Spatial confinement: a green pathway to promote the oxidation processes for organic pollutants removal from water

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Abstract

Organic pollutants removal from water is pressing owing to the great demand for clean water. Oxidation processes (OPs) are the commonly used method. However, the efficiency of most OPs is limited owing to the poor mass transfer process. Spatial confinement is a burgeoning way to solve this limitation by use of nanoreactor. Spatial confinement in OPs would (i) alter the transport characteristics of protons and charges; (ii) bring about molecular orientation and rearrangement; (iii) cause the dynamic redistribution of active sites in catalyst and reduce the entropic barrier that is high in unconfined space. So far, spatial confinement has been utilized for various OPs, such as Fenton, persulfate, and photocatalytic oxidation. A comprehensive summary and discussion on the fundamental mechanisms of spatial confinement mediated OPs is needed. Herein, the application, performance and mechanisms of spatial confinement mediated OPs are overviewed firstly. Subsequently, the features of spatial confinement and their effects on OPs are discussed in detail. Furthermore, environmental influences (including environmental pH, organic matter and inorganic ions) are studied with analyzing their intrinsic connection with the features of spatial confinement in OPs. Lastly, challenges and future development direction of spatial confinement mediated OPs are proposed.

Keywords: Spatial confinement, oxidation process, organic polluted water, mass transfer, local enrichment of substances

1. Introduction

Large amount of persistent organics released into surface and ground water cause serious pollution and pose a significant threat to living organisms. Oxidation processes (OPs) are frequently used for organics removal (Song et al. 2022, Yang et al. 2020). Organics are attacked by the oxidizing radicals generated in OPs, like hydroxyl radicals (•OH, 2.8 V vs. SHE) and singlet oxygen ($^1O_2$, 1.1 V vs. SHE) (Yi et al. 2021, Zhou et al. 2019). However, the generation of radicals is slow (Zhang et al. 2022), and only a few radicals participate in organics degradation (Li et al. 2022). Great efforts have been made to overcome these restrictions, such as adding cocatalyst, increasing oxidants concentration (e.g., peroxymonosulfate and H_2O_2) or introducing external energy (e.g., solar, thermal and electric energy) (Wei et al. 2022a). Nevertheless, these strategies could not achieve the satisfactory efficiency of OPs in actual wastewater treatment due to poor mass transfer process (Yi et al. 2022b). Therefore, the broad application of OPs in practical settings is restricted (Li et al. 2019b).

As a means to accelerate the OPs, spatial confinement has attracted much attention in recent years (Shang et al. 2022). When the size of spatial restriction is at nanometer scale or smaller, known as spatial confinement, the phase behavior of matter in confined space will be different from in the bulk phase, which has a great effect on oxidation reaction. In the beginning, traditional spatial restriction at nanometer scale was utilized to improve OPs. Materials with special scaffolds contribute to multiple confined structures, including holes, cavities, or well-defined structures (e.g., tubes or layered structure). With the development of nanotechnology, spatial confinement has been extended to the atomic level restriction like unsaturated coordination of atomic species (Lin et al. 2020). Spatial confinement shortens reactant diffusion distance to achieve faster mass and heat transfer (Faucher et al. 2019), and enhances covalent and noncovalent interaction between the guest molecules and the reaction surface, especially those distance-dependent intermolecular forces like electrostatic interaction (Chen et al. 2014). Moreover, by enhancing the interaction, spatial confinement further promotes their individual behavior like accumulation, distribution and binding (Zhou et al. 2020b). These contribute to the enrichment of reactants, which promotes oxidation reaction thermodynamically.

The size of restricted space plays an important role in the confinement effect for OPs improvement. When OP is confined in a space with the size decreased to several nanometers or even small, in addition to enrichment of reactants, the electronic transport characteristics could be altered obviously, leading to the change of oxidation system, especially the valence electron structure, which may even contribute to the quantum mutation (Ma et al. 2022a, Rajadell et al. 2017). Consequently, the oxidation reaction could be improved thermodynamically and kinetically, and the improvement is obvious. For instance, the reaction kinetics of confined Fenton OP inside nanoscale (< 20 nm) channels improved 820 times compared to the unconfined Fenton OP (Zhang et al. 2020b). On one hand, the confined space enhances the utilization efficiency of enriched reactive radicals in OPs. The generated reactive radicals are easily quenched by ubiquitous natural organic matter (NOM) and bicarbonate, carbonate and other substances existing in environment, leading to ultrashort lifetimes (10^{-6}-10^{-9} s) and transfer distance (Chen et al. 2019). It was reported that •OH radicals generated from catalyst surface would be consumed within 25 nm of mass transfer distance in aqueous phase, thus 25 nm is the critical size to optimize the confinement effect (Zhang et al. 2020b). On the other hand, the energy barriers of oxidation reaction could be reduced under spatial confinement (Panić et al. 2018). Spatial confinement also makes the solid electron donor/receptor more active (Ding et al. 2018) and accelerates electron transport by regulating the surface electron properties (Chen et al. 2017). These enable spatial confinement to adjust the reaction kinetics to achieve efficient OPs.

For spatial confinement mediated OPs, the precise match between the size/shape of confined space and substrate is of great significance. Additionally, the nature of oxidation catalysts, the hydration properties of pollutant, environment pH, and redox potential also affect the OPs (Hu et al. 2020b, Liu et al. 2020a). The OPs are elusive under spatial confinement. Using spatial confinement to promote OPs must combine fundamental research with technology applications. The relationship between the differences made by spatial confinement and their implications in OPs for organics removal needs systematical illustration. In this review, the application of spatial confinement in OPs for organics removal is summarized firstly. Subsequently, the features of spatial confinement and their effects on OPs are discussed. Furthermore, environmental influences are studied with analyzing their intrinsic connection with the features of spatial confinement in OPs. Lastly, the challenges and future development of spatial confinement mediated OPs in actual wastewater treatment are proposed.

2. Application of spatial confinement in oxidation process

Amounts of OPs have been improved by use of spatial confinement, including Fenton OP, persulfate OP, photocatalytic OP and others like ozone, electrocaltalysis and spontaneous OPs. Materials with various structures, such as holes, cavities, or well-defined structures, have been used to provide confined structure. The confined structure and its match degree with substrates have great effects on the performance of OPs. The effects are diverse in different OPs, which is investigated with analyzing concrete OPs in this section. The causes of confinement for the variation of reaction efficiency is also discussed.

2.1 Fenton oxidation

2.1.1 Radicals mediated Fenton OP

Fenton OPs mediated by •OH radicals are widely employed in the treatment of organics polluted water (Li et al. 2015, Shin et al. 2008). The coordination environment of Fenton catalysts could affect the redox potentials of Fenton OPs and binding behaviors with H_2O_2, leading to different yield of •OH (Kamitani 2021). •OH concentration plays an decisive role in Fenton OP. It is worth noting that the existence time of •OH in aqueous phase is ultrashort (~ 10 us) owing to scavenging by NOMs.

This limits the transfer of •OH from the generating site to target organics (Qu et al. 2022b, Zhang et al. 2017). Because of the short lifetime, •OH concentration in the bulk phase is low, cannot meet the required amount of high-efficient Fenton OPs in organics degradation (Zeng et al. 2014).

Vast works focus on the improvement of surface catalytic performance (Tan et al. 2022, Zhou et al. 2020c). Nevertheless, this strategy cannot improve the transfer efficiency of •OH from the generated sites to target pollutants (Li et al. 2021b). Utilizing confined structure as nanoreactor for Fenton OPs can shorten the mass transfer distance of •OH and reduce •OH consumption in transfer process. For instance, magnetic Ti_3C_2-based MXene nanosheets were used to confine nanoscale zero-valent iron particles (nZVI@Ti_3C_2) to catalyze Fenton OPs for ranitidine degradation (Ma et al. 2021). This confined structure enriched local •OH production from H_2O_2 activation and promoted the embeddedness of ranitidine molecules in the reaction region (i.e., confined lamellar space), and then improved the collision frequency of these reactants to achieve high degradation efficiency. Additionally, anodized aluminum oxide (AAO) was used to confine Fe_3O_4 to construct Fe_3O_4-AAO nanoreactor with uniformly sized and cylindrical parallel channels (Figure 1a) (Zhang et al. 2020b). In 14 h of Fenton OPs, there were no catalyst deactivation, low iron leaching (<19 ug/L) and little pH change (<0.05). The half-life of para-chlorobenzoic acid (p-CBA) decomposition was shortened to about 14 s in the Fe_3O_4-AAO nanoreactor with pore size < 20 nm, much less than in the bulk oxidative system with suspended Fe_3O_4 in water (~3.2 h). The size of confined space has an impact on Fenton OPs. •OH concentration confined in the smaller pore range at 20 nm is higher than the pore range at 200 nm, leading to faster oxidation reaction. The extent of spatial confinement on •OH mediated Fenton OPs kinetics depends on •OH concentration and the contact of reactants with •OH.

Furthermore, the spatial confinement can give Fenton OPs "selectivity". The configuration with designed porous materials can block organic molecules larger than the pores, which can reduce the catalyst fouling and •OH quenching by macromolecular NOM (Sun et al. 2018). Zhang et al. (2021e) used ZrO_2/TiO_2 ceramic membrane (CM) to embed iron oxychloride (FeOCl), which can block the organics with molecular weight larger than 300 kDa (Figure 1b). The distance of FeOCl interlayers is 7.92 Å, larger than the average size of H_2O_2 precursor molecules (2.5 Å) (Herber and Cassell 1982). This enables H_2O_2 entry to produce •OH. Large surface area available for reaction contributes to the high •OH concentration inside CM. Additionally, only a little NOM with van der Waals diameter < 7.92 Å can enter FeOCl-CM pores, leading to reduced deactivation of •OH and FeOCl sites. FeOCl-CM confined the Fenton OPs within the membrane pores (size at ~20 nm), realizing "selective exposure" and "domain limited oxidation" of internal •OH to small organics, and showed a near-complete destruction of organics through single-pass treatment.

2.1.2 Nonradicals mediated Fenton-like OP

Beside •OH radicals mediated Fenton OPs, nonradical pathway is also worthy of attention under spatial confinement. Yang et al. (2019) found a $^1O_2$ mediated iron-based Fenton-like OP in a nanoreactor formed by Fe_2O_3 nanoparticles (~2 nm) confined in the multiwalled CNT (Fe_2O_3@MWCNT) with ~7 nm inner diameter. To explore the effect of spatial confinement, Fe_2O_3 nanoparticles were distributed on the MWCNT (Fe_2O_3/MWCNT) outer surface as another structure. The electron spin resonance (ESR) spectra was used to identify the active species generated in various OPs. •OH but no $^1O_2$ were detected in unconfined OPs over Fe_2O_3 and Fe_2O_3/MWCNT. In contrast, nearly no •OH but $^1O_2$ were detected in confined Fenton OPs over Fe_2O_3@MWCNT (Figure 2) (Yang et al. 2019). Moreover, the ~7 nm size impeded the adsorption of many organic macromolecules into the MWCNT. The oxidation rate was linearly proportional to the adsorption affinity of organics on MWCNT inner surface. Compared to other confined Fenton OPs (Table 1), this $^1O_2$ mediated Fenton OP showed high pH tolerance, which can maintain oxidation performance at pH value up to 9.0.

Spatial confinement inside MWCNTs changes the Fenton reaction pathway to generate $^1O_2$ but not •OH. We speculate that there are two stages in the mechanism: (i) Two H_2O_2 molecules are required for the reaction to generate $^1O_2$. In the confined space, H_2O_2 are enriched locally, promoting the reaction to generate $^1O_2$. (ii) Electronic state is different in the inner and outer surface of MWCNT. The inner surface is electron deficient. When confined in MWCNT, the conversion of

Fe(III)/Fe(II) that needs the participation of electrons might be inhibited, subsequently the reaction of Fe(II) and H_2O_2 to generate •OH was inhibited.

2.2 Persulfate oxidation

Persulfate OP, including peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$), is also an alternative to degrade organic pollutants (Gao et al. 2022, Mei et al. 2020, Wei et al. 2022b). Compared with H_2O_2, most PMS and PDS strong oxidants are in the solid form, which are easier to be stored and transported (Qu et al. 2022a). Direct reaction of persulfates with organics is slow. To obtain efficient persulfate OP, activate persulfates to generate reactive species like $\bullet SO_4^-$, •OH, and $^1O_2$ is critical (Liu et al. 2022b). Apply various catalysts is a commonly used method to active persulfates (Huang et al. 2021a, Zhou et al. 2020a). Achieving high exposure of active surfaces and edges of catalyst is crucial for persulfates activation (Xu et al. 2022b, Yi et al. 2022a).

Confined structure effectively utilizes the considerable specific surface area to achieve this goal (Cao et al. 2020). And the confinement can realize quick cycling of metals in different valence states, like Fe(III)/Fe(II) cycle (Wang et al. 2020b). Amounts of persulfate OPs have been improved by spatial confinement (Table 2). Chen et al. (2019) assembled MoS_2 nanosheets into a lamellar membrane. This two-dimensional (2D) structure provided large surface area, well-preserved the active sites ($Mo^{2+} \rightarrow Mo^{6+}$) on surface, and shortened the diffusion distance of organics in nano-sized interspacings, resulting in the increased efficiency of PMS activation.

Total degradation of BPA over lamellar MoS_2 membrane/PMS system just needs ~60.4 ms. $•SO_4^-$ and •OH dominates the oxidation reaction for bisphenol A (BPA) removal (Chen et al. 2019). Li et al. (2021a) presented a yolk-shell structured $CoTiO_3@Co_3O_4$ with high permeability for guest molecules/ions diffusion (Figure 3a). $•SO_4^-$, $^1O_2$ and •OH were detected via ESR in PMS activation over $CoTiO_3@Co_3O_4$. $•SO_4^-$ and $^1O_2$ are the dominating reactive species for the oxidation degradation of rhodamine B (RhB).

Notably, the confined structure also influences the activation pathway of PMS. In most persulfate OPs, $•SO_4^-$, $^1O_2$ and •OH are generated and participate in organics oxidation. Generally, PMS was activated via the cleavage of O-O bond to generate $•SO_4^-$, and •OH was generated via $•SO_4^-$ while $^1O_2$ was generated from the self reaction of $•SO_5^-$ (Chen et al. 2019). Interestingly, it was found that when the space size was reduced to angstrom scale, spontaneous dissociation of PMS via S-O bond cleavage could be promoted to generate more $^1O_2$ (Meng et al. (2022).

Meng et al. (2022) synthesized an angstrom-confined Co-TiO_x laminar membrane to activate PMS for ranitidine degradation (Figure 3b). $•SO_4^-$, $^1O_2$ and •OH are the main reactive oxygen species. The adsorption energy (E_{ads}) of PMS molecule on Co-TiO_x membrane nanochannels increases with the constriction of interlayer free spacing, indicating more efficient adsorption. DFT calculations found the S-O bond length increased with the decrease of interlayer free spacing size, indicating easier cleavage of S-O bond in PMS. 5.8 Å is the critical size value for the spontaneous

(G-$ZnFe_2O_4$) photocatalyst was synthesized. The interconnected graphene network provided transport channel for photogenerated electrons from $ZnFe_2O_4$, and acted as an electron reservoir to inhibit the recombination of electrons and holes. The confined mesoporous structure with ultrasmall grain size promoted the exposure of $ZnFe_2O_4$ crystallized (311) plane and the adsorption of organic pollutants. G-$ZnFe_2O_4$ can quickly degrade methylene blue (MB) and the degradation rate reached 1.924×10^{-7} mol g^{-1} s^{-1}. Ma et al. (2022b) also fabricated Co/La decorated g-C_3N_4 nanosheets (Co/La@g-C_3N_4) with layer confinement, showing outstanding oxygen activation. The spatial confinement provided by g-C_3N_4 layers promotes the reactants enrichment and the contact with active sites, contributing to high photocatalytic performance for tetracycline (TC) degradation. Besides, Liu et al. (2022a) prepared a confined pyrite cinder-based FeOCl (PyC/FeOCl) catalyst that showed good performance on ciprofloxacin (CIP) degradation. Bai et al. (2022) synthesized a confined perylene diimide (PDA)@CNT photocatalyst for remarkably boosted degradation of diclofenac. The confinement effect of CNTs make PDA@CNT grow sequentially to form supramolecules. Electrostatic interaction formed by dispersion forces dominates the stabilization process. The conjugation of PDA constructed a 3D pathway (CNT → CNT, CNT → PDA, and PDA → PDA), which allowed for electrons transfer to the CNT plane that formed an internal electric field to accelerate the transport of photogenerated electrons and holes (Figure 4a) (Bai et al. 2022).

In addition to directly improve the excitation processes of photocatalysts, spatial the application of spatial confinement brings about a change on pH and behavior of organics and ions. In turn, environmental pH, co-exist organics and ions also affect the application of spatial confinement. Environmental pH plays an important role in the transport of protons and charge. The electrostatic interaction between the reactants and reactive surface is affected by the co-existed organics and inorganic ions (Falkowska et al. 2018). In this section, environmental influences are studied with analyzing their intrinsic connection with confinement features in OPs (Figure 7).

4.1 Environmental pH

Transport of protons and charges affects environmental pH, while environmental pH influences the function of spatial confinement on OPs improvement. It was found that protons can quickly transferred under spatial confinement (Shi et al. 2020, Wang et al. 2021b). Environmental pH and the pH at point of zero charge determine proton transfer process. When environmental pH is less than the zero charge point of catalyst, the catalyst surface is negative charged (Zhang et al. 2021c). At this point, protons acting as the counterions transfer to the negative charged surface to achieve interfacial charge balance (Macha et al. 2019). Furthermore, pH alters the charge distribution of catalyst surface, which affects the adsorption of organics. For example, Yao et al. (2021) found a negative correlation between pH value and perfluorooctanoic acid (PFOA) oxidation efficiency, presumably because the reduced adsorption. PFOA (the acid dissociation constant is 2.8) is more likely to show deprotonation state and catalyst surface tends to be negatively charged with the increased pH value. The

Aquino et al. 2019). Influence of spatial confinement on solvation status that may affect the adsorption and oxidation reaction needs further discussion.

ii) Secondary pollution. Owing to the added chemical reactants and incomplete degradation of organic pollutants, secondary pollution often occurs in OPs. The addition of chemical reactants needs to be control. More importantly, the transformation products should be detected and identified to get the possible reaction pathways. The toxicity test and risk evaluation of transformation products is indispensable. Besides, potential pollution caused by the added catalysts is also a noteworthy issue. For example, MOF catalysts were constructed by the coordination of metal and organics. Theoretically, strong acid/alkali or high temperature can promote the decomposition of MOF, which might generate harmful organics. And the recycling of catalysts remains a concern for large-scale application.

iii) Advanced test methods and fundamental research. Spatial confinement effect are mostly studied via computational simulation (Tunuguntla et al. 2016). Molecular dynamics simulations were used to explore the process that spatial confinement denatures protein helices (Sorin and Pande 2006). Molecular dynamics simulations combined with interfacial charge balance theory were used to study proton density redistribution (Zhang et al. 2021c). Advanced characterization and test methods are lacked. Moreover, owing to the complexity of water matrix and the difficulty of transition state capture and identification in OPs, relevant studies on the effect of spatial confinement on the transition states are inadequate (Qian et al. 2020a, Zhang et al. 2021d). To study spatial confinement effect on OPs more accurately, more fundamental research is needed.

iv) Controllable cost. Various materials are utilized as the support for spatial confinement mediated OPs, like CNTs, MOFs, and natural porous zeolites. The selection of supporting materials to provide confined structure is important. There are many aspects to be consider, such as the match degree between confined structure and substrate, the stability and applicability of materials in various conditions, and production cost. Furthermore, the cost of confined catalyst in supporting materials also needs control. From the aspect of actual application, the economic efficiency of spatial confinement mediated OPs is very important. Therefore, the selected catalyst and supporting materials should be rich in resources, cheap in price, stable in property and eco-friendly.

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