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

Jia-Cheng E. Yang^{a,b,1}, Huachun Lan^{a,d,1}, Xiao-Qiong Lin^a, 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 $\text{MnO}_x/\text{SBA-15}$ (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 $\text{MnO}_x/\text{SBA-15}$.

ARTICLE INFO

Article history:

Received 28 October 2015

Received in revised form 5 January 2016

Accepted 6 January 2016

Available online 11 January 2016

Keywords:

MnO_x

SBA-15

Oxone

Butyl paraben (BPB)

Synthetic conditions

ABSTRACT

Heterogeneous catalysts prepared under different conditions usually demonstrate different catalytic performance, but the underlying influences are not well addressed. Therefore, $\text{MnO}_x/\text{SBA-15}$ (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 $\text{Mn}/\text{SBA-15}$ weight ratio, calcination temperature and time altered the physicochemical 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. $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ 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.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Research in manganese oxides (MnO_x) is extremely increasing due to their wide applications in energy exploration and environ-

* Corresponding author. Tel.: +86 592 6190762; fax: +86 592 6190977.

E-mail address: mlfu@iue.ac.cn (M.-L. Fu).

¹ Equal contribution to this work.

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_x 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_2O_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/transferring environmental contaminants or for catalytically evolving O_2 in energy devices [11–19].

More recently, catalytically decomposing/activating oxidants (such as H_2O_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_2O_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 [4,23,24,31,32]. 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 molecule sieves were first synthesized. Then, various MS composites were made by an integrated route of ultrasonically impregnating in an aqueous solution of $\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ 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 (Y,Z), 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 $0.45 \mu\text{m}$ cellulose acetate membranes. All experiments were carried out in duplicate or triplicate by rotating in rotary vibrator at 300 rpm/min under aerobic conditions ($298 \pm 2 \text{ K}$). 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 ($2.7 \mu\text{m}$, $4 \times 100 \text{ mm}$, 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 K α , $\lambda = 0.15406$ 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). N $_2$ -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 K α X-ray source. The zeta potentials of samples were tested using a ZetaPALS analyzer (Malvern, United Kingdom) to estimate their points of zero charge (pH $_{PZC}$). 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 $2\theta \approx 22.5^\circ$ 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 $a_{\{100\}}$ values are observed for MS materials (See Table S1). This might be the result of the modification processes of SBA-15 with MnO $_x$, and to some extent, in reverse, confirms the successful immobilization of MnO $_x$ in/on silica support. On the other hand, the wide and dumpy peaks at $2\theta \approx 22.5^\circ$ are clearly detected for SBA-15 and MS composites, showing that amorphous structures existed in SBA-15 and its modification with MnO $_x$ 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 -Mn $_2$ O $_3$ phase (see XRD patterns in Fig. S1), typical peaks indexed for α -Mn $_2$ O $_3$ phase cannot be clearly observed for all MS composites. However, some weak peaks appeared at

31 $\sim$ 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 MnO $_x$ species formed in SBA-15 are too low to be detected clearly by XRD characterization; (2) MnO $_x$ phases are amorphous [12]; and (3) the MnO $_x$ species might exist as other forms of oxidation states except for the α -Mn $_2$ O $_3$ 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 m 2 /g, 5.44 nm and 1.02 cm 3 /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 $P/P_0 \approx 0.85$ indicate the mesoporous features of as-synthesized SBA-15 [35]. In general, MS $_x$ (823,3) materials show the similar adsorption/desorption isotherms and hysteresis loops (Fig. S3). The decrease both in quantities of N $_2$ adsorption and in relative pressures also proves the success of supporting MnO $_x$ in/on SBA-15 without changing its mesoporous characteristics. On the other side, this suggests partial filling of the mesopores by MnO $_x$ 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/SiO $_2$ weight ratios (Table 1). The increased BET pore sizes (from 5.54 to 6.65 nm), on one hand, indicate that some MnO $_x$ nanocrystals or sub-nanocrystals had probably formed inside the channels of SBA-15 matrix, and on the other hand, they imply that the MnO $_x$ 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., MnO $_x$) 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 MS $_x$ (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] – has also been observed in this study. Herein, it should be noted that additional tests of MS $_x$ (Y,Z) composites were not carried out to characterize their porous features based on our hypothesis that calcination temperature and time of MS $_x$ 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., MS $_x$ (823,3) (Figs. 2, S4 and S5). SEM images (Fig. 2(a)) shows that the as-prepared SBA-15 sieves consist of many rod-like components with distinct edges and relatively uniform sizes of ~ 0.8 μ m in length, which aggregate into wheat and rope-like macrostructures (Fig. S4). However, when MnO $_x$ 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 MnO $_x$ particles. The estimated length of SBA-15 and MS based on TEM images ranges from 0.72 to 0.8 μ m, which agrees well with the observation of SEM images; while the channels before and after

Fig. 1. XRD patterns of SBA-15 and $MS_x(Y,Z)$ composites with different Mn/SBA-15 weight ratios (a), calcination temperatures (b) and hours (c).

Table 1

Brunauer–Emmett–Teller (BET) surface areas, BET pore sizes, Barrett–Joyner–Halenda (BJH) pore volumes and pH_{PZC} values of SBA-15 and $MS_x(823,3)$.

Samples	BET surface area (m^2/g)	BET pore size (nm)	BJH pore volume (cm^3/g)	pH_{PZC}
SBA-15	702.81	5.44	1.02	2.75
$MS_2(823,3)$	475.03	6.52	0.80	2.30
$MS_4(823,3)$	457.86	6.33	0.76	2.25
$MS_6(823,3)$	448.58	6.36	0.75	2.55
$MS_8(823,3)$	416.50	6.65	0.73	2.70
$MS_{10}(823,3)$	409.42	6.59	0.71	2.60

supporting are both estimated to 85–95 Å (see typical demonstrations in Fig. 2(c) and (d)), in line with those calculated using XRD data. Moreover, the estimated values of pH_{PZC} for $MS_x(823,3)$ composites (Table 1) indicated that the decorating processes of MnO_x with different contents for SBA-15 did not change its surface charge. The tests on the zeta potentials of MS_8 composites calcinated under different temperatures and hours were not further performed given their same content.

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 MnO_x within MS composites (Table 2, Figs. S6 and S7). For example, MnO_x particles with 31.84% of Mn(IV), 20.72% of Mn(III) and 47.44% of Mn(II) were formed within $MS_8(823,3)$, indicating the co-presence of MnO , Mn_3O_4 , Mn_2O_3 and MnO_2 species. Interestingly, it is found that, regardless the types of MnO_x 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 MnO_x particles. Furthermore, previous work shows that the formation processes and the kinds of MnO_x species formed on the silica support KIT-6 are highly temperature-dependent with MnO_2 , Mn_2O_3 and Mn_3O_4 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 MnO_x 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 MnO_x 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 $MS_x(823,3)$ composites.

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 MnO_x particles (0.04 g/L) is found to be far lower than that of supported ones with an equal amount, i.e., $MS_8(823,3)$. The enhancement of catalytic Oxone efficacy may result from the higher dispersion of MnO_x 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 $MS_x(823,3)$ composites decreased with Mn/SBA-15 weight ratios increased (Table 1), which could not explain why $MS_8(823,3)$ showed the best catalytic Oxone performance. In addition, the effect of zeta potentials of $MS_x(823,3)$ can be also ruled out due to the negligible changes of the values of pH_{PZC} (Table 1) and the removal of BPB caused by the adsorption of MS composites with the increased Mn/SBA-15 weight ratios (Fig. S8). The reasonable explanation for such trend may be that the increase of

Fig. 2. Representative SEM (a, b) and TEM (c, d) images of SBA-15 and MS₈(823,3).

Table 2

XPS analysis on surface Mn compositions of MS₈(Y,3), MS₈(823,Z) and aged MS₈(823,3).

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	54.17	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

Mn/SBA-15 weight ratios altered the types and the amounts of active species (i.e., SO_4^- and OH^-) 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^- 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_2O_3 and Mn_3O_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_2O_3 and Mn_3O_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 MS₈(823,3) and Oxone, initial pH values of solutions and types of quenching agents) and regeneration of MS₈(823,3) on catalytic efficacy of MS–Oxone systems for BPB removal were examined.

3.3.1. Influence of MS₈(823,3) and Oxone dosages

It's shown that BPB removal rate first increased with increasing the dosages of MS₈(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 MS₈(823,3), which controls the formation and the numbers of active species for BPB removal. On the other

Fig. 3. Influences of Mn/SBA-15 weight ratios, calcination temperatures and hours on catalytic Oxone efficacy of MS composites towards BPB removal (reaction conditions, except if noted otherwise: 80 mL of 25.74 μ M BPB solution, pH 6.5 ± 0.2 , 0.5 g/L MS composites, 5 mM Oxone, reaction time 175 min and solution temperature 298 ± 2 K).

Fig. 4. EPR signals ($\text{DMPO-SO}_4^{\bullet-}$ ($\blacktriangle$) and $\text{DMPO-OH}^{\bullet}$ ($\square$) adducts) detected in Oxone–MS systems at reaction time of 10 min for various MS composites (a1 for $\text{MS}_2(823,3)$, a2 for $\text{MS}_4(823,3)$, a3 for $\text{MS}_6(823,3)$, a4 for $\text{MS}_8(823,3)$ and a5 for $\text{MS}_{10}(823,3)$; b1 for $\text{MS}_8(723,3)$, b2 for $\text{MS}_8(823,3)$, b3 for $\text{MS}_8(923,3)$ and b4 for $\text{MS}_8(1023,3)$; c1 for $\text{MS}_8(823,1)$, c2 for $\text{MS}_8(823,3)$, c3 for $\text{MS}_8(823,5)$ and c4 for $\text{MS}_8(823,7)$) (5 mM Oxone, pH 6.5 ± 0.2 , 0.5 g/L MS composites, 0.2 M DMPO).

hand, when the usage of $\text{MS}_8(823,3)$ 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 $\text{SO}_4^{\bullet-}$ [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 $\text{MS}_8(823,3)$ –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_{PZC} of $\text{MS}_8(823,3)$ and the pK_a of BPB [46]. But this is not the case as an

Fig. 5. Influences of $\text{MS}_8(823,3)$ 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 $\text{MS}_8(823,3)$, 5 mM Oxone, reaction time 175 min and solution temperature 298 ± 2 K).

unexpected trend was observed for BPB removal rate as a function of solution pH. In a given range, $\text{MS}_8(823,3)$ –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. S9). This can be explained by the fact that strong base induced–Oxone can produce active species [47], which contributed to BPB removal. Compared to Oxone alone, the lower BPB removal by MS–Oxone at initial pH of 11.43 was likely due to the presence of Lewis acid sites of MS, which could absorb a large amount of OH^- ions in aquatic matrix, thus reducing the activation ability of base towards Oxone for BPB removal (Fig. S13). In general, $\text{MS}_8(823,3)$ –Oxone system can still maintain its high reaction efficacy towards BPB removal in a wide range of solution pH.

3.3.3. Influence of quenching agents

Previous studies indicate that activated persulfate-based oxidation systems can produce $\text{SO}_4^{\cdot-}$, $\text{SO}_5^{\cdot-}$ and $\text{OH}^{\cdot}$ [48–53]. Therefore, quenching experiments were carried out to elucidate the types of active species and evaluate their effects on BPB removal under weak acidic environment. Fig. 5(d) shows that the introductions of methanol and TBA both resulted in a decrease of BPB removal rate, suggesting the co-existence of $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ in MS–Oxone

system, in agreement with EPR tests (Fig. 6a3–c3). In detail, when 38.6 mM methanol or TBA were introduced BPB solutions, the removal rates were reduced by 15.14% and 17.67%, respectively, compared to the case without adding methanol or TBA. This relatively lower inhibition of methanol than TBA suggests that $\text{OH}^{\cdot}$ was formed in aquatic MS–Oxone system via the reaction of $\text{SO}_4^{\cdot-}$ 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 affinitive behavior with $\text{SO}_4^{\cdot-}/\text{OH}^{\cdot}$ in spite of the presence of competitors.

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 MnO_x without regeneration suffered a great decrease of catalytic Oxone performance towards phenol removal [23], and our primary studies shows that aged $\text{MS}_8(823,3)$ 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 $\text{SO}_4^{\cdot-}/\text{OH}^{\cdot}$ 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 $\text{MS}_8(823,3)$ was first filtered after each recycle with washing using a large amount of deionized water, then drying it at 343 K, followed by a thermal activation process under 823 K for 2 h. The regenerated sample was then used to catalytically degrade BPB. The above procedures were carried out for six times under the identical reaction conditions. As depicted in Fig. 7, $\text{MS}_8(823,3)$ exhibited excellent catalytic Oxone efficacy over six recycle experiments and the removal efficiency of BPB in solutions can be up to 98.4% in the sixth recycle. Note that the average

Fig. 6. EPR signals ($\text{DMPO-SO}_4^{\bullet-}$ (▲) and $\text{DMPO-OH}^{\bullet}$ (□) adducts) detected in Oxone- $\text{MS}_8(823,3)$ systems at different reaction time under varied initial solution pH values: 2.93 (a1–c1), 4.30 (a2–c2), 6.50 (a3–c3), 8.19 (a4–c4), 9.95 (a5–c5) and 11.43 (a6–c6)) (5 mM Oxone, 0.5 g/L $\text{MS}_8(823,3)$, 0.2 M DMPO).

valence of Mn of fifth activated $\text{MS}_8(823,3)$ is lower than that of aged one (Table 2), indicating that the thermal treatment partially removed the oxygen-containing substrates on aged MS (like $-\text{OH}$ groups and byproducts on MS), which thus contribute to BPB removal without declined efficiency. In addition, Mn releasing from $\text{MS}_8(823,3)$ sample over the courses of BPB removal was measured and the concentrations of Mn ions in solutions were lower than $80 \mu\text{g/L}$, 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 $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$, confirmed by the hyperfine splitting of $\text{DMPO-SO}_4^{\bullet-}$ and

$\text{DMPO-OH}^{\bullet}$ adducts obtained by simulation (refer to $\alpha^N = 13.82$ G, $\alpha_{\beta}^H = 10.1$ G, $\alpha_{\gamma}^H = 1.41$, $\alpha_{\delta}^H = 0.83$, and $g\text{-factor} = 2.0059$ for $\text{DMPO-SO}_4^{\bullet-}$, while $\alpha^N = \alpha_{\beta}^H = 14.9$ G, and $g\text{-factor} = 2.0057$ for $\text{DMPO-OH}^{\bullet}$ [55]) (see Figs. 4 and 6). The amount of $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$ 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

Fig. 7. Reuse of $\text{MS}_8(823,3)$ for catalytic Oxone removal of BPB (reaction conditions, except if noted otherwise: 160 mL of $25.74 \mu\text{M}$ BPB solution, pH 6.5 ± 0.2 , 0.5 g/L $\text{MS}_8(823,3)$, 5 mM Oxone, reaction time 175 min and solution temperature 298 ± 2 K).

Fig. 8. Schematic diagram for synthetic conditions-regulated Oxone activation by MS composites.

synthetic conditions and catalytic Oxone efficacies of MS composites and therefore produced an optimized MS composite, i.e., MS₈(823,3). The TOC removal for BPB by fresh MS₈(823,3)–Oxone system under the reaction conditions of Fig. 7 can be up to 73.7% over the reaction time of 240 min (data not shown here). Additionally, the variations of EPR signals indicated that solution pH also played a vital role in BPB removal via the change of active radicals in aquatic MS–Oxone system (see Figs. 5(c), 6 and S13). All in all, this study implies that MS-catalytically induced Oxone decomposition in aquatic matrix can produce radicals like SO₄^{•−} and OH[•] responsible for BPB removal, and that the synthetic conditions-regulated physicochemical features like oxidation state of Mn species in MS controlled the catalytic Oxone performance by the tuning the formation of active radicals in aquatic MS–Oxone system.

4. Conclusions

Synthetic conditions-regulated physicochemical features and catalytic Oxone 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 MnO_x 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 Oxone efficacy of MS towards BPB with different removal efficiencies. Meanwhile, MS and Oxone dosages, initial pH values of BPB solutions and the quenching agents demonstrated varied influences on the catalytic removal ability of MS–Oxone 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.

Acknowledgments

The authors acknowledge Mr. Bin Xu, Ms. Jia-Ni Wang and Mr. Zi-Xiao Hong, IUE, CAS, Xiamen, and Ms. La-Jia Yu in Xiamen University, Xiamen, China, respectively, for their help with electron microscope, XRD, BET, and EPR measurements. This research was

partially supported by National Natural Science Foundation of China (Nos. 51278481 and 51478449), Natural Science Foundation of Fujian Province (No. 2013J01213), and Xiamen Science & Technology Major Program (No. 3502Z20131018).

Appendix A. Supplementary data

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

References

- [1] K. Zhang, X. Han, Z. Hu, X. Zhang, Z. Tao, J. Chen, Nanostructured Mn-based oxides for electrochemical energy storage and conversion, *Chem. Soc. Rev.* 44 (2015) 699–728.
- [2] K. Lin, W. Liu, J. Gan, Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways, *Environ. Sci. Technol.* 43 (2009) 3860–3864.
- [3] R. Chen, J. Yu, W. Xiao, Hierarchically porous MnO₂ microspheres with enhanced adsorption performance, *J. Mater. Chem. A* 1 (2013) 11682–11690.
- [4] E. Saputra, S. Muhammad, H. Sun, H.M. Ang, M.O. Tade, S. Wang, Different crystallographic one-dimensional MnO₂ nanomaterials and their superior performance in catalytic phenol degradation, *Environ. Sci. Technol.* 47 (2013) 5882–5887.
- [5] F. Wang, H. Dai, J. Deng, G. Bai, K. Ji, Y. Liu, Manganese oxides with rod-, wire-, tube-, and flower-like morphologies: highly effective catalysts for the removal of toluene, *Environ. Sci. Technol.* 46 (2012) 4034–4041.
- [6] Y. Wang, H. Sun, H.M. Ang, M.O. Tade, S. Wang, 3D-hierarchically structured MnO₂ for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: structure dependence and mechanism, *Appl. Catal. B Environ.* 164 (2015) 159–167.
- [7] Y. Yao, C. Xu, S. Yu, D. Zhang, S. Wang, Facile synthesis of Mn₃O₄-reduced graphene oxide hybrids for catalytic decomposition of aqueous organics, *Ind. Eng. Chem. Res.* 52 (2013) 3637–3645.
- [8] Y. Wang, H. Sun, H.M. Ang, M.O. Tade, S. Wang, Synthesis of magnetic core/shell carbon nanosphere supported manganese catalysts for oxidation of organics in water by peroxymonosulfate, *J. Colloid Interface Sci.* 433 (2014) 68–75.
- [9] Y. Li, J. Qu, F. Gao, S. Lv, L. Shi, C. He, J. Sun, In situ fabrication of Mn₃O₄ decorated graphene oxide as a synergistic catalyst for degradation of methylene blue, *Appl. Catal. B Environ.* 162 (2015) 268–274.
- [10] J. Qu, L. Shi, C. He, F. Gao, B. Li, Q. Zhou, H. Hu, G. Shao, X. Wang, J. Qiu, Highly efficient synthesis of graphene/MnO₂ hybrids and their application for ultrafast oxidative decomposition of methylene blue, *Carbon* 66 (2014) 485–492.
- [11] N.N. Tušar, D. Maučec, M. Rangus, I. Arčon, M. Mazaj, M. Cotman, A. Pintar, V. Kaučič, Manganese functionalized silicate nanoparticles as a Fenton-type catalyst for water purification by advanced oxidation processes (AOP), *Adv. Funct. Mater.* 22 (2012) 820–826.
- [12] F. Jiao, H. Frei, Nanostructured manganese oxide clusters supported on mesoporous silica as efficient oxygen-evolving catalysts, *Chem. Commun.* 46 (2010) 2920–2922.
- [13] Q. Sun, L. Li, H. Yan, X. Hong, K.S. Hui, Z. Pan, Influence of the surface hydroxyl groups of MnO_x/SBA-15 on heterogeneous catalytic ozonation of oxalic acid, *Chem. Eng. J.* 242 (2014) 348–356.
- [14] J. Li, N. Yan, Z. Qu, S. Qiao, S. Yang, Y. Guo, P. Liu, J. Jia, Catalytic oxidation of elemental mercury over the modified catalyst Mn/α-Al₂O₃ at lower temperatures, *Environ. Sci. Technol.* 44 (2010) 426–431.
- [15] L. Yang, C. Hu, Y. Nie, J. Qu, Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide, *Environ. Sci. Technol.* 43 (2009) 2525–2529.
- [16] S. Xing, C. Hu, J. Qu, H. He, M. Yang, Characterization and reactivity of MnO_x supported on mesoporous zirconia for herbicide 2,4-D mineralization with ozone, *Environ. Sci. Technol.* 42 (2008) 3363–3368.
- [17] H. Zhao, H. Cui, M. Fu, Synthesis of core-shell structured Fe₃O₄@α-MnO₂ microspheres for efficient catalytic degradation of ciprofloxacin, *RSC Adv.* 4 (2014) 39472–39475.
- [18] X. Chen, K.F. Lam, K.L. Yeung, Selective removal of chromium from different aqueous systems using magnetic MCM-41 nanosorbents, *Chem. Eng. J.* 172 (2011) 728–734.
- [19] S. Maeno, Q. Zhu, M. Sasaki, T. Miyamoto, M. Fukushima, Monopersulfate oxidation of tetrabromobisphenol A by an iron(III)-phthalocyaninetetrasulfate catalyst coordinated to imidazole functionalized silica particles, *J. Mol. Catal. A Chem.* 400 (2015) 56–63.
- [20] L. Hu, X. Yang, S. Dang, An easily recyclable Co/SBA-15 catalyst: Heterogeneous activation of peroxymonosulfate for the degradation of phenol in water, *Appl. Catal. B Environ.* 102 (2011) 19–26.
- [21] L. Hu, F. Yang, W. Lu, Y. Hao, H. Yuan, Heterogeneous activation of oxone with CoMg/SBA-15 for the degradation of dye Rhodamine B in aqueous solution, *Appl. Catal. B Environ.* 134–135 (2013) 7–18.
- [22] P. Shukla, H. Sun, S. Wang, H.M. Ang, M.O. Tade, Co-SBA-15 for heterogeneous oxidation of phenol with sulfate radical for wastewater treatment, *Catal. Today* 175 (2011) 380–385.

- [23] E. Saputra, S. Muhammad, H. Sun, H. Ang, M.O. Tade, S. Wang, Manganese oxides at different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions, *Appl. Catal. B Environ.* 142–143 (2013) 729–735.
- [24] E. Saputra, S. Muhammad, H. Sun, H. Ang, M.O. Tade, S. Wang, Shape-controlled activation of peroxymonosulfate by single crystal α - Mn_2O_3 for catalytic phenol degradation in aqueous solution, *Appl. Catal. B Environ.* 154–155 (2014) 246–251.
- [25] D. Tang, G. Zhang, S. Guo, Efficient activation of peroxymonosulfate by manganese oxide for the degradation of azo dye at ambient condition, *J. Colloid Interf. Sci.* 454 (2015) 44–51.
- [26] F. Gong, L. Wang, D. Li, F. Zhou, Y. Yao, W. Lu, S. Huang, W. Chen, An effective heterogeneous iron-based catalyst to activate peroxymonosulfate for organic contaminants removal, *Chem. Eng. J.* 267 (2015) 102–110.
- [27] G. Wei, X. Liang, Z. He, Y. Liao, Z. Xie, P. Liu, S. Ji, H. He, D. Li, J. Zhang, Heterogeneous activation of Oxone by substituted magnetites $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ (Cr, Mn Co, Ni) for degradation of acid orange II at neutral pH, *J. Mol. Catal. A Chem.* 398 (2015) 86–94.
- [28] G.P. Anipsitakis, D.D. Dionysiou, M.A. Gonzalez, Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions, *Environ. Sci. Technol.* 40 (2006) 1000–1007.
- [29] G.P. Anipsitakis, D.D. Dionysiou, Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt, *Environ. Sci. Technol.* 37 (2003) 4790–4797.
- [30] J. Liu, Z. Zhao, P. Shao, F. Cui, Activation of peroxymonosulfate with magnetic Fe_3O_4 - MnO_2 core-shell nanocomposites for 4-chlorophenol degradation, *Chem. Eng. J.* 262 (2015) 854–861.
- [31] S. Luo, L. Duan, B. Sun, M. Wei, X. Li, A. Xu, Manganese oxide octahedral molecular sieve (OMS-2) as an effective catalyst for degradation of organic dyes in aqueous solutions in the presence of peroxymonosulfate, *Appl. Catal. B Environ.* 164 (2015) 92–99.
- [32] G. Wang, B. Huang, Z. Lou, Z. Wang, X. Qin, X. Zhang, Y. Dai, Valence state heterojunction $\text{Mn}_3\text{O}_4/\text{MnCO}_3$: Photo and thermal synergistic catalyst, *Appl. Catal. B Environ.* 180 (2016) 6–12.
- [33] J. Zhang, B. Sun, X. Xiong, N. Gao, W. Song, E. Du, X. Guan, G. Zhou, Removal of emerging pollutants by Ru/TiO_2 -catalyzed permanganate oxidation, *Water Res.* 63 (2014) 262–270.
- [34] J. Zhang, B. Sun, X. Guan, H. Wang, H. Bao, Y. Huang, J. Qiao, G. Zhou, Ruthenium nanoparticles supported on CeO_2 for catalytic permanganate oxidation of butylparaben, *Environ. Sci. Technol.* 47 (2013) 13011–13019.
- [35] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science* 279 (1998) 548–552.
- [36] Q. Tao, Z. Xu, J. Wang, F. Liu, H. Wan, S. Zheng, Adsorption of humic acid to aminopropyl functionalized SBA-15, *Microporous Mesoporous Mater.* 131 (2010) 177–185.
- [37] A. Moses Ezhil Raj, S.G. Victoria, V.B. Jothy, C. Ravidhas, J. Wollschl Ger, M. Suendorf, M. Neumann, M. Jayachandran, C. Sanjeeviraja, XRD and XPS characterization of mixed valence Mn_3O_4 hausmannite thin films prepared by chemical spray pyrolysis technique, *Appl. Surf. Sci.* 256 (2010) 2920–2926.
- [38] C. Reed, Y. Lee, S.T. Oyama, Structure and oxidation state of silica-supported manganese oxide catalysts and reactivity for acetone oxidation with ozone, *J. Phys. Chem. B* 110 (2006) 4207–4216.
- [39] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.* 257 (2011) 2717–2730.
- [40] H.W. Nesbitt, D. Banerjee, Interpretation of XPS $\text{Mn}(2p)$ spectra of Mn oxyhydroxides and constraints on the mechanism of MnO_2 precipitation, *Am. Mineral.* 83 (1998) 305–315.
- [41] G. Fang, C. Liu, J. Gao, D.D. Dionysiou, D. Zhou, Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation, *Environ. Sci. Technol.* 49 (2015) 5645–5653.
- [42] G. Fang, D.D. Dionysiou, S.R. Al-Abed, D. Zhou, Superoxide radical driving the activation of persulfate by magnetite nanoparticles: implications for the degradation of PCBs, *Appl. Catal. B Environ.* 129 (2013) 325–332.
- [43] C. Tan, N. Gao, Y. Deng, J. Deng, S. Zhou, J. Li, X. Xin, Radical induced degradation of acetaminophen with Fe_3O_4 magnetic nanoparticles as heterogeneous activator of peroxymonosulfate, *J. Hazard. Mater.* 276 (2014) 452–460.
- [44] Y. Guan, J. Ma, X. Li, J. Fang, L. Chen, Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/peroxymonosulfate system, *Environ. Sci. Technol.* 45 (2011) 9308–9314.
- [45] J. Yan, L. Han, W. Gao, S. Xue, M. Chen, Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene, *Bioresour. Technol.* 175 (2015) 269–274.
- [46] R. Daghrir, A. Dimboukou-Mpira, B. Seyhi, P. Drogui, Photocatalytic degradation of butyl-paraben: optimization, toxicity and kinetic studies, *Sci. Total Environ.* 490 (2014) 223–234.
- [47] O.S. Furman, A.L. Teel, R.J. Watts, Mechanism of base activation of persulfate, *Environ. Sci. Technol.* 44 (2010) 6423–6428.
- [48] Y. Ji, C. Dong, D. Kong, J. Lu, Q. Zhou, Heat-activated persulfate oxidation of atrazine: implications for remediation of groundwater contaminated by herbicides, *Chem. Eng. J.* 263 (2015) 45–54.
- [49] L.J. Xu, W. Chu, L. Gan, Environmental application of graphene-based CoFe_2O_4 as an activator of peroxymonosulfate for the degradation of a plasticizer, *Chem. Eng. J.* 263 (2015) 435–443.
- [50] P. Avetta, A. Pensato, M. Minella, M. Malandrino, V. Maurino, C. Minero, K. Hanna, D. Vione, Activation of persulfate by irradiated magnetite: Implications for the degradation of phenol under heterogeneous photo-Fenton-like conditions, *Environ. Sci. Technol.* 49 (2015) 1043–1050.
- [51] T. Zhang, Y. Chen, Y. Wang, J. Le Roux, Y. Yang, J. Croué, Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation, *Environ. Sci. Technol.* 48 (2014) 5868–5875.
- [52] J. Zou, J. Ma, L. Chen, X. Li, Y. Guan, P. Xie, C. Pan, Rapid acceleration of ferrous iron/peroxymonosulfate oxidation of organic pollutants by promoting Fe(III)/Fe(II) cycle with hydroxylamine, *Environ. Sci. Technol.* 47 (2013) 11685–11691.
- [53] C. Luo, J. Ma, J. Jiang, Y. Liu, Y. Song, Y. Yang, Y. Guan, D. Wu, Simulation and comparative study on the oxidation kinetics of atrazine by $\text{UV}/\text{H}_2\text{O}_2$, UV/HSO_5^- and $\text{UV}/\text{S}_2\text{O}_8^{2-}$, *Water Res.* 80 (2015) 99–108.
- [54] Ministry of Environmental Protection of the People's Republic China, Discharge standard of pollutants for municipal wastewater treatment plant, GB 18918-2002, 2002.
- [55] Y. Kirino, T. Ohkuma, T. Kwan, Spin trapping with 5,5-dimethylpyrroline-N-oxide in aqueous solution, *Chem. Pharm. Bull.* 29 (1981) 29–34.