

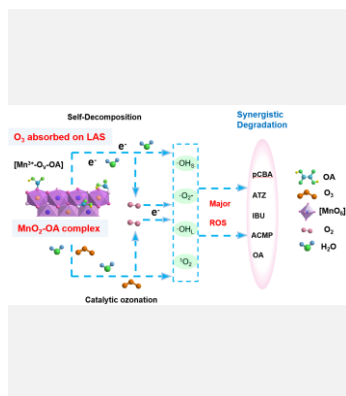
# Unravelling the role of manganese oxides and oxalic acid complex in catalytic ozonation: Structural properties and mechanistic insights

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The complexation between metal oxides and organic acid plays an important role in the water treatment. However, the mechanism of complex in catalytic ozonation process (HCO) has not been studied yet. In this study, manganese oxide-oxalic acid (MnO<sub>2</sub>-OA) complex was constructed and used in HCO for different pollutants degradation (MnO<sub>2</sub>/OA/O<sub>3</sub>). The addition of OA enhanced not only k value of MnO<sub>2</sub>/OA/O<sub>3</sub> process, but also had advantageous effects on co-degradation of contaminant and OA. Systematic characterization techniques (XPS, H<sub>2</sub>-TPR, and etc.) confirmed the enhanced electron transfer ability and redox property of MnO<sub>2</sub>-OA complex. Probe experiments quantified the contribution of various radicals for atrazine degradation. Finally, a feasible mechanism involving solid-liquid interface reaction was elaborated, which presented a potential strategy improving catalytic ozonation performance.

## Introduction

Heterogeneous catalytic ozonation (HCO), one of advanced oxidation processes (AOPs), has been widely employed to degrade and mineralize many recalcitrant organic pollutants owing to its advantages of shorter reaction time, low energy consumption, and mild operate conditions [1]. So far, solid catalyst utilized for HCO can be commonly divided into four categories including metals on supports, carbonaceous materials, minerals, and metal oxides [2]. Manganese oxides (MnOx), a commonly occurring metal oxide in nature, have excellent physicochemical properties [3]. Particularly, manganese dioxide (MnO<sub>2</sub>) has exhibited excellent catalytic ozonation activity for the degradation of refractory pollutants [4].

Oxalic acid (OA) is a common organic acid ligand that has very low reactivity with O<sub>3</sub> ( $k_{O_3,OA} \leq 0.04 \text{ M}^{-1} \text{ S}^{-1}$ ,  $k_{OH,OA} \approx 10^6 \text{ M}^{-1} \text{ S}^{-1}$ ) [5]. Moreover, OA can directly form complexes with MnOx to promote the degradation efficiency of organic compounds. Our previous study [6] revealed that copper oxide supported  $\beta$ -MnO<sub>2</sub> composites (Cu<sub>1</sub>Mn<sub>180</sub>) could obtain great catalytic ozonation performance with 87.5% of OA removal efficiency in 30 min at pH 6.0. However, no noticeable degradation of OA was observed within the initial five minutes. Therefore, it was reasonable to suspect that  $\beta$ -MnO<sub>2</sub> and OA formed the complex ( $\beta$ -MnO<sub>2</sub>-OA) at the beginning of the reaction, which significantly influenced the degradation of OA in HCO process.

In this study, different structural MnO<sub>2</sub> was synthesized by a hydrothermal method and used for constructing MnO<sub>2</sub>-OA complex in the HCO process. The formation, interaction, and surface

physicochemical properties between MnO<sub>2</sub> and OA were explored and revealed by a series of characterization methods. Additionally, the influence of the ratio of MnO<sub>2</sub> dosage and OA concentration on pollutant degradation was discussed the HCO process. Probe methods were employed to further evaluate the contribution of various radicals in catalytic HCO system. Ultimately, a feasible interface mechanism of MnO<sub>2</sub>-OA complex in HCO process was elucidated.

## Material and Methods

All chemicals used in the experiments including manganese sulfate (MnSO<sub>4</sub>), ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), and potassium permanganate (KMnO<sub>4</sub>), tert-butanol (purity  $\geq 99.7\%$ ), p-benzoquinone (BQ) were of analytical grade.

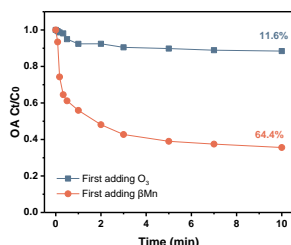
Batch ozonation experiments were performed in 250 mL glass beaker. All samples (1.5 mL) of the experiments were taken out at a certain time interval under stirring (400 rpm). Then quenched with excess Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.01 M) to remove spare O<sub>3</sub> content. After filtered by 0.45  $\mu\text{m}$  filter, the samples were further determined through High Performance Liquid Chromatography (HPLC).

## Results and Discussion

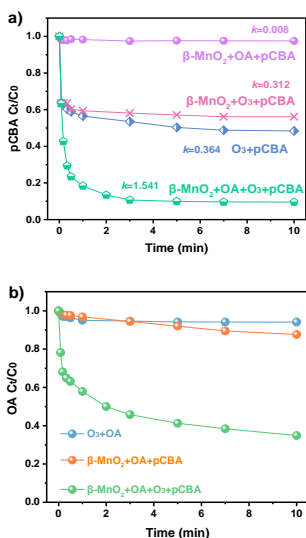
According to Fig.1, adding  $\beta$ -MnO<sub>2</sub> to the OA solution before ozonation could facilitate the formation of  $\beta$ -MnO<sub>2</sub>-OA complex, which would strengthen the catalytic ozonation activity.

As illustrated in Fig.2(a), O<sub>3</sub> alone could achieve 51.6% of pCBA degradation in 10 min, while it was partially inhibited in the  $\beta$ -MnO<sub>2</sub>/O<sub>3</sub> system (43.8%). Notably, the optimum catalytic ozonation

performance with 90.4% of pCBA degradation was obtained in the  $\beta$ -MnO<sub>2</sub>/OA/O<sub>3</sub> process. Meanwhile, the degradation of OA in  $\beta$ -MnO<sub>2</sub>/OA/O<sub>3</sub> system could reach to 65.14% (Fig.2(b)).



**Figure 1.** The effect of the adding sequence of  $\beta$ -MnO<sub>2</sub> and O<sub>3</sub> solution on catalytic ozone activity. Experimental conditions:  $[\beta\text{-MnO}_2]=50\text{ mg L}^{-1}$ ,  $[\text{OA}]_0=10\text{ mg L}^{-1}$ ,  $[\text{O}_3]=2\text{ mg L}^{-1}$ ,  $\text{pH}_0=4.0 \pm 0.2$ .



**Figure 2.** a) pCBA removal efficiency, b) OA degradation efficiency in different processes. Experimental conditions:  $[\text{pCBA}]_0=0.1\text{ mg L}^{-1}$ ,  $[\beta\text{-MnO}_2]=50\text{ mg L}^{-1}$ ,  $[\text{OA}]_0=10\text{ mg L}^{-1}$ ,  $[\text{O}_3]=2\text{ mg L}^{-1}$ ,  $\text{pH}_0=4.0 \pm 0.2$ .

## Conclusions

The complexation of MnO<sub>2</sub> and OA would facilitate electron transfer ability, enhance the redox property, and create more active Ov of catalyst, thus resulting in excellent catalytic performance. In addition, radical scavenger experiments demonstrated that the degradation of pCBA was probably main due to the coexistence of  $\cdot\text{OH}$ ,  $\text{O}_2^{\cdot-}$  and  $^1\text{O}_2$ .

## Acknowledgments

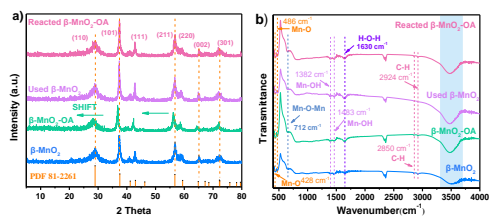
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The crystal structures of pristine  $\beta$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub>-OA complex were characterized by XRD pattern. As described in Fig.3(a), the diffraction peaks at the value of  $2\theta = 28.6^\circ, 37.2^\circ, 42.8^\circ, 56.7^\circ, 59.3^\circ, 64.8^\circ,$  and  $72.2^\circ$  were indexed to (110), (101), (111), (211), (220), (002), and (301) planes of a typical  $1 \times 1$  tunnel structure of  $\beta$ -MnO<sub>2</sub> (PDF 81-2261). By contrast, no other characteristic peaks were found in the image of  $\beta$ -MnO<sub>2</sub>-OA complex, but a slight shift to the lower angle, which meant that the inter-planner distance become long. The changes in micro lattice structure proved the possibility of complexation between  $\beta$ -MnO<sub>2</sub> and OA, via the substitution of atoms with different atomic diameters.

The FT-IR analysis in the range between 400 and 4000  $\text{cm}^{-1}$  was conducted in Fig.3(b). Same peaks of  $\beta$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub>-OA complex found at 428  $\text{cm}^{-1}$ , 486  $\text{cm}^{-1}$ , at 712  $\text{cm}^{-1}$ , 1382  $\text{cm}^{-1}$ , 1483  $\text{cm}^{-1}$ , 1630  $\text{cm}^{-1}$ , and 3500  $\text{cm}^{-1}$  could be related to the vibrations of Mn-O bonds, Mn-O-Mn bonds, O-H bonds, H-O-H bonds, and the surface-adsorbed water species and hydroxyl groups, respectively, confirming the structural integrity of catalyst after the generation of  $\beta$ -MnO<sub>2</sub>-OA complex. It could be noticed that the more intensified peaks of -OH groups were observed in  $\beta$ -MnO<sub>2</sub>-OA complex, due to the intercalation of tunnel structure by a small amount of water molecules in complex formation process.



**Figure 3.** XRD patterns a) and FT-IR images b) of different catalysts.