Synthetic conditions-regulated catalytic Oxone efficacy of MnO$_x$/SBA-15 towards butyl paraben (BPB) removal under heterogeneous conditions

Jia-Cheng E. Yang$^{a,b,1}$, Huachun Lan$^{a,d,1}$, Xiao-Qiong Lina, Baoling Yuan$^c$, Ming-Lai Fu$^{a,⇑}$

$^a$Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment (IUE), Chinese Academy of Sciences, Xiamen 361021, China
$^b$University of Chinese Academy of Sciences, Beijing 100039, China
$^c$College of Civil Engineering, Huaqiao University, Xiamen 361020, China
$^d$Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS
- Catalytic Oxone efficacy of MnO$_x$/SBA-15 (MS) towards butyl paraben (BPB) was probed.
- Synthetic conditions controlled the catalytic Oxone performance of MS composites.
- Operating factors affected BPB removal by MS–Oxone system.
- Aged MS can be regenerated by a thermal treatment.

GRAPHICAL ABSTRACT

Pioneering work on systematically probing the synthetic conditions-regulated catalytic Oxone efficacy of MnO$_x$/SBA-15.

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ABSTRACT

Heterogeneous catalysts prepared under different conditions usually demonstrate different catalytic performance, but the underlying influences are not well addressed. Therefore, MnO$_x$/SBA-15 (MS) composites were fabricated under different synthetic conditions to probe the links between their changes in physicochemical features and catalytic Oxone efficacies, using butyl paraben (BPB) as a probe chemical. Characterization results demonstrated that the changes of Mn/SBA-15 weight ratio, calcination temperature and time altered the physico–chemical characteristics of MS composites such as the specific surface area and the types/amounts of MnO$_x$ species of MS composites. Further studies showed that these synthetic conditions had affected the catalytic Oxone performance of MS composites towards BPB removal through changing the types or the amounts of active radicals. The catalytic Oxone efficacy of the optimized MS was highly dependent on the changes of the dosages of MS and Oxone and the initial pH values of BPB solutions. SO$_4^-$ and OH$^-$ were identified as the main reactive species of MS–Oxone system responsible for BPB removal. Additionally, the thermally activated MS demonstrated excellent catalytic Oxone efficacy during its recycles. These findings will increase the knowledge regarding the “synthetic conditions – physicochemical characteristics – application” centered-relationships of heterogeneous catalysts for water treatment.

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1. Introduction

Research in manganese oxides (MnO$_x$) is extremely increasing due to their wide applications in energy exploration and environ-
mental remediation [1]. Among these applications, using MnO$_x$ as adsorbents, oxidizing agents or catalysts to remove various environmentally important pollutants is such a case. For example, MnO$_2$ has been shown to have oxidative and adsorption capacity towards endocrine disruption compounds and organic dyes [2,3]. Meanwhile, MnO$_2$ has also been demonstrated as a prominent catalyst to degrade organic pollutants in water and air [4–8]. However, MnO$_x$ in its bare forms has some intrinsic structural drawbacks like aggregation and poor stability, which inevitably limit its practical applications. Pre-immobilizing MnO$_x$ precursors onto/into porous substrates to fabricate hybrid materials provides an alternative approach to alleviating the aforementioned defects. Such MnO$_x$-based composites are expected to furnish better performance than individual components. Graphene oxide supported MnO$_x$ composite is just one of these examples, where a better reaction activity of the supported MnO$_x$ was observed than its bare powders for the catalytic removal of methylene blue in the presence of H$_2$O$_2$ [9,10]. Apart from the porous carbonaceous vehicles, alumina, zirconia iron oxides, and monox materials are also used as promising supporters for dispersing guest metal species like MnO$_x$ to develop hybrid systems with some interesting properties either for efficiently decomposing/activating environmental contaminants or for catalytically evolving O$_2$ in energy devices [11–19].

More recently, catalytically decomposing/activating oxidants (such as H$_2$O$_2$, O$_3$ and Oxone) using metallic active species decorated ordered mesoporous silica supporters has also received much attention because of their improved performance towards the destruction of refractory organics and their acceptable cost in wastewater treatment. Porous silica supported MnO$_x$ composites, for instance, possess better catalytic ability to decompose H$_2$O$_2$ and O$_3$ to form active radicals for water purification [11,13]. In addition, Co and Co/Mg decorated SBA-15 hybrids were found to provide higher catalytic Oxone efficacy during the treatment of wastewater containing organic chemicals and the hybrid catalysts exhibited excellent stability over their recycle processes [20–22]. Although the catalytic Oxone efficacy of MnO$_x$ or other metal-based composites toward the removal of commonly found organic contaminants such as phenols and dyes has been demonstrated in previous work [4,23–30], yet, thus far, such information on the catalytic Oxone performance of MnO$_x$ decorated SBA-15 composite for the removal of pharmaceutical and personal care products (PPCPs) is still unavailable.

It is also evidenced that bare MnO$_x$ with different valence states, morphologies and crystal phases often shows different catalytic performance against the decomposition of organic substrates [24,31,32]. On the other side, MnO$_x$ formed within porous silica was reported to possess different oxide states [11–13], which resulted in varied catalytic performance. In this context, it can be anticipated that MnO$_x$/SBA-15 (MS) composite with varied metallic active species could exhibit differentiated catalytic Oxone efficacy. Furthermore, at current stage some key questions still remain unknown: (1) how do the physicochemical features of MS composites evolve when their synthetic conditions were changed? (2) What is the response of MS composites with varied properties towards the catalytic Oxone efficacy? and (3) How is the catalytic Oxone performance of the optimized MS composite against the removal of PPCPs? Revealing these issues is of great importance to increase our knowledge of the synthetic conditions-regulated catalytic performance of MS composite, which, in turn, improves the cost-effectiveness of designing desired MS composites with high performance for wastewater management.

Taking the above questions into account, a series of experiments, i.e., preparing MS composites under differing conditions, characterizing their physicochemical features and evaluating their catalytic Oxone efficacy, were specifically designed. To the best of our knowledge, this is the pioneering work aiming at systematically probing the links between synthetic conditions and physicochemical properties in MS–Oxone reaction system for the removal of PPCPs. Butyl paraben (BPB), as one of the most commonly used parabens in personal care chemicals, was selected as a probe compound to test the catalytic activity and properties of the composites due to its wide presence in aquatic media and physiological risk to organisms [33,34].

2. Materials and methods

2.1. Chemicals

Unless otherwise specified, all chemicals from commercial suppliers were of analytical grade and used without any purification. Deionized water produced in lab was used to prepare various solutions.

2.2. Materials synthesis

Based on the general principles [35], mesoporous SBA-15 molecular sieves were first synthesized. Then, various MS composites were made by an integrated route of ultrasonically impregnating an aqueous solution of Mn(CH$_3$COOH)$_2$·4H$_2$O at room temperature for 90 min, drying at 373 K overnight and calcinating at different temperatures and hours [13]. The resultant composites prepared under varied synthetic conditions were labeled as MS$_x$(YZ), where X, Y and Z stand for the weight ratio of Mn/SBA-15 (wt%), calcination temperature (K) and time (h), respectively. For comparison, bare MnO$_x$ particles were also prepared by directly calcinating manganese acetate at 823 K for 3 h.

2.3. Batch experiments

Four types of BPB removal experiments were carried out in current study: (a) experiments concerning the effects of synthetic conditions, (b) experiments regarding the effects of operating parameters, (c) quenching experiments using methanol and tert butyl alcohol (TBA) as probe compounds, and (d) recycle experiments. Batch removal experiments, except recycle experiments, were conducted in 100-mL flat conical flasks with ground-in glass stoppers, each of which contained 80 mL of BPB solutions. Recycle experiments were performed in 250-mL flat conical flasks containing 160 mL of BPB solutions. The initial pH values of target samples were adjusted in advance with HNO$_3$ and NaOH dilute solutions. BPB removal was initiated when MS composites and Oxone with different dosages were introduced into the glass flasks. At determined intervals (up to 175 min), 2 mL of reaction samples were withdrawn for BPB residue analysis, each of which was quickly quenched with 0.5 mL of methanol, followed by filtering using 0.45 µm cellulose acetate membranes. All experiments were carried out in duplicate or triplicate by rotating in rotary vibrator at 300 rpm/min under aerobic conditions (298 ± 2 K). All the data points are the average values of two or three determinations, and the error bars are based on the results of replicate experiments with 95% confidence level. Additionally, parallel control experiments were also performed.

The residual concentrations of BPB in solutions were analyzed using a high performance liquid chromatography (HPLC) system (Agilent 1260, USA) equipped with a diode array detector and a Poroshell 120 EC-C18 column (2.7 µm, 4 × 100 mm, Agilent). The mobile phase was a mixture of 55/45 (v/v) acetonitrile–water with a flow rate of 1 mL/min at 303 K. The concentrations of Mn ions (released from MS) in BPB solutions were measured by atomic absorption spectroscopy (AAS) (Thermo M6, USA) with a hydrogen flame detector. The total organic carbon (TOC) of the BPB solution
before and after reaction was analyzed by a TOC-Vmp apparatus (Shimadzu, Japan). The free radicals generated in MS-Oxone systems were detected by an EMX 10/12 electron paramagnetic resonance (EPR) spectrometer (Bruker, Germany) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap under following conditions: center field, 3410.0 G; resonance frequency, 9.837 GHz; microwave power, 19.87 mW and attenuation setting, 10 dB.

2.4. Characterization

The X-ray diffraction (XRD) spectra of samples were recorded on an X’Pert PRO diffractor (PANalytical, Holland, Cu Kα, λ = 0.15406 nm) with 40 kV accelerating voltage and 40 mA current. The small-angle data were collected from 0.6° to 3° (2θ) with a scan speed of 0.6°/min, while the wide ones were collected from 5° to 80° (2θ) with a scan speed of 6°/min. The scanning electron microscopy (SEM) images of SBA-15 and MS composites were obtained by an S-4800 (Hitachi, Japan), whereas the transmission electron microscopy (TEM) images of powder samples were determined on an S-7650 equipment (Hitachi, Japan). N2-adsorption/desorption isotherms of as-prepared samples were measured by an ASAP 2020M + C apparatus (Micromeritics, USA) at 77 K. The surface elemental compositions of samples were characterized by X-ray photoelectron spectroscopy (XPS) operated on a Kratos Amicus spectrometer (Shimadzu, Japan) equipped with Mg Kα X-ray source. The zeta potentials of samples were tested using a ZetaPALS analyzer (Malvern, United Kingdom) to estimate their points of zero charge (pHPC). Prior to zeta-potential tests, all aqueous samples (~3 g/L) with varied pH values were equilibrated for at least 24 h.

3. Results and discussion

3.1. Synthetic conditions-regulated evolutions of physicochemical features

3.1.1. Crystal phase

The powder XRD patterns of MS composites and SBA-15 are depicted in Fig. 1. The small-angle XRD of resultant SBA-15 exhibits three well-resolved peaks that are ascribed to [100], [110] and [200] reflections of its p6mm hexagonal symmetry structures. Additional weak diffraction peak appearing at 2θ ≈ 22.5° in wide-angle XRD pattern suggests the presence of amorphous character of SBA-15. The as-prepared SBA-15 has a d[100] spacing of 93.74 Å coupling with an unit-cell parameter of a = 108.24 Å. All these findings are well consistent with reported publications [35,36]. More interestingly, the obtained MS composites derived from SBA-15 also have p6mm hexagonal morphology due to the presence of distinct [100], [110] and [200] reflections, indicating that MS composites generally maintained the intrinsic structures of SBA-15 over the decorating processes under varying conditions. However, slightly larger 2θ values (corresponding to the peaks of [100], [110] and [200] reflections (Fig. 1)) with slightly decreased d[100] and 2θ[100] values are observed for MS materials (See Table S1). This might be the result of the modification processes of SBA-15 with MnOx and to some extent, in reverse, confirms the successful immobilization of MnOx in/on silica support. On the other hand, the wide and dumpy peaks at 2θ ≈ 22.5° are clearly detected for SBA-15 and MS composites, showing that amorphous structures existed in SBA-15 and its modification with MnOx species did not destroy these original structures. Although directly calcinating manganese acetate at 823 K for 3 h can result in the formation of α-Mn3O4 phase (see XRD patterns in Fig. S1), typical peaks indexed for α-Mn3O4 phase cannot be clearly observed for all MS composites. However, some weak peaks appeared at 31 ~ 36.5° can be detected for MS composites obtained under higher Mn/SBA-15 weight ratios and calcination temperatures and longer calcination time. Both of the two observations could be possibly attributed to the facts that: (1) the amount of MnOx species formed in SBA-15 are too low to be detected clearly by XRD characterization; (2) MnOx phases are amorphous [12]; and (3) the MnOx species might exist as other forms of oxidation states except for the α-Mn3O4 phase [12].

3.1.2. Porous structure

The calculated Brunauer–Emmett–Teller (BET) surface area, BET pore size and Barrett–Joyner–Halenda (BJH) pore volume of SBA-15 are 702.81 m²/g, 5.44 nm and 1.02 cm³/g, respectively (Table 1), which have good agreement with the reported results [13]. Three well-differentiated stages of adsorption isotherm of SBA-15, i.e., monolayer-multilayer adsorption, capillary condensation, and multilayer adsorption on the outer surfaces of SBA-15, are clearly observed (Fig. S3). The type-IV hysteresis loop and capillary condensation occurring at a higher relative pressure of P/P0 ~ 0.85 indicate the mesoporous features of as-synthesized SBA-15 [35]. In general, MSn(823,3) materials show the similar adsorption/desorption isotherms and hysteresis loops (Fig. S3). The decrease both in quantities of N2 adsorption and in relative pressures also prove the success of supporting MnOx in/on SBA-15 without changing its mesoporous characteristics. On the other side, this suggests partial filling of the mesopores by MnOx particles, which can be confirmed by the decreased BET surface areas and BJH pore volumes, and the extent of filling can be enhanced with the increase of Mn/SiO2 weight ratios (Table 1). The increased BET pore sizes (from 5.54 to 6.65 nm), on one hand, indicate that some MnOx nanocrystals or sub-nanocrystals had probably formed inside the channels of SBA-15 matrix, and on the other hand, they imply that the MnOx species formed had exerted a limited influence on the pore structures due to the higher stability of the channels in SBA-15 matrix. Thus, the mesoporous characteristics of SBA-15 played a key role in regulating the formation of active species (i.e., MnOx) while maintaining its hexagonal structures, which undoubtedly increased the dispersion and stability of target active species. In addition, the finding that the pore sizes of SBA-15 or MSn(823,3) determined by BET method are smaller than their corresponding d[100] spacings measured by XRD technique – ascribing to the fact that the latter contains the thickness of pore wall [35] – also been observed in this study. Herein, it should be noted that additional tests of MSn(Y/Z) composites were not carried out to characterize their porous features based on our hypothesis that calcination temperature and time of MnOx composites with the same content exert little influence on their porous structures.

3.1.3. Morphology

SEM and TEM characterizations were conducted to study the morphologies of SBA-15 and the optimized MS, i.e., MS8(823,3) (Figs. 2, S4 and S5). SEM images (Fig. 2(a)) show that the as-prepared SBA-15 sieves consist of many rod-like components with distinct edges and relatively uniform sizes of ~0.8 μm in length, which aggregate into wheat and rope-like macrostructures (Fig. S4). However, when MnOx particles were introduced SBA-15 supporters, the rope-like aggregates turned into relatively individual particles without detectable edges but with some tiny particles on their surfaces (Fig. 2(b)). This observation implies that decorating processes could induce slight changes of surface morphologies of SBA-15 samples to some extent. TEM images (Fig. 2(c) and (d) and S5) exhibit that the SBA-15 samples maintained their mesoporous structures with many 1D channels after immobilizing with MnOx particles. The estimated length of SBA-15 and MS based on TEM images ranges from 0.72 to 0.8 μm, which agrees well with the observation of SEM images; while the channels before and after
amounts of MnO species. Interestingly, it is found that, as the main species under calcination conditions at 673–773 K, the varied valence states of Mn with changed calcination temperatures and time on catalytic Oxone efficacy of MS composites towards BPB removal in aquatic solutions are provided to probe their synthetic conditions-controlled catalytic Oxone performance (Figs. 3 and S8).

3.2. Synthetic conditions-regulated catalytic Oxone efficacy of MS composites

The influences of Mn/SBA-15 weight ratios, calcination temperatures and time on catalytic Oxone efficacy of MS composites towards BPB removal in aquatic solutions are provided to probe their synthetic conditions-controlled catalytic Oxone performance (Figs. 3 and S8).

3.2.1. Influence of Mn/SBA-15 weight ratios

It is evidenced that the loss of BPB caused by its evaporation, the adsorption of MS composites and SBA-15 and the oxidation of Oxone can be neglected (Fig. S8), and the BPB removal is mainly attributed to the catalytic oxidation of MS–Oxone systems (Fig. 3). In addition, the catalytic activity of bare MnO2 particles (0.04 g/L) is found to be far lower than that of supported ones with an equal amount, i.e., MS8(823,3). The enhancement of catalytic Oxone efficacy may result from the higher dispersion of MnO2 species formed in/on silica supporters (refer to Figs. S2 and 2). As shown in Fig. 3 (a) and S8 (Inset), the BPB removal rate first increased with the increase of Mn/SBA-15 weight ratios, and then decreased when the Mn/SBA-15 weight ratio exceeded 8 wt%. For such trend in BPB removal, the effects of the changes of surface morphologies and pore characteristics caused by Mn/SBA-15 weight ratios can be excluded. Two possible reasons are provided: (1) the evolutions of surface morphologies with the changes of Mn/SBA-15 weight ratios are not obvious from the observations of SEM characterizations (data not shown here); (2) the BET surface areas and BJH pore volumes of MS8(823,3) composites decreased with Mn/SBA-15 weight ratios increased (Table 1), which could not explain why MS8(823,3) showed the best catalytic Oxone performance. Hence, we did not perform extra XPS tests for MS8(823,3) composites.

Table 1
Brønsted–Emmett–Teller (BET) surface areas, BET pore sizes, Barrett–Joyner–Halenda (BJH) pore volumes and pH_{PZC} values of SBA-15 and MS/(823,3).

| Samples   | BET surface area (m²/g) | BET pore size (nm) | BJH pore volume (cm³/g) | pH_{PZC} |
|-----------|-------------------------|--------------------|--------------------------|---------|
| SBA-15    | 475.03                  | 6.69               | 1.02                     | 2.75    |
| MS2(823,3)| 437.86                  | 6.33               | 0.76                     | 2.25    |
| MS4(823,3)| 448.58                  | 6.36               | 0.75                     | 2.55    |
| MS6(823,3)| 416.50                  | 6.65               | 0.73                     | 2.70    |
| MS8(823,3)| 409.42                  | 6.59               | 0.71                     | 2.60    |
| MS10(823,3)| 416.50                | 6.65               | 0.73                     | 2.70    |

3.1.4. Valence state information

XPS characterizations for various MS composites were analyzed based on previous work [37–40], and the results confirm the presence of mixed oxidation states of MnO2 within MS composites (Table 2, Figs. S6 and S7). For example, MnO2 particles with 31.84% of Mn(IV), 20.72% of Mn(III) and 47.44% of Mn(II) were formed within MS8(823,3), indicating the co-presence of MnO2, Mn3O4, Mn2O3 and MnO2 species. Interestingly, it is found that, regardless the types of MnO2 species, the average valence of Mn generally decreased with calcination temperature or time increased, which is the same as the reported conclusions [12,38]. The varied valence states of Mn with changed calcination procedures are results of the formation of different MnO2 particles. Furthermore, previous work shows that the formation processes and the kinds of MnO2 species formed on the silica support KIT-6 are highly temperature-dependent with MnO2, Mn3O4 and Mn2O3 as the main species under calcination conditions at 673–773 K, 873–973 K and 1073–1173 K, respectively [12]. Thereby, it is reasonable to understand that the changes in the types and the amounts of MnO2 species caused by different calcination procedures induced the variations of average oxidation states of Mn, which undoubtedly will regulate its diversity in catalytic properties (discuss later). In addition, the changes of MnO2 loadings with silica were also reported to induce the changes of oxidation state for Mn [29]. Hence, we did not perform extra XPS tests for MS8(823,3) composites.

Fig. 1. XRD patterns of SBA-15 and MS (YZ) composites with different Mn/SBA-15 weight ratios (a), calcination temperatures (b) and hours (c).
Mn/SBA-15 weight ratios altered the types and the amounts of active species (i.e., SO$_4^{2-}$/C$_5^{2-}$/C$_0^{2-}$ and OH$_2^{2-}$/C$_5^{2-}$/C$_0^{2-}$) formed in MS–Oxone systems (see Figs. 4(a), S10(a), S11(a), and S12) [41–43], thus leading to an optimized Mn/SBA-15 weight ratio for MS–Oxone reaction systems under other conditions unchanged, and another reason might be the self-scavenging of SO$_4^{2-}$/C$_5^{2-}$/C$_0^{2-}$ radicals occurred in the case of MS10(823,3)–Oxone system (Fig. S12) [42].

3.2.2. Influence of calcination temperature and time

Previous work indicates that calcination temperature is a key factor for controlling the catalytic performance of MnO$_x$ clusters decorated mesoporous silica for O$_2$ evolution [12]. So, we suspected that calcination procedures of MS composites might also play a significant role in their catalytic Oxone efficacy toward BPB removal and designed such experiments accordingly. It’s clear that, in the initial stages, increasing calcination temperature or time of MS composites both resulted in the increased catalytic Oxone removal efficiencies of BPB, while, beyond the extreme point, further increase whether in calcination temperature or in time gave an unfavorable effect on their catalytic performance towards BPB removal (Fig. 3(b) and (c)). The variations in the types and the amounts of MnO$_x$ species within MS – which controlled the formation of active radicals in MS–Oxone systems (see Figs. 4, S10, S11, and S12) – would contribute to such phenomenon. Indeed, differentiated MnO$_x$ species of MS with changed oxidation states can be observed in current study where Mn$_2$O$_3$ and Mn$_3$O$_4$ are suspected as the main species of MS8(823,3) (refer to XPS analysis in Section 3.1.4). Moreover, previous work indicated that the catalytic decomposition of Oxone was closely associated with the oxidation states of bare MnO$_x$ particles with a conclusion that Mn$_2$O$_3$ and Mn$_3$O$_4$ are more effective for Oxone activation than MnO$_2$ [23]. Hence, it is understandable that the changes of MnO$_x$ species in oxidation states could control the types and the amounts of free radicals formed in MS–Oxone systems, thus regulating their catalytic Oxone removal ability of BPB.

3.3. Evaluation on catalytic Oxone efficacy of MS toward BPB

To better understand the performance of the optimized MS, influences of operating parameters (i.e., dosages of MS$_8$(823,3) and Oxone, initial pH values of solutions and types of quenching agents) and regeneration of MS$_8$(823,3) on catalytic efficacy of MS–Oxone systems for BPB removal were examined.

3.3.1. Influence of MS$_8$(823,3) and Oxone dosages

It’s shown that BPB removal rate first increased with increasing the dosages of MS$_8$(823,3) and then became flat (Fig. 5(a)). This trend is due to a trade-off between a given dosage of Oxone and the varied dosages of MS$_8$(823,3), which controls the formation and the numbers of active species for BPB removal. On the other hand, further increasing the dosage of Oxone gave a favorable effect on the catalytic performance of MS–Oxone systems. Indeed, differentiated Oxone dosages altered the types and the amounts of active species formed in MS–Oxone systems (see Figs. 4(a), S10(a), S11(a), and S12) [41–43], thus leading to the optimized Mn/SBA-15 weight ratio for MS–Oxone reaction systems under other conditions unchanged.

![Fig. 2. Representative SEM (a, b) and TEM (c, d) images of SBA-15 and MS$_8$(823,3).](image)

**Table 2**

| Samples       | Valence state of Mn (%) | Average valence of Mn |
|---------------|-------------------------|-----------------------|
|               | IV                      | III                   | II                    |
| MS$_8$(723,3) | 32.25                   | 26.30                 | 41.45                 | 2.908 |
| MS$_8$(823,3) | 31.84                   | 20.72                 | 47.44                 | 2.844 |
| MS$_8$(923,3) | 19.93                   | 25.90                 | 44.17                 | 2.658 |
| MS$_8$(1023,3)| 0.00                    | 51.69                 | 48.31                 | 2.517 |
| MS$_8$(823,1) | 31.40                   | 27.16                 | 41.44                 | 2.900 |
| MS$_8$(823,5) | 28.19                   | 27.92                 | 43.89                 | 2.843 |
| MS$_8$(823,7) | 26.41                   | 27.09                 | 46.50                 | 2.799 |
| Aged MS$_8$(823,3) | 58.20                   | 31.40                 | 10.76                 | 3.474 |
| 5th activated MS$_8$(823,3) | 48.25                   | 33.46                 | 18.29                 | 3.299 |
hand, when the usage of MS8(823,3) was fixed, decreasing or increasing the amounts of Oxone would result in a declined removal rate of BPB when the amount of Oxone was below 7.5 mM (Fig. 5(b)). This is because, on one hand, inadequate amounts of Oxone would confine the amounts of active species; on the other side, adequate amounts would lead to a self-scavenging of active species like SO4\(^{2-}\)/C5\(^{2-}\)/C0\(^{2-}\) [42], which would also result in the reduction of the formation of active species. Nevertheless, when the amount of Oxone exceeded 7.5 mM, increasing its amount led to an enhanced BPB removal rate. This might be a result of a trade-off between the self-scavenging of active species and the re-formation of active species for MS8(823,3)–Oxone system under a given reaction condition.

3.3.2. Influence of solution pH

As depicted in Fig. 5(c), initial pH values of solutions ranging from acidic to moderately alkaline conditions generally exerted more favorable effect on BPB removal for MS–Oxone reaction systems than those of extremely alkaline ones. Different reasons were explored to explain the effects of the solution pH on persulfate-based oxidation systems [31,42,44,45]. For current reaction system, the role of electrostatic interactions between MS particles and BPB molecules could not explain such trend. If so, when solution pH increased, BPB removal rate would first increased with its maximum expected at solution pH of 4–5 and then decreased accordingly in the light of the pH \(pK_a\) of MS8(823,3) and the \(pK_a\) of BPB [46]. But this is not the case as an
unexpected trend was observed for BPB removal rate as a function of solution pH. In a given range, MS8(823,3)–Oxone system had a maximum removal efficacy of BPB at initial pH of 2.93, then experienced a slightly decreased removal efficacy with a relatively low point at pH of 4.3 – which had been elevated with an end of a relatively balanced point at solution pH of 6.5–9.95 and then reduced when solution pH was further increased to 11.43. The effect of initial pH values on BPB removal by Oxone alone can also be excluded except the pH of 11.43 (see Fig. S9). Such pH-induced trend was also reported in reaction system of persulfate and magnetite nanoparticles [42]. One reasonable explanation is that the variations of solution pH changed the types and the amounts of active species in MS–Oxone systems [45], which had been confirmed by our EPR tests (see Figs. 6 and S13). Note that BPB removal by Oxone alone can be reached 95.5% at initial pH values of 11.43 (see Fig. S13). In general, MS8(823,3)–Oxone system can still maintain its high reaction efficacy towards BPB removal in a wide range of solution pH.

3.3.4. Influence of regeneration

Evaluating the stability and reusability of a catalyst is of great significance to its practical application. Previous study indicates that MnO2 without regeneration suffered a great decrease of catalytic Oxone performance towards phenol removal [23], and our primary studies shows that aged MS8(823,3) without post-treatment demonstrated a deactivation over the catalytic Oxone removal process of BPB (data not shown here), which might be ascribed to the oxidation of Mn by SO4

\[\text{OH}^+ \] in MS–Oxone reaction system (evidenced by XPS analysis in Table 2 and Fig. S7(d)) and the deposition of intermediate products on MS surface. Hence, we employed a thermal process to activate the aged MS composite. Typically, the aged MS8(823,3) was first filtered after each recycle with hydroxide at the solution pH of 6.5 [31,45,47]. Nevertheless, significant reduction of BPB removal was not observed when further increasing the concentrations of methanol or TBA. This implies that BPB has a good affinity behavior with SO4

\[\text{OH}^+ \] in spite of the presence of competitors.

Fig. 5. Influences of MS8(823,3) dosages (a), Oxone dosages (b), initial pH values (c) and quenching agents (d) on catalytic Oxone efficacy of MS composites towards BPB removal (reaction conditions, except if noted otherwise: 80 mL of 25.74 μM BPB solution, pH 6.5 ± 0.2, 0.5 g/L MS8(823,3), 5 mM Oxone, reaction time 175 min and solution temperature 298 ± 2 K).
valence of Mn of fifth activated MS$_8$(823,3) is lower than that of aged one (Table 2), indicating that the thermal treatment partially removed the oxygen-containing substrates on aged MS (like $\text{A}_\text{OH}$ groups and byproducts on MS), which thus contribute to BPB removal without declined efficiency. In addition, Mn releasing from MS$_8$(823,3) sample over the courses of BPB removal was measured and the concentrations of Mn ions in solutions were lower than 80 $\mu$g/L, which were far below the regulated values issued by Chinese government [54]. Taken together, the optimized MS composite can be reused by a thermal treatment.

3.4. Oxone activation mechanisms by MS composites

Fig. 8 depicts the synthetic conditions-regulated Oxone activation process by MS composites. Once MS composite introduced, Oxone in aquatic matrix was quickly decomposed to produce various active radicals. The dominating radicals were SO$_4^-$ and OH, confirmed by the hyperfine splitting of DMPO–SO$_4^-$ and DMPO–OH adducts obtained by simulation (refer to $\alpha^N = 13.82$ G, $\alpha^H = 10.1$ G, $\alpha^H = 1.41$, $\alpha^H = 0.83$, and $g$-factor = 2.0059 for DMPO–SO$_4^-$, while $\alpha^N = \alpha^H = 14.9$ G, and $g$-factor = 2.0057 for DMPO–OH [55]) (see Figs. 4 and 6). The amount of SO$_4^-$ and OH will gradually decrease with reaction time increasing in aquatic MS–Oxone system (see Figs. 4, 6 and S10–S14). The catalytically activating role of MS in the generation of radicals can be evidenced by the absence of EPR signals in MS-excluded Oxone system (data not shown here). For aquatic MS–Oxone system, whether the synthetic conditions of MS composites or the amounts of MS/Oxone and the changes of solution chemistry like initial pH, all of them can induce the changes of catalytic Oxone efficacy towards BPB removal. For instance, in this work, synthetic conditions of MS composites changed the amount/types of MnO$_x$ species and the oxidation state of Mn within silica matrix (see Section 3.1.4). These changes were then considered as driving factors dominating the generation of active radicals in aquatic MS–Oxone systems (Fig. 4 and S10–S12), which resulted in a trade-off between...
4. Conclusions

Synthetic conditions-regulated physicochemical features and catalytic Ozone efficacy of MS composites were systematically probed. In detail, the weight ratios of Mn/SBA-15 induced the changes of porous structures rather than the surface morphologies and charge, while the calcination processes mainly controlled the types and amounts of MnOx formed on SBA-15 support and thus regulated the average valence of Mn. These synthetic conditions-regulated physicochemical features are identified as key factors for controlling the catalytic Ozone efficacy of MS towards BPB with different removal efficiencies. Meanwhile, MS and Ozone dosages, initial pH values of BPB solutions and the quenching agents demonstrated varied influences on the catalytic removal ability of MS–Ozone systems towards BPB. Moreover, the aged MS can be reused by a thermal process. All in all, this paper highlights the importance of comprehensively understanding the synthetic conditions of heterogeneous catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/jcej.2016.01.007.

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