



Ranitidine abatement in chemically activated persulfate systems: Assessment of industrial iron waste for sustainable applications

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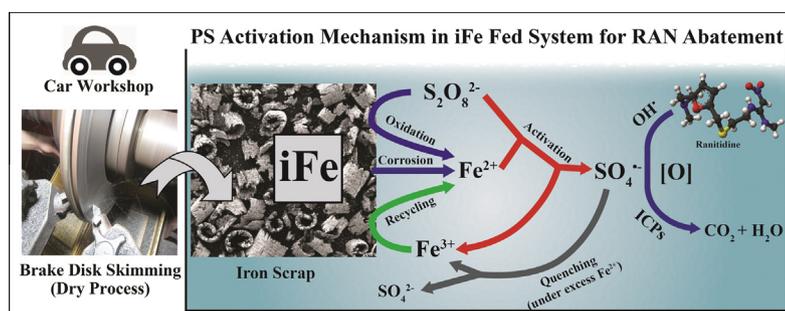
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HIGHLIGHTS

- cFe was substituted by iFe for sustainable PS-activation processes.
- Ranitidine was successfully degraded in iFe/PS systems even at high [I].
- No negative effect was exerted on RAN degradation by Cl^- or Br^- (up to 1 mM).
- The reaction stoichiometric efficiency was greater than 72% in most systems.
- TOC removal reached up to 91% when PS and iFe amounts were excessively increased.

GRAPHICAL ABSTRACT



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ABSTRACT

This work assessed the use of industrial iron waste in the activation of persulfate (PS) (100 μM) into sulfate radicals (SRs) for the removal of ranitidine (RAN) (28.5 μM) from aqueous systems. The released iron corrosion products (ICPs) e.g. mainly Fe^{2+} species are responsible of PS activation. The optimal molar ratio of Fe^{2+} :PS was found to be 1:1. A comparative study between industrial iron (iFe) and commercial iron (cFe) at 2 successive experimental runs showed that iFe has some advantages over cFe in terms of sustainability and less sludge formation. At low load of iFe (1 mg/20 mL), RAN removal was 95% over one hour of reaction time with a ratio of released Fe^{2+} :PS of only 0.16:1.00. This system was evaluated at different ionic strength [I] conditions with NaClO_4 neutral electrolyte, as well as in the presence of Cl^- and Br^- , the main seawater components. Results showed that at elevated [I] conditions, the rate of RAN degradation has decreased. However, in the presence of Cl^- and Br^- , with optimum levels of 1.0 mM at [I] = 100 mM, RAN removal was enhanced rather than quenched. The total organic carbon (TOC) was analyzed at different PS:iFe molar ratios. Although degradation was successful at a very low iFe load, mineralization was negligible. However, RAN co-precipitation with in-situ formed ICPS improved TOC removal at higher iFe levels. The HPLC/MS chromatograms showed the presence of an oxidized RAN intermediate detected at 331 m/z that dissipated gradually throughout the treatment.

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1. Introduction

Ranitidine (RAN) is an H_2 receptor antagonist widely used in treatment of peptic ulcer and gastroesophageal reflux diseases.

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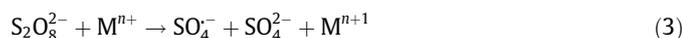
Given the essential need of this drug for basic human health [1], it is among the most prescribed pharmaceuticals in the world [2,3]. It reaches water systems mainly through excretion e.g. 30–70% remained intact [4,5]. Eventually, RAN has been encountered in the aquatic environment at a maximal detected concentration of 1 $\mu\text{g/L}$ [6]. It was pervasively identified in water [7,8], and was proved to be a precursor of N-Nitrosodimethylamine (NDMA),

a potent carcinogen, upon chloramination (>77% molar conversion) [9]. As a result, it was included in priority compounds list [10]. Under direct exposure to sunlight, RAN can be transformed into photo-products that are more stable and of higher risk potential [11]. In conventional wastewater treatment plants (WWTPs), RAN showed low biodegradability [12]; therefore, alternative methods are needed to increase its removal efficiency. In this study, RAN degradation has been tested through advanced oxidation processes (AOPs) by iron-based chemically activated persulfate.

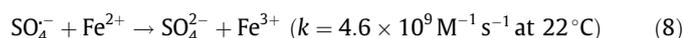
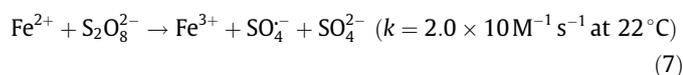
Persulfate (PS) is the newest oxidant that is being utilized for in situ chemical oxidation (ISCO) in groundwater and soil remediation [13]. It has received a significant attention as a strong oxidant ($E^0 = 2.1$ V) (Eq. (1)), capable of substituting hydrogen peroxide (H_2O_2) ($E^0 = 1.8$ V) [14]



The reactivity of PS is enhanced by various activators including heat [15–19], UV light (Eq. (2)) [20], hydrogen peroxide [21] and transition metals (Eq. (3)) [22,23]. As a result, strongly reactive sulfate radicals (SRs) ($E^0 = 2.5$ – 3.1 V) are generated capable of decomposing and mineralizing organic contaminants



PS activation by transition metals is more applicable than by heat and UV light for in-situ technology. Many metals as Co(II) and Ag(I) conjugated with PS showed effective contaminant decomposition along with successful SR-generation [24], but their toxicity and high cost have significantly limited their application. On the contrary, Fe^0 is a non-toxic and a cheap alternative activator that provides progressive release of Fe^{2+} through Fe^0 dissociation (Eqs. (4) and (5)), or via direct reaction with PS (Eq. (6)) [25]. Although Fe^0 application without oxidant feeding was successful in removing different contaminants [26–30], this however requires a very high Fe^0 load (e.g. 40 g/L) that causes more sludge formation without achieving full removal extent [31]. The mechanism of Fe^0 toward organic contaminants is assumed to follow oxidation/reduction [32,33], and/or adsorption/co-precipitation routes [34–37]. In Fe^0/PS systems, reactive radicals are generated using fewer amounts of iron capable of inducing complete contaminant removal [38]. Very recent studies performed free-radical analysis by electron paramagnetic resonance (EPR) spectroscopy and proved the formation of both SRs and hydroxyl radicals (HRs) in iron-based persulfate activated systems [39,40] as in homogeneous PS activated systems e.g. heat or UV activation. However, the process of SR-generation from PS activation by Fe^{2+} (Eq. (7)) can be deactivated by a quenching reaction with excess Fe^{2+} (Eq. (8)) [38]. Therefore, the Fe:PS ratio is a key factor that should be optimized to overcome the loss of SRs in the quenching pathway



Over the last decade, Fe^0 -activated PS has received an increasing attention for the degradation of several types of contaminants (e.g. pharmaceuticals). For instant, Ghauch et al. has studied the Fe^0 -PS activation on sulfamethoxazole (SMX) degradation. His work has demonstrated complete SMX degradation and up to 37% mineralization over one hour [38]. In another study, Ayoub and Ghauch have modified iron by plating catalytic metals (e.g. Ag, Co) on the Fe^0 surface e.g. case of bimetallic and trimetallic systems [41]. In the present study, micrometric industrial iron waste was used as a heterogeneous metallic system for PS activation. The occurrence of elements other than Fe makes this system similar to iron plated systems. Metals different from Fe could play catalytic role in sustaining iron corrosion through the formation of micro galvanic cells therefore accelerating the substrate removal [42]; however, Fe remains the only contributor to PS activation.

Throughout this investigation, (i) the Fe^{2+} :PS ratio was optimized, (ii) the industrial iron (iFe) was compared to commercial iron (cFe) with respect to RAN degradation extent and sustainability, reaction stoichiometric efficiency ((RSE): ratio of the concentration of RAN degraded to the concentration of PS consumed over a time interval), and final dissolved iron species, (iii) the impact of environmental conditions, such as ionic strength [I] and ionic content (Cl^- , Br^-), was assessed and the kinetics of RAN degradation was followed, (iv) the total organic carbon (TOC) was measured under different PS:iFe molar ratios, (v) the transformation products were identified and plausible degradation mechanisms were elucidated.

2. Materials and methods

2.1. Chemicals

Ranitidine hydrochloride ($C_{13}H_{22}N_4O_3S \cdot HCl$), sodium persulfate (PS) ($Na_2S_2O_8$, $\geq 99.0\%$), and potassium iodide (KI) (puriss, 99.0–100.5%) were purchased from Sigma–Aldrich (India, France, and Germany, respectively). Commercial iron (puriss 99.5%, fine powder < 150 μm) and iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (puriss, 99.5–104.5%) were obtained from Riedel–Haen (Germany), while iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) (purum $\geq 98\%$) was acquired from Fluka (Switzerland). Industrial iron powders were collected from RYMCO car workshop (Lebanon), grinded and sieved to the size of 53–150 μm . Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$) (ACS reagent, 98%) was purchased from Sigma–Aldrich (France) and used as a background electrolyte. To assess the ionic additives effect, sodium bromide (NaBr) and sodium chloride (NaCl) were acquired from HIMEDIA and Fluka, respectively. Ammonium acetate ($C_2H_7NO_2$, $\geq 98.0\%$, puriss ACS reagent), sodium hydrogen carbonate ($NaHCO_3$) and hydrochloric acid (HCl) were purchased from Fluka (Netherlands). Methanol of HPLC grade was from Sigma–Aldrich (Germany). Millipore deionized water (DI) was used in the preparation of all solutions.

2.2. Chemical analysis

RAN analysis was carried out on an Agilent 1100 Series Liquid Chromatography (LC) equipped with a diode array (DAD) and an MS detector (MSD) as previously described [16,18,43]. The LC mobile phase consisted of methanol: (10 mM) ammonium acetate (aq) of (40:60) (v/v) and was kept under isocratic mode at a flow rate of 0.8 mL/min. The injection volume was 50 μL taken from 0.5 mL aliquots pre-filtered on a 0.45 μm PTFE 13 mm disc filters (Jaytee Biosciences Ltd., UK) and placed in a 2 mL Agilent vial. Under these conditions, RAN was eluted at a retention time of 5.3 min. It revealed two λ_{max} at 230 nm and 320 nm; the latter

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