# **Efficient Degradation of 2,4-Dichlorophenol on Activation** of Peroxymonosulfate Mediated by MnO<sub>2</sub>

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Received: 3 October 2020 / Accepted: 8 January 2021 / Published online: 8 February 2021 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC part of Springer Nature 2021

#### **Abstract**



Sulfate radical based-advanced oxidation process has received increasing interest in the remediation of wastewater and contaminated soil. In this study, degradation of 2, 4-dichlorophenol (2, 4-DCP) was investigated over peroxymonosulfate (PMS) activation by MnO<sub>2</sub>, which was prepared by liquid-phase oxidation method. The prepared MnO<sub>2</sub> was characterized by transition electron microscopy, X-ray diffraction,  $N<sub>2</sub>$  adsorption–desorption, and X-ray photoelectron spectroscopy. Characterization results showed that  $\alpha$ -MnO<sub>2</sub> exhibited the highest surface area and Mn (III) content. The PMS activation by MnO<sub>2</sub> in 2, 4-DCP degradation followed the order of  $\alpha$ -MnO<sub>2</sub>>  $\gamma$ -MnO<sub>2</sub>> β-MnO<sub>2</sub>, which is dependent on the properties of  $MnO<sub>2</sub>$  including crystal structure, surface area and Mn (III) content. Influences of initial concentration of 2, 4-DCP, PMS and MnO<sub>2</sub> dosage, pH and co-existing inorganic ions on the degradation were examined. Electron paramagnetic resonance (EPR) and quenching experiments with ethanol and tert-butanol suggested that sulfate radicals were the dominant radicals in the process. Findings in this study indicated that  $\alpha$ -MnO<sub>2</sub> was an attractive catalyst for activation of PMS to degrade 2, 4-DCP in aqueous solution.

**Keywords** Manganese oxides · 2, 4-dichlorophenol · Peroxymonosulfate · Activation · Degradation

Chlorophenols as chemical raw materials are typically used in leather, dyes, pesticide and fungicides (Chen et al. [2013](#page-5-0); Zhou et al. [2018\)](#page-7-0), which have been listed as priority pollutants by the United States Environmental Protection Agency (Chen et al. [2018\)](#page-5-1). The discharged chlorophenols in wastewater have caused serious environmental concerns due to the toxicity, persistence and carcinogenicity (Zhang et al. [2015a](#page-7-1); Zhao et al. [2016](#page-7-2)). Hence, it is highly demanded to develop efective methods for chlorophenols removal from water.

Many treatment techniques including adsorption (Chen et al. [2012](#page-5-2); Xu et al. [2012\)](#page-6-0), hydrodechlorination (Jin et al. [2011](#page-6-1); Zhou et al. [2014](#page-7-3)), photocatalysis (Bayarri et al. [2005](#page-5-3); Liu et al. [2012](#page-6-2)), advanced oxidation processes (Jia et al.

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[2015](#page-6-3); Karci et al. [2012](#page-6-4)) and biological methods (Eker and Kargi [2008](#page-5-4); Wang et al. [2015c\)](#page-6-5), have been used to treat 2, 4-DCP. In recent years, sulfate radical-based advanced oxidation process has attracted great attention for the treatment of a wide range of organic pollutants (Anipsitakis and Dionysiou [2003;](#page-5-5) Ghanbari and Moradi [2017](#page-5-6); Zhou et al. [2018b](#page-7-4)). Sulfate radicals have higher redox potential (2.5–3.1 V), wider range of solution pH, and longer life time (30–40 μs) than hydroxyl radicals. Sulfate radicals could be generated from the activation of peroxymonosulfate (PMS) and peroxydisulfate (PDS) via UV, heat, carbon-based materials and ransition metals (Fang et al. [2015;](#page-5-7) Wang and Wang [2018](#page-6-6)).

Various transition metal catalysts  $(Co^{2+}, Cu^{2+}, Ag^+, V^{3+})$ et al.) have been reported to activate PMS (Nfodzo and Choi [2011](#page-6-7); Wang and Wang [2018](#page-6-6)). Cobalt-based materials have been recognized as one of the most efective options for the activation of PMS. However, the leaching of cobalt oxides from cobalt-based materials posed risks to human health and environment. Consequently, it is necessary to develop environmental-friendly catalysts for PMS activation. Manganese oxides, due to low toxicity, abundance in natural stock and environmental friendliness, have been widely used in oxidation reaction for treatment of organic pollutants (Saputra

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et al. [2013;](#page-6-8) Wang et al. [2015a](#page-6-9); Zhou et al. [1998\)](#page-7-5). Moreover, manganese dioxides are promising catalysts in activation persulfate for degradation of organic contaminants. Saputra et al. reported that  $Mn_2O_3$  was the best catalyst in activating PMS for phenol degradation (Saputra et al. [2013](#page-6-8)). As reported,  $\alpha$ -MnO<sub>2</sub> showed outstanding catalytic activity in activation of PDS and PMS for degradation of phenol and dye (Liu et al. [2016;](#page-6-10) Saputra et al. [2012;](#page-6-11) Zhao et al. [2016](#page-7-2)).

However, to the best of our knowledge, there are few studies to compare the structure of  $MnO<sub>2</sub>$  on PMS activation and chlorophenols degradation in  $MnO<sub>2</sub>/PMS$  system. In this study, three types of  $MnO<sub>2</sub>$  with different structural properties were synthesized and their performances in activation of PMS for 2, 4-dichlorophenol (2, 4-DCP) degradation were investigated. The dominant radicals were identifed by electron paramagnetic resonance (EPR) spectra and free radical quenching studies. Furthermore, several infuence factors were investigated, including 2, 4-DCP concentration,  $MnO<sub>2</sub>$ dosage, PMS concentration, pH and co-existing inorganic ions.

### **Materials and Methods**

2, 4-Dichlorophenol, 2-chlorophenol, phenol and 5, 5-dimethyl-1-pyrrolidine *N*-oxide (DMPO, 97%) were purchased from Sigma-Aldrich. Sodium PMS (available as a triple potassium salt with the commercial name of Oxone®,  $2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>$  was obtained from Alfa Aesar. Ethanol (EtOH) and acetonitrile (chromatography grade) were purchased from Merck. Tertiary butanol (TBA) was obtained from Aladdin Chemistry Co. Ltd.  $MnSO<sub>4</sub>$ ,  $(NH_4)_2S_2O_8$ ,  $(NH_4)_2SO_4$ , HCl and NaOH were purchased from Nanjing Chemical Reagents Co. Ltd. All other reagents were chemical grade or higher and were used without further purification. Deionized water with a resistivity of 18  $M\Omega$ cm−1 was used for preparing aqueous solutions.

The synthesis of  $MnO<sub>2</sub>$  was conducted based on liquidphase oxidation method according to literature (Wang and Li [2003](#page-6-12)). Details of synthesis and characterization are listed in Text S1 in Supporting Information (SI).

The degradation of 2, 4-DCP was carried out in a 250 mL three-necked flask at  $25 \pm 0.5$  °C with a waterbath. Briefly, 50 mg of  $MnO<sub>2</sub>$  was added into 250 mL solution with 20 mg/L of 2, 4-DCP and 1.63 mM PMS under stirring (1400 rpm) and parallel experiment were carried out simultaneously. Control experiments with only  $MnO<sub>2</sub>$  or PMS were performed under the same condition. A 0.5 mL of samples were collected at selected time intervals (5, 10, 15, 20, 30, 40, 50, 60, 90 and 120 min) and then mixed with 0.5 mL ethanol to quench the reaction. After fltered with 0.45 μm membrane flter, the concentration of solute in an aliquot was analyzed by high-performance liquid chromatography (Agilent 1200, USA) with an ultraviolet detector at wavelength of 270 nm using a  $4.6 \times 150$  mm HC-C18 column. The mobile phase was 60% acetonitrile and 40% water (v/v).

# **Results and Discussion**

Transmission electron microscope (TEM) images of three MnO<sub>2</sub> are presented in Fig. [1](#page-1-0). Obviously,  $\alpha$ -MnO<sub>2</sub> is ribbonlike nanowires with diameters around 10 nm and lengths ranging between 40 and 200 nm. TEM images of  $β$ -MnO<sub>2</sub> demonstrated that it was nanorods with average diameters of 100 nm, while  $\gamma$ -MnO<sub>2</sub> showed a nanofiber structure with the diameters of 10–30 nm. The Brunauer–Emmett–Teller (BET) surface areas were 96.9, 15.2, and 72.3 m<sup>2</sup>/g for  $\alpha$ -,  $β$ - and γ-MnO<sub>2</sub>, respectively. Clearly, α-MnO<sub>2</sub> has the largest BET surface area.

<span id="page-1-0"></span>

**Fig. 1** TEM images of different structures of  $MnO<sub>2</sub>$ 

As shown in Fig. [2](#page-2-0), the XRD patterns of the  $MnO<sub>2</sub>$  were in according with the inorganic crystallographic database of XRD patterns of α-MnO<sub>2</sub> (JCPDS 44-0141), β-MnO<sub>2</sub> (JCPDS 24-0735) and  $\gamma$ -MnO<sub>2</sub> (JCPDS 14-0664) (Huang et al. [2019;](#page-6-13) Wang and Li [2003](#page-6-12); Wang et al. [2015b\)](#page-6-14). For all the MnO<sub>2</sub>, the strong bands at 473, 519 and 715 cm<sup>-1</sup> were observed in FTIR spectra (Fig. S1), which were assigned to the Mn–O lattice vibration (Kang et al. [2007](#page-6-15); Kim and Stair [2004\)](#page-6-16). The weak peak around  $1105 \text{ cm}^{-1}$  was assigned to the vibration of Mn (III)-O bond (Kang et al. [2007\)](#page-6-15).

The XPS spectra of MnO<sub>2</sub> in the Mn  $2p3/2$  regions are presented in Fig. S2. The Mn 2p3/2 spectra were divided into two peaks at binding energies of 642.4 eV and 641.3 eV, which were assigned to Mn (IV) and Mn (III) species (Peng et al. [2017](#page-6-17)), respectively. The ftting results of Mn 2p3/2 spectrums of Mn (III) and Mn (IV) are summarized in Table S1. Clearly, the abundance of Mn (III) species decreased in the order:  $\alpha$ -MnO<sub>2</sub>>γ-MnO<sub>2</sub>>β-MnO<sub>2</sub>.

Batch experiments were performed to investigate the degradation of 2, 4-DCP in  $MnO<sub>2</sub>/PMS$  system. The result is presented in Fig. [3](#page-2-1). Clearly, only about 4.6% of 2, 4-DCP was degraded in PMS system within 120 min, suggesting that 2,4-DCP could not be degraded efectively by PMS without activation. In the system with  $\alpha$ -MnO<sub>2</sub> alone, approximately 37.3% of 2, 4-DCP was removed from the solution, indicating that  $\alpha$ -MnO<sub>2</sub> has direct oxidation ability for degradation of 2, 4-DCP. The degradation of 2, 4-DCP with different dosages of  $\alpha$ -MnO<sub>2</sub> were compared in Fig. S3. The degradation efficiency increased from  $52.2\%$  to  $88.1\%$ as the dosage of  $\alpha$ -MnO<sub>2</sub> increasing from 0.20 to 1.0 g/L within 720 min, which further validated the direct oxidation of 2, 4-DCP by  $MnO<sub>2</sub>$ . The direct oxidation mechanisms of  $MnO<sub>2</sub>$  have been well studied in previous studies (Im et al. [2015;](#page-6-18) Lin et al. [2009](#page-6-19); Saputra et al. [2013;](#page-6-8) Septian and Shin [2019](#page-6-20); Zhang et al. [2008;](#page-7-6) Zhang and Huang [2003;](#page-7-7) Zhu



<span id="page-2-0"></span>**Fig. 2**  $XRD$  patterns of different structures of  $MnO<sub>2</sub>$ 



<span id="page-2-1"></span>Fig. 3 Degradation of 2, 4-DCP in  $\alpha$ -MnO<sub>2</sub>/PMS process. Reaction conditions:  $[2, 4-DCP]=20$  mg/L,  $[PMS]=1.63$  mM,  $[\alpha\text{-}MnO_2] = 0.2 \text{ g/L}, \text{pH } 7.0, \text{T} = 25 \text{ }^{\circ}\text{C}$ 

et al. [2019b\)](#page-7-8). Thus, direct oxidation will not be discussed in our study. It is note that 99% of 2, 4-DCP was degraded in  $\alpha$ -MnO<sub>2</sub>/PMS system within 120 min, which is significantly higher than the reported degradation efficiency (around  $75\%$ ) for 2, 4-DCP with persulfate activation by α-MnO<sub>2</sub> nanowire (Zhao et al. [2016\)](#page-7-2). The results indicated that  $MnO<sub>2</sub>$  exhibited an excellent catalytic ability to activate PMS to degrade 2, 4-DCP.

Degradation of 2, 4-DCP using  $\alpha$ -, β- and γ-MnO<sub>2</sub> as activation reagents were compared in Fig. [4.](#page-2-2) The degradation efficiency of 2, 4-DCP was  $88.6\%$ , 76.6% and  $85.5\%$  for  $\alpha$ -, β- and λ-MnO<sub>2</sub>, respectively. This phenomenon may be related to the Mn (III) content and crystal structure of  $MnO<sub>2</sub>$ . The sulfate radicals  $(SO<sub>4</sub><sup>−</sup>)$  and hydroxyl radicals  $(\cdot OH)$  are



<span id="page-2-2"></span>**Fig. 4** Degradation of 2, 4-DCP on activation of PMS by different  $MnO_2$ . Reaction conditions: [2, 4-DCP]=20 mg/L, [PMS] = 0.33 mM, [α-, β-, and γ-MnO<sub>2</sub>] = 0.04 g/L, pH 7.0, T = 25 °C

$$
HSO_5^- + 2MnO_2 \to SO_5^{--} + OH^- + Mn_2O_3 \tag{1}
$$

$$
HSO_5^- + Mn_2O_3 \rightarrow SO_4^{--} + H^+ + 2MnO_2 \tag{2}
$$

$$
SO_4^{\bullet-} + H_2O \rightarrow \bullet OH + H^+ + SO_4^{2-}
$$
 (3)

Obviously,  $SO_4^{\bullet-}$  is formed from PMS activation by Mn(III) and  $HSO_5^{\rightarrow}$  is formed by Mn(IV). Moreover, and  $SO_4^{\bullet-}$  has a higher redox potential than  $HSO_5^{\bullet-}$  (Oh et al. [2016](#page-6-23)). Hence, the higher the content of Mn (III), the more SO∙− <sup>4</sup> were produced for degradation reaction. As mentioned above,  $\alpha$ -MnO<sub>2</sub> has the highest content (62.3%) of Mn (III), leading to the highest degradation efficiency. Additionally, Mn (III) forms weaker and more fexible Mn–O bonds due to the occupation of the antibonding  $e_{\varphi}$  orbital, which are more catalytically reactive (Robinson et al. [2013](#page-6-24)). In contrast, βand  $\gamma$ -MnO<sub>2</sub> with stronger Mn(IV)-O bonds are more stable and infexible, leading to the low oxidation potential. This further explained why  $\alpha$ -MnO<sub>2</sub> showed the highest catalytic activity.

The unique tunnel structure of  $\alpha$ -MnO<sub>2</sub> is also responsible for the extraordinarily strong catalytic reactivity (Huang et al. [2019](#page-6-13), [2018](#page-6-25); Zhang et al. [2015b\)](#page-7-9). α-MnO<sub>2</sub> with  $(2\times2)$ tunnel structure displayed larger tunnel sizes than  $γ$ -MnO<sub>2</sub> with  $(1 \times 1)$  and  $(1 \times 2)$  tunnel structure, and  $\beta$ - MnO<sub>2</sub> with  $(1 \times 1)$  tunnel structure. Additionally,  $\alpha$ -MnO<sub>2</sub> exhibited the largest surface area, which would provide more active sites and enhance the catalytic performance.

EPR studies were performed to identify the reactive radical species in  $MnO<sub>2</sub>/PMS$  system. EPR spectroscopy coupled with DMPO as a spin-trapping agent was used to detect free radicals. As shown in Fig. [5](#page-3-2), DMPO-OH (four lines, 1:2:2:1) signal with hyperfne splitting constants of  $a_H = a_N = 4.7$ G was observed in PMS system. The generation of DMPO-OH signals suggested ∙OH was formed in PMS solution at ambient temperature without activator, which was consistent with previous studies (Shukla et al. [2010\)](#page-6-26).

However, no DMPO-OH and DMPO-SO $_4$  signals were observed in MnO<sub>2</sub>/PMS system. Instead, a typical seven line spectrum with the intensity ratio of 1:2:1:2:1:2:1 signal was detected, which was identifed the characters of 5-tert-butoxycarbonyl-methyl-2-oxo-pyrroline-1-oxyl (DMPOX). The generation of DMPOX was possibly oxidation of DMPO by many strong oxidizing substances as reported in previous studies (Du et al. [2019](#page-5-8); Xie et al. [2019\)](#page-6-27). It is should be noted that the formation of DMPOX did not indicated that ∙OH and SO∙− <sup>4</sup> were absent. It is mainly because that the DMPO

<span id="page-3-0"></span>

<span id="page-3-2"></span><span id="page-3-1"></span>**Fig. 5** EPR spectra of DMPO-radical adducts in diferent reaction systems

oxidation is difficult to be detected due to its low sensitivity or short life time (Wang et al. [2017;](#page-6-28) Xie et al. [2019;](#page-6-27) Zhu et al. [2019a\)](#page-7-10).

Radical quenching experiments by adding EtOH and TBA were conducted to examine the main reactive species. EtOH is a well-known quenching agent for both •OH ( $k_{\text{OH}} = 1.2 - 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and SO<sup> $\text{C}_4$ </sup>  $(k_{SO_4^-} = 1.6 - 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$ . TBA is used to quench •OH  $(k_{\rm oH}^{\prime} = 3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}, k_{\rm SO_4^{\prime}} = 4 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$ (Huang et al. [2017](#page-6-29); Liang and Su [2009\)](#page-6-30). As shown in Fig. S4, the degradation of 2, 4-DCP was signifcantly inhibited after the addition of 0.02 M EtOH, but only slightly inhibited after addition of 0.02 M TBA. The results indicated that SO∙− <sup>4</sup> was the dominant reactive species for PMS activation by crystalline  $MnO<sub>2</sub>$ , which was consistent with previous reports (Liu et al. [2016;](#page-6-10) Luo et al. [2015](#page-6-31); Wang and Chen [2015](#page-6-32)).

Reactant adsorption on catalyst surface is considered as the prerequisite step for heterogeneous catalysis reaction. Therefore, concentration of adsorbed reactants is related to the reaction rate. Degradation reactions with diferent initial 2, 4-DCP concentration were compared in Fig. [6](#page-4-0)a. Clearly, the reaction rate was positively related to the concentration of 2, 4-DCP adsorbed on  $MnO<sub>2</sub>$ . The results are fitted by the Langmuir–Hinshelwood model (Dong et al. [2019;](#page-5-9) Konstantinou and Albanis [2004](#page-6-33)) as following reaction Eqs. ([4,](#page-3-3) [5\)](#page-3-4)

<span id="page-3-3"></span>
$$
r_0 = k\theta_s = k\frac{bC_0}{1 + bC_0} \tag{4}
$$

<span id="page-3-4"></span>
$$
\frac{1}{r_0} = \frac{1}{kbC_0} + \frac{1}{k}
$$
 (5)



<span id="page-4-0"></span>**Fig. 6 a** Efect of initial 2, 4-DCP concentrations; **b** linear plot of  $1/r_0$  versus  $1/C_0$ . Reaction conditions: [PMS] = 1.63 mM,  $[\alpha\text{-}MnO_2] = 0.2 \text{ g/L}, \text{pH } 7.0, \text{T} = 25 \text{ }^{\circ}\text{C}$ 

where  $r_0$  is the initial reaction rate,  $C_0$  is the initial 2,4-DCP concentration,  $\theta_s$  is the surface coverage of 2,4-DCP adsorption, *k* is the reaction rate constant, and *b* is the adsorption constant for 2,4-DCP. As shown in Fig. [6b](#page-4-0), the plot of  $1/r_0$  versus  $1/C_0$  presented a linear relation with a higher  $R^2$  (0.9989), reflecting that the degradation of 2, 4-DCP well follows the Langmuir–Hinshelwood model.

The impact of  $\alpha$ -MnO<sub>2</sub> dosage on 2, 4-DCP degradation is displayed in Fig. S5. The degradation of 2, 4-DCP was remarkably influenced by the dosage of  $\alpha$ -MnO<sub>2</sub>. The degradation efficiency increased from 89.0% to 99.2% with the increase of  $\alpha$ -MnO<sub>2</sub> dose from 0.04 to 0.20 g/L. The enhancement of the degradation efficiency should be ascribed to more generation of radicals due to increased reactive sites with  $MnO<sub>2</sub>$  addition. The effect of PMS concentration for the degradation of 2, 4-DCP is present in Fig. S6. As shown in Fig. S6, the degradation efficiency of 2, 4-DCP increased with the increasing of PMS concentration. This owes to more SO∙− <sup>4</sup> generated with the increasing



<span id="page-4-1"></span>Fig. 7 Effect of influencing factors for 2, 4-DCP degradation in α-MnO<sub>2</sub>/PMS process **a** Dose of α-MnO<sub>2</sub>. Reaction conditions: [2, 4-DCP]=20 mg/L, [PMS]=1.63 mM, pH 7.0,  $T=25$  °C. **b** Concentration of PMS. Reaction conditions: [2, 4-DCP]=20 mg/L, [α-MnO<sub>2</sub>]=0.04 g/L, pH 7.0, T=25 °C. **c** Initial pH, Reaction conditions: [2, 4-DCP]=20 mg/L, [PMS]=0.33 mM, [α-MnO<sub>2</sub>] = 0.04 g/L, T = 25 °C

concentration of PMS, when the reactive sites on the surface of catalyst are sufficient to activate PMS (Feng et al. [2015](#page-5-10); Liu et al. [2016;](#page-6-10) Tan et al. [2014\)](#page-6-34).

The effect of solution pH on 2, 4-DCP degradation in  $\alpha$ -MnO<sub>2</sub>/PMS system is presented in Fig. [7](#page-4-1). The degradation efficiency was  $96.3\%$  at pH 7. However, the degradation efficiency were decreased to  $85.7\%$  and  $24.7\%$  at pH 3.0 and pH 10.0 in the same reaction process. Solution pH governed the dissociation of 2, 4-DCP ( $pK_a$ =7.85 (Schwarzenbach et al.  $2003$ )) and PMS ( $pK_a$  of 9.4 for  $H_2SO_5$  (Guan et al. [2011](#page-5-11))). Dissociated 2, 4-DCP may enhance electron donating strength for oxidants under acidic and neutral conditions. Similarly, PMS is mainly presented in the form of  $HSO_5^-$ , which is favorable for the reaction Eq. ([1\)](#page-3-0). In addition, solution pH affected surface charge of the  $\alpha$ -MnO<sub>2</sub> (point of zero charge of 4.5, (Prélot et al. [2003](#page-6-36))), and then afected interaction between  $\alpha$ -MnO<sub>2</sub> surface and PMS (Wang et al. [2018](#page-6-22)). The electrostatic repulsions interaction between the  $MnO<sub>2</sub>$  surface and  $HSO<sub>5</sub><sup>-</sup>$  increased at alkaline condition, leading to suppressed generation of reactive free radicals (Liu et al. [2015](#page-6-21)), because. Moreover, PMS was unstable and self-decomposition of PMS occurred in the presence of high concentration of hydroxide ions (Ahmadi and Ghanbari [2019](#page-5-12); Ghanbari and Martínez-Huitle [2019](#page-5-13)). Therefore, the degradation of 2, 4-DCP decreased signifcantly under alkaline conditions.

The impacts of selected inorganic ions  $(Cl<sup>-</sup>$  and  $NO<sub>3</sub><sup>-</sup>$ ), which commonly occurr in the environment, on 2, 4-DCP degradation were examined. As shown in Fig. [8](#page-5-14), the degradation efficiency of 2, 4-DCP was enhanced with the addition



<span id="page-5-14"></span>**Fig. 8** Efect of co-existing inorganic ions on the degradation of 2, 4-DCP

of Cl<sup>−</sup> and NO<sub>3</sub><sup>−</sup>. Cl<sup>−</sup> has different effects on the degradation of contaminants. For instance, Qin et al. reported that the presence of Cl− greatly inhibited the degradation of DDT (Qin et al. [2016\)](#page-6-37). While, Anipsitakis et al. reported opposite conclusion that Cl− facilitated the degradation of phenolic compounds by SO<sup> $\text{ }$ </sup> (Anipsitakis et al. [2006](#page-5-15)). As a fact, Cl<sup>−</sup> could be oxidized by  $SO_4^{\text{--}}$  to form Cl<sup>•</sup> according to following reaction (Eq.  $(6)$  $(6)$ ), which favored the degradation of 2, 4-DCP (Liang et al. [2006\)](#page-6-38).

$$
SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \tag{6}
$$

In addition, the degradation efficiency of  $2$ , 4-DCP significantly increased from 85.7% to 94.6% after adding  $NO_3^-$ . The enhanced effect in the presence of  $NO_3^-$  is owing to the active oxygen produced in the degradation process (Hu and Long [2016;](#page-5-17) Huang et al. [2009;](#page-6-39) Zhu et al. [2019a](#page-7-10)).

In this study,  $MnO<sub>2</sub>$  with different structures were prepared and activation of PMS for the removal of 2, 4-DCP from water was studied systematically. The prepared  $\alpha$ -MnO<sub>2</sub> showed excellent activity to activate PMS for 2, 4-DCP degradation because of the larger tunnel size, higher BET surface area and Mn (III) content. The degradation mechanisms included direct oxidation by  $MnO<sub>2</sub>$  and catalytic oxidation by radicals (•OH and  $SO_4^{\bullet-}$ ). The degradation of 2, 4-DCP was facilitated at lower solution pH and the presence of Cl− and NO3 −. Additionally, sulfate radicals were the main reactive species responsible for the degradation of 2, 4-DCP in  $MnO<sub>2</sub>/PMS$  system.

**Supplementary Information** The online version of this article [\(https://](https://doi.org/10.1007/s00128-021-03109-7) [doi.org/10.1007/s00128-021-03109-7](https://doi.org/10.1007/s00128-021-03109-7)) contains supplementary material, which is available to authorized users.

**Acknowledgements** This work was supported by the National Key Research and Development Program of China (NO. 2018YFC1803100), Scientifc Research Project of Nanjing Xiaozhuang University (NO. 2017NXY46), Excellent Science and Technology Innovation Group of Jiangsu Province, Innovative Practice of Environmental Engineering Subject Based on New Engineering Construction.

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