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VIEWS & COMMENTS

Oxidant or catalyst for oxidation? The role of manganese oxides in the activation of peroxymonosulfate (PMS)

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Abstract Manganese oxides (MnO_x) have been demonstrated to be effective materials to activate Oxone (i.e., PMS) to degrade various contaminants. However, the contribution of direct oxidation by MnO_x to the total contaminant degradation under acidic conditions was often neglected in the published work, which has resulted in different and even conflicting interpretations of the reaction mechanisms. Here, the role of MnO_x (as both oxidants and catalysts) in the activation of Oxone was briefly discussed. The findings offered new insights into the reaction mechanisms in PMS-MnO_x and provided a more accurate approach to examine contaminant degradation for water/wastewater treatment.

Keywords Peroxymonosulfate, Manganese oxides, Catalyst, Oxidant

The world is facing a water crisis, which requires affordable technologies to obtain clean water around the world. Advanced oxidation processes (AOPs) have been widely regarded as an important technology for removing various pollutants. Recently, $SO_4^{\bullet -}$ produced from peroxymonosulfate (PMS) has received increasing attention due to its high redox potential (2.5–3.1 V) and longer life time (30–40 μs) than $^{\bullet}OH$ (Huang et al., 2019). In the past seven years, manganese oxides (MnO_x) have been often examined and demonstrated to be effective in Oxone activation due to their high abundance, low toxicity, and environmental friendliness. Numerous properties of MnO_x that might influence the reactivity have been investigated, such as phase structure, Mn oxidation state, particle shape, oxygen species, reduction potential, surface area, and conductivity. All of these findings enabled us to obtain a mechanistic understanding of the catalytic oxidation processes.

In MnO_2-PMS systems, Oxone ($KHSO_5$•$0.5KHSO_4$ •$0.5K_2SO_4$) is commonly employed to provide PMS, which can substantially lower the solution pH when buffer is not used, resulting in a significant enhancement of the direct oxidative reactivity. Recently, both the direct oxidative reactivity and catalytic reactivity were reported to be involved in the activation of Oxone by MnO_x (Huang et al., 2019). As shown in Fig. 1(a), the direct oxidative reactivity accounted for 25.2, 7.4, 34.1, and 94.5% of the total reactivity of α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2 at pH 3.07, respectively (Huang et al., 2019). This result indicated that direct oxidation played an important role in the total reactivity, especially for δ-MnO_2.

However, we surprisingly found that among 62 journal articles published in the past seven years, 36 of them (58% as of 05/25/2019) did not consider the contribution of direct oxidation by the MnO_x under acidic conditions (i.e., MnO_x as oxidants), and only attributed the overall reactivity to catalytic reactivity (i.e., MnO_x as catalysts). This might have resulted in different and even conflicting interpretations of the involved mechanisms. For instance, some studies obtained the XPS spectra to show that Mn (III) was partially transformed to Mn(IV) after the reaction (Khan et al., 2018), whereas others reported that Mn(IV) was partially converted to Mn(III) (Luo et al., 2015). However, all of these studies attributed the changes to the catalytic reactivity only. We believe that the contradictory results were because of the different contributions of catalytic versus direct oxidative reactivity. It has been shown that in the PMS-MnO_2 systems, the catalytic reaction resulted in increasing Mn(IV)% and decreasing Mn(III)%, whereas the direct oxidation led to the opposite results (Huang et al., 2019). Therefore, depending on the relative contributions of direct vs. catalytic oxidation, the changes in the abundance of different Mn species would be expected to be different. Given the growing interest in the PMS-MnO_x systems, we believe it is timely to point out this important overlook, so future researchers could obtain more accurate understanding of the reactivity and

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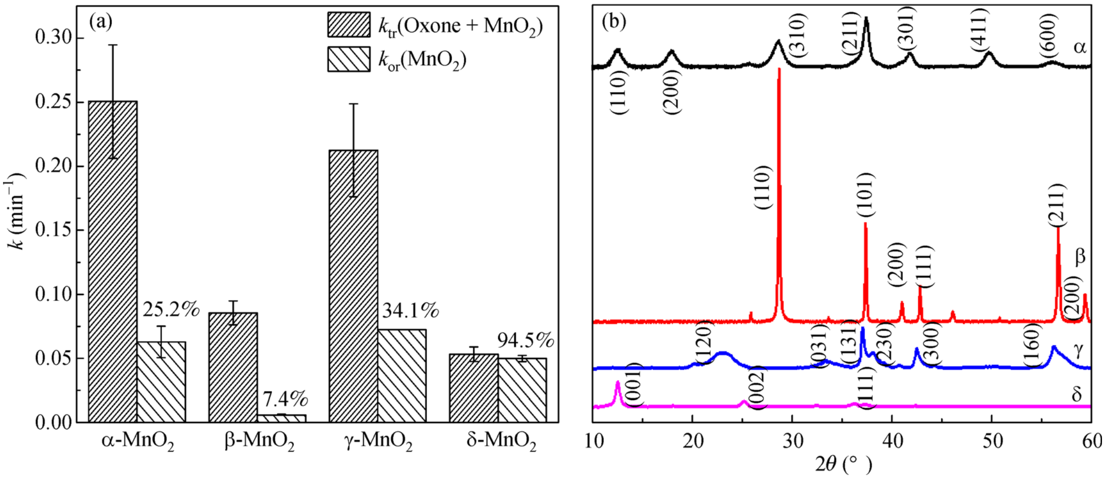


Fig. 1 (a) Pseudo-first-order reaction rate constants of bisphenol A (BPA) degradation by Oxone-MnO$_2$ (total reactivity: k_{tr}) and MnO$_2$ (direct oxidative reactivity: k_{or}) at pH 3.07; (b) XRD patterns of different structures of MnO$_2$ (Huang et al., 2019).

mechanisms of Mn-based catalysts.

In fact, long before the increasing number of research examining the activation of PMS by MnO$_x$ as catalysts, MnO$_x$ had been widely investigated as oxidants themselves in direct oxidation of different contaminants. The detailed reaction mechanisms of aromatic compounds (ArXH) by MnO$_2$ (denoted as $>$ Mn^{IV}) are summarized in Eqs. (1)–(5) (Zhang et al., 2008), where either the precursor complex formation (Eq. 1) or the electron transfer reaction (Eq. 2) is the rate limiting step. It has been well-known that the oxidative reactivity of MnO$_x$ increased substantially with decreasing pH, mainly because pH can affect the reduction potential and surface charge of MnO$_x$, which in turn affected the oxidative reactivity. Moreover, the surface properties of MnO$_x$ can affect their direct oxidative reactivity, and it has been revealed that the amount of surface Mn(III) was key to the direct oxidative reactivity at pH 5 (Huang et al., 2018).

$$> \mathrm{Mn^{IV}} + \mathrm{ArXH} \rightleftharpoons (> \mathrm{Mn^{IV}},\ \mathrm{ArXH}) \tag{1}$$

$$(> \mathrm{Mn^{IV}} + \mathrm{ArXH}) \rightleftharpoons (> \mathrm{Mn^{III}},\ \mathrm{ArH}\bullet) + \mathrm{H^+} \tag{2}$$

$$(> \mathrm{Mn^{III}},\ \mathrm{ArX}\bullet) \rightleftharpoons\ > \mathrm{Mn^{III}} + \mathrm{ArH}\bullet \tag{3}$$

$$\mathrm{ArX}\bullet \longrightarrow \mathrm{products} \tag{4}$$

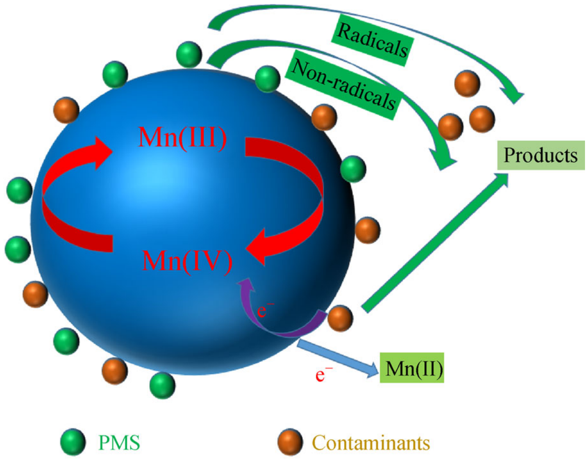
$$> \mathrm{Mn^{III}} \longrightarrow\ > \mathrm{Mn^{II}} \tag{5}$$

Therefore, the reported contaminant degradation in PMS-MnO$_x$ in many previous papers was in fact a sum of both catalytic oxidation by PMS/MnO$_2$ and direct oxidation by MnO$_2$. The relative contribution of direct vs. catalytic oxidation depends on the nature of the MnO$_x$ (Huang et al., 2019). Based on the XRD spectra (Fig. 1(b)) and HRTEM (Huang et al., 2019), α-, β-, and γ-MnO$_2$ are crystalline MnO$_2$, while δ -MnO$_2$ is a less crystalline MnO$_2$. It was found that the crystallinity of MnO$_x$ was a dominant factor in determining whether MnO$_x$ reacted as an oxidant or a catalyst in the activation of Oxone. For δ-MnO$_2$, the major role of Oxone was actually to lower the solution pH (just like any other acids) to lead to the higher reactivity of the MnO$_2$. Therefore, the major role of δ-MnO$_2$ was an oxidant in PMS-MnO$_2$, while that of β-MnO$_2$ was a catalyst because it was poorly reactive as a direct oxidant. α- and γ-MnO$_2$ acted as both oxidants and catalysts. The less crystalline or amorphous structures might have destabilized MnO$_x$ thermodynamically, which made them stronger oxidants but weaker catalysts (Sabri et al., 2018).

The crystallinity of MnO$_x$ also influenced the generation of radicals in the PMS-MnO$_x$ systems. It was shown that $SO_4^{\bullet -}$, $^{\bullet}OH$ and $^1O_2$ were all generated in PMS-crystalline MnO$_2$, while only $^1O_2$ was generated in PMS-less crystalline MnO$_2$ (Huang et al., 2019). Moreover, a non-radical mechanism based on the direct electron transfer between PMS-MnO$_2$ and the contaminant was reported in the activation of Oxone by an amorphous MnO$_2$ (Wang et al., 2018). Therefore, it seems that $SO_4^{\bullet -}$ and $^{\bullet}OH$ were only produced when crystalline MnO$_2$ was the catalyst, although further research is needed to verify this conclusion.

In addition, pH can influence the role of MnO$_x$ in the activation of Oxone because the direct oxidation was negligible as compared with the catalytic reactivity at near neutral and alkaline pH (Huang et al., 2019). Therefore, the major role of MnO$_x$ in Oxone-MnO$_x$ is a catalyst under those pH conditions. To accurately quantify the catalytic reactivity of MnO$_x$ in the activation of Oxone, it is better to employ appropriate buffers to maintain the solution pH; otherwise, the addition of Oxone will significantly lower the pH to within the acidic range. If no buffer is used for various reasons, then the solution pH of the MnO_x control experiments for quantifying the direct oxidative reactivity of MnO_x should be adjusted to the same value as that in the Oxone-MnO_x system.

In conclusion, it is essential to consider the role of MnO_x as both oxidants and catalysts (Scheme 1) to better understand the reaction mechanisms, products, and reactivity of Oxone-MnO_x. The direct oxidative reactivity of MnO_x has been overlooked in a number of recent studies, which requires us to carefully re-interpret some of the reported results obtained under acidic conditions.



Scheme 1 Reaction mechanisms in the degradation of contaminants by PMS-MnO_x.

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