Chemically and thermally activated persulfate for theophylline degradation and application to pharmaceutical factory effluent†

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Degradation of PPCPs by AOPs has gained major interest in the past decade. In this work, theophylline (TP) oxidation was studied in thermally (TAP) and chemically (CAP) activated persulfate systems, separately and in combination (TCAP). For [TP]₀ = 10 mg L⁻¹, (i) TAP resulted in 60% TP degradation at [PS]₀ = 5 mM and T = 60 °C after 60 min of reaction and (ii) CAP showed slight degradation at room temperature; however, (iii) TCAP resulted in complete TP degradation for [PS]₀ = [Fe²⁺]₀ = 2 mM at T = 60 °C following a pseudo-first order reaction rate with calculated k_{obs} = 5.6 (±0.4) × 10⁻² min⁻¹. In the TCAP system, the [PS]₀ : [Fe²⁺]₀ ratio of 1 : 1 presented the best results. A positive correlation was obtained between the TP degradation rate and increasing temperature and [PS]₀, and a negative correlation was obtained with increasing pH.

Both chloride and humic acid inhibited the degradation process, while nitrates enhanced it. TP dissolved in spring, sea and waste water simulating real effluents showed lower degradation rates than in DI water. Waste water caused the highest inhibition (k_{obs} = 2.6 (±0.6) × 10⁻⁴ min⁻¹). Finally, the TCAP system was tested on a real factory effluent highly charged with TP, e.g. [TP]₀ = 160 mg L⁻¹, with successful degradation under the conditions of 60 °C and [PS]₀ = [Fe²⁺]₀ = 50 mM.

1. Introduction

Theophylline (TP), or 1,3-dimethyl-7H-purine-2,6-dione, is a crystalline compound that is used in the treatment of respiratory diseases such as asthma and wheezing; it is also found in trace amounts in normal diet foods, such as tea and cocoa beans.1,2 TP belongs to the pharmaceuticals and personal care products (PPCPs) family, whose members have gained global attention in the past few decades as emerging contaminants. This increased attention is attributed to the discovery of PPCPs in ground and surface water, aided by advancements in analytical techniques which enable their detection at previously undetectable concentrations.3 The presence of PPCPs in water, even at low concentrations, poses environmental hazards and possible public health risks. Among these risks are bioaccumulation, such as the accumulation of lipophilic PPCPs in aquatic organisms4,5 and the development of antibiotic resistance,6 in addition to uncertain synergistic/antagonist effects of long term exposure to mixtures of pharmaceuticals at low concentrations.7 TP is introduced into nature by several pathways, such as from untreated pharmaceutical production plant wastewater effluents, in addition to domestic wastewater, which can contain TP from direct disposal of the drug and from urine excretion; this contributes to the pollution of water bodies by TP.8,9

To solve the problem of water contamination by several pollutants, water treatment plants are integrated to treat wastewater discharges from domestic, agricultural and industrial sources. Conventional water treatment methods include, but are not limited to, carbon adsorption, chemical precipitation, evaporation and ion exchange.10 It has been shown that conventional methods do not treat PPCPs efficiently; PPCPs are resistant to such treatment and have been detected in drinking water.11–13 One of the pharmaceuticals detected in water is TP. It was found in spring water in Lebanon, possibly due to the discharge of untreated waste water.14 TP degradation has been studied during the past decades by several methods, including degradation by means of ferrate(VI)15 and a metal organic framework (Pd@MIL-100(Fe)) with visible light (λ ≥ 420 nm),16 UV/H₂O₂,17,18 and UV/TiO₂ nanobelts.19 Novel water treatment methods include advanced oxidation processes (AOPs), which have been proved to be significantly efficient in removing persistent organic compounds. A wide variety of techniques involving different oxidants and different methods of activation are used in AOPs; examples include Fenton,20 photo-Fenton,21 UV/PS,22,23 Fe/PS,24,25 and heat/PS26–29 systems, in addition to alkaline/PS and alkaline/peroxymonosulfate30 systems. PS and H₂O₂ are the two most commonly used effective oxidants in AOPs; however, PS poses some advantages over H₂O₂ in terms of cost, safety in handling, and ease of access in some regions. PS
is effective in degrading several pharmaceuticals; however, to our knowledge, it has not been tested by other research groups to treat TP. The main PS activation methods are UV, chemical, and heat activation, which generate highly reactive sulfate radicals (SRS) (eqn (1)-(3)). Our research group has recently studied TP degradation by UV-activated PS.

In this study, TP degradation by thermally activated PS (TAP) and chemically activated PS (CAP) was studied separately as well as in a combined thermally and chemically activated PS (TCAP) system. The combination of activation techniques was applied, for the first time, to simulated effluents and to a real highly concentrated pharmaceutical effluent collected from a local pharmaceutical factory. The degradation process was optimized by testing several parameters in order to obtain efficient degradation within a reasonable time at an affordable cost. Finally, charge distribution and frontier orbital calculations were investigated in order to better elucidate the TP degradation mechanism by oxidative radical species in solution.

\[
\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} \text{ (thermal activation) } 30 ^\circ C < T < 99 ^\circ C \quad (1)
\]

\[
\text{S}_2\text{O}_8^{2-} + \text{Fe}^{3+} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{Fe}^{3+} \text{ (chemical activation) } (2)
\]

\[
\text{S}_2\text{O}_8^{2-} + h\nu \rightarrow 2\text{SO}_4^{2-} \text{ (UV activation) } (3)
\]

2. Materials and methods

2.1. Chemicals

Theophylline (C$_7$H$_8$N$_4$O$_2$) (C$_7$H$_8$N$_4$O$_2$ ≥99%) and sodium persulfate (PS) (Na$_2$S$_2$O$_8$ ≥99.0%), were obtained from Sigma-Aldrich (China and France, respectively). Methanol (MeOH, CH$_3$OH) and tert-butyl alcohol (TBA) of HPLC grade were purchased from Sigma-Aldrich (Germany). MeOH was used as the mobile phase for chromatographic analysis in combination with deionized water (DI). Ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O), used as a chemical activator for PS, was obtained from Fluka (Switzerland). HCl (37%) was obtained from Fluka (Netherlands) and used to dissolve FeCl$_2$ in the preparation of stock solutions. To evaluate the effects of ionic additives, sodium chloride (NaCl) was purchased from Fluka (Netherlands), and sodium nitrate (NaNO$_3$) was obtained from Sigma-Aldrich (Germany). DI water was used for the preparation of all solutions in this study.

2.2. Chemical analysis: TP quantification and identification

High performance liquid chromatography (HPLC, Agilent 1100 series) was used for TP quantification. The HPLC was equipped with a thermo-electrically cooled autosampler unit, a quaternary pump, a vacuum degasser, and a thermally controlled column. Separation of TP from other by-products was enabled by the use of a C-18 reverse phase column (Discovery® HS, 5 µm; 4.6 mm internal diameter × 250 mm length) connected to a guard column (HS C-18, 5 µm; 4.0 mm internal diameter, 20 mm length) (Pennsylvania, USA). The temperature of the column was set at 30 °C, while that of the autosampler compartment was set at 4 °C. A column flow rate of 0.5 mL min$^{-1}$ was used with a mobile phase consisting of water and MeOH (70 : 30 ratio) maintained in isocratic mode. The injection volume was set at 80 µL. A diode-array detector for the quantification of TP was coupled to the HPLC. For the aforementioned conditions, the TP retention time was observed to be 12 min. All samples were filtered using 0.45 µm PTFE 13 mm disc filters (Jaytee Biosciences Ltd., UK) before HPLC analysis. Selected TP chemical properties in addition to the calibration curve and the corresponding LINEST output are summarized in ESI Fig. 1S (a-c). Identification of the degradation and transformation products of TP was performed on an Ultimate 3000 RSLC Thermo Scientific HPLC-MS/MS connected to a Q Exactive Orbitrap. A Hypersil GOLD C18 150 column (100 × 2.1 mm, 1.9 µm) was used for separation. The injection volume was set as 2 µL and the elution process was performed at a flow rate of 0.3 mL min$^{-1}$ using DI water (containing 0.1% formic acid) as eluent A and methanol as eluent B. The mass spectrometer was operated in positive ionization mode. The auxiliary gas heater temperature was set as 350 °C and the capillary temperature was 320 °C.

2.3. Experimental setup

The experimental setup consisted of 200 mL Erlenmeyer flasks used as reactors and immersed in a controlled-temperature water bath. The latter was equipped with an orbital shaker (Wise Bath WSB-30) and amended with a homemade Plexiglas cover plate with the capacity to hold all the Erlenmeyer flasks by their necks in order to prevent the reactors from falling (Fig. 2S†). The experimental setup could accommodate up to 12 reactors at a time, and all experiments were performed in triplicate. The reactors were efficiently submerged in the water bath to ensure that their temperatures matched that of the surrounding water. This was further guaranteed by the measurement of the inner temperature of the reactor using a thermometer. The temperatures tested were room temperature in addition to 40 °C to 75 °C. To ensure proper homogenization and heat distribution, the orbital shaker was set at 70 revolutions per minute throughout the experiments.

2.4. Experimental procedure

The stock solutions were prepared as follows: TP (100 mg L$^{-1}$) was prepared by dissolving 100 mg of dry TP powder in 1 L of DI water; PS (100 mM) was prepared by dissolving 2.38 g of sodium persulfate in 100 mL of DI; FeCl$_2$ (80 mM) was prepared by dissolving 3.1808 g of FeCl$_2$·4H$_2$O in concentrated HCl (37%) in a 250 mL volumetric flask, followed by the addition of DI. The stock solutions were prepared weekly and stored in the dark at 4 °C. The water bath was turned on before the experiments to attain the required temperature. The reactors outside the water bath were each filled with predetermined amounts of prepared concentrated stock solutions of TP and matrix solution when required, in addition to DI water. Each obtained solution was mixed and preheated in the water bath to reach the desired temperature. Finally, the experiment was initiated by adding FeCl$_2$ (20 mM) and PS (100 mM) stock solutions, reaching a final
reactor volume of 200 mL. Samples were withdrawn using a clean 1 mL syringe from every reactor, then filtered using a 0.45 μm PTFE 13 mm disc filter and stored in 2 mL HPLC vials. To quench any further oxidation reactions after sample withdrawal, vials were placed in an ice bath to prevent further thermal activation of PS.26 In fact, a slight decline in the stability of TP in aqueous solutions. In real water sample experiments was pre-filtered using a 1 μm ashless glass fiber filter.

2.5. Calculation of charge distributions and frontier orbitals

The theoretical calculations were performed using the Gaussian 09 program with density functional theory. The Becke 3-parameter Lee–Yang–Parr (B3LYP) functional was used with the 6-311++(2d,2p) basis set. First, the molecular parameters of theophylline molecule were optimized using the mentioned level of theory. Second, at the same level of theory, the frontier electron densities and Mulliken charge distributions were obtained utilizing the optimized parameters.

3. Results and discussion

3.1. Thermal activation of PS (TAP system)

3.1.1. Thermal stability of TP and effects of [PS]0

To test the stability and behaviour of TP molecules under thermal stress, control experiments were conducted in a PS-free medium with [TP]0 = 10 mg L⁻¹ at different temperatures (40–75 °C) for a total reaction time of 60 min.

As can be noted in Fig. 3S, heat did not significantly affect the stability of TP in aqueous solutions. In fact, a slight decline in the concentration of TP was observed, with a maximum of about 5% for T = 40–75 °C, demonstrating the thermal stability of TP.

Table 1: % TP degradation in the TAP system at T = 55–75 °C and different [PS]0, and in the CAP system at room temperature. Experimental conditions: [PS]0 = 0.25–5 mM, [PS]0 : [Fe²⁺]0 ratios = 1 : 10, 1 : 5 and 1 : 1, and [TP]0 = 10 mg L⁻¹ for all studied cases

| Activation method | [TP]0 (mg L⁻¹) | T (°C) | [PS]0 (mM) | [Fe²⁺]0 (mM) | % degradation at t = 60 min | pH/i-pHf |
|-------------------|---------------|--------|------------|--------------|---------------------------|----------|
| TA                | 10            | 55     | 2          | —            | 14                        | 3.83/3.69 |
|                   |               | 60     | 0.25       | —            | 3                         | 4.30/4.56 |
|                   |               |        | 1          | 12           |                           | 3.87/3.75 |
|                   |               |        | 2          | 28           |                           | 3.83/3.58 |
|                   |               |        | 5          | 60           |                           | 3.41/3.05 |
|                   |               | 65     | 2          | 45           |                           | 3.57/3.46 |
|                   |               | 70     | 65         | 100          |                           | 3.57/3.22 |
|                   |               | 75     | 70         | 100          |                           | 3.50/3.22 |
| CA                | 10            | 20     | 0.25       | 0.025        | 0.5                       | 3.48/3.83 |
|                   |               |        | 0.125      | —            | 2.97/2.84                 |          |
|                   |               |        | 0.25       | 5            | 2.81/2.54                 |          |
|                   |               |        | 0.1        | 4            | 2.96/3.18                 |          |
|                   |               |        | 0.05       | —            | 2.43/2.30                 |          |
|                   |               |        | 1          | 2            | 2.23/2.12                 |          |
|                   |               |        | 5          | 4            | 2.59/2.76                 |          |
|                   |               |        | 0.25       | 1            | 1.84/1.79                 |          |
|                   |               |        | 5          | 2            | 1.65/1.54                 |          |

*Check Fig. 4S, Fig. 1a. b Check Fig. 5S*
system; however, they used half the [PS]₀ used in this work, e.g. 1 mM. The uncertainties reported for ln(A) and Eₐ were determined using the LINEST function of Microsoft Excel.

\[
\ln \left( \frac{[TP]}{[TP]₀} \right) = -k_{obs}t \tag{4}
\]

\[
\ln(k_{obs}) = \ln(A) - \frac{Eₐ}{RT} \tag{5}
\]

3.2. Chemical activation of PS (CAP system)

To test the effectiveness of CAP for TP degradation at room temperature, a solution of [TP]₀ = 10 mg L⁻¹ was subjected to [PS]₀ = 0.25, 1 and 5 mM activated by Fe²⁺ with [PS]₀ : [Fe²⁺]₀ ratios of 10 : 1, 2 : 1 and 1 : 1 at favorable acidic pH to ensure Fe²⁺ solubility. Under all conditions tested, only negligible degradation of TP was observed (Fig. 5S†), with a maximum of 5% TP degradation noted at 60 min for the case of [PS]₀ = 0.25 mM and a [PS]₀ : [Fe²⁺]₀ ratio of 1 : 1, as summarized in Table 1. Thus, TP is demonstrated to be relatively resistant to the CAP system at room temperature compared to other organic contaminants. For example, Oh et al. obtained incomplete degradation of polyvinyl alcohol utilizing Fe²⁺-based CAP at room temperature and used a higher reaction temperature to secure significant degradation of the contaminant. This can be explained by the common scavenging effect of SO₄²⁻ by Fe²⁺ to form the less effective Fe³⁺ ion (eqn (6)) in addition to the recalcitrant character of the TP molecule.

\[
\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} \tag{6}
\]

3.3. Combined thermal and chemical activation of PS (TCAP system)

Because both TAP and CAP systems showed low to negligible performance in degrading TP in aqueous solutions, both activation methods were combined into a thermally and chemically activated PS (TCAP) system. This system was tested for different [PS]₀ : [Fe²⁺]₀ ratios, [PS]₀ values and temperatures in order to positively or negatively confirm any synergistic effect that can be obtained upon combination of both PS activation techniques.

3.3.1. Effects of [PS]₀ : [Fe²⁺]₀ ratio and [PS]₀. TP degradation was studied at different [PS]₀ : [Fe²⁺]₀ ratios and [PS]₀ values. [PS]₀ : [Fe²⁺]₀ ratios of 10 : 1, 2 : 1 and 1 : 1 were tested at [PS]₀ = 0.25, 1 and 5 mM, [TP]₀ = 10 mg L⁻¹ and T = 60 °C. kₕobs was calculated for the pseudo-first order kinetics model according to eqn (4), as demonstrated in previous work (Text S3, Table 3). In fact, the reaction at the early stage can be considered to be zero order in the first five minutes; however, as the reaction proceeds, degradation by-products form and the reaction follows pseudo-first order kinetics. As depicted in Fig. 2 and Table 2, the 1 : 1 [PS]₀ : [Fe²⁺]₀ ratio showed the highest degradation rate in the three tested [PS]₀ conditions, followed by the 2 : 1 and 10 : 1 ratios.
Table 2: Effects of the [PS]₀ : [Fe²⁺]₀ ratio on TP degradation in a TCAP system. Initial and final pH values are presented for every case. Experimental conditions: [PS]₀ = 0.25, 1.0 and 5 mM, [PS]₀ : [Fe²⁺]₀ ratios of 1 : 1, 2 : 1 and 10 : 1, and T = 60 °C.

| [PS]₀ : [Fe²⁺]₀ | [PS]₀ mM | [Fe²⁺]₀ mM | pH₁/pH₁ |
|-----------------|----------|------------|----------|
| 10 : 1          | 0.25     | 0.025      | 3.5/0.30 |
| 1 : 1           | 0.1      | 0.025      | 2.79/2.7 |
| 5 : 1           | 0.5      | 0.025      | 2.19/2.07|
| 2 : 1           | 0.25     | 0.125      | 2.97/2.85|
| 1 : 2           | 0.25     | 0.5        | 2.53/2.9 |
| 5 : 2           | 0.25     | 0.25       | 1.84/1.79|
| 1 : 5           | 0.25     | 0.025      | 2.81/2.54|
| 1 : 10          | 1        | 0.025      | 2.23/2.12|
| 5 : 10          | 5        | 0.025      | 1.63/1.54|

Different studies have shown the effectiveness of different [PS]₀ : [Fe²⁺]₀ ratios. The optimum ratio obtained varies depending on different parameters, such as the target analyte, the method of iron addition, and the state/morphology of the added iron. For example, a study by Oh et al. showed that 1 : 1 [PS]₀ : [Fe²⁺]₀ was the optimum ratio for the degradation of polyvinyl alcohol by CAP. Also, Naim and Ghauch (2016) showed that 1 : 1 [PS]₀ : [Fe²⁺]₀ was the most effective ratio to yield full ranitidine degradation in almost 10 min. On the other hand, Shang et al. obtained 10 : 1 [PS]₀ : [Fe²⁺]₀ as the optimum ratio for degrading diatrizoate in a CAP system.

In order to study the effects of [PS]₀ on TP degradation, different [PS]₀ concentrations were used (0.25 to 5 mM) while maintaining a constant [PS]₀ : [Fe²⁺]₀ ratio of 1 : 1 and [TP]₀ = 10 mg L⁻¹ at T = 60 °C. Fig. 3 and Table 3 show that the higher the [PS]₀, the greater the observed rate constant kₜₔ. For example, kₜₔ increased by 32 fold when [PS]₀ increased from 0.25 mM to 5.0 mM with good correlation (R² = 0.9879), as shown in the inset of Fig. 3. This observation can be explained by the production of a greater amount of SO₄²⁻ upon increasing [PS]₀ (Fig. 3).

3.3.2. Effects of temperature and determination of the activation energy. To study the effects of temperature on TP degradation in TCAP systems, the same conditions as before (Section 3.3.1) were adopted; however, in addition to the temperature reaction variation: [TP]₀ = 10 mg L⁻¹, [PS]₀ = [Fe²⁺]₀ = 2 mM and T = 55 °C to 75 °C. As can be noted in Fig. 4a, complete TP degradation occurred in only 10 min at 75 °C, while up to 50 min were required at 60 °C. However, at 55 °C, only partial TP degradation, e.g. 83%, was obtained after 1 h of reaction. The results also showed that as the temperature increased from 55 °C to 75 °C, kₜₔ increased by 44 fold from 1.9 (±0.1) × 10⁻² min⁻¹ to 8.3 (±0.1) × 10⁻¹ min⁻¹.

The TCAP system, like the investigated TAP system (Section 3.1.2), showed excellent fitting with the Arrhenius equation,

\[
\ln(kₜₔ) = -\frac{E_a}{R} \frac{1}{T} + \ln(A)
\]

(R² = 0.9795)
where the calculated ln(Δ) and the apparent activation energy $E_A$ were greater than those calculated in the absence of $Fe^{2+}$, e.g. 61 (±5) kJ mol$^{-1}$ and 178 (±14) kJ mol$^{-1}$, respectively (Fig. 4b). This should not be surprising, as one might expect a lower activation energy in the presence of $Fe^{2+}$. In fact, $Fe^{2+}$ does not play the role of a catalyst to decrease the reaction rate and the reaction temperature is the only factor that affects the yield of $SO_4^{2-}$. For example, as the reaction temperature increased from $40 \degree C$ to $50 \degree C$ (or $60 \degree C$), the % degradation of TP improved from 29% to 45% and 100%, respectively, at $pH_f = 6.0$ ($\pm 0.3$) and the apparent activation energy $E_A$ in the presence of $Fe^{2+}$ is 2.48 $\pm 2.01$ (Fig. 5 and Table 4).

| pH adjustment | $pH_e$ | $pH_{ps}$ | $pH_f$ | $k_{obs}$ (min$^{-1}$) |
|---------------|-------|-----------|-------|-----------------------|
| −             | 2.48  | 2.01      | 2.20  | 4.9 ($\pm 0.4$) × 10$^{-2}$ |
| +             | 3.04  | 2.19      | 2.39  | 1.7 ($\pm 0.1$) × 10$^{-2}$ |
| +             | 4.79  | 2.23      | 2.93  | 1.09 ($\pm 0.6$) × 10$^{-2}$ |
| +             | 7.07  | 2.81      | 5.06  | 6.0 ($\pm 0.3$) × 10$^{-3}$ |

$a$ $pH_i$ is measured before PS addition. $b$ $pH_{ps}$ is measured after PS addition.

3.4. Effects of pH adjustment of the TCAP system

To study the effects of pH on the TP degradation process in the TCAP system, the initial pH ($pH_i$) was adjusted to values of around 3, 5 and 7 using NaOH solution before the addition of PS. The subsequent PS addition caused a further decrease in pH ($pH_{ps}$) (Fig. 5 and Table 4). The use of a buffer solution was not possible because an organic buffer would compete with TP on the PS present in the solution; on the other hand, an inorganic buffer, such as phosphate buffer, would cause interference by complexing with $Fe^{2+}$. The effect of initial pH is important to study because the effluent to be treated may contain traces of acid or base from the reactor cleaning process; however, most pharmaceutical production plants use deionized water for production. This was further clarified by comparing the case of pH 7 in the TCAP system to that of the TAP system at the same $[PS]_0$ = 2 mM. In fact, $k_{obs}$ is $6.0$ ($\pm 0.3$) × 10$^{-3}$ for the former and $5.52$ ($\pm 0.08$) × 10$^{-3}$ min$^{-1}$ for the latter (Table 1S). These values can be explained by the insignificant effects of $Fe^{2+}$ in the TCAP system adjusted initially to neutral pH. Thus, the studied TP system is very sensitive to pH variations. These results can be compared to a solar/$Fe^{2+}$/PS system investigated by Nie et al. In fact, the authors found a decrease in the degradation rate of chloramphenicol by around 70% when the reaction pH increased from 3 to 9.

3.5. Additive and matrix effects in the TCAP system

In order to test the effects of $Cl^-$, $NO_3^-$, and HA additives on the degradation rate of TP, the experimental conditions that yielded full TP degradation in 1 h at 60 °C were chosen as previously determined (Fig. 3).

3.5.1. Effects of sodium chloride. Different concentrations of saline solutions spiked with TP were investigated in the TCAP system. The resulting TP solutions had NaCl concentrations of 0, 200, 2000 and 20 000 mg L$^{-1}$ to mimic the conditions of...
distilled, fresh, brackish and saline water, respectively, according to Gorrell et al. and EPA data.\(^{47,48}\) It should be noted that chloride was present in all solutions at a concentration of 4 mM from FeCl\(_2\) (Fe\(^{2+}\) source) because FeCl\(_2\) was used as a source of Fe\(^{2+}\).

As can be noted from Fig. 6, the calculated \(k_{\text{obs}}\) for the cases of DI and fresh water were almost equal, showing a very slight positive effect of low [NaCl\(_0\)] in solution. However, the results also showed that higher [NaCl\(_0\)] caused inhibition of the degradation process, where \(k_{\text{obs}}\) decreased from 5.6 (±0.4) \times 10^{-2} \text{ min}^{-1}\) in the case of DI water to 3.0 (±0.2) \times 10^{-2} \text{ min}^{-1}\) and 8.0 (±0.5) \times 10^{-3} \text{ min}^{-1}\) in the cases of brackish and saline water, respectively (Fig. 6a and Table 5). Moreover, although a decrease in \(k_{\text{obs}}\) was noticed for fresh water, almost complete TP degradation was achieved in 60 min. The decrease in \(k_{\text{obs}}\) is attributed to the quenching of SO\(_4^{2-}\) (\(E^*= 2.437 \pm 0.019\) V) by Cl\(^-\) to produce Cl\(^-\) (\(E^* = 2.432 \pm 0.018\) V), which in turn reacts to produce Cl\(_2\)^\(-\) (\(E^* = 2.126 \pm 0.017\) V) (eqn (9) and (10)). The latter radical formed has lower redox potential and is thus less effective in terms of oxidation of TP and its transformation products compared to SO\(_4^{2-}\).\(^{49-51}\)

Different studies have showed varied effects of Cl\(^-\) on degradation processes. For example, Fan et al. observed enhancement in the degradation of sulfamethazine,\(^{52}\) whereas Norzaee et al. observed inhibition of penicillin G degradation,\(^{53}\) both in TAP systems. Wang et al. observed inhibition of acetaminophen degradation at low chloride concentrations and enhancement at high concentrations, while Amasha et al. noted inhibition of ketoprofen degradation, both in Fe\(^{2+}/\text{PS}\) systems.\(^{54,55}\) The increased degradation in the presence of Cl\(^-\) can be explained by the formation of Cl\(^-\), which has a redox potential close to that of SO\(_4^{2-}\), in addition to the formation of reactive HO\(^*\) (eqn (9) and (11)–(13)).\(^{50,51}\)

\[
\text{SO}_4^{2-} + \text{Cl}^- \rightleftharpoons \text{Cl}^- + \text{SO}_4^{2-}, \ k_f = 4.7 \times 10^8, \ k_b = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}
\] (9)

\[
\text{Cl}^- + \text{Cl}_2^- \rightleftharpoons \text{Cl}_2^- + \text{Cl}^- , \ k_f = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}, \ k_b = 4.2 \times 10^4 \text{ s}^{-1}
\] (10)

\[
\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{ClOH}^* + \text{H}^+, \ k_{\text{f[H}_2\text{O}]} = 1.6 \times 10^5 \text{ s}^{-1}, \ k_b = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}
\] (11)

\[
\text{HOCl}^- \rightleftharpoons \text{HO}^- + \text{Cl}^-, \ k_f = 6.1 \times 10^9 \text{ s}^{-1}, \ k_b = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}
\] (12)

\[
\text{HOCl}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{Cl}^-, \ k_f = 2.1 \times 10^{10}, \ k_b = 1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}
\] (13)

3.5.2. Effects of nitrates. Nitrate is one of the most commonly present ions in different water bodies, such as groundwater, due to the excessive use of fertilizers.\(^{55}\) Accordingly, the effects of [NO\(_3^-\)] = 1, 10 and 100 mg L\(^{-1}\) on TP degradation in the TCAP system were tested. The results showed that the reaction rate increased in the presence of [NO\(_3^-\)], where \(k_{\text{obs}}\) increased by 6 fold from 5.6 (±0.4) \times 10^{-2} \text{ min}^{-1}\) to 1.0 (±0.1) \times 10^{-1} \text{ min}^{-1}\) in DI media and [NO\(_3^-\)] = 1 mg L\(^{-1}\), respectively, and then slightly decreased for [NO\(_3^-\)] = 10 and

| Matrix     | Unit       | \(k_{\text{obs}} \times 10^{-2} \text{ (min}^{-1})\) | pHf/pHf |
|------------|------------|-----------------------------------------------|---------|
| No additive| mg L\(^{-1}\) | 5.6 (±0.4)                                      | 1.85/1.53 |
| [NaCl] = 200 |           | 6.5 (±0.5)                                      | 1.82/1.56 |
| [NaCl] = 2000 |          | 3.0 (±0.2)                                      | 1.81/1.62 |
| [NaCl] = 20 000 |         | 0.8 (±0.05)                                     | 1.78/1.56 |
| [NO\(_3^-\)] = 1 |          | 10.0 (±0.1)                                     | 1.81/1.71 |
| [NO\(_3^-\)] = 10 |          | 9.0 (±0.1)                                      | 1.79/1.71 |
| [NO\(_3^-\)] = 100 |         | 7.6 (±0.7)                                      | 1.78/1.70 |
| [HA] = 0.5 |            | 1.68 (±0.07)                                    | 1.84/1.97 |
| [HA] = 5 |             | 2.1 (±0.1)                                      | 1.83/1.95 |
| [HA] = 20 |              | 2.2 (±0.1)                                      | 1.81/1.94 |
100 mg L\(^{-1}\) to values of 9.0 (\(\pm\)0.1) \(\times\) 10\(^{-2}\) min\(^{-1}\) and 7.6 (\(\pm\)0.7) \(\times\) 10\(^{-2}\) min\(^{-1}\), respectively (Fig. 6b and Table 5).

The increase in TP degradation in the presence of nitrates can be attributed to the formation of NO\(_3^-\), which is considered to have significant oxidation redox potential (\(E^{\text{red}}_{1/2} = 2.50\) V) and can react with TP.\(^{22}\) Therefore, although nitrates react with SO\(_4^{2-}\) and quench them, the formation of NO\(_3^-\) appears to compensate for the decrease in [SO\(_4^{2-}\)] (eqn (14)). However, the increase in [NO\(_3^-\)] also results in an increase of [NO\(_3^-\)], which can subsequently undergo self-quenching reactions; this decreases [NO\(_3^-\)] and, as a result, decreases the degradation rate. Ghauch et al. also noted an increase in the naproxen degradation rate by 154.3% in the presence of [NO\(_3^-\)] = 5 mg L\(^{-1}\) in a TAP system.\(^{26}\)

\[
\text{SO}_4^{2-} + \text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3^-
\] (14)

### 3.5.3. Effects of humic acid (HA)

One widely present type of natural organic matter (NOM) is humic acid (HA).\(^{45}\) TP degradation in the TCAP system was studied in the presence of [HA]\(_0\) = 0.5, 5 and 20 mg L\(^{-1}\), which are in the typical naturally existing range.\(^{26}\) The results show that HA inhibited the degradation rate, where \(k_{obs}\) decreased by almost 3 fold when [HA]\(_0\) = 0.5 mg L\(^{-1}\) compared to HA-free medium. After that, the increase in [HA]\(_0\) caused no significant change in \(k_{obs}\) (Fig. 6c and Table 5). The inhibition in TP degradation can be explained by the competitiveness of active radicals, where NOM quenches SO\(_4^{2-}\) due to the presence of electron-rich sites.\(^{37}\) Liu et al. noted a significant decrease in reaction rate with increasing [HA] during sulfachloropyridazine degradation in a TAP system.\(^{37}\) Amasha et al. noted enhanced ketoprofen degradation in a CAP system at [HA]\(_0\) = 0.5, which was explained by the possible reductive ability of HA towards transition metals which, in the case of a CAP system, can regenerate Fe\(^{2+}\) from Fe\(^{3+}\).\(^{34,36}\) Thus, for the case of TP degradation in the TCAP system, the cease in the decrease in \(k_{obs}\) with increasing [HA]\(_0\) can be explained by the counter effects of HA: at higher concentrations, HA contributes more to the re-generation of Fe\(^{2+}\), which counteracts its radical-quenching properties.

### 3.6. Case of natural water matrices: spring, sea, and waste water in the TCAP system

The degradation of TP was studied in media of natural sea, spring, and waste water (SW, SpW and WW) obtained from locations at coordinates of 33°44′17.9″N 35°34′12.5″E, 33°54′11.1″N 35°28′44.8″E and 33°54′08.2″N 35°29′05.0″E, respectively. The experimental conditions are as follows: [PS]\(_0\) = 5 mM, [Fe\(^{2+}\)]\(_0\) = 0.5 mM, and TP were added in adequate amounts to each water medium so that [TP]\(_0\) = 10 mg L\(^{-1}\). A [PS]\(_0\) : [Fe\(^{2+}\)]\(_0\) ratio of 10 : 1 was used instead of the optimum obtained ratio of 1 : 1 in order to decrease the use of Fe\(^{2+}\), e.g., Fe(OH)\(_2\) in neutral media.\(^{45}\) These conditions were adopted because natural water matrices are buffered to around neutral pH (Table 6), mainly because of the presence of bicarbonate. The results showed that TP degradation was inhibited in the three tested cases compared to the DI matrix case, where \(k_{obs}\) was 1.5 (\(\pm\)0.1) \(\times\) 10\(^{-1}\) min\(^{-1}\), with WW showing \(-\)570 fold inhibition in terms of \(k_{obs}\) = 2.6 (\(\pm\)0.6) \(\times\) 10\(^{-4}\) min\(^{-1}\), followed by SpW \(-\)14 fold and SW \(-\)10 fold, \(k_{obs}\) = 1.1 (\(\pm\)0.1) \(\times\) 10\(^{-2}\) and 1.54 (\(\pm\)0.09) \(\times\) 10\(^{-2}\) min\(^{-1}\), respectively (Fig. 7).

![Degradation of TP in real water samples: spring, sea and waste water. Experimental conditions: [TP]_0 = 10 mg L^{-1}, [PS]_0 = 5 mM and [Fe^{2+}]_0 = 0.5 mM. Error bars are calculated as \(t_0 \sqrt{n}\), where absent bars fall within the symbols.](image-url)
One reason for the inhibition of the degradation of TP in the three investigated cases is the neutral to slightly basic pH values (7 to 8.2); this pH range causes the complexation and precipitation of Fe$^{2+}$, e.g. as Fe(OH)$_2$, where natural water media act as buffer solutions compared to DI medium, which becomes acidic (pH $\approx 2$) immediately after the addition of PS and Fe$^{2+}$ solutions. The inhibition was the highest in the case of the WW matrix, where WW possessed the highest values of total and fecal coliforms, chlorides, turbidity and total suspended and dissolved solids among the three studied matrices. The organic and inorganic material present in WW competes with TP in reacting with SO$_4^{2-}$, thus inhibiting TP degradation. Additionally, chlorides acted as quenchers in the studied TCAP system (Section 3.5.1), and WW showed the highest [Cl$^-$] present. It should be noted that total elimination of coliforms was observed in the WW and SW (Table 6) systems; this is probably due to the heat factor in addition to the activity of the SO$_4^{2-}$ present. Effluents of pharmaceutical production plants, after discharge, may be mixed with several water matrices with different properties. In addition, the water used for initial cleaning operations may be of natural origin and not DI water. The results presented in this section show that it is crucial to clean mixing reactors in pharmaceutical production facilities with distilled water (Section 3.3.5); thus, it is crucial for industries to utilize adequate amounts of distilled (DI) water in rinsing apparatuses and tools used during syntheses and mixing processes for efficient and cost-effective effluent treatment.

3.7. Economic study. The cost of factory effluent treatment utilizing the TCAP system was estimated. The electric energy required to heat the solution in addition to the reagent price were considered to be the main contributors to the total cost of operation (eqn (15)).

$$\text{Total system cost} = \text{electricity energy cost} + \text{reagent cost}$$

Electric energy per order ($E_{EO}$) was defined as the electric energy required to degrade contaminants by one order of magnitude, for example from 10 mg L$^{-1}$ to 1 mg L$^{-1}$, in one cubic meter of contaminated water or air; this was calculated using eqn (16) for a batch system:

$$E_{EO} = \frac{P \times t \times 1000}{V \times \log \left( \frac{C_i}{C_f} \right)}$$

where $P$ is the power supplied to the system in kW, $t$ is the duration of the treatment in hours, $V$ is the volume treated in L, $C_i$ and $C_f$ are the initial and final concentrations, respectively.

### Table 7 Degradation of TP by TCAP in real pharmaceutical effluent containing [TP]$_0$ = 160 mg L$^{-1}$. Experimental conditions: [PS]$_0$ = 25–100 mM, [PS]$_0$ : [Fe$^{2+}$]$_0$ ratio of 1 : 1, and $T = 60$ °C. $k_{obs}$ is calculated for the pseudo-first order reaction rate.

| [PS]$_0$ mM | [Fe$^{2+}$]$_0$ mM | $T$ °C | $k_{obs}$ min$^{-1}$ | pH$_i$/pH$_f$ |
|-------------|------------------|-------|-------------------|-------------|
| 25          | 25               | 60    | 1.4 (±0.1) \times 10^{-2} | 1.17/1.08   |
| 50          | 50               |       | 4.5 (±0.2) \times 10^{-2} | 0.85/0.78   |
| 75          | 75               |       | 1.16 (±0.05) \times 10^{-1} | 0.67/0.60   |
| 100         | 100              |       | 1.65 (±0.09) \times 10^{-1} | 0.58/0.48   |
and 1000 is a conversion factor from L to m³. Thus, $E_{EO}$ is obtained in kW h per m³ per order. Additionally, eqn (16) was simplified by substituting the first-order reaction rate eqn (17) in eqn (16) and changing the unit of time. Thus, the following simplification was performed (eqn (16)–(19)):

$$\log \frac{C}{C_t} = \frac{P}{V} \times \frac{1000}{k_{obs} \times t}$$  \hspace{1cm} (17)

$$E_{EO} = \frac{P \times t \times 1000}{V \times 0.4343 \times k_{obs} \times t \times 60}$$  \hspace{1cm} (18)

$$E_{EO} = \frac{38.4 \times P}{V \times k_{obs}}$$  \hspace{1cm} (19)

The resulting simplified eqn (19) shows $P$ in kW, $V$ in L, and $k_{obs}$ in min⁻¹. Power was calculated based on the energy and time needed to heat the reactors. The energy required for this heating was calculated using eqn (20), where $Q$ is the energy in J, $m$ is the mass of water in g (200 g), $C$ is the specific heat capacity of water (4.186 J g⁻¹ °C⁻¹), and $\Delta T$ (35 °C) is the temperature difference for heating from 25 °C to 60 °C. $Q$ was found to be 29.3 kJ.

$$Q = mC\Delta T$$  \hspace{1cm} (20)

Power was calculated utilizing eqn (21), where $t$ is the time in seconds needed to heat the solution to the desired temperature. Experimentally, 12 min were required to heat the 200 mL reactor from room temperature to 60 °C. Thus, $P = 0.122$ kW.

$$P = \frac{Q}{t}$$  \hspace{1cm} (21)

The $E_{EO}$ was calculated for each of the four different $[PS]_0$ values, and the results are presented in Table 8. The electrical energy cost was estimated utilizing electricity cost rates in Lebanon, with the Electricité du Liban (EDL) average rate of 255 LBP per kW h equivalent to 0.169 $ per kW h at the current conversion rate, as well as in the US, where the average electricity cost rate for the industrial sector is 0.0709 $ per kW h. The costs of the reagents were calculated using wholesale prices in every case (Table S1†). The total system cost can thus be obtained (eqn (15)) and is presented in detail in Fig. 9. It was observed that as $[PS]_0$ increases, the reagent cost increases, while the electric cost due to heating decreases. Consequently, the choice of $[PS]_0$ for the treatment of factory effluent can be based on the estimated total cost, where the case of $[PS]_0 = 50$ mM gave the lowest total cost of 56.8 and 73.8 $ per m³ based on electricity prices in the US and in Lebanon, respectively (Fig. 9 and Table 8).

Amasha et al. obtained a total cost of 44.414 $ per m³ for degradation of ketoprofen (7.87 μM, 2.00 mg L⁻¹) in a TAP system, with $[PS]_0 = 1$ mM and $T = 60$ °C. The lower total cost obtained by the mentioned study can be attributed to the fact that no Fe²⁺ was used, so the reagent price was lower; in addition, the degradation was performed in DI and not in factory effluent, where competitive reactions take place between SO₄²⁻ and the excipients present (Section 3.7.1).

### 3.8. Effects of MeOH and TBA quenchers

Radical scavenging by methanol (MeOH) and tert-butyl-alcohol (TBA) was tested in the TAP system to determine the effectiveness of the produced $SO₄^{2-}$ and HO· in the degradation of TP. Different concentrations of MeOH and TBA (400, 800 mM) were added separately to reactors containing $[TP]_0 = 10$ mg L⁻¹.

| $[PS]_0$ mM | $k_{obs}$ min⁻¹ | $E_{EO}$ kW h per m³ per order | Electricity cost (US), $ per m³ per order | Electricity cost (Lebanon), $ per m³ per order | Reagent cost*, $ per m³ | Total cost (US), $ per m³ | Total cost (Lebanon), $ per m³ |
|---|---|---|---|---|---|---|---|
| 25 | $1.4 (±0.1) \times 10^{-2}$ | 558 | 39.6 | 94.4 | 22.2 | 61.8 | 116.6 |
| 50 | $4.5 (±0.2) \times 10^{-2}$ | 174 | 12.3 | 29.4 | 44.5 | 56.8 | 73.8 |
| 75 | $1.16 (±0.05) \times 10^{-1}$ | 67.4 | 4.8 | 11.4 | 66.7 | 71.5 | 78.1 |
| 100 | $1.65 (±0.09) \times 10^{-1}$ | 47.4 | 3.4 | 8.0 | 88.9 | 92.3 | 96.9 |

* Check Table 1S.

Fig. 9 Treatment cost of pharmaceutical effluent contaminated with TP using a TAP system. The electricity, reagent and total costs are presented (based on US electricity cost). Experimental conditions: $[TP]_0 = 160$ mg L⁻¹, $[PS]_0 = 25–100$ mM, $[PS]_0 : [Fe^{2+}]_0$ ratio of 1 : 1 and $T = 60$ °C.
and \([\text{PS}]_0 = [\text{Fe}^{2+}]_0 = 2 \text{ mM}\). The experiments were conducted in tight reactors using rubber stoppers in order to prevent substantial loss of MeOH \((k_H = 230 \text{ mol kg}^{-1} \text{ bar}^{-1})\) and TBA \((k_H = 83 \text{ mol kg}^{-1} \text{ bar}^{-1})\) from the reactor due to heat. It is known that MeOH quenches both \(\text{SO}_4^{2-}\) and \(\text{HO}^+\) radicals, whereas TBA mainly quenches \(\text{HO}^+\). Fig. 10 shows that MeOH and TBA caused increased inhibition as their concentrations increased. This is due to the increase in competition between the quenchers and TP to react with the radicals present in the medium. Wang et al. also obtained a positive correlation between inhibition extent and the concentrations of TBA and MeOH used in a TAP system. In the case of 800 mM quenchers used (quencher/PS: 400/1), TBA and MeOH caused almost total quenching due to their high concentrations. However, when 400 mM quenchers were used (Quencher/PS: 200/1), MeOH caused slightly more quenching than TBA. We can deduce that \(\text{HO}^+\) is the major reactive species when degrading TP in a TCAP system.

### 3.9. Suggested degradation pathway

A theoretical study of the degradation pathway utilizing frontier orbitals and charge distribution was conducted. Frontier molecular orbital theory shows that electrophilic reactions are more likely to occur for atoms with higher values of the highest

![Fig. 11](image-url) **(a)** TP atomic labeling and numbering. **(b)** HOMO and **(c)** LUMO of TP with isovalue 0.05.

### Table 9 The computed values of the FEDs for the HOMO and LUMO in addition to the Mulliken charge distributions

| Atom | \(\text{FED}_{\text{HOMO}} + \text{FED}_{\text{LUMO}}\) | \(2\text{FED}_{\text{HOMO}}\) | \(2\text{FED}_{\text{LUMO}}\) | Mulliken charge |
|------|---------------------|---------------------|---------------------|-----------------|
| 1C   | 0.27                | 0.45                | 0.08                | 0.35            |
| 2C   | 0.23                | 0.19                | 0.27                | 0.11            |
| 3C   | 0.38                | 0.17                | 0.58                | 0.25            |
| 4N   | 0.17                | 0.13                | 0.21                | -0.21           |
| 5N   | 0.05                | 0.01                | 0.10                | -0.25           |
| 6C   | 0.02                | 0.04                | 0.01                | 0.56            |
| 7O   | 0.18                | 0.17                | 0.19                | -0.66           |
| 8O   | 0.10                | 0.20                | 0.00                | -0.67           |
| 9N   | 0.25                | 0.38                | 0.11                | -0.26           |
| 10C  | 0.01                | 0.01                | 0.01                | -0.21           |
| 11H  | 0.00                | 0.00                | 0.00                | 0.14            |
| 12H  | 0.01                | 0.02                | 0.00                | 0.14            |
| 13H  | 0.01                | 0.02                | 0.00                | 0.14            |
| 14C  | 0.00                | 0.00                | 0.00                | -0.15           |
| 15H  | 0.00                | 0.00                | 0.00                | 0.15            |
| 16H  | 0.01                | 0.00                | 0.02                | 0.14            |
| 17H  | 0.01                | 0.00                | 0.02                | 0.14            |
| 18N  | 0.01                | 0.01                | 0.01                | -0.47           |
| 19C  | 0.28                | 0.19                | 0.36                | 0.29            |
| 20H  | 0.00                | 0.00                | 0.00                | 0.23            |
| 21H  | 0.00                | 0.00                | 0.00                | 0.25            |
| 22H  | —                   | —                   | —                   | —               |
occupied molecular orbital (HOMO), while nucleophilic reactions are prone to occur for atoms with higher values of the lowest unoccupied molecular orbital (LUMO). Consequently, several studies suggest that atoms with a higher \( \text{FEDHOMO}^+ \) are more easily oxidized, and those with a higher \( \text{FEDHOMO}^+ + \text{FEDLUMO}^+ \) are more susceptible to addition reactions. The \( \text{FEDHOMO}^+ \), \( \text{FEDHOMO}^+ \), and Mulliken charge distributions were calculated for TP and are presented along with the atom numbering and the isodensity surfaces of frontier molecular orbital theory in Fig. 11 and Table 9. For TP, 1C showed the highest \( \text{FEDHOMO}^+ \), followed by 9N, 8O, 2C, 19C, 3C and 7O. Therefore, attack by oxidants is expected to occur readily on 1C, 19C and 3C; however, it was noted that 19C is the least sterically hindered of the three atoms. Thus, addition reactions are expected to occur more readily at 1C, 19C and 9N, while addition reactions will mostly take place at 1C, 19C and 3C; however, it was noted that 19C is the least sterically hindered of the three atoms. Thus, addition reactions are expected to occur more readily at 19C, such as the formation of hydroxylated products. Consequently, addition reactions are expected to occur more readily on 2C, 19C, 9N, 2C, 7O and 4N. Thus, addition reactions will mostly take place at 1C, 19C and 3C; however, it was noted that 19C is the least sterically hindered of the three atoms. Thus, addition reactions are expected to occur more readily at 19C, such as the formation of hydroxylated products. Consequently, addition reactions are expected to occur more readily on 2C, 19C, 9N, 2C, 7O and 4N. Thus, addition reactions will mostly take place at 1C, 19C and 3C; however, it was noted that 19C is the least sterically hindered of the three atoms. Thus, addition reactions are expected to occur more readily at 19C, such as the formation of hydroxylated products. Consequently, addition reactions are expected to occur more readily on 2C, 19C, 9N, 2C, 7O and 4N. Thus, addition reactions will mostly take place at 1C, 19C and 3C; however, it was noted that 19C is the least sterically hindered of the three atoms. Thus, addition reactions are expected to occur more readily at 19C.

Demethylation is initiated by hydrogen abstraction at 10C and 14C, which is followed by \( \text{HO}^- \) attack. BP2 is formed through demethylation and saturation of double bonds. Ultimately, mineralization is expected, which was obtained in similar AOP studies.

4. Conclusions

In this study, TP degradation was tested in systems of TAP, CAP and TCAP. TAP resulted in incomplete (60%) TP degradation at \( t = 60 \text{ min} \) for \([\text{PS}]_0 = 5 \text{ mM} \) and \( T = 60 \degree \text{ C} \). The CAP system was not effective at room temperature, where a maximum of 5% TP degradation was observed at \( t = 60 \text{ min} \) for \([\text{PS}]_0 = [\text{Fe}^{II}]_0 = 0.25 \text{ mM} \). To obtain better efficiency, the two methods of PS activation were combined in a TCAP system, which resulted in complete TP degradation at \( T = 60 \degree \text{ C} \) and \([\text{PS}]_0 = [\text{Fe}^{II}]_0 = 2 \text{ mM} \). The reaction followed a pseudo-first order reaction rate, with \( k_{\text{obs}} = 5.6 \pm 0.4 \times 10^{-2} \text{ min}^{-1} \). The effects of \([\text{PS}]_0 : [\text{Fe}^{II}]_0 \) ratio, \([\text{PS}]_0 \) and temperature were tested, where the 1 : 1 ratio gave optimum results, and the degradation rate increased with increasing \([\text{PS}]_0 \) and temperature. Salinity inhibited the degradation process, while nitrates slightly enhanced the process. The presence of HAs inhibited TP degradation. TP was dissolved in real water samples of spring, sea and waste water, which showed lower degradation rates in comparison with DI water medium. Real factory effluent containing TP was obtained and showed total degradation of \([TP]_0 = 160 \text{ mg L}^{-1} \) within 180 and 40 min for \([\text{PS}]_0 = [\text{Fe}^{II}]_0 = 25 \text{ and } 100 \text{ mM} \). The degradation cost was estimated to 56.8 $ per m\text{m}^3$, for electricity price rates in the US at \([\text{PS}]_0 = [\text{Fe}^{II}]_0 = 50 \text{ mM} \). A degradation mechanism involving \textit{in situ} evolved reactive oxidative species, mainly sulfate and hydroxyl radicals, was also suggested based on LC/MS/MS HRAM analyses supported by frontier molecular orbital theory calculations.

Conflicts of interest

There are no conflicts to declare.
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