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Transformation of antimicrobial agent sulfamethazine by peroxymonosulfate: Radical vs. nonradical mechanisms

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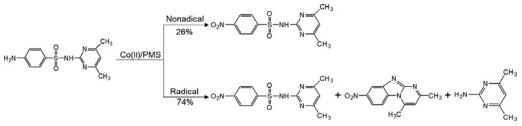
HIGHLIGHTS

- SMZ can be transformed by PMS oxidation, leading to nitrated products.
- PMS oxidation was significant during the removal of SMZ in Co(II)/PMS process.
- Anilinic compounds underwent similar nitration upon reaction with PMS.
- Nitrated products appeared more recalcitrant.

GRAPHICAL ABSTRACT



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ABSTRACT

Peroxymonosulfate (PMS) is increasingly used as an oxidant for in situ remediation of organic contaminants in soil and groundwater. In this study we demonstrated that sulfamethazine (SMZ) could be transformed by PMS in the absence of any activators. Such transformation was ascribed to the oxidation by PMS per se, rather than free radicals ($SO_4^{\bullet-}$ or HO•), superoxide ($O_2^{\bullet-}$), or singlet oxygen ($^1O_2$). The aniline moiety of SMZ molecule was the reactive site for PMS oxidation, leading to the formation of nitrated products. This nitration pathway in fact played a significant role in the removal of SMZ in activated PMS oxidation processes. For instance, it contributed 26% of the total SMZ transformation, while $SO_4^{\bullet-}$ contributed the other 74% during the removal of SMZ, in Co(II)/PMS oxidation process with initial PMS and Co(II) concentrations of 1.0 mM and 0.1 μM, respectively. Similar nitration reaction also occurred to other sulfonamide antibiotics bearing an aniline moiety upon the reaction with PMS. Since nitrated sulfonamide antibiotics appear more persistent than the parent compounds and may cause other environmental problems, such a pathway should not be desired. Therefore, PMS might not be an ideal oxidant for the treatment of sulfonamide antibiotics and other compounds having aniline moieties, especially in subsurface remediation practices where efficient activation of PMS represents a major challenge.

1. Introduction

In situ chemical oxidation (ISCO) has become an established technology for the remediation of contaminated soil and groundwater (Tsitonaki et al., 2010). Peroxymonosulfate (PMS) and peroxydisulfate (PDS) are the most effective ISCO oxidant sources. PMS and PDS can be regarded as the derivatives of H_2O_2 in which one or two of the H-atoms are replaced by sulfonic moieties (Anipsitakis and Dionysiou, 2003; Yang et al., 2010). The distance of the O—O bond in PMS is 1.460 Å, which is close to that of H_2O_2 (1.458 Å) (Flanagan et al., 1984). As an alternative of chlorine-based bleaching agent, PMS is widely used in paper and pulp industry. In addition, it can be used as the cleaning agent along with chlorine in pools and spas disinfection, with the dosage of approximately 1–2 pounds per 10,000 gallon pool water (Anipsitakis and Dionysiou, 2003; Jang et al., 2010). Although PMS is thermodynamically a strong oxidant with a redox potential of 1.82 V (vs. NHE), its direct reaction with most organic compounds is

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slow (Betterton and Hoffmann, 1990). In ISCO practices, PMS is usually activated appropriately to produce sulfate radical ($SO_4^{\bullet-}$), which has a redox potential of 2.5–3.1 V (vs. NHE). $SO_4^{\bullet-}$ can react with a variety of organic compounds with second-order rate constants ranging from 10^6 to 10^9 M^{-1} s^{-1} (Anipsitakis and Dionysiou, 2003; Furman et al., 2010; Neta et al., 1988). Compared with hydroxyl radical (HO•, 2.7 V in acid solution and 1.8 V in neutral solution), $SO_4^{\bullet-}$ has a wider operational pH range (Guan et al., 2011; Usman et al., 2012). Generally, transition metals (e.g., Fe^{2+} and Co^{2+}) or metal oxides (e.g., CuO, Co_3O_4, and $CuFe_2O_4$) are used to activate PMS to generate $SO_4^{\bullet-}$ (Fan et al., 2017; Guan et al., 2013; Hu et al., 2017; Ji et al., 2011; Tan et al., 2014; T. Zhang et al., 2016). Some carbon-based materials such as graphene and carbon nanotube were also demonstrated capable to activate PMS (Chen et al., 2018; Liu et al., 2016; Zhang et al., 2017). Recently, it was found that PMS could be activated by benzoquinone to generate singlet oxygen ($^1O_2$), which showed high reactivity toward electron-rich compounds such as phenols, sulfides, and amines (Zhou et al., 2015).

Sulfonamide antimicrobial agents are widely used in animal husbandry, fishery, and human health (Kümmerer, 2009a; Wright, 2003). The molecules of sulfonamide antibiotics comprise an aniline moiety and a heterocyclic ring bridged by a sulfonamide group. Table S1 (Supporting data) shows the molecular structures of some sulfonamide antibiotics used in medicine. It was revealed that approximately 30–85% of sulfonamide antibiotics are excreted unchanged via urine and feces by humans and animals and then released to the environment through municipal discharge and land application of animal wastes (Kemper, 2008; Sarmah et al., 2006; Voulvoulis, 2005; Zhang et al., 2015). Microbial degradation of sulfonamide antibiotics is generally slow due to their antibiotic nature (Kümmerer, 2009a; Lapworth et al., 2012). As a result, sulfonamide antibiotics are widely detected in the environment, such as surface waters, ground waters, soils, and sediments, with concentrations ranging from sub μg L^{-1} to ng L^{-1} level (Baran et al., 2011). The effects of residual antibiotics to the environment and public health are chronic, but cannot be ignored, because they can induce the development of antibiotic resistant genes and pose risks to ecosystems and human health (Crane et al., 2006; Kümmerer, 2009b; Rizzo et al., 2013). Therefore, effective and economic treatment technologies are desired to minimize the risks of sulfonamide antibiotics.

Previous studies demonstrated that sulfonamide antibiotics could be effectively removed in activated PMS and PDS oxidation processes, such as heat/PDS, UV/PDS, UV/PMS, and $CuCo_2O_4$/PMS (Fan et al., 2015; Feng et al., 2015; Ji et al., 2015; Yang et al., 2017; Yao et al., 2017). During these processes, the degradation of sulfonamide antibiotics was assumed to be attributed to the reactions with $SO_4^{\bullet-}$. The reactions between sulfonamide antibiotics and $SO_4^{\bullet-}$ are diffusion-controlled with the second-order rate constants as high as 10^9 M^{-1} s^{-1} (R. Zhang et al., 2016). Upon reaction with $SO_4^{\bullet-}$, the antibiotics are transformed through various pathways including sulfonamide bond cleavage, hydroxylation, nitration, and intramolecular Smiles rearrangement (Ismail et al., 2017; Ji et al., 2015; Ji et al., 2017b; Mahdi Ahmed et al., 2012). In a recent study, it was found that sulfonamide antibiotics could be removed by PMS in the absence of activators, but the underlying mechanisms were not well understood (Cui et al., 2016). In the present study, we demonstrated that such removal was due to the direct oxidation by PMS, generating nitrated products of higher persistence. This mechanism is in fact significant in activated PMS oxidation process and has been largely overlooked. The data of this study are of significance in evaluating the use of PMS for ISCO applications.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade or better. PMS (available as oxone, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) was purchased from Aladdin (Shanghai, China). Sulfamethazine (SMZ, ≥99%), 4-nitro-sulfamethazine (4-nitro-SMZ, 98%), aniline (99.0%), nitrobenzene, nitrosobenzene, sulfanilamide (99.0%), 2-amino-4,6-dimethylpyrimidine (ADPD, 98%), sulfamethoxazole (SMX, 99%), sulfapyridine (SPD, 99%), sulfadiazine (SDZ, 99%), sulfachloropyridazine (SCP, 98%), furfuryl alcohol (FFA, 98%), superoxide dismutase (SOD, from bovine erythrocytes), and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) were all obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade methanol (MeOH) and formic acid were purchased from Fisher (Waltham, MA, USA). Stock solutions of SMZ (150 μM), PMS (100 mM), and $CoSO_4$ (0.1 mM) were prepared by dissolving the reagents in Milli-Q water (18.2 MΩ cm) produced in a Millipore Super-Q water purification system.

2.2. Removal of SMZ and related compounds by PMS

The degradation of SMZ by PMS oxidation was conducted in 40-mL borosilicate glass vials as batch reactors at 25 °C. Reactions were initiated by dosing appropriate amount of PMS stock solution to the solution containing 15 μM SMZ. PMS doses of 0.5 mM to 4.0 mM were examined. The pH of the solution was maintained at 7.0 ± 0.2 with 10 mM phosphate buffer during the reaction, in order to simulate natural conditions. An aliquot of 1.0 mL sample was collected periodically, quenched with 20 μL $Na_2S_2O_3$ (1 M) immediately. The samples were stored in 4 °C refrigerator before further analysis for the residual SMZ. In order to identify the reactive species responsible for the removal of SMZ, the reaction was performed in the presence of MeOH, FFA, and SOD as the probes of free radicals (HO• and $SO_4^{\bullet-}$), $^1O_2$ and superoxide ($O_2^{\bullet-}$), respectively. The concentrations for MeOH and FFA were 10 mM and 1 mM, respectively. The quantity of SOD was 1 kU. Each time only one probe compound was spiked. Initial SMZ and PMS concentrations were 15 μM and 1.0 mM, respectively. All experiments were performed in triplicates and the data were averaged. Standard error of the mean was calculated and included as error bar for each data point.

The degradation of other related chemicals including four other sulfonamide antibiotics (i.e., SMX, SDZ, SPD, and SCP) and sub-structural moieties of SMZ (i.e., aniline, sulfanilamide, and ADPD) by PMS was examined individually. Initial concentration of aniline was 40 μM, the other compounds were all 15 μM. PMS dose was 1.0 mM. Other conditions and treatment were same as described above.

2.3. Removal of SMZ and related compounds by Co(II)/PMS

Removal of SMZ and aniline as well as their nitrated products including nitrosobenzene, nitrobenzene, and 4-nitro-SMZ in Co(II)/PMS oxidation process was explored. Co(II) was added as $CoSO_4$ at concentration of 0.1 μM. Initial PMS concentration was 1.0 mM. Initial concentrations of aniline, nitrosobenzene, and nitrobenzene were 100 μM; SMZ and 4-nitro-SMZ were 15 μM. Only one chemical was presented in the reactor each time. Degradation of SMZ in Co(II)/PMS process was also performed in the presence of 1 M MeOH in order to determine the contribution of free radicals to its removal. Other conditions and treatment were same as described above.

2.4. Quantification of SMZ and related compounds

The concentrations of SMZ and related compounds in the samples were quantified by a Hitachi L-2000 high performance liquid chromatography (HPLC, Hitachi, Japan) equipped with an Agilent ZORBAX Eclipse Plus C18 column (5 μm, 250 mm × 4.6 mm i.d.) and an L-2455 diode array detector. Isocratic elution for the analysis of SMZ, 4-nitro-SMZ, nitrosobenzene, and nitrobenzene consisted of 70% H_2O with 0.1% formic acid (v/v) and 30% MeOH with 0.1% formic acid (v/v). The elution for aniline, sulfanilamide, and ADPD consisted of water and methanol with a ratio of 95:5 (v/v). The flow rate was 1 mL min^{-1}.