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Sulfate radical advanced oxidation processes: activation methods and application to industrial wastewater treatment[†]

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Abstract: Industrial wastewater (IWW) generation is a serious problem when set free into environment in absence of appropriate treatment, therefore, industries spot for structured, easy and low-cost treatment processes. This review intends to present the applicability of sulfate radicals advanced oxidation processes (SR-AOPs) for IWW treatment. Different peroxymonosulfate (PMS), persulfate (PS) activation methods are addressed. Laboratory, pilot-scale enforcement of SR-AOPs in IWW treatment, with focus on the advantages and disadvantages of these processes, are presented.

Keywords: Oxidation potential; persulfate; peroxymonosulfate; UV activation

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1. Introduction

Industrial wastewaters (IWW) are derived from industrial activities, which comprehend dairy or breweries, paper industry, wine and olive production, among others. The physicochemical characteristics of these wastewaters are very wide range, with organic content reaching thousands mg/L, large pH range, and low biodegradability (Table 1). Therefore, an efficient strategy is required to degrade the organic content present [1,2]. Some authors criticized the widely use of physical or chemical processes due to the high solid waste, secondary contamination production. Therefore a necessity is imposed to search effective and environmentally friendly solutions to remove these organic contaminants, providing greater approach for removal of hazardous wastes before the wastewater is released into aquatic environments [3].

Advanced oxidation processes (AOPs) are an efficient process for pollutants degradation, based on hydroxyl radicals ($HO^{\bullet}$) generation. These radicals are extremely reactive, suited to oxidize an ample scope of contaminants, such as refractory contaminants, to innocuous compounds or reach thorough mineralization to CO_2, H_2O, and inorganic ions [2,4,5].

Considering the different AOPs, in this review it will be studied the application of sulfate radical AOPs (SR-AOPs) for IWW treatment. The interest in persulfate began around 2000 [6], since then, SR-AOPs have progressively attracted attention, complementing HR-AOPs. Sulfate radicals are produced with persulfate salts as chemical oxidants [7]. Peroxymonosulfate (HSO_5^-, PMS) and persulfate ($S_2O_8^{2-}$, PS) are operated as sources for SR-AOPs. Oxone ($2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$) generates PMS, while sodium persulfate ($Na_2S_2O_8$) and potassium persulfate ($K_2S_2O_8$) generates PS [4].

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Table 1. Physicochemical characteristics of industrial wastewaters. COD – chemical oxygen demand, BOD_5 – biochemical oxygen demand and BOD_5/COD – biodegradability.

IWW	COD	BOD_5	pH	BOD_5/COD
	mg O_2/L	mg O_2/L		
Landfill leachate	3000	< 300	> 7.5	< 0.1
Pharmaceutical	375 – 32 500	200 – 6000	3.9 – 9.2	0.1 – 0.6
Pulp and paper	900 – 3791	102 – 1197	6.5 – 10	< 0.2
Textile	300 – 12 000	188 – 550	2 – 13.5	< 0.4
Winery	11 886 – 15 553	6570 – 8858	5.3	< 0.3
Olive mill	12 000 – 220 000	3400 – 100 000	3.9 – 5.2	0.2 – 0.5
Dairy	4000 – 6000	2800 – 4480	6.5 – 12	> 0.5

PMS (white solid powder) is the active principle of $2KHSO_5{\bullet}KHSO_4{\bullet}K_2SO_4$. Presents stability with pH < 6 or pH = 12 and poor stability with pH = 9, due to half HSO_5^- decomposing to SO_5^{2-} [8]. PMS is quickly dissolved in water, with solubility > 250 g L^{-1}, acidic water solution, asymmetrical structure, distance O-O bond = 1.453 Å (bond energy ≈ 140–213.3 kJ/mol [8–11], and the oxidation potential of HSO_5^- ($E^0_{\frac{HSO_5^-}{HSO_4^-}}$=1.82 V) is higher than hydrogen peroxide ($E^0_{H_2O_2/H_2O}$=1.78 V), although lower than hydroxyl radical ($E^0_{HO^{\bullet}}$=2.80 V) [7].

PS (colorless, white crystal), with high stability is readily dissolved in water, solubility = 730 g L^{-1} [12], acidic water solution, symmetrical structure, O-O bond distance = 1.497 Å, bond energy = 140 kJ/mol [8,9]. Peroxydisulfate (PDS, $S_2O_8^{2-}$), is often found in the form of sodium persulfate, potassium persulfate, and ammonium persulfate ($(NH_4)_2S_2O_8$) [13]. Persulfate anion ($S_2O_8^{2-}$) is a strong oxidant ($E^0_{S_2O_8^{2-}/SO_4^{\bullet-}}$=2.01 V), activated by heat, light, ultrasound or catalyst, producing sulfate radicals ($SO_4^{\bullet-}$) [14,15].

In a Web of Science search using keywords "sulfate radicals", "Fenton" and "industrial wastewater", results showed 212 articles published involving the treatment of IWW by sulfate radicals, against 1622 articles involving treatment of IWW by Fenton, which shows a necessity to study sulfate radicals. The aim of this work is to present a review of the different sulfate radicals activation processes, evaluate the efficient of SR-AOPs in the treatment of IWW and highlight the advantages and disadvantages associated with the application of these radicals.

2. Activation methods

A number of methods are able to activate PS and PMS, such as heat, alkaline, radiation and transition metals [16].

2.1. Thermal activation

As observed, O-O bong energy was estimated in 140–213.3 kJ/mol, therefore, a high amount of energy is required. Energy input with elevated temperature (> 50 °C) application, causes O-O bond break to generate sulfate radicals as Equation 1 and Equation 2 [8]:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \qquad (1)$$

$$HSO_5^- \rightarrow SO_4^{\bullet-} + HO^{\bullet} \qquad (2)$$

2.2. Alkaline activation

In alkaline conditions, PS can be transformed in sulfate radicals, which further generates hydroxyl radicals. Liang and Su [17] and Yang et al., [18] observed inter-conversions among $SO_4^{\bullet-}$ and $HO^{\bullet}$: (1) pH < 7: $SO_4^{\bullet-}$ - prevalent radical; (2) pH = 9: $SO_4^{\bullet-}$ and $HO^{\bullet}$ - both present; (3) pH > 9: $HO^{\bullet}$ - dominating radical. PDS alkaline activation, O-O bond nucleophilic attack is design, main mechanism, shown in Equation 3 and Equation 4:

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + HO_2^- + H^+ \quad (3)$$

$$S_2O_8^{2-} + HO_2^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-} + H^+ \quad (4)$$

2.3. Radiation activation

PS and PMS activation is obtained by ultraviolet, gamma ray and ultrasonic radiation. sulfate radicals quantum yields decreases with UV wavelength increase (248 to 351 nm) [19], maximal quantum yield 1.4 (248 and 253.7 nm). Equation 5 – Equation 6 shows O–O bond fission by ultraviolet radiation [8], as follows:

$$S_2O_8^{2-} + UV/US \rightarrow 2SO_4^{\bullet-} \quad (5)$$

$$HSO_5^- + UV/US \rightarrow SO_4^{\bullet-} + HO^\bullet \quad (6)$$

2.4. Transition metal ions and metal oxide activation

Persulfate can be activated by transition metals like silver, copper, iron, zinc, cobalt and manganese. For PS and PMS activation by metal ions and metal oxide, a reduction mechanism takes place, as observed in Equation 7 and Equation 8 [8]:

$$S_2O_8^{2-} + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-} \quad (7)$$

$$HSO_5^- + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + HO^- \quad (8)$$

3. Application of sulfate radicals in wastewater treatment

Table 2 presents studies for treatment of IWW, employing sulfate radicals. It is shown the operational conditions and the attained efficiencies. In Jorge et al., [20], PMS was activated by cobalt ions in a UV-A LED reactor, for the treatment of WW. The conditions revealed to be effective for sulfate radical activation, with 82.3% COD removal. In a different work, olive mill wastewater (OMW) was treated by persulfate, activated by catalyst addition (Fe^{2+})[21]. Results showed that at near neutral conditions, persulfate (PS) could be activated, reaching 46.7% COD removal. In Rodríguez-Chueca et al., [22], real winery wastewater management by a solar-KPS-Fe^{2+} process, with results showing the highest TOC removal with 25/25 KPS/Fe^{2+}. Results showed that KPS was able to be activated by solar radiation, achieving high $SO_4^{\bullet-}$ radical generation, which in turn showed high efficiency to degrade the non-biodegradable matter existing in the WW. In Can-Güven et al., [23], paper mill wastewater treatment was performed, comparing an Fe^{2+}-PS vs heat-PS activation. Results showed that catalyst activation had higher efficiency regarding heat activation, although catalyst activation was dependent on the pH. When compared with studies involving application of HR-AOPs [24,25] for the treatment of IWW, results show a high consumption of H_2O_2, which increases treatment costs in comparison with the consumption of PMS and PDS.

Table 2. Application of sulfate radicals in wastewater treatment.

IWW	Operational conditions	Results	References
Winery wastewater (WW)	[PMS] = 5.88 mM $[Co^{2+}]$ = 5 mM pH = 6.0 UV-A LED (32.7 W m^{-2})	CODrem = 82.3%	Jorge et al., [20]
Olive mill wastewater (OMW)	[PS] = 206 mM $[Fe^{2+}]$ = 70 mM pH = 5.0 Time = 95 min	CODrem = 46.7%	Sinan Ateşa et al., [21]
Winery wastewater (WW)	[KPS] = 25 mM $[Fe^{2+}]$ = 25 mM pH = 4.5 Time = 180 min	TOCrem = 64%	Rodríguez-Chueca et al., [22]
Paper mill wastewater (PMW)	COD_{PMW} = 11700 mg O_2/L PS:COD ratio = 8.9 $[Fe^{2+}]$ = 100 mM pH = 3.0 Time = 92.92 min	CODrem = 72.7%	Can-Güven et al., [23]
Olive mill wastewater (OMW)	COD_{OMW} = 800 mg O_2/L [PS] = 600 mg/L $[Fe^{2+}]$ = 300 mg/L pH = 5.0	CODrem = 39%	Domingues et al., [26]
Municipal landfill leachate (MLL)	COD_{MLL} = 5650 mg O_2/L [PS] = 500 mg/L $[Fe^{2+}]$ = 100 mg/L pH = 3 Time = 120 min Voltage – 3 V	CODrem = 87.8%	Nidheesh et al., [27]

4. Benefits and limitations

The use of persulfate and peroxymonosulfate has several advantages in organic matter degradation: (1) they are reliable at ambient temperature, handle effortless [7], (2) $SO_4^{\bullet -}$ possess equal or even higher redox potential (2.5–3.1 V) than $HO^{\bullet}$ radicals [28], (3) higher selectivity, longer half-life (30–40 μs), than $HO^{\bullet}$ radicals (20 ns) [29]. However, there are several drawbacks associated with sulfate radical generation: (1) in heat activation, which involves increasing temperatures, it is accelerated the rate of reaction, however it can result in very aggressive oxidizing conditions and high energy consumption [6], (2) finite penetration of ultraviolet into water, unusable in subsurface, affecting UV-activated PS and PMS reactions, (3) difficulty of metal ions recovery in PS and PMS activation in homogeneous catalysis [8,30].

5. Conclusions

This work's main objective was systematized different activation methods used for sulfate radical generation. In addition, it was evaluated if SR-AOPs could be a viable alternative for the treatment of IWW. It is concluded an extraordinarily large absence of studies involving the treatment of IWW by SR-AOPs, in comparison to HR-AOPs. It can be concluded that sulfate radicals can be activated by different methods, and that these methods can be applied in the treatment of IWW. SR-AOPs allow to obtain similar results to HR-AOPs, with less oxidant consumption.

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