Aldol condensation followed by ozonation to reduce phenolic compounds in coking wastewater

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Abstract. To treat the coking wastewater with phenolic compounds over 3000 mg/L, the biological method cannot be directly employed due to the toxicity to microorganisms and other methods are usually expensive. In this study, the aldol condensation followed by ozonation was developed to reduce the phenolic compounds in the wastewater from a coal coking plant in Gansu Province of China. For the aldol condensation reaction, the removal efficiency of phenolic compounds increases with increasing the molar ratio of formaldehyde to phenol (F/P), reaction time, reaction temperature, and acidity or alkalinity. Under alkaline conditions the removal efficiency of phenolic compounds is higher than under acid conditions. If the reaction temperature, reaction time, F/P and pH values of the aldol condensation are respectively 95°C, 3 hours, 2.0 and 10.5, the concentration of phenolic compounds decreases from 9018.3 mg/L to 1901.2 mg/L after precipitation separation of phenolic resins. Subsequently adjusting the pH value to 7 further reduces the concentration of phenolic compounds to 764.7 mg/L. Thereafter 2 hours ozonation further reduces the concentration of phenolic compounds to 22 mg/L, resulting in total removal efficiency of 99.75%. The ozonation removes phenolic compounds with methyl/ethyl substituent on benzene ring easier than phenol.

1. Introduction
The coking wastewater pollution has been cared about by more and more people. It is generated from the coal coking, coal gasification, production of refined benzene and by-product recovery processes [1]. It is a complex mixture of hazardous and toxic organic compounds, with high concentration of phenol, cyanide, thiocyanate, polycyclic aromatic hydrocarbons, heterocyclic compounds and ammonia nitrogen. Most of these compounds are difficult to be degraded [2]. Among these pollutants, phenolic compounds account for 80% of chemical oxygen demand (COD) and 60% of total organic carbon (TOC), which has strong negative impacts on environment and human's life [3]. In particular, phenolic compounds are lethal to most creatures even at very low concentrations because they can make cells lose vitality, coagulate proteins, and cause tissue damage and necrosis [4]. Hence, to remove phenolic compounds from the coking wastewater is crucial.

Currently, some treatment methods including physical, chemical and biological processes have been developed to remove phenolic compounds. The adsorption, extraction, distillation and membrane
separation are prevalent physical treatments for removing phenolic compounds [5]. But the adsorption may induce the risk of secondary pollution such as the burning of natural adsorbent and the treatment of resins, and the inhibition may occur at high concentration of phenolic compounds [6]. For the extraction process, the mixing, emulsification and loss of solvent are urgent problems to be solved [7]. Both the distillation and the membrane separation need expensive operating cost. Chemical methods mainly include oxidation treatments such as electrochemical oxidation, Fenton oxidation, advanced oxidation, and ozonation. The Fenton oxidation faces the safety problem of hydrogen peroxide and the corrosion of ferrous sulphate. The electrochemical and advanced oxidation need relative high materials cost [8]. In comparison, ozone is a powerful oxidant which can effectively assault the initial molecular structure of organics containing conjugated double bonds or aromatic rings [9]. In the ozonation process, the only secondary pollution may result from the catalyst. Once the catalyst is used, the cost and life of catalyst should also be considered. Therefore, it is worth investigating the efficiency of direct ozonation to reduce phenolic compounds in absence of catalyst. For the biological method, the enzymatic treatment and activated sludge systems are widely used. But the coking wastewater contains so high concentration of phenolic compounds (generally over 3000 mg/L) that most of microorganisms cannot survive. Thus, the commonly used biological method cannot be directly used to treat the coking wastewater [10]. Even if the concentration of phenolic compounds is very low, the most contentious issue of enzymatic treatment is inefficient because of enzyme inactivation [11]. The competitive microorganism in activated sludge systems grows rapidly, and a large majority of helpful microorganisms cannot survive. Therefore, the coking wastewater without removing phenolic compounds cannot directly enter the activated sludge system [12].

In this study, the aldol condensation followed by the ozonation method without catalyst was adopted as an effective way to reduce the phenolic compounds in coking wastewater. The combination of the two methods has some advantages. The pre-treatment of coking wastewater containing high concentration of phenolic compounds by the condensation with formaldehyde can not only achieve good removal effect, but also be economic and simply operated. In addition, the catalyst can be a hydroxide anion in aldol condensation [13]. The coking wastewater is generally alkaline which is favourable to the condensation. Additionally, the ozonation can further reduce the concentration of phenolic compounds and remove the excess formaldehyde in the reaction system. The direct ozonation reaction without catalyst avoids the problems of catalyst failure and secondary pollution.

2. Experimental

2.1. Materials and instrument

The quality analysis results of the coking wastewater produced by a coal coking plant in GanSu Province, China are listed in Table 1, containing high content of COD, phenolic compounds, NH$_3$-N and small amounts of metal ions such as Na$^+$, Ca$^{2+}$, K$^+$ and Mg$^{2+}$.

| Water quality | pH | COD  | Ammonia nitrogen | Total nitrogen | Total sulfide | Total cyanide | Total phenol | Na$^+$ | Mg$^{2+}$ | K$^+$ | Ca$^{2+}$ |
|---------------|----|------|------------------|----------------|--------------|---------------|--------------|--------|----------|--------|----------|
| Value (mg/L)  | 9.0| 7.1×10$^4$ | 527 | 1.2×10$^3$ | 111 | <0.004 | 9018.3 | 5.3×10$^3$ | 0.8 | 2.0 | 2.3 |

The samples were filtered through a 0.45 micron syringe filter prior to all measurements. The metal ions in coking wastewater were determined by ICP-MS (inductively coupled plasma mass spectrometry, ICP-MS-2030, Shimadzu). The concentration of phenolic compounds in the wastewater were determined by 4-aminoantipyrine colorimetry and measured by a UV-vis spectrophotometer (ultraviolet–visible spectroscopy, Lambda 25, PerkinElmer) [14]. The COD value was calibrated via the potassium dichromate method (HJ828-2017, China), using a COD testing instrument (DR1010, HACH) [15]. The pH value of gastric juice was measured by a pH meter (PB-10, Sartorius). All
reagents were purchased from Aladdin Chemical Co. Ltd., in which dichloromethane reagent is chromatographically pure, while others are analytical grade.

2.2. Removal of phenolic compounds with formaldehyde

Acid condition: A certain amount of hydrochloric acid was added to 200 mL coking wastewater to adjust the pH value < 7, then the mixed solution was put into a port flask and was heated to 70 °C. Thereafter, a certain amount of formaldehyde solution was added. Meanwhile the temperature gradually rose to 80 °C at the rate of 2 °C/min. 30 minutes later the system was heated to the reaction temperature and maintained for several hours. At the end, the concentration of phenolic compounds in the clear liquid was measured after the reaction products were centrifuged and filtered. In order to optimize the reaction conditions, a series of experiments were carried out by changing the molar ratio of formaldehyde to phenol (F/P), the reaction time and temperature, and pH.

Alkali condition: The experimental method of alkali-catalyzed reaction was similar to that in acid-catalyzed condition, just replacing hydrochloric acid with ammonia water as catalyst.

2.3. Removal of phenolic compounds with ozone

The residual phenolic compounds were further treated by continuous ozonation process using a 200 mL one-necked flask as an ozonation reactor containing 100 mL coking wastewater treated by aldol condensation. The ozone was generated by a corona discharge ozone generator (AKO-5G, Qingdao, China) using pure oxygen as feed gas. The concentration of ozone in the ozonized gas was adjusted by the gas flow rate and the discharge current in the ozonation cell. After ozone concentration stabilized within 5 min, started timing for the experiment. The flow rate of oxygen gas was 500 mL/min and the power of the ozonator was 50 Hz. The continuous ozonation process lasted for 240 min for all experiments. During the ozonation, 2 mL of the sample was taken out from the sampling port every 60 min for measuring the concentration of phenolic compounds.

The samples before and after ozonation were extracted by dichloromethane, and then the liquid phase was separated, dried and purified with anhydrous sodium sulfate. Finally, the organic phase was concentrated to 2 mL by the rotary evaporator for analysis. All prepared samples were analyzed by a GC-MS instrument (gas chromatography-mass spectrometer, Agilent 7890A/5975C) equipped with a HP-INNOWAX capillary column (50 m × 0.25 mm × 0.25 μm). The analysis conditions were as follows. The flow rate of the carrier gas (He) was 1 mL/min. The temperature of gasification compartment was maintained at 280 °C. The temperature of the MS ion source was 200 °C with electron energy of 70 eV. After sample injection, the temperature of oven was increased from 60 °C to 300 °C with an increment of 5 °C/min and maintained for 10 min.

3. Results and discussion

3.1. The removal efficiency of phenolic compounds by aldol condensation

Figure 1 illustrates the effects of processing parameters on the removal efficiency of phenolic compounds that is the amount of removed phenolic compounds divided by the amount of phenolic compounds before treatment. Generally the removal efficiency under alkali catalysis is significantly higher than that under acid catalysis. In figure 1(a) the F/P value is set to be 1, 2, 3 and 4 respectively since F/P is usually in the range of 0.5 - 4.5 [16]. Whether under the condition of acid catalysis or alkali catalysis, the removal efficiency increases with increasing the F/P value. Further With the increase of formaldehyde, the removal efficiency of phenolic compounds by acid catalysis increases more than by alkali catalysis. As the F/P value increases from 2 to 3, the removal efficiency rises from 62.4% to 66.4% with pH=2 and from 78.9% to 80.4% with pH = 10.5. When the F/P value equals 4, the removal efficiency is highest for both pH=2 and pH=10.5. However, for engineering applications the F/P value is not proper to be 1 or 4. If F/P is no more than one the aldol condensation hardly produce the phenolic resin with network structure which is easy to precipitate [17]. In addition, formaldehyde is a strong carcinogen and its excessive addition can bring secondary pollution to coking
wastewater and increase the COD value. Therefore, the F/P of 3 is suggested for the reaction under acid catalysis and the F/P of 2 is reasonable to be selected under alkali catalysis. In figure 1(b) the removal efficiency increases by prolonging the reaction time. However, if the reaction time increases from 3 to 4 hours, the removal efficiency at pH=10.5 hardly increases. Therefore, it is practical to select the reaction time of 3 h. In figure 1(c) the removal efficiency increases as the temperature rises. When pH=10.5 and the reaction temperature rises from 90 °C to 95 °C, the removal efficiency increases slightly. Since the boiling point of water is 100 °C and higher temperature may cause higher energy consumption, it is appropriate to choose 95 °C as the reaction temperature. In figure 1(d) the removal efficiency increases with increasing the acidity or alkalinity. The acid catalyst promotes dehydration of hydroxymethylphenols to generate hydroxybenzyl positive ions which react with phenol, resulting in the linkage between the two phenols by methylene bridge. Under acid catalysis, the reaction rate of methylene activation of formaldehyde is faster than that of hydroxymethylation to form linear thermoplastic phenolic resin [18]. The alkali catalyst can accelerate the rate of hydroxymethylation and thermosetting phenolic resin can be formed [19]. It should be noted that in coking plant in China, ammonium hydroxide is commonly used to cool coke oven gas, which leads to the coking wastewater being strongly alkaline. Because the coking wastewater itself contains ammonia, the ammonia water is used as catalyst to avoid introducing other alkalis into the wastewater. Since the pH value is hard to exceed 10.5 except that the volume of ammonium water is more than half of the volume of wastewater, the pH value controlled at 10.5 is an efficient and economical way.

![Figure 1. Removal efficiency of phenolic compounds versus processing parameters.](image)

Therefore, the proper conditions are as follows: the reaction temperature, reaction time, F/P and pH values are 95 °C, 3 hours, 2.0 and 10.5 respectively. Under these conditions, the concentration of phenolic compounds decreases from 9018.3 mg/L to 1901.2 mg/L after aldol condensation. In industry in order to recycle ammonia and reduce ammonia nitrogen, the coking wastewater will undergo an ammonia distillation process until the pH value is close to 7. In this study adjusting the pH value to 7 by adding hydrochloric acid further reduces the concentration of phenolic compounds from 1901.2 mg/L to 764.7 mg/L because more phenolic resins precipitate, resulting in the final removal efficiency
of 91.52% by the condensation. The wastewater containing 764.7 mg/L phenolic compounds is further treated by the ozone oxidation method, which is described below.

### 3.2. Further phenolic compounds removed by ozone oxidation

Table 2. The removal efficiency of phenolic compounds by ozone oxidation.

| Reaction time (h) | Concentration of phenolic compounds (mg/L) | Removal efficiency of phenolic compounds (%) |
|------------------|-------------------------------------------|---------------------------------------------|
| 1                | 61.8                                      | 91.92                                       |
| 2                | 22.4                                      | 97.07                                       |
| 3                | 21.4                                      | 97.20                                       |
| 4                | 20.7                                      | 97.29                                       |

Table 3. The organic components in wastewater treated by ozonation with different reaction times.

| No. | Matching substances     | Relative percentage (wt.%) | Concentration (mg/L) |
|-----|-------------------------|-----------------------------|----------------------|
|     |                         | 0 hour | 1 hour | 2 hours | 0 hour | 1 hour | 2 hours |
| 1   | Phenol                  | 16.82  | 16.46  | 11.75   | 561.18 | 53.86  | 22.40   |
| 2   | 2-methyl-phenol         | 1.38   | 0      | 0       | 46.04  | 0      | 0       |
| 3   | 4-methyl-phenol         | 4.13   | 1.78   | 0       | 137.79 | 5.81   | 0       |
| 4   | 4-ethyl-phenol          | 0.37   | 0.65   | 0       | 12.34  | 2.13   | 0       |
| 5   | 2,3-dimethyl-phenol     | 0.22   | 0      | 0       | 7.34   | 0      | 0       |
| 6   | Acetic acid             | 12.59  | 21.18  | 30.90   | 420.05 | 69.30  | 58.92   |
| 7   | Propanoic acid          | 2.84   | 9.31   | 14.07   | 94.75  | 30.45  | 26.84   |
| 8   | 2-methyl-propanoic acid | 0.38   | 0      | 0       | 12.68  | 0      | 0       |
| 9   | Butanoic acid           | 2.82   | 6.18   | 7.81    | 94.09  | 20.22  | 14.89   |
| 10  | 2-methyl-2-propenoic acid| 1.21  | 0      | 0       | 40.37  | 0      | 0       |
| 11  | Pentanoic acid          | 1.48   | 1.65   | 1.95    | 49.38  | 5.41   | 3.72    |
| 12  | 2,2-dimethyl-propanoic acid| 0.61 | 0      | 0       | 20.35  | 0      | 0       |
| 13  | Hexanoic acid           | 0.57   | 1.03   | 1.03    | 19.02  | 3.35   | 1.97    |
| 14  | Octanoic acid           | 1.31   | 0      | 0       | 43.71  | 0      | 0       |
| 15  | n-nonanoic acid         | 0.27   | 0      | 0       | 9.01   | 0      | 0       |
| 16  | Benzoic acid            | 39.7   | 17.67  | 15.17   | 1324.55| 57.82  | 28.94   |
| 17  | 3-methyl-benzoic acid   | 5.22   | 5.83   | 0       | 174.16 | 19.06  | 0       |
| 18  | 3,4-dimethyl-benzoic acid| 2.47  | 0      | 0       | 82.41  | 0      | 0       |
| 19  | Acetamide               | 1.25   | 3.63   | 4.52    | 41.70  | 11.89  | 8.62    |
| 20  | Propanamide             | 0.82   | 0.67   | 0.98    | 27.36  | 2.19   | 1.87    |
| 21  | Methenamine              | 3.54   | 13.96  | 11.82   | 118.11 | 45.66  | 22.54   |

The result of ozone oxidation is shown in Table 2. The removal efficiency of phenolic compounds increases with increasing the oxidation reaction time. If the reaction time is prolonged from 1h increased to two hours, the removal efficiency increases by 5.15%. But as the reaction time extends from two hours to three hours the removal efficiency only enhance by 0.13%, implying that the
reaction time is appropriate to be two hours. After 2 hours ozonation reaction, the concentration of phenolic compounds decreases from 764.7 to 22.4 mg/L, which means that the residual phenolic compounds after the condensation further reduce by 97.07% with ozonation and the total removal efficiency reaches 99.75%.

The relative percentages and estimated concentrations of organic components are listed in Table 3. The substance and its relative percentage are characterized by GC-MS. The estimated concentration of each substance is the product of the concentration of phenolic compounds and its relative percentage divided by the sum relative percentage of phenolic compounds. The m-methylphenol, p-methylphenol and p-ethylphenol are completely removed after 2 hours ozonation, in accord with that the phenolic compounds containing electron repellent group have higher ozonation rate than that containing electron acceptor group [20]. In addition, other substances are also reduced significantly by direct ozonation. However, carboxylic acids still exist in the treated wastewater and need further treatment.

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