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Thermally activated persulfate-based Advanced Oxidation Processes – recent progress and challenges in mineralization of persistent organic chemicals: a review

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Thermally activated persulfate (TAP) finds application in Advanced Oxidation Processes for the removal of pollutants from contaminated water and soil. This paper reviewed the various cases of TAP in the environmental remediation. The pollutants such as individual pharmaceuticals, biocides, cyclic organic compounds, and dyes are considered in this review. It is interesting to note that most of the organic compounds undergo complete degradation at a high temperature of 70°C with a first-order reaction kinetics. The influence of operating parameters such as temperature, persulfate concentration, initial pH, and degradation behavior in the presence of natural water constituents are also discussed. In addition, several processes to reduce the temperature of TAP are highlighted.

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Introduction

The industrial and domestic wastewater contains number of pollutants, while many of them are persistent

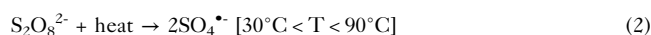
to the single treatment techniques. Advanced Oxidation Processes (AOPs) are one of the key methods for the treatment of wastewater containing recalcitrant pollutants [1,2]. Currently, big attention is made on persulfates ($S_2O_8^{2-}$, PS) based AOPs [3–9]. This type of oxidants demands effective activation (Eq. 1) to produce radical species which are able to degrade persistent organic pollutants. The commonly used activators are acoustic (US) and hydrodynamic cavitation (HC), transition metal ions and related catalyst, carbon-based catalyst, UV light, alkaline and thermal activation [4,5,10–17].



Often simple PS activation method which can be implemented on a large-scale basis is highly required. In this regard, thermal activation of PS has high potential of applicability.

Thermally-activated persulfates for the removal of organic contaminants

Thermal activation is one of the simplest and an effective method for PS activation to generate reactive species [18]. Since the bond energy of peroxide (O–O) in PS is 140–213.3 kJ mol⁻¹, a thermal activation at a temperature of > 30°C is sufficient to break the O–O bond for the generation of sulfate anion radicals ($SO_4^{\bullet-}$) (Eq. 2) [4]. These $SO_4^{\bullet-}$ radicals can be further converted to hydroxyl radicals ($\bullet OH$), which are also an effective species (Eq. 3) [19]. The generation of $SO_4^{\bullet-}$ and $\bullet OH$ radicals can be represented as given below:



Reaction described by Eq. (3) is a slow process (< 2 × 10⁻³ s⁻¹) under normal condition; however, the thermal processes enhance the conversion of $SO_4^{\bullet-}$ to $\bullet OH$. Therefore, the advantage of the thermally activated PS (TAP) is the involvement of selective reactive species, $SO_4^{\bullet-}$ and nonselective reactive species, $\bullet OH$. Furthermore, the evolution of these reactive species depends on the pH of the solution. The speciation of the

radical species revealed that the $\text{SO}_4^{\bullet-}$ species are the predominant species formed at $\text{pH} < 7$, whereas both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ are present when the pH is increased to 9 [20]. The alkaline pH favors $\bullet\text{OH}$ in the reaction medium as the major species. The studies also reported that among the various peroxide-based oxidants, PS is very common in thermal activation processes [6,8,15,21,22].

Parameters affecting the degradation of organic pollutants in wastewater and soil

TAP method has been tested for a number of pollutants ranging from chlorinated solvents to the emerging contaminants. The removal of various pollutants using TAP and the parameters studied in the processes are given in Table 1.

Analysis of the collected data suggests that the most of the degradation processes follows the pseudo-first-order kinetics. Fan et al. reported the degradation of sulfamethazine using TAP. The complete degradation of the pollutant was observed in 120 min of treatment at 60°C [23]. TAP method has been reported for various recalcitrant pollutants like sulfachloropyridazine, *p*-nitrophenol, phenol, benzoic acid, ibuprofen, parabens, phthalates, perfluorooctanoic acid, atrazine, diuron, and dinitrodiazophenol (Table 1). Waldemer et al. reported similar techniques for the removal of chlorinated ethenes (tetrachloroethene (PCE), cis-1,2-dichloroethene (cis-DCE), trans-1,2-dichloroethene (trans-DCE), and trichloroethene (TCE)), rapid removal was observed in 60 min of the treatment. Complete removal was reported for almost all the tested pollutants [25].

Along with removal of organic pollutants the TAP has also proven to be effective for removal of total organic carbon (TOC). Luo et al. have studied the removal of Congo red (CR) dye via TAP and reported around 98% decolorization along with 84% TOC removal [53]. Amasha et al. reported the effect of initial PS concentration ($[\text{PS}]_0$) on TOC removal during degradation of nonsteroidal anti-inflammatory drugs using TAP process. The increase in mineralization with increasing $[\text{PS}]_0$ was observed with maximum TOC removal of 75% at 60 min was treatment at 60°C and $[\text{PS}]_0 = 5 \text{ mM}$ [55]. Similar trend in mineralization was also reported by Dominguez et al. with $[\text{PS}]_0$. They have also noted the enhancement in extent of mineralization with increasing temperature [56]. However, with increasing temperature, an increase in cost of process along with unproductive decomposition of PS is also inevitable (See Section *Temperature*). Moreover, in most of the cases such as degradation of propranolol, antipyrine, methyl and ethyl parabens (EtP), diuron, triclosan, only about 10–25% TOC removal was reported with TAP. On the contrary, 90–100% degradation was noted for the

forementioned contaminants [24,27,29,39,41]. This indicates that the contaminant's degradation is substantially faster than their mineralization, which implies that the by-products generated are resistant to PS oxidation. But, upon the application of one or two activators along with heat for PS activation tremendous enhancement in rates of contaminant degradation and mineralization was reported, thereby addressing the issue of contaminant mineralization. Rayaroth et al. have attempted the degradation of reactive black 5 using a sulfidized nanoscale zerovalent iron and combined sulfidized nanoscale zerovalent iron–PS system. The results indicated that, when only sulfidized nanoscale zerovalent iron was used 25% degradation and 10% TOC removal was obtained. Whereas, 100% degradation and 90% TOC removal was achieved with combined sulfidized nanoscale zerovalent iron–PS system [57]. Zhang et al. noted 85.81% TOC removal using thermal and metal ions co-activated PS used for degradation of *p*-nitrophenol [45].

The PS dosage is also an important parameter that can affect the quality of treated water and the operating cost of TAP. Thus, for the practical application of TAP it is necessary to use the optimized PS dosage in accordance with the reaction stoichiometric efficiency (RSE). The RSE is defined as the number of moles of organic pollutant degraded divided by the number of moles of PS consumed and often plays an important role in the evaluation of the oxidation efficiency for TAP [53]. Amasha et al. have studied the degradation of ketoprofen using TAP ($[\text{PS}]_0 = 0.25\text{--}5 \text{ mM}$). They have obtained maximum value of % RSE to be 33.2% at $[\text{PS}]_0 = 1 \text{ mM}$ and $T = 60^\circ\text{C}$. They noted significant decrease in % RSE with increasing $[\text{PS}]_0$ above 1 mM. Also, the efficacy of TAP system was found to be higher than Fe^{2+}/PS system and lower than UV/PS system [55]. Ghauch et al. have used RSE to determine whether acidic, neutral or basic pH condition is the optimum for degradation of ibuprofen using TAP. The results have shown that the optimum ibuprofen removal was obtained at neutral pH (RSE = 0.65) followed by pH = 9.0 (RSE = 0.25) and pH = 4.0 (RSE = 0.09). This higher RSE at neutral pH of 7.0 suggests that the produced $\text{SO}_4^{\bullet-}$ are directly used for oxidation of ibuprofen through electron transfer or H-abstraction via indirectly produced $\bullet\text{OH}$. Lowest RSE implies that the very few $\text{SO}_4^{\bullet-}$ produced through acidic catalysis are involved in the oxidation of ibuprofen and the rest reacts with phosphate or with each other. In case of pH 9.0, some of the $\text{SO}_4^{\bullet-}$ produced reacts with hydroxyl species increasing PS consumption which in turn results in lower IBU degradation [30]. In another study, Ghauch et al. suggested that the RSE values evaluated at similar operating conditions for various pollutants can also help in the interpretation of the kinetics law and the role of dissolved species involved in the oxidation mechanisms.

Table 1

Performance of TAP process reported for the degradation of various recalcitrant pollutants.

Type of pollutant	Pollutant (Real/Synthetic)	Experimental condition	% Removal, rate constant, and activation energy	Ref.
Pharmaceutical Active Ingredients	Sulfachloropyridazine (Synthetic)	$C_0 = 3.51 \mu\text{M}$, [PS] = $140 \mu\text{M}$, $T = 40^\circ\text{C}$, $\text{pH} = 3$, Time = 180 min	100%, 0.178 min^{-1} $155 \pm 15 \text{ kJ mol}^{-1}$	[26]
	Propranolol (Synthetic)	$C_0 = 0.025 \text{ mM}$, [PS] = 1 mM , $T = 70^\circ\text{C}$, $\text{pH} = 7$, Time = 50 min	100%, 0.193 min^{-1} , 99.0 kJ mol^{-1} , TOC removal(%) = 13.6	[24]
	Antipyrine (Synthetic)	$C_0 = 0.2 \text{ mM}$, [PS] = 4 mM , $T = 70^\circ\text{C}$, $\text{pH} = 5.4$, Time = 120 min	100%, 0.004 s^{-1} , $139.5 \pm 9.7 \text{ kJ mol}^{-1}$, TOC removal(%) = 12.5	[27]
	Chloramphenicol (Synthetic)	$C_0 = 0.0265 \text{ mM}$, [PS] = 1.85 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 160 min	100%, 0.059 min^{-1} , $103.1 \text{ kJ mol}^{-1}$, TOC removal(%) = 90	[28]
	Methyl-parabens (MeP) and EtP (Synthetic)	$C_0 = 20 \mu\text{M}$, [PS] = 1 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 240 min	100%, $17.67 \times 10^{-3} \text{ min}^{-1}$ and $18.37 \times 10^{-3} \text{ min}^{-1}$ for MeP and EtP, 95.2 and 98.9 kJ mol^{-1} for MeP and EtP, TOC removal(%) for MeP = 10.2 , TOC removal(%) for EtP = 15	[29]
	Ibuprofen (Synthetic)	$C_0 = 20.36 \mu\text{M}$, [PS] = 1 mM , $T = 70^\circ\text{C}$, $\text{pH} = 7$, Time = 60 min	100%, 0.192 min^{-1} , $168 (\pm 9.5) \text{ kJ mol}^{-1}$	[30]
	Carbamazepine (Synthetic)	$C_0 = 40 \mu\text{M}$, [PS] = 1 mM , $T = 60^\circ\text{C}$, $\text{pH} = 5$, Time = 120 min	100%, 0.0566 min^{-1} , $120.4 \pm 2.6 \text{ kJ mol}^{-1}$	[31]
	Chloroxylenol (Synthetic)	$C_0 = 1.5 \text{ mM}$, [PS] = 75 mM , $T = 60^\circ\text{C}$, $\text{pH} = 5$, Time = 120 min	100%, 0.02886 min^{-1} , $130.4 \text{ kJ mol}^{-1}$	[32]
	Losartan (Synthetic)	$C_0 = 500 \text{ mg L}^{-1}$, [PS] = 50 mg L^{-1} , $T = 50^\circ\text{C}$, $\text{pH} = 5$, Time = 45 min	100%, 0.0678 min^{-1} , $112.70 \text{ kJ mol}^{-1}$	[33]
	Bisoprolol (Synthetic)	$C_0 = 50 \mu\text{M}$, [PS] = 1 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 60 min	100%, $8.47 \pm 0.31 \text{ min}^{-1}$, $119.8 (\pm 10.8) \text{ kJ mol}^{-1}$	[34]
	ROX (Synthetic)	$C_0 = 50 \mu\text{M}$, [PS] = 2 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 480 min	98%, 0.0025 min^{-1} , $102.4 \pm 0.6 \text{ kJ mol}^{-1}$.	[35]
	Sulfamethazole (Synthetic)	$C_0 = 100 \text{ mg L}^{-1}$, [PS] = 5 mM , $T = 70^\circ\text{C}$, $\text{pH} = 4.6$, Time = 480 min	99%, 0.01 min^{-1} , 103 kJ mol^{-1}	[36]
	Ibuprofen (IBP) in a soil system (Synthetic)	$C_0 = 48.4\text{--}46.0 \mu\text{M kg}^{-1}$, [PS] = 20 mM kg^{-1} , $\text{pH} = 7.75$, $T = 50^\circ\text{C}$, Time = 120 min	81.9%, 0.0164 min^{-1} , $132.12 \text{ kJ mol}^{-1}$	[18]
	Sulfamethazine (Synthetic)	$C_0 = 30 \mu\text{M}$, [PS] = 2 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 120 min	100%, 0.84 min^{-1} , 126 kJ mol^{-1}	[23]
	Naproxen (Real)	$C_0 = 50 \mu\text{M}$; [PS] = 10 mM , $T = 70^\circ\text{C}$, Time = 120 min	$155.03 (\pm 26.4) \text{ kJ mol}^{-1}$, degradation rate = $1.286 \times 10^{-2} \text{ mM min}^{-1}$, TOC removal(%) = 100	[37]

Table 1 (continued)

Type of pollutant	Pollutant (Real/Synthetic)	Experimental condition	% Removal, rate constant, and activation energy	Ref.
Pesticides	Thiamethoxam (Synthetic)	$C_0 = 2 \text{ mg L}^{-1}$, [PS] = 100 mg L^{-1} , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 120 min	100% , 0.2 min^{-1} , $103.1 \text{ kJ mol}^{-1}$, $108.7 \text{ kJ mol}^{-1}$, TOC removal (%) = 95	[38]
	Diuron (Synthetic)	$C_0 = 0.0375 \text{ mM}$, [PS] = 0.375 mM , $T = 60^\circ\text{C}$, $\text{pH} = 5.1$, Time = 180 min	TOC removal (%) = 95	[39]
	Atrazine (Synthetic)	$C_0 = 50 \mu\text{M}$, [PS] = 2 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 120 min	$166.7 \pm 0.8 \text{ kJ mol}^{-1}$, TOC removal (%) = 15 98% , 0.028 min^{-1} , 141 kJ mol^{-1}	[40]
Industrial contaminants	Triclosan (Real)	$C_0 = 0.031 \text{ mM}$, [PS] = 0.155 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 500 min	100% , 0.0097 min^{-1} , $121.12 \text{ kJ mol}^{-1}$, TOC removal (%) = 11.5	[41]
	Simazine (Synthetic)	$C_0 = 10 \mu\text{M}$, [PS] = 0.1 mM , $T = 65^\circ\text{C}$, $\text{pH} = 5$, Time = 120 min	99% , 0.05 min^{-1} , $118.45 \text{ kJ mol}^{-1}$	[42]
	Soils contaminated with HCHs (Real)	15 g of polluted soil (α -HCH = 254 mg kg^{-1} and β -HCH = 99 mg kg^{-1}), [PS] = 80 g L^{-1} , $T = 55^\circ\text{C}$, Time = 9 days	83%	[43]
	Phthalate esters (DEP and dibutyl phthalate (DBP)) (Synthetic)	$C_0 = 2 \mu\text{M}$, [PS] = $500 \mu\text{M}$, $T = 60^\circ\text{C}$, $\text{pH} = 5.8$, Time = 60 min	0.4396 min^{-1} , $125.4 \pm 18.6 \text{ kJ mol}^{-1}$ and $146.1 \pm 14.3 \text{ kJ mol}^{-1}$ for DEP and DBP respectively.	[44]
	<i>p</i> -nitrophenol (Synthetic)	$C_0 = 0.72 \text{ mM}$, [PS] = 30 mM , $T = 70^\circ\text{C}$, $\text{pH} = 7$, Time = 180 min	100% , 0.027 min^{-1} , $127.8 (\pm 1.56) \text{ kJ mol}^{-1}$, TOC removal (%) = 85.8	[45]
	Chlorinated Ethenes (Synthetic)	$C_0 = 4.5 \times 10^{-5} \text{ M}$, [PS] = $4.5 \times 10^{-4} \text{ M}$, $T = 70^\circ\text{C}$, $\text{pH} = 7$, Time = 8 hours	100% , 0.967 hours^{-1} , 101 kJ mol^{-1} for PCE, 108 kJ mol^{-1} for TCE, 144 kJ mol^{-1} for <i>cis</i> -DCE, and 141 kJ mol^{-1} for <i>trans</i> -DCE.	[25]
	Bisphenol A (Synthetic)	$C_0 = 220 \mu\text{g L}^{-1}$, [PS] = 625 mg L^{-1} , $T = 70^\circ\text{C}$, $\text{pH} = 6.5$, Time = 60 min	100% , 1.73 min^{-1} , $133.5 \text{ kJ mol}^{-1}$	[46]
	Bisphenol S (Synthetic)	$C_0 = 25 \mu\text{M}$, [PS] = 0.5 mM , $T = 60^\circ\text{C}$, $\text{pH} = 7$, Time = 180 min	TOC removal (%) = 28 99% , 0.02 min^{-1} , $(112.9 \pm 6.8) \text{ kJ mol}^{-1}$,	[47]
Chlorinated Solvents in Sandy Soil (Synthetic) [TCE, <i>cis</i> -1,2-DCE, 1,1,1-trichloroethane (TCA), and 1,2-dichloroethane (1,2-DCA)]	Perfluorooctanoic acid (Synthetic)	$C_0 = 0.5 \mu\text{M}$, [PS] = 10 mM , $T = 85^\circ\text{C}$, $\text{pH} = 7$, Time = 30 hours	TOC removal (%) = 27 93.5% , $9.15 \times 10^{-2} \text{ hours}^{-1}$, 60 kJ mol^{-1}	[48]
	Bisphenol A (BPA) in soil (Synthetic)	25 mL water and 25 g soil 7 μL mixed contaminated solution (TCE- 81.8 mg L^{-1} , <i>cis</i> -1,2-DCE- 71.2 mg L^{-1} , TCA- 75.0 mg L^{-1} , and 1,2-DCA- 70.6 mg L^{-1}), [PS] = 20 g L^{-1} , Time = 72 hours	79.5% , $0.0035 \text{ hours}^{-1}$	[49]
	Total petroleum hydrocarbon (TPH) in soil (Synthetic)	BPA in soil = 31.93 mg kg^{-1} , [PS] = 8 mM , $C_0 = 5 \text{ mg L}^{-1}$, Biochar ₀ = 1 g L^{-1} , $\text{pH} = 7$, $T = 25^\circ\text{C}$, Time = 150 min ultrasonic power = 200 W , [PS] = 1 M , $10 \text{ gm} = \text{testing}$ soil ($19\ 850 \text{ mg kg}^{-1}$), $\text{pH} = 7$, water:soil ratio = 1:1, $T = 50^\circ\text{C}$, Time = 72 hours	98.5%	[50]
			78.2% , $7.44 \times 10^6 \text{ kg mg}^{-1} \text{ hours}^{-1}$	[12]

Table 1 (continued)

Type of pollutant	Pollutant (Real/Synthetic)	Experimental condition	% Removal, rate constant, and activation energy	Ref.
Dyes	Acid Blue 92 (Synthetic)	$C_0 = 100 \text{ mg L}^{-1}$, [PS] = 0.5 mM, T = 60°C, pH = 4.6, Time = 80 min	65%, 0.0018 min ⁻¹ , 17.38 kJ mol ⁻¹ , TOC removal (%) = 89.2	[51]
	Methylene blue (Synthetic)	$C_0 = 311.8 \mu\text{M}$, [PS] ₀ = 10 mM, [SPS] ₀ /[Cl] ₀ > 640, T = 70°C, Time = 20 min	100%, 107.4 (± 24.4) kJ mol ⁻¹	[52]
Radiographic contrast medium	CR (Synthetic)	$C_0 = 20 \text{ mg L}^{-1}$, [PS] = 1 mM, T = 60°C, pH = 7, Time = 180 min	98%, $9.156 \times 10^{-2} \text{ min}^{-1}$, 76 (± 0.8) kJ mol ⁻¹	[53]
	Iohexol (Synthetic)	$C_0 = 0.01 \text{ mM}$, [PS] = 0.25 mM, T = 60°C, pH = 7, Time = 180 min	100%, $1.5 \times 10^{-4} \text{ s}^{-1}$, 122.2 ± 2.8 kJ mol ⁻¹ , TOC removal (%) = 3.7	[54]

As lower RSE values can indicate lower consumption of PS towards pollutant degradation resulting in lower reaction rate constants and vice-a-versa [37]. This highlights that the estimation of RSE is an important aspect for the degradation of organic pollutants with TAP.

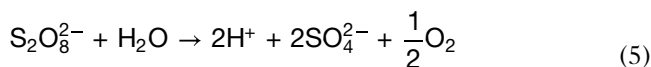
Temperature

The critical parameter in this process is temperature. In most of the studies, the temperature was varied from 20 to 70°C; however, most effective processes were reported for temperatures of at least 60°C [58]. Higher temperature causes high abundance of reactive species as well as increases the reaction rate for the interaction of reactive species with pollutants [18]. However, high temperature of treatment increases energy consumption. Thus, for the real applications, most of the studies were performed in temperature range of 40–60°C [59]. The temperature effect is also useful in the calculation of activation energy using the Arrhenius equation (Eq. 4) [34,51].

$$\ln k_{\text{obs}} = \ln A - E_a/RT \quad (4)$$

In this equation k_{obs} is the rate constant obtained from the pseudo-first-order kinetics, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. As given in Table 1, the calculated E_a for the PS oxidation of pollutants was in the range of 95–180 kJ mol⁻¹ [34–36,39,51,58].

Moreover, raising the temperature not only results in excess consumption of energy but also leads to some side reactions due to the unproductive decomposition of PS. Dominguez et al. state that the PS activation takes place by two parallel reactions; 1) the reaction resulting in the formation of $\text{SO}_4^{\bullet-}$ (Eq. 2), and 2) the unproductive decomposition of PS as given in Eq. (5) [3,56].



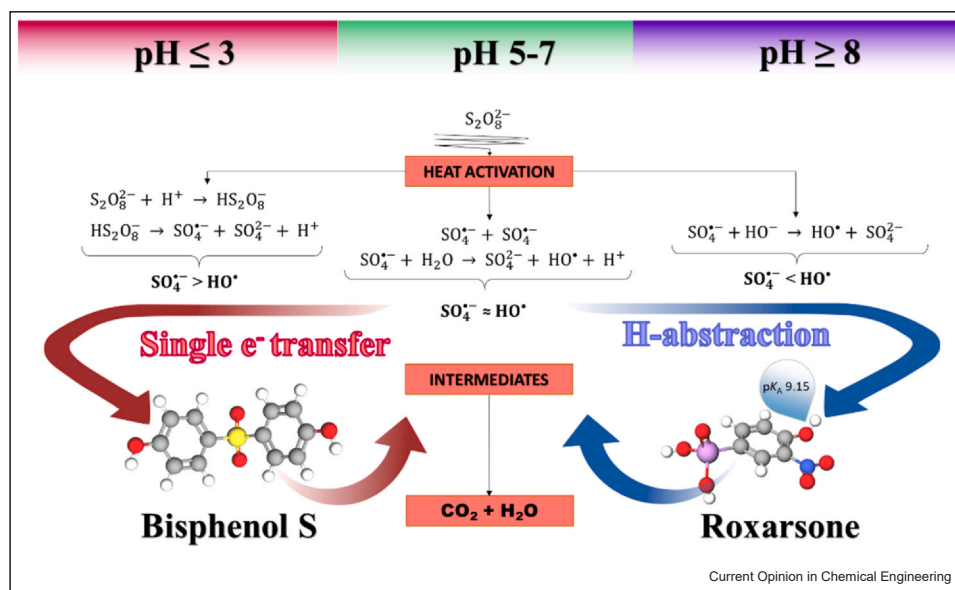
Goulden and Anthony and Dominguez et al. have reported that, the higher temperatures favors the rate of PS decomposition over that of PS oxidation as the E_a for PS decomposition was estimated as 128.48–140.16 kJ mol⁻¹ whereas E_a for oxidation of pollutants by PS was found to be 102.4–115.72 kJ mol⁻¹ [56,60].

Initial pH

pH is another important parameter in any oxidation process. Under acidic pH, the H^+ ions react with PS to generate more easily oxidizing species, $\text{SO}_4^{\bullet-}$ as given in the Eqs. (6) and (7) [52].



Figure 1



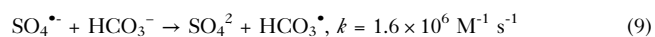
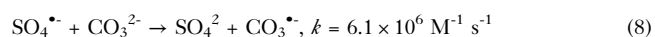
Reactive species involved in the TAP method under varying pH and their reaction towards model compound.

As can be seen from Figure 1, the major reactive species involved under acidic pH is $\text{SO}_4^{\bullet-}$. On the other hand, when the pH is increased in such cases, the decomposition of PS decreases which can affect the degradation rate [18]. The high pH range accelerates the conversion of $\text{SO}_4^{\bullet-}$ to $\cdot\text{OH}$ and the removal rate depends on the reactivity of pollutants towards $\cdot\text{OH}$ and the stability of $\cdot\text{OH}$ at alkaline pH conditions [52]. Being a selective oxidant, electron transfer is the main reaction of $\text{SO}_4^{\bullet-}$ [23]. This is clear in the case of Bisphenol S, where the higher degradation was observed at acidic pH and decreased with an increase in pH [47]. On the other hand, $\cdot\text{OH}$ reacts nonselectively preferentially via addition to C=C double bonds, electron transfer and H-abstraction from C-H, N-H, or O-H bonds. Furthermore, the ionization and speciation of pollutants also played an important role in the degradation of pollutants. For instance, sulfamethazine, pK_a values at 2.79 and 7.45 for the amine group and NH group of sulfonamide group, respectively. The protonation at the amine group restricted the delocalization of lone pair of electrons from through the aromatic rings and reduced the reactivity towards the electrophilic reactive species [23]. In contrast to this, the oxidation was enhanced by the electron-withdrawing effect on aniline by the deprotonation of NH of sulfonamide group. In the case of roxarsone (ROX), it has three pK_a values such as 3.45, 5.95 and 9.15 for arsenic and hydroxyl groups, respectively. The electron density around the aromatic ring increased with the increase of pH due to the deprotonation. These factors increased the removal efficiency by facilitating the reaction with reactive species [35,41].

The difference in the degradation of selected contaminants at varying pHs is given in Figure 1.

Applicability of the thermally activated persulfates in real systems

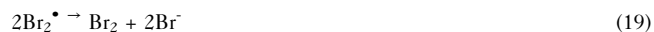
Many real samples contain several organic matrices and inorganic ions in large amounts which affects the removal of pollutants due to the scavenging of the reactive species by the ions [61]. For example, the bicarbonate ions and organic matrix inhibited the removal of pollutants due to the scavenging of the reactive species by the ions as presented in Eqs. (8)–(10) [5,18,47].



In addition, many other adverse effects of the inorganic ions on the degradation of pollutants in TAP were also observed. The chloride and bicarbonate ions, decreased the degradations for the pollutants such as bisphenol S [47], BPA [50], simazine [42], losartan [33], carbamazepine [31], thiamethoxam [38], etc. However, in the case of triclosan, ROX, chloroxylenol an inhibition in the degradation was observed at the lower concentration of Cl^- ion and an increase in the concentration enhanced the degradation [32,35,41]. The Cl^- ions scavenge the reactive species to form reactive chlorine species such as Cl^{\bullet} ($E^0 = 2.4 \text{ V}$), and $\text{Cl}_2^{\bullet-}$ ($E^0 = 2.4 \text{ V}$) and HOCl (E^0

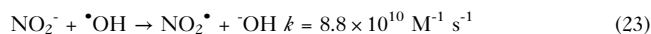
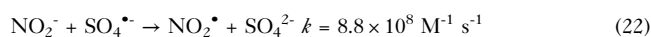
= 1.48 V) (Eqs. 11–14) which are having lower reactivity compared to the oxygen species. This reaction inhibited the degradation of the target pollutants. On the other hand, high concentration of Cl^- increases the concentration of reactive chlorine species in the medium. This may enhance the degradation of the pollutant. The inorganic ions like nitrite ions affect the transformation of phenols, as it forms nitro derivatives of the parent pollutants [62,63]. It is reported that nitrite ions in PS-based degradation processes generates a variety of toxic nitro-products [64]. Thus, it necessitates the consideration to appropriately address this kind of processes.

Wang et al. investigated the influence of Br^- on the degradation of diethyl phthalate (DEP) [44]. The process resulted in the formation of brominated disinfection by-products (Br-DBPs) such as dibromoacetonitrile and bromoform in the presence of Br^- ions and natural organic matter (NOM) in the solution. However, only bromoform was detected in the absence of NOM. The reactive bromine species formed by the scavenging reaction of Br^- and the reactive species ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) are capable to react with the phenolic group of the parent compound, intermediate by-product, and NOM to form Br-DBPs (Eqs. 15–21) [44,65,66].



Another issue associated with the degradation of pollutants in the PS-based processes is the interferences from the mineralized nitrogen species. It is observed in the case of ROX, which contains nitro-group in the structure. In this case, nitro-group initially undergoes denitration processes to release the nitrite ion in the solution. These nitrite ions further scavenge $\text{SO}_4^{\bullet-}$ radicals in the medium to form nitrite radicals (Eqs. 22 and 23), which

can react with the target pollutants to form the nitro-products [63].



In the same way, the organic matrix such as humic acid contains many electron-rich centers [55]. The bimolecular rate constant for the reaction of organic matrix with reactive species is $2.35 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ respectively for $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$. Therefore, the reactive species can be directed towards these species instead of the pollutants. Another possible effect of NOM is their ability to adsorb the pollutants through complexation reaction. This may reduce their availability in the reaction medium for the reaction with the reactive species [66]. As a result, the degradation of the pollutants can decrease to a large extent in the case of TAP process.

Synergistic application of thermally activated persulfate with other activators

Further research is being carried out to enhance the performance of TAP to implement the process to the contaminated soil sites and wastewater streams. Recently, application of more than one activator along with the heat to activate the PS is reported. Although TAP is an efficient process, the use of combined/hybrid processes can change the pathway of pollutant decomposition, mineralization, and, therefore, the toxicity of the transformation products [33]. The alkalies, Fe^{2+} metal ions, catalysts, cavitation, binary oxidants, etc. are some of the recent approaches employed to enhance the removal efficiency of TAP [21,59,67,68]. Can-Guven et al. have studied the possibility of sequential treatment methods such as coagulation and TAP process for the treatment of landfill leachate. PS-peroxide (PS/PO) binary system had been used in this study and offered 98% of chemical oxygen demand (COD) removal, which is far better than the individual system. The TAP with binary system generated abundant of reactive oxidation species such as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ [67]. Checa-Fernandez et al. attempted treatment of real soil contaminated with hexachlorocyclohexanes (α -HCH and β -HCH) using combined thermal and alkaline activation of PS. At the optimized operating conditions of $\text{pH} > 12$, simultaneous addition of PS and NaOH, 50°C , $\text{PS} = 40 \text{ g L}^{-1}$, liquid/soil ratio = 2, $\text{NaOH/PS} = 2$ and 100 rpm, they have achieved 100% conversion of α -HCH while 81% conversion of β -HCH with a dechlorination degree of 94% in 3 days. [69]. Further, Garcia-Cervilla et al. have studied the remediation of soil contaminated with lindane via alkaline activated PS. Around 70–96% conversion of chlorinated organic compounds was reported after 21 days with 400 mM PS and 400 mM NaOH. Also, the presence of oxidation by-products such as chlorinated or

aromatic organic compounds was not detected [70]. This suggests that the synergistic activation of PS by alkali and temperature can be opted as an effective method for the remediation of HCHs in the soil. The cavitation is an emerging method for the activation of several oxidants, including PS [16,71]. A high temperature obtained near the collapsing cavitation bubbles is sufficient for the pyrolytic cleavage of the water molecule to the respective reactive species as well as thermal-activation of oxidants. Lebig-Elhadi et al. performed the degradation of a pesticide, thiamethoxam using the combination of thermal and ultrasound activation for PS (US-TAP). It provided complete removal of the pollutants in 60 min [38]. However, the energy requirement for TAP is lesser as compared to the US-TAP system. The activating nanomaterial, MnO₂ in conjunction with TAP has been tested for the removal of organic contaminants. The system was highly effective for the removal of contaminants (heterocyclic groups, aniline, carboxyphenyl and azo benzene) irrespective of its structure. An important advantage of MnO₂-TAP system is that it can be operated at a temperature of 50°C [59]. The combination of US, TAP, and an Fe containing material Fe₃O₄@AC have further resulted in the reduction of the operational temperature to 30°C with a complete removal of organics. In this case, the predominating form responsible for degradation was singlet oxygen, ¹O₂ [68]. The temperature could also be reduced with the use of carbon catalysts in the TAP system. The temperature promoted the water oxidation on the surface of carbon catalyst [72]. The pretreatment of perfluorooctanesulfonic acid contaminated soil with alkali resulted in the enhancement of the removal in TAP process [73].

Though TAP and TAP along with other PS activators has proven to be efficient in terms of pollutants and TOC abatement, the feasibility of using a method in the oxidation of wastewater as an alternative to the other traditional and advanced treatment methods is determined by the evaluation of cost based on the electrical energy and oxidizing agent consumption [74]. A common approach to calculate the energy requirements of physicochemical processes is the calculation of energy per order (EEO). EEO defines the energy required to reduce the concentration of an organic pollutant by an order of magnitude in one cubic meter of wastewater [33]. In line with this the efficiency of the TAP or TAP hybrid systems can be evaluated through TOC removal and pollutant degradation, the electrical energy consumed, PS consumed, and total cost. Ioannidi et al. [33] have showed the cost effectiveness and feasibility of US-TAP process for the removal of losartan present in environmental water matrices. They have noted a prominent effect on the removal of losartan especially in various water matrices with US-TAP. The synergy between the processes is likely due to the additional

generation of reactive species from the direct sonolysis of water and PS and the thermal decomposition of pollutants in the cavitating bubbles. The competitive EEO of 3.981×10^3 kWh/m³/order for the decomposition of 500 µg/L losartan in wastewater was reported by Ioannidi et al. [33]. Whereas, the EEO reported by Patidar and Srivastava for the degradation of ofloxacin with only US was 28.572×10^3 kWh/m³/order, with US/UV/H₂O₂ was 3.942×10^3 kWh/m³/order and with US/UV/H₂O₂/TiO₂ was 1.191×10^3 kWh/m³/order [75]. This implies that if PS is co-activated with heat, US and metal nanoparticle catalyst the dramatic decrease in EEO and increase in TOC removal and pollutant degradation can be achieved. However, application of US requires large amounts of energy, making it viable only in particular cases. An alternative to the US is the use of HC, which has significantly fewer energy needs and allows easier scaling up compared to conventional ultrasonic chemistry [16]. Yabalak has estimated the electrical energy consumption for the remediation of agrochemical wastewater with TAP as 529.5 kWhm⁻³ and stated its competitiveness in comparison with various AOPs [74]. Ushani et al. have mentioned that the PS activation with Fe²⁺ can be more significant than other transition metals. As the application of naturally found iron minerals for PS activation has shown significant reduction in the cost to 37 000 \$ per year with 75% efficacy [9]. Further, Zhou et al. have shown that the sludge dewaterability of 50% was obtained with only [•]OH and SO₄^{•-}, whereas, its combination with Fe⁰ resulted in the 29% saving of the expenses (\$155 600 per year) in comparison with the conventional Fenton process [76]. Based on the reports, the TAP and TAP hybrid processes were found to be feasible on the basis of cost required for the requirement of oxidizing agent and its primary treatments. However, the energy requirement for the process is considerable to overcome hazardous effects of micropollutants.

Conclusion and future prospective

Thermally activated PS is one of promising possible alternatives to classic AOPs to degrade the persistent organic pollutants. Lower temperature values below 60°C are preferable in order to avoid large excess of energy for heating. In most of the cases, the extent of pollutant degradation is brought above 90%, in some cases the degradation efficiency even achieves the complete mineralization. The concentration ratio of PS to organic pollutant seems to be needed in the range of 20–500. It needs to be further optimized based on the organic load. Values below five are preferred to name the process economic in relation to oxidant usage and costs. The presence of bicarbonates and chloride anions have unfavorable effect and very few cases reported the favorable impact on degradation kinetics. In many papers this aspect was not studied. It limits the spectrum of data

obtained from presented studies, as sometimes chloride ions were reported to improve the degradation in AOPs.

Moreover, presence of nitrite ions causes generation of nitro-products and many brominated disinfection by-products in the presence of NOM. Thus, the water constituent should be monitored before the real scale application and proper measures should be taken to reduce the formation of toxic by-products. Another important challenge in the real application of TAP is the requirement of the high temperature input. The authors should address the aspects of energy/heat recovery from discharged effluents to improve energy balance. However, the addition of nanomaterials in the TAP process can reduce the temperature requirement to 30–50°C. Therefore, such kind of techniques will be more suitable for the treatment of organic pollutants contaminated site.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
 - of outstanding interest
1. Wang JL, Xu LJ: **Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application.** *Crit Rev Environ Sci Technol* 2012, **42**:251-325, <https://doi.org/10.1080/10643389.2010.507698>
 2. Boczkaj G, Fernandes A: **Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review.** *Chem Eng J* 2017, **320**:608-633, <https://doi.org/10.1016/J.CEJ.2017.03.084>
 3. Kolthoff IM, Miller IK: **The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium.** *J Am Chem Soc* 1951, **73**:3055-3059, <https://doi.org/10.1021/ja011151a024>
 4. Wang J, Wang S: **Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants.** *Chem Eng J* 2018, **334**:1502-1517, <https://doi.org/10.1016/J.CEJ.2017.11.059>
 5. Rayaroth MP, Lee CS, Aravind UK, Aravindakumar CT, Chang YS: **Oxidative degradation of benzoic acid using Fe0- and sulfidized Fe0-activated persulfate: a comparative study.** *Chem Eng J* 2017, **315**:426-436, <https://doi.org/10.1016/j.cej.2017.01.031>
 6. Ike IA, Linden KG, Orbell JD, Duke M: **Critical review of the science and sustainability of persulphate advanced oxidation processes.** *Chem Eng J* 2018, **338**:651-669, <https://doi.org/10.1016/j.cej.2018.01.034>
 7. Matzek LW, Carter KE: **Activated persulfate for organic chemical degradation: a review.** *Chemosphere* 2016, **151**:178-188, <https://doi.org/10.1016/j.chemosphere.2016.02.055>
 8. Waclawek S, Lutze HV, Grübel K, Padil VVT, Černík M, Dionysiou DD: **Chemistry of persulfates in water and wastewater treatment: a review.** *Chem Eng J* 2017, **330**:44-62, <https://doi.org/10.1016/j.cej.2017.07.132>
 9. Ushani U, Lu X, Wang J, Zhang Z, Dai J, Tan Y, Wang S, Li W, Niu C, Cai T, Wang N, Zhen G: **Sulfate radicals-based advanced oxidation technology in various environmental remediation: a state-of-the-art review.** *Chem Eng J* 2020, **402**:126232, <https://doi.org/10.1016/j.cej.2020.126232>
 10. Qian Y, Guo X, Zhang Y, Peng Y, Sun P, Huang CH, Niu J, Zhou X, Crittenden JC: **Perfluorooctanoic acid degradation using UV-persulfate process: modeling of the degradation and chlorate formation.** *Environ Sci Technol* 2016, **50**:772-781, <https://doi.org/10.1021/acs.est.5b03715>
 11. Yabalak E, Elneccar F: **Evaluation of watermelon peel, banana peel and bay leaves hydrochars as green catalysts in the degradation of malachite green by thermally activated persulfate oxidation method.** *J Environ Manag* 2022, **304**:114311, <https://doi.org/10.1016/j.jenvman.2021.114311>
 12. Li YT, Zhang JJ, Li YH, Chen JL, Du WY: **Treatment of soil contaminated with petroleum hydrocarbons using activated persulfate oxidation, ultrasound, and heat: a kinetic and thermodynamic study.** *Chem Eng J* 2022, **428**:131336, <https://doi.org/10.1016/j.cej.2021.131336>
 13. Preethi J, Rajesh Banu V, Godvin Sharmila S, Kavitha S, Varjani G, Kumar M, Gunasekaran: **Alkali activated persulfate mediated extracellular organic release on enzyme secreting bacterial pretreatment for efficient hydrogen production.** *Bioresour Technol* 2021, **341**:125810, <https://doi.org/10.1016/j.biortech.2021.125810>
 14. Soltani RDC, Mahmoudi M, Boczkaj G, Khataee A: **Activation of peroxymonosulfate using carbon black nano-spheres/calcium alginate hydrogel matrix for degradation of acetaminophen: Fe3O4 co-immobilization and microbial community response.** *J Ind Eng Chem* 2020, **91**:240-251, <https://doi.org/10.1016/J.JIEC.2020.08.006>
 15. Park S, Lee LS, Medina VF, Zull A, Waisner S: **Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation.** *Chemosphere* 2016, **145**:376-383, <https://doi.org/10.1016/j.chemosphere.2015.11.097>
 16. Fedorov K, Sun X, Boczkaj G: **Combination of hydrodynamic cavitation and SR-AOPs for simultaneous degradation of BTEX in water.** *Chem Eng J* 2020, **417**:128081, <https://doi.org/10.1016/j.cej.2020.128081>
 17. Wei Z, Villamena FA, Weavers LK: **Kinetics and mechanism of ultrasonic activation of persulfate: an in situ EPR spin trapping study.** *Environ Sci Technol* 2017, **51**:3410-3417, <https://doi.org/10.1021/acs.est.6b05392>
 18. Liu Y, Wang S, Wu Y, Chen H, Shi Y, Liu M, Dong W: **Degradation of ibuprofen by thermally activated persulfate in soil systems.** *Chem Eng J* 2019, **356**:799-810, <https://doi.org/10.1016/j.cej.2018.09.002>
 19. Yabalak E, Ozay Y, Vatanpour V, Dizge N: **Membrane concentrate management for textile wastewater with thermally activated persulfate oxidation method.** *Water Environ J* 2021, **35**:1281-1292, <https://doi.org/10.1111/wej.12718>
 20. Liang C, Su HW: **Identification of sulfate and hydroxyl radicals in thermally activated persulfate.** *Ind Eng Chem Res* 2009, **48**:5558-5562, <https://doi.org/10.1021/ie9002848>
 21. Zhao D, Liao X, Yan X, Huling SG, Chai T, Tao H: **Effect and mechanism of persulfate activated by different methods for PAHs removal in soil.** *J Hazard Mater* 2013, **254-255**:228-235, <https://doi.org/10.1016/j.jhazmat.2013.03.056>

22. Calenciuc C, Fdez-Sanromán A, Lama G, Annamalai S, Sanromán A, Pazos M: **Recent developments in advanced oxidation processes for organics-polluted soil reclamation.** *Catalysts* 2022, **12**:64, <https://doi.org/10.3390/catal12010064> 1-24.
23. Fan Y, Ji Y, Kong D, Lu J, Zhou Q: **Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process.** *J Hazard Mater* 2015, **300**:39-47, <https://doi.org/10.1016/j.jhazmat.2015.06.058>
24. Qiong Gao Y, Nan Fang J, Yun Gao N, Nong Yi X, Mao W, Zhang J: **Kinetic and mechanistic investigations of the degradation of propranolol in heat activated persulfate process.** *RSC Adv* 2018, **8**:41163-41171, <https://doi.org/10.1039/c8ra08488b>
25. Waldemer RH, Tratnyek PG, Johnson RL, Nurmi JT: **Oxidation of chlorinated ethenes by heat-activated persulfate: kinetics and products.** *Environ Sci Technol* 2007, **41**:1010-1015, <https://doi.org/10.1021/es062237m>
26. Liu L, Lin S, Zhang W, Farooq U, Shen G, Hu S: **Kinetic and mechanistic investigations of the degradation of sulfachloropyridazine in heat-activated persulfate oxidation process.** *Chem Eng J* 2018, **346**:515-524, <https://doi.org/10.1016/j.cej.2018.04.068>
27. Tan C, Gao N, Deng Y, Li L, Deng J, Zhou S: **Kinetic oxidation of antipyrine in heat-activated persulfate.** *Desalin Water Treat* 2015, **53**:263-271, <https://doi.org/10.1080/19443994.2013.848414>
28. Nie M, Yang Y, Zhang Z, Yan C, Wang X, Li H, Dong W: **Degradation of chloramphenicol by thermally activated persulfate in aqueous solution.** *Chem Eng J* 2014, **246**:373-382, <https://doi.org/10.1016/J.CEJ.2014.02.047>
29. Chen Y, Deng P, Xie P, Shang R, Wang Z, Wang S: **Heat-activated persulfate oxidation of methyl- and ethyl-parabens: effect, kinetics, and mechanism.** *Chemosphere* 2017, **168**:1628-1636, <https://doi.org/10.1016/j.chemosphere.2016.11.143>
30. Ghauch A, Tuqan AM, Kibbi N: **Ibuprofen removal by heated persulfate in aqueous solution: a kinetics study.** *Chem Eng J* 2012, **197**:483-492, <https://doi.org/10.1016/j.cej.2012.05.051>
31. Deng J, Shao Y, Gao N, Deng Y, Zhou S, Hu X: **Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water.** *Chem Eng J* 2013, **228**:765-771, <https://doi.org/10.1016/j.cej.2013.05.044>
32. Sun Y, Zhao J, Zhang BT, Li J, Shi Y, Zhang Y: **Oxidative degradation of chloroxylenol in aqueous solution by thermally activated persulfate: kinetics, mechanisms and toxicities.** *Chem Eng J* 2019, **368**:553-563, <https://doi.org/10.1016/j.cej.2019.02.208>
33. Ioannidi A, Arvaniti OS, Nika MC, Aalizadeh R, Thomaidis NS, Mantzavinos D, Frontistis Z: **Removal of drug losartan in environmental aquatic matrices by heat-activated persulfate: kinetics, transformation products and synergistic effects.** *Chemosphere* 2022, **287**:131952, <https://doi.org/10.1016/j.chemosphere.2021.131952>
34. Ghauch A, Tuqan AM: **Oxidation of bisoprolol in heated persulfate/H₂O systems: kinetics and products.** *Chem Eng J* 2012, **183**:162-171, <https://doi.org/10.1016/j.cej.2011.12.048>
35. Ji Y, Shi Y, Kong D, Lu J: **Degradation of roxarsone in a sulfate radical mediated oxidation process and formation of polynitrated by-products.** *RSC Adv* 2016, **6**:82040-82048, <https://doi.org/10.1039/c6ra17764f>
36. Milh H, Schoenaers B, Stesmans A, Cabooter D, Dewil R: **Degradation of sulfamethoxazole by heat-activated persulfate oxidation: elucidation of the degradation mechanism and influence of process parameters.** *Chem Eng J* 2020, **379**:122234, <https://doi.org/10.1016/j.cej.2019.122234>.
This paper reported the degradation of sulfamethoxazole. It covers all the possible parameters that are affecting the process. The product analysis and toxicity analysis are the important highlight of this paper.
37. Ghauch A, Tuqan AM, Kibbi N: **Naproxen abatement by thermally activated persulfate in aqueous systems.** *Chem Eng J* 2015, **279**:861-873, <https://doi.org/10.1016/j.cej.2015.05.067>
38. Lebik-Elhadi H, Frontistis Z, Ait-Amar H, Madjene F, Mantzavinos D: **Degradation of pesticide thiamethoxam by heat — activated and ultrasound — activated persulfate: effect of key operating parameters and the water matrix.** *Process Saf Environ Prot* 2020, **134**:197-207, <https://doi.org/10.1016/j.psep.2019.11.041>.
This paper reported the combined effect of heat and ultrasound on the activation of PS. The cavitation process generated high temperature in side the reaction medium and the external source of heat further enhanced the activation and the subsequent oxidation of pollutants.
39. Tan C, Gao N, Deng Y, An N, Deng J: **Heat-activated persulfate oxidation of diuron in water.** *Chem Eng J* 2012, **203**:294-300, <https://doi.org/10.1016/j.cej.2012.07.005>
40. Ji Y, Dong C, Kong D, Lu J, Zhou Q: **Heat-activated persulfate oxidation of atrazine: implications for remediation of groundwater contaminated by herbicides.** *Chem Eng J* 2015, **263**:45-54, <https://doi.org/10.1016/j.cej.2014.10.097>
41. Gao H, Chen J, Zhang Y, Zhou X: **Sulfate radicals induced degradation of Triclosan in thermally activated persulfate system.** *Chem Eng J* 2016, **306**:522-530, <https://doi.org/10.1016/j.cej.2016.07.080>
42. Ren W, Huang X, Wang L, Liu X, Zhou Z, Wang Y, Lin C, He M, Ouyang W: **Degradation of simazine by heat-activated peroxydisulfate process: a coherent study on kinetics, radicals and models.** *Chem Eng J* 2021, **426**:131876, <https://doi.org/10.1016/j.cej.2021.131876>.
This paper has utilised a steady-state model and unsteady-state model to describe the heat activated PS. and thus opened theoretical reference for the heat activated PS process for various environmental applications.
43. Dominguez CM, Checa-Fernandez A, Romero A, Santos A: **Degradation of HCHs by thermally activated persulfate in soil system: effect of temperature and oxidant concentration.** *J Environ Chem Eng* 2021, **9**:105668, <https://doi.org/10.1016/j.jece.2021.105668>
44. Wang Z, Shao Y, Gao N, Lu X, An N: **Degradation kinetic of phthalate esters and the formation of brominated byproducts in heat-activated persulfate system.** *Chem Eng J* 2019, **359**:1086-1096, <https://doi.org/10.1016/j.cej.2018.11.075>
45. Zhang M, Chen X, Zhou H, Murugananthan M, Zhang Y: **Degradation of p-nitrophenol by heat and metal ions co-activated persulfate.** *Chem Eng J* 2015, **264**:39-47, <https://doi.org/10.1016/j.cej.2014.11.060>
46. Potakis N, Frontistis Z, Antonopoulou M, Konstantinou I, Mantzavinos D: **Oxidation of bisphenol A in water by heat-activated persulfate.** *J Environ Manag* 2017, **195**:125-132, <https://doi.org/10.1016/J.JENVMAN.2016.05.045>
47. Wang Q, Lu X, Cao Y, Ma J, Jiang J, Bai X, Hu T: **Degradation of Bisphenol S by heat activated persulfate: kinetics study, transformation pathways and influences of co-existing chemicals.** *Chem Eng J* 2017, **328**:236-245, <https://doi.org/10.1016/j.cej.2017.07.041>
48. Liu CS, Higgins CP, Wang F, Shih K: **Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by persulfate activation in water.** *Sep Purif Technol* 2012, **91**:46-51, <https://doi.org/10.1016/j.seppur.2011.09.047>
49. Liu J, Gong X, Song S, Zhang F, Lu C: **Heat-activated persulfate oxidation of chlorinated solvents in sandy soil.** *J Spectrosc* 2014, **2014**:578638, <https://doi.org/10.1155/2014/578638>
50. Liu J, Jiang S, Chen D, Dai G, Wei D, Shu Y: **Activation of persulfate with biochar for degradation of bisphenol A in soil.** *Chem Eng J* 2020, **381**:122637, <https://doi.org/10.1016/j.cej.2019.122637>
51. Ahmadi S, Igwegbe CA, Rahdar S: **The application of thermally activated persulfate for degradation of Acid Blue 92 in aqueous solution.** *Int J Ind Chem* 2019, **10**:249-260, <https://doi.org/10.1007/s40090-019-0188-1>
52. Ghauch A, Tuqan AM, Kibbi N, Geryes S: **Methylene blue discoloration by heated persulfate in aqueous solution.** *Chem Eng J* 2012, **213**:259-271, <https://doi.org/10.1016/j.cej.2012.09.122>
53. Luo C, Wu D, Gan L, Cheng X, Ma Q, Tan F, Gao J, Zhou W, Wang S, Zhang F, Ma J: **Oxidation of Congo red by thermally activated**

- persulfate process: kinetics and transformation pathway.** *Sep Purif Technol* 2020, **244**:116839, <https://doi.org/10.1016/j.seppur.2020.116839>
54. Hu CY, Hou YZ, Lin YL, Deng YG, Hua SJ, Du YF, Chen CW, Wu CH: **Investigation of iohexol degradation kinetics by using heat-activated persulfate.** *Chem Eng J* 2020, **379**:122403, <https://doi.org/10.1016/j.cej.2019.122403>
 55. Amasha M, Baalbaki A, Ghauch A: **A comparative study of the common persulfate activation techniques for the complete degradation of an NSAID: the case of ketoprofen.** *Chem Eng J* 2018, **350**:395-410, <https://doi.org/10.1016/j.cej.2018.05.118>
 56. Dominguez CM, Romero A, Lorenzo D, Santos A: **Thermally activated persulfate for the chemical oxidation of chlorinated organic compounds in groundwater.** *J Environ Manag* 2020, **261**:110240, <https://doi.org/10.1016/j.jenvman.2020.110240>
 57. Rayaroth MP, Oh D, Lee CS, Kang YG, Chang YS: **In situ chemical oxidation of contaminated groundwater using a sulfidized nanoscale zerovalent iron-persulfate system: insights from a box-type study.** *Chemosphere* 2020, **257**:127117, <https://doi.org/10.1016/j.chemosphere.2020.127117>
 58. Shuchi SB, Suhan MBK, Bin Humayun S, Haque ME, Islam MS: **Heat-activated potassium persulfate treatment of Sudan Black B dye: degradation kinetic and thermodynamic studies.** *J Water Process Eng* 2021, **39**:101690, <https://doi.org/10.1016/j.jwpe.2020.101690>
 59. Zhou T, Du J, Wang Z, Xiao G, Luo L, Faheem M, Ling H, Bao J: **Degradation of sulfamethoxazole by MnO₂/heat-activated persulfate: kinetics, synergistic effect and reaction mechanism.** *Chem Eng J Adv* 2022, **9**:100200, <https://doi.org/10.1016/j.cej.2021.100200>
 60. Goulden PD, Anthony DHJ: **Kinetics of uncatalyzed peroxydisulfate oxidation of organic material in fresh water.** *Anal Chem* 1978, **50**:953-958, <https://doi.org/10.1021/ac50029a032>
 61. Rayaroth MP, Aravind UK, Aravindakumar CT: **Effect of inorganic ions on the ultrasound initiated degradation and product formation of triphenylmethane dyes.** *Ultrason Sonochem* 2018, **48**:482-491, <https://doi.org/10.1016/j.ultsonch.2018.07.009>
 62. Wu Y, Bu L, Duan X, Zhu S, Kong M, Zhu N, Zhou S: **Mini review on the roles of nitrate/nitrite in advanced oxidation processes: radicals transformation and products formation.** *J Clean Prod* 2020, **273**:123065, <https://doi.org/10.1016/j.jclepro.2020.123065>
 63. Rayaroth MP, Aravindakumar CT, Shah NS, Boczkaj G: **Advanced oxidation processes (AOPs) based wastewater treatment – unexpected nitration side reactions – a serious environmental issue: a review.** *Chem Eng J* 2022, **430**:133002, <https://doi.org/10.1016/j.cej.2021.133002>.
This paper reviewed the formation of nitro-products especially for the nitrogen containing organic pollutants in various AOPs. The heat activated PS also generating such unexpected products. This review detailed the mechanism for the nitroproduct formation and their environmental impacts
 64. Yang P, Ji Y, Lu J, Huang Q: **Formation of nitrophenolic byproducts during heat-activated peroxydisulfate oxidation in the presence of natural organic matter and nitrite.** *Environ Sci Technol* 2019, **53**:4255-4264, <https://doi.org/10.1021/acs.est.8b06967>
 65. Manz KE, Adams TJ, Carter KE: **Furfural degradation through heat-activated persulfate: impacts of simulated brine and elevated pressures.** *Chem Eng J* 2018, **353**:727-735, <https://doi.org/10.1016/j.cej.2018.07.142>
 66. Wang Z, Shao Y, Gao N, Xu B, An N, Lu X: **Comprehensive study on the formation of brominated byproducts during heat-activated persulfate degradation.** *Chem Eng J* 2020, **381**:122660, <https://doi.org/10.1016/j.cej.2019.122660>.
This paper reported the formation of brominated disinfection by-products during the degradation of phthalates in the presence of Br- and organic matters. The intermediates of phthalates formed during the degradation had a prominent role on the formation of Br-DBPs. This paper has relevant terms of environmental point of view
 67. Can-Güven E, Yazici Guvenc S, Varank G: **Sequential coagulation and heat activated persulfate-peroxide binary oxidation process for landfill leachate treatment.** *J Water Process Eng* 2021, **42**:102202, <https://doi.org/10.1016/j.jwpe.2021.102202>
 68. Liu L, Yang C, Tan W, Wang Y, Wang Y: **Degradation of Acid Red 73 by activated persulfate in a Heat/Fe₃O₄@AC system with ultrasound intensification.** *ACS Omega* 2020, **5**:13739-13750, <https://doi.org/10.1021/acsomega.0c00903>
 69. Checa-Fernández A, Santos A, Romero A, Dominguez CM: **Remediation of real soil polluted with hexachlorocyclohexanes (α -HCH and β -HCH) using combined thermal and alkaline activation of persulfate: optimization of the operating conditions.** *Sep Purif Technol* 2021, **270**:118795, <https://doi.org/10.1016/j.seppur.2021.118795>
 70. García-Cervilla R, Santos A, Romero A, Lorenzo D: **Remediation of soil contaminated by lindane wastes using alkaline activated persulfate: kinetic model.** *Chem Eng J* 2020, **393**:124646, <https://doi.org/10.1016/j.cej.2020.124646>
 71. Fedorov K, Plata-Gryl M, Khan JA, Boczkaj G: **Ultrasound-assisted heterogeneous activation of persulfate and peroxymonosulfate by asphaltene for the degradation of BTEX in water.** *J Hazard Mater* 2020, **397**:122804, <https://doi.org/10.1016/j.jhazmat.2020.122804>
 72. Duan X, Indrawirawan S, Kang J, Tian W, Zhang H: **Synergy of carbocatalytic and heat activation of persulfate for evolution of reactive radicals toward metal-free oxidation.** *Catal Today* 2020, **355**:319-324, <https://doi.org/10.1016/j.cattod.2019.02.051>
 73. Shojaei M, Kumar N, Chaobol S, Wu K, Crimi M, Guelfo J: **Enhanced recovery of Per- And Polyfluoroalkyl Substances (PFASs) from impacted soils using heat activated persulfate.** *Environ Sci Technol* 2021, **55**:9805-9816, <https://doi.org/10.1021/acs.est.0c08069>
 74. Yabalak E: **Treatment of agrochemical wastewater by thermally activated persulfate oxidation method: evaluation of energy and reagent consumption.** *J Environ Chem Eng* 2021, **9**:105201, <https://doi.org/10.1016/j.jece.2021.105201>
 75. Patidar R, Srivastava VC: **Mechanistic and kinetic insights of synergistic mineralization of ofloxacin using a sono-photo hybrid process.** *Chem Eng J* 2021, **403**:125736, <https://doi.org/10.1016/j.cej.2020.125736>
 76. Zhen G, Lu X, Su L, Kobayashi T, Kumar G, Zhou T, Xu K, Li YY, Zhu X, Zhao Y: **Unraveling the catalyzing behaviors of different iron species (Fe²⁺ vs. Fe⁰) in activating persulfate-based oxidation process with implications to waste activated sludge dewaterability.** *Water Res* 2018, **134**:101-114, <https://doi.org/10.1016/j.watres.2018.01.072>