



Impact Persulfate on COD Analyze and Possibility Use it as Oxidant of Leachate

Soubh AM*

School of Environment, University of Tehran, Tehran, Iran

*Corresponding author: Alaa Mohamad Soubh, School of Environment, College of Engineering, University of Tehran, Tehran, Iran, Tel: (+963) 932238708; Email: soubh@ut.ac.ir; Alaa.sobh1984@yahoo.com

Research Article

Volume 3 Issue 4

Received Date: September 03, 2020

Published Date: November 02, 2020

DOI: 10.23880/oajwx-16000146

Abstract

In this research, the performance of persulfate (PS) for the removal the chemical oxygen demand (COD) of raw leachate landfill was studied. The experiments were conducted in a batch reactor. The effects pH (2-11), PS/COD ratio (2-10), and reaction time (0-240 min) on the removal of leachate landfill. The Maximum removal efficiencies of COD and NH₃ at optimize operational conditions (pH 4, PS/COD ratio: 6 and reaction time: 45 min) were 48.33% and 45.83%, respectively.

Keywords: Persulfate; COD; Leachate landfill

Introduction

The annual level of municipal solid waste generation is expected to reach 2.2 billion tons in 2025 [1]. This high amount of solid waste will generate the remarkable volume of landfill leachate, containing a various spectrum of pollutants, which will lead to serious shocks to the environment, especially natural resources if not treated appropriately [2]. Traditional treatment methods are not useful for leachates, which contain high organic loading and refractory compounds.

The chemical oxidation techniques are usually used to treat the complex organic materials, which could not be treated by the usual methods and during which the resistant organic substances are degraded [3]. Persulfate or peroxydisulfate (PS, S₂O₈²⁻) has a strong redox potential (E° = 2.01 V) [4,5]; consequently, it is useful for oxidation of many organic pollutants [6-8]. However, direct oxidation rates using peroxydisulfate are often low, especially those related to refractory contaminants [9].

The use of sulfate radical-based advanced oxidation processes (SR-AOPs) has achieved promising results in terms of removing a large spectrum of pollutants [10,11]. Several

studies have indicated the success of their use in treatment of landfill leachate [4,12,13]. Deng and Ezyske used PS to treat a mature leachate, with an emphasis of concurrent removal of refractory organics and ammonia. The findings of this study refer that PS is a promising landfill leachate treatment method [10,14,15]. In this search, due to the properties of PS, the PS employed for the treatment of real landfill leachate and the effect of PS on COD analyze was studied.

Materials and Methods

Materials

Fresh leachate was obtained from Aradkouh's landfill located in Tehran, Iran. This landfill accommodates 8000 tons solid waste per day [16]. The mean values for some parameters of studied leachate are given in Table 1. It should be noted that in this investigation the samples have been stored in plastic tight vessels at temperature 4°C in order to prevent from occurrence possible changes in physical, chemical, and biologic properties up to time of conducting experiment after transferring leachate to laboratory. All chemicals employed for analysis were of analytical grade and obtained from reliable companies.

Parameters	units	Min.
COD	mg L ⁻¹	1800
NH ₃ -N	mg L ⁻¹	96
TS	mg L ⁻¹	820
EC	mS/cm	16.5
pH	-	8.5
Color	Gardner	8
BOD ₅	mg L ⁻¹	650
TDS	mg L ⁻¹	1600
TVS	mg L ⁻¹	900

Table 1: Specifications of used leachate.

Analytical Methods

COD concentration and color were determined using a UV/ Vis spectrophotometer (HACH, DR 5000). BOD₅ was determined by a BOD measurement system (OxDirect). A Metrohm 691 pH meter was used to measure the pH of solutions. Electrical conductivity (EC) and total dissolved solids (TDS) were measured with a multimeter equipped with a conductivity electrode (WTW COND 7110, inoLab).

Batch oxidation Experiments

All experiments were performed in the batch mode. Briefly, 25 mL of leachate solution was transferred to a 50-mL glass flask, to which the sodium persulfate dissolved in 10

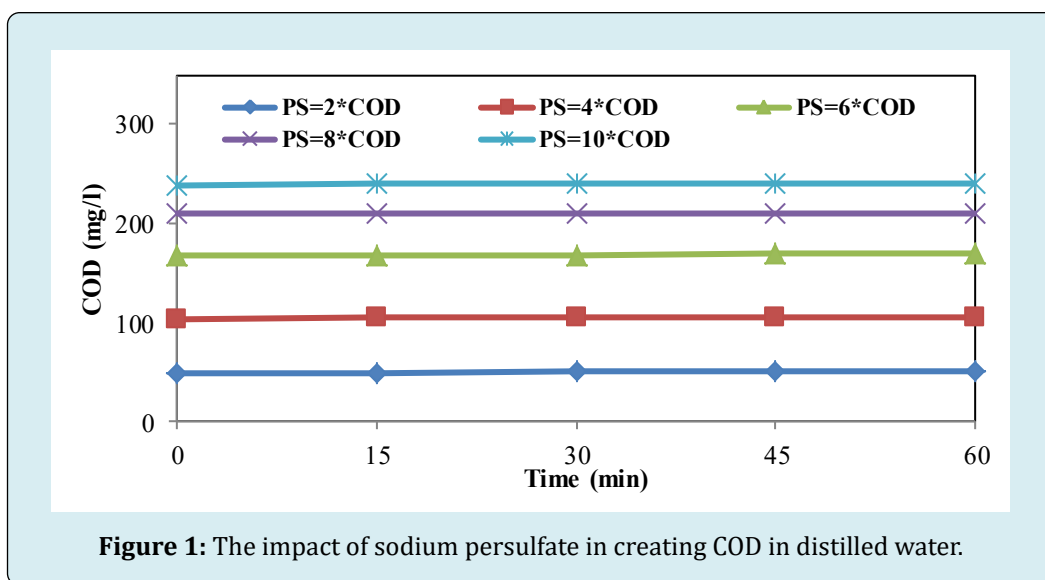
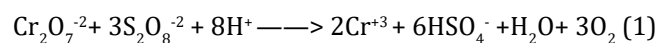
mL of the leachate had been added. Afterward, the mixture was stirred at 150 rpm. Finally, the concentrations of COD and NH₃ were determined at specified time intervals. Sulfuric acid and sodium hydroxide solutions (2 mol L⁻¹) were used to adjust the pH of solutions. The effect of essential parameters on the removal efficiency was also investigated. The effect of pH was studied in the range of 2–11. For studying the other essential factors, the degradation tests were also done at the specified ranges (PS/ COD ratio: 2-10; contact time: 0-240 min).

Results and Discussion

Interference of PS with COD

Some of mineral agents such as chloride, bromide, iodide, Iron (II), sulfide, and manganese ions are oxidized during COD test and cause occurrence of error in results of COD test [17].

As shown in Figure 1, adding of PS equal to 2, 4, 6, 8, and 10 times of COD₀ of leachate caused increase in COD by 52, 106, 170, 210, and 240 mg/l respectively almost during the period studied. According to equation (1), PS can react with dichromate, Cr₂O₇²⁻. In the course of the oxidation–reduction reaction, each chromium atom goes from an oxidation state of +6 to +3 in the released ion Cr³⁺ which in turn causes an increase in reading COD analyze.



In order to study of interference of PS with COD of leachate, the effect of previous concentrations was studied during the period studied. The COD increased only slightly

at first but by beginning of mixing and over time, the COD decreased as the reaction progressed. This phenomenon is caused by nature of leachate and starting degradation of

the existing organic materials in this system by persulfate, which leads to reduced COD in leachate over the time and progress trend of oxidation reaction as well. However, adding persulfate at first moment of this reaction may increase COD in leachate, its effect has been ignored in this study.

pH Effect

In sulfate radical-based advanced oxidation processes (SR-AOPs) like other advanced oxidation processes (AOPs), changes in pH affect the type and quantity of radicals produced, i.e. active ingredient in treatment of the organic

compounds [18-20]. The removal efficiencies of COD and NH_3 have been studied at different pH values (2,4,7,9, and 11). As shown in (Figure 2), the removal efficiency for COD and NH_3 at pH 4.0 were 35.00 and 32.30%, respectively and the removal efficiency at pH 4.0 was bigger than that at pH 7.0. As result to Under acidic conditions, the presence of H^+ may cause further breakdown of PS into $\text{SO}_4^{\cdot-}$, according to Eq. 2 and Eq. 3 [21,22]. The results at pH 2.0 were very close to those at pH 3.0. This can be explained, at strong acidic condition (pH=2.0), the presence of proton with high concentrations could lead to scavenging some of produced sulfate radical [23,24].

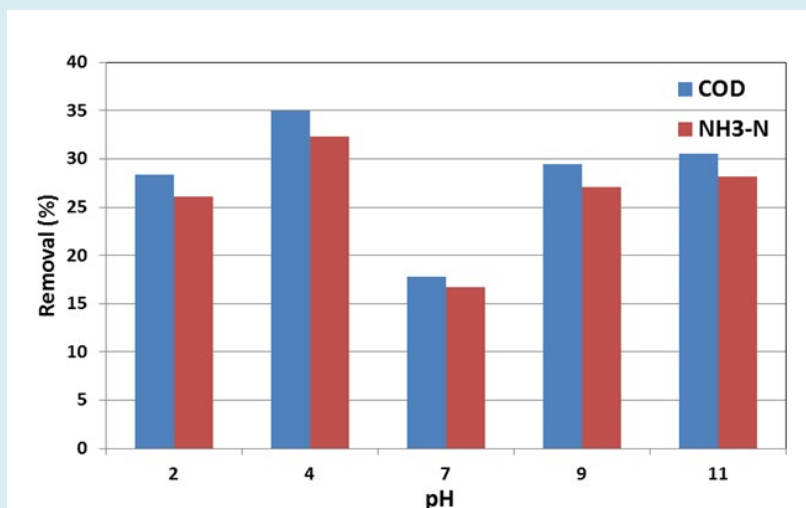
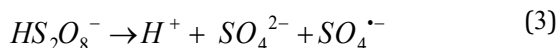


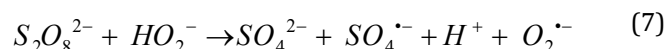
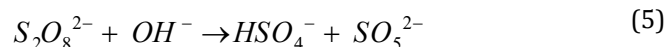
Figure 2: Effect of pH on the COD and NH_3 removal (PS/COD ratio of 4; reaction time of 60 min).

By increasing the pH to 7, production of sulfate radical was almost entirely stopped. The removal efficiencies were 17.78 and 16.67.25% for COD and NH_3 , respectively. In accordance with Eq.4, PS anions, under these conditions, often hydrolyze to hydrogen peroxide ($E^\circ = 1.77 \text{ V}$), which is less efficient oxidant than PS ($E^\circ = 2.01 \text{ V}$) [25-27].



By increasing the pH from 7 to 9, the removal efficiencies of COD (29.44%) and NH_3 (27.08%) increased and at pH 11.0 the removal efficiency of increased just slightly and did not exceed more than 2%. In alkaline medium, SO_5^{2-} is formed through reaction between hydroxide and persulfate ions (Eq. 5). Afterwards, SO_5^{2-} hydrolyzes to hydroperoxide anions (HO_2^-) in accordance with Eq. 6. Finally, the hydroperoxide

anions can active persulfate to initiate sulfate radical formation (Eq.7), [27,28].



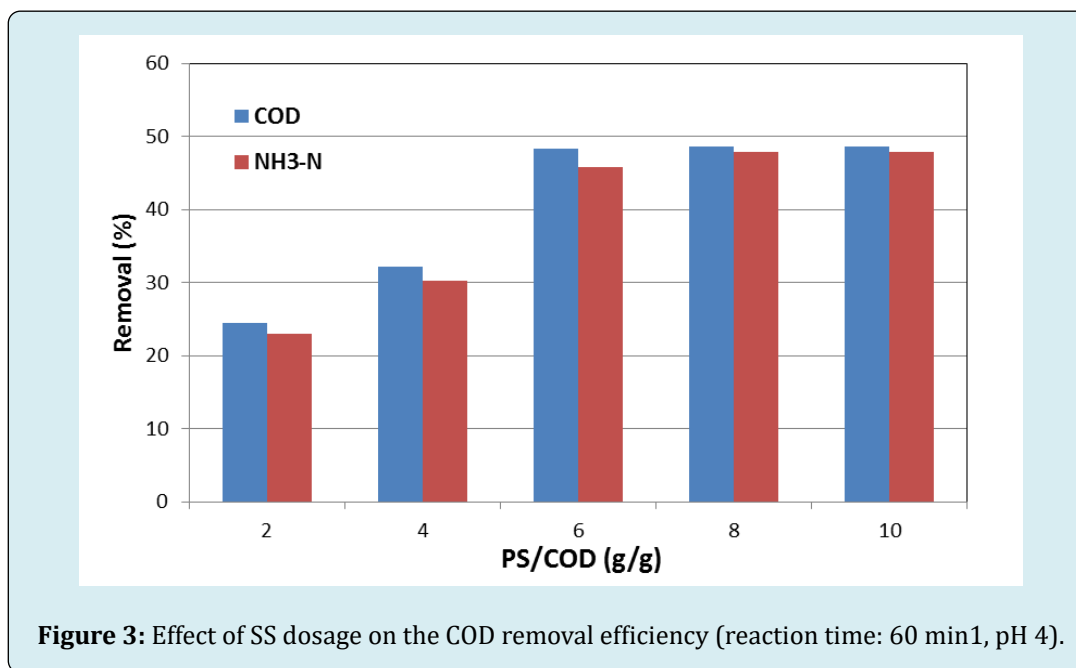
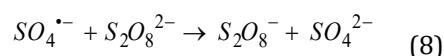
In the present study, pH 4 was selected to conduct the experiments.

Effect of PS/COD dosages

The effect of PS dosage on the removal of COD studied Figure 3. As can be seen in Figure 3, by increasing the PS/COD ratio from 2 to 6, the removal efficiencies of COD and NH_3 increased significantly from 24.44% to 48.33% and 22.92% to 45.83%, respectively. This is due to the increase

in generating of sulfate radical, and then there was stability in removal efficiency, because the sulfate radical can be discouraged at high concentration of PS, according to Eq. 8 [29]. The PS/COD ratio of 6 was selected to perform following

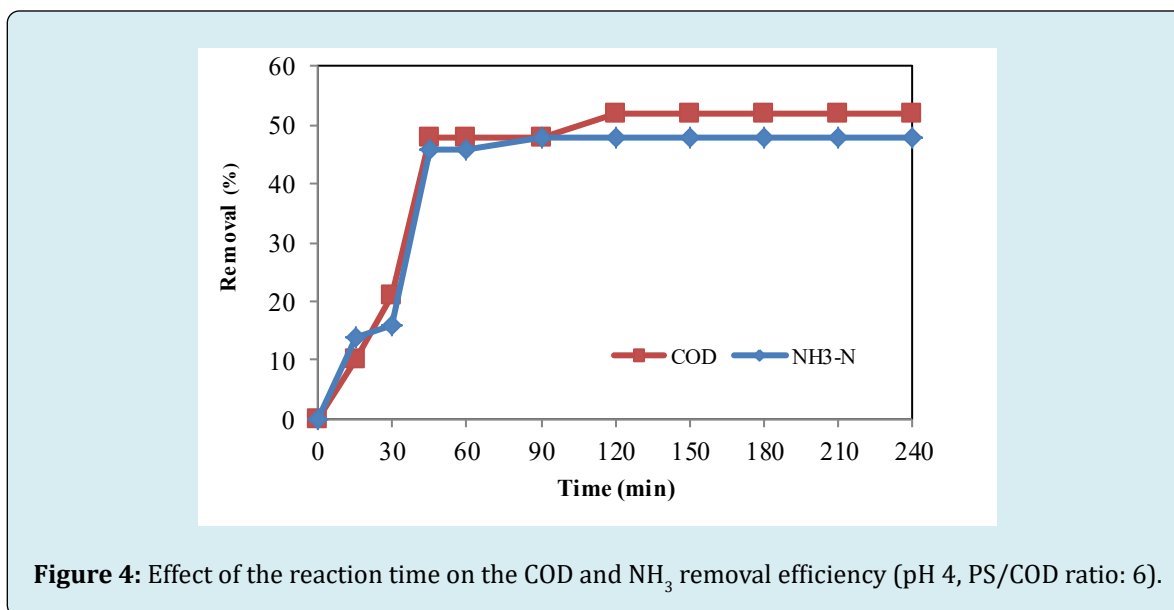
experiments.



Effect of Reaction Time

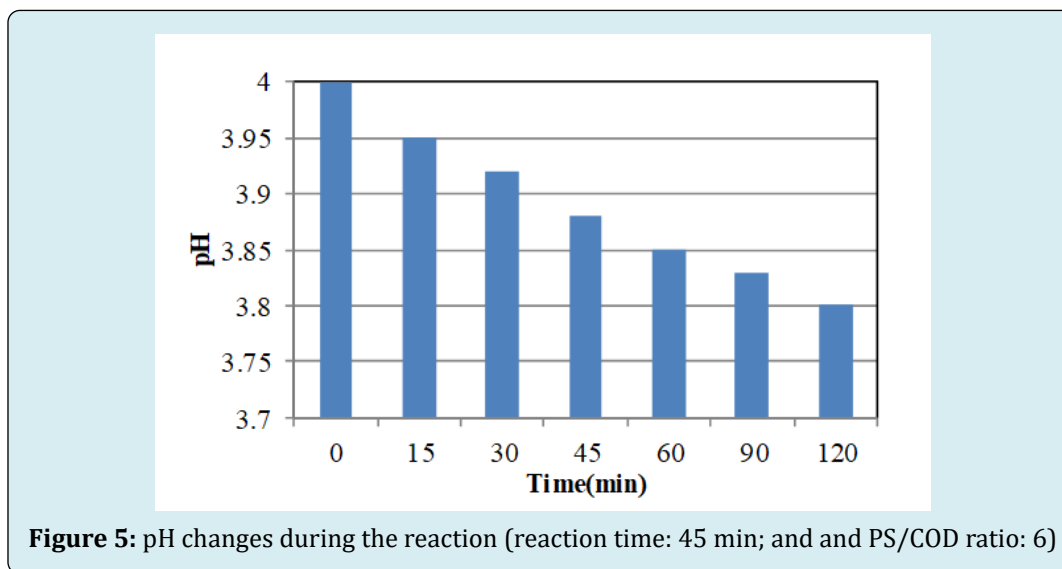
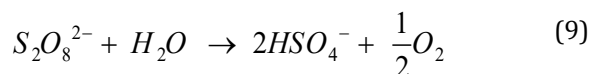
In order to use the full potential of persulfate to remove COD and NH₃, the effect of time was studied in the range of 0-240 min at the most efficient conditions, Figure 4, (pH 4

and PS/COD ratio: 6). By increasing the reaction time up to 45 min, the removal efficiencies of COD increased. After that, no significant change in removal efficiencies was observed. Thus, the reaction time of 45 min was selected as the optimum reaction time.



Variations in pH after PS addition

The pH changes in preceding conditions have been studied Figure 5. The addition of persulfate alone causes a decrease the pH of solution gradually from 4 to 3.8, which can due to produce the of positive ions resulting from decomposition of PS, according to Eq.8 and Eq. 9 [30].



Conclusion

This study investigated the possibility of using PS oxidation for leachate treatment. Experiments indicate the possibility of using PS as a primary treatment for leachate treatment. Also, the use of water is activators in order to activate of PS.

Acknowledgements

This research has been done in Graduate Faculty of Environment, University of Tehran.

References

1. Hoornweg D, Bhada-Tata P (2012) What a Waste: A Global Review of Solid Waste Management. Urban Dev Ser Knowl Pap, World Bank.
2. Naveen BP, Mahapatra DM, Sitharam TG, Sivapullaiah PV, Ramachandra TV (2017) Physico-chemical and biological characterization of urban municipal landfill leachate. Environ Pollut 220: 1-12.
3. Monteagudo JM, Duran A, Gonzalez R, Exposito AJ (2015) In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe²⁺ ions, and H₂O₂. Appl Catal B Environ 176-177: 120-129.
4. Amr ASS, Aziz HA, Adlan MN, Bashir MJK (2013) Pretreatment of stabilized leachate using ozone/persulfate oxidation process. Chem Eng J 221: 492-499.
5. Zhen G, Lu X, Zhao Y, Chai X, Niu D (2012) Enhanced dewaterability of sewage sludge in the presence of Fe(II)-activated persulfate oxidation. Bioresour Technol 116: 259-265.
6. Oh SY, Kang SG, Kim DW, Chiu PC (2011) Degradation of 2,4-dinitrotoluene by persulfate activated with iron sulfides. Chem Eng J 172(2-3): 641-646.
7. Hussain I, Zhang Y, Huang S, Du X (2012) Degradation of p-chloroaniline by persulfate activated with zero-valent iron. Chem Eng J 203: 269-276.
8. Liang HY, Zhang YQ, Huang SB, Hussain I (2013) Oxidative degradation of p-chloroaniline by copper oxidate activated persulfate. Chem Eng J 218: 384-391.
9. Oh SY, Kim HW, Park JM, Park HS, Yoon C (2009) Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe²⁺, and zero-valent iron. J Hazard Mater 168(1): 346-351.
10. Deng Y, Ezyske CM (2011) Sulfate radical-advanced

- oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate. *Water Res* 45(18): 6189-6194.
11. Liu C, Wu B, Chen X (2018) Sulfate radical-based oxidation for sludge treatment: A review. *Chem Eng J* 335: 865-875.
 12. Chou YC, Lo SL, Kuo J, Yeh CJ (2015) Microwave-enhanced persulfate oxidation to treat mature landfill leachate. *J Hazard Mater* 284: 83-91.
 13. Hilles AH, Amr SSA, Hussein RA, El-Sebaie OD, Arafa AI (2016) Performance of combined sodium persulfate/ H_2O_2 based advanced oxidation process in stabilized landfill leachate treatment. *J Environ Manage* 166: 493-498.
 14. Soubh AM, Baghdadi M, Abdoli MA, Aminzadeh B (2018) Activation of Persulfate Using an Industrial Iron-Rich Sludge as an Efficient Nanocatalyst for Landfill. *Catalysts* 8(5): 218.
 15. Soubh A, Mokhtarani N (2016) The post treatment of composting leachate with a combination of ozone and persulfate oxidation processes. *Rsc Adv* 6: 76113-76122.
 16. Soubh AM, Baghdadi M, Abdoli MA, Aminzadeh B (2018) Zero-valent iron nano fibers (ZVINFs) immobilized on the surface of reduced ultra-large graphene oxide (rULGO) as a persulfate activator for treatment of landfill leachate. *J Environ Chem Eng* 6(5): 6568-6579.
 17. Belkin S, Brenner A, Abeliovich A (1992) Effect of inorganic constituents on chemical oxygen demand-II. Organic carbon to halogen ratios determine halogen interference. *Water Research* 26(12): 1583-1588.
 18. Liang C, Wang ZS, Bruell CJ (2007) Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere* 66(1): 106-113.
 19. Soubh AM (2019) Assessment of Steel Slag as a Persulfate Activator for Treatment of Landfill Leachate. *Open Access J Waste Manag Xenobiotics* 2: 1-6.
 20. Soubh AM, Baghdadi M, Abdoli MA, Aminzadeh B (2019) Assessment of Converter Sludge from Esfahan Steel Company as a Persulfate Nano-Activator for Permeable Reactive Barriers (Prbs) in Landfill Leachate Treatment. *Pollution* 5(2): 395-409.
 21. Huling SG, Ko S, Park S, Kan E (2011) Persulfate oxidation of MTBE- and chloroform-spent granular activated carbon. *J Hazard Mater* 192(3): 1484-1490.
 22. Ahmad A, Gu X, Li L, Lv S, Xu Y, et al. (2015) Efficient degradation of trichloroethylene in water using persulfate activated by reduced graphene oxide-iron nanocomposite. *Environ Sci Pollut Res* 22: 17876-17885.
 23. Ahmadi M, Ghanbari F (2018) Combination of UVC-LEDs and ultrasound for peroxymonosulfate activation to degrade synthetic dye: influence of promotional and inhibitory agents and application for real wastewater. *Environ Sci Pollut Res* 25: 6003-6014.
 24. Ahmadi M, Ghanbari F, Alvarez A, Silva Martinez S (2017) UV-LEDs assisted peroxymonosulfate/ Fe^{2+} for oxidative removal of carmoisine: The effect of chloride ion. *Korean J Chem Eng* 34: 2154-2161.
 25. Kolthoff IM, Miller IK (1951) The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium. *J Am Chem Soc* 73(7): 3055-3059.
 26. House DA (1962) Kinetics and Mechanism of Oxidations by Peroxydisulfate. *Chem Rev* 62(3): 185-203.
 27. Liang C, Guo YY (2012) Remediation of diesel-contaminated soils using persulfate under alkaline condition. *Water Air Soil Pollut* 223: 4605-4614.
 28. Furman OS, Teel AMYL, Watts RJ (2010) Mechanism of Base Activation of Persulfate. *Environ. Sci. Technol* 44(16): 6423-6428.
 29. Deng J, Shao Y, Gao N, Deng Y, Tan C, et al. (2013) Zero-valent iron/persulfate(Fe^0/PS) oxidation acetaminophen in water. *Int J Environ Sci Technol* 11: 881-890.
 30. Kusic H, Peternel I, Koprivanac N, Bozic AL (2011) Iron-Activated Persulfate Oxidation of an Azo Dye in Model Wastewater: Influence of Iron Activator Type on Process Optimization. *J Environ Eng* 137(6): 454-463.

