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Applications and factors influencing of the persulfate-based advanced oxidation processes for the remediation of groundwater and soil contaminated with organic compounds

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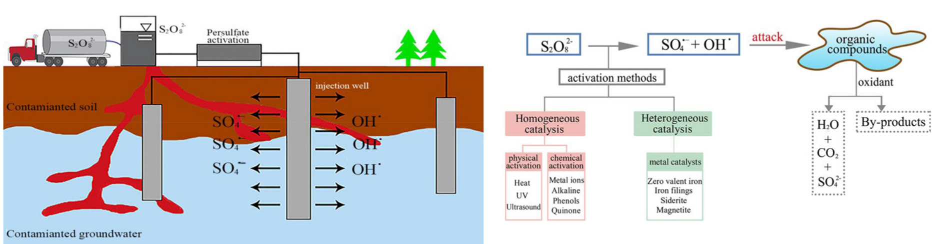
GRAPHICAL ABSTRACT



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ABSTRACT

Persulfate is the latest oxidant which is being used increasingly for the remediation of groundwater and soil contaminated with organic compounds. It is of great significant to offer readers a general summary about different methods of activating persulfate, mainly including heat-activated, metal ions-activated, UV-activated, and alkaline-activated. Meanwhile, in addition to persulfate concentration as an influencing factor for persulfate oxidation process, selected information like temperature, anions, cations, pH, and humic acid are presented and discussed. The last section focuses on the advantages of different activated persulfate processes, and the suggestions and research needs for persulfate-based advanced oxidation in the remediation of polluted groundwater and soil.

1. Introduction

As a significant part of ecological environment, groundwaterand soils are not only core resources which humans sustain life and livelihood, but also the data storehouse of biogeochemical cycles [1–4]. At present, groundwater and soil contaminated with organic compounds (e.g., antibiotics, polycyclic aromatic hydrocarbons, herbicides, parabens, phenolic compounds) are becoming more and more serious [4–6]. Fortunately, the public and the governments have realized the potential dangers of organic compounds posed to the health of human beings and environment [7,8]. Thus, the remediation of groundwater and soil contaminated with organic compounds has become the common opinion of the public and governments [9–12].

Recently, a lot of work has been done in the development of technologies for the remediation of groundwater and soil, and some innovative solutions for efficient removal of organic contaminants have

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been studied to reduce contents of organic contaminants to an acceptable and safe level [13,14]. In fact, in those treatment techniques, it is widely accepted that chemical oxidation has the latent capacity to pretreat or rapidly treat groundwater and soil contaminated with organic compounds [15]. The purpose of chemical oxidation is to mineralize organic contaminants to inorganics and H_2O, and CO_2, finally, transform them into biodegradable or harmless products [1,16,17]. Over the past decade, plenty of studies have been addressed to this goal and pointed out the outstanding role of an unique treatment technology of persulfate-based advanced oxidation, which always operated at near ambient pressure and temperature [18,19].

Persulfate-based advanced oxidation is an increasingly growing field for the remediation of groundwater and soil contaminated with organic compounds [20]. Peroxydisulfate ($S_2O_8{}^{2-}$), usually referred to as persulfate, which is the latest persulfate based advanced chemical oxidant and successfully gets extensive applications, and has usually showed great results [21,22]. Since persulfuric acid ($H_2S_2O_8$) was found by Marcelin Berthelot (a French chemist) in 1878 [23], persulfate-based advanced oxidation could be a valid, promising, and cost-effective technology for the remediation of groundwater and soil contaminated with organic compounds. The advantage of persulfate-based advanced oxidation is more "environmental-friendly" than other biological and chemical processes, because persulfate-based advanced oxidation neither produces a mass of hazardous sludge nor transfers contaminants from one phase to others [19]. Besides, the persulfate-based advanced oxidation method could degrade most organic compounds into biodegradable or harmless products [24].

For persulfate-based advanced oxidation, the heat, alkaline, metal ions, UV and other means activated decomposition of persulfate to engender two strong oxidants called sulfate free radical ($SO_4{\cdot}^-$) and hydroxyl radical ($OH\cdot$) [17,25–29]. The $SO_4{\cdot}^-$ and $OH\cdot$, which engendered by activating persulfate, and have a strong oxidation ability and can degrade the overwhelming majority of the organic compounds in ideal circumstances [30]. What's more, the $SO_4{\cdot}^-$ and $OH\cdot$ play an important role in the degradation of hard-degradable organic compounds [31], actually $OH^{\cdot}$ often dominant when using alkaline activated persulfate [30]. Because of this special advantage, persulfate is increasingly and widely used for the remediation of polluted water and soil with an extensive range of organic compounds [32–34]. Some studies have suggested that sulfate free radicals can last a long time, which can prolong the contact with organic compounds and enhance the degradation efficiency [30,35].

The objective of this study is to summarize and discuss the persulfate-based advanced oxidation method for the remediation of groundwater and soil contaminated with antibiotics, polycyclic aromatic hydrocarbons, herbicides, parabens, phenolic compounds. The activation methods, influencing factors and perspective of persulfate-based advanced oxidation in the remediation system will also be introduced. Meanwhile, challenges confronted in the application of persulfate-based advanced oxidation are discussed in the conclusion and perspective.

2. Research findings and practical observations concerning persulfate-based advanced oxidation

Persulfate-based advanced oxidation is a novel technique with few field applications recorded in the literature. However, activated persulfate oxidation technology has huge potential in environmental engineering and could have widespread application for environmental remediation with organic compounds [36–38]. Furthermore, it is focused on the current research in environmental protection field, mainly including the remediation of groundwater and soils contaminated by organic compounds and treatment of refractory organic wastewater [39]. Fig. 1 provides an illustration to help us to understand this method. Laboratory experiments, full-scale field projects, and pilot field studies have used different methods of activating persulfate in order to get a better compliance with the concrete treatment conditions. In fact, the technology of activating persulfate is divided into homogeneous catalysis and heterogeneous catalysis. Homogeneous catalysis mainly includes physical activation (e.g., heat, UV, ultrasound) and chemical activation (e.g., metal ions, alkaline, phenols, quinone). And heterogeneous catalysis mainly involves metal catalysts (e.g., cobalt-based, iron–based, manganese-based) and carbon catalysts (e.g., carbon nanotubes, nanodiamonds). In general, homogeneous catalysis is more frequently used. The following activation methods are most commonly used: (i) heat, (ii) metal ions, (iii) UV, (iv) alkaline. In addition, like other oxidants, persulfate is used in-situ by injecting an oxidant solution into underground (Fig. 2).

For the great majority the in-situ applications, the persulfate activation is an essential condition for the effective and successful degradation of organic compounds. But the documentation of activated persulfate which describes the degradation mechanisms of organic compounds is poor. Fortunately, a great number of results come from laboratory experiments in which effects of different activation ways on the activation efficiency of persulfate were tested. These findings are conducive to future researches [30].

3. Homogeneous catalysis

3.1. Physical activation

3.1.1. Heat-activated persulfate based advanced oxidation processes

Persulfate forms two sulfate free radicals through fracture of the peroxide bond because of absorption of heat energy [23]. And the activation energies for reactions are 100–116 kJ/mol, 119–129 kJ/mol, and 134–139 kJ/mol under acidic, neutral, and basic conditions, respectively [40] (Fig. 3).

The technique of heat-activated persulfate has been used for remedying groundwater and soil contaminated with organic compounds, and heat-activation is a hot spot in the research of persulfate activation technology due to its high efficiency and be able to degrade an extensive range of contaminants [30]. What's more, it has been well studied of heat-activated persulfate in some laboratory researches (Table 1

3.1.1.1. Remediation of antibiotics. Recently, the widespread occurrence of groundwater micropollutants such as antibiotics has raised serious concern about latent adverse effects on human health and aquatic ecosystems [41–43]. The main sources for the appearance of antibiotics in groundwater are municipal landfill leaching, land application of biosolids, and wastewater treatment plant effluents [44,45]. Therefore, antibiotics would be widely distributed in the groundwater, resulting in affecting ecosystem by the antibiotic-resistant genes' proliferation [46]. The environment and human health might be influenced by the groundwater contaminated with antibiotics [47]. In 2015, Ji et al. used heat-activated persulfate to remove SMX (SMX is sulfamethoxazole, a broad-spectrum antibiotic) [48]. Additionally, they indicated that the aniline moiety of SMX can be firstly attacked by $SO_4{\cdot}^-$, producing a radical cation $SMX{\cdot}^+$. Then it passed through further reactions involving aniline moiety oxidation, sulfonamide S—N bond fracture, hydroxylation and coupling reaction, forming a series of special intermediate products [48]. In 2015, Fan et al. investigated the removal process of sulfamethazine (SMZ) by heat-activated persulfate [49]. Based on radical scavenging tests, $SO_4{\cdot}^-$ was predominant oxidizing species, while $OH\cdot$ had little effect. Meanwhile, they found that both lower pH and higher pH had an inhibitory effect on the removal of SMZ, and the optimal pH range for removal SMZ was 7.0–9.0 [49].

3.1.1.2. Remediation of polycyclic aromatic hydrocarbons (PAHs). PAHs are a kind of hydrophobic organic molecules composing of 3–6 benzene rings, and PAHs are known for their carcinogenicity and highly toxicity.