



Assessment of bimetallic and trimetallic iron-based systems for persulfate activation: Application to sulfamethoxazole degradation



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HIGHLIGHTS

- Sulfamethoxazole is fully degraded in Fe⁰/PS systems at room temperature.
- PS activation by iron particles minimizes the formation of by-products.
- Plated systems AgFe, CoFe, AgCoFe and CoAgFe maintain PS in solution longer time.
- Bimetallic and trimetallic systems improve the RSE in disturbed systems.
- AOPs based on Fe⁰ and plated Fe⁰ PS activation decreased the formation of sludge.

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ABSTRACT

This work investigated the potential of different iron-based systems to activate persulfate (PS) into sulfate radicals (SRs) through catalytic electron transfer. SRs were then used to degrade sulfamethoxazole (SMX) in water. PS activators like Fe²⁺, Fe⁰, AgFe and CoFe (bimetallics), AgCoFe and CoAgFe (trimetallics) were tested on SMX solution (39.5 μM) spiked with PS (1.0 mM). Results on SMX degradation showed better kinetics and efficiency in case of non-plated iron particles used compared to bimetallic and trimetallic systems as well as Fe²⁺ at early stage of the reaction. Direct and sequential addition of Fe²⁺ resulted in better reaction stoichiometric efficiency (RSE) however did not yield full SMX degradation in contrast to metallic particles. Bimetallic and trimetallic systems showed higher RSE than Fe⁰ initially due to less PS consumption while maintaining acceptable SMX degradation rate. Smooth corrosion was responsible of progressive release of iron corrosion products for SRs production. However, in case of improved corrosion, generated SRs were quenched by an excess of iron-based activators which negatively affected the RSE. SMX mineralization was greatly improved in oxic solution rather than in anoxic medium. This work demonstrated the potential of iron-based systems to sustain PS longer in oxic solutions without the production of heavy sludge or formation of transformation products that can burden the treatment process.

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1. Introduction

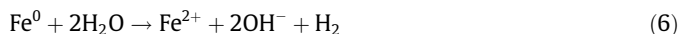
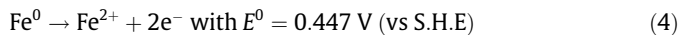
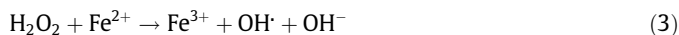
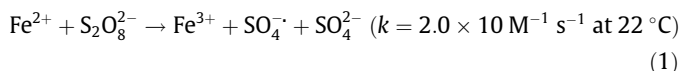
Pharmaceutical and personal care products (PPCP) are a class of compounds that include pharmaceutical drugs, cosmetic ingredients, food supplements, and ingredients in other consumer products such as shampoos and lotions [1,2]. Several studies have evidenced the widespread of emerging pharmaceuticals; in particular, sulfamethoxazole (SMX) [3]. SMX is an antimicrobial agent typically used to remediate and prohibit diseases in animals; also, promote growth and weight gain in livestock [4]. SMX abatement by conventional water treatment methods such as adsorption,

coagulation, and biodegradation is very difficult due to their limitations in efficiently removing active pharmaceutical molecules (APMs) [5,6]. For the last two decades, Fe⁰ has been extensively used for water decontamination however high Fe⁰ loads (up to 40 g L⁻¹) were necessary in order to induce formation of iron corrosion products (ICPs) responsible for the removal of contaminants through adsorption, sequestration, co-precipitation, reduction and oxidation [7–15]. Such high loads generated lot of sludge that needs to be correctly disposed. Accordingly, an alternative has been recently proposed [16] reducing considerably iron loads while feeding the medium with persulfate (PS). The latter generates SRs (Eq. (1)) and hydroxyl radicals (HRs) (Eq. (2)) in a similar fashion as Fenton's reaction (Eq. (3)) [17–20]. Fe⁰ has been shown to improve the activation of PS through the release of ICPs

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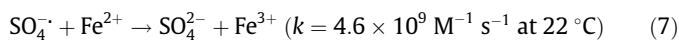
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(e.g. Fe^{2+} and nascent iron oxides) during the corrosion process (Eqs. 4–6) [16,21].



Although advanced oxidation processes (AOPs) using O_3 [22], H_2O_2 [23,24], and KMnO_4 [25] have shown good performances in wastewater remediation, they exhibited however high operational cost in addition to other well-known drawbacks [26–28]. In contrast, PS has been recently considered in order to improve underground water quality especially when it comes to reach non-accessible zones of an aquifer. In real situations, injection of PS into aquifers can progressively release SRs to oxidize micro-contaminants present in water [17,20,29,30].

PS anion ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant, highly soluble in water and relatively stable at room temperature [28]. It can be easily activated to produce SRs (Eq. 1) of greater standard potential ($E^0 = 2.6 \text{ V}$) than PS ($E^0 = 2.1 \text{ V}$) and H_2O_2 ($E^0 = 1.76 \text{ V}$) as well at neutral pH [31,32]. Activation can occur via photolysis [33], microwaves [34], heat [35], electron beam [36], ultrasonication [37], and reaction with a metal ion. The latter can be directly supplied to the medium in the form of a salt or indirectly as zero-valent metal (ZVM e.g. Fe^0) able to corrode in aqueous solution. However, ions' release should not be in excess so as to avoid SRs quenching (Eq. (7)). In addition, direct reaction between Fe^0 and PS is likely to happen (Eq. 8). This yields (1) rapid consumption of PS and (2) improved Fe^0 corrosion releasing quickly and abundantly Fe^{2+} in the medium responsible for more SRs quenching [16].



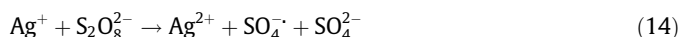
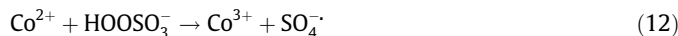
Furthermore, the resulting pH is more influenced by PS activation rather than iron corrosion. In fact, PS activation yields bisulfate of (HSO_4^-) acidic properties ($\text{pK}_a = 1.92$) (Eqs. (9) and (10)) while Fe^0 corrosion produces hydroxyl species (Eqs. (5) and (6)) of basic properties.



The acidic medium favors the dissolution of iron oxides and the liberation of Fe^{3+} . The latter can adsorb at the surface of iron particles to produce Fe^{2+} PS activator (Eq. (11)) in a catalytic way. However, sustaining iron corrosion could be enhanced through the deposition of an additional metal on the surface of iron particles creating thereby bimetallic and trimetallic systems [12,38–42]. These systems might possess additional properties that enhance the activation of PS into SRs in a sustainable way [43]. They can also be used instead of direct Fe^{2+} spiking providing therefore longer PS lifetime in solution [18].



In this work, Ag and Co ions were chosen for plating on iron particles based on the work done by Dionysiou's group [44] (Eqs. (12)–(14)). An attempt of using these metallic systems for PS activation is carried out. The efficiency of the chosen AOP will be tested on SMX molecule as typical recalcitrant pharmaceutical probe.



To our knowledge, this is the first time that such bimetallic (AgFe and CoFe) and trimetallic (AgCoFe and CoAgFe) systems are used to activate PS. We investigated throughout this work (i) the impact of dissolved oxygen, metal molecularity, plating order and metal load on SMX removal and PS activation, (ii) the % RSE and (iii) the presence or absence of transformation products formed during the oxidation process.

2. Materials and methods

2.1. Chemicals

SMX was obtained from Sigma Aldrich (USA), sodium persulfate (PS) ($\text{Na}_2\text{S}_2\text{O}_8$, 99%) from Chem-Lab (Belgium). Potassium iodide (KI) (puriss, 99–100.5%) and iron particles (puriss 99.5%, fine powder, and $<150 \mu\text{m}$) were purchased from Riedel-de-Haen (Germany). Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), silver nitrate (AgNO_3) and iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were acquired from Sigma Aldrich (USA). Ammonium acetate ($\text{C}_2\text{H}_7\text{NO}_2$, >98%, puriss ACS reagent), sodium hydrogen carbonate (NaHCO_3) and hydrochloric acid (HCl) were from Fluka (Netherlands). HPLC solvent (methanol) is of HPLC grade and purchased from Sigma. Millipore deionized water (DI) was used throughout this work.

2.2. Chemical analysis

The quantification of SMX was performed on an Agilent 1100 Series LC/MS system as previously described [12,45–47]. The mobile phase consisted of 50:50 (v/v) 10 mM ammonium acetate and methanol under isocratic mode. The flow rate and injection volume were 0.5 mL min^{-1} and $25 \mu\text{L}$ respectively. SMX was eluted at 6.5 min and showed maximum absorbance around 262 nm. Persulfate anions were determined at $\lambda_{\text{max}} = 352 \text{ nm}$ using a Nanodrop 2000cUV-VIS Spectrophotometer (Thermo Scientific) in accordance with the procedure developed by Liang and collaborators [48]. Total iron was quantified on a calibration curve ($2\text{--}50 \text{ mg L}^{-1}$) using an Atomic Absorption Spectrometer (Thermo labsystems Solaar). Metallic systems were characterized by a Scanning Electron Microscope (SEM) (Tescan, Czech Republic). Surface morphology and elemental composition were studied by the mean of a Tescan Mira 3 LMU. For Co characterization in all plated metallic systems (CoFe, CoAgFe and AgCoFe), a low beam voltage of 10 KV was chosen so as to analyze the outer layer of plated iron particles without getting deeper into iron core particles; otherwise, Co emission will be hindered by Fe emission peaks (K_α and L_α). However, for metallic systems exempted from Co (e.g. Fe and AgFe), characterization was successful at low and high voltages as well (10–20 KV). Mineralization of SMX was measured by a total organic carbon (TOC) analyzer (GE 5310C) equipped with an auto-sampler and a CO_2 conductivity detector. Samples were centrifuged at 4000 g and filtered prior to analysis. A minimum volume of 17 mL was required for each analysis.

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