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Treatment of Coking Wastewater by α-MnO$_2$/Peroxymonosulfate Process via Direct Electron Transfer Mechanism

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Abstract: Side reactions between free radicals and impurities decelerate the catalytic degradation of organic contaminants from coking wastewater by Advanced Oxidation Processes (AOPs). Herein, we report the disposal of coking wastewater by α-MnO$_2$/PMS process via a direct electron transfer mechanism in this study. By the removal assays of the target compound of phenol, the PMS mediated electron transfer mechanism was identified as the dominated one. Water quality parameters including initial pH, common anions and natural organic matters demonstrated limited influences on phenol degradation. Afterwards, α-MnO$_2$/PMS process was applied on the disposal of coking wastewater. The treatment not only eliminated organic contaminants with COD removal of 73.8% but also enhanced BOD$_5$/COD from 0.172 to 0.419, within 180 min of reaction under conditions of 50 g/L α-MnO$_2$, 50 mM PMS and pH$_0$ 7.0. COD removal decreased only 1.1% after five-time cycle application, suggesting a good reuse performance. A quadratic polynomial regression model was further built to optimize the reaction conditions. By the model, the dosage of α-MnO$_2$ was identified as the most important parameters to enhance the performance. The optimal reaction conditions were calculated as 50 g/L α-MnO$_2$, 50 mM PMS and pH$_0$ 6.5, under which COD removal of 74.6% was predicted. All aforementioned results suggested that the α-MnO$_2$/PMS process is a promising catalytic oxidation technology for the disposal of coking wastewater with good practical potentials.

Keywords: alpha manganese dioxide; peroxymonosulfate; electron transfer; catalytic oxidation; coking wastewater

1. Introduction

Coal is the most important energy resource in China because it accounts for at least 70% of China's energy consumption [1]. Coking wastewater generates from coal coking, by-products recovery, refinement processes and coal gas purification in coal plants [2]. To yield 1 ton of coal, 0.31–4.00 m^3 of coking wastewater is reported to be produced [3,4]. At present, approximately 0.3 billion tons of coking wastewater is generated every year in China [5]. In view of the whole world, the yield is 0.75 billion tons per year [4]. The discharged Chemical Oxygen Demand (COD) from coking wastewater every year accounts for more than 1.5% of that from the total wastewater [5]. More importantly, it is one of the most

cumbersome wastewaters handled by human beings, being typically characterized by high toxicity, low biodegradability, high nitrogen and COD concentrations, as well as its complex compositions [6]. Thus, coking wastewater emerges as an on-going challenge in the field of wastewater treatment [7]. The development for the disposal of coking wastewater attracts a lot of attentions [8].
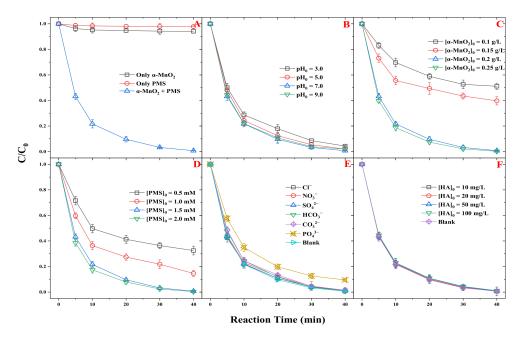
Coking water contains organic contaminants involving phenols, pyrrole, furan, naphthalene, polycyclic aromatic hydrocarbon and other refractory components [9,10]. China issued a strict discharge standard for coking wastewater (GB 16171-2012) [11]. Treatment of coking wastewater has become more and more sophisticated, evolving from simple mechanical approaches prevalent during the 1950s to 1960s to the boom of biochemical technology during the 1980s to 1990s [12]. However, disposed by biochemical technologies, coking wastewater may not meet the discharge standard due to its low biodegradability: non-biodegradable constituents account for over 40% of total organic compounds, and also large amounts of refractory organics [5,13]. In addition, disadvantages including low efficiency, unstable operation and potential second pollutions have impeded the practical applications of other traditional technologies such as physicochemical ones [14,15]. In the last decade, Advanced Oxidation Processes (AOPs) have emerged as one of the most promising technologies for the elimination of organic contaminants in coking wastewater [16,17]. For instance, homogeneous AOPs were reported to be efficient in disposing of coking wastewater. For example, Fenton oxidation treatment was reported to achieve COD, phenol and cyanide removal of 84.66%, 88.46% and 79.34%, respectively, in coking wastewater [18]. In another case, a the Fenton-denitrification process was employed to eliminate both organic contaminants and total nitrogen [19]. However, drawbacks including the narrow pH window of the reaction and quenching of reactive oxygen species (ROS) by a homogeneous activator limited their applications. Thus, heterogeneous AOPs were employed in more cases. For instance, manganese oxide ore acidic oxidation was employed to efficiently degrade the organic contaminants in coking wastewater [20]. In another study, a process of O_3/H_2O_2/Fe-shavings, which coupled catalytic ozonation and Fenton-like oxidation with Fe-shaving wastes reused, demonstrated high efficiency in the treatment of coking wastewater secondary biochemical effluent [11]. Unfortunately, due to the strong quenching effects of impurities on ROS, especially free radicals, huge amounts of reaction reagents and power were consumed to achieve high efficiency. Even worse, the disposal performance was not that stable due to the variable physicochemical properties of coking wastewater. Inorganic pollutants including sulfate, chlorides, cyanides and nitrides are widely dispersed in coking wastewater [11]. In addition, coking wastewater is characterized by its high alkalinity and hardness [14]. In all homogeneous AOPs and even some heterogeneous ones, the elimination efficiencies of contaminants varied extensively with changeable water matrix parameters such as reaction pHs, natural organic matter (NOM) and anions [21,22]. Furthermore, a human carcinogen was widely reported to be generated via the oxidation of Br^- by free radicals in AOPs [21,23]. The complications in removing the refractory organics and the inhibitory effects of inorganic compounds are stumbling blocks for the effective disposal of coking wastewater.

To overcome the aforementioned limitations, a heterogeneous system with stable performance and degradation products in low toxicity was eagerly desired. Sulfate radicals-based AOPs (SR-AOPs) were widely employed due to the high stability that benefits the storage and transportation, wide reactivity with contaminants and relatively lower cost demand [24–29]. In some peroxymonosulfate (PMS)-based systems, non-radical species such as singlet oxygen [30–32], metastable PMS [33–35] and non-radical routes such as direct electron transfer from pollutants to PMS [36,37] were reported to dominate the removal of organic contaminants. In such systems, side reactions between free radicals and the co-existing inorganic impurities could be avoided [38,39]. MnO_2 was widely employed as highly efficient PMS activator [40,41]. The mechanism of organic degradation was highly dependent on its crystal facets [42]. Very recently, we disclosed the underlying mechanism of PMS activation by a series of crystallographic MnO_2 as oxidation by surface bound

metastable PMS and direct electron transfer from organic contaminants to surface Mn(IV, III) [34]. We employed the most reactive one, α-MnO$_2$, as a PMS activator towards the disposal of coking wastewater in this study. In our research hypothesis, refractory contaminants would be highly-efficiently degraded via non-radical pathways, with low dosages of reaction reagents and negligible influences from impurities in wastewater. Inspired by the advantage of quickly analyzing the interactions between multiple parameters, optimizing and predicting the experimental parameters with a low number of experiments, the response surface method (RSM) was employed to optimize the reaction conditions of the α-MnO$_2$/PMS process [11,13]. Due to the fact that phenols were reported to account for more than 80% of the total COD in coking wastewater [14], we chose phenol as the model compound to uncover the mechanism of our system to degrade organic contaminants. By the aforementioned efforts, we aim to propose a strategy to treat coking wastewater via a non-radical mechanism by the α-MnO$_2$/PMS process and evaluate its potential practical applications.

2. Results and Discussion

2.1. Degradation of Phenol by α-MnO$_2$/PMS Process

Before the experiments of phenol degradation, the successful synthesis of α-MnO$_2$ was confirmed by scanning electron microscope (SEM, Figure S1) and X-ray diffraction (XRD, Figure S2). Initial assays were carried out to test the removal of phenol by only α-MnO$_2$, only PMS or α-MnO$_2$/PMS system (Figure 1A). Only 5.9% of phenol was removed via adsorption by α-MnO$_2$, suggesting that the adsorption capacity of α-MnO$_2$ was low. In our previous study, the surface area of α-MnO$_2$ was demonstrated as 34.1 m^2/g [34]. The sluggish adsorption of phenol was most likely attributed to the low surface area of α-MnO$_2$. A lower phenol removal of 2.2% was achieved only in the PMS group. This result was consistent with previous studies, suggesting that PMS was obtuse to degrade refractory organic compounds without activation [26,43,44]. Phenol removal dramatically increased to 99.3% when α-MnO$_2$ was introduced only into the PMS group, suggesting that α-MnO$_2$ successfully activated PMS.

Figure 1. Removal of phenol by only α-MnO$_2$, only PMS or α-MnO$_2$/PMS system (**A**), effects of pH (**B**), α-MnO$_2$ dosage (**C**), PMS dosage (**D**), common anions (**E**) and HA concentration (**F**) on phenol removal by α-MnO$_2$/PMS system. Reaction conditions: [α-MnO$_2$]$_0$ = 0.2 g/L, [PMS]$_0$ = 1.5 mM, [phenol]$_0$ = 20 mg/L, pH$_0$ = 7.0, Temperature = 30 °C, [anions]$_0$ = 5.0 mM.

Effects of initial pH on phenol removal were then evaluated (Figure 1B). Along with the initial pH increase from 3.0 to 7.0, phenol removal increased from 95.7% to 99.3%. When the initial pH further increased to 9.0, phenol removal decreased to 98.1%. The pH-independent performance was consistent with that in our previous work which employed manganese anode slag as the PMS activator [45]. The aforementioned results can be attributed to two reasons. Firstly, PMS mainly exists as HSO_5^- at pH_0 3.0 and 5.0 and the stabilization effect between HSO_5^- and H^+ might reduce the effective activation of PMS [46]. Then, point of zero charge (pH_{PZC}) of α-MnO_2 was determined to be 7.9 (Figure S3). At a pH_0 of 9.0, the electro-negative surface of α-MnO_2 is not conducive to the contact of HSO_5^- and SO_5^{2-} [26]. Electron transfer was identified as one of the major mechanisms to degrade phenol in our system (*vide infra* in Section 2.2); thus, ineffective contact between PMS and α-MnO_2 might delay the degradation of phenol [47]. Since that even at pH_0 3.0, 95.7% of phenol was eliminated, we concluded that the influence of the initial pH on the performance of the α-MnO_2/PMS system was weak. Furthermore, the concentration of leached Mn at pH_0 3.0, 5.0, 7.0 and 9.0 was revealed as 0.15, 0.07, 0.02 and 0.01 ppm, respectively (Figure S4), which were far below the highest limit in Chinese Integrated Wastewater Discharge Standard (GB8978-1996) and Sanitary Standard in China for Drinking Water (GB5749-2006) [45]. The results suggested that the α-MnO_2/PMS process uses a green strategy to eliminate organic contaminants without the second pollution of metal leaching.

Then, the effects of α-MnO_2 (Figure 1C) and PMS (Figure 1D) dosages were studied. Phenol removal increased from 48.9% to 99.8% along with the increase in α-MnO_2 dosage from 0.1 to 0.25 g/L. With respect to PMS dosage, along with its increase from 0.5 to 2.0 mM, phenol removal increased from 67.5% to 99.7%. The results suggested that with higher dosages of α-MnO_2 or PMS, we could achieve higher phenol removal. The increase in phenol removal with higher α-MnO_2 dosage was attributed to additional reactive sites for catalytic reactions [28]. The increase with higher PMS dosage was attributed to more frequent contact between PMS and reactive sites [25].

The impacts of common anions on phenol degradation were further disclosed (Figure 1E). Most anions demonstrated limited influence since phenol removal of 98.7%, 98.6%, 99.2%, 99.3%, 98.5% was achieved in the presence of 5.0 mM of Cl^-, NO_3^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}, respectively. Free radicals including sulfate radicals ($SO_4^{\bullet-}$, E^0 = 2.5–3.1 V) and hydroxyl radicals ($OH^{\bullet-}$, E^0 = 1.9–2.7 V) were reported to be transferred to radicals with lower reactivity such as nitrate radicals ($NO_3^\bullet$, E^0 = 2.0–2.2 V) in the presence of the aforementioned anions (Equations (1)–(7)) [24,48,49]. Based on this fact, the degradation reaction should be partly decelerated. The unusual phenomena should be attributed to two reasons. Firstly, in the case of Cl^-, the quenching reaction (Equation (1)) was reported to be reversible and the rate constants of the forward and reverse pathway are similar [48]. Under a high concentration of $SO_4^{\bullet-}$, certain amounts of $SO_4^{\bullet-}$ was quenched, which may help to avoid its self-quenching. Under a low concentration, the reverse pathway will undergo, which may facilitate the regeneration of $SO_4^{\bullet-}$ and maintain the reaction efficiency [24]. Secondly, according to the non-radical dominated mechanism (*vide infra* in Section 2.2), free radicals did not contribute too much to phenol degradation. Thus, the quenching effects of free radicals by common anions were negligible in this case, while, in the presence of PO_4^{3-}, phenol removal significantly decreased to 90.5%. This phenomenon was attributed to the inhibition effects on the formation of surface-bound PMS complex due to the substitution of surface hydroxyl groups by phosphate [33,50,51]. The formation of BrO_3^- was further tested in the presence of Br^- (Figure S5). BrO_3^- was reported to be formatted via the chain reactions between Br^- and free radicals such as sulfate radicals (Equations (8)–(14)) [21,52]. In a typical free radicals-based system, Mn(II)/PMS, 1.27 mM of BrO_3^- was formatted, while in α-MnO_2/PMS system, the concentration of BrO_3^- during the whole reaction was under the detection limit. The results suggested that it was favored by the non-radical dominated mechanism, no BrO_3^-, which is a potent carcinogen subjected to strict regulation globally, generated in α-MnO_2/PMS system.

$$Cl^- + SO_4^{\bullet-} \leftrightarrow Cl^\bullet + SO_4^{2-}, k_{forward} = 2.47 - 6.6 \times 10^8 \ M^{-1} \ s^{-1}, k_{backward} = 2.5 \times 10^8 \ M^{-1} \ s^{-1} \tag{1}$$

$$NO_3^- + SO_4^{\bullet-} \rightarrow NO_3^\bullet + SO_4^{2-}, k = 5.5 \times 10^5 \ M^{-1} \ s^{-1} \tag{2}$$

$$NO_3^- + OH^\bullet \rightarrow NO_3^\bullet + OH^-, k < 5.0 \times 10^5 \ M^{-1} \ s^{-1} \tag{3}$$

$$CO_3^{2-} + SO_4^{\bullet-} \rightarrow CO_3^{\bullet-} + SO_4^{2-}, k = 6.1 \times 10^6 \ M^{-1} \ s^{-1} \tag{4}$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{\bullet-} + OH^-, k = 3.9 \times 10^8 \ M^{-1} \ s^{-1} \tag{5}$$

$$HCO_3^- + SO_4^{\bullet-} \rightarrow HCO_3^\bullet + SO_4^{2-}, k = 9.1 \times 10^6 \ M^{-1} \ s^{-1} \tag{6}$$

$$HCO_3^- + OH^\bullet \rightarrow HCO_3^\bullet + OH^-, k = 8.5 \times 10^8 \ M^{-1} \ s^{-1} \tag{7}$$

$$Br^- + SO_4^{\bullet-} \rightarrow Br^\bullet + SO_4^{2-}, k = 3.5 \times 10^9 \ M^{-1} \ s^{-1} \tag{8}$$

$$Br^- + Br^\bullet \rightarrow Br_2^{\bullet-}, k = 1.2 \times 10^{10} \ M^{-1} \ s^{-1} \tag{9}$$

$$Br_2^{\bullet-} + Br^\bullet \rightarrow Br_2 + Br^-, k = 2.0 \times 10^9 \ M^{-1} \ s^{-1} \tag{10}$$

$$Br_2^{\bullet-} + Br_2^{\bullet-} \rightarrow Br_2 + 2Br^-, k = 1.9 \times 10^9 \ M^{-1} \ s^{-1} \tag{11}$$

$$Br^\bullet + Br^\bullet \rightarrow Br_2, k = 1.0 \times 10^9 \ M^{-1} \ s^{-1} \tag{12}$$

$$Br_2 + H_2O \rightarrow HBrO + H^+ + Br^-, k = 1.6 \times 10^{10} \ M^{-1} \ s^{-1} \tag{13}$$

$$HBrO + 4SO_4^{\bullet-} + 2H_2O \rightarrow BrO_3^- + 4SO_4^{2-} + 5H^+ \tag{14}$$

The effects of Natural Organic Matters (NOMs) on phenol removal were disclosed with humic acid (HA) as representative NOMs. Phenol removal was tested as 99.5%, 99.3%, 99.2% and 98.9% in the presence of 10, 20, 50 and 100 mg/L HA, respectively. The results suggested that nearly no effects of HA on phenol removal, which was significantly distinguished with phenomena in free radicals-based systems [25,27]. The result suggested that the α-MnO$_2$/PMS process is a promising approach for the treatment of real wastewaters with a high amount of background organic matter. To further evaluate the effects of water matrices, phenol removal was tested in tap water and lake water (Figure S6). We found that similar phenol removal of 99.1% was achieved in tap water. Even in lake water with a higher concentration of impurities, a satisfying phenol removal of 98.2% was achieved.
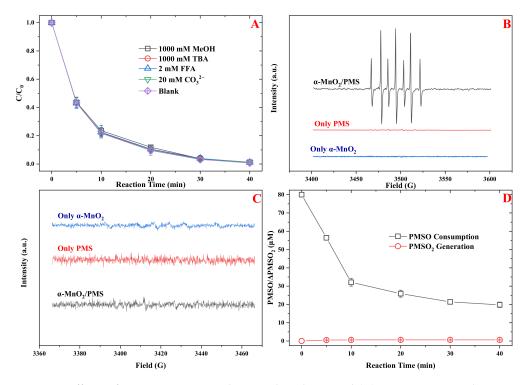
All aforementioned results suggested that PMS was successfully activated by α-MnO$_2$. More importantly, the performance of the α-MnO$_2$/PMS system remained highly efficient and stable in complex water matrices.

2.2. Non-Radical Mechanism of α-MnO$_2$/PMS Process

To identify the dominated reactive oxidative species (ROS) in α-MnO$_2$/PMS system, quenching studies were firstly carried out (Figure 2A). Methanol (MeOH) was employed as the scavenger of SO$_4^{\bullet-}$ ($k = 2.5 \times 10^7 \ M^{-1} \ s^{-1}$) and also OH$^\bullet$ ($k = 9.7 \times 10^8 \ M^{-1} \ s^{-1}$) [25]. Tert-butyl alcohol (TBA) was employed as the scavenger of OH$^\bullet$ ($k = 6.0 \times 10^8 \ M^{-1} \ s^{-1}$) [27]. Furfuryl alcohol (FFA) was applied as the scavenger of singlet oxygen ($^1O_2$, $k = 1.2 \times 10^8$ $M^{-1} \ s^{-1}$) [53]. CO$_3^{2-}$ (20 mM) was employed as the scavenger of superoxide radicals (O$_2^{\bullet-}$, $k = 5.0 \times 10^8 \ M^{-1} \ s^{-1}$) [54]. Phenol removal was demonstrated as 98.7%, 99.1%, 98.9% and 98.8% in the presence of 1000 mM MeOH, 1000 mM TBA, 2 mM FFA and 20 Mm CO$_3^{2-}$, which was similar as that without any scavenger. The phenomena suggested that all common ROS including SO$_4^{\bullet-}$, OH$^\bullet$, $^1O_2$ and O$_2^{\bullet-}$ did not participate in the degradation of phenol. Electron paramagnetic resonance (EPR) experiments with 5,5-dimethylpyrrolineN-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) as spin-trapping reagents were further conducted to confirm the conclusion. As illustrated in Figure 2B, both the signals DMPO-SO$_4^{\bullet-}$ and DMPO-OH$^\bullet$ remained silent, ruling free radicals as major ROS again. Surprisingly, in the group of α-MnO$_2$/PMS, a typical heptet signal with special hyperfine splitting constants of $\alpha_N = 7.3 \pm 0.1 \ G$ and $\alpha_H = 3.9 \pm 0.1 \ G$
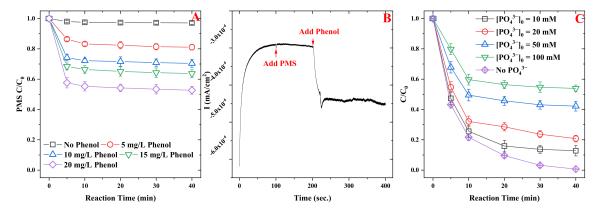
was found, indicating the generation of 5,5-dimethyl-1-pyrrolidone-2-oxyl (DMPOX) [55]. DMPOX was widely reported to be generated via direct oxidation of DMPO in the absence of free radicals [56,57]. In the case employed TEMP as the spin-trapping reagent, no signal of TEMP-$^1O_2$ was detected (Figure 2C). Phenol removal assays were also carried out in D_2O (Figure S7). Additionally, 99.5% of phenol was removed following a first-order kinetic model with the rate constant of 0.123 min^{-1}, which was consistent with the removal (99.3%) and rate constant (0.119 min^{-1}) in deionized water. The half-life of $^1O_2$ in D_2O is almost 10 times higher than that in deionized water, while the removal of organic contaminants in $^1O_2$ dominated systems was reported to be accelerated [58]. The EPR spectra and results in D_2O experiments ruled out $^1O_2$ as major ROS again. Very recently, high-valent metal-oxo species emerged as a novel ROS to degrade organic contaminants [59]. Via the oxidation by high-valent metal-oxo species through oxygen transfer, methyl phenyl sulfoxide (PMSO) could correspond to sulfone product and methyl phenyl sulfone ($PMSO_2$) [60]. Thus, the PMSO oxidation experiments were carried out (Figure 2D). Large amount of PMSO was consumed (60.2 μM); however, no $PMSO_2$ was generated. Thus, we can conclude that high-valent metal-oxo species did not participate in the degradation of phenol in this case.

Figure 2. Effects of various ROS quencher on phenol removal (**A**), EPR spectra in the presence of DMPO (**B**), EPR spectra in the presence of TEMP (**C**) and PMSO consumption and $PMSO_2$ generation in α-MnO_2/PMS system (**D**). Reaction conditions: [α-MnO_2]$_0$ = 0.2 g/L, [PMS]$_0$ = 1.5 mM, [phenol]$_0$ = 20 mg/L, pH$_0$ = 7.0, Temperature = 30 °C.

Based on the aforementioned phenomena that all common ROS did not contribute to phenol degradation, a direct electron transfer mechanism was considered by us. The mediated electron transfer reaction occurs when PMS and organic pollutants simultaneously participate in the reaction, while the ROS generation could be triggered in the absence of organic contaminants [61]. Thus, to further disclose the degradation mechanism of phenol, PMS decomposition was firstly measured (Figure 3A). In the absence of phenol, 2.9% of PMS was decomposed. After injection of phenol into the reaction, PMS decomposition increased from 18.9% to 47.3% along with the increased amounts of injected phenol from 5 to 20 mg/L. The phenomena clearly indicated that pollutants remarkably promoted the electron transfer process in α-MnO_2/PMS system [62]. The chronoamperometric electrochemical measurements further elucidated the electron transfer mechanism (Figure 3B). No

significant change in current was observed after the addition of PMS at 100 s in the i-t curve. However, the current changed dramatically after the addition of phenol at 200 s, indicating that PMS and phenol acted as electron acceptor and donor, respectively, on the surface of α-MnO$_2$ to trigger the electron transfer reaction, which was consistent with the PMS decomposition experiment [63]. For gain further insight into the PMS mediated electron transfer mechanism, the effects of phosphate at a higher concentration on phenol removal were studied (Figure 3C). Phenol removal rapidly decreased from 99.3% to 87.2%, 79.2%, 57.8% and 47.1% when phosphate concentration increased from 0 to 10, 20, 50 and 100 mM, respectively. It is well known that surface hydroxyl groups were readily substituted by phosphate, thereby inhibiting the formation of surface-bound PMS complexes [33]. The results suggested that surface hydroxyl groups are major adsorption sites for PMS in the electron transfer process.
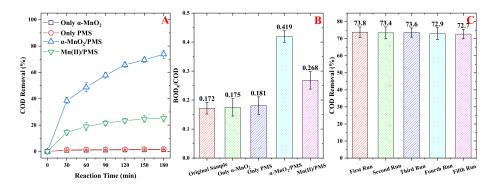

Figure 3. Decomposition of PMS in the presence of various concentrations of phenol (**A**), i-t curve of α-MnO$_2$ (**B**), degradation of phenol in the presence of higher concentration of PO$_4$$^{3-}$ (**C**). Reaction conditions: [α-MnO$_2$]$_0$ = 0.2 g/L, [PMS]$_0$ = 1.5 mM, [phenol]$_0$ = 0–20 mg/L, pH$_0$ = 7.0, [PO$_4$$^{3-}$]$_0$ = 0–100 mM Temperature = 30 °C.

In summary, all aforementioned data identified PMS mediated electron transfer as the dominated mechanism for phenol degradation.

2.3. Disposal of Coking Wastewater by α-MnO$_2$/PMS Process

Since the α-MnO$_2$/PMS process demonstrated a satisfying performance in the removal of phenol, it has good potential to eliminate organic contaminants from coking wastewater. Thus, further efforts were paid to study its performance on the disposal of coking wastewater. Firstly, COD removal was measured (Figure 4A). Only α-MnO$_2$ and only PMS performed very sluggishly, with COD removal of 1.4% and 1.8%, respectively. In the α-MnO$_2$/PMS process, 73.8% of COD was removed within 180 min of reaction. Mn(II)/PMS, a typical free radicals-based system, was performed as a comparison. Only 25.3% of COD was removed in the Mn(II)/PMS system. The results indicated that the non-radical α-MnO$_2$/PMS process was more efficient and robust in the disposal of real wastewater, with a high concentration of interfering substances. Considering that biochemical technologies are combined with AOPs in some cases to guarantee that the water quality of effluent can reach the discharge standard [6], the performance of the α-MnO$_2$/PMS process to enhance the biodegradability index (BOD$_5$/COD) was further tested (Figure 4B). BOD$_5$/COD of the original sample, the sample only in α-MnO$_2$, only PMS and Mn(II)/PMS groups were tested as low as 0.172, 0.175, 0.181 and 0.268, respectively. The value increased significantly to 0.419 after treatment by the α-MnO$_2$/PMS process. The results suggested that organic compounds which are refractory to biodegradation were efficiently degraded into intermediates with higher biodegradability [64]. To further confirm the practical potentials of the α-MnO$_2$/PMS process, reuse performance of α-MnO$_2$ was evaluated (Figure 4C). The performance was nearly consistent in the five-cycle application because 73.8%, 73.4%,

73.6%, 72.9% and 72.7% of COD was removed in the first, second, third, fourth and fifth run of the α-MnO$_2$/PMS process. The good reuse performance was widely reported in AOPs dominated by direct electron transfer mechanism due to the fact that little change in the structure of the heterogeneous catalysts occurred during the activation [65,66].

Figure 4. Removal of COD from coking wastewater (**A**), enhancement of the biodegradability index (**B**), and the reuse performance of α-MnO$_2$/PMS process (**C**). Reaction conditions: [α-MnO$_2$]$_0$ = 50 g/L, [Mn(II)]$_0$ = 50 mM, [PMS]$_0$ = 50 mM, pH$_0$ = 7.0, Temperature = 30 °C.

We further studied the effects of reaction conditions including the dosage of catalyst (X_1), the dosage of PMS (X_2) and initial pH (X_3) on COD removal (Y) by the results of seventeen sets of single-factor experiments (Table S1). The experimental results were fitted by polynomial regression, and a quadratic polynomial regression model was fitted to predict the COD removal, as shown in Equation (15).

$$Y = 1.44354\,X_1 + 0.15375\,X_2 - 4.05526\,X_3 - 0.00767\,X_1X_2 - 0.00083\,X_1X_3 + 0.05722\,X_2X_3 + 0.00018\,X_1^2 + 0.00994X_2^2 + 0.21757X_3^2 + 8.32209 \tag{15}$$

ANOVA analysis was employed to analyze the significance and adequacy of the experimental data (Table 1) [11]. *F* value and *p* value were 17.451 and 0.0005, respectively, indicating that aforementioned model was statistically significant [67]. *F* value and *p* value of the lack of fit was 7.660 and 0.2164, indicating that the term was not significant. To further test the significance of the model, error statistical analysis was performed on the fitted regression equations (Table 2). The multivariate correlation coefficient (R^2) and the adjusted determination correlation coefficient (adj-R^2) of the model was as high as 98.74% and 96.26%, respectively, verifying the significance of the model [13]. The low coefficient of variation (C.V.) was as low as 3.7%, indicating the high accuracy and reliability of the model [68]. *F* value of X_1, X_2 and X_3 was 131.051, 79.751 and 22.955, while *p* value was <0.0001, 0.0008 and 0.0020, respectively. The results suggested that the linear effect of X_1, X_2 and X_3 on COD removal was significant, indicating that the three factors effect COD removal significantly in an order of catalyst dosage > PMS dosage > initial pH value [12]. In summary, we can conclude that the polynomial regression model can well predict COD removal from coking wastewater by the α-MnO$_2$/PMS process.

Table 1. Analysis of variance for the response surface optimization.

Source	Sum of Squares	df	Mean Square	F Value	p Value	
Model	5351.403	9	594.600	17.451	0.0005	significant
X_1	4465.125	1	4465.125	131.051	<0.0001	
X_2	782.101	1	782.101	79.751	0.0008	
X_3	25.600	1	25.600	22.955	0.0020	
X_1X_2	21.160	1	21.160	0.621	0.4565	
X_1X_3	0.010	1	0.010	0.001	0.9868	
X_2X_3	26.523	1	26.523	0.778	0.4069	

Table 1. *Cont.*

Source	Sum of Squares	df	Mean Square	*F* Value	*p* Value	
$X_1{}^2$	0.022	1	0.022	0.001	0.9803	
$X_2{}^2$	20.788	1	20.788	0.610	0.4603	
$X_3{}^2$	14.933	1	14.9338	0.438	0.5291	
Residual	238.502	7	34.072			
Lack of Fit	238.495	5	47.699	7.660	0.2154	not significant
Pure Error	0.007	2	0.003			
Cor Total	5589.905	16				

Table 2. Results of error statistical analysis.

R-Squared	Mean	Adj *R*-Squared	C.V.%	Pred *R*-Squared	PRESS	Adeq Precisior
0.9874	58.21	0.9626	3.7	0.7007	2791.36	14.977

The RSM 3D response contour maps of COD removal and their corresponding contour maps are provided in Figure 5. In the 3D response contour maps which evaluate the interaction among the response variable and the two factors, the interaction was stronger when the maps were steeper [69]. The map formed a good "slope" surface in Figure 5A, suggesting the dosage of catalyst and the dosage of PMS had significant effects on COD removal. From the contour map (Figure 5B), we found that COD removal increased monotonously along with the increase in the dosage of catalyst and that of PMS. In addition, the increase in the dosage of catalyst was more significant to the increase in COD removal than the increase in the dosage of PMS. In Figure 5C, a good "slope" surface was also illustrated. However, in the contour map (Figure 5D), we found that COD removal increased along with the increase in initial pH in the window of 3.0 to 6.5 and then decreased when the initial pH further increased. The results were similar with those in phenol removal assays (*vide supra* in Figure 1B). In Figure 5E, indicating the interaction among the COD removal, the dosage of PMS and the initial pH, the 3D map became much gentler. The results once again proved that the dosage of catalyst is the most important factor to manipulate COD removal from coking wastewater [70]. In the contour map (Figure 5F), the initial pH of 6.5 was once again proved as the optimal pH value for COD removal. Based on the RSM 3D response contour maps and the model, we identified the optimal parameters for the α-MnO$_2$/PMS process to remove COD from coking wastewater to be 50 g/L catalyst, 50 mM PMS and an initial pH of 6.5. Under the aforementioned reaction condition, COD removal of 74.6% was predicted to be achieved.

Based on the aforementioned achievements, some issues on the policies for the disposal and discharge of coking wastewater can be suggested. Firstly, AOPs via a non-radical mechanism can be listed as one of the standard technologies or technology units combined with traditional ones to dispose coking wastewater. Secondly, concentrations of impurities in wastewater, especially that of phosphate, should be carefully controlled in the influence of AOPs technologies. Last but not least, the yield of potential toxic degradation intermediates or products in the effluent also need to be carefully controlled.

Figure 5. 3D response surface contour of COD removal between the dosage of Cat. and the dosage of PMS (**A**), the dosage of Cat. and initial pH (**C**), the dosage of PMS and initial pH (**E**) and the corresponding contour maps (**B**,**D**,**F**).

3. Materials and Methods

3.1. Materials

The coking wastewater was collected locally in Hubei Province, PR China. Its physico-chemical properties are provided in Table 3. α-MnO$_2$ was synthesized via the procedure described in our previous work [34]. The details can be found in Text S1. Tap and lake water were sampled in the campus of Huazhong University of Science and Technology, Wuhan, P.R. China. Their physico-chemical properties are provided in Tables S2 and S3, respectively.

Table 3. Physicochemical properties of the coking wastewater.

Parameters	Values *
pH value	7.17 ± 0.25
Electrical Conductivity (mS/cm)	13.46 ± 0.97
Alkalinity (mg $CaCO_3$/L)	3349.00 ± 102.37
COD (mg/L)	1135.00 ± 47.90
BOD_5 (mg/L)	195.00 ± 16.30
TOC (mg/L)	298.45 ± 21.40
Total phenol (mg/L)	377.35 ± 37.80
CN^- (mg/L)	83.20 ± 14.60
SCN^- (mg/L)	115.70 ± 19.80
Cl^- (mg/L)	297.40 ± 31.20
NH_4^+-N (mg/L)	178.50 ± 11.90
Total nitrogen (mg/L)	276.60 ± 24.80

* Value $\pm$ standard deviation.

3.2. Chemicals

Ultrapure water (18.0 MΩ cm) used in all experiments was produced by a Millipore Milli-Q system (USA). Potassium permanganate ($KMnO_4$), manganese sulfate ($MnSO_4$), sodium phosphate (Na_3PO_4), nitric acid (HNO_3), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), sodium nitrate ($NaNO_3$) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Peroxymonosulfate (PMS, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$, 47%), phenol, humic acid (HA), tert-butyl alcohol (TBA), methanol (MeOH, CH_3OH), furfuryl alcohol (FFA), acetonitrile, N-diethyl-p-phenylenediamine (DPD), deuterated water (D_2O) 5,5-dimethylpyrrolineN-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidinol (TEMP) and methyl phenyl sulfoxide (PMSO) were obtained from Adamas Reagent Co. All chemicals and reagents in this study were of analytical grade and used without further purification.

3.3. Characterization of α-MnO_2

The X-ray diffraction (XRD) data were obtained using an 08 x'pert3 powder diffractometer with graphite monochromatized Cu Kα radiation. The structure and morphology were examined with a SEM (ZEISS Gemini 300, Carl Zeiss AG, Oberkochen, Baden-Württemberg, Germany). Furthermore, a zeta potential analyzer (Nanotrac Wave, Microtrac, Montgomeryville, PA, USA) was performed to record the surface charge of catalysts in water. The metal ions leaching was measured by inductive coupled plasma-optical emission spectrometry (ICP-OES, Optima 8300, PerkinElmer, Waltham, MA, USA). Electrochemical experiments were plotted on a CHI760 Electrochemical workstation (78738, CH Instrument Company, Austin, TX, USA) using a standard three-electrode cell (glassy carbon electrode as the working electrode, Ag/AgCl (4 M KCl) as a reference electrode and platinum wire electrode as a counter electrode). The solution containing 5.0 mM $[Fe(CN)_6]^{3-}/^{4-}$ and 0.1 M KCl was selected as the electrolyte solution. Firstly, the mixture of 20 mg of α-MnO_2, 0.2 mL of Nafion (5 wt%) and 2 mL EtOH was sonicated for an hour. Afterwards, 20 mL of the mixture was dropped on the glassy carbon electrode and dried in a 60 °C vacuum oven.

3.4. Experiments to Remove Phenol

Assays to remove phenol were performed in a 100 mL glass beaker which was placed in a water bath at 30 °C with constant magnetic stirring. In a typical procedure, 20 mL of phenol stock solution was transferred to the beaker, followed by the injection of catalyst and PMS. Initial pH was immediately adjusted by nitric acid and sodium hydroxide if needed. Subsequently, 1 mL of the reaction solution was withdrawn at predetermined time intervals and analyzed immediately after being filtered through a 0.22 μm nylon filter. All experiments were performed in triplicate.

3.5. Experiments to Treat Coking Wastewater

Assays to treat coking wastewater were conducted in a 500 mL glass beaker in a water bath at 30 °C with constant magnetic stirring. In a typical procedure, 250 mL of coking wastewater was transferred to the beaker, followed by the injection of the catalyst and PMS. The initial pH was immediately adjusted by nitric acid and sodium hydroxide if needed. Subsequently, 10 mL of the coking wastewater was withdrawn at predetermined time intervals and analyzed immediately after being filtered through a 0.22 μm nylon filter. All experiments were performed in triplicate.

To find out how the reaction conditions effects COD removal, the three key parameters including catalyst dosage, PMS dosage and initial pH were selected to develop the prediction model. Based on the data from seventeen sets of preliminary experiments, the RSM model combined with the Box–Behnken experimental design (BBD) was employed to design the experiment sets and optimize COD removal by our system. All the RSM results were analyzed by Design Expert Program (Version 13.0.0.0).

3.6. Analytic Technologies

The concentration of phenol was determined by a high-performance liquid chromatography (HPLC-Agilent 1200) with C18 column and ultraviolet (UV) detector. Acetonitrile (15%) and ultra-pure water (85%) at a flow rate of 1 mL/min were used as the mobile phase. A detection wavelength of 254 nm was used to analyze the concentration. For electrochemical studies, the powdered catalysts were first dispersed in ethanol. A droplet of highly disperse catalyst (5 μL) was dropped onto the glassy electrode and then dried at 105 °C. This procedure was repeated three times. Quenching studies, EPR tests and PMSO oxidation experiments were carried out to identify the dominated ROS. Details can be found in Text S2. The concentration of PMS was examined by the DPD method [71]. Details can be found in Text S3. COD was evaluated by the dichromate method in accordance with the standard methods issued by the China National Environmental Protection Agency [72]. BOD_5 was measured using a BOD analyzer (Trak TM II, Hach Co., Loveland, CO, USA). pH was measured using a pH meter (Hach Sension 1, Hach Co., Loveland, CO, USA).

4. Conclusions

A α-MnO_2/PMS process was employed to efficiently dispose coking wastewater in this study. ROS including sulfate radicals, hydroxyl radicals, superoxide radicals and singlet oxygen were ruled out as contributors to degrade organic matter. PMS mediated electron transfer was identified as the major mechanism of organic degradation. Favored by the electron transfer mechanism, water parameters including initial pH, common anions and natural organic matters showed limited effects on the degradation reaction. In the treatment of coking wastewater, a satisfying COD removal of 73.8% of COD was removed within 180 min of reaction with 50 g/L α-MnO_2 and 50 mM PMS at pH_0 7.0. Furthermore, the biodegradability of coking wastewater was remarkably enhanced due to BOD_5/COD increasing from 0.172 to 0.419 after the treatment. The reuse performance was good as COD removal decreased only 1.1% after the five-time cycle application. Employing COD removal as the dependent variable, a quadratic polynomial regression model was further built to optimize the reaction conditions. By the model, we found the dosage of α-MnO_2 as the most important parameters to enhance the performance. The optimal reaction conditions were identified as 50 g/L α-MnO_2, 50 mM PMS and pH_0 6.5 by the model. Under such reaction conditions, COD removal of 74.6% was predicted to be achieved. By all aforementioned efforts, α-MnO_2/PMS process was proved as a promising technology for the disposal of coking wastewater and supported its potential full-scale application.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12111359/s1, Text S1: Details of synthesis procedures of α-MnO_2; Text S2: Identification of dominated ROS; Text S3: Details of the detection of PMS concentration; Figure S1: SEM image of α-MnO_2; Figure S2: XRD pattern of α-MnO_2; Figure S3: Zeta potential in the

pH range from 3.0 to 11.0; Figure S4: Leaching of Mn in pH window of 3.0 to 9.0; Figure S5: Formation of BrO_3^- in the presence of Br^-; Figure S6: Removal of phenol by α-MnO_2/PMS system in deionized water, tap water or lake water; Figure S7: Phenol removal in D_2O and deionized water and first-order kinetic model fitting results of the phenol removal; Table S1: Box-Behnken design and results of COD removal; Table S2: Physico-chemical properties of the tap water; Table S3: Physico-chemical properties of the lake water. Reference [34] is cited in the Supplementary Materials.

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