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High increase in biodegradability of coking wastewater enhanced by Mn ore tailings in Fenton/O₃ combined processes

H. Liu¹  · T. Xu¹ · C. Li¹ · W. Liu¹ · E. Lichtfouse^{2,3}

Abstract

Coking wastewater contains high concentration of organic pollutants and seriously endangers the natural ecological balance and human health. This study proposes a novel pre-treatment method that can significantly improve removal efficiency of organic pollutants in coking wastewater by the concept of “treating waste with waste.” Three two-step advanced oxidation processes were proposed by combining Fenton, ozonation with manganese tailings: (i) O₃/Mn tailings + H₂O₂, (ii) O₃/Mn tailings + Fenton and (iii) Fenton + O₃/Mn tailings. Results show that (1) Fenton + O₃/Mn tailings presented the best removal efficiency in the three combined processes. The reaction process was carried out by first performing Fenton reaction on the wastewater for 65 min, and then, the reaction wastewater was subjected to ozone and manganese tailings mixed reaction for 30 min, and the chemical oxygen demand (COD) and chromaticity were reduced by 61.0% and 96.1%, respectively. (2) After pre-treated with Fenton, the biodegradability of the wastewater can be significantly increased. When Fenton + O₃/Mn ore tailings were used to pre-treat the raw water, the biodegradability (BOD₅/COD) of the wastewater was increased to 0.54. It is proved that the combined process Fenton + O₃/Mn ore tailings has better performance than the ordinary single advanced oxidation process. Compared with the existing methods, the addition of manganese tailings containing manganese oxides as catalytic free radicals can significantly improve the treatment activity of advanced oxidation process (AOPS).

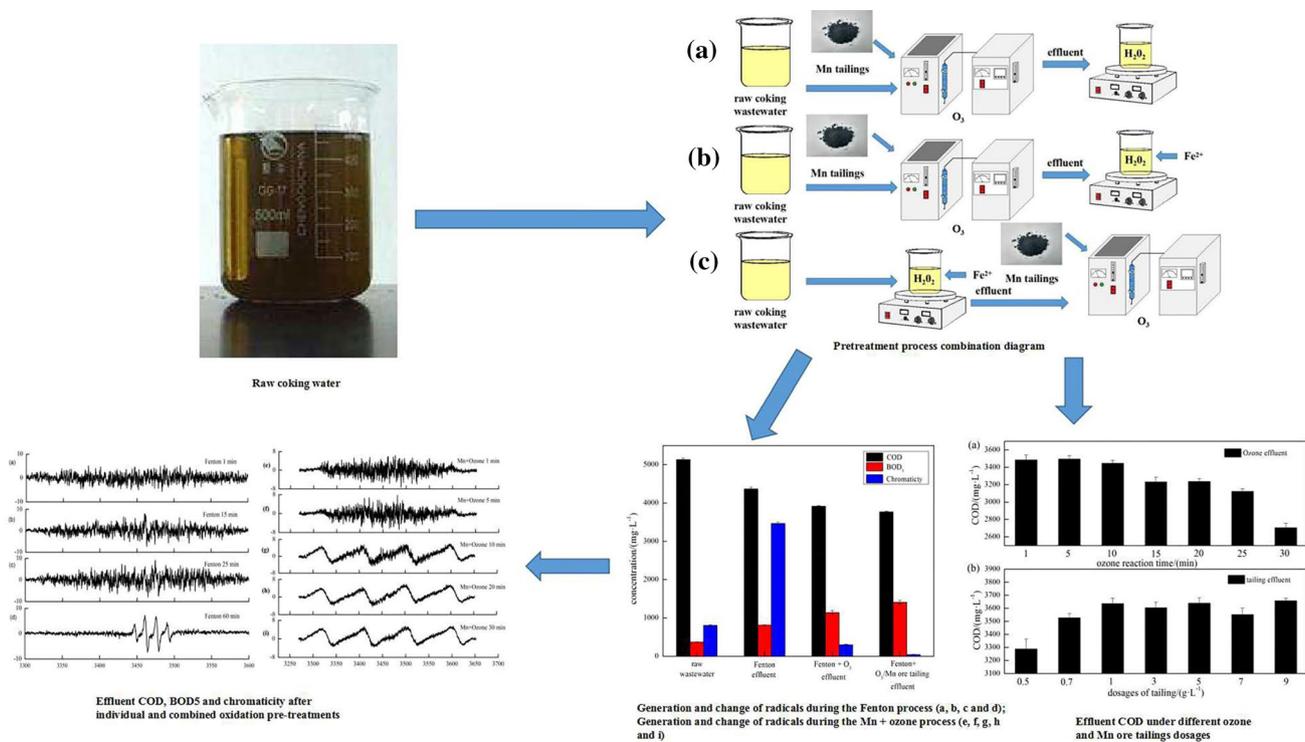
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Graphic abstract



Keywords Coking wastewater · Pre-treatment processes · Biodegradability · Mn ore tailing · Combined advanced oxidation process (AOP)

Introduction

Coking wastewater is mainly produced from the process of high-temperature carbonization of coal, by-production recovery and refining, gas purification and other production processes (Meng et al. 2017). In China, for example, many coke plants and coal gasification plants cause annual discharge of 300 million tons of coking wastewater, which is one of the main sources of industrial wastewater discharge (Lungen 2005). Coking wastewater contains inorganic pollutants (ammonia, fluoride, cyanide, thiocyanate, heavy metals, etc.) and high concentrations of organic pollutants (phenol, amine, oil, naphthalene, quinoline, pyridine, etc.) (Lim et al. 2003; Wenzl et al. 2006). Most of these compounds are refractory, highly concentrated, toxic, mutative and carcinogenic and may produce long-term environmental and ecological impacts.

A certain number of refractory and inhibitory organic compounds (ammonia nitrogen, oily substances, volatile phenols and cyanide) in coking wastewater are highly concentrated, especially in the practical engineering treatment;

large amount of cyanide contained in the coking wastewater often results in failure of the biological treatment processes since it is difficult for microorganisms to survive (Li and Zhao 2001); pre-treatment processes are necessary to reduce toxic and harmful substances and further strengthen the biodegradability of coking wastewater. The conventional pre-treatment methods include ammonium stripping, extraction, flotation and advanced oxidation processes (AOPs). The performance of the ammonium stripping process is difficult to control, and the process is easily affected by conventional indicators such as pH in the coking wastewater, resulting in unstable treatment (Guštin and Marinšeklogar 2011). The flotation process is mainly restricted by conventional factors such as coagulation and contact time (Santo et al. 2012).

Advanced oxidation methods have been applied in wastewater treatments, e.g., Fenton, ozonation, wet catalytic oxidation, photochemical oxidation and electrochemical oxidation (Asghar et al. 2015). Ozone (O₃) is considered to be one of the most powerful oxidants in alkaline solutions and is widely used for disinfection and elimination of organic compounds in water and wastewater

(Barriga-Ordóñez et al. 2006; Turhan and Uzman 2008). O_3 molecules can react with organic compounds by direct oxidation, thereby improving the biodegradability of inhibitory compounds (Bijan and Mohseni 2005; Zhang et al. 2014). Fenton is the most widely used AOP, mainly using divalent iron ions catalyzing hydrogen peroxide and producing hydroxyl radicals ($\cdot OH$). Hydroxyl radicals have strong oxidizing power and can degrade organic matter in wastewater. However, the removal of COD and ammonia nitrogen from coking wastewater by ozonation alone is insufficient, and its application is constrained by high equipment and operating costs. In the single Fenton process, low utilization of hydrogen peroxide and strict pH (2.0–4.0) is necessary, causing the process complex and expensive (Feng et al. 2006). Performances of single treatment technologies are limited due to complexity of the real coking wastewater; thus, the combination of different treatment units is necessary. The combination of Fenton and membrane treatment process could simultaneously remove organic matter and recover struvite from wastewater (Kumar and Pal 2012, 2013). At optimum operating conditions, maximum removal rates for COD, phenol and cyanide reached 84.7%, 88.5% and 79.3%, respectively (Verma and Chaudhari 2020), while the COD removal rate can reach 71.0% when coking wastewater pre-treated with a combination of electro-Fenton process (Zhao et al. 2019).

Manganese ore tailings were produced hundreds of thousands of tons every year in China, due to the exploitation of manganese ores. It causes serious environmental problems, such as occupying land resources, damaging the natural landscape, inducing geological disasters and producing chemical wastes (Liu et al. 2012). Manganese ore tailings may also be used as oxidant in wastewater treatment, which provides not only an effective residual management option for manganese ore tailings, but also a beneficial approach for the ecology environment. It has been reported that transition metals such as copper (Cu), manganese (Mn) and their oxides could be a replacement for iron ions in the Fenton process (Faweya and Oniya 2012; Su et al. 2016). Therefore, the application of Mn ore tailings in combined advanced oxidation processes might be a promising pre-treatment for coking wastewater, by disposing Mn ore tailings and coking wastewater simultaneously with a low cost. In a Mn-AOP system, Mn ore tailings can act as catalysts and generate $\cdot OH$ by consuming hydrogen peroxide. Although traditional AOPs and their combination processes have been widely used for the pre-treatment of coking wastewater, the Mn-AOP is rarely reported.

This study aims to screen a suitable cost-effective process disposing Mn ore tailings and coking wastewater simultaneously by using Mn in the ore tailings as a catalyst combining with AOPs. Three combination processes were investigated, i.e., (i) O_3 /Mn ore tailings + H_2O_2 , (ii) O_3 /Mn ore tailings + Fenton and (iii) Fenton + O_3 /Mn tailings. In this paper, the treatment characteristics and reaction mechanism of advanced oxidation combined with manganese tailings as catalyst were studied.

Materials and methods

Characteristics of coking wastewater

The raw coking wastewater was collected from the equation tank of QJ Coking Chemical Plant (Yunnan, China), and it is an untreated production wastewater produced during the tar processing, mainly consists of steam condensate and crude gas final cooling water. Its characteristics are listed as follows: COD of $5100.0 \pm 100.0 \text{ mg L}^{-1}$, BOD_5 of $370.0 \pm 20.0 \text{ mg L}^{-1}$, pH of 6.5–6.8, NH_4^+-N of $430.0 \pm 10.0 \text{ mg L}^{-1}$ and chromaticity of $800.0 \pm 50.0 \text{ mg L}^{-1}$.

Characteristics of Mn ore tailings

The raw Mn ore tailings were obtained from a mine in Guangxi, China. The main components of the tailing are SiO_2 (silicon dioxide) and MnO_2 (Mn dioxide). Shape and structure of the tailing were identified by SEM (scanning electron microscope) in our previous research (Liu et al. 2015). Before used in experiments, the tailings were dried at $105^\circ C$ for 24 h and then sieved through a 100–200 mesh sieve.

Experimental methods

Comparison of individual and combined oxidation pre-treatments

For individual Fenton pre-treatments, initially 100 mL of coking wastewater was put into a glass breaker of 250 mL and the pH was adjusted to 4.0 using 1 M HCl solution. Then, hydrogen peroxide and $FeSO_4$ were added to each breaker to make the final concentration of 2 g L^{-1} and 0.7 g L^{-1} , respectively, under moderate mixing (150 rpm)

with magnetic stirring apparatus (HJ-6, Jintan, China). After the Fenton treatment run for 2 h, O₃ was applied at a flow rate of 2 L min⁻¹ for 30 min. The O₃ concentration was 25 mg L⁻¹, which was supplied by using an O₃ generator (YH-X-15P, Aoyang, China). Another trial was performed by combining Fenton and O₃/Mn ore tailings oxidation. After Fenton reaction, 0.2 g of Mn ore tailings was added to 100 mL Fenton effluent, and then subject to 30 min of O₃ reaction. The flow rate of O₃ was 1.5 L min⁻¹.

Three trials of two-step combined oxidation processes

Three combination methods were conducted, i.e., (i) O₃/Mn ore tailings + H₂O₂, (ii) O₃/Mn ore tailings + Fenton and (iii) Fenton + O₃/Mn ore tailings. The combination (i) is shown in Fig. S1a: 100 mL raw coking wastewater was treated with O₃/Mn ore tailings for 30 min, then added 2 g L⁻¹ of H₂O₂ to the solution and reacted for 2 h. The combination (ii) is represented in Fig. S1b: 100 mL raw coking wastewater was treated with O₃/Mn ore tailings for 30 min; then, Fenton reagent with 2 g L⁻¹ hydrogen peroxide and 0.7 g L⁻¹ FeSO₄ was put to the effluent, reacting for 2 h. The combination (iii) is presented in Fig. S1c: 100 mL of raw coking wastewater was treated with Fenton reagent with 2 g L⁻¹ hydrogen peroxide and 0.7 g L⁻¹ FeSO₄ for 2 h; then, the effluent was treated with O₃/Mn ore tailings for 30 min. All three reaction conditions were controlled to room temperature, and the profiles of chromaticity and other indicators during the reaction were investigated.

Optimization of each oxidation step for combination (iii)

To further improve the efficiency of the combined oxidation process (iii), each step was optimized sequentially. Firstly, the mass ratio of hydrogen peroxide and Fe²⁺ was optimized via operational runs with the initial dosage mass ratios of 1:2, 1:1, 2:1, 4:1, 6:1, 8:1 and 10:1, respectively, while the H₂O₂ dosage is optimized from 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 g L⁻¹. The ozonation contact time was optimized from 15, 20, 25 and 30 min, and the dosage of Mn ore tailings was optimized from 0.5, 0.7, 1.0, 3.0, 5.0, 7.0 and 9.0 g L⁻¹. The used Mn ore tailings were recovered from the reaction mixture by filtration and then washed with distilled water for three times and dried at 105 °C for 24 h and then screened through a 100–200 mesh sieve.

Recycling of the used Mn ore tailing

The used Mn ore tailings were recovered from the reaction mixture by filtration washed with distilled water for three times and dried at 105 °C for 24 h in a vacuum oven and then screened through a 100–200 mesh sieve. The reuse experiments were performed according to the process of the combination (iii). After reuse, the Mn ore tailing was added in a glass breaker with 100 ml pure water under moderate mixing rate (150 rpm) with magnetic stirring apparatus to detect residue metal ions in the leaching solution.

Analytical methods

COD was digested by a Hach reagent tube (model 20–1500 mg/L) and was measured by a matching spectrophotometer; BOD₅ is determined by a dilution inoculation method, while the ozone concentration was determined by the KI solution (10 g L⁻¹) method; the chromaticity is determined by the dilution factor method, and pH was measured using a Mettler Toledo FE20. Phenol, phenylamine and other organic components in the coking wastewater were determined by a gas chromatography–mass spectrometer (GC–MS, Agilent Technologies 7890A, USA). The samples were extracted using CH₂Cl₂, filtered through a 0.45 μL syringe filter (PTFE) and then separated using a 30 m × 250 μm capillary chromatographic column. Helium of 1.0 mL min⁻¹ was used as carrier gas with a splitless injection volume of 2 μL and inlet temperature of 250 °C. The oven temperature was programmed at 40 °C for 5 min and then ramped at 10 °C min⁻¹ to 150 °C with 2 min, increased at a rate of 5 °C min⁻¹ to 280 °C, and kept for 3 min (Liu et al. 2016a). Radicals and metal ions were detected with

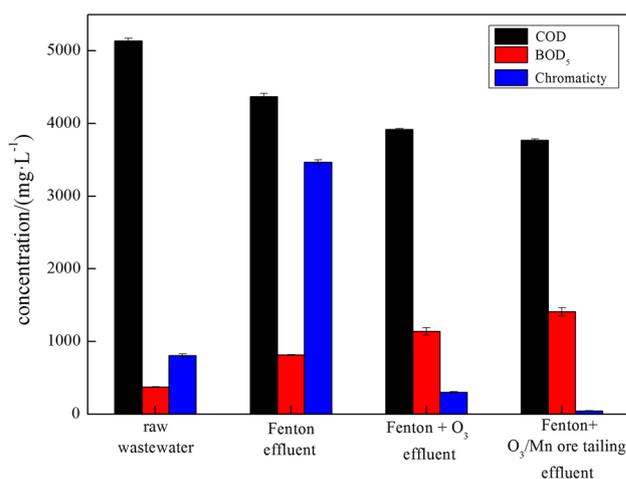


Fig. 1 Effluent COD (chemical oxygen demand), BOD₅ (biochemical oxygen demand) and chromaticity after individual and combined oxidation pre-treatments (note the increase in BOD₅ and the decrease in COD)

a Micro-ESR (Active Spectrum Inc, USA) using 100 mM of DMPO (5,5-dimethyl-1-pyrroline N-oxide) and ICP-MS (inductively coupled plasma mass spectrometry) (PE/Nexlon 300X, PE, USA). Other chemical and physical parameters of the water sample were determined according to the standard methods (Gilcreas 1966).

Results and discussion

Enhancing effect of Mn ore tailings on Fenton and ozonation

From results shown in Fig. 1, COD removal rate of the individual Fenton oxidation was only around 15%, meanwhile the chromaticity was increased from 800 to 3500 due to iron blue formation by reaction of iron in Fenton and cyanide in coking wastewater. Figure 1 also indicates that the combination of Fenton with ozonation and/or the Mn ore tailings can largely enhance the pre-treatment performance. This is because manganese tailings promote catalytic oxidation of organic wastewater and can remove phenols, sulfides and COD in coking wastewater. O_3 is highly oxidizing and can react quickly with organic matter to achieve COD removal. Compared with the single Fenton method, COD decreased by 496 mg L^{-1} , BOD_5 increased by 331 mg L^{-1} and chromaticity decreased by 3200, respectively, when using Fenton + O_3 as the pre-treatment process. Surprisingly, COD decreased by 617 mg L^{-1} , BOD_5 increased by 593 mg L^{-1}

and chromaticity decreased by 3460, respectively, when using Fenton + O_3 /Mn tailings as the pre-treatment process. Two options are obviously available to improve the pollutants removal efficiencies of coking wastewater: (1) optimizing the Fenton reaction conditions; (2) combining Mn ore tailings with the traditional oxidation processes such as Fenton and ozonation.

Figure 2 illustrates the optimization results of the Fenton process by using effluent COD as a model parameter at different H_2O_2/Fe^{2+} ratios and reaction times. As shown in Fig. 2a, the different ratios of hydrogen peroxide and ferrous ion had a significant effect on effluent COD. Higher COD removal rate could be obtained when the ratio is 1:1. The reaction time of Fenton has a positive effect on the removal of COD, but when the reaction time reaches 65 min, the effluent COD is relatively stable. It is shown that at 65 min, the reaction has been completed and the maximum removal rate of COD is achieved (Fig. 2b). Hydroxyl radicals produced by the Fenton reagent have a strong oxidizing capacity and can react with organic matter quickly in the early period. The effect of H_2O_2 concentration on removal of COD was investigated in the range of $1.0\text{--}7.0 \text{ g L}^{-1}$ as shown in Fig. 2c. With the increase in H_2O_2 dosage, effluent COD of the coking wastewater decreased due to the higher concentration of hydrogen peroxide that can produce more $\cdot OH$ (Peng et al. 2017; Zhu et al. 2011). At the same time, excessive concentration of H_2O_2 is not an option considering the cost factor. When the concentration of H_2O_2 exceeds 5.0 g L^{-1} , Fe^{2+}

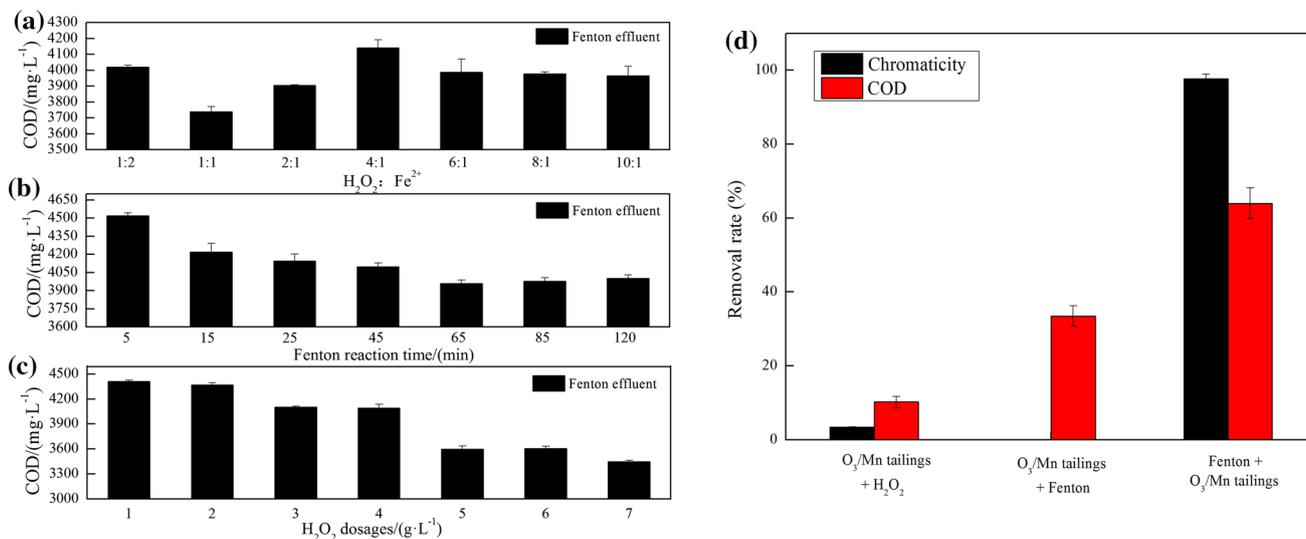


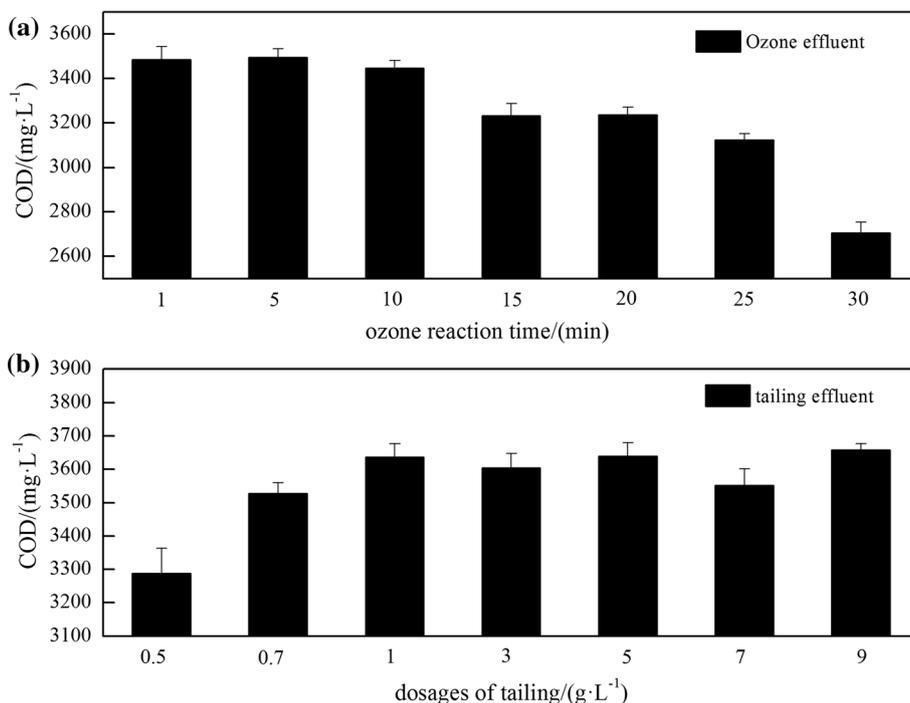
Fig. 2 Effluent COD (chemical oxygen demand) after different Fenton conditions (a–c); effluent COD (chemical oxygen demand) and chromaticity of different combination processes (d) (note the decrease in COD)

is almost completely consumed, and the effluent COD is maintained at 3400–3500 mg L⁻¹. Through the optimization of Fenton process, the removal rate of COD in effluent was increased from 21.5 to 30.0%.

Based on the best Fenton results obtained from the above reaction, three complex oxidation experiments were carried out. The experimental control O₃ concentration and contact time were 25 mg L⁻¹, 30 min, respectively, while the manganese tailings dosage and reaction time were 0.5 g L⁻¹ and 30 min, respectively. Figure 2d indicates that COD and chromaticity removal rates varied greatly with different combined oxidation processes. For the first group of experiments, Mn ore tailings were dosed simultaneously with subject to 30 min of ozonation and then reacted for 30 min with hydrogen peroxide. Removal rates of COD and chromaticity are only 9.3% and 3.3%, respectively, for the first group of experiments. For the second group of experiments, Mn ore tailings were dosed simultaneously with subject to ozonation for 30 min; Fenton reagent was then added and reacted for 30 min. Removal rates of COD and chromaticity are slightly lower than the second group of experiments. For the third group of experiments, the Fenton process started 30 min before the Mn ore tailings were dosed and subject to ozonation for 30 min at the same time. Removal rate of COD and chromaticity is 61.0% and 96.7%, respectively.

Due to the complexity of the degradable organic matter in the coking wastewater, the individual oxidation process cannot remove all the organic matters. Researches had found that O₃ combined with the Fenton reagent (O₃/Fenton) showed a high oxidation rate due to synergistic effects while it can produce a large number of ·OH in the O₃/Fenton process (Asaithambi et al. 2017; Li et al. 2015). Compared the second combination (ii) with the third combination (iii), Fenton reagent, O₃ and Mn tailings were all introduced to the combined system with different reaction sequences. Mn oxides are potential oxidizing agents of natural and xenobiotic organic compounds which make them important participants in oxidation–reduction reactions. In addition, the structure of Mn ore tailing surface is uneven and can absorb organics effectively (Liu et al. 2015); the adsorption process follows the pseudo-second-order model (Zheng and Tang 1999). The Mn(III) released by Mn ore tailings will convert into Mn(II) after reacting with phenols under acid condition, but the Mn(II) shown inconspicuous catalysis as it is difficult to determine whether phenols reactant molecules participate in the release of Mn(II) (Stone 1987). For the third group of experiments, Fenton was applied first to degrade organic matter and convert macromolecules into small molecules, then Mn ore tailing was dosed to the system. On the one hand, the released Mn(II) can react with hydrogen peroxide that is not fully reacted in Fenton and produce ·OH; on the

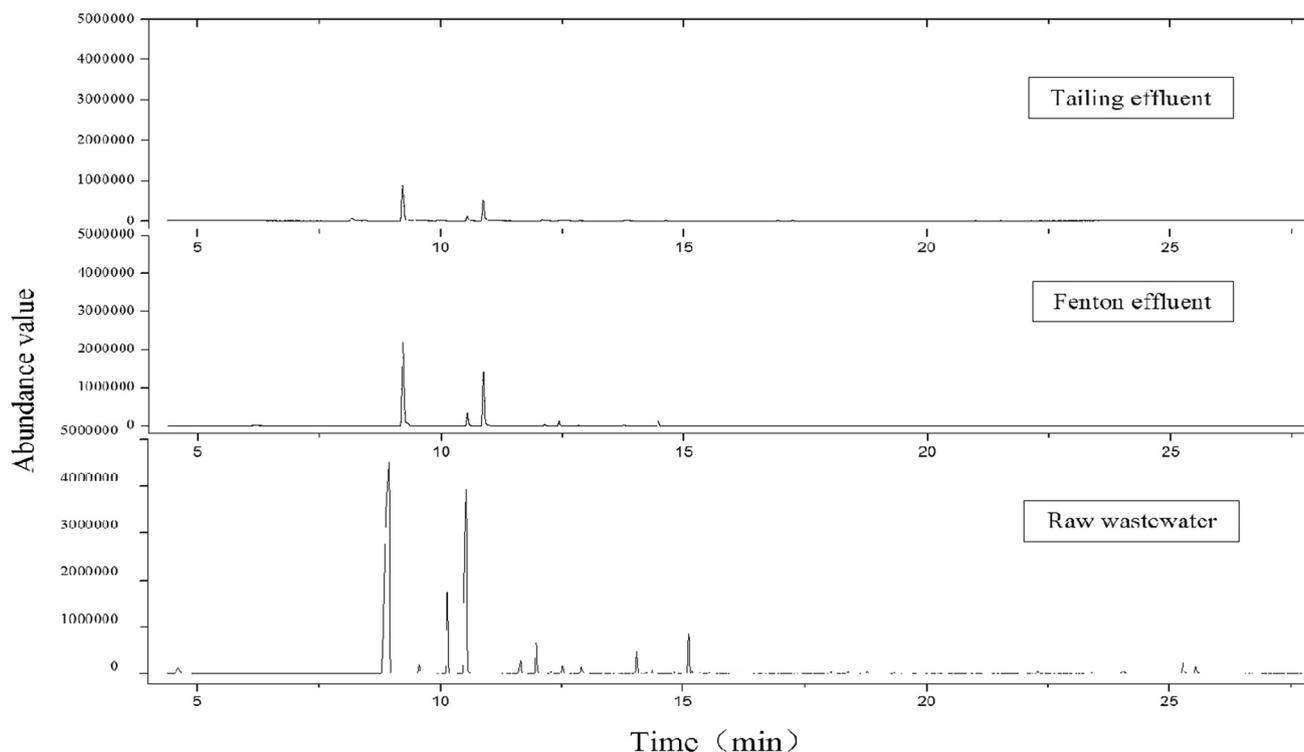
Fig. 3 Effluent COD (chemical oxygen demand) under different ozone and Mn ore tailings dosages (note the changes of COD)



other hand, the remained Mn(III) can be used as catalyst to convert hydrogen peroxide into superoxide radical ($O_2^{\cdot-}$). Some studies also reported that iron and Mn oxides can take full advantage of H_2O_2 to degrade organics in the redox process (Chen et al. 2017).

Role of ozone and Mn ore tailing in the combined oxidation processes

The profiles of COD removal efficiency with different ozonation reaction times and dosages of Mn tailings at pH 4.0 are shown in Fig. 3. The initial O_3 concentration of the reaction is 25 mg L^{-1} . COD removal efficiency of the combined



Main pollutants	Peak time (min)	peak area (raw wastewater)	Peak area (Fenton effluent)	Removal rate (%)	Peak area (ozone effluent)	Removal rate (%)
phenol	8.931	272849586	74926948	72.5	31979357	88.3
aniline	9.554	4691767	3045343	35.1	1362246	71.0
dimethylphenol	10.149	35078307	7180099	79.5	3099294	91.2
2- methyl- pyridine	10.535	136252575	33396112	75.5	13458046	90.1
quinoline	14.027	8514297	1452245	82.9	843256	90.1
indole	15.112	14645444	2858492	80.5	1083759	92.6

Fig. 4 GC–MS (gas chromatography–mass spectrometer) results of raw wastewater, Fenton effluent and tailing effluent (note the contaminant components at the peak location)

process increased with the reaction time in a three-stage pattern (Fig. 3a). Barely any COD removal was observed in this study when the reaction time was less than 10 min. Once the reaction time exceeded 15 min, the COD removal efficiency increased to 10%, while the COD removal efficiency increased to 28% after 30 min of reaction. The reaction rate of the ozonation process is mainly limited by the transfer step in the early stage of the reaction (Li et al. 2016a); with the increase in reaction time, a certain amount of O_3 was dosed and more $\cdot OH$ appeared; thus, a corresponding number of target organic compounds were degraded.

As shown in Fig. 3b, the dosages of Mn tailings also had a significant influence on the oxidation process. When the dosage of Mn tailings was between 0.5 and 1.0 $g L^{-1}$, the effluent COD increased with the dosages amount and it reached a relatively stable level when the dosage of tailings was 1.0 $g L^{-1}$. The result is comparable to the literature statement that the loaded Mn contents can increase the catalytic strength of the oxidation process, but it posed negative influence on the catalytic activity when the Mn contents exceeded to some extent (Huang et al. 2017). The Mn ore tailings used in this study not only contain Fe/Mn oxides but also large amount of SiO_2 ; excessive SiO_2 covering the surface of Fe/Mn oxides can lead to incomplete reaction.

Treatment characteristics and mechanisms of the combined oxidation process

Composition of the raw wastewater, Fenton effluent and Fenton + O_3 /Mn ore tailings effluent under the optimal

operational conditions are demonstrated in Fig. 4. According to the GC-MS database, the organic pollutants in coking wastewater include phenol, aniline, dimethylphenol, 2-methylpyridine, quinoline and indole. Phenol and aniline were chosen as the typical organic pollutions due to their harmful toxicity and long-remaining property (Liu et al. 2016b). Comparing the raw wastewater with Fenton effluent and Fenton + O_3 /Mn ore tailings effluent, the organic pollutants can be removed greatly, especially by the combined oxidation process with a suitable reaction time. Most macromolecular organic matters were disappeared after treatment by the Fenton process with a reaction time of 15 min; the pollution peak is no longer obvious after treated by the combined oxidation process with proper reaction times. The removal rate of phenol and aniline in the Fenton method is 72.5% and 35.1%, respectively, and the removal rate of dimethylphenol, 2-methylpyridine, quinoline and indole is about 80.0%.

Coking wastewater contains a large number of macromolecules organic matter in the pre-reaction. The $\cdot OH$ produced by Fenton reagent can combine with organic matters and destroy organic chemicals, converting the large macromolecules into small molecules, such as H_2O and CO_2 (Ma et al. 2009). The Fenton method used for removing aniline had been reported by (Zhou et al. 2012). The results presented here are consistent with those of Chu et al. (2012), which reported that during the advanced Fenton oxidation using iron powder and H_2O_2 , organic compounds such as quinoline and bifuran can react with $\cdot OH$ and be removed completely; thus, no radicals can be detected for the first 25 min of the Fenton process, but a typical signal of $\cdot OH$ can be detected at the reaction time of 1 h (Fig. 5a-d).

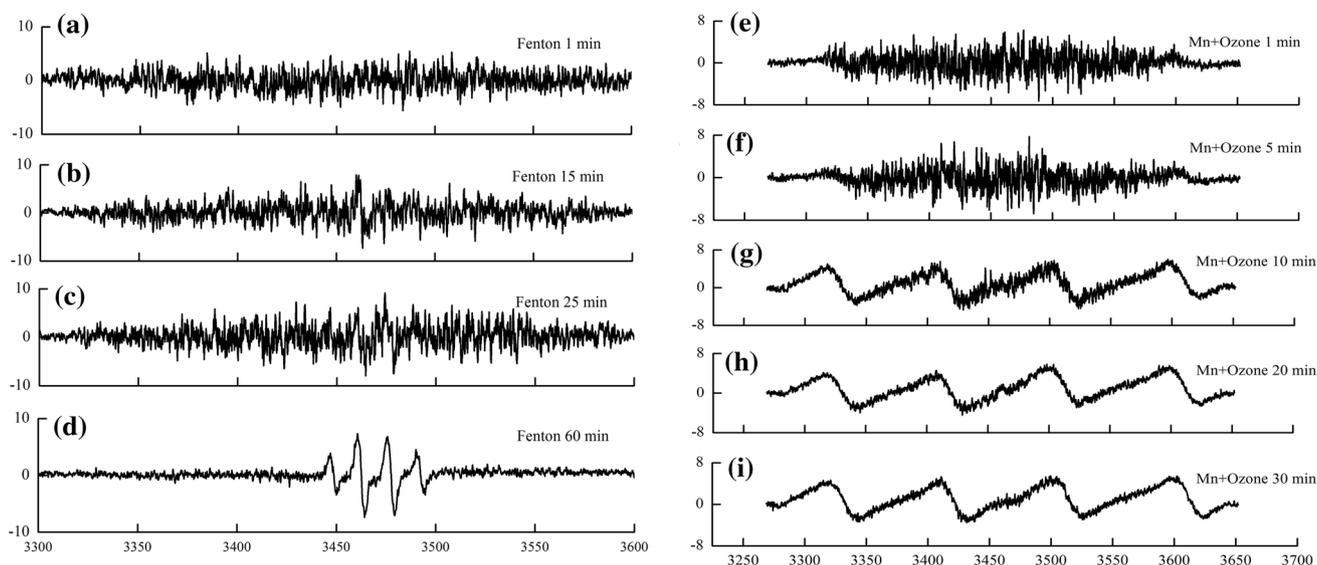
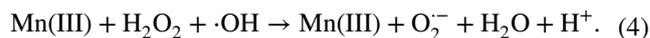
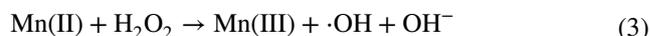
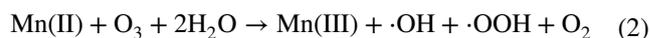
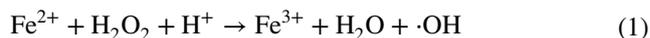


Fig. 5 Generation and change of radicals during the Fenton process (a-d); generation and change of radicals during the Mn ore tailings + ozone process (e-i) (note the changes of BOD/COD)

The removal rate of dimethylphenol for aniline after O₃/Mn tailings reaction increased from 35.1 to 71.0%, which was twice as effective as the Fenton process. As shown in Fig. 5e–i, the ·OH radical peak disappeared immediately in the first 5 min and later no radicals can be detected due to strong absorption of the Mn ore tailings that absorb ·OH remained in solution to the surface of the manganese ore. With the increase in O₃ dosage, more ·OH were generated in the study system since the Mn oxides can accelerate decomposition of O₃ to ·OH (Xing et al. 2016). A typical signal of O₂^{·-} can be detected, and the signal intensity tends to be increased and more obviously after 10 min of reaction, because the generated ·OH are transformed into O₂^{·-} under the catalysis of Mn ore tailings (Li et al. 2016b). MnO_x can remove organic pollutants more effectively under the condition of heterogeneous catalytic ozonation (Jiang et al. 2016). Due to the large surface of Mn ore tailing, the main catalysis and oxidation reaction were supposed to occur on the surface, following by the direct contact of pollutants with molecular O₃ and O₂^{·-}. The result is consistent with a previously study which indicated that when Mn oxide with carbon materials was used as catalysts for the

ozonation of oxalic acid, the reaction mechanisms included both surface reaction and liquid bulk reactions involving ·OH radicals (Orge et al. 2012). Equations (1)–(4) are the main reactions in the combined AOPs (Berlett et al. 1990; Li et al. 2016b; Schönherr et al. 2017).



After pre-treatment, the biochemical tests of coking wastewater were carried out using BOD₅ inoculation method with results shown in Table 1. The BOD₅/COD value (B/C) of raw coking wastewater is only 0.073, which is difficult to treat biochemically. After the Fenton oxidation, the B/C value is promoted to 0.247; but the low pH value after Fenton treatment is harmful to the subsequent biochemical treatment. Finally, after Mn ore tailings and ozonation treatment, the B/C value of the coking wastewater can increase to 0.539 while O₃ oxidation was effective in reducing toxicity of two quaternary ammonium compounds and improved their biodegradability. A study also indicated that with single ozonation at pH 9.0 the biodegradability of a landfill leachate can be increased from 0.05 to 0.33 (Amaral-Silva et al. 2016). Biodegradability of the treated effluent, measured as a ratio of BOD₅ to COD, improved about 2–3 folds in 30 min due to O₃/H₂O₂ oxidation (Khan et al. 2017).

Table 1 Effluent COD (chemical oxygen demand) and BOD₅ (biochemical oxygen demand) under different pre-treatments (note the comparison of different pre-treatment results)

	Raw wastewater	Fenton effluent	Fenton + O ₃ / Mn ore tailings effluent
COD (mg L ⁻¹)	5100 ± 100	3560 ± 80	2717 ± 65
BOD ₅ (mg L ⁻¹)	372.3 ± 7.1	879.3 ± 13.2	1464.5 ± 17.5
BOD ₅ /COD	0.073	0.247	0.539

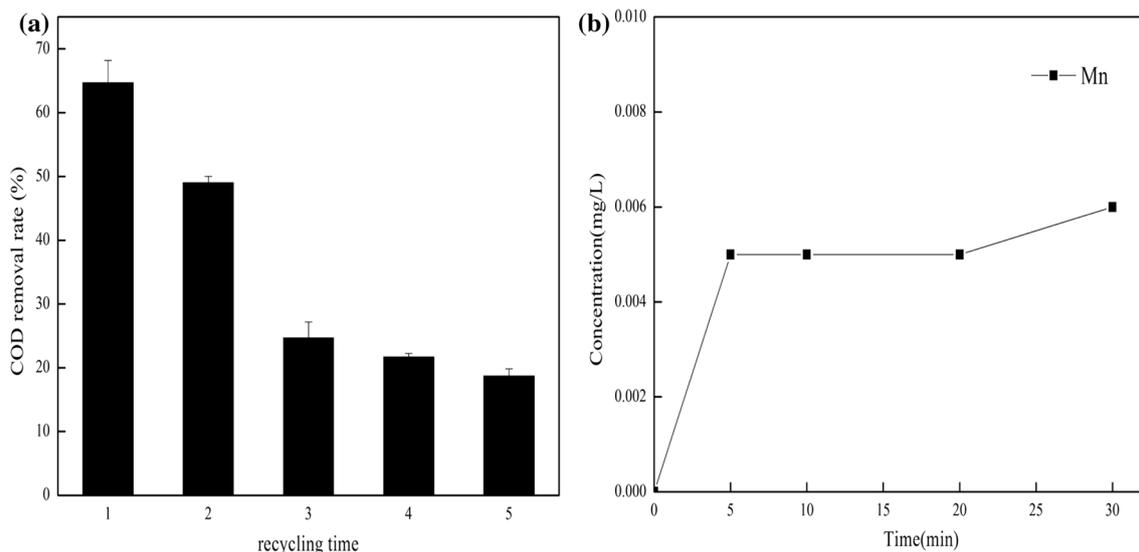


Fig. 6 Recycling (a) and leaching (b) profiles of Mn ore tailings

The recycling of manganese ore tailings is an important resource utilization. In the process of mine development, there are many environmental problems, endangering human health and destroying the ecological environment. Therefore, it is of far-reaching resource significance for the reuse of manganese ore tailings. The experiments concerning recycling and reusing of Mn ore tailing residue were carried out after the pre-treatment, and the results are shown in Fig. 6a. The removal rate of COD is about 65% when using Mn ore tailing for the first time, and it decreased with the increase in recycling time. The removal rate is less than 25% when the recycling time exceeds 3. In our previous research, the surface of Mn ore tailing turned smoother as the reaction progressed, during treatment of low concentration coking wastewater, which resulted in the decrease in catalysis effects (Liu et al. 2015). Mn oxides were applied as heterogeneous catalysts and were recovered by filtration, washed with distilled water and ethyl ether repeatedly previously; it showed that the activity of the catalyst reduced insignificantly after 4 times of reuse (Qi et al. 2011). Concentration of residue metal ions of the Mn ore tailing representing as in the leaching solution is shown in Fig. 6b. From the results, only Mn can be detected, but its concentration does not significantly change with the leaching time. The concentration was 0.005 mg L⁻¹ when the leaching time is 5 min, while it remains almost constant until 20 min; Mn concentration increased only by 0.001 mg L⁻¹ when the leaching time was 30 min. The experimental data indicate that the leaching content of manganese tailings in water is low; considering the operational and recycling cost of full-scale projects, manganese tailings can be processed into filter materials for filling in practical engineering applications. A reactor filled with filter material increases contact of O₃/Mn and the coking wastewater, improves the oxidation efficiency and can effectively reduce sludge production amount. Also, it is convenient for recycling of waste filter materials after recycling. Because Mg²⁺ cannot destroy the unity of crystal structure, MgO has little effect on the characteristics of ceramsite (Zou et al. 2009). It can be combined with other materials to produce high-performance ceramsite, reducing the cost of sludge disposal, which is consistent with sustainable development philosophy.

The combined Mn-AOPs process can not only solve the disposal problem of manganese tailings, but also reduce the chemical dosage cost; compared to traditional technologies, it can save 30–50% of operating cost and realize economic benefits after calculation, with a total operation cost of 3.77 RMB-Yuan per pre-treated wastewater (m³).

Conclusion

A novel combined process AOP using Mn ore tailings treating coking wastewater was proved to be feasible. Fenton and ozonation were chosen as model oxidation technologies combining with Mn ore tailings. The optimal combination process is initial Fenton oxidation followed by Mn tailings assisted ozonation (Fenton + O₃/Mn ore tailings), where its COD and chromaticity removal rates can reach 61.0% and 96.7%, respectively. Mn ore tailing improves efficiency of AOPs using Mn oxides as a catalyst for the formation of free radicals ($\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$) and oxidation of organic compounds. Oxidation and radicals mainly took place on the surface of Mn ore tailings.

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Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest.

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Supplementary Material

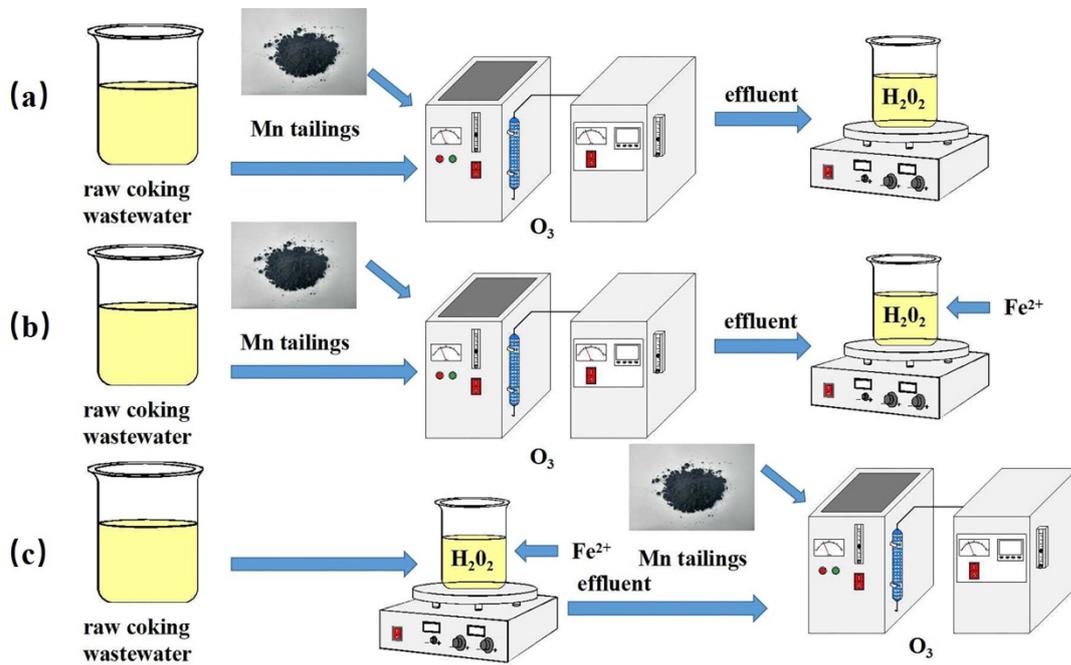


Figure S1. Diagram of the study combination processes (a) O_3 /Mn ore tailings + H_2O_2 ; (b) O_3 /Mn ore tailings + Fenton and (c) Fenton + O_3 /Mn ore tailings

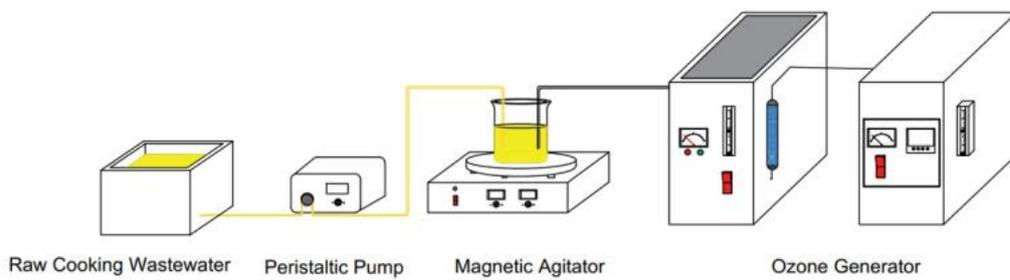


Figure S2. Diagram of the study combination process