol, while medium adsorption (40–60 %) of ciprofloxacin and clindamycin was found. The rest of the pollutants exhibited very low adsorption (<25 %) on the zeolite A. Indeed, the ZA achieved a total removed amount (TRA value) of 11.5 ng (see Table S8 and Eqs. S6-S7), indicating a low global adsorption capability (Fig. 3); which can be related to its low surface area (~19 m^2 g^{-1}) and charges on the surface (Table S2).

As the zeolite A is hydrophilic (i.e., SiO_2/Al_3O_2 ratio <2), it has a low ability to adsorb diverse pharmaceuticals (which is also consistent with

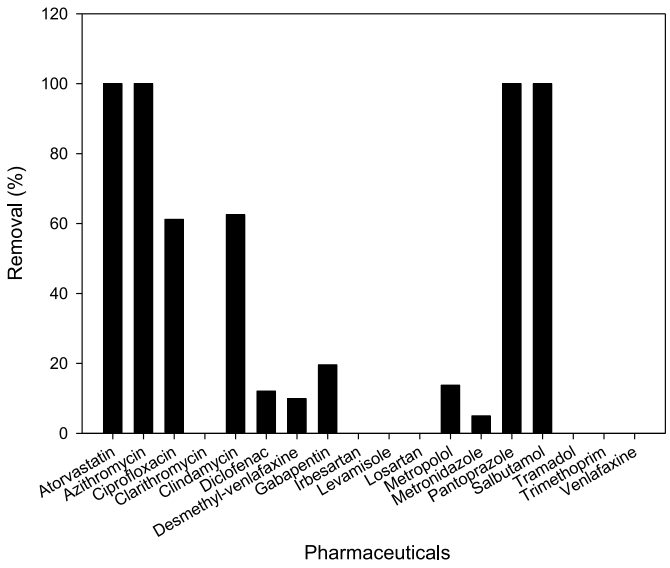

Fig. 3. Removal of the target pollutants in EMWTP by adsorption on ZA (0.2 g L^{-1}) after 60 min of treatment.

the results previously presented for the model compounds in Fig. 1A). At the experimental pH of the EMWTP (which is 7.2, Table S1), the ZA surface is negatively charged (pHpzc: 3.8). Then, the adsorption of pharmaceuticals such as azithromycin, ciprofloxacin, clindamycin, metoprolol, pantoprazole, and salbutamol (which are positively charged, Table S9) is explained by electrostatic attractions toward the ZA surface.

Also, it is important to consider that, in a complex matrix such as EMWTP, the presence of inorganic cations (e.g., Fe^{2+}) or even other non-target organic compounds could play a role as mediator substances in the adsorption of the pharmaceuticals. For instance, some inorganic species such as iron cations can act as a bridge between the zeolite and the pharmaceuticals (via chemical binding) (Russo et al., 2021; Serna-Galvis et al., 2024). This could be the case of atorvastatin or diclofenac, which can interact with iron cations adsorbed on ZA through the deprotonated carboxylic acid moiety. Moreover, other organic compounds in the water matrix, such as surfactants, could generate new and different interactions (e.g., hydrophobic interactions mediated by surfactants) (Krajišnik et al., 2013; Serna-Galvis et al., 2024), thus favoring some adsorption of compounds such as diclofenac, desmethyl venlafaxine, gabapentin or metronidazole.

3.2.3. Elimination of pharmaceuticals under the action of PMS

The degradation of the pharmaceuticals in EMWTP by the PMS was also tested. Fig. 4 presents the degradation of the target pollutants under the PMS addition to the water sample. After 60 min of treatment, atorvastatin, azithromycin, ciprofloxacin, clarithromycin, clindamycin, diclofenac, desmethyl venlafaxine, pantoprazole, and salbutamol had high degradation percentages (>80 %). At the same treatment time, gabapentin, irbesartan, levamisole, and trimethoprim showed moderate degradation percentages (35–60 %), and the other pharmaceuticals presented eliminations by PMS lower than 25 %. Hence, the PMS addition achieved a TRA of 27.5 ng (Table S8).

Pharmaceuticals such as azithromycin, clarithromycin, clindamycin, desmethyl venlafaxine, gabapentin, venlafaxine, metoprolol, salbutamol, tramadol, and trimethoprim have amine moieties, which can experience direct oxidation by PMS. Also, PMS can transform sulfide and thioether groups into sulfoxides and sulfones (Ruiz et al., 2019; Yang et al., 2018), which could be the case with clindamycin, levamisole, and pantoprazole.

The interaction of aniline moiety with PMS leads to nitro group formation (Jiang et al., 2018). This degradation mechanism could be involved in the removal of diclofenac by PMS. Peroxymonosulfate is also a hydroxylating agent of aromatic rings (Ruiz et al., 2019). For example, PMS reacts with phenol to form hydroquinone (Yang et al., 2018). Thus, part of the degradation of the desmethyl venlafaxine, venlafaxine, irbesartan, losartan, metoprolol, pantoprazole, salbutamol, tramadol, and trimethoprim (Fig. 4) may be related to the interaction of PMS with the aromatic rings on those pollutants.

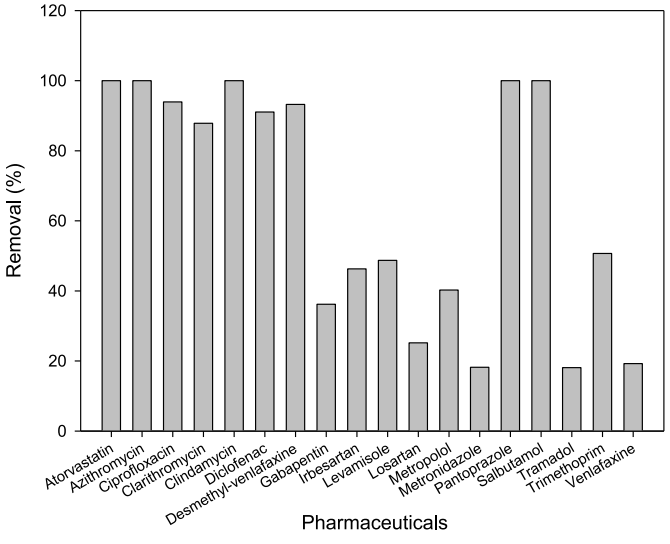

Fig. 4. Degradation of the pharmaceuticals in EMWTP by action of PMS (500 μmol L^{-1}) after 60 min of treatment.

3.2.4. Removal of the pharmaceuticals by the PMS/ZA process

The PMS/ZA system was applied to the EMWTP effluent and Fig. 5 shows the elimination of the target pollutants after 60 min of treatment. The PMS/ZA system induced removals >75 % for most of the target pollutants (11 out of 18). Also, the PMS/ZA system achieved a TRA of 30.9 ng (Table S8). In such a system, there is a mixture of phenomena: adsorption on ZA, direct oxidation by PMS, attacks of ROS from the interaction of PMS with ZA, or PMS with some matrix components (e.g., PMS/iron ions or PMS/chloride ions, as demonstrated in Section 3.1.3).

As demonstrated in Section 3.1.3, $^1O_2$ is produced by the interaction of PMS with ZA, and this ROS can transform ciprofloxacin and diclofenac. Also, singlet oxygen can introduce oxygen atoms on pyrrole and imidazole moieties on pollutants such as atorvastatin, pantoprazole, and losartan (Kim et al., 2012). Moreover, singlet oxygen could react with venlafaxine and its metabolite by attacking and modifying the amine group on these pollutants (Alshammari et al., 2024).

In the EMWTP, matrix components such as iron or chloride ions promote the formation of HO•, SO_4•-, or HClO (Eqs. (1)–(3)), which could have some contribution to degrade the target pollutants in the EMWTP sample. Sulfate radicals can fastly react with aromatic rings, carboxyl groups (Lee et al., 2020), and heteroatoms (e.g., N or S) in reduced forms (Serna-Galvis et al., 2017a). Then, sulfate radical reacts with pharmaceuticals such as ciprofloxacin, carbamazepine, diclofenac, metoprolol, metronidazole, salbutamol, sulfamethoxazole, and venlafaxine at rate constants ranged between 10^8 and 10^{10} M^{-1} s^{-1} (Wojnárovits and Takács, 2019).

In the case of HO•, this typically induces hydrogen abstraction, oxidation of amines or thioethers, and addition to pi-systems (e.g., aromatic rings or double bonds) on the pollutants. Hence, the hydroxyl radical can react with pharmaceuticals such as carbamazepine, ciprofloxacin, diclofenac, sulfamethoxazole, and trimethoprim at rate constants in orders of 10^9 M^{-1} s^{-1} (Wols and Hofman-Caris, 2012). On the other hand, the small amounts of the generated HClO could participate by attacking pharmaceuticals such as ciprofloxacin, diclofenac, metoprolol, or trimethoprim (Serna-Galvis et al., 2017b).

3.3. Extent of the PMS/ZA treatment

3.3.1. Environmental risk decreasing after treatment

The treatment of the EMWTP by the PMS/ZA system led to a significant decrease in the occurrence criterion for atorvastatin, azithromycin, ciprofloxacin, clarithromycin, clindamycin, desmethyl venlafaxine, and venlafaxine (Table S10). Furthermore, the HQ and HQ_{mix} values (see Table S11) were also diminished regarding the initial values (see Table S11) after the treatment using the PMS/ZA process. Indeed, the HQ_{mix} (considering the dilution factor) was lower than 0.1. Furthermore, it is important to note that the change in the HQ values (represented by ΔHQ in Table S11) was very high for environmentally concerning pharmaceuticals such as azithromycin, diclofenac, trimethoprim, and clarithromycin. Thus, the occurrence values and risk quotients after the treatment suggest that the PMS/ZA system decreased environmental risk associated with the presence of the target pharmaceuticals.

3.3.2. EMWTP bleaching/discoloration and phytotoxicity test

To go beyond the degradation of pharmaceuticals, during the effluent treatment, other parameters were analyzed. Thus, the α_{254} and α_{410} (which are non-specific surrogates of compounds having aromatic rings or unsaturated carbon bonds in EMWTP, and the color of the water

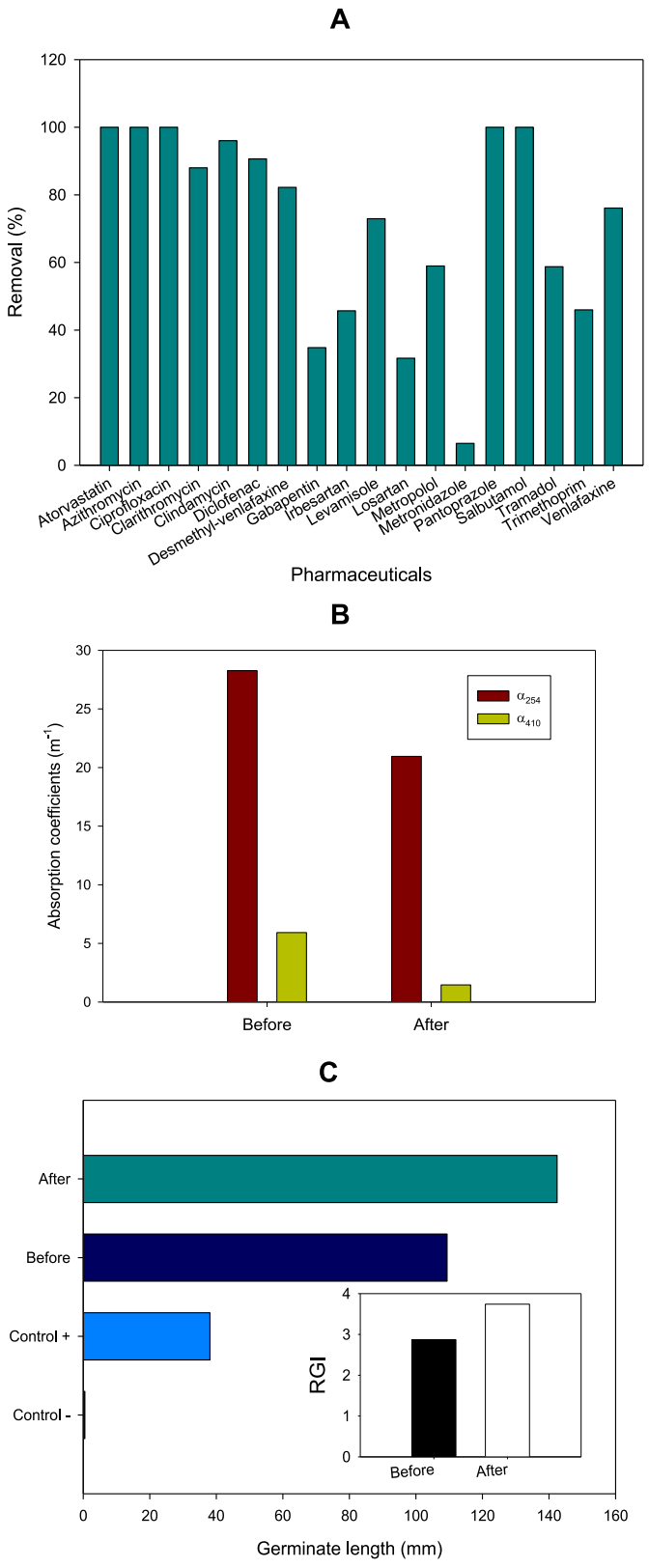

Fig. 5. Degradation of the pharmaceuticals in EMWTP by the PMS/ZA process and treatment extent. **A.** Removal efficiency. **B.** Spectral absorption coefficients (α) before and after treatment by the PMS/ZA process. **C.** Phytotoxicity results before and after the treatment by the PMS/ZA process (inset: relative growth index-RGI). Experimental conditions: [ZA] = 0.2 g L^{-1}, [PMS] = 500 μmol L^{-1}, treatment time = 60 min.

sample, respectively) were measured. Fig. 5B presents the values of spectral absorption coefficients of EMWTP before and after the treatment by the PMS/ZA process.

Most pharmaceuticals in the EMWTP contribute to the α_{254} parameter. Furthermore, many dyes are not degraded by the classical processes in the wastewater treatment plants (WWTP) (Magdaleno et al., 2024), contributing to the color of the effluent, represented by the α_{410} parameter. According to Fig. 5B, there was a ~26 % reduction of α_{254} by the PMS/ZA process, indicating partial removal and/or transformation of the aromatic nature of the pollutants (Prada-Vásquez et al., 2024). In turn, a strong change in the α_{410} parameter (it was decreased by ~72 %, Fig. 5B) was obtained, indicating that the treated sample was significantly bleached by the process action.

The decrease in specific absorption coefficients by the action of the PMS/ZA process can be linked to the simultaneous participation of PMS and the other degradation species (e.g., $^1O_2$). For instance, PMS alone can attack aromatic or alkene structures, leading to hydroxylation and epoxidation of the compounds, and the interaction of PMS with aniline-type moieties produces nitro groups (Jiang et al., 2018; Yang et al., 2018), causing a decrease of α_{254}. Besides, the adsorption of pollutants having aromatic rings (e.g., atorvastatin, ciprofloxacin, pantoprazole, or salbutamol) could have some contribution to decreasing the α_{254} parameter.

The singlet oxygen can oxidize benzene rings on pharmaceuticals, e.g., phenolic structures, and double bonds (Díez-Mato et al., 2014; Li et al., 2023), also supporting the decrease of α_{254} observed in Fig. 5B. Moreover, sulfate radical or hydroxyl radical can promote the hydroxylation of aromatic rings and hypochlorous acid can induce chlorination of the benzene moieties, thus facilitating the α_{254} diminution.

Regarding the decrease of α_{410}, we can mention that the adsorption of some compounds responsible for color on ZA is plausible (Al-dahri et al., 2022; Thongkam et al., 2021). Besides, PMS, $^1O_2$, and radical species have a high affinity to amines, sulfide, and azo groups typically present in coloring substances, which degradation can explain the EMWTP discoloration (i.e., the strong decrease of α_{410}) (Lei et al., 2016; Zuo et al., 2022).

On the other hand, if the treated EMWTP is reclaimed/reused for irrigation crops, the phytotoxicity must be assessed. Thus, the phytotoxicity of the raw and treated EMWTP against tomato seeds was determined (Fig. 5C). Table S12 presents the analyses of variance (ANOVAs) for the statistical comparison of the average values of the germinate lengths. Before treatment, EMWTP had an RGI value > 1.2 (i.e., the sample had stimulating effects on the seeds' germination). This can be associated with the presence of some nutrients (N, C, P) in the raw EMWTP, which can promote the germination of tomato seeds. Moreover, the RGI for the treated EMWTP was higher than that for the sample before treatment.

The PMS/ZA process degraded the pharmaceuticals and other matrix components, generating products less phytotoxic than the parent compounds. Hence, these results denote the beneficial effects of the EMWTP treatment using the PMS/ZA system. Our results are in agreement with other previous works, which also report the increase of seed growth (i.e., phytotoxicity reduction) after the treatment of effluents from WWTPs by PMS-based processes (Berruti et al., 2023; Guerra-Rodríguez et al., 2021).

Finally, it is important to highlight that this research represents a first approach to evaluate the combined action of ZA with PMS in an actual EMWTP, which seems to be promissory (as shown in Figs. 4 and 5). Future work should be focused on quantifying the target pharmaceuticals at several treatment times under optimizing operational parameters (e.g., zeolite dose and PMS concentration). Also, the variability of the sample should be evaluated by treating different EMWTP samples to provide a wider panorama of the capability of the PMS/ZA system to deal with diverse loads of pollutants. Moreover, it is worth noting that most zeolites are environmentally friendly catalysts but the recovery of and reuse of the zeolite are relevant topics that must be considered for a

future scaling up of the PMS/ZA system.

4. Conclusions

From this research work, it can be proposed the following final remarks:

- The model compounds allowed an understanding of the fundamental aspects of the PMS/ZA process, revealing that removal/degradation of pollutants mainly occurred through the direct attacks of PMS and reactive species coming from the interaction of PMS with the zeolite (i.e., $^1O_2$) or PMS with the matrix components, with minor participation of the target pollutants adsorption on the zeolite.
- The environmental risk analysis for the EMWTP sample showed that the target compounds offered hazards such as high occurrence, as a consequence of the high consumption and excretion, and low removal efficiency of the processes in the wastewater treatment plant. Among the considered pharmaceuticals, atorvastatin, clarithromycin, diclofenac, irbesartan, and losartan presented high potentiality for bioaccumulation.
- The hazard quotient without dilution, for ten of eighteen target pollutants, was >1, indicating that pharmaceuticals such as atorvastatin, azithromycin, ciprofloxacin, and diclofenac represent a high toxicological risk to aquatic species placed close to the discharge point. Nevertheless, when the dilution factor was considered, the HQ values strongly decreased to a low risk but the HQ_{mix} was >0.1, indicating that the mixture of the pharmaceuticals has a moderate risk of inducing toxic effects on aquatic species.
- For most of the target pollutants (11 out of 18) the PMS/ZA system induced removals >75 % after 60 min of treatment. Indeed, the degradation of the pharmaceuticals in the EMWTP achieved 30.9 ng of the total removed amount (TRA).
- The PMS/ZA led to the EMWTP sample discoloration and this catalytic process degraded the pharmaceuticals and other matrix components, generating products less phytotoxic than the parent compounds. Hence, these results denote the beneficial effects of the EMWTP treatment using the PMS/ZA system.

CRediT authorship contribution statement

Efraím A. Serna-Galvis: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ana M. Botero-Coy:** Writing – review & editing, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Johana Arboleda-Echavarría:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Adriana Echavarría-Isaza:** Writing – review & editing, Resources, Methodology, Conceptualization. **Félix Hernández:** Writing – review & editing, Resources, Project administration, Methodology, Data curation, Conceptualization. **Ricardo A. Torres-Palma:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2025.145550.

Data availability

Data will be made available on request.

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