Comparison between UV and VUV photolysis for the pre- and post-treatment of coking wastewater

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ABSTRACT

In this study, ultraviolet (UV) and vacuum ultraviolet (VUV) photolysis were investigated for the pre-treatment and post-treatment of coking wastewater. First, 6-fold diluted raw coking wastewater was irradiated by UV and VUV. It was found that 15.9%–35.4% total organic carbon (TOC) was removed after 24 hr irradiation. The irradiated effluent could be degraded by the acclimated activated sludge. Even though the VUV photolysis removed more chemical oxygen demand (COD) than UV, the UV-irradiated effluent demonstrated better biodegradability. After 4 hr UV irradiation, the biological oxygen demand BOD$_5$/COD ratio of irradiated coking wastewater increased from 0.163 to 0.224, and its toxicity decreased to the greatest extent. Second, the biologically treated coking wastewater was irradiated by UV and VUV. Both of them were able to remove 37%–47% TOC within 8 hr irradiation. Compared to UV, VUV photolysis could significantly improve the transparency of the bio-treated effluent. VUV also reduced 7% more ammonia nitrogen (NH$_4^+$–N), 17% more nitrite nitrogen (NO$_2^-$–N), and 18% more total nitrogen (TN) than UV, producing 35% less nitrite nitrogen (NO$_3^-$–N) as a result. In conclusion, UV irradiation was better in improving the biodegradability of coking wastewater, while VUV was more effective at photolyzing the residual organic compounds and inorganic N-species in the bio-treated effluent.

Introduction

Coke plays an important role in iron and steelmaking; there are many coke plants throughout China. Pollution caused by coking wastewater is a serious problem throughout the world, especially in China. This wastewater contains high concentrations of phenolic compounds and toxic contaminants, such as ammonia, cyanide, polycyclic aromatic hydrocarbons (PAHs), nitrogen heterocyclic compounds (NHCs), etc. (Luthy et al., 1983; Qian et al., 1994). Even after biological treatment, the water quality usually cannot meet discharge standards, i.e., the Integrated Wastewater Discharge Standard (GB8978-1996) and the Emission Standard of Pollutants for Coking Chemical Industry (GB 16171-1996) (Feng et al., 2005). In addition, China issued a new discharge standard in 2012, the Emission Standard of Pollutants for Coking Chemical Industry (GB 16171-2012), which is more stringent and requires plants not to drain, but to reuse the treated coking wastewater instead.

With regard to advanced oxidation technologies (AOTs), the physicochemical technology of ultraviolet (UV 254 nm) and vacuum ultraviolet (VUV 185 + 254 nm) photolysis has shown advantages in the elimination of toxic contaminants existing in coking wastewater, such as phenol (Alapi and Dombi, 2007; Alapi et al., 2008), quinoline and isoquinoline (Zhu, 2007; Zhu et al., 2009), and does not require additional chemicals. Al-Momani et al. (2002) successfully used VUV photolysis in the pre-treatment of textile dyes and practical textile wastewater. Buchanan et al.
(2005, 2008) compared the potential of UV and VUV for the removal of natural organic matters (NOMs) in drinking water, probed into the mechanisms, and examined the effect of VUV-BAC (biologically activated carbon column) treatment. They found that VUV irradiation was more effective than UV irradiation prior to biological treatment for the removal of NOMs due to rapid formation of biodegradable compounds and mineralization. In our lab, we employed two-stage anoxic–oxic biofilm reactors to treat coking wastewater and applied UV (254 nm) and VUV (185 + 254 nm) to irradiate the effluent separately (Xing et al., 2012). VUV was found more effective than UV in reducing the residual organic compounds and inorganic nitrogen compounds in the bio-treated effluent (Xing et al., 2012; Zoschke et al., 2014).

In order to determine whether and how UV or VUV photolysis could be employed in coking wastewater treatment, in this study UV and VUV were investigated for the pre-treatment and post-treatment of coking wastewater. The research objective is to assess the feasibility of this technology and to identify which one is more suitable for pre- or post-treatment.

1. Materials and methods

1.1. Wastewater and sludge

The raw coking wastewater and coking activated sludge were collected from a coking factory in Hebei Province, northern China. The wastewater was dark brown with obnoxious odor. The sludge was further cultivated and acclimated to the coking wastewater. After pre-study, 6-fold diluted coking wastewater was used as the influent in this study. Table 1 lists the characteristics of the influent.

In order to use UV and VUV as the post-treatment, biologically treated coking wastewater was generated by a biofilm reactor system (Xing et al., 2012). The characteristics of the bio-treated coking wastewater are detailed in Table 1.

1.2. Experimental setup

Fig. 1 shows the batch photolysis reactors, which were two cylindrical vessels made of glass with the same diameter of 60 mm, length of 200 mm and effective volume of 0.4 L. The reactors were equipped with two lamps with identical physical dimensions: UV lamp with main wavelength of 254 nm, and vacuum UV lamp with wavelengths of 254 nm (95%) and 185 nm (5%). Their power densities were respectively 18.5 × 100 μW/cm² and 29.5 × 100 μW/cm². Each lamp was fixed at the center of a photolysis reactor with a quartz tube protective jacket. Both reactors were covered with aluminum foil for UV safety.

1.3. Photolysis experiments

VUV and UV lights were applied separately to photolyze the diluted raw coking wastewater as pre-treatment and the bio-treated coking wastewater as advanced treatment. In each experiment, 250 mL wastewater was added to a photolysis reactor, and mixed and aerated by air (DO, 4–5 mg/L) during the irradiation. Samples were obtained at intervals and analyzed promptly.

1.4. Degradation experiments

The 6-fold diluted coking wastewater was first irradiated by UV or VUV for 24 hr. Then the irradiated effluents were degraded by the acclimated activated sludge in shaking flasks. The volume ratio of the effluent and the sludge was 100:20 (V/V). Both flasks were shaken in a rotator at 110 r/min and 25°C, and sampled at 24 hr and 48 hr for COD analysis.

### Table 1 – Characteristics of the coking wastewater.

<table>
<thead>
<tr>
<th>Water quality index</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>TOC (mg/L)</th>
<th>NO$_3^-$N (mg/L)</th>
<th>NO$_2^-$N (mg/L)</th>
<th>NH$_4^+$N (mg/L)</th>
<th>TN (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6× diluted raw coking wastewater</td>
<td>8.3–8.8</td>
<td>262.7–452</td>
<td>78.6–99.3</td>
<td>1.6–1.9</td>
<td>0.04–0.5</td>
<td>30.8–50.2</td>
<td>69.8–76.7</td>
</tr>
<tr>
<td>Bio-treated coking wastewater</td>
<td>7.3–7.6</td>
<td>40–60</td>
<td>11.7–18.6</td>
<td>0.1–0.8</td>
<td>7.4–26.8</td>
<td>16.4–38.9</td>
<td>32.7–53.8</td>
</tr>
</tbody>
</table>
1.5. Analytical methods

COD was determined according to the standard methods (APHA, 1998) with a COD analyzer (HACH, USA). Ammonia nitrogen (NH₄⁺-N), nitrite nitrogen (NO₂⁻-N), nitrate nitrogen (NO₃⁻-N), total nitrogen (TN) and biological oxygen demand for 5 days (BOD₅) were detected according to the Chinese National Standard methods (APHA, 1998). DO was examined by a Portable dissolved oxygen probe (Thermo, USA) probe. TOC analysis was performed on a TOC analyzer (Shimadzu, Japan). The Ultraviolet-visible spectroscopy (Shimadzu, Japan) spectra of the samples were recorded, i.e., the absorbances from 200 nm to 400 nm were detected after different irradiation times. The acute toxicity of the wastewater was assessed by triphenyl-tetrazolium chloride (TTC) dehydrogenase activity (DHA) tests (Yu et al., 2005).

2. Results and discussion

2.1. Pre-treatment of the diluted coking wastewater by UV and VUV irradiation

Fig. 2 displays the TOC variation throughout UV and VUV photolysis. 15.9%–35.4% of TOC was removed after 24 hr irradiation. UV photolysis reached its stable stage after 4 hr. VUV was more effective than UV, as the TOC removal efficiency improved as much as about 20% after 8 hr VUV irradiation. Fig. 3 shows the variations of UV-Vis spectra of wastewater after UV and VUV irradiation. It can be observed that the absorption peaks at 210–230 nm and 270 nm became weaker along with the irradiation time, which indicated that the phenolic organics were decomposed during the photolysis (Wang et al., 2008). Comparing the samples’ absorbance after UV or VUV photolysis, VUV produced effluent with lower absorbance, which was consistent with the TOC removal results.

After photolysis, the irradiated wastewaters were employed in a biodegradation experiment and biodegradability analysis.

As shown in Fig. 4, even though the VUV photolysis removed more COD than UV, the UV-irradiated wastewater could be better degraded by the acclimated activated sludge. The BOD₅/COD ratio in Fig. 5 also demonstrated that UV-irradiated wastewater had better biodegradability after 4 hr and 12 hr irradiation, as the ratio increased from 0.163 to 0.224 and 0.241.
When Al-Momani et al (2002) applied VUV photolysis in the biodegradability enhancement of textile wastewater, its BOD5/COD ratio increased up to 0.22. Although the BOD5/COD ratio did not reach 0.4, a value usually considered as the threshold of being readily biodegradable, this kind of technology can also achieve the abatement of COD or TOC.

Besides biodegradability, toxicity was another indicator to evaluate the characteristics of irradiated wastewater in this study. In the DHA test, triphenyl formazan (TF) could be produced from TTC, and generally, the DHA was positively correlated with the TF absorbance (Kim et al., 1994). Fig. 6 shows the TF absorbance of UV and VUV-irradiated wastewater. In general terms, the DHA of VUV-irradiated coking wastewater decreased as the irradiation time increased; but the TF absorbance experienced an apparent increase of up to 4 hr UV irradiation, and then dropped gradually afterward. Although the biodegradability and toxicity of the UV-irradiated wastewater slightly improved, the subsequent biodegradation performance should be further tested with a biological reactor.

Considering the mechanism of ultraviolet photolysis, since VUV (λ = 185 nm) carries more energy than UV (λ = 254 nm), it might over-oxidize the organic compounds in the coking wastewater, making them unavailable for further biodegradation. In addition to directly attacking the organic bonds, VUV photolysis could generate free radicals (.OH), which easily reacts with O2 to form O3, and consequently initiates advanced oxidation (Kano et al., 2003). The greater effectiveness of VUV irradiation might be a consequence of the in situ formation of hydroxyl radicals via the photolysis of water at 185 nm and the subsequent formation of ozone (Buchanan et al., 2005).

2.2. Advanced treatment of the bio-treated coking wastewater by UV and VUV irradiation

In order to determine if UV or VUV photolysis could be used as advanced treatment, the bio-treated coking wastewater was subsequently irradiated by UV and VUV. Fig. 7 shows that the TOC of the bio-treated effluent decreased as the irradiation time increased. VUV also demonstrated higher removal efficiency. A notable phenomenon was that, while the effluent irradiated by UV light always had a light-yellow color, the effluent became transparent after 12 hr VUV irradiation (Fig. 8) and 57% of COD was eliminated at the same time. Many researchers estimated
that humic substances might be the major refractory organic and color-causing compounds in coking wastewater effluent according to fluorescence excitation emission matrix (EEM) (Zhao et al., 2009; Xing et al., 2012) and $^{13}$C nuclear magnetic resonance spectrometry ($^{13}$C NMR) analysis (Ni et al., 2008; Lai et al., 2009).

In addition to the organic compound removal, UV and VUV could also effectively reduce the NH$_4^+$-N, NO$_2^-$-N, and TN in the bio-treated effluent. However, a large amount of NO$_3^-$-N was produced by both UV and VUV irradiation. The removal rates of different inorganic nitrogen compounds are summarized in Table 2.

After 12 hr UV irradiation, 17.2% of NH$_4^+$-N, 58.6% of NO$_2^-$-N, and 12.7% of TN were removed, while 85.0% of NO$_3^-$-N was formed. With regard to 12 hr VUV irradiation, 23.9% of NH$_4^+$-N, 75.4% of NO$_2^-$-N, and 30.8% of TN were eliminated, while 50.0% of NO$_3^-$-N was produced. Compared with UV, VUV not only removed more NH$_4^+$-N, NO$_2^-$-N, and TN, but also generated less NO$_3^-$-N. A previous study found that NH$_4^+$-N could be oxidized to NO$_3^-$-N at longer irradiation time when the solution contained O$_2$ (Gonzalez et al., 2004; Buchanan et al., 2006). Further investigations should be done to identify the mechanism of the transformation.

3. Conclusions

Both UV and VUV were able to reduce TOC in diluted or bio-treated coking wastewater. However, VUV had a higher photolysis rate than UV, with the difference of about 20% as pre-treatment and 10% for advanced treatment. UV-irradiated coking wastewater demonstrated better biodegradability than VUV-irradiated wastewater did. For the 4 hr UV-irradiated wastewater, its BOD$_5$/COD ratio increased from 0.163 to 0.224, and its toxicity decreased to the greatest extent; but the toxicity of VUV-irradiated coking wastewater slightly increased. Therefore, UV is more appropriate than VUV for the pre-treatment of diluted coking wastewater.

As for the advanced treatment, VUV photolysis not only eliminated 57% of COD, but also realized total color removal after 12 hr irradiation. Compared with UV, VUV not only removed more NH$_4^+$-N, NO$_2^-$-N, and TN, but also generated 35% less NO$_3^-$-N. These results suggest that VUV photolysis is very promising for advanced treatment combined with an existing biological treatment.

Acknowledgments

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REFERENCES


Table 2 – Removal rates of inorganic-N compounds after UV and VUV irradiation.

<table>
<thead>
<tr>
<th>Irradiation time (hr)</th>
<th>UV irradiation (%)</th>
<th>VUV irradiation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>NO$_2^-$</td>
</tr>
<tr>
<td>4</td>
<td>10.49</td>
<td>32.48</td>
</tr>
<tr>
<td>8</td>
<td>13.64</td>
<td>48.54</td>
</tr>
<tr>
<td>12</td>
<td>17.23</td>
<td>58.66</td>
</tr>
</tbody>
</table>

$^a$ Negative results presented the increase of NO$_3^-$.


