METABISULFITE AS UNCONVENTIONAL REAGENT FOR OXIDATIONS CATALYZED BY Fe-TAML®

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Micropollutants, such as pesticides, pharmaceuticals, and personal care products are persistent and biologically active substances. They are ubiquitous in aquatic environments and can jeopardize the life of plants, animals, and humans (Carvalho et al., 2015). Advanced oxidation processes (AOPs) are among the most efficient treatment methods to degrade micropollutants in water. For example, the Fenton process has been widely applied for the degradation of a large range of recalcitrant and/or non-biodegradable pollutants in industrial wastewaters (Pignatello et al., 2006). The main reactions involved in Fenton oxidation cause the formation of reactive species such as - mainly - hydroxyl radicals and/or superoxidized iron species (Haber and Weiss, 1932; Pignatello et al., 2006; Vione et al., 2013). The Fenton process works best in the pH range 2.5 - 4, with the highest rates usually observed around pH 3. The low pH implies important technical and economical drawbacks that hinder the application of the classic Fenton process in real-world (Minella et al., 2018).

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 (Collins, 2002). Fe-TAML® - a biodegradable, homogeneous tetra-amido macrocyclic ligand catalyst containing iron(III) - has a large spectrum of applications in the removal 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 (Ghosh et al., 2008). In this sense, oxidation by Fe-TAML® or other similar catalysts is advantageous compared to a typical Fenton process.

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®.
Metabisulfite showed the highest efficiency among the three tested reagents, and its reactivity was similar to that of H_2O_2. However, metabisulfite is a cheaper, safer, and cleaner reagent compared to H_2O_2. A comprehensive study of the activity of metabisulfite with Fe-TAML® was carried out towards the oxidative degradation of eight contaminants of emerging concern (Figure 1). 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 highest 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.

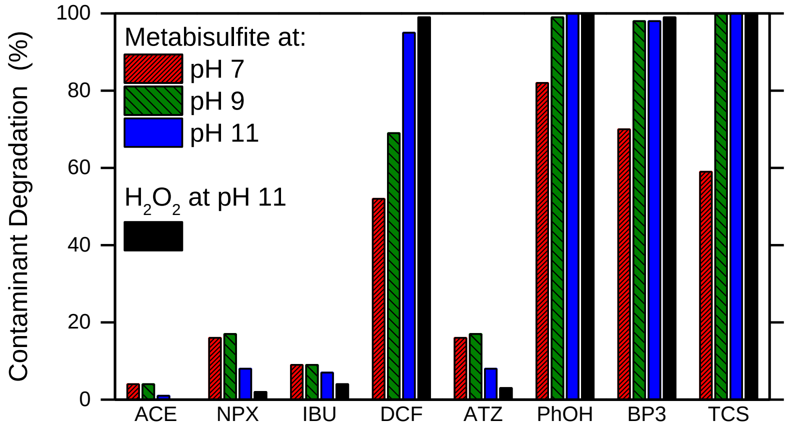

Figure 1. Degradation % of contaminants of emerging concern. Metabisulfite or H_2O_2 were used as reagents at different pH values. The reactions were carried out for 60 min in phosphate buffer (10 mM) by adding 0.1 mM of reagent every 10 minutes. Initial conditions were [Fe-TAML®] = 0.01 mM; [Contaminant] = 0.1 mM. ACE: Acesulfame K; ATZ = atrazine; DCF = diclofenac; IBU = ibuprofen; NPX = naproxen; BP3 = oxybenzone; PhOH = phenol; TCS = triclosan.

Fe-TAML® is a well-known green catalyst for the oxidative degradation of various organic contaminants, however, the discovery of cleaner and safer reagents different from those previously proposed – mainly H_2O_2 – is a breakthrough in the field of AOPs, because it opens the route towards greener cleaning systems.

References

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