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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.

## Addresses

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## Introduction

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

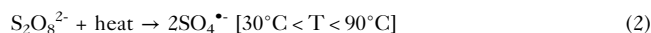
to the single treatment techniques. Advanced Oxidation Processes (AOPs) are one of the key methods for the treatment of wastewater containing recalcitrant pollutants [1,2]. Currently, big attention is made on persulfates ( $S_2O_8^{2-}$ , PS) based AOPs [3–9]. This type of oxidants demands effective 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<sup>-1</sup>, 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 ( $< 2 \times 10^{-3} \text{ s}^{-1}$ ) 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  $\text{pH}$  is increased to 9 [20]. The alkaline  $\text{pH}$  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  $60^\circ\text{C}$  [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  $60^\circ\text{C}$  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  $\text{Fe}^{2+}/\text{PS}$  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  $\text{pH} = 9.0$  (RSE = 0.25) and  $\text{pH} = 4.0$  (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  $\text{pH} 9.0$ , 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 <sub>0</sub> = 3.51 μM, [PS] = 140 μM, T = 40°C, pH = 3, Time = 180 min	100%, 0.178 min <sup>-1</sup> , 155 ± 15 kJ mol <sup>-1</sup>	[26]
	Propranolol (Synthetic)	C <sub>0</sub> = 0.025 mM, [PS] = 1 mM, T = 70°C, pH = 7, Time = 50 min	100%, 0.193 min <sup>-1</sup> , 99.0 kJ mol <sup>-1</sup>	[24]
	Antipyrine (Synthetic)	C <sub>0</sub> = 0.2 mM, [PS] = 4 mM, T = 70°C, pH = 5.4, Time = 120 min	TOC removal(%) = 13.6 100%, 0.004 s <sup>-1</sup> , 139.5 ± 9.7 kJ mol <sup>-1</sup>	[27]
	Chloramphenicol (Synthetic)	C <sub>0</sub> = 0.0265 mM, [PS] = 1.85 mM, T = 60°C, pH = 7, Time = 160 min	TOC removal(%) = 12.5 100%, 0.059 min <sup>-1</sup> , 103.1 kJ mol <sup>-1</sup>	[28]
	Methyl-parabens (MeP) and EtP (Synthetic)	C <sub>0</sub> = 20 μM, [PS] = 1 mM, T = 60°C, pH = 7, Time = 240 min	TOC removal(%) = 90 100%, 17.67 × 10 <sup>-3</sup> min <sup>-1</sup> and 18.37 × 10 <sup>-3</sup> min <sup>-1</sup> for MeP and EtP, 95.2 and 98.9 kJ mol <sup>-1</sup> for MeP and EtP, TOC removal(%) for MeP = 10.2, TOC removal(%) for EtP = 15	[29]
	Ibuprofen (Synthetic)	C <sub>0</sub> = 20.36 μM, [PS] = 1 mM, T = 70°C, pH = 7, Time = 60 min	100%, 0.192 min <sup>-1</sup> , 168( ± 9.5) kJ mol <sup>-1</sup>	[30]
	Carbamazepine (Synthetic)	C <sub>0</sub> = 40 μM, [PS] = 1 mM, T = 60°C, pH = 5, Time = 120 min	100%, 0.0566 min <sup>-1</sup> , 120.4 ± 2.6 kJ mol <sup>-1</sup>	[31]
	Chloroxylenol (Synthetic)	C <sub>0</sub> = 1.5 mM, [PS] = 75 mM, T = 60°C, pH = 5, Time = 120 min	100%, 0.02886 min <sup>-1</sup> , 130.4 kJ mol <sup>-1</sup>	[32]
	Losartan (Synthetic)	C <sub>0</sub> = 500 mg L <sup>-1</sup> , [PS] = 50 mg L <sup>-1</sup> , T = 50°C, pH = 5, Time = 45 min	100%, 0.0678 min <sup>-1</sup> , 112.70 kJ mol <sup>-1</sup>	[33]
	Bisoprolol (Synthetic)	C <sub>0</sub> = 50 μM, [PS] = 1 mM, T = 60°C, pH = 7, Time = 60 min	100%, 8.47 ± 0.31 min <sup>-1</sup> , 119.8( ± 10.8) kJ mol <sup>-1</sup>	[34]
Sulfamethaxazole (Synthetic)	ROX (Synthetic)	C <sub>0</sub> = 50 μM, [PS] = 2 mM, T = 60°C, pH = 7, Time = 480 min	98%, 0.0025 min <sup>-1</sup> , 102.4 ± 0.6 kJ mol <sup>-1</sup>	[35]
	Sulfamethaxazole (Synthetic)	C <sub>0</sub> = 100 mg L <sup>-1</sup> , [PS] = 5 mM, T = 70°C, pH = 4.6, Time = 480 min	99%, 0.01 min <sup>-1</sup> , 103 kJ mol <sup>-1</sup>	[36]
	Ibuprofen (IBP) in a soil system (Synthetic)	C <sub>0</sub> = 48.4–46.0 μM kg <sup>-1</sup> , [PS] = 20 mM kg <sup>-1</sup> , pH = 7.75, T = 50°C, Time = 120 min	81.9%, 0.0164 min <sup>-1</sup> , 132.12 kJ mol <sup>-1</sup>	[18]
	Sulfamethazine (Synthetic)	C <sub>0</sub> = 30 μM, [PS] = 2 mM, T = 60°C, pH = 7, Time = 120 min	100%, 0.84 min <sup>-1</sup> , 126 kJ mol <sup>-1</sup>	[23]
	Naproxen (Real)	C <sub>0</sub> = 50 μM; [PS] = 10 mM, T = 70°C, Time = 120 min	155.03 ( ± 26.4) kJ mol <sup>-1</sup> , degradation rate = 1.286 × 10 <sup>-2</sup> mM min <sup>-1</sup> , 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] = $100 \text{ mg L}^{-1}$ , T = $60^\circ\text{C}$ , pH = 7, Time = 120 min	100%, $0.2 \text{ min}^{-1}$ , $103.1 \text{ kJ mol}^{-1}$ , $108.7 \text{ kJ mol}^{-1}$ , TOC removal (%) = 95	[38]
	Diuron (Synthetic)	$C_0 = 0.0375 \text{ mM}$ , [PS] = $0.375 \text{ mM}$ , T = $60^\circ\text{C}$ , pH = 5.1, Time = 180 min	90%, $0.233 \text{ min}^{-1}$ , $166.7 \pm 0.8 \text{ kJ mol}^{-1}$ , TOC removal (%) = 15	[39]
	Atrazine (Synthetic)	$C_0 = 50 \text{ }\mu\text{M}$ , [PS] = 2 mM, T = $60^\circ\text{C}$ , pH = 7, Time = 120 min	$98\% \pm 0.028 \text{ min}^{-1}$ , $141 \text{ kJ mol}^{-1}$	[40]
	Triclosan (Real)	$C_0 = 0.031 \text{ mM}$ , [PS] = $0.155 \text{ mM}$ , T = $60^\circ\text{C}$ , pH = 7, Time = 500 min	100%, $0.0097 \text{ min}^{-1}$ , $121.12 \text{ kJ mol}^{-1}$ , TOC removal (%) = 11.5	[41]
	Simazine (Synthetic)	$C_0 = 10 \text{ }\mu\text{M}$ , [PS] = 0.1 mM, T = $65^\circ\text{C}$ , pH = 5, Time = 120 min	99%, $0.05 \text{ min}^{-1}$ , $118.45 \text{ kJ mol}^{-1}$	[42]
Industrial contaminants	Soils contaminated with HCHs (Real)	15 g of polluted soil ( $\alpha$ -HCH = $254 \text{ mg kg}^{-1}$ and $\beta$ -HCH = $99 \text{ mg kg}^{-1}$ ), [PS] = $80 \text{ g L}^{-1}$ , T = $55^\circ\text{C}$ , Time = 9 days	83%	[43]
	Phthalate esters (DEP and dibutyl phthalate (DBP)) (Synthetic)	$C_0 = 2 \text{ }\mu\text{M}$ , [PS] = 500 $\mu\text{M}$ , T = $60^\circ\text{C}$ , pH = 5.8, Time = 60 min	$0.4396 \text{ min}^{-1}$ , $125.4 \pm 18.6 \text{ kJ mol}^{-1}$ 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 = $70^\circ\text{C}$ , pH = 7, Time = 180 min	100%, $0.027 \text{ min}^{-1}$ , $127.8 (\pm 1.56) \text{ kJ mol}^{-1}$ , 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 = $70^\circ\text{C}$ , pH = 7, Time = 8 hours	100%, $0.967 \text{ hours}^{-1}$ , $101 \text{ kJ mol}^{-1}$ for PCE, $108 \text{ kJ mol}^{-1}$ for TCE, $144 \text{ kJ mol}^{-1}$ for cis-DCE, and $141 \text{ kJ mol}^{-1}$ for trans-DCE.	[25]
	Bisphenol A (Synthetic)	$C_0 = 220 \text{ }\mu\text{g L}^{-1}$ , [PS] = $625 \text{ mg L}^{-1}$ , T = $70^\circ\text{C}$ , pH = 6.5, Time = 60 min	100%, $1.73 \text{ min}^{-1}$ , $133.5 \text{ kJ mol}^{-1}$	[46]
	Bisphenol S (Synthetic)	$C_0 = 25 \text{ }\mu\text{M}$ , [PS] = 0.5 mM, T = $60^\circ\text{C}$ , pH = 7, Time = 180 min	TOC removal (%) = 28 $99\% \pm 0.02 \text{ min}^{-1}$ , $(112.9 \pm 6.8) \text{ kJ mol}^{-1}$ ,	[47]
	Perfluorooctanoic acid (Synthetic)	$C_0 = 0.5 \text{ }\mu\text{M}$ , [PS] = 10 mM, T = $85^\circ\text{C}$ , pH = 7, Time = 30 hours	TOC removal (%) = 27 $93.5\%$ , $9.15 \times 10^{-2} \text{ hours}^{-1}$ , $60 \text{ kJ mol}^{-1}$	[48]
	Chlorinated Solvents in Sandy Soil (Synthetic) [TCE, cis-1,2-DCE, 1,1,1-trichloroethane (TCA), and 1,2-dichloroethane (1,2-DCA)]	25 mL water and 25 g soil 7 $\mu\text{L}$ mixed contaminated solution (TCE- $81.8 \text{ mg L}^{-1}$ , cis-1,2-DCE- $71.2 \text{ mg L}^{-1}$ , TCA- $75.0 \text{ mg L}^{-1}$ , and 1,2-DCA- $70.6 \text{ mg L}^{-1}$ ), [PS] = 20 $\text{g L}^{-1}$ , Time = 72 hours	$79.5\% \pm 0.0035 \text{ hours}^{-1}$	[49]
	Bisphenol A (BPA) in soil (Synthetic)	BPA in soil = $31.93 \text{ mg kg}^{-1}$ , [PS] = 8 mM, $C_0 = 5 \text{ mg L}^{-1}$ , Biochar <sub>0</sub> = $1 \text{ g L}^{-1}$ , pH = 7, T = $25^\circ\text{C}$ , Time = 150 min	98.5%	[50]
	Total petroleum hydrocarbon (TPH) in soil (Synthetic)	ultrasonic power = 200 W, [PS] = 1 M, 10 gm = testing soil ( $19.850 \text{ mg kg}^{-1}$ ), pH = 7, water:soil ratio = 1:1, T = $50^\circ\text{C}$ , Time = 72 hours	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 <sup>-1</sup> , 17.38 kJ mol <sup>-1</sup> , TOC removal (%) = 89.2	[51]
	Methylene blue (Synthetic)	$C_0 = 311.8 \text{ } \mu\text{M}$ , [PS] <sub>0</sub> = 10 mM, [SPS] <sub>0</sub> /[Cl] <sub>0</sub> ≥ 640, T = 70°C, Time = 20 min	100%, 107.4 ( ± 24.4) kJ mol <sup>-1</sup>	[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 × 10 <sup>-2</sup> min <sup>-1</sup> , 76 ( ± 0.8) kJ mol <sup>-1</sup>	[53]
	Iohexol (Synthetic)	$C_0 = 0.01 \text{ mM}$ , [PS] = 0.25 mM, T = 60°C, pH = 7, Time = 180 min	100%, 1.5 × 10 <sup>-4</sup> s <sup>-1</sup> , 122.2 ± 2.8 kJ mol <sup>-1</sup> , 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.

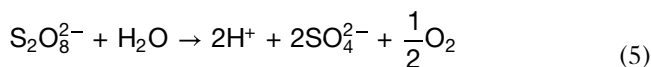
### Temperature

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  $k_{\text{obs}}$  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<sup>-1</sup> [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<sup>-1</sup> whereas  $E_a$  for oxidation of pollutants by PS was found to be 102.4–115.72 kJ mol<sup>-1</sup> [56,60].

### Initial pH

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

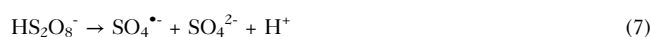
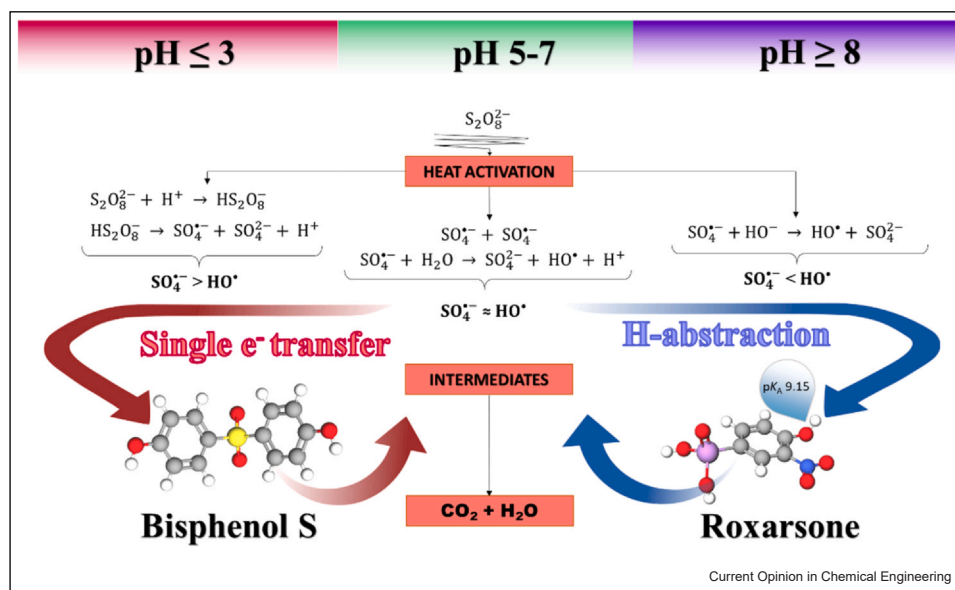




Figure 1



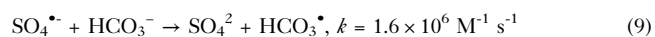
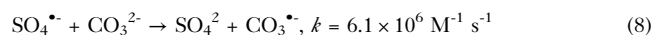
Reactive species involved in the TAP method under varying pH and their reaction towards model compound.

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,  $\text{pK}_a$  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  $\text{pK}_a$  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  $\text{Cl}^-$  ion and an increase in the concentration enhanced the degradation [32,35,41]. The  $\text{Cl}^-$  ions scavenge the reactive species to form reactive chlorine species such as  $\text{Cl}^{\bullet}$  ( $E^0 = 2.4 \text{ V}$ ), and  $\text{Cl}_2^{\bullet-}$  ( $E^0 = 2.4 \text{ V}$ ) and  $\text{HOCl}$  ( $E^0$

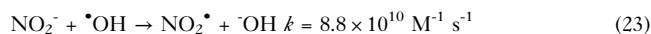
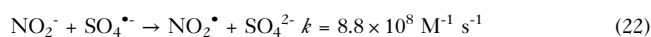
= 1.48 V) (Eqs. 11–14) which are having lower reactivity compared to the oxygen species. This reaction inhibited the degradation of the target pollutants. On the other hand, high concentration of  $\text{Cl}^-$  increases the concentration of reactive chlorine species in the medium. This may enhance 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  $\text{Br}^-$  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  $\text{Br}^-$  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  $\text{Br}^-$  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,  $\text{Fe}^{2+}$  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 ( $\alpha$ -HCH and  $\beta$ -HCH) using combined thermal and alkaline activation of PS. At the optimized operating conditions of  $\text{pH} > 12$ , simultaneous addition of PS and NaOH,  $50^\circ\text{C}$ ,  $\text{PS} = 40 \text{ g L}^{-1}$ , liquid/soil ratio = 2,  $\text{NaOH/PS} = 2$  and 100 rpm, they have achieved 100% conversion of  $\alpha$ -HCH while 81% conversion of  $\beta$ -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, MnO<sub>2</sub> 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 MnO<sub>2</sub>-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 Fe<sub>3</sub>O<sub>4</sub>@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, <sup>1</sup>O<sub>2</sub> [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  $3.981 \times 10^3$  kWh/m<sup>3</sup>/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  $28.572 \times 10^3$  kWh/m<sup>3</sup>/order, with US/UV/H<sub>2</sub>O<sub>2</sub> was  $3.942 \times 10^3$  kWh/m<sup>3</sup>/order and with US/UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> was  $1.191 \times 10^3$  kWh/m<sup>3</sup>/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<sup>-3</sup> and stated its competitiveness in comparison with various AOPs [74]. Ushani et al. have mentioned that the PS activation with Fe<sup>2+</sup> 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 SO<sub>4</sub>•<sup>-</sup>, whereas, its combination with Fe<sup>0</sup> 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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