

# Mineralization of petrochemical wastewater after biological treatment by ozonation catalyzed with divalent iron tartaric acid chelate

Song Wang, Genwang Zhu, Zhongchen Yu, Chenxi Li, Dan Wang and Xiaoling Cao

## ABSTRACT

The petrochemical wastewater includes many toxic organic compounds, which are refractory substances. It is difficult for the wastewater to meet discharge standards after biological treatment, therefore, the further effective treatment of post-biochemical petrochemical wastewater has become an urgent problem to be solved. This study used iron tartaric acid chelate (ITC) catalytic ozonation to treat the petrochemical wastewater. Various key factors were investigated, such as hydraulic retention time (HRT), catalyst dosage, ozone concentration, initial pH values and oxidation efficiency. The kinetics of catalytic ozonation were established. The results indicate that the chemical oxygen demand (COD) removal rate reached a maximum of 58.5%, when the  $\text{Fe}^{2+}$  dosage is  $0.25 \text{ mmol L}^{-1}$ , the initial pH value is neutral, the liquid phase ozone concentration is about  $1.95 \text{ mg L}^{-1}$ , and HRT is equal to 180 min. In addition, when HRT is equal to 90 min, the B/C ratio of wastewater increases to 0.31, the catalytic ozone reaches maximum oxidation efficiency, and the most economical HRT was 90 min. Finally, the kinetics of ITC catalytic ozonation catalyzed with ITC is consistent with the pseudo-first-order kinetic reaction, and its rate constant is  $0.00484 \text{ min}^{-1}$ .

**Key words** | catalytic ozonation, chelate, kinetic, petrochemical wastewater

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## HIGHLIGHTS

- The low-cost and environmentally friendly tartaric acid is used as the chelating agent in the homogeneous catalytic oxidation reaction.
- Under neutral conditions, after the treatment of petrochemical wastewater by catalytic ozonation, the biodegradability of petrochemical wastewater has been significantly improved.
- Various key factors were investigated, such as hydraulic retention time (HRT), catalyst dosage, ozone concentration, initial pH values and oxidation efficiency.
- The kinetics of catalytic ozonation was established.

## INTRODUCTION

With the development of industry and population growth, freshwater resources have been becoming scarcer (Schwarzenbach *et al.* 2006; Shannon *et al.* 2008; Wu *et al.* 2015). Toxic and hazardous substances emitted from different industries to natural water bodies have exacerbated the water crisis (Maiti *et al.* 2019). Especially, aquatic organisms

and water ecosystem are seriously threatened by non-standard discharge of petrochemical wastewaters, which contain various kinds of hazardous matters and petroleum hydrocarbons. In Daqing Xinghua Park, the petrochemical wastewater after biological treatment (PWBT) seriously exceeds the standard, their discharge into surrounding

water bodies causes serious threat and damage to the water quality and environment. Therefore, the further effective treatment of PWBT has become an urgent problem to be solved.

In the last few decades, the advanced oxidation process (AOPs) have been regarded as effective techniques for treating organic pollutants (Boczkaj & Fernandes 2017; Gaḡol *et al.* 2018b; Khan *et al.* 2020). AOPs were first reported by Glaze & Kang (1989), who stated that AOPs are capable of generation of highly reactive species named hydroxyl radicals ( $\cdot\text{OH}$ ).  $\cdot\text{OH}$ , possesses a high oxidation potential ( $E^0 = 2.07 \text{ V}$ ), is capable of oxidizing the majority of the organic compounds (Litter 2005). In earlier reports, different oxidants in AOPs, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), persulfate and ozone ( $\text{O}_3$ ), have been compared (Chong *et al.* 2010).  $\text{H}_2\text{O}_2$  requires careful control of pH (2.5–4.0) and incurs a financial cost.  $\text{Cl}^-$  inhibits the destruction of organic contaminants by persulfate based AOPs (Huang *et al.* 2016). The above disadvantages make the use of  $\text{H}_2\text{O}_2$  and persulfate difficult in industrialized applications. However,  $\cdot\text{OH}$  and sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) have a better effect on the treatment of volatile organic compounds that are toxic and persistent in the environment (Fernandes *et al.* 2019a, 2019c). The preference of the  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  for degradation of oxygen containing VOCs had different behavior depending on the group of compounds and should be considered in future research for combined radical processes (Fernandes *et al.* 2018, 2019b). In recent years, with the improvement of the efficiency of catalytic ozone, the reports about employing ozone to treat organic wastewater treatment are gradually increased (Pines & Reckhow 2002). However, there are still many organic compounds that barely react directly with ozone (Wu *et al.* 2015). Fortunately, some reaction conditions or catalysts can initiate chain reaction of ozone oxidation to produce  $\cdot\text{OH}$ , which are less selective reaction with most organic compounds in many reactions (Schwarzenbach *et al.* 2006). Because the free radical-dominated reaction is completely different from the traditional chemical process in water treatment (chemical flocculation, chlorination and electrolysis etc.), and the oxidation reaction involved by free radicals is faster and more efficient (Boczkaj *et al.* 2018; Gaḡol *et al.* 2018a, 2019). Therefore, this kind of water treatment technology involving free radicals is called advanced oxidation processes. In order to improve ozonation efficiency, some other assisted catalysis techniques have introduced in AOPs, such as peroxone ( $\text{H}_2\text{O}_2/\text{O}_3$ ), ozone at alkaline condition, ultraviolet radiation-assisted ozonation, hydrodynamic cavitation in combination with ozone and catalytic

ozonation (Boczkaj & Fernandes 2017; Khan *et al.* 2020). On the one hand, hydrodynamic cavitation in combination with ozone has received extensive attention because it can improve the mass transfer efficiency of liquid-phase ozone. (Gaḡol *et al.* 2018b). On the other hand, catalytic ozonation has been a hot topic because it can effectively improve the utilization of ozone (Lovato *et al.* 2016). In the previous three decades, the application of AOPs to solve environmental problems has received extensive attention, especially in combination with transition metal catalysts (Yang *et al.* 2014). Lv *et al.* (2012) reported a magnetic iron oxide nanoparticle for catalytic ozonation to treat organic pollutants in water. The results have shown that the removal rate of 2,4-dichlorophenoxyacetic acid reached 93% within 20 min. Cernigoj *et al.* (2010) found that multiple oxides have a synergistic effect for catalytic ozonation, which tends to produce free radicals to degrade organic matter more quickly. But, the release and wastage of metal ions (iron, cobalt, and manganese) will decrease the stability and activity of the catalyst. When the pH exceeds 4.0, the catalyst in the oxidation system tends to form metal sludge, which will cause deactivation of the catalyst (Maiti *et al.* 2019).

In order to make the metal ion catalyst work efficiently at higher pH conditions, some chelating agents and metal ions are added into the oxidation system. The compound agent can reduce the metal ions concentration level exposed to the oxidation system and release metal ions slowly. Therefore, a suitable compound agent is effective in increasing the efficiency of ozonation catalyzed with the metal ions (Bourgin *et al.* 2017). Chen & Pignatello (1997) used picolinic acid as the chelating agent to enhance  $\text{Fe}^{3+}$  catalytic efficiency. The result showed that the removal rate of organic matter reached 95% by  $\text{Fe}^{3+}$  catalyzing  $\text{H}_2\text{O}_2$ . Canals *et al.* (2013) studied six metal coordination chelates with N-based ligands, which were used as compound agents to synergize  $\text{Fe}^{2+}$  catalyst, and catalyzed  $\text{H}_2\text{O}_2$  to degrade organic substrates at neutral condition. The results indicated that the highest degradation efficiency of organic substrates reached 99.6%. Although compound agents could effectively increase the catalytic efficiency and pH adaptation range of metal ions, there are many shortcomings to be considered. For example, most of the organic compound agents (phenanthroline, ethylene diamine tetraacetic acid, nitrilotriacetic acid etc.) are refractory organic compounds. Although the use of these chelating agents can play a good role in masking metal ions, they cannot be recovered during the water treatment process, and new organic pollutants are introduced into the water (Soltermann *et al.* 2015; Sharma & Feng 2017). Tartaric acid is widely present in higher plants and is

also a common food additive. Therefore, tartaric acid as a masking agent in water treatment can effectively solve the problem of secondary pollution (Han *et al.* 2015; Serna-Galvis *et al.* 2016).

In order to reduce secondary pollution during water treatment to the greatest extent, in this paper tartaric acid, which is ubiquitous in higher plants, is used as chelating agent, and chelated with divalent iron to form ITC. A new method of ozonation of PWBT catalyzed by ITC was proposed. The influence of different factors on catalytic ozone performance was investigated, and the kinetic model is also discussed.

## MATERIALS AND METHODS

### Materials

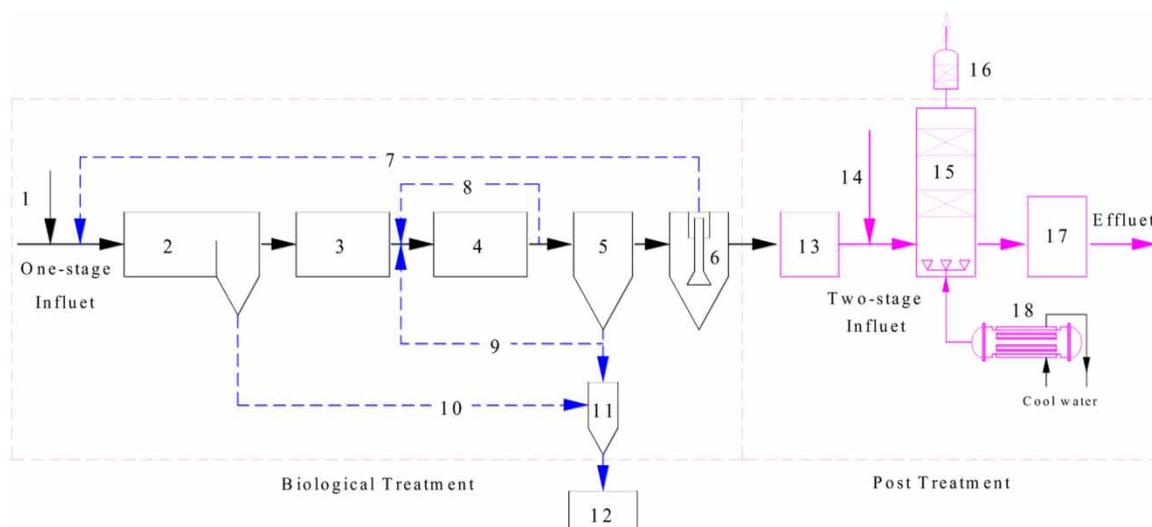
The ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sodium hydroxide ( $\text{NaOH}$ ) and phenanthroline were purchased from DAMAO (Tianjin, China). Tartaric acid and ammonium iron(II) sulfate were obtained from Quanrui reagent (Shenyang, China). Silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) and mercury(II) sulfate ( $\text{HgSO}_4$ ) were purchased from Kermel Chemical Reagent Company (Tianjin, China). The carbonyl iron powder ( $\text{Fe}(\text{CO})_5$ ) was obtained from China Metallurgical Research Institute. All chemicals used in this study were of commercially available analytical grade.

### Petrochemical wastewater after the biological treatment

The entire wastewater treatment process in Xinghua Park is shown in Figure 1. Petrochemical wastewater after biological treatment (PWBT) has been biologically treated at the wastewater treatment plant in Xinghua Park. The major contaminants of PWBT are phenols, nitrile compounds and petroleum-based organic pollutants. The detailed water parameters of PWBT are as follows: pH value range is 7.5–8.5, chemical oxygen demand (COD) concentration is 100–120  $\text{mg L}^{-1}$ , biochemical oxygen demand (BOD) concentration is 10–15  $\text{mg L}^{-1}$ , suspended solids (SS) is 20–40  $\text{mg L}^{-1}$ , oil content is 2.5–5.8  $\text{mg L}^{-1}$ , cyanide concentration is 0.03–0.1  $\text{mg L}^{-1}$ , ammonia nitrogen concentration is 15–20  $\text{mg L}^{-1}$ .

### Experimental apparatus

The ozonation of PWBT catalyzed by ITC was tested in a cylindrical organic glass reactor with an inner diameter of 10.8 cm and a height of 135.0 cm. 0.2  $\text{mmol L}^{-1}$   $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.4  $\text{mmol L}^{-1}$  tartaric acid were added. The oxygen-rich gas is produced by oxygenator, the concentration of oxygen is  $90 \pm 3\%$ , the volumetric flowrate of ozone containing gas is 0.2–0.4  $\text{m}^3 \text{h}^{-1}$ . The gas phase ozone with a flux ranging from 10 to 70  $\text{mg L}^{-1}$  was produced from a generator (CF-G3–10 g, Qingdao Guolin Technology Co., Ltd, Qingdao, China), and the corresponding liquid



**Figure 1** | Schematic diagram of wastewater treatment process in Xinghua Park. 1 Add acid or alkali liquor, 2 multifunctional regulation tank, 3 EGSB reactor, 4  $\text{A}^2/\text{O}$  biofilm reactor, 5 clarifier, 6 Dynasand filter, 7 wastewater with sludge, 8 mixed liquor recycle, 9 return activated sludge, 10 discharge sludge, 11 sludge tank, 12 sludge dewatering, 13 water tank, 14 ITC catalyst, 15 catalyzed ozonation reactor, 16 ozone destroyer, 17 biological activated carbon tank, 18 ozonator.

phase ozone concentration range was 0.9 to 3.6 mg L<sup>-1</sup>. The oxygen source is provided by an oxygen generator (OCG30, SYSMED Co., Ltd, Shenyang, China). The hydraulic retention time (HRT) was 180 minutes. Water samples were taken for further analysis at different time intervals (Figure 2).

### Analysis methods

The concentrations of O<sub>3</sub> in the gas and aqueous solution were respectively measured with the iodometric titration method and indigo method (Bader & Hoigné 1981). The COD removal rate of PWBT and the BOD/COD ratio (B/C) were used as indexes. The COD of the PWBT was obtained by the potassium dichromate method. Briefly, potassium dichromate was used as a strong oxidant for oxidation of organic matter under acidic conditions and 150 °C temperature for 2 h. After that, the excessive potassium dichromate was determined by titration with ammonium iron(II) sulfate (Jaafarzadeh *et al.* 2017). The five-day biochemical oxygen demand (BOD<sub>5</sub>) was analyzed by iodometry method according to GB/T 7488–1987 of PR China. Briefly, the BOD<sub>5</sub> was determined through the oxygen consumption of bacteria breaking down organic matter in the sample over a 5-day period under standardized conditions (Chen *et al.* 2016). The concentration of irons was determined by o-phenanthroline spectrophotometry using a 752N UV-vis spectrophotometer (Shanghai Lengguang Technology) at 510 nm. The biodegradability was measured using B/C. The pH of succinonitrile solution was adjusted by adding 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.1 mol L<sup>-1</sup> NaOH, and determined by using a PHS-3C pH meter (Rex Instrument Factory, Shanghai, China).

## RESULTS AND DISCUSSION

### Selection of catalyst

The optimum molar ratio of tartaric acid and ferrous chloride was 2:1 at pH 7.0. Therefore, the initial reaction conditions are the following: initial pH value was 7.0, the concentration of liquid phase O<sub>3</sub> was 1.8–2.0 mg L<sup>-1</sup> and HRT was 150 min. The catalyst is combined with 0.2 mmol L<sup>-1</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O and 0.4 mmol L<sup>-1</sup> tartaric acid. In the other batch experiments, carbonyl iron powder of the same iron molar equivalent was used as catalyst. The result is shown in Figure 3.

It can be seen from Figure 3, when the HRT is 150 min, the COD removal rate of PWBT in the two oxidation systems with catalyst (42.3 and 58.8%) are both significantly higher than that of the ozone system alone (5.8%). This illustrates that both catalysts can improve the efficiency of ozone treatment for PWBT. Among them, ITC has expressed stronger catalytic performance (58.8%) than carbonyl iron powder (42.3%). Under the masking effect of tartaric acid, the Fe<sup>2+</sup> will not be oxidized quickly, so that the Fe<sup>2+</sup> in the catalytic system can maintain stable and efficient catalytic performance for a long time (Hoek & Sachtler 1979).

### Experimental influencing factors

The catalyst dosage is an important factor in catalytic reaction. Therefore, the concentration of ITC added to the reaction systems are 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 mmol L<sup>-1</sup>, respectively. The results are shown in Figure 4.

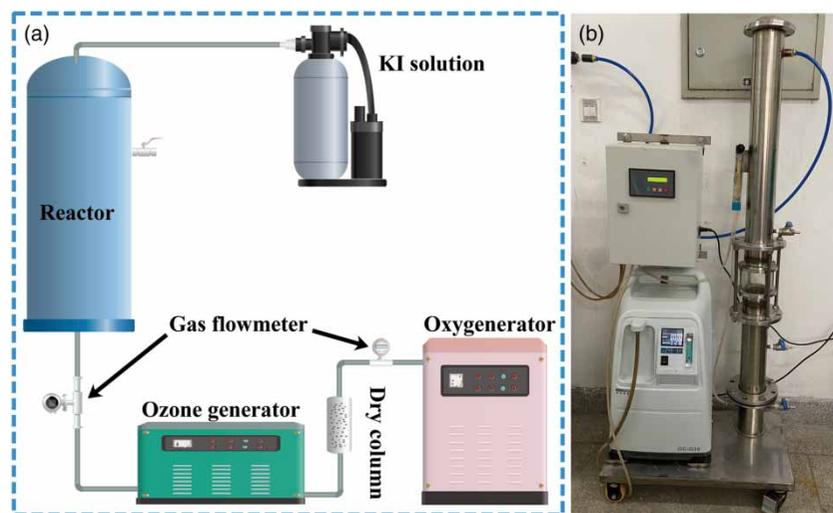


Figure 2 | Experimental apparatus for ozonation: (a) schematic, (b) photography.

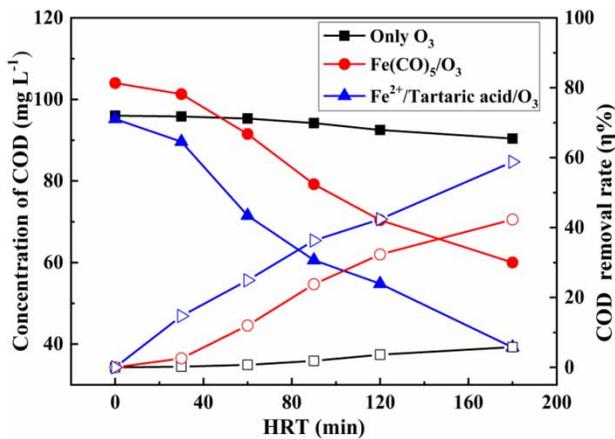


Figure 3 | COD removal rate of PWBT at different catalysts.

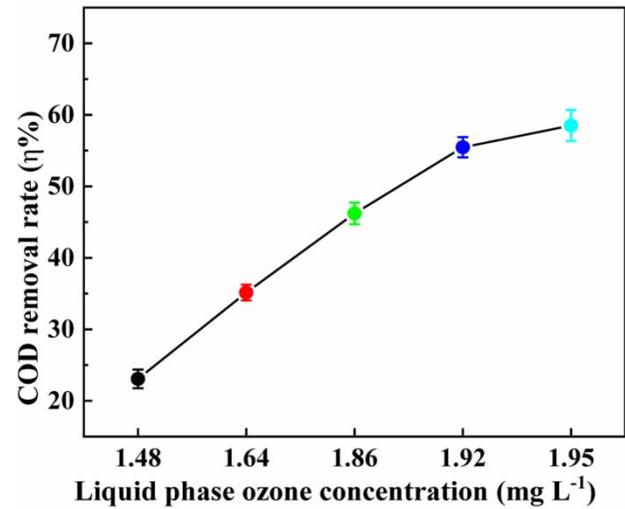


Figure 5 | COD removal rate of PWBT with different liquid phase concentrations of ozone.

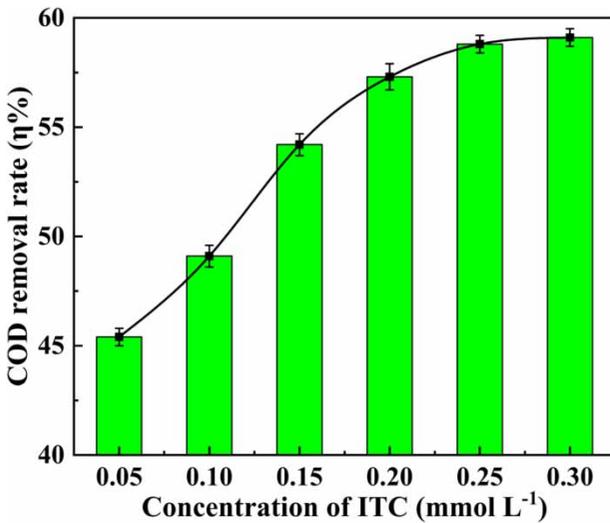


Figure 4 | COD removal rate of PWBT with different catalyst dosages.

Figure 4 shows that with the increase of catalyst dosage, the COD removal rate of PWBT increased. When the catalyst dosage was  $0.25 \text{ mmol L}^{-1}$ , the COD removal rate of PWBT reached 58.8%. However, when the catalyst dosage added exceeds  $0.25 \text{ mmol L}^{-1}$ , the COD removal rate increases slowly (59.1%). This may be because the solubility product of  $\text{Fe}(\text{OH})_2$  is a constant, and excessive  $\text{Fe}^{2+}$  will generate a precipitate through Equations (1) and (2) instead of acting as catalyst.

In the ozone oxidation process of PWBT, the dosage of oxidant is an important factor for COD removal rate of PWBT. Therefore, the COD removal rates of PWBT with different liquid phase concentrations of ozone have been studied (Figure 5).

It can be seen in Figure 5 that with the increase of liquid phase ozone concentrations, the COD removal rate of PWBT increased gradually, from 23.1 to 58.8%. Starting from an ozone concentration of  $1.92 \text{ mg L}^{-1}$ , the COD removal rate of PWBT began to slow down, from 57.6 to 58.8%, only increasing by 1.2%. This may be limited to the rate of decomposition of ozone to generate radicals (Burbano *et al.* 2005).

It is well known that pH is an important factor in liquid reaction. Therefore, the COD removal rate of PWBT at different initial pH has been studied (Figure 6).

The result of Figure 6 shows that the COD removal rate of PWBT increased. The highest COD removal rate of PWBT increases with the increase of initial pH when pH is less than 7.0. The optimal pH values for the COD removal

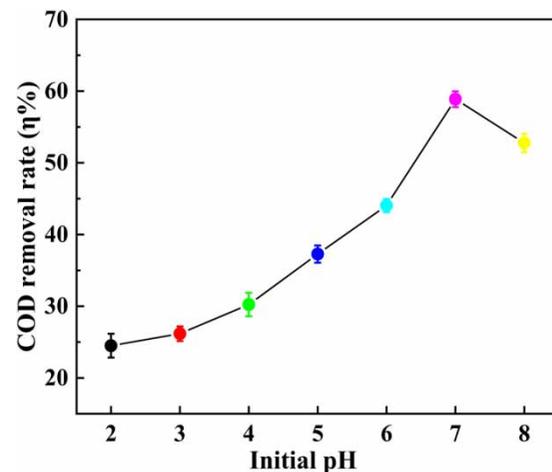
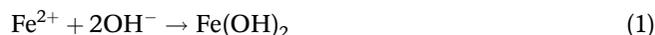


Figure 6 | COD removal rate of PWBT at different initial pH.

rate of PWBT (58.8%) is about 6.98. After that, the COD removal rate of PWBT decreases significantly. The reason is that  $\text{Fe}^{2+}$  strongly tends to produce  $\text{Fe}(\text{OH})_2$  under alkaline conditions and then be quickly oxidized to  $\text{Fe}(\text{OH})_3$  precipitate (Equations (1) and (2)) (Bokare & Choi 2014). The final result is a decrease in the COD removal rate of PWBT.



### Improvement of biodegradability

In general, the cost of chemical treatment increases with the consumption of chemical reagents. It is the most economical option to apply biological treatment after appropriate chemical treatment. On the other hand, some volatile oxygen-containing organic compounds mainly composed of small organic carboxylic acids are generated during the ozonation treatment of organic wastewater. These oxygenated organic compounds are easily degraded by microorganisms. Therefore, in the complete process flow, the wastewater after ozonation will be further processed by the biological activated carbon process to eliminate the oxygenated organic compounds generated in the oxidation process. In order to save the cost of treatment, Eckenfelder (2002) had proposed the concept of efficiency of treatment (ET) which is based on the ability of the oxidant to produce an acceptable organic by-product without significant ultimate conversion of organic carbon to carbon dioxide. In addition, B/C is an important index to appraise the biodegradation of wastewater. Therefore, B/C at different HRT was employed to evaluate ET of ozonation (Figure 7).

Figure 7 shows that although the COD concentration ( $39.2 \text{ mg L}^{-1}$ ) of PWBT after ozonation meets discharge standards, the cost and HRT of treatment are uneconomical. Although COD removal rate was only 36.3% when HRT was 90 min, B/C had the largest increase from 0.09 to 0.31. This phenomenon can be explained that the refractory organic matters in PWBT was decomposed to acceptable organic by-product by ITC catalytic ozone. Therefore, the most economical way to treat PWBT is to use ozonation for 90 min and then employ biological treatment.

### Mechanism for the PWBT degradation in $\text{O}_3/\text{ITC}$

The iron ion catalytic degradation mechanism of organic compounds by iron ion is accompanied by a cycle of

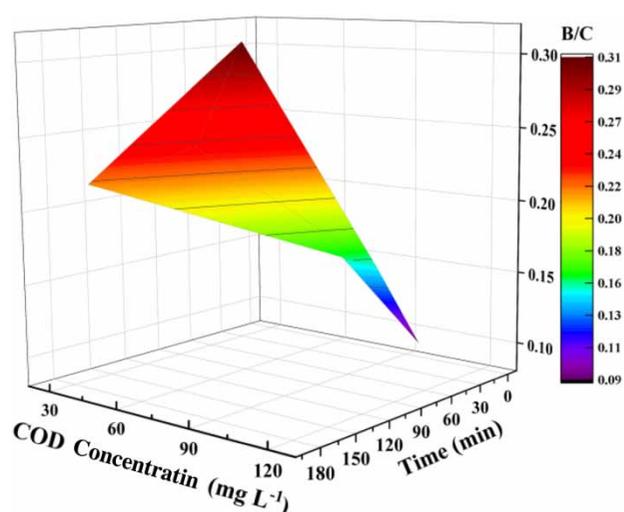


Figure 7 | The value of B/C in organic transformation.

$\text{Fe}^{2+}/\text{Fe}^{3+}$  (Walling 1975). The homogeneous catalyzed reactions of metal ions are shown in Table 1. In a typical procedure,  $\text{Fe}^{2+}$  can be rapidly oxidized by liquid phase ozone to high-valent iron oxides  $\text{FeO}^{2+}(\text{Fe}(\text{IV}))$ . Subsequently,  $\text{FeO}^{2+}(\text{Fe}(\text{IV}))$  reacts with water or  $\text{Fe}^{2+}$  to generate  $\text{Fe}^{3+}$  and  $\cdot\text{OH}$ . It has to be pointed out that the constant of reaction (2) is first order and, consequently, reaction (2) can be faster than reaction (1) or any other second order elementary step presented in the text depending on reactant concentration (Piera et al. 2000). This is the initiation phase of the free radical chain reactions. In the amplification phase of the free radical chain reactions, other free radicals are generated and the  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ . In this catalytic ozonation reaction process, the generated  $\cdot\text{OH}$  oxidize organic pollutants, while the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  circulate.

Whitlow & Roth (1988) established the kinetic model of ozonation by empirical equation through a series of experiments.

$$-\frac{dC}{dt} = k_n \cdot C^n \quad (3)$$

In this equation,  $-\frac{dC}{dt}$  = organic matter oxidation rate,  $k_n$  = synthetic reaction rate constant,  $C$  = reactant concentration,  $n$  = order of reaction.

In order to characterize the degree of mineralization of organic pollutants catalytic ozonation by chelate, COD is used as an index of mineralization degree. Therefore, the Equation (3) can be transformed into Equation (4).

$$-\frac{dC_{(\text{COD})}}{dt} = k_n \cdot C_{(\text{COD})}^n \quad (4)$$

**Table 1** | Principal reactions in kinetic model

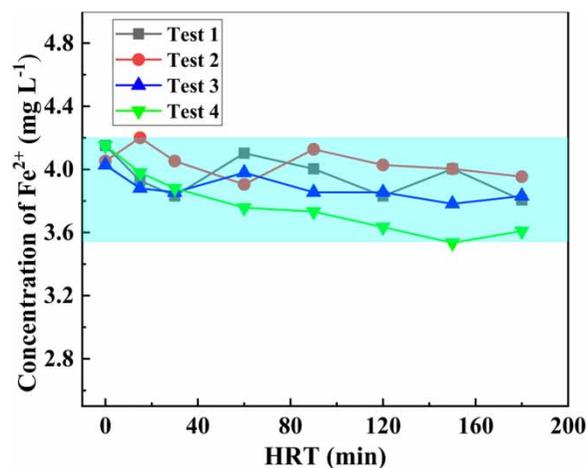
No.	Reactions	Rate constant	References
1	$\text{Fe}^{2+} + \text{O}_3 \rightarrow \text{FeO}^{2+} (\text{Fe(IV)}) + \text{O}_2$	$k = (8.2 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Løgager <i>et al.</i> (1992)
2	$\text{FeO}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$	$k = (1.3 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$	Løgager <i>et al.</i> (1992)
3	$\text{FeO}^{2+} + \text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}$	$k = 4.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Pang <i>et al.</i> (2011)
4	$\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$	$k = (3.0\text{--}4.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Kusic <i>et al.</i> (2011)
5	$\text{Fe}^{3+} + \text{HO}_2\cdot \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	$k = 0.1\text{--}3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Sehested <i>et al.</i> (1984)
6	$\text{HO}_2\cdot \rightarrow \text{O}_2\cdot^- + \text{H}^+$	$k = 5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Chen & Pignatello (1997)
7	$\text{Fe}^{3+} + \text{O}_2\cdot^- \rightarrow \text{Fe}^{2+} + \text{O}_2$	$k = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Chen & Pignatello (1997)
8	$\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Chen & Pignatello (1997)
9	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k = (4.2\text{--}5.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Kang <i>et al.</i> (2002)
10	$\text{HO}_2\cdot + \text{O}_2\cdot^- \rightarrow \text{HO}_2^- + \text{O}_2$	$k = 9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Burbano <i>et al.</i> (2005)
11	$\text{O}_2\cdot^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \cdot\text{OH} + \text{O}_2$	$k = 0.13 \text{ M}^{-1} \text{ s}^{-1}$	Gallard & De Laat (2000)
12	$\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{OH} + \text{O}_2$	$k = 3.0 \text{ M}^{-1} \text{ s}^{-1}$	Crittenden <i>et al.</i> (1999)
13	$\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{HO}_2\cdot + \text{OH}^-$	$k = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Crittenden <i>et al.</i> (1999)
14	$\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Grymonpré <i>et al.</i> (2001)
15	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2\cdot^- + \text{H}_2\text{O}$	$k = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Crittenden <i>et al.</i> (1999)
16	$\cdot\text{OH} + \text{O}_2\cdot^- \rightarrow \text{O}_2 + \text{OH}^-$	$k = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Grymonpré <i>et al.</i> (2001)
17	$\cdot\text{OH} + \text{O}_3 \rightarrow \text{HO}_2\cdot + \text{O}_2$	$k = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Crittenden <i>et al.</i> (1999)

In this equation,  $-\frac{dC_{(\text{COD})}}{dt}$  = decomposition of organic pollutant COD,  $C_{(\text{COD})}$  = COD value.

In general, the order of decomposition of organic compounds by oxidant ( $\cdot\text{OH}$  or  $\text{O}_3$ ) is second-order (Cano Quiroz *et al.* 2011; Guo *et al.* 2016). Benitez *et al.* (1999) used the least squares method to analyze the experimental data of a large number of catalytic ozone oxidation organic compounds and also got such a conclusion. In the chelate catalytic ozone reaction, the main oxidant reacting with organic compounds is  $\cdot\text{OH}$ , so the equation of second-order reaction is as follows.

$$-\frac{dC_{(\text{COD})}}{dt} = k_A \cdot \text{OH} \cdot C_{(\text{OH})} \cdot C_{(\text{COD})} \quad (5)$$

Because  $\cdot\text{OH}$  reacts very quickly with other substances, it becomes a rate-limiting reaction. According to Table 1, in the case of excess liquid phase ozone, the concentration of  $\cdot\text{OH}$  is determined by concentration of  $\text{Fe}^{2+}$ . Therefore, four parallel tests show that the largest change in the  $\text{Fe}^{2+}$  at different times was 4th groups, which decreased to  $0.616 \text{ mg L}^{-1}$ . This result indicates that tartaric acid is effective chelating agent for  $\text{Fe}^{2+}$ . On the other hand, the concentration of the  $\text{Fe}^{2+}$  varies very little (Figure 8). It can be explained that the amount of  $\cdot\text{OH}$  in this system remains basically unchanged; that is, the concentration of  $\cdot\text{OH}$  can be regarded as a constant.

**Figure 8** | Concentration of  $\text{Fe}^{2+}$  in different time systems.

Because the concentration of  $\cdot\text{OH}$  can be a constant, the pseudo first order reaction equation of the ITC catalytic ozonation of the PWBT can be expressed by Equations (6)–(8).

$$-\frac{dC_{(\text{COD})}}{dt} = k_{(\text{COD})} \cdot C_{(\text{COD})} \quad (6)$$

$$-\int_{C_{(\text{COD})}^0}^{C_{(\text{COD})}^t} \frac{1}{C_{(\text{COD})}} dC_{(\text{COD})} = \int_0^t k_{(\text{COD})} dt \quad (7)$$

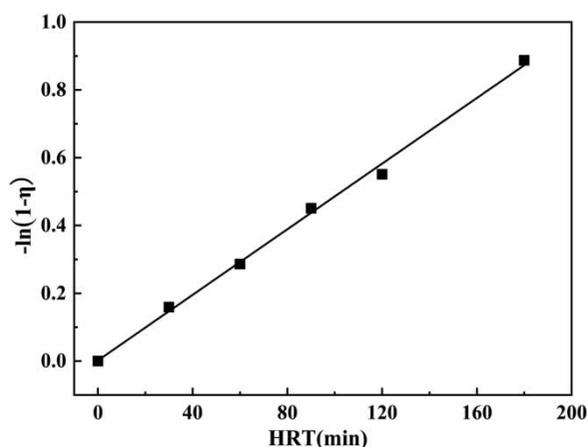


Figure 9 | First-order linear fitting curve.

where  $k_{(\text{COD})}$  represents the pseudo-first-order rate constant. After integration with the boundary conditions  $C_{(\text{COD})} = C_{(\text{COD})0}$  for  $t = 0$ , and  $C_{(\text{COD})} = C_{(\text{COD})}$  for  $t = t$ , this equation leads to

$$-\ln \frac{C_{(\text{COD})}}{C_{(\text{COD})0}} = -\ln(1 - \eta) = k_{(\text{COD})} \cdot t \quad (8)$$

$C_{(\text{COD})}$  = COD value,  $C_{(\text{COD})0}$  = Initial COD value,  $\eta$  = COD removal rate,  $k_{(\text{COD})}$  = synthetic reaction rate constant.

In order to determine the reaction rate constant, the organic wastewater was oxidized by ozone under the optimum reaction conditions, and the reaction rate constant was obtained under the optimum reaction conditions, as shown in Figure 9.

Figure 9 shows the first order linear fitting equation of function and its parameters when pH was 7.0, liquid ozone concentration was  $1.92 \text{ mg L}^{-1}$  and HRT was 180 min. The pseudo-first-order synthetic reaction rate constant is  $0.00484 \text{ min}^{-1}$ , which indicates that ITC could catalyze ozone effectively to produce  $\cdot\text{OH}$  to oxidize PWBT.

## CONCLUSION

Compared with single ozone, carbonyl iron powder and ITC catalytic ozonation of PWBT are improved significantly. When pH was 7.0, the ITC concentration was  $0.2 \text{ mmol L}^{-1}$ , the liquid phase ozone concentration was  $1.9 \text{ mg L}^{-1}$ , and the HRT was 180 min, the COD removal rate of PWBT reached 58.8%. By monitoring  $\text{Fe}^{2+}$  concentration in the reaction system, it can be seen that the  $\text{Fe}^{2+}$  maintained a

high concentration. It evidences that tartaric acid can protect  $\text{Fe}^{2+}$  effectively in the oxidation process. In addition, when HRT was equal to 90 min, the B/C ratio of wastewater increased to 0.31, the catalytic ozone reached maximum oxidation efficiency, and the most economical HRT was 90 min. The kinetics of ITC catalytic ozonation of PWBT was studied. The result shows that the degradation of PWBT follows pseudo-first-order kinetics. The reaction rate constant is  $0.00484 \text{ (min)}^{-1}$ , which indicates that the ITC can catalyze ozone to generate  $\cdot\text{OH}$  to degrade PWBT. This study has theoretical significance and application value for the refractory wastewater treatment and opens up a new way to meet the standard discharge of petrochemical wastewater.

## ACKNOWLEDGEMENTS

The study was financially supported by PetroChina Innovation Foundation (No. 2016D-5007-0604), Natural Science Foundation of Heilongjiang Province (No. B2015012), Applied Technology Research and Development Project of Heilongjiang Province (No. GC13C305).

## COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no competing interests.

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First received 10 February 2020; accepted in revised form 29 May 2020. Available online 15 June 2020