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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.

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(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/cm^2 and 29.5 × 100 μW/cm^2. 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.

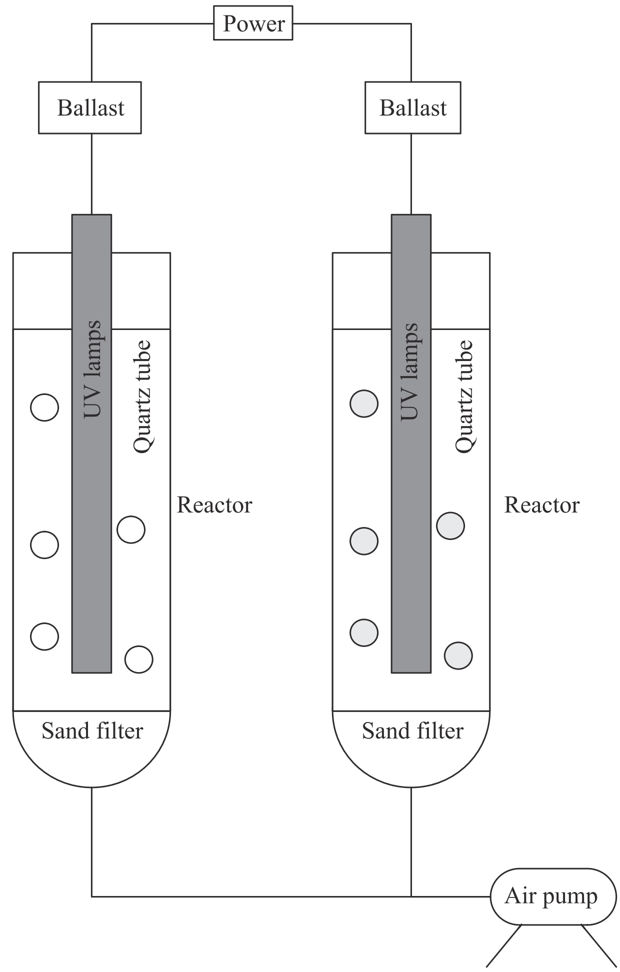

Fig. 1 – Schematic diagram of the experiment equipment for ultraviolet (UV) and vacuum ultraviolet (VUV) photo-biodegradation.

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.
COD: chemical oxygen demand; TOC: total organic carbon; NO_3^--N: nitrate nitrogen; NO_2^--N: nitrite nitrogen; NH_4^+-N: ammonia nitrogen; TN: total nitrogen; BOD5: biological oxygen demand.

Water quality index	pH	COD (mg/L)	TOC (mg/L)	NO_3^-–N (mg/L)	NO_2^-–N (mg/L)	NH_4^+–N (mg/L)	TN (mg/L)
6× diluted raw coking wastewater	8.3–8.8	262.7–452	78.6–99.3	1.6–1.9	0.04–0.5	30.8–50.2	69.8–76.7
Bio-treated coking wastewater	7.3–7.6	40–60	11.7–18.6	0.1–0.8	7.4–26.8	16.4–38.9	32.7–53.8