ACS ENVIRONMENTAL Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/environau Perspective

Non-negligible Organic Carbon Transfer during Organic Pollutant Degradation Processes by Advanced Oxidation Technologies

Published as part of ACS Environmental Au special issue "2024 Rising Stars in Environmental Research".

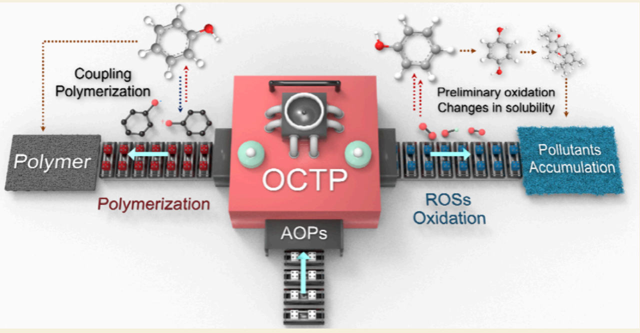
Zhuan Chen and Mingyang Xing*

Cite This: *ACS Environ. Au* 2025, 5, 148−151

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Heterogeneous Fenton and Fenton-like reactions, as one of the significant development directions of advanced oxidation processes (AOPs), still have some limitations that hinder their large-scale practical application. Organic carbon transfer processes (OCTPs) in AOPs including direct oxidation transfer processes (DOTPs) and changes in the solubility of pollutant reaction intermediates can lead to a significant accumulation of organics on the catalyst. The accumulation of organics severely impacts the sustainability of the catalyst and may lead to erroneous guidance about the mineralization rate of the reaction system. This perspective provides a comprehensive overview of recent research on OCTPs and presents new viewpoints and research directions for heterogeneous AOPs.



KEYWORDS: *advanced oxidation process, environmental remediation, pollutant degradation, organic carbon transfer, polymerization*

Due to their persistence and bioaccumulation, organic pollutants are difficult to degrade naturally, making environmental pollution issues increasingly complex. Nowadays, there is an urgent need to develop efficient technologies for the treatment of organic pollutants. By generating highly reactive radicals, advanced oxidation processes (AOPs) can efficiently degrade organic pollutants from water and have been widely used in the treatment of industrial wastewater.[1] The key features of AOPs are their rapid reaction rates and remarkable treatment efficacy, making them particularly suitable for the treatment of recalcitrant organic pollutants. Consequently, AOPs play a crucial role in enhancing the efficiency of environmental remediation and have become an essential tool for addressing environmental pollution issues.[2] As one of the key directions in the development of AOPs, heterogeneous AOPs still face challenges such as poor long-term stability of the oxidation systems and difficulty in recycling active sites.[3] The underlying causes of these issues remain unclear, and effective solutions are urgently needed. On the other side, the mechanisms underlying the degradation of pollutants by AOPs remain unclear yet. The reaction mechanisms involved in these processes are complex, and the evolution of organic pollutants within highly reactive systems is difficult to study comprehensively. For instance, current research has extensively focused on the selective generation of singlet oxygen ($^1O_2$) in Fenton-like systems. Unlike hydroxyl radicals (•OH) and other reactive oxygen species (ROS) with high oxidative potentials, $^1O_2$ is able to selectively oxidize easily oxidizable pollutants. However, with the oxidation degree of pollutant molecules increasing, the energy required for further oxidation also rises significantly. From the perspective of thermodynamics, the low oxidation potential of $^1O_2$ does not support achieving high mineralization rates of organic pollutants in such systems, which contradicts the conclusions of many researches. One possible reason is that in many heterogeneous AOP systems currently at the laboratory stage the complete range of ROS types is difficult to detect comprehensively. •OH, due to its high oxidative potential and short lifespan, is difficult to detect in some AOPs, particularly in heterogeneous Fenton-like reaction systems. According to the report by Yu et al., adsorbed •OH is present on the surface of CoP catalysts in photocatalytic Fenton systems.[4] This adsorbed •OH is difficult to detect directly by electron-paramagnetic resonance (EPR) spectroscopy but can cooperate with $^1O_2$ in the system to oxidize and mineralize organic pollutants. In such oxidation systems, organic pollutants can usually be preliminarily

Received: July 29, 2024
Revised: December 11, 2024
Accepted: December 16, 2024
Published: January 7, 2025

oxidized by $^1O_2$ and form corresponding hydroxylation products, such as catechol, hydroquinone, and resorcinol. And hydroxylation products can be further oxidized and mineralized by adsorbed •OH. On the other hand, in various heterogeneous AOPs, an organic carbon transfer process (OCTP) on the catalyst surface is common, in fact leading to the removal of chemical oxygen demand (COD) from the water and, consequently, high mineralization rates in the reaction solution. Zhang et al. demonstrated that, in some heterogeneous Fenton-like reaction systems, phenolic organic pollutants such as phenol could undergo coupling or polymerization reactions with the addition of a small amount of oxidant.[5,6] The resulting macromolecular polymers aggregate on the catalyst surface, thereby removing pollutants from the wastewater. However, most of the current research on advanced oxidation processes primarily focuses on the oxidation of organic compounds in the reaction solution while neglecting the accumulation of these organic carbon substances on the catalyst surface.

Since 2022, Zhang et al. have proposed a direct oxidation transfer process (DOTP) mechanism for the direct removal of organic pollutants from contaminated water through polymerization reactions.[5] This mechanism introduces a polymerization reaction of pollutants present in Fenton-like reactions under low oxidant dosage conditions. In the DOTP, a small amount of oxidant first interacts with the catalyst and subsequently reacts with pollutant molecules to generate active intermediates, such as phenoxy radicals or phenoxonium ions. These active intermediates can then initiate free radical or cationic polymerization of the pollutant molecules. This process requires only the oxidant to act as an initiator for the polymerization reaction; therefore, DOTP is based on a minor amount of oxidant. Simultaneously, the removal of organic pollutants from water through the DOTP does not mineralize the pollutants. Instead, the organic pollutants generally accumulate on the catalyst surface through the polymerization reaction. DOTP using this low oxidant can be extended to various metal oxides and halides, such as BiOI, FeOCl, VOCl, and other low-cost, environmentally friendly materials.[7]

In addition to DOTP, the accumulation of oxidation products of organic pollutants on the surface of solid materials is common during the degradation of pollutants in most heterogeneous AOPs. In recent studies, we found that the oxidative intermediates of organic pollutants tended to accumulate on the surface of solid materials with poor hydrophilicity due to the water solubility changes of organic pollutant molecules in many heterogeneous Fenton and Fenton-like reactions. Distinguishing from the polymerization reaction of pollutants in the DOTP, this process primarily involves the oxidation of pollutants and includes partial mineralization of organic pollutants. It mainly describes that the energy required for the oxidation of organic pollutant molecules increases with the degree of oxidation in AOPs. Therefore, in reaction systems dominated by singlet oxygen with a low oxidation potential, such OCTP phenomena are particularly prevalent. On the other hand, the oxidation products of organic pollutant molecules vary in form, leading to numerous organic reactions among the products. These postreaction products may exhibit a significant decrease in water solubility and are more likely to accumulate on the surface of solid materials present in the reaction system, which are less hydrophilic. The proportion of organics accumulating on the catalysts after the reaction is related to several factors, such as the hydrophilicity of the solid materials in the reaction system and the amount of oxidant in the reaction system. The oxidation degree of organic pollutants in the reaction system increases with the rising amount of oxidant, while the proportion of organics accumulating on the catalysts first increases and then decreases. This is because the aggregation of reaction intermediates on the catalyst surface requires only partial oxidation of pollutant molecules, whereas a high mineralization rate would diminish this phenomenon. At specific oxidant dosages, the aggregation of pollutants becomes the primary reason for the removal of COD from contaminated wastewater. On the other hand, solid materials with weak hydrophilicity are more suitable for this accumulation because the water solubility of the pollutant molecules after the reaction will significantly decrease. Both DOTP and OCTP caused by changes in the water solubility of reaction intermediates can lead to catalyst deactivation. However, the catalyst's activity can be restored through simple washing. Since the organic compounds accumulated on the catalyst surface are not homogeneous, solvents with varying polarities, such as methanol, toluene, and dichloromethane, should be used for washing.

In addition to low oxidation potential reaction systems, OCTP also occurs in traditional Fenton reactions dominated by •OH. When nonreactive solid substances such as TiO_2 are added to the conventional homogeneous Fenton reaction for the degradation of phenol, the mass of TiO_2 significantly increases after the reaction and the COD of TiO_2 increases from 1 to 180 mg/L. The significant increase in COD on TiO_2 indicates the aggregation of a substantial amount of organic matter on its surface. This implies that the aggregation of reaction intermediates also occurs in reaction systems dominated by high oxidation potential active oxygen species. Essentially, OCTP is related to the mineralization rate of pollutants, and at specific oxidant dosages, high oxidation potential reaction systems similarly fail to achieve high mineralization rates, thereby leading to the occurrence of OCTP. In addition, homogeneous Fenton reactions can also induce the polymerization of pollutants molecules. In recent studies, we found that when aniline is added to the Fenton reaction, flaky solids appear in the reaction system (Figure 1). The formation of these solids in the reaction system is relatively slow, typically requiring up to a week of stirring the reaction solution. In fact, the traditional Fenton reaction is a process that produces both active oxygen species and iron sludge. Therefore, the presence of various OCTPs in the reaction system may also be based on the formation of iron sludge nanoparticles in homogeneous Fenton reactions. Iron sludge nanoparticles can continuously adsorb weakly polar molecules or polymers in the reaction system, thereby removing COD from the reaction solution.

Both OCTP based on DOTP and changes in the water solubility of pollutant reaction intermediates essentially require the catalyst to activate the oxidant to initiate the process. Therefore, OCTP fundamentally remains a type of process within AOPs (Figure 2). Additionally, the preliminary oxidation (hydroxylation of phenolic substances) or transformation (formation of phenoxy radicals/phenoxonium ions) of pollutant molecules by the oxidant is a necessary step for the occurrence of OCTP. Meanwhile, the OCTP can create the false appearance of organic pollutants mineralization in the reaction solution. However, rational utilization of the OCTP

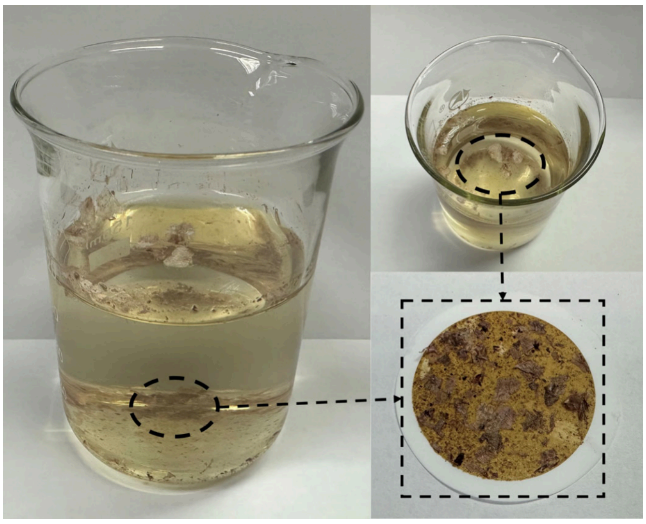


Figure 1. Solid substances generated during the traditional Fenton reaction for the degradation of aniline.

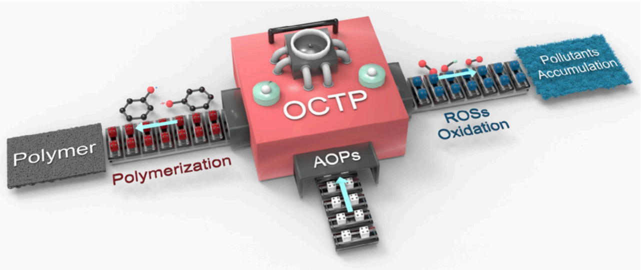


Figure 2. Process of polymerization and accumulation of pollutants in AOPs.

mechanism can significantly enhance the efficiency of AOP systems, allowing the removal of more pollutants with a smaller amount of oxidant. Therefore, the study of OCTP is indispensable in the degradation of organic pollutants with AOPs. In the process of treating organic pollutants with heterogeneous AOPs, more attention needs to be given to the following aspects:

(1) According to the Sabatier principle, ensuring the adsorption and oxidation of pollutant molecules on the catalyst surface while enhancing the desorption rate of oxidation products is one of the key factors for maintaining the high efficiency of heterogeneous AOPs in activating oxidants to degrade pollutants.[8]

(2) From the perspective of thermodynamics, the rapid removal of organic pollutants and COD in heterogeneous AOPs may imply rapid deactivation of the catalyst.[9] At this point, examining the OCTP in the system should be a very important part of the research. In heterogeneous AOPs dominated by low oxidation potential ROS, the presence of the OCTP phenomenon must be carefully studied if there are no adsorbed ROS in the reaction system.

(3) In the widely studied various heterogeneous AOPs, the sustainability of the catalyst needs to be more rigorously examined. Including cycling experiments in numerous studies does not, in fact, demonstrate the stability of the catalyst. Conducting long-term degradation experiments over extended periods is a better method for assessing the catalyst's continuous activation of oxidants for pollutant degradation in water. Furthermore, merely evaluating the mineralization rate of organic pollutants in the reaction liquid is insufficient; it is also essential to measure the changes in total organic carbon and COD of the solid materials before and after reaction, as these are crucial aspects of the research process.

(4) If it is necessary to reduce an OCTP in the reaction system, by combining the correlation between the OCTP and material hydrophilicity, regulating the catalyst to a superhydrophilic surface can effectively reduce the occurrence of an OCTP. On the other hand, an effective way to reduce an OCTP is to increase the mineralization rate of organic pollutants. There are two ways to improve the mineralization rate of pollutants: (1) coupling long-lived non radical ROS such as singlet oxygen with adsorbed ROS to mineralize pollutants; (2) improve the utilization rate of oxidants, increase the relative concentration of ROS, and achieve high mineralization rate.

(5) Based on key factors such as the hydrophilicity of materials and the water solubility of pollutants that affect an OCTP, for some difficult to dissolve micropollutants, selecting suitable hydrophilic and hydrophobic materials may enhance the adsorption and degradation of such pollutants through OCTPs.

■ AUTHOR INFORMATION

Corresponding Author

Mingyang Xing − *Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China; Shanghai Engineering Research Center for Multimedia Environmental Catalysis and Resource Utilization, East China University of Science and Technology, Shanghai 200237, China;* orcid.org/0000-0002-0518-2849; Email: mingyangxing@ecust.edu.cn

Author

Zhuan Chen − *Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsenvironau.4c00063

Author Contributions

CRediT: **Zhuan Chen** writing - original draft; **Mingyang Xing** conceptualization, funding acquisition, investigation, methodology, supervision, writing - review & editing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 22325602, 22176060) and sponsored by Program of Shanghai Academic/Technology

Research Leader (23XD1421000). The authors thank Research Center of Analysis and Test of East China University of Science and Technology for the help on the characterization.

REFERENCES

(1) Zhang, S.; Zheng, H.; Tratnyek, P. G. Advanced redox processes for sustainable water treatment. *Nature Water* **2023**, *1* (8), 666−681.

(2) Li, Y.; Dong, H.; Li, L.; Tang, L.; Tian, R.; Li, R.; Chen, J.; Xie, Q.; Jin, Z.; Xiao, J.; et al. Recent advances in waste water treatment through transition metal sulfides-based advanced oxidation processes. *Water Res.* **2021**, *192*, No. 116850.

(3) Thomas, N.; Dionysiou, D. D.; Pillai, S. C. Heterogeneous Fenton catalysts: A review of recent advances. *J. Hazard. Mater.* **2021**, *404*, No. 124082.

(4) Yu, H.; Liu, D.; Wang, H.; Yu, H.; Yan, Q.; Ji, J.; Zhang, J.; Xing, M. Singlet oxygen synergistic surface-adsorbed hydroxyl radicals for phenol degradation in CoP catalytic photo-Fenton. *Chin. J. Catal.* **2022**, *43* (10), 2678−2689.

(5) Zhang, Y.-J.; Huang, G.-X.; Winter, L. R.; Chen, J.-J.; Tian, L.; Mei, S.-C.; Zhang, Z.; Chen, F.; Guo, Z.-Y.; Ji, R.; et al. Simultaneous nanocatalytic surface activation of pollutants and oxidants for highly efficient water decontamination. *Nat. Commun.* **2022**, *13* (1), 3005.

(6) Zhang, Y.-J.; Chen, J.-J.; Huang, G.-X.; Li, W.-W.; Yu, H.-Q.; Elimelech, M. Distinguishing homogeneous advanced oxidation processes in bulk water from heterogeneous surface reactions in organic oxidation. *Proc. Natl. Acad. Sci. U. S. A.* **2023**, *120* (20), No. e2302407120.

(7) Zhang, Y.-J.; Tao, J.-S.; Hu, Y.; Huang, G.-X.; Pan, Y.; Li, W.-W.; Chen, J.-J.; Yu, H.-Q. Metal oxyhalide-based heterogeneous catalytic water purification with ultralow H2O2 consumption. *Nature Water* **2024**, *2*, 770.

(8) Hu, S.; Li, W.-X. Sabatier principle of metal-support interaction for design of ultrastable metal nanocatalysts. *Science* **2021**, *374* (6573), 1360−1365.

(9) Vaiss, V. S.; Fonseca, C. G.; Antunes, F. P.; Chinelatto, L. S., Jr; Chiaro, S. S.; Souza, W. F.; Leitão, A. A. Experimental and theoretical study of deactivated HDT catalysts by Si species deposited on their surfaces: Models proposition, structural and thermodynamic analysis. *J. Catal.* **2020**, *389*, 578−591.