



Review on Using Persulfate as an Activator for Wastewater Treatment

Soubh AM* and Kerhaili YH

Department of Food Technology, Tartous University, Tartous, Syria

*Corresponding author: Alaa Mohamad Soubh, Department of Food Technology, Faculty of Technical Engineering, Tartous University, Tartous, Syria, Email: Alaasoubh@tartous-univ.edu.sy

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Abstract

Persulfate (PS, S2O8²⁻) has a standard oxidation potential making it use for treatment of a wide range of pollutants. It is also used within Advanced oxidation processes (AOPs), where Sulfate radicals (SR) can be effectively generated through PS activation by physical methods (such as heating, UV) and chemical methods (including transition metal ions, alkaline conditions), as well as coupling activation methods. Overall, SR-AOPs not limited applied to the treatment of refractory organics in wastewater but also are efficient in dealing with novel/emerging pollutants.

Keywords: Persulfate; Sulfate Radicals; Activation; Treatment

Introduction

The large increase in the population and the accompanying great development in the oil, chemical and food industries, This led to the generation of large quantities of wastewater containing large types of pollutants with complex structures that are difficult to decompose [1-4].

Because the industrial wastewater composition varies depending on where it is formed, there is no specific method or technique for its treatment [5]. Generally accepted treatments for leachates mainly includes: (a) chemical and physical methods such as chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/flotation, and air stripping [6] (b) aerobic and anaerobic processes [7-9]. Various methods, including physical, chemical and biological ones for treating this type of wastewater have been used [10]. Due to its resistance to degradability; most of these methods did not give the desired results [11].

The advanced oxidation processes (AOPs) are the most commonly used techniques for removal of contaminants

from effluents [11-13]. Hydroxyl radical-based advanced oxidation processes (HR-AOPs) attenuate lots of organic substances through conversion into CO₂ and H₂O [14-16]. Persulfate (S₂O₈²⁻) is the strongest member of the peroxygen family, which has a standard oxidation potential (E°) of 2.01 V [17-20] Therefore, in recent years, it has been increasingly used for the chemical oxidation of organic contaminants [12,21] and it has been able to remove the organics and ammonia from landfill leachates. Sulfate radical based advanced oxidation processes (SR-AOPs) are occurred when persulfate ion is activated [14,22], and the sulfate radical (E° = 2.4 V) is generated [23]. Transition metals, ozone, heat, or ultraviolet light irradiation are generally used for persulfate activation.

Typically persulfate anions can be activated to generate the intermediate sulfate free radical (SO₄^{•-}) oxidant using transition metals, heat or ultraviolet light irradiation, pH and ozone [9].

In this manuscript, the most important methods of activating persulfate will be highlighted and also the possibility of using it in the treatment of wastewater.

The Mechanism of Activation of Persulfate and the Generation of Sulfate Radical

Properties of Persulfate

Peroxydisulfate or persulfate anion ($S_2O_8^{2-}$) is a strong oxidant ($E_0 = 2.01$ V), which can be found in the form of three salts: ammonia, potassium and sodium [24,25]. The application of sodium persulfate ($Na_2S_2O_8$) is mostly favored since this salt has aqueous solubility as high as 730 g per kg of H_2O at 25 °C. The use of ammonia persulfate can lead to the secondary contamination caused by residual concentrations of ammonia, whereas the use of potassium persulfate may be ineffective especially for in situ applications due to its low solubility [9].

Persulfate Activation Mechanisms

Persulfate is stable at room temperature and its direct oxidation reactions are slow showing a negligible efficacy for water treatment. Thus, it needs activation, which thereupon results in generation of sulfate radicals ($SO_4^{\cdot-}$) selectively degrading organic pollutants. Without activation, persulfate may react with some organic compounds, although the process efficacy is lower than the one of the activated persulfate. This may be explained by the higher oxidation potential of $SO_4^{\cdot-}$ ($E_0 = 2.60$ V) [26].

However, the overall extent of $SO_4^{\cdot-}$ generation depends on the type of activation used Figure 1. The following paragraphs give an overview of different persulfate activation mechanisms with emphasis on the main advantages and disadvantages.

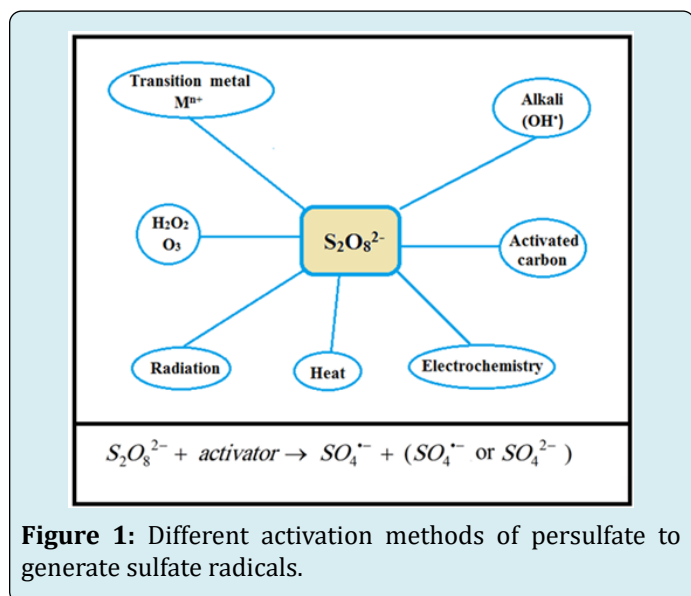
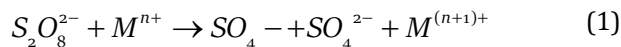


Figure 1: Different activation methods of persulfate to generate sulfate radicals.

Transition metal-activated persulfate: Typically persulfate

anions can be activated to generate the intermediate sulfate free radical ($SO_4^{\cdot-}$) oxidant using transition metals (Equation (1)), where Ag^+ , Co^{2+} , Ce^{3+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , V^{3+} and Ru^{3+} are the most efficient transition metal ions for the first reaction [9,27,28].

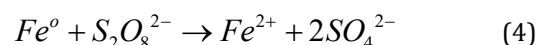
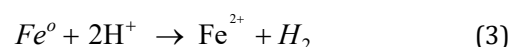
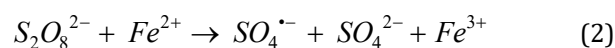


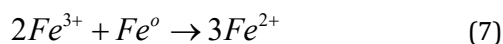
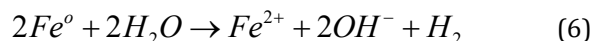
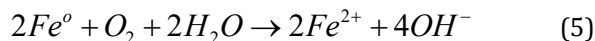
Heterogeneous metal-bearing species-activated persulfate: Heterogeneous activation of persulfate is an alternative to homogeneous transition metals to avoid the formation of metal hydroxide sludge. It must be noted that the quantity of the latter strongly depends how well are the treatment conditions optimized or controlled.

Recently, zero-valent iron (ZVI, Fe (0)) has been used as a promising catalyst and as an alternate source of Fe (II) [21,29]. In addition, it has the advantages including low cost and being non-toxic to the environment [30]. In addition to being a catalyst, it has a distinct role in transforming Fe (III) into Fe(II) [31]. nZVI has been reported to be effective in activating persulfate for the degradation of alkyl phenol polyethoxylate [32], bentazon (BTZ) [33], amicarbazone (AMZ) [34], acetaminophen [35], dye reactive blue 19 (RB19) [36], and aniline [37]. nZVI also achieved promising results when it was used as an activator of PS for the degradation of organic compounds [38], such as sulfamethazine (SMT) [39], trichloroethene (TCE) [40], and 2,4-dichlorophenol (DCP) [41].

Because of the higher surface area, nZVI showed more efficient results than ZVI in micrometer scales [42,43]. nZVI without any support is less stable and tends to be agglomerated and oxidized [44,45]. To overcome this disadvantage and to enhance their effectiveness in the removal of contaminants, composites of nZVI with some substances, such as resin [46], kaolinite [47], biochar [30] chitosan/silica [48], carbon [49], and graphene [50] have been used.

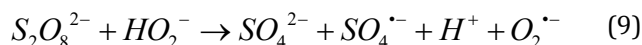
Fe (II) is considered as a homogeneous catalyst for activation of persulfate ions, which produce a stronger oxidant, i.e., sulfate radical ($SO_4^{\cdot-}$) according to Equation 2, ZVINFs is converted to Fe (II) according to several mechanisms: (1) corrosion in acidic medium through reaction with H^+ (Equation 3); (2) exchanging electrons with $S_2O_8^{2-}$ (Equation 4); (3) corrosion through reaction with oxygen and water (Equation 5 and Equation 6); (4) reaction of generated Fe (III) in solution with Fe^0 (Equation 7) [29,35].



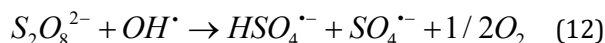
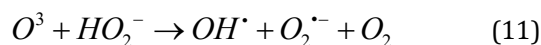
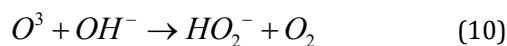


Carbon-activated persulfate: To overcome this metal leaching problem, recent studies have emerged using carbonaceous materials as an alternative strategy for persulfate activation. The advantages of carbonaceous materials over metal based catalysts can be briefly categorized into the following categories: (1) non-toxicity due to their metal-free nature, completely preventing leaching of toxic metal ions. (2) Good chemical and thermal stability to withstand harsh reaction conditions – they can operate over a wide range of pH without the structure collapsing. (3) A high surface area with suitable pore volumes that facilitates the adsorption of pollutants into the catalyst's active sites. (4) Malleable surface charge which provides control over the selection of a specific water pollutant. However, the catalytic activity of pristine carbonaceous materials is usually poor compared to that of the well-established metal-based catalysts, a consequence of the ambiguous active centers, inherent structural complexity and nonstoichiometric structure of the bulk carbonaceous material due to its graphitic degree, porosity, oxygen functionality and the presence of impurities. Therefore, various modulation strategies have been introduced to further control the surface characteristics of carbonaceous materials, such as size, morphology, and porous and electronic structure, which in turn manipulate their performance as persulfate activators [51].

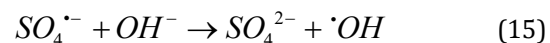
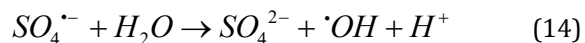
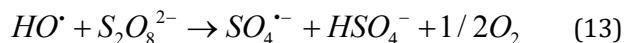
Alkali-activated persulfate: The hydroxide anions activates persulfate to initiate sulfate radical formation, according to Equation 8 & 9 [52].



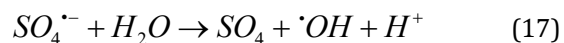
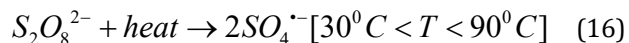
Oxidant-activated persulfate: In O_3 /persulfate process, when adding PS to solution, it reacts with OH^\bullet , according to Equation (10), which formed from decomposing ozone under alkane condition, according to Equations 11 & 12 [53]. This led to an improvement in the efficiency of removal.



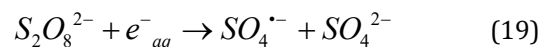
Hydrogen Peroxide can activate persulfate for soil remediation [54]. The knowledge about the interaction between two oxidants is still scarce, but it is proposed that H_2O_2 is decomposed into HO^\bullet , which are then activating persulfate to generate $SO_4^{\bullet-}$ (Equation 13). Another suggestion is that the exothermic reactions of H_2O_2 propagate $SO_4^{\bullet-}$ formation by heat. In turn, $SO_4^{\bullet-}$ can increase the formation of HO^\bullet , which results in a multiradical system (Equations 14-15) [54].



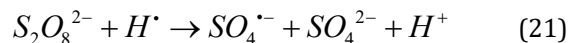
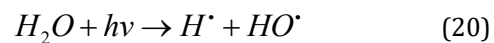
Thermally-activated persulfate: Thermal activation is one of the simplest and an effective method for PS activation to generate reactive species. Since the bond energy of peroxide (O-O) in PS is 140–213.3 kJ mol⁻¹, a thermal activation at a temperature of >30°C is sufficient to break the O-O bond for the generation of sulfate anion radicals ($SO_4^{\bullet-}$) (Equation 16). These $SO_4^{\bullet-}$ radicals can be further converted to hydroxyl radicals ($\bullet OH$), which are also an effective species (Equation 14). The generation of $SO_4^{\bullet-}$ and $\bullet OH$ radicals can be represented as given below [55].



Radiation-activated persulfate: This activation type is similar to heat-activated persulfate, when UV radiation (Equation 18), gamma-radiation (Equation 19) or pulse radiolysis (Equation 19) induces the cleavage of peroxide bond generating a pair of sulfate radicals [54].



The activation of persulfate by UV-light may involve second mechanism according to the reaction given in Equation 19: an electron can be produced from water exposure to UV, and persulfate is then activated by electron transfer Equations 20 & 21.



Electrochemically-activated persulfate: Persulfate activation by transition metal electrode-involving system in aqueous environment consists of simple chain reactions. First, the process is initiated with the production of transition

metal by anodic corrosion, which activates persulfate and can be regenerated on a cathode [56]. This method may help to overcome the problem of transition metal accumulation on the in the activated persulfate system, where the electrolysis of water takes place on the cathode consisting of OH⁻ [56].

Conclusion

In this manuscript, the mechanism of using persulfate for treatment of pollutants was highlighted. Also, the possibility of activating it was shown, where the sulfate radicals it is generated. It also explains the mechanism activated by activators such as (transition metal ions, heterogeneous metal, carbon, alkali, oxidant, thermally, radiation and electrochemically).

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