

# **The organic pollutant characteristics of Lurgi coal gasification wastewater before and after ozonation**

**Chunrong Wang, Qi Zhang, Longxin Jiang, Zhifei Hou**

*School of Chemical and Environmental Engineering, China University of Mining and Technology*

*(Beijing), Beijing 100083, China*

Correspondence should be addressed to C.R. Wang; [wcrzgz@126.com](mailto:wcrzgz@126.com)

## **Experimental details**

### *Pretreatment of resins*

Before testing for resin fractionation, Amberlite XAD-8 nonionic resin, Dowex50WX2 ( $\text{H}^+$  cation exchange) and Amberlite IRA-958 ( $\text{Cl}^-$  anion exchange) were rinsed three times in alternating  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl. The three resins were then Soxhlet-extracted with methanol for 24 h to remove the organic matter. Following Soxhlet-extraction, the resins were dipped in Milli-Q water. The

subsequent rinse steps were as follows.

(1) XAD-8: 10 mL (wet volume) of XAD-8 resin were added into the glass column, after which Milli-Q water was added until the liquid level exceeded that of the resins. The XAD-8 resin was then rinsed three times, alternating  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl each time, after which Milli-Q water was added into the glass column until the TOC of the leachate was consistent with that of the Milli-Q water.

(2) Dowex50WX2: 10 mL (wet volume) of Dowex50WX2 resin was added into the glass column and rinsed three times, alternating  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl each time. Milli-Q water was then added into the glass column until the TOC of the leachate was consistent with that of Milli-Q water. The Dowex50WX2 was then rinsed with about 100 mL  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{H}_3\text{PO}_4$  to transform it into a saturated acid group state. Finally, the resin was rinsed with Milli-Q water until the leachate pH was approximately neutral.

(3) Amberlite IRA-958: 10 mL (wet volume) of IRA-958 resin was added into the glass column and rinsed three times, alternating  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl and  $1 \text{ mol}\cdot\text{L}^{-1}$   $\text{NH}_4\text{OH}$  each time, after which Milli-Q water was added into the glass column until the TOC of acerbic leachate was consistent with that of Milli-Q water. The IRA-958 was then rinsed with about 100 mL  $1 \text{ mol}\cdot\text{L}^{-1}$   $\text{NH}_4\text{OH}$  to transform into a saturated basic group state. Finally, the resin was rinsed with Milli-Q water until the leachate pH was approximately neutral.

*Organic matter fractionation procedure*

The organic matter fractionation procedure included the following steps: after the raw water was passed through a 0.45  $\mu\text{m}$  cellulose membrane, the solution pH was adjusted to 10, then flowed through the XAD-8 resin column slowly. The dissolved organics that were adsorbed onto the XAD-8 resin were hydrophobic organic bases (HoB). The elution process was conducted with 100 mL 0.1 mol·L<sup>-1</sup> HCl. Similarly, the sample was acquired through a XAD-8 resin column, after which the solution pH was adjusted to 2. The dissolved organic material that remained on the resin after the water sample flowed through the column was hydrophobic organic acid (HoA). The elution process was conducted with 100 mL 0.1 mol·L<sup>-1</sup> NaOH. When the elution was completed, the resin was air dried for 12 h, then extracted. The hydrophobic organic neutral (HoN) fraction was then extracted from the resin with a Soxhlet extractor over 24 h, after which the excess methanol was removed by vacuum evaporation at 40°C and the sample was then diluted with Milli-Q water to 100 mL. The water samples were passed through the XAD-8 resin for a second time, then through the Dowex50 resin, which absorbed the hydrophilic bases (HiB). The elution process was subsequently conducted with 100 mL 0.1 mol·L<sup>-1</sup> NaOH, after which the samples were passed through IRA985 resin and the hydrophilic neutral (HiN) contents were acquired while the hydrophilic acid (HiA) remained on the resin. The elution process was also conducted with 100 mL 0.1 mol·L<sup>-1</sup> NaOH.

Figure 1S shows the degradation of COD and the removal of chromaticity during ozonation. In the first 60 min, the degradation of COD in ozonation was around 8.07%, and the removal of chromaticity was similar to that of COD. After 60 min, the degradation of COD and the removal of chromaticity increased quickly. In 120 min, the degradation of COD reached 30.45%, while the removal of chromaticity reached 68.40%. The results indicated that chroma was removed effectively by ozonation, but only slight COD degradation occurred. Because of the dipole structure, ozone only

destroyed the double bonds in the organic molecules. Therefore, the high molecular weight organics were only degraded to small organics, which led to the slight degradation of COD.

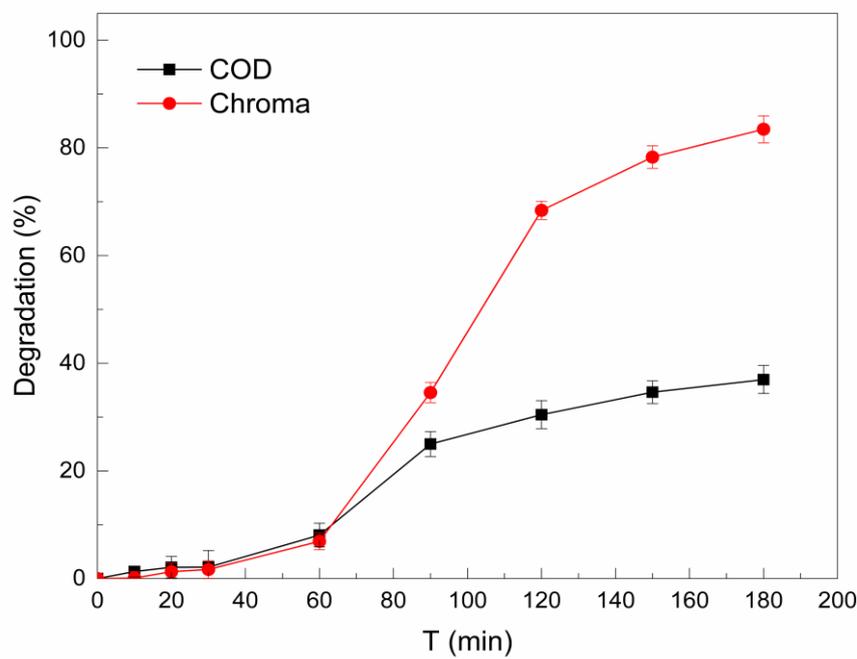


FIGURE.1S: Relationship between ozonation effect and reaction time.

The effectiveness of ozonation under a wide range of pH (from acidic to alkaline) was optimized because pH is one of the most important factors influencing its effects. Under acidic conditions, the direct oxidation of ozone was the primary oxidation pathway, which was quite slow. However, under high pH conditions, this direct oxidation promoted the decomposition of ozone and generation of  $\cdot\text{OH}$ , which quickly reacted with organic matter. As the real wastewater, the pH in the samples was usually influenced by existing  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . The presence of inorganic anions as

hydroxyl radical scavengers could effectively inhibit the degradation of organic compounds by ozonation and catalytic ozonation. Under low pH conditions, the decomposition of anions effectively enhanced the removal of COD. Therefore, the degradation of COD at pH=4 was higher than the degradation of COD at pH=7. Under high pH conditions, the anions were not decomposed, which inhibited the degradation of COD. Accordingly, the degradation of COD at pH=7 was higher than that at pH=9 and 11.

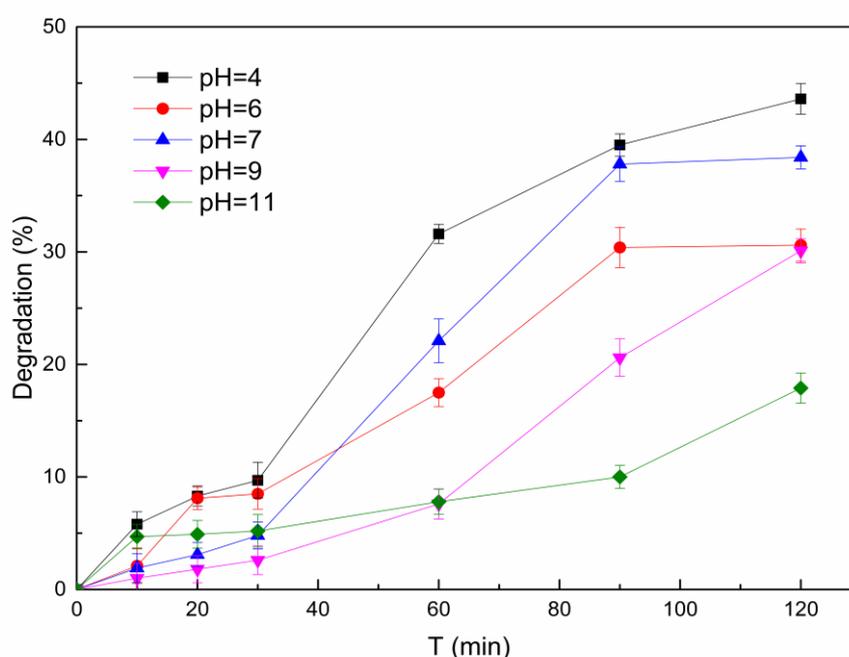


FIGURE.2S: Influence of pH on COD removal.

Ozone, which is one of the most important elements in the ecosystem, can directly oxidize or be decomposed to produce  $\cdot\text{OH}$  for indirect oxidation to remove organic materials in the wastewater. Even though increased dosages of ozone were provided, the degradation of COD was not better. During the initial reaction stage, as the dosage of ozone increased, COD removal by ozonation was significantly enhanced. As shown in Figure 3S, the degradation of COD at an ozone level of 1.6

g/h was 28.92%, which was higher than under other conditions in the first 60 min. However, as the dosage of ozone increased, the removal of COD changed slightly in response to different dosages after 60 min. During actual wastewater treatment, when the ozone concentration reaches equilibrium additional ozone does not enhance the degradation, which causes a great waste of ozone. Thus, 1.02 g/h was selected as the optimum ozone level.

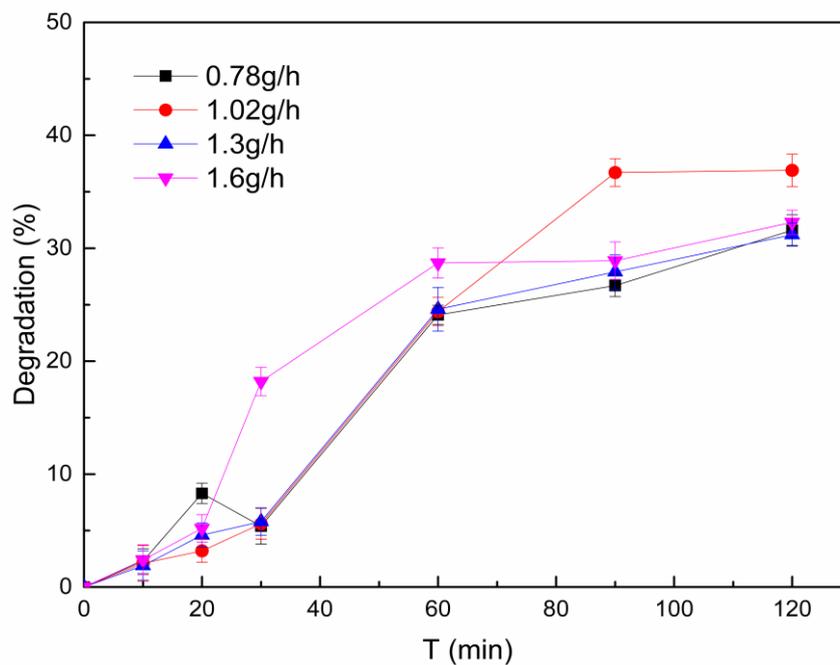


FIGURE.3S: Influence of ozone dosage on COD removal.

Ventilation influenced the removal of COD, primarily from the following two aspects. When the concentration of ozone was constant, gas flux increased the dosage of ozone, thereby promoting the degradation of organic materials. However, when ventilation levels were exorbitant, the bubbles were quickly distributed in the wastewater and the ozone did not have a chance to completely dissolve, resulting in

ozone dissipation. As shown in Figure 4S, ozonation significantly enhanced degradation of organic compounds from 19.42% to 40.13% at ventilation levels of 1 L/min to 3 L/min. However, increasing the ventilation caused the efficiency of aeration to rapidly decline, resulting in the degradation of COD decreasing to 34.20% at 4 L/min. Thus, 3 L/min was selected as the optimum condition for ventilation.

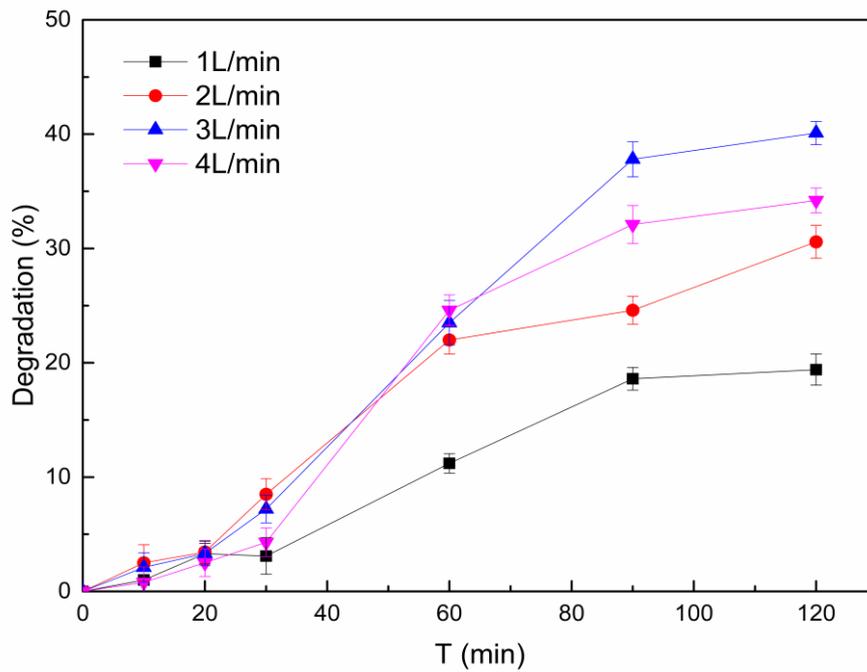


FIGURE.4S: Influence of aeration on COD removal rate.