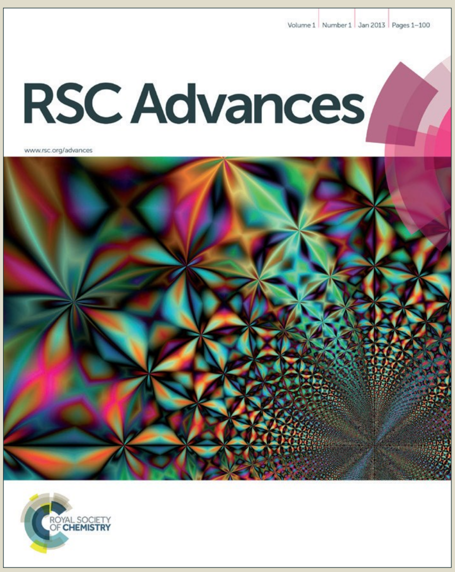
RSC Advances



Study on the Treatment of Simulated Coking Wastewater by O_3 and O_3/Fenton Processes in a Rotating Packed Bed

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Abstract

In this study, simulated coking wastewater was treated by the O_3/Fenton process in a rotating packed bed (RPB) and the results were compared with those by the O_3 process. Contrast experiments indicated that the degradation rates of phenol, aniline, quinoline and NH_3-N in the wastewater reached 100%, 100%, 95.68% and 100% respectively under the optimum operating conditions in the O_3/Fenton process and were much higher than those in the O_3 process. The BOD_5/COD value of the simulated coking wastewater treated in the O_3/Fenton process reached 0.46 and was 135% higher than that in the O_3 process. The degradation pathways of phenol, aniline, quinoline and NH_3-N in the simulated coking wastewater were also discussed. The results indicated that a combination of the advanced oxidation processes and the RPB can enhance the treatment efficiency of coking wastewater.

Keywords: O_3/Fenton process, Rotating packed bed, Coking wastewater, Degradation, Biodegradability

1. Introduction

Coking wastewater is one of the largest industrial wastewater with many poorly biodegradable organics including phenol, aniline, quinoline, as well as inorganic ammonia, which are refractory and cause difficulties in biochemical treatment.[1-2] Therefore, coking wastewater treatment processes are complex, and combined treatment processes with various chemical and physical methods are usually adopted in order to achieve a certain effect, resulting in high operation costs.

In recent years, a variety of new technologies have emerged for the treatment of wastewater with complex components, among which advanced oxidation processes (AOPs), based on chain reactions of hydroxyl radicals with pollutants, have attracted wide attention due to their high efficiency and non-selectivity.[3] The most commonly used AOPs include O_3, Fenton, O_3/Fenton, O_3/H_2O_2, and so on.[4-9] It was reported that AOPs are efficient methods for coking wastewater treatment.[10-12] In O_3-related AOPs, pollutants are degraded by reacting with O_3 molecules (direct oxidation) or with hydroxyl radicals (indirect oxidation), which are stronger oxidants produced through chain reactions of ozone.[13]

High gravity technology is carried out in a rotation packed bed (RPB), which creates a simulated high gravity environment using centrifugal force generated by the rotation of a rotor in the RPB. Liquid flowing through the porous packing in the rotor is split into micro- or nano-droplets, threads and thin films, and there is a huge and violently renewed gas-liquid interface, leading to a significant intensification of mass transfer and micromixing[14-15]. It is known that O_3-related AOPs are limited by O_3 absorption into water[16]. Thus high gravity technology can be used to intensify these processes to improve the treatment effect of wastewater.

This study employed the O_3 and O_3/ Fenton AOPs and an RPB as the reactor to treat a simulated coking wastewater containing phenol, aniline, quinoline and ammonia. The effect of different operating conditions on the degradation of phenol, aniline, quinoline and ammonia was investigated, in an attempt to provide a new process for the treatment of coking wastewater.

2. Experimental Section

2.1 Materials

The simulated coking wastewater was prepared in the laboratory and its composition and properties are shown in Table 1.

The chemical reagents used in the experiments include ferrous sulfate heptahydrate, hydrogen peroxide (30%, w/w), sodium hydroxide, sulfuric acid (98%), phenol (≥99.0%), aniline (≥99.5%), quinolone (≥99.5%) and ammonia (≥99.0%). They are of analytical grade and were purchased from Beijing Chemical Works, China. One mol/L of sodium hydroxide and l mol/L of sulfuric acid were used to adjust pH value of the solution.

Table 1. Composition and properties of the simulated coking wastewater.

Parameter	Value
Phenol (mg/L)	100
Aniline (mg/L)	100
Quinoline (mg/L)	50
NH_3-N (mg/L)	83
pH	6.58
Chemical oxygen demand (COD) (mg/L)	588
Biochemical oxygen demand after 5 days (BOD_5) (mg/L)	147
BOD_5/COD	0.25

The RPB consists mainly of a stationary casing and a packed rotor. The rotor has an inner diameter of 40 mm, an outer diameter of 120 mm, and an axial length of 15 mm. The diameter of the casing is 170 mm. Stainless steel wire mesh (Beijing Hongyahong Mesh Sale Center, Beijing, China) was used as the packing material. For further information on the RPB, please refer to our previous paper.[17]

2.2 Experimental procedures

The experimental setup is shown in Fig. 1. The simulated coking wastewater was adjusted to a certain pH value and divided into two portions with equal volume, one of which was added with a certain amount of H_2O_2, and the other with a certain amount of $FeSO_4 \cdot 7H_2O$. The two liquid streams were simultaneously pumped into the RPB via two respective liquid inlets with the same flow rate, while the ozone-containing gas was produced by an ozone generator and introduced into the RPB via a gas inlet. The liquid streams and gas stream contacted countercurrently in the RPB to achieve the mixing of liquid streams and the absorption of O_3 into the liquid as well as the degradation of the pollutants. The remaining O_3 in the gas stream exiting the gas outlet was absorbed by the KI solution. Samples were taken at the liquid outlet to analyze the pollutant concentration, COD and BOD_5.

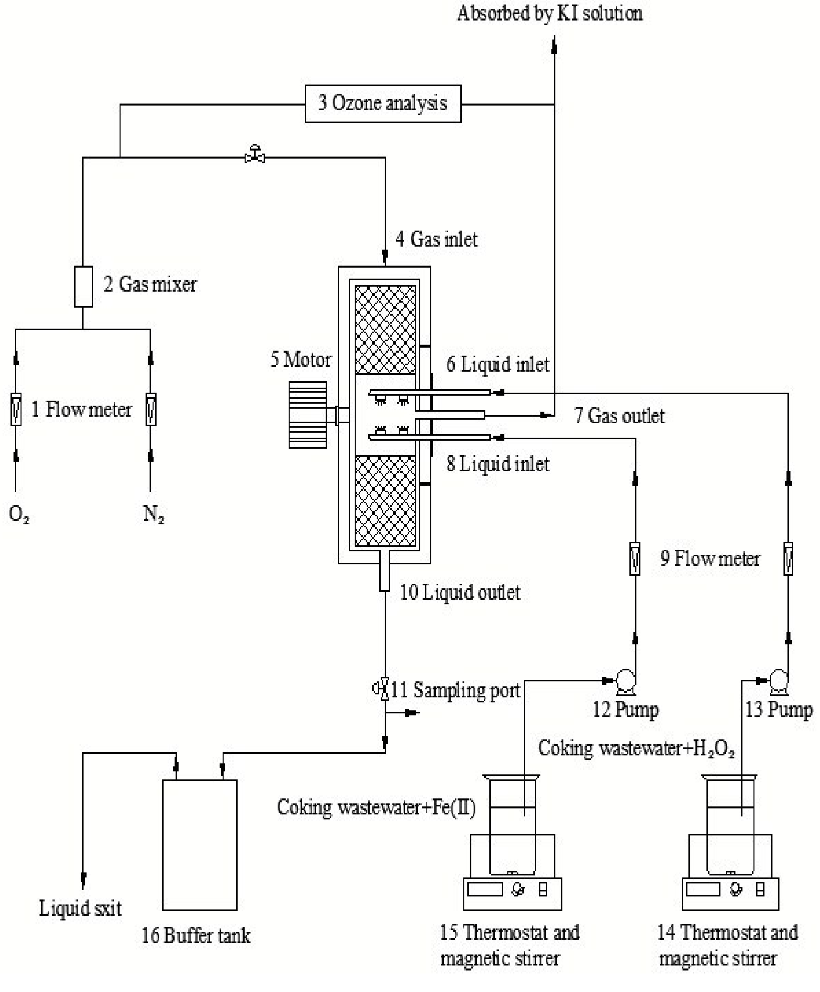


Fig. 1. Experimental setup for the treatment of simulated coking wastewater in an RPB with the O_3/Fenton process.

2.3. Analytical Methods

Ozone concentration was analyzed by a dual ultraviolet ozone concentration detector (LM S-150, Guangzhou Li Mei Co., China).

COD was measured in terms of the Chinese Standard GB HJ/T 399-2007 (Water quality—Determination of the chemical oxygen demand—Fast digestion-Spectrophotometric method, which is similar to the method by APHA[18]), and COD removal rate was calculated according to the following equation (1):

$$\eta = \frac{(COD_i - COD_0)}{COD_0} \times 100\% \quad (1)$$

where COD_0 is the initial COD value of the wastewater, mg/L; COD_i is the COD value of the liquid samples taken at the liquid outlet of the RPB, mg/L.

BOD_5 was measured in terms of the Chinese Standard GB 7488-87 (Water quality—Determination of biochemical oxygen demand after 5 days—Dilution and seeding method, which is based on ISO 5815:1983[19]), and BOD_5 removal rate was calculated according to the following equation (2):

$$BOD_5 = [(C_1 - C_2) - \frac{V_t - V_e}{V_t}(C_3 - C_4)]\frac{V_t}{V_e} \quad (2)$$

where C_1, C_2: dissolved oxygen concentration measured immediately after the test specimen was prepared, and measured after the test specimen was cultivated for 5 days, respectively, mg/L.

C_3, C_4: dissolved oxygen concentration in a blank water specimen measured immediately after the specimen was prepared, and measured after the specimen was cultivated for 5 days, respectively, mg/L.

V_e, V_t: sample volume in the test specimen and total volume of the test specimen, respectively, mL.

BOD_5/COD (B/C) is the ratio of BOD_5 to COD. B/C is a biodegradable index, and a high B/C means high biodegradability of organic matters in wastewater. In general, wastewater is suitable for biological treatment when B/C is higher than 0.3.

Phenol, aniline and quinoline concentrations were measured with a high performance liquid chromatograph (Waters 2695, USA), while NH_3-N concentration was determined by a portable ammonia meter (GDYS-101SA, Xiaotiane Instrument Co. Ltd., Changchun, China).

3. Results and Discussion

3.1 Effect of rotation speed

The effect of rotation speed on COD removal in the O_3 and O_3/Fenton processes is presented in Fig. 2. It can be seen that the highest COD removal rates of 39.36% and 17.5% were reached at the rotation speed of 1000 rpm in the O_3 and O_3/Fenton processes, respectively. When the rotation speed increased initially, liquid was split into smaller droplets and thinner films, leading to a larger gas-liquid interface and better absorption of O_3 and thus higher COD removal rate. Nevertheless, a further increase in the rotation speed resulted in a reduction in liquid residence time in the RPB and thus a decrease in the COD removal. It is also found from Fig. 2 that the O_3/Fenton process has better effect on the COD removal than the O_3 process due to the presence of H_2O_2 and Fe^{2+} to enhance the generation of hydroxyl radicals.

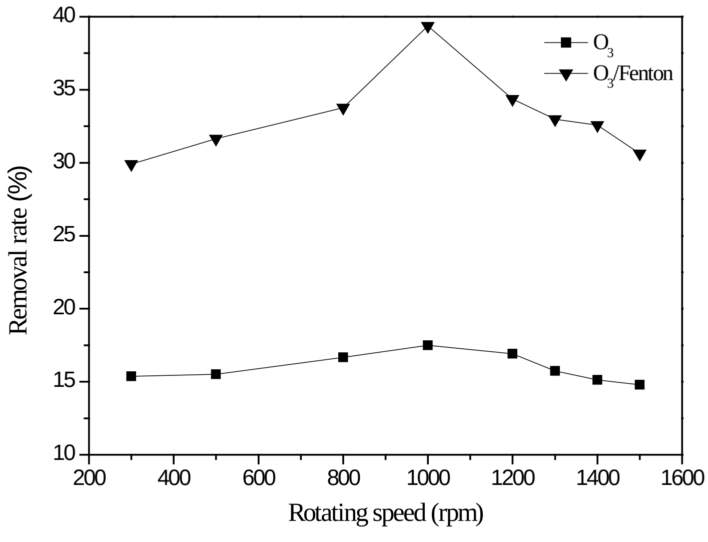


Fig. 2. Effect of rotation speed on the COD removal rate.

(C_{O3} =30 mg/L, pH = 6.58, $C_{Fe(II)}$=0.4 mmol/L, C_{H2O2} =6.5 mmol/L, G=150 L/h, L = 30 L/h).

The B/C values were 0.24 and 0.38 at the rotation speed of 1000 rpm in the O_3

and O_3/Fenton processes respectively, indicating that the wastewater treated by the O_3/Fenton process is suitable for subsequent bio-treatment.

A large amount of hydroxyl radicals is generated in the O_3/Fenton process through the reaction of O_3 with Fenton. The synergic mechanism of O_3 and Fenton is shown by the following equations (3-12).[20-23]

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + \cdot O_3^- \quad (3)$$

$$\cdot O_3^- + H^+ \rightarrow O_2 + \cdot OH \quad (4)$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (5)$$

$$FeO^{2+} + O_3 + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (6)$$

$$H_2O_2 \rightarrow H^+ + HO_2^- \quad (7)$$

$$O_3 + HO_2^- \rightarrow O_2 + \cdot OH + O_2^- \quad (8)$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \quad (9)$$

$$O_3^- + H^+ \rightarrow \cdot HO_3 \quad (10)$$

$$\cdot HO_3 \rightarrow O_2 + \cdot OH \quad (11)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (12)$$

3.2 Effect of gas flow rate

The effect of gas flow rate on the phenol, aniline, quinoline, NH_3-N removal in the O_3 and O_3/Fenton processes is presented in Fig. 3. It can be seen from Fig. 3 that the degradation of the pollutants increased with an increasing gas flow rate and tended to stability at the gas flow rate of 300 L/h in both the O_3 and O_3 /Fenton processes. The phenol, aniline, quinoline, NH_3-N degradation rates reached 61.97%, 98.78%, 60.0 % and 100% respectively at the gas flow rate of 300 L/h in the O_3 process, while their degradation rates reached 91.51%, 100%, 88.78% and 100% at the gas flow rate of 300 L/h in the O_3 /Fenton process, indicating that the O_3 /Fenton process has better effect than the O_3 process. As the gas flow rate increased, the pollutant degradation rates increased because higher gas flow rate provided more ozone and higher mass transfer driving force, promoting the mass transfer between ozone and liquid and accelerating the degradation of the pollutants.

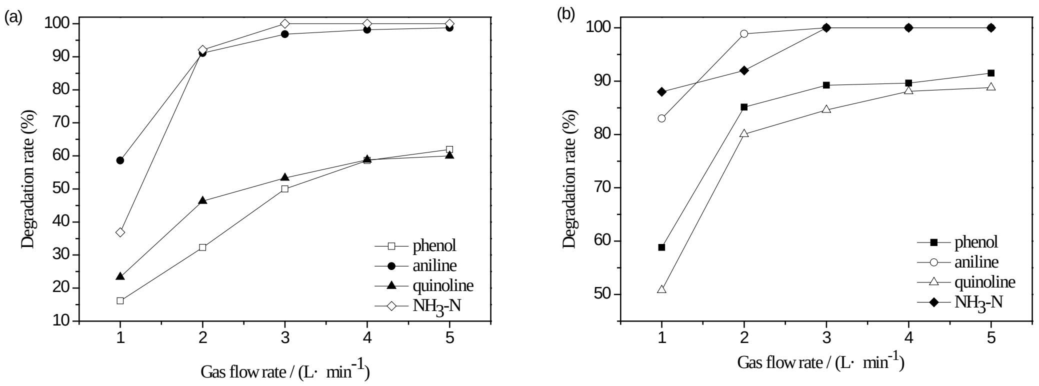


Fig. 3. Effect of gas flow rate on pollutants degradation in the O_3 process (a) and O_3/Fenton process (b).

(C_{O3} =30mg/L, R=1000rpm, pH=6.58, L=20 L/h, $C_{Fe(II)}$=0.4 mM/L, C_{H2O2}=6.5mM/L)

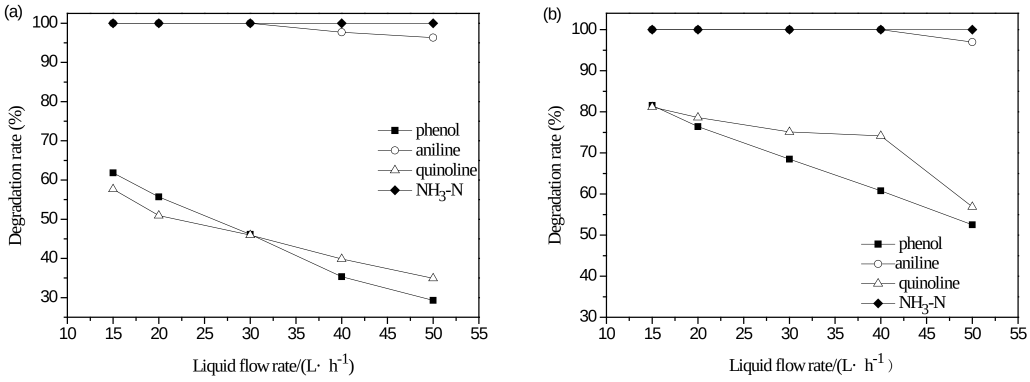
The effect of the gas flow rate on the B/C value in the O_3/Fenton process is given in Table 2, which shows that the B/C value at the gas flow rate of 300 L/h reached 0.43 and was higher than that at the gas flow rate of 150 L/h, indicating that the treated water is suitable for subsequent bio-treatment.

Table 2. Effect of gas flow rate on the B/C value in the O_3/Fenton process.

Gas flow rate	150 (L/h)	300 (L/h)
COD (mg/L)	418.7	366.8
BOD (mg/L)	159.1	157.7
B/C	0.38	0.43

3.3 Effect of liquid flow rate

The effect of liquid flow rate on the phenol, aniline, quinoline, NH_3-N removal in the O_3 and O_3/Fenton processes is presented in Fig. 4. It can be seen from Fig. 4(a) that the pollutants degradation rate decreased as the liquid flow rate increased. An increase in the liquid flow rate led to lower gas-liquid ratio, resulting in reduced ozone mass transfer into per volume liquid. In addition, higher liquid flow rate caused



larger liquid droplet size and shorter residence time of the liquid in the reactor.[14] All these were unfavorable for mass transfer between ozone and the liquid and consequently resulted in decrease in the removal rates of the pollutants.

Fig. 4. Effect of liquid flow rate on pollutants degradation in the O_3 process (a) and O_3/Fenton process (b).

(C_{O3} =30mg/L, R=1000rpm, pH=6.58, G=300 L/h, $C_{Fe(II)}$=0.4 mM/L, C_{H2O2}=6.5mM/L)

In order to maintain a reasonable throughput capacity, the suitable liquid flow rate was determined as 20 L/h in this study. Fig. 4 also demonstrates that the O_3 /Fenton process has better effect than the O_3 process with the degradation rates of phenol and quinoline reaching 76.4% and 78.63% respectively in the O_3 /Fenton process but 55.69% and 50.96% respectively in the O_3 process at the liquid flow rate of 20 L/h.

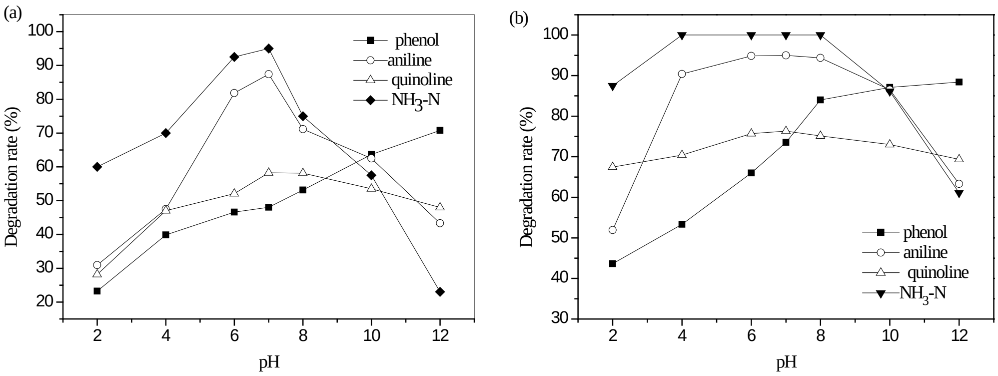
Table 3 gives the effect of the liquid flow rate on the B/C value and shows that the B/C value reached 0.43 at the liquid flow rate of 20 L/h in the O_3/Fenton process, indicating a high biodegradability.

Table 3. Effect of liquid flow rate on the B/C value in the O_3/Fenton process.

Liquid flow rate	20 (L/h)	50 (L/h)
COD (mg/L)	373.4	449
BOD (mg/L)	160.6	152.7
B/C	0.43	0.34

3.4 Effect of initial pH

The solution pH plays an important role in the reaction of organic compounds with ozone. The effect of initial pH on the phenol, aniline, quinoline, NH_3-N removal in the O_3 and O_3/Fenton processes is presented in Fig. 5, which indicates that the highest aniline, quinoline, NH_3-N degradation rates were attained at the initial pH 7 in both processes. At a lower pH, the scavenging effect of hydroxyl radicals by H^+ becomes obvious and H_2O_2 reacted with H^+ to form $H_3O_2^+$, leading to an improved stability of H_2O_2 and weakened degradation effect.[24] The pollutants degradation increased with a rising pH until 7 because the increase of hydroxyl ion concentration enhanced the formation of hydroxyl radical, a more active oxidant than ozone, through hydroxyl ion reaction with O_3.[15] In addition, the increase of pH to 7 in the O_3/Fenton process led to coagulation whereby the pollutants were also removed by



complexation reactions due to the conversion of Fe^{2+} and Fe^{3+} to $Fe(OH)_n$ type structures.[25]

Fig. 5. Effect of initial pH on pollutants degradation in the O_3 process (a) and O_3/Fenton process (b).

(C_{O3} =47mg/L, R=1000rpm, L=20L/h, G=300 L/h, $C_{Fe(II)}$=0.4mM/L , C_{H2O2}=6.5mM/L)

When the pH was higher than 7, the degradation of phenol constantly increased, while the degradation of aniline, quinoline, NH_3-N decreased with an increasing pH. The increasing phenol degradation rate can be explained by the reaction of phenol with more hydroxyl radicals induced by the increasing hydroxyl ion concentration. It is deduced that aniline and quinoline exist as the emprotid that is active and easy to react with hydroxyl ions in acidic condition, but they exist as stable molecules in basic condition, leading to a decreasing degradation rate with increasing pH[26].

It can be seen from Fig. 5 that the phenol, aniline, quinoline, NH_3-N degradation rates reached 70.78%, 87.41%, 58.25 % and 95.0% respectively at the initial pH of 7 in the O_3 process, while they increased to 88.39%, 94.97%, 76.31% and 100% respectively at the initial pH of 7 in the O_3 /Fenton process. These results confirmed that the O_3 /Fenton process has a higher efficiency for coking wastewater treatment.

The B/C values of the wastewater treated at different initial pH in the O_3 /Fenton process are given in Table 4, which indicates that the highest B/C value of 0.49 was attained at the pH 7. The natural pH of the simulated coking wastewater is 6.58, which is close to 7 and was chosen as a suitable pH because there was no need to adjust the pH of the wastewater with reagents.

Table 4. Effect of initial pH on the B/C value in the O_3/Fenton process.

pH	3	5	6	7	9	12
COD (mg/L)	424.3	419.5	400.1	386.6	422.4	426.5
BOD (mg/L)	148.5	155.2	176.2	190.2	167.2	153.5
B/C	0.35	0.37	0.44	0.49	0.40	0.36

3.5 Effect of Fe(II) concentration

The effect of Fe(II) concentration on the phenol, aniline, quinoline, NH_3-N removal in the O_3/Fenton process is presented in Fig. 6. It can be seen from Fig. 6 that the phenol, aniline, quinolone and NH_3-N degradation rates reached 100%, 100%, 95.68% and 100% respectively at the Fe(II) concentration of 0.4 mM/L in the O_3 /Fenton process. The combination of Fe (II) and hydrogen peroxide can promote the generation of hydroxyl radicals and improve the oxidation efficiency (eqs (3)-(12)). Therefore, the increase in Fe(II) concentration enhanced the formation of hydroxyl radicals, thus boosting coking wastewater degradation. However, when Fe(II) concentration exceeded 0.4 mM/L, hydroxyl radicals were consumed by the excess Fe(II) (eqs (13) and (14)), leading to a decrease in coking wastewater degradation efficiency. The optimum Fe(II) concentration was thus determined as 0.4 mM/L.

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (13)$$

$$Fe^{2+} + FeO^{2+} + 2H^+ \rightarrow 2\ Fe^{3+} + H_2O \quad (14)$$

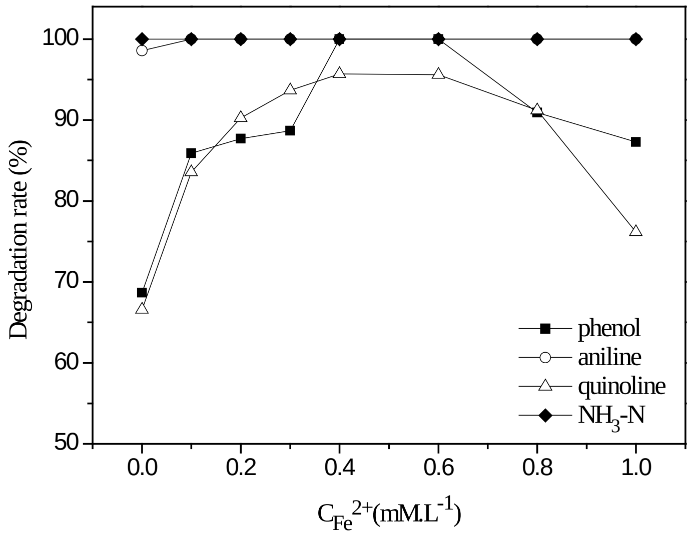


Fig. 6. Effect of Fe(II) concentration on pollutants degradation in the O_3/Fenton process.

(C_{O3} =47mg/L, R=1000rpm, pH=6.58, L=20L/h, G=300 L/h, C_{H2O2}=6.5mM/L)

Higher degradation rate and B/C value can be attained in the O_3/Fenton process due to the synergic effect of O_3 and Fenton reagent. Table 5 indicates that the B/C value reached 0.46 at the Fe(II) concentration of 0.4 mM/L, compared to 0.35 and 0.38 at the Fe(II) concentration of zero and 0.8 mM/L respectively, confirming that 0.4 mM/L was a suitable Fe(II) concentration.

Table 5. Effect of Fe(II) concentration on the B/C value in the O_3/Fenton process.

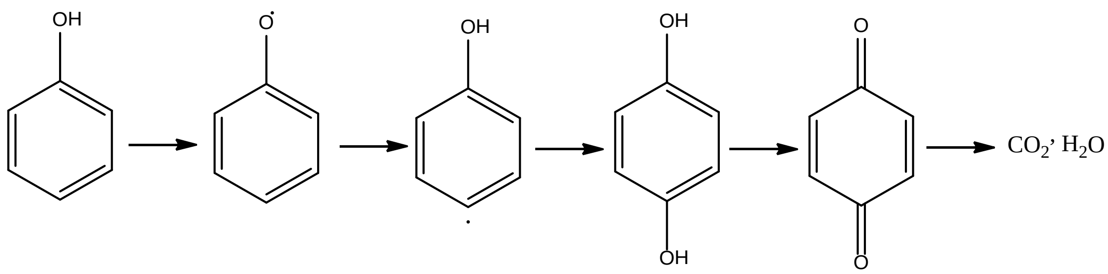
Fe(II) concentration	0	0.4 (mM/L)	0.8 (mM/L)
COD (mg/L)	440.6	392.6	418.8
BOD (mg/L)	154.2	180.6	159.1
B/C	0.35	0.46	0.38

3.6 Degradation pathways

The degradation pathways of the coking wastewater are complex and involve mainly the oxidative ring-opening reaction, nitration reaction, and so on. In the O_3/Fenton process, the Fenton reagent with Fe^{2+} and H_2O_2 can catalyze O_3 decomposition to produce hydroxyl radicals and thus improve the degradation efficiency of the coking wastewater significantly.

1) Phenol degradation pathway

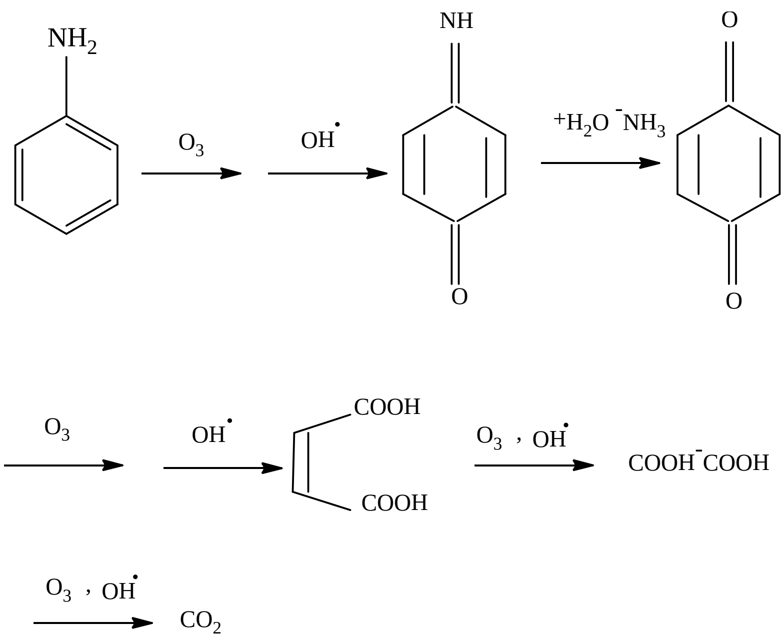
The mechanism of oxidative degradation of phenol is shown in Scheme 1. Intermediates are generated by the attack of hydroxyl radicals on phenol, and the main intermediate is hydroquinone. Then the generated quinone substances are further oxidized to form small molecular substances through ring-opening reaction and eventually converted into carbon dioxide and water. [27, 28]



(Scheme 1)

2) Aniline degradation pathway

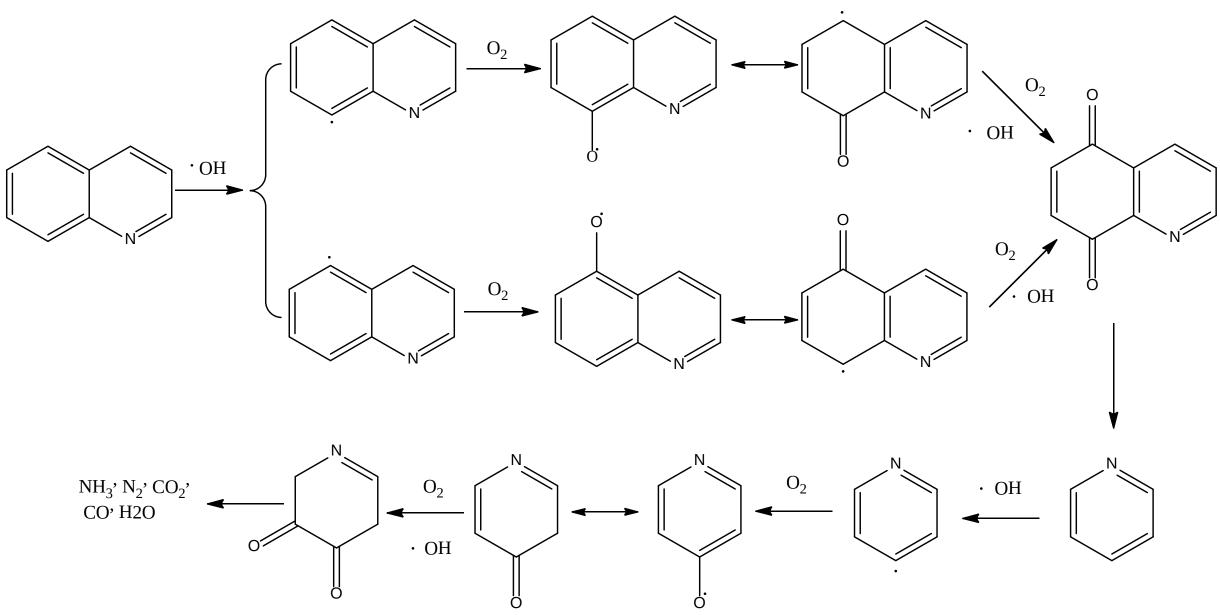
Aniline mineralization is initiated by the attack of O_3 and/or ·OH on aniline to yield mainly benzoquinonimine and some nitrobenzene. Þ-benzoquinone is subsequently produced by hydrolytic decomposition of benzoquinonimine. Further degradation of Þ-benzoquinone, as well as of nitrobenzene with release of NO_3^-, leads to the formation of maleic acid which is mineralized to CO_2[29, 30]. The mechanism of oxidative degradation of aniline is shown in Scheme 2.



(Scheme 2)

3) Quinoline degradation pathway

The mechanism of oxidative degradation of quinoline is shown in Scheme 3. Hydroxyl radicals attack preferentially C3 and C6 sites at the benzene ring to activate quinoline, which are quickly oxidized to form 5, 8-dicarbonyl quinolone. Aldehyde and acid are released through the ring-opening reaction of 5, 8-dicarbonyl quinolone, and by-products, mainly pyridine, are produced. With the attack of hydroxyl radicals and O_2 on pyridine, NH_3, N_2, CO_2, CO, H_2O and other small molecule compounds are generated. [31]



(Scheme 3)

4) NH_3-N degradation pathway

As shown in the following equations 15 and 16, NH_3 is removed by the reaction with O_3 and hydroxyl radicals, and N_2 and NO_3^- are produced. It is also found that hydroxyl radical concentration in the solution has a great influence on the degradation rate of NH_3-N. [32]

$$NH_3 + O_3 \rightarrow N_2 + H_2O \quad (15)$$

$$NH_3 + \cdot OH \rightarrow N_2 + H_2O + NO_3^- + H^+ \quad (16)$$

4. Conclusions

The degradation of simulated coking wastewater by the O_3/Fenton process in the RPB was investigated in this study. The O_3/Fenton process was compared with the O_3 process, and it is found that the O_3/Fenton process was more effective due to the synergistic effect of O_3 and Fenton. The optimum operating conditions for the degradation of phenol, aniline, quinoline and NH_3-N in the coking wastewater were determined as rotation speed of 1000 rpm, gas flow rate of 300 L/h, liquid flow rate of 20L/h, $C_{Fe(II)}$ of 0.4 mM/L, C_{H2O2} of 6.5 mM/L and pH of 6.58. Under these conditions, phenol, aniline, quinoline and NH_3-N removal rates in the O_3/Fenton process reached 100%, 100%, 95.68% and 100%, respectively, which are much higher than those in the O_3 process. The BOD_5/COD value of the simulated coking wastewater treated by the O_3/Fenton process reached 0.46 and was 135% higher than that treated by the O_3 process. It can be deduced that the O_3/Fenton process in an RPB is a feasible way to increase biodegradability in the treatment of coking wastewater.

Acknowledgments

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