



A titration method for determining individual oxidant concentration in the dual sodium persulfate and hydrogen peroxide oxidation system

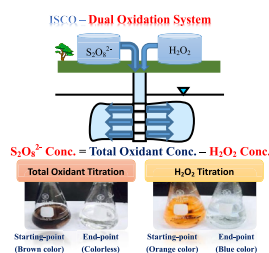
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HIGHLIGHTS

- A dual $S_2O_8^{2-}$ and H_2O_2 oxidation system is applied as an ISCO process.
- An iodometric titration method was developed for measuring total oxidant concentration.
- Ceric sulfate titration can be used to measure H_2O_2 in the dual oxidation system.
- $S_2O_8^{2-}$ concentration can be determined by subtraction of H_2O_2 from total oxidant.
- The concentration deviations are limited to within 10% of the theoretical value.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of a dual oxidation system, which combines sodium persulfate ($Na_2S_2O_8$, SPS) and hydrogen peroxide (H_2O_2 , HP) is increasing as an in-situ chemical oxidation (ISCO) process for soil and groundwater remediation. An analytical method was assessed in this study for determining individual oxidant concentration in order to understand the interactions, and variations in the concentrations, of SPS and HP in aqueous systems containing both SPS and HP. The iodometric titration method was demonstrated to be capable of measuring total oxidant (SPS + HP) concentration; while the ceric sulfate titration method can be used specifically for measuring HP in the dual oxidation system without interfering with the iodometric titration. Therefore, SPS concentration can be deduced by subtraction of the HP concentration from the total oxidant concentration. Direct iodometric titration for determination of total oxidant at concentration above 20 mM exhibited <8% concentration. Based on the results of indirect determination of SPS in the dual oxidation system, an approximate 10% concentration variation was expected. This research may serve as a reference for measuring oxidant variations in this ISCO dual oxidant application.

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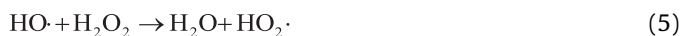
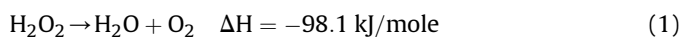
1. Introduction

Sodium persulfate ($Na_2S_2O_8^{2-}$, SPS) and hydrogen peroxide (H_2O_2 , HP) are both commonly used in situ chemical oxidation (ISCO) as oxidants for the remediation of soil and groundwater contamination. SPS and HP activations, e.g., with transition metals

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(Liang et al., 2004; Lin et al., 2016) and ultraviolet light (Lin et al., 2011), can generate highly reactive radicals such as the hydroxyl radical ($\text{HO}\cdot$) or the sulfate radical ($\text{SO}_4\cdot^-$) to degrade organic contaminants into less harmful substances. Recently, a dual oxidation system, which combines SPS and HP reagents, was implemented as an ISCO process for removal of contaminants such as polychlorinated biphenyls (Goi and Viisimaa, 2015), carbofuran (Chu et al., 2006), naproxen (Dulova et al., 2016), and levofloxacin (Epold and Dulova, 2015). Ko et al. (2012) and Epold and Dulova (2015) postulated that the reaction mechanism in the dual SPS/HP oxidation system could be attributed to several synergistic reactions between the persulfate anion ($\text{S}_2\text{O}_8^{2-}$) and H_2O_2 . The reaction may be induced by the decomposition heat of H_2O_2 (Eq. (1)), which thermally activates $\text{S}_2\text{O}_8^{2-}$ as shown in Eq. (2). It should be noted that HP decomposes exothermically and 1 mol of HP could generate 98.1 kJ (Eq. (1)). The temperature attained by HP decomposition is a function of HP concentration. For example, complete decomposition of 9.5% HP (3.19 M) in 1 L of water generates 75.1 kcal, which may induce a temperature rise from 25 °C to 100 °C. Therefore, the potential for the decomposition heat of HP to thermally activate SPS would depend on the HP concentration and the extent of HP decomposition. Upon $\text{SO}_4\cdot^-$ formation, a series of radical initiation reactions occur starting with $\text{SO}_4\cdot^-/\text{H}_2\text{O}$ then interconversion into $\text{HO}\cdot$ (Eq. (3)) and subsequent generations of hydroperoxide radical ($\text{HO}_2\cdot$) (Eqs. (4)–(6)).

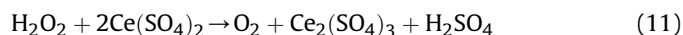
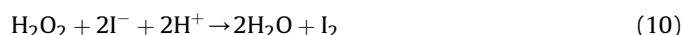


Alternatively, H_2O_2 can also directly activate $\text{S}_2\text{O}_8^{2-}$ to generate $\text{SO}_4\cdot^-$ through Eq. (7) (Epold and Dulova, 2015), which is followed by a series of radical initiations reactions as described in Eqs. (3)–(6). Because of various radicals formed in the SPS/HP dual oxidation system, that are applicable for degrading a variety of organic contaminants, this system has gained much attention from environmental engineers. Even though the dual SPS/HP system has been extensively researched, the interaction between $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 , in the dual $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 system, has not yet been reported, based on our recent literature survey. Therefore, an appropriate analytical method to measure individual oxidant in the dual oxidation system was assessed in this study.



Among available SPS measurement methods, which were reported in the compilation by Liang et al. (2008), the iodometric SPS titration (Kolthoff and Carr, 1953) and SPS spectrophotometric methods (Liang et al., 2008) are promising as simple and rapid ways to measure SPS in ISCO application. These two methods mainly determine SPS by means of persulfate anion ($E^0(\text{S}_2\text{O}_8^{2-}/2\text{SO}_4^{2-}) = 2.01 \text{ V}$) oxidation of iodide (I^-) ($E^0(\text{I}^-/\text{I}_2) = -0.54 \text{ V}$) (Latimer, 1952) to formation of iodine (I_2) by Eq. (8), which can then be quantitatively determined by titration with thiosulfate (Eq. (9)), or by a spectrophotometric measurement at the wavelength of 352 or 400 nm. In a similar manner, H_2O_2 ($E^0(\text{H}_2\text{O}_2/2\text{H}_2\text{O}) = 1.77 \text{ V}$

(Latimer, 1952)) can also be measured using the iodometric titration method in accordance with Eq. (10) (Kolthoff and Carr, 1953; Klassen et al., 1994). Therefore, it is theoretically possible that the iodometric titration method can be used for determining total oxidant concentration (SPS + HP) in the dual oxidation system. Furthermore, in order to differentiate SPS from HP, the ceric sulfate (IV) H_2O_2 titration method was evaluated for the determination of HP according to Eq. (11), in which Ce(IV) ($E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.61 \text{ V}$ (Latimer, 1952)) is reacted specifically with HP (Furman and Wallace, 1929), but is not able to oxidize $\text{S}_2\text{O}_8^{2-}$ in the dual oxidation system, and therefore would not interfere with the iodometric total oxidant concentration determination.



In brief summary, the methods evaluated for determining oxidants in this study included: (1) SPS iodometric titration method and SPS spectrophotometric method for measuring SPS alone, (2) ceric sulfate titration method for measuring HP alone, (3) total oxidant titration method (a modified iodometric method) for measuring total oxidants (SPS + HP), and (4) in the SPS + HP mixture solution, the total oxidant titration method is used for measuring SPS + HP, and the ceric sulfate titration method is used for measuring HP. Thereafter the SPS concentration is deduced from the difference between these two measurements. In an effort to develop an appropriate SPS/HP analytical method, this study aimed to investigate the measurement of (1) total oxidant concentration using the iodometric titration and spectrophotometric methods and (2) only the HP concentration using the ceric sulfate (IV) titration method in the dual oxidation system. Based on this approach, the SPS concentration can be deduced by subtraction of the HP concentration from total oxidant concentration.

2. Materials and methods

2.1. Materials

All chemicals used in the experiments were analytical reagent grade. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 99\%$) was purchased from Merck. Potassium iodide (KI, $\geq 99.5\%$) was purchased from UNION Taiwan. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.5\%$), starch ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$, ACS grade) and hydrogen peroxide (H_2O_2 , 34.5–36.5%) were purchased from Riedel-de Haën. Salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, ≥ 99.8), sodium bicarbonate (NaHCO_3 , $\geq 99.7\%$) and acetic acid (CH_3COOH , $\geq 99.7\%$) were purchased from J. T. Baker. Cerium (IV) sulfate ($\text{Ce}(\text{SO}_4)_2$, $\geq 97.0\%$) was purchased from Alfa Aesar. 1,10-phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, $\geq 99.0\%$), Ferroin indicator solution ($\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{SO}_4$, 0.1 wt% in H_2O), sodium bicarbonate (NaHCO_3 , $\geq 99.7\%$) and sulfuric acid (H_2SO_4 , 95.0–97.0%) were purchased from Sigma-Aldrich. Water purified by Millipore reverse osmosis (RO) purification system was used for preparation of reagents.

2.2. Apparatus

25 mL burettes with subdivision marks of 0.05 mL and accuracy $\pm 0.03 \text{ mL}$ (BRAND® BLAUBRAND® burette, straight stopcock) were used for titration. A visible light spectrophotometer (HACH DR/

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