Persulfate activation technology based on carbon-based catalyst for removal of phenolic pollutants from water

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Abstract. Phenolic compounds constitute a broad category of extensively utilized chemical entities, the environmental residue of which has elicited substantial concerns regarding its deleterious impacts on natural ecology and human health. Over the past years, persulfate-based advanced oxidation technology (PS-AOPs), attributable to its effective degradation capacity for organic contaminants in aqueous environments, has garnered increasing interest among the scientific community. Relative to metal-based catalysts, their carbon-based counterparts possess distinct advantages such as non-toxicity, robust pH adaptability, appropriate pore volume, and extensive specific surface area, and have thus found considerable applications in activating PS for the removal of phenolic pollutants in water. This article provides a comprehensive review of recent research advancements concerning the use of carbon-based catalysts— including graphene, activated carbon, biochar, and metal-carbon composite materials — for the activation of PS aimed at phenolic pollutant removal. Additionally, it suggests potential trajectories for future investigations in this field.

Keywords. phenolic compounds, advanced oxidation technology, persulfate, carbon-based catalyst, water pollution treatment.

1. Introduction

With the advent of scientific and technological advancements, phenolic compounds have been increasingly utilized in the manufacturing of a broad spectrum of industrial products, encompassing paints, fertilizers, surfactants, and more [1]. Concurrently, escalating concerns are being raised due to the mounting prominence of water pollution issues instigated by the migration and transformation of these phenolic compounds. The presence of phenolic compounds can detrimentally influence the taste and odor of drinking water. Furthermore, a substantial proportion of phenolic substances are acknowledged as toxic carcinogens, capable of inducing adverse impacts on various biological processes even at low concentration levels — for example, interference with reproductive and neural operations — thus posing considerable threats to both the ecological milieu and human health [2,3,4]. Numerous global organizations, including the United States Environmental Protection Agency (EPA) and the European Union (EU), have categorized phenolic compounds as priority pollutants, setting thresholds for wastewater and drinking water at $1mg \cdot L^{-1}$ and $0.001mg \cdot L^{-1}$ respectively [5]. Phenolic substances are characterized by their ubiquity, accumulation in living organisms, and persistence [6]. They are highly soluble in water and are capable of migrating to groundwater [7]. Owing to the challenge associated with the cracking of the benzene ring, these compounds exhibit resistance to biodegradation [8]. The high organic concentration typically found in phenol-containing wastewater contributes to elevated treatment costs [9], thus underscoring the pressing necessity for the efficient removal of phenolic pollutants from water. Advanced oxidation technology (AOPs), acknowledged for its potent oxidation capacity and low selectivity, has found widespread applications in the oxidation removal of refractory organic matter [10]. The conventional Fenton process predominantly employs Fe^{2+} ions as catalysts for activating H_2O_2, generating hydroxyl radicals ($^{\bullet}OH$) capable of attacking organic pollutants indiscriminately. However, the easy decomposition of H_2O_2 and the concomitant accumulation of iron sludge during the Fenton process limit its development and application.

In recent years, persulfate-based advanced oxidation technologies (PS-AOPs) have emerged as a focal area of research within the field of water treatment. Persulfate (PMS) or persulfate (PDS) are

white solids at room temperature, exhibiting stable physical and chemical properties that facilitate large-scale application. The activation process instigates the breakage of peroxy bonds (O−O) in PS molecules, triggering a chain reaction that produces reactive oxygen species (ROS) such as sulfate radicals ($SO_4^{\bullet-}$), hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{\bullet-}$), and singlet oxygen ($^1O_2$). $SO_4^{\bullet-}$ showcases a high REDOX potential (E_0=2.5~3.1V), a long half-life (30~40μs), a wide pH tolerance range, and non-selective oxidation characteristics [11,12,13].

PS activation can be achieved through various means including light energy, electric energy, transition metals, and carbon materials. While transition metal-based catalysts often exhibit significant activation properties by providing 3d electrons or empty 3d orbits, their application on a larger scale is hindered due to metal dissolution and ensuing secondary pollution [14,15]. Contrarily, carbon-based catalysts, compared to transition metal-based counterparts, offer distinct advantages: (1) safety, by evading the potential for ion leaching as a non-metallic material, (2) robust pH adaptability, ensuring stable structure across a wide pH range, and (3) suitable pore volume and expansive specific surface area, facilitating the efficient adsorption of oxidants/contaminants at the active site [16,17,18,19]. Consequently, the carbon material/PS system is being touted as a promising AOPs technology. This paper endeavors to provide a comprehensive review of the most recent research advancements in the field of phenolic pollutant removal via the activation of PS with carbon-based catalysts. It examines the structural features and catalytic activities of diverse carbon-based catalysts, thereby presenting a broad analysis of the current state of knowledge and potential future directions in this rapidly evolving field. The review will also delve into the mechanics of catalyst activation, elucidating the underlying processes that render these carbon-based materials such effective agents in the context of advanced oxidation procedures. It is anticipated that this synthesis of current research will serve as a foundation for further studies and provide a trajectory for the design and development of increasingly effective, efficient, and sustainable strategies for water treatment.

2. Research progress of carbon materials

2.1. Carbon materials and derivatives

The spectrum of carbon materials is wide and varied, encompassing entities such as graphene, activated carbon, biochar, among others. Factors such as the nature of the raw materials, the strategies employed for preparation, and the methods for modification can induce considerable variations in the pore structure and surface functional groups of these carbon materials. These differences, in turn, can profoundly influence the reaction mechanism and overall efficiency of the oxidation process. This underscores the importance of nuanced understanding and manipulation of these factors to optimize the utility of carbon-based catalysts in the context of advanced oxidation procedures. Future research should continue to investigate the intricate interplay between the properties of carbon materials and their efficacy in removing phenolic pollutants, striving to enhance both the theoretical understanding and practical applications in this area of study[20].

2.1.1 Graphene

Carbon materials encompass a diverse array of structures, including nanographenes and their derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO), all of which have demonstrated significant promise as PS activators in previous research. Specifically, GO derivatives, due to the presence of structural defects, have shown to activate PS more effectively than other carbon catalysts (such as graphite and carbon nanotubes), contributing to the degradation of phenol (PhOH) and 2,4-dichlorophenol (2,4-DCP) [21].In a noteworthy study, Duan et al. discovered that rGO-900/PMS was capable of entirely removing PhOH within a span of 150 minutes. They also noted a positive correlation between the synthesis temperature of rGO and the activation efficiency of PMS [22]. Further extending this line of investigation, Sun et al. demonstrated that rGO materials in a powdered form were particularly effective at promoting PMS activation [23].Additional support for the efficacy of rGO as a catalyst in this context comes from the work of Cruz-Alcalde et al., who

found that membrane catalysts developed using powdered rGO can effectively remove PhOH. This removal efficacy can be attributed to the ability of rGO to directly adsorb PhOH, with the removal rate of PhOH positively associated with the dose of rGO. Moreover, when rGO was combined with PDS, there was an additional enhancement in PhOH removal [24].Pedrosa et al. further added to this growing body of knowledge by using melamine to create nitrogen-doped GO powder that can activate PDS to remove PhOH. The process of nitrogen doping disrupted the sp^2 hybrid carbon arrangement and generated new active sites, leading to an increased rate of PhOH removal [25].These research findings highlight the diverse methods that can be employed to optimize the capabilities of carbon-based materials as catalysts in PS activation. They also underscore the immense potential these materials hold in advancing the field of water treatment technology.

2.1.2 Activated Carbon

Activated carbon (AC), characterized by its high porosity, large specific surface area, low cost, environmentally friendly nature, and abundant functional groups on its surface, has demonstrated significant activation properties [26]. For instance, Guo et al. employed a one-pot method to prepare sulfur-doped AC (S-AC) in situ, which was used to activate PDS for the removal of pentachlorophenol (PCP) from water. S-AC-800, characterized by a higher proportion of sp^2 hybrid structure, carbonyl groups, and defect sites, showed excellent catalytic activity for PCP degradation. Removal of sulfonyl groups increased the reduction degree of S-AC-800, facilitating electron transfer from carbon to PDS. Doped sulfur atoms altered the spin density of carbon atoms, generating more active sites, undermining the chemical inertness of carbon, and promoting electron transfer, which further improved the activation ability of S-AC [27]. A study conducted by Septian et al. introduced a simple grinding technique to prepare colloidal activated carbon (CAC), exhibiting a large specific surface area and proving to be an exceptional metal-free catalyst for PS activation [28]. Their research showed that the PhOH removal rate of the PDS/CAC system reached 100%, surpassing that of both the PDS/AC system (90.1%) and the conventional PDS/Fe^{2+} system (27.9%). PhOH removal occurred both in the bulk solution and on the CAC surface. The research also suggested that changes in particle size triggered a shift in the mechanism, with the main active species produced by AC and CAC activation of PDS being $^{\bullet}OH$ and $O_2^{\bullet-}$ [28]. AlMasud et al. explored the degradation of PhOH in an aqueous solution by a PDS and calcium peroxide (CP) bi-oxidant (DuO_x) using ball-milled activated carbon (ACBM) as a catalyst. Their experiment showed that the order of PDS and CP could affect the pH of the reaction system, thus impacting the activity of the reaction. In the ACBM/PDS/CP system, the primary active species were non-free radical species ($^1O_2$), with only a few being $SO_4^{\bullet-}$ and $^{\bullet}OH$ [29].Collectively, these studies underscore the potential of activated carbon, in its various forms and modifications, as a highly effective PS activator for the removal of phenolic pollutants from water. They also offer valuable insights into how different methods and materials can be used to enhance the activation properties of AC.

2.1.3 Biochar

Biochar (BC), extensively utilized in agriculture for carbon sequestration and as a fertilizer amendment, is regarded as a promising carbon material [30,31]. BC is a porous carbon material derived from the thermal treatment of biomass materials under a specific atmosphere [30]. The characteristics of BC are predominantly determined by its surface oxygen-containing functional groups (OFGs), including carboxylic groups, phenolic hydroxyl groups, hydroxyl groups, lactones, carboxylic anhydrides, and cyclic peroxide groups [32,33,34,35]. The surface charge and REDOX properties of BC are chiefly dictated by its carboxyl and phenolic hydroxyl groups [36]. Studies have evidenced that the presence of carboxyl, hydroxyl, and carbonyl groups can amplify the degradation potential of BC-activated PS towards organic pollutants [37,38].Research conducted by Miserli et al. demonstrated that the degradation rate did not substantially increase when Fe^{2+} was present in the BC/PDS system compared to the BC/Fe^{2+}/PDS system, indicating that BC plays a significant role in the activation and degradation of PDS. The degradation rate of phenols was found to be mainly influenced by the amount of BC rather than the amount of PDS [39]. The mineral content of BC was also observed to

affect the PhOH degradation rate. Liang et al. reported that different minerals in BC presented varying activation characteristics. Iron-bearing minerals facilitated the degradation of PhOH, whereas calcium-containing minerals greatly reduced the formation of $^{\bullet}OH$ causing an overall decline in PhOH degradation by inherent minerals. Magnesium and potassium did not affect PhOH degradation. The demineralization of BC further improved the PhOH degradation rate in the BC/PDS system [40]. The arrangement of BC's mesoporous structure also affects the removal rate of phenols. For instance, Sun et al. found that bovine bone char (BBCs) has an ordered mesoporous structure and can partner with PDS to achieve complete degradation of PhOH within 180 minutes. A large number of defect sites and functional groups on BBC700 are beneficial for ROS production and electron transfer. The BC700/PDS system exhibited an impressive PhOH mineralization rate (89.6±1.85%) and strong resistance to water pH and multiple co-existing components [41]. Furthermore, Zhang et al. prepared mesoporous BC through the calcination of bagasse modified by KOH and $CaCl_2$, and activated PDS by Ca/BS-800-KOH for the surface oxidative degradation of PhOH. Ca/BS-800-KOH acted as a medium to stimulate electron transfer between PhOH (electron donor) and PDS (electron acceptor), wherein Ca expedited the electron transfer rate on the Ca/BS-800-KOH surface. This process demonstrated an excellent removal rate of 90% (k=0.0404min^{-1}) within 60 minutes at a relatively low dose (0.066g/L) [42]. These findings highlight the potential of biochar as a robust activator in PS-based systems for efficient phenolic pollutants removal from water.

2.2. Metal-carbon composite materials

Metal oxide-carbon composites have been extensively employed as heterogeneous catalysts in SR-AOPs in recent years, as numerous studies have shown that combination with carbon carriers facilitates the dispersion, catalytic performance, and stability of metal oxides [43,44,45].

.Iron/carbon composites possess not only the common advantages of iron-based supported catalysts (such as non-toxicity, high dispersion, high catalytic activity, easy separation, and good stability), but the carbon components can also participate in the activation of PS, thereby improving catalytic activity further [46,47,48,49]. For instance, Yu et al. studied the removal efficiency of bisphenol A (BPA) using PDS activated by Fe_3O_4-modified ball milling biochar (Fe_3O_4@MBC). The abundance of oxygen-containing groups, enhanced graphitization and mesopore structure of MBC800, and the Fe^{3+}/Fe^{2+} conversion of Fe_3O_4 particles facilitated the activation of PDS to generate ROS. Also, the outstanding electrochemical performance expedited the electron transfer between the catalyst and PDS, promoting the degradation of BPA in the Fe_3O_4@MBC800/PDS system. Fe_3O_4@MBC800 demonstrated resistance to interference (including pH, anions, cations, and humic acids) and good catalytic reusability and stability [50]. Hadi et al. successfully fabricated a magnetized activated carbon (MPHAC) catalyst using pomegranate peel and explored the removal efficiency of 4-chlorophenol (4-CP) in water by the MPHAC/PDS system. Fe_3O_4 particles on the catalyst surface can induce the production of iron ions, enhancing the activation of PDS and the formation of $SO_4^{\bullet-}$. The produced $SO_4^{\bullet-}$ reacts with the H_2O molecule, resulting in the generation of an active $^{\bullet}OH$. $SO_4^{\bullet-}$ and $^{\bullet}OH$ react with 4-CP molecules to form intermediate compounds that initiate the degradation of the intermediates to H_2O and CO_2 [51]. Nguyen and Oh discovered that $SO_4^{\bullet-}$ and $^{\bullet}OH$ participatedin PhOH degradation when BC activated PDS in the presence of zero-valent iron (Fe(0)). In the Fe(0)-BC-PDS system, the graphite structure of the sp^2 covalent carbon network and the oxygen-containing functional groups on BC significantly enhanced PhOH degradation [55].

The good electron transfer ability of cupric oxide makes it a promising heterogeneous catalyst for SR-AOPs [56,57,58]. However, the unmodified CuO/carbon composite supported CuO tablets will agglomerate, thus affecting the catalytic activity [59]. Ma et al., for the first time, synthesized a nano-scale magnetic supported composite metal oxide Fe_3O_4-CuO@LAC catalyst using lignite active coke (LAC) as the carrier and Fe_3O_4-CuO composite metal oxide as the main active substance, which can effectively activate PDS to remove hydroquinone (HQ).The removal of HQ by Fe_3O_4-CuO@LAC is mainly dominated by $SO_4^{\bullet-}$, but the effect of $^{\bullet}OH$ cannot be ignored. $SO_4^{\bullet-}$ and $^{\bullet}OH$ first attack contaminants, then degrade and mineralize HQ. $^1O_2$ also degrades HQ via non-radical pathways. Due

to the circulation of Cu(II) and Fe(III) in the reaction system, the generation rate and concentration of ROS increase, leading to subsequent degradation reactions and promoting the efficient degradation of the system [60]. Qian et al. developed a novel graphene-Schiff base copper complex (Cu(salen)) for the activation of PDS to remove triclosan (TCS) from aqueous solutions. On the basis of Cu(salen), the authors also found that the activation of PDS in the polyphase amine-reduced graphene-copper oxide system (DArGO-Cu) can produce $SO_4^{\bullet-}$ and rapidly convert to $^{\bullet}OH$. In catalysis, graphene can not only serve as the carrier of Cu(salen), but also establish hydrophobic microregions to stabilize the catalytic active site in the reaction [61]. Li et al prepared a series of uniformly dispersed Cu-Cu_xO composites (Cu-Cu_xO@C), Cu-Cu_xO@C-700 containing polyvalent copper components, the co-presence of polyvalent copper ions played an important role in the activation of PDS [62]. Cu-Cu_xO@C-700 realizes the PhOH removal process with a k_{obs} value greater than 0.40min^{-1}. This excellent catalytic activity is mainly attributed to the synergistic effect of carbon matrix adsorption and electron transfer of polyvalent copper active center [63].

3. Conclusion and outlook

(1) Indeed, while carbon-based catalysts are showing promise in the field of water treatment by activating persulfate (PS) to remove phenolic pollutants, some challenges still need to be addressed to enhance the practical applicability of this technique:

(2) Performance in Real-World Applications: Many of the existing studies have been conducted using laboratory-simulated wastewater, which tends to have lower organic content and water volume compared to real-world wastewater. Therefore, future research needs to test the performance of these carbon-based catalysts in more realistic conditions. This could involve using actual wastewater samples from various sources (such as industrial or residential waste streams) to examine how well these catalysts perform in the presence of other potential contaminants and at larger volumes.

(3) Ease of Recovery: The majority of carbon catalysts used in these applications are in powdered form, which can be challenging to recover after use, particularly in large-scale applications. Future research and development should look into modifying the form, property, or composition of these carbon materials to ease their recovery. For instance, carbon materials could be configured into films or beads that can be more easily retrieved from the water after treatment. Additionally, the use of magnetic carbon materials could offer an innovative solution for easy recovery using magnetic separation techniques.

Environmental Impact Assessment: Another essential aspect that needs further attention is a comprehensive environmental impact assessment of carbon-based catalysts/persulfate systems. While these catalysts are seen as environmentally friendly due to their non-toxic nature and good pH adaptability, there is still a need to thoroughly evaluate the potential environmental impact of these systems. This could include assessing the lifecycle of these catalysts (from production to disposal), their potential to produce harmful by-products, and their long-term stability and effectiveness in various environmental conditions.

The future of PS-activated AOPs using carbon-based catalysts for water treatment seems promising, but addressing these challenges will be critical for its successful implementation on a large scale.

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