Metabisulfite as an Unconventional Reagent for Green Oxidation of Emerging Contaminants Using an Iron-Based Catalyst

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ABSTRACT: In this work, contaminants of emerging concern were catalytically degraded in the homogeneous phase with the use of unconventional green reagents. Three reagents, namely, sulfite, metabisulfite, and persulfate, were tested and compared with conventional hydrogen peroxide in the degradation process activated by Fe-TAML. The latter is a biodegradable, homogeneous tetra-amido macrocyclic ligand catalyst containing iron(III). Metabisulfite showed the highest efficiency among the three tested reagents, and its reactivity was similar to that of H2O2. However, metabisulfite is a safer and cleaner reagent compared to H2O2. A comprehensive study of the activity of metabisulfite with Fe-TAML was carried out toward the oxidative degradation of eight contaminants of emerging concern. The catalytic process was tested at different pH values (7, 9, and 11). Metabisulfite showed the highest activity at pH 11, completely degrading some of the tested micropollutants, but in several cases, the system was active at pH 9 as well. In particular, metabisulfite showed the best efficiency toward phenolic compounds. A preliminary study on the reaction mechanism and the nature of the active species in the Fe-TAML/metabisulfite system was also conducted, highlighting that a high-valent iron-oxo species might be involved in the degradation pathways.

1. INTRODUCTION

Micropollutants, such as pesticides, pharmaceuticals, and personal care products, are products that are naturally and biologically active substances. They are ubiquitous in aquatic environments and can jeopardize the life of plants, animals, and humans. The Fenton reaction is a promising advanced oxidation process to reduce micropollutants in water, and it has been proven effective for the degradation of a wide variety of recalcitrant and/or non-biodegradable contaminants in industrial wastewaters. The main reactions involved in Fentonmediated oxidation are mainly hydroxyl radicals and/or superoxided iron species. The Fenton process works best in the pH range of 2.5–4, with the highest degradation rates usually observed around pH 3.5

Living organisms metabolize micropollutants and potentially toxic endogenous and exogenous compounds with cytochrome P450, an iron-based family of enzymes. On this basis, Collins and co-workers have developed an innovative catalyst for water decontamination, the Fe-TAML activator, which mimics the oxidative activity of cytochrome P450 by forming a stable iron-oxo species in water when it reacts with peroxides. Fe-TAML has a large spectrum of applications in the remediation of recalcitrant micropollutants and pathogens from water. Its reaction usually takes place at room temperature and it is most effective in the pH range 7.5–11, with the highest rates usually observed around pH 10–11. An oxidation process that is efficient under basic conditions may be more promising and useful than a process operating under acidic conditions (e.g., the traditional Fenton process), for two main reasons: (i) it does not require pH adjustments when the water effluent is already alkaline, as in the case of some industrial effluents; and (ii) it allows the coprecipitation of inorganic cations (e.g., toxic metals) potentially present in the effluent, thus reducing the need of an ad hoc treatment step and preventing their possible interfering activity. In this sense, oxidation by Fe-TAML or other similar catalysts as tools to improve the Fenton reaction is potentially advantageous compared to a classic Fenton process.

Hydrogen peroxide is preferentially used as the Fenton reagent because of its relatively low cost, availability on the market, and fair environmental compatibility. Hydrogen peroxide is also the preferred reagent in the case of oxidations activated by Fe-TAML. In addition to hydrogen peroxide, Fe-TAML can activate hypochlorite, organic peroxides, and oxone. However, not all these alternative reagents are convenient in every circumstance. For instance, hypochlorite may lead to the formation of potentially carcinogenic chlorinated byproducts.

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besides being explosive and unsafe, have a high cost. Therefore, they may not be easily employed to treat large flow rates, which are commonly encountered in wastewater treatment plants. While being the current best choice, hydrogen peroxide has also important limitations related to operational safety, particularly when it is used in large amounts and concentrations. H2O2 is highly reactive, and it forms explosive mixtures upon contact with organic compounds. Furthermore, it is corrosive and irritant for eyes, mucous membranes and skin, and its relatively high vapor pressure poses health risks by inhalation even following short exposure. H2O2 has also been classified as a known animal carcinogen, with unknown relevance on humans. Finally, the thermodynamic instability of H2O2 results in a relatively short shelf life, especially when stored in concentrated solutions and exposed to ambient temperatures. For all these reasons, research is needed to identify more benign reagents that combine all of the positive features of hydrogen peroxide while minimizing safety hazards and operational burdens.

In preliminary tests, we found that benign species, such as sulfite and metabisulfite, can be effectively activated by Fe-TAML toward the degradation of micropollutants. Despite its activity as a reductant, sulfite can be activated toward the oxidative degradation of organic compounds. Furthermore, it is corrosive and irritant for eyes, mucous membranes and skin, and its relatively high vapor pressure poses health risks by inhalation even following short exposure. H2O2 has also been classified as a known animal carcinogen, with unknown relevance on humans. Finally, the thermodynamic instability of H2O2 results in a relatively short shelf life, especially when stored in concentrated solutions and exposed to ambient temperatures. For all these reasons, research is needed to identify more benign reagents that combine all of the positive features of hydrogen peroxide while minimizing safety hazards and operational burdens.

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2. RESULTS AND DISCUSSION

2.1. Performance of Different Reagents toward the Degradation of Phenol. The activity of hydrogen peroxide in the degradation of various classes of contaminants with Fe-TAML is widely reported in the literature. Therefore, here, H2O2 was used as a comparative standard. Figure 1 shows the catalytic degradation of phenol in three-step addition experiments, using Fe-TAML and sulfite (SO32−, Figure 1a), metabisulfite (S2O52−, Figure 1b), persulfate (S2O82−, Figure 1c), and hydrogen peroxide (Figure 1d, only one addition) as reagents. After each addition of metabisulfite (one every 10 min, i.e., at 0, 10, and 20 min reaction time), there was significant phenol degradation, soon followed by stabilization of the phenol concentration, with an overall step-wise trend that closely mirrored the step-wise S2O52−-additions. This finding is
similar to recent results, obtained in the framework of the traditional Fenton reaction.\textsuperscript{32} Duplicates and triplicates of these tests are presented in Figure S1 of the Supporting Information. The replicate tests showed high robustness, implying the reproducibility of the adopted experimental procedures. All of the reactions were quenched by decreasing the pH to a final value <3. Under acidic conditions, demetallation (decomplexation of the Fe-TAML complex) is promoted and the catalytic reaction is stopped as a consequence, also considering the limited reactivity of Fe(III) species with H$_2$O$_2$ and similar reagents under very acidic conditions.\textsuperscript{33}

Metabisulfito was more effective than sulfite toward phenol degradation, and the highest degradation efficiency for the two reagents was achieved at pH 11. On the other hand, persulfate did not show any activity toward the degradation of phenol (further insights below). Table S1 of the Supporting Information reports the degradation percentages reached at the end of the degradation experiments for all of the investigated conditions. Wherever a significant reactivity was observed (i.e., with sulfite, metabisulfito, and mainly hydrogen peroxide), phenol degradation was very fast immediately after the addition of the reagent. It then followed a rapid stabilization of the substrate concentration. This behavior prevented the details of the degradation kinetics to be monitored with the used experimental setup, which was based on sample aliquots withdrawal from the reaction beaker, quenching of the reaction, and successive high-performance liquid chromatography (HPLC) quantification of the residual substrate concentration. As a consequence, we could not measure the initial reaction rate. However, we could easily measure the degradation percentage, which is the most relevant information in the framework of water treatment. Additionally, such an approach allowed us to obtain sufficient insight into the reaction mechanism (vide infra). The first step of the reaction might be investigated by using the rather outmoded (and, unfortunately, not easily found nowadays) stopped-flow technique, which has proven, for instance, suitable for the investigation of the dark traditional Fenton process.\textsuperscript{34}

In general, the degradation efficiency was higher at basic pH values. Because phenol undergoes acid–base equilibrium ($pK_a$ 9.95),\textsuperscript{35} at pH 9, the phenolate anion (PhO$^-$) starts to be significantly present, while at pH 11, it prevails. Phenolate is more easily oxidized than neutral PhOH. In the case of H$_2$O$_2$, an almost complete degradation of phenol took place at both pH 9 and 11 with just one hydrogen peroxide addition. In contrast, at pH 7, the H$_2$O$_2$ treatment was less effective. The pH trend of the degradation efficiency was consistent with that reported by Collins et al. when using H$_2$O$_2$\textsuperscript{12} please see further details in the Supporting Information.

Interestingly, the system containing Fe-TAML + persulfate was unable to induce significant degradation of phenol at any of the investigated pH values. It may be reasonable to assume that the inactivity of persulfate depends on poor complexation capability (steric hindrance) of the persulfate anion with the metal center of Fe-TAML (vide infra).\textsuperscript{36,37}

The reported results suggest that metabisulfito is less effective than hydrogen peroxide in the degradation of phenol, but it is the most effective among the alternative reagents investigated here. Because of the lower cost and hazards of metabisulfito compared to H$_2$O$_2$, its reaction conditions were optimized, and its potential as a H$_2$O$_2$ substitute was further investigated for the degradation of other contaminants of emerging concern (CECs). Some phenol degradation experiments were carried out to identify the experimental conditions able to maximize its transformation with metabisulfito. In particular, we wanted to assess whether the best degradation conditions could be reached with multistep additions of metabisulfito at relatively low concentration, or with a single addition of the reagent at higher concentration. Figure 2 shows the results of the experiments carried out with Fe-TAML and metabisulfito at different pH values (7, 9, and 11), with only one addition of the reagent at concentrations of 0.3 mM (Figure 2a) and 0.1 mM (Figure 2b; this latter experiment is similar to the first addition step reported in Figure 1b). Phenol concentration was monitored for up to 60 min. As expected, the reaction was very fast in the first 1–2 min after the addition of the reagent and it followed a rapid stabilization of phenol concentration afterward. The overall degradation performance was better when the concentration of metabisulfito was higher (i.e., 0.3 mM), but the best results were definitely achieved when the same overall amount of metabisulfito was added in three separate steps (100% degradation, see Figure 1b), rather than in a single addition (80% degradation, Figure 2a). It is reasonable to assume that, in the case of a single large addition, the reagent itself partly scavenges the reactive species, as often observed in the classic Fenton process (note that metabisulfito has a reducing character). In fact, within the same time interval, more reagent (higher concentration of metabisulfito)

Figure 2. Degradation of phenol with metabisulfito as the reagent. The reactions were carried out in phosphate buffer (10 mM), with initial concentrations [Fe-TAML] = 0.01 mM; [PhOH] = 0.1 mM, and adding one aliquot of metabisulfito with initial concentrations of (a) 0.3 and (b) 0.1 mM.
is available to react with the reactive species present in the system, compared with the addition of the same overall amount of the reagent in separate steps. Based on these results, the multiple addition approach appears to be the most rational way to use the \(\text{S}_2\text{O}_5^{2−}\) reagent, and it was chosen hereafter to perform the degradation of the contaminants under study.

2.2. Comparison of Metabisulfite (\(\text{S}_2\text{O}_5^{2−}\)) and Hydrogen Peroxide in the Degradation of CECs. The ability of Fe-TAML to activate metabisulfite was tested against the degradation of additional micropollutants. Figure 3 shows the percentage of contaminant degradation after 1 h reaction time, when metabisulfite was used as the reagent at different pH values (7, 9, and 11). The reaction was carried out by adding 0.1 mM of the reagent every 10 min for a total of three additions (at 0, 10, and 20 min). Initial conditions were [Fe-TAML] = 0.01 mM and [contaminant] = 0.1 mM.

![Figure 3](image-url) 

**Figure 3.** Degradation percentage of the studied CEC. Metabisulfite or \(\text{H}_2\text{O}_2\) were used as reagents at different pH values. The reactions were carried out for 60 min in phosphate buffer (10 mM), by adding 0.1 mM of the reagent every 10 min for a total of three additions (at 0, 10, and 20 min). Initial conditions were [Fe-TAML] = 0.01 mM and [contaminant] = 0.1 mM.

Supporting Information to see results from some test replicates.

Previous literature has reported that Fe-TAML forms an iron-oxo active species with peroxides. The iron-oxo species is electrophilic, and it tends to react with electron-rich compounds that are easily oxidized. Coming back to our data, the complete degradation of PhOH and the inactivity of the process toward ACE (see Figure 3) are consistent with a peculiar role of oxidants with middle-high redox potential (such as iron-oxo species, vide infra) in both the Fe-TAML/\(\text{H}_2\text{O}_2\) and the Fe-TAML/\(\text{S}_2\text{O}_5^{2−}\) chemistry. Indeed, PhOH is definitely electron richer than ACE (see also the electrochemical evidences reported below). The results, in terms of the Fe-TAML + \(\text{H}_2\text{O}_2\) reaction efficiency, may thus be rationalized with the different electronic structure of the contaminants, in agreement with Chen and White. Then, because metabisulfite showed the same efficiency trend as \(\text{H}_2\text{O}_2\) toward the chosen contaminants, we can tentatively assume as a working hypothesis that there is a close analogy between the reactive species involved in the two cases.

Interestingly, when the Fe-TAML + \(\text{S}_2\text{O}_5^{2−}\) process led to quantitative or almost quantitative substrate transformation (i.e., with PhOH, BP3, and TCS), the degradation efficiency was very similar at both pH 9 and 11, while the degradation at pH 7 was less effective. Conversely, when the degradation was inefficient (i.e., with ACE, NPX, IBU, and ATZ), it was so at all of the tested pH values. DCF is the only instance in which we observed a gradual increase of the degradation efficiency throughout the entire interval of increasing pH. Differently from DCF, the phenolic compounds PhOH, BP3, and TCS undergo acid–base equilibria in the pH interval 7–11, thereby yielding the corresponding easily oxidized phenolates at high pH. For this reason, the case of DCF, which does not undergo acid–base equilibrium changes between pH 7 and 11, is likely to better reflect the genuine pH trend of the Fe-TAML + \(\text{S}_2\text{O}_5^{2−}\) reactivity. Note that a low Fe-TAML activity at pH 7 has already been reported in a previous paper describing the Fe-TAML activation of \(\text{H}_2\text{O}_2\).

Different from the classic Fenton reaction at acidic pH, which is mainly driven by the production of hydroxyl radicals and is usually poorly selective toward different pollutants, the Fe-TAML-activated process was definitely more selective (see Figure 3). On the one hand, this means that a smaller number of contaminants can be targeted with Fe-TAML-Fenton compared to \(\text{Fe}^{2+} + \text{H}_2\text{O}_2\). However, higher selectivity (i.e., the ability of the catalyst to discriminate amongst different compounds) might improve the degradation efficiency of target contaminants in a multipolluted aqueous environment, especially in the presence of interfering agents, such as the inherently harmless organic matter. Organic matter usually does not require a dedicated degradation step, but it is accidentally degraded by hydroxyl radicals and, by consuming them, it may inhibit the traditional Fenton process. In contrast, by virtue of higher selectivity, iron-oxo-based treatments may be less prone to interferences from organic matter.

2.3. Discussion on the Nature of the Active Species and the Reaction Mechanism. While it is accepted that systems containing Fe-TAML + \(\text{H}_2\text{O}_2\) have an iron-oxo species as reactive transient, there is no piece of information concerning the behavior of Fe-TAML + \(\text{S}_2\text{O}_5^{2−}\), or the nature of the resulting active species. Indeed, this system is here described for the first time. As mentioned above, Fe-TAML +

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H$_2$O$_2$ and Fe-TAML + S$_2$O$_5$$^2$− had analogous reactivity at pH 11 toward the studied substrates. Therefore, it is reasonable to hypothesize that the formed active species share some similarities. Tests were conducted to assess whether the main active species of Fe-TAML + S$_2$O$_5$$^2$− has radical or nonradical nature. Although we could not rely on any previous report concerning the S$_2$O$_5$$^2$−-based Fenton process, possible reactive radical species in, for example, sulfito-based Fenton systems are hydroxyl (•OH) and sulfate (SO$_4$•−).44 In contrast, a Fe-based oxidant could trigger a nonradical pathway, in analogy with Fe-TAML + H$_2$O$_2$.

To get mechanistic insight into the studied process, tert-butanol (t-BuOH) and isopropyl alcohol (2-PrOH) were added into the solution as radical scavengers during the transformation of phenol. 2-PrOH is very reactive with hydroxyl radicals (k = 1.9 × 10$^9$ M$^{-1}$ s$^{-1}$) and significantly less so with sulfate radicals (k = 4 × 10$^7$ M$^{-1}$ s$^{-1}$).45 On the other hand, t-BuOH shows similar reactivity with both •OH (k = 4 × 10$^8$ M$^{-1}$ s$^{-1}$) and SO$_4$•− (k = 3.6 × 10$^8$ M$^{-1}$ s$^{-1}$).13,45

Different phenol degradation experiments were thus carried out with Fe-TAML and metabisulfite, in the presence of t-BuOH and 2-PrOH. Scavenger/phenol concentration ratios of 400:1 (t-BuOH) and 1330:1 (2-PrOH) were used. Considering the reaction rate constants of phenol/phenolate with •OH (k$_{PhOH}$ and k$_{PhO}^-$ ≈ 10$^{10}$ M$^{-1}$ s$^{-1}$) and SO$_4$•− (k$_{PhOH}$ = 2.2 × 10$^9$ M$^{-1}$ s$^{-1}$, k$_{PhO}^-$ unknown but possibly similar, and <10$^{10}$ M$^{-1}$ s$^{-1}$),13 it is expected that t-BuOH causes a ∼95% inhibition of phenol degradation if •OH is the reactive species (i.e., the degradation should be ∼20 times lower with the alcohol). Moreover, almost total quenching by t-BuOH is
should be quantitative with well-known properties of a nonradical nature. By analogy, the behavior of SO\textsubscript{4}\textsuperscript{2-} alcohols would be due to the slight reactivity of the iron-oxo species. Further evidence is provided by the limited, observed inhibition of the degradation process by Fe-TAML + S\textsubscript{2}O\textsubscript{5}\textsuperscript{2-}. This is consistent with the occurrence of either OH or SO\textsubscript{4}\textsuperscript{2-} as the main reactive species, especially at the higher pH value (11), where we would expect inhibition to be much more evident in the case of a dominant role of the hydroxyl and sulfate radicals as reactive species of the process. Moreover, the two alcohols produced very similar and limited e\textsuperscript{-}S\textsuperscript{2}O\textsubscript{5}\textsuperscript{2-} as reactive species of the process. In the case of unreactive persulfate, the coordination of iron(III) species may be too stable for resonance, and the corresponding π* orbital of the O=S fragment would be too distant from the iron center, while the latter may be sterically hindered because of the geometry of the persulfate molecule.

Table 1. Onset Potential for the Oxidation of the Studied Contaminants of Emerging Concern\textsuperscript{a}

<table>
<thead>
<tr>
<th>compound</th>
<th>oxidation onset (V vs Ag/AgCl)</th>
<th>oxidation onset (1st scan, V vs Ag/AgCl)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACE</td>
<td>0.90</td>
<td>0.90</td>
<td>Although an anodic current onset can be appreciated for ACE, the oxidation current is always very low and an anodic peak is never observed. In fact, for the analytical determination of ACE, Pierini et al.\textsuperscript{46} have exploited its reduction. Because of limited solubility in CH\textsubscript{3}CN, the same measurement was repeated in water at pH 10. No anodic current was observed compared with the blank run.</td>
</tr>
<tr>
<td>NPX</td>
<td>0.80</td>
<td>0.25</td>
<td>An additional oxidation peak could be appreciated on the first scan only. The potential of the anodic peak observed in the successive scans corresponds with literature data\textsuperscript{47}.</td>
</tr>
<tr>
<td>IBU</td>
<td>1.62</td>
<td>1.62</td>
<td>The oxidation onset potential corresponds very well to the results of Lima et al.,\textsuperscript{50} obtained using a boron-doped diamond.</td>
</tr>
<tr>
<td>DCF</td>
<td>0.05</td>
<td>0.05</td>
<td>The results obtained are coherent with the literature.\textsuperscript{50} Nevertheless, in that report, the authors reported significantly larger sensitivity in the 0 V/0.6 V potential window thanks to the modification of the glassy carbon electrode.</td>
</tr>
<tr>
<td>ATZ</td>
<td>1.75</td>
<td>1.75</td>
<td>ATZ is only oxidized at a very positive potential. In fact, for ATZ determination, Svorc et al.\textsuperscript{51} exploited its reduction.</td>
</tr>
<tr>
<td>PhOH</td>
<td>0.70</td>
<td>0.80</td>
<td>The oxidation onset potential decreases on successive scans because of the formation of catechol and hydroquinone\textsuperscript{52}.</td>
</tr>
<tr>
<td>BP3</td>
<td>0.90</td>
<td>1.25</td>
<td>The anodic peak at 1.05 V (with corresponding oxidation onset at 0.9 V) is only observed if the potential is previously swept below 0 V. The main oxidation onset corresponds very well to the results reported by Suyer et al.\textsuperscript{53}.</td>
</tr>
<tr>
<td>TCS</td>
<td>0.60</td>
<td>0.60</td>
<td>Very similar values have been found by Fotouhi et al.\textsuperscript{54}.</td>
</tr>
</tbody>
</table>

*The onset potential is reported for both the first and the successive scans of the CVs.*

expected in the case of SO\textsubscript{4}\textsuperscript{2-}. Similarly, inhibition by PrOH should be quantitative with *OH, and in the order of ~90% with SO\textsubscript{4}\textsuperscript{2-}.

The results shown in Figure 4a,b indicate that the alcohols caused limited inhibition of phenol degradation by Fe-TAML + S\textsubscript{2}O\textsubscript{5}\textsuperscript{2-} at pH 7 and practically no inhibition at pH 11. These results are not consistent with the occurrence of either *OH or SO\textsubscript{4}\textsuperscript{2-} as the main reactive species, especially at the higher pH value (11), where we would expect inhibition to be much more evident in the case of a dominant role of the hydroxyl and sulfate radicals as reactive species of the process. Moreover, the two alcohols produced very similar and limited effects on the degradation of BP3, with both Fe-TAML + H\textsubscript{2}O\textsubscript{2} and Fe-TAML + S\textsubscript{2}O\textsubscript{5}\textsuperscript{2-}, at both pH 7 and 11 (see Figure 4c–f). This analogy in behavior further suggests that similar reactive species may be involved in Fe-TAML + H\textsubscript{2}O\textsubscript{2} and Fe-TAML + S\textsubscript{2}O\textsubscript{5}\textsuperscript{2-}. In the case of Fe-TAML + H\textsubscript{2}O\textsubscript{2}, the reactive species is well known to be of a nonradical nature.\textsuperscript{10,12,38} By analogy, and given the overall results, it is reasonable to believe that an iron-oxo species may also occur in Fe-TAML + S\textsubscript{2}O\textsubscript{5}\textsuperscript{2-}. The limited, observed inhibition of the degradation process by alcohols would be due to the slight reactivity of the iron-oxo species (less oxidant with respect to *OH or SO\textsubscript{4}\textsuperscript{2-}, vide infra) toward PrOH and t-BuOH, with no need to invoke radical-based reactions.

A tentative outline of the mechanism of activation of H\textsubscript{2}O\textsubscript{2} by Fe-TAML has already been proposed (Figure 5).\textsuperscript{12} It has been reported that the activation of H\textsubscript{2}O\textsubscript{2} occurs via the heterolytic cleavage of its O=O bond, after coordination to the iron center. The cleavage of the O=O bond is reasonably helped by proton transfer, followed by water release and formation of an iron-oxo complex.\textsuperscript{52} Taking inspiration from the hydrogen peroxide activation mechanism, in the case of the Fe-TAML/metabisulfite system, it is reasonable to suggest that the initial formation of the Fe–O=O–SR intermediate may be followed by heterolytic O–S cleavage, yielding the related iron-oxo species (Figure 5b). This would also tentatively explain why persulfate was not activated by Fe-TAML (Figure 1c). In the case of unreactive persulfate, the coordination of iron(III) should involve either sulfonyl or peroxy oxygen. The former may be too stable for resonance, and the corresponding π* orbital of the O–S fragment would be too distant from the reducing Fe(III) center, while the latter may be sterically hindered because of the geometry of the persulfate molecule.
Although this outline looks reasonable and agrees with the experimental data, further work is needed to confirm this rationalization and the related mechanisms.

The oxidation potentials recorded for the CECs studied in the present work by using the cyclic voltammetry (CV) technique (Table 1) are coherent with the mechanism here proposed. All of the CECs under study have oxidation onset potentials between 0.05 and 1.75 V versus Ag/AgCl. The reported values were obtained by averaging three CV scans (see Figures S10–S17 of the Supporting Information for the raw CV data).

These results are coherent with previously published values, although the experimental conditions are not fully comparable. The radicals •OH or SO4•− have more positive reduction potentials (2.5 V or above vs SHE, i.e., at least 2.2 V vs Ag/AgCl) in the pH window under investigation; thus, they are not operational during the electrochemical oxidation process at the glassy carbon electrode in CH3CN. Conversely, kinetic limitations could impede some oxidation and the substrate could activate additional mechanisms, which are not operational during the electrochemical oxidation processes at the glassy carbon electrode in CH3CN. Conversely, kinetic limitations could impede some oxidation reactions, although they are thermodynamically possible.

3. EXPERIMENTAL SECTION

3.1. Chemicals. Fe(III)-TAML was purchased from GreenOx Catalysts Inc. (Pittsburgh, PA, U.S.A.) Sodium phosphate tribasic was obtained from Carlo Erba (Italy). All of the other reagents, buffer solutions, and solvents were purchased from Sigma-Aldrich. Water was of Milli-Q quality (total organic carbon (TOC) 2 ppb, resistivity ≥18.2 MΩ cm).

3.2. Preparation of the Fe-TAML Stock Solution. A stock solution of Fe-TAML was prepared by dissolving 520 mg of Fe-TAML in 20 mL of a sodium hydroxide solution (0.05 M). The supernatant of this solution was used for further experiments. UV–vis analysis was carried out to determine the effective Fe-TAML concentration at pH 7, by measuring light absorbance at 360 nm. From the known Fe-TAML absorption coefficient (6600 M⁻¹ cm⁻¹), a stock solution with a concentration of 3.1 mM was prepared. The stability of the catalyst in solution was spectrophotometrically checked every month. The stock solution was stored refrigerated (4 °C) under the N₂ atmosphere.

3.3. Protocol of the Oxidation Experiments. Three different reagents (sodium sulfite, SO₃²⁻, potassium metabisulfite, S₂O₅²⁻, and sodium persulfate, S₄O₆²⁻) were preliminarily tested, and their reactivity was compared with that of hydrogen peroxide. The most reactive compound, namely, metabisulfite, was then chosen to carry out further degradation experiments on several contaminants. Finally, the reaction mechanism with metabisulfite was investigated. The degradation experiments were carried out at room temperature, under continuous stirring for a maximum of 60 min. Reactions were tested at different pH values (7, 9, and 11) in 10 mL of phosphate buffer (total concentration 0.01 M). Under such conditions, the demetallation of Fe-TAML via the general acid mechanism can be considered negligible. As shown in previous literature reports, the demetallation kinetics of Fe-TAML increases as the pH decreases, or as the concentration of the buffering agents increases at constant pH. For these reasons, the phosphate buffer concentration used in this study was as low as reported in previous works. It is important to note that the mechanism of demetallation has not yet been fully understood.

Unless otherwise stated, the default initial concentrations in the experiments were as follows: 0.01 mM of Fe-TAML, 0.1 mM of the target contaminant, and 0.1 mM of the reagent (H₂O₂, SO₃²⁻, S₂O₅²⁻, or S₄O₆²⁻). During some tests, step-wise additions of the reagent corresponding each to a 0.1 mM concentration in the reaction system were made every 10 min, for a total of three additions. In all of these latter cases, the overall molar ratio of the Fe-TAML/contaminant/reagent was 1:10:30. All of the reactions were quenched by decreasing the pH to a final value <3. Under acidic conditions, demetallation is promoted and the catalytic reaction is stopped as a consequence. In some experiments involving metabisulfite, control tests were performed by analysis of the solutions immediately following reaction and without acidification.

3.4. Analytical Methods. UV–vis spectrophotometric measurements were performed using a Cary 100 Scan double-beam instrument (Varian). The concentrations of contaminants in solution were monitored by HPLC coupled with diode array detection (HPLC-DAD). The adopted Lachrom Elite instrument (VWR-Hitachi) was equipped with a L-2200 Autosampler (injection volume 60 μL), a L-2130 quaternary pump for low-pressure gradients, a L-2300 column oven (set at 40 °C), and a L-2455 DAD detector. The column was a RP-C18 LiChroCART (VWR Int., length 125 mm, diameter 4 mm), packed with LiChrospher 100 RP-18 (5 μm diameter).

The different test contaminants were always eluted in isocratic mode, with a mixture of A = 5.7 mmol L⁻¹ H₃PO₄ in water and B = methanol, at a flow rate of 1 mL min⁻¹. The following conditions were used (tλ = detection wavelength, tR = retention time): ACE (5% B, λ = 220 nm and tR = 4 min); ATZ (60% B, λ = 221 nm and tR = 4.5 min); diclofenac (DCF, 65% B, λ = 275 nm and tR = 8 min); ibuprofen (IBU, 70% B, λ = 222 nm and tR = 6 min); NPX (60% B, λ = 220 nm and tR = 6 min); oxybenzone (aka benzophenone-3, BP3, 70% B, λ = 280 nm and tR = 5 min); phenol (PhOH, 30% B, λ = 271 nm).
and \( t_R = 5.5 \text{ min} \); triclosan (TCS, 70% B, \( \lambda = 280 \text{ nm} \) and \( t_R = 9.6 \text{ min} \)).

Note that the study of the degradation of the investigated substrates cannot be considered in terms of the evolution of the TOC in solution, because (i) the Fe-TAML catalyst is in the homogeneous form and (ii) the organic TAML ligand increases the overall TOC value, thereby interfering with the assessment of contaminant mineralization. Still, the studied systems are unlikely to achieve substrate mineralization, as suggested by the occurrence of several unknown HPLC peaks, presumably accounted for by transformation intermediates (more hydrophilic than the original substrates on the basis of their chromatographic retention times), even at long reaction times.

3.5. Electrochemical Measurements. The redox properties and stability of the investigated substrates were electrochemically investigated. The electrochemical experiments were carried out through a standard photoelectrochemical setup and a computer-controlled potentiostat (PGSTAT12, Autolab). The electrochemical cell was a conventional three-electrode cell. The counter and reference electrodes were a glassy carbon rod (diameter 2 mm, length 75 mm) and a Ag/AgCl/KCl (3 M) electrode, respectively. The working electrode was a 5 mm diameter glassy carbon disk. The electrolytic solution was 0.1 M NaClO4 in CH3CN, purged with nitrogen gas. CVs were recorded between −0.4 and 2.0 V, at a scan rate of 100 mV s\(^{-1}\). To better detect the onset of the anodic current, CVs were recorded on 10 mM solutions of each studied compound, with the exceptions of ATZ and ACE. In the latter cases, CVs were recorded on saturated CH3CN solutions. The CVs here reported are the average of at least three successive scans, unless otherwise stated.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03088.

Degradation percentages in all of the investigated conditions, together with the most significant experimental parameters; kinetic trends obtained from replicate experiments of the degradation of phenol, using metabisulfitre as a reagent; details about the degradation efficiency of the Fe-TAML/hydrogen peroxide system as a function of \( p_H^2 \); kinetic trends in the degradation of the different CECs; values of the degradation percentage of CEC from replicate experiments; and CV data from measurements performed with different CECs (PDF)

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■ ABBREVIATIONS

TAML, tetra-amido macrocyclic ligand; CEC, contaminants of emerging concern; ACE, acesulfame K; NPX, naproxen; IBU, ibuprofen; DCF, diclofenac; ATZ, atrazine; PhOH, phenol; TCS, triclosan; BP3, oxybenzone (benzophenone-3)

■ REFERENCES


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Notes
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