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博士学位论文

焦化废水处理系统中挥发性和半挥发性污染物：排放特征与健康风险

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Volatile and semi-volatile pollutants in coking wastewater treatment systems: emission characteristics and health risks

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Abstract

Coking wastewater is an important source of volatile and semi-Volatile organic compounds (VOCs and SVOCs), which poses an adverse effect to human health. However, few studies have been carried out on the fate and emissions of VOCs and SVOCs in the coking wastewater treatment plants (WWTPs). In this thesis, the occurrence, fate, transformation, and emission characteristics of 60 VOCs and VOCs, including phenols, BTEX, Polycyclic aromatic hydrocarbons (PAHs), and substituted Polycyclic aromatic hydrocarbons (SPAHs), were studied in coking WWTP and succeeding central WWTP using GC-MS. At the same time, 130 unknown VOCs and SVOCs were identified by suspect and non-target screening with a two-dimensional gas chromatography-mass spectrometry (GC×GC-MS), and the potential health hazards and environmental effects were also evaluated. The main results are as follows:

First, a dynamic verification method of headspace solid-phase microextraction-gas chromatography-triple quadrupole mass spectrometry (HS-SPME-GC-MS/MS) was established for qualitative and quantitative analysis of 43 VOCs and SVOCs in wastewater from a coking plant in Hebei Province. The 43 VOCs and SVOCs were detected in the raw coking wastewater, and the concentration of total phenols was the highest (178.67mg·L^{-1}), of which 3-cresol was the main one (42.9mg·L^{-1}). Among 43 VOCs and SVOCs, 23 were identified in the biological effluent, including 11 PAHs, seven phenols, five benzenes, and anilines.

Secondly, the occurrence and distribution of 43 VOCs and SVOCs in the wastewater system of 5 coking plants and the succeeding central WWTP in Inner Mongolia were studied using GC-MS. Besides, the fate and emission characteristics of 43 VOCs and SVOCs have been determined in coking plant C and central WWTP. Though biological treatment removes most of the 43 VOCs and SVOCs, the emissions of BTEX and some other compounds in the atmosphere are still great attention. The total emissions of VOCs and SVOCs from Plant C and the central WWTP are 1640 and 784 g·d^{-1}, respectively. The mass balance calculation results of

coking plant C show that biodegradation was the main removal pathway for all the target compounds (56.6-99.9%) except BTEX, chlorinated phenols, and high molecular weight (MW) of PAHs. The chlorinated phenols and HMW-PAHs were mainly removed through sorption on activated sludge (51.8-73.2% and 60.2-75.9%, respectively). The health risk assessment results shown that Benzene from the equalization basins of plant C and central WWTP exhibited the highest inhalation carcinogenic risks (LCR) ($1.4\times10^{-3}$and 3.2×10^{-4}, respectively), which above the acceptable level for human health recommended by the U.S.EPA (1×10^{-6}). In contrast, Benzo (a) pyrene (BaP) exhibited the highest inhalation non-cancer risks with a hazard index (HI) as high ratio as 70 and 30, respectively. At the same time, the excess sludge generated during wastewater treatment should also be carefully handled since it adsorbs abundant PAHs and chlorinated phenols (58,000and 3,500μg/g; and 622 and 54 μg/g at coking plant C and central WWTP, respectively).

Thirdly, the distribution, fate and transformation of substituted PAHs (SPAHs), including oxygenated-PAHs (OPAHs), methyl-PAHs (MPAHs), and nitrated-PAHs (NPAHs) in the wastewater treatment system of a coking plant E and central WWTP in Inner Mongolia were studied using GC-MS. Biodegradation is the main removal pathway for most LMW-MPAH, LMW-PAH, and part of LMW-OPAH and LMW-NPAH. The average concentrations of total SPAHs in the air above coking plant E (8.1 $\mu g\cdot m^{-3}$) and central WWTP (3.3 $\mu g\cdot m^{-3}$) were markedly higher than those in the ambient air of other urban and industrial areas. The mass balance calculation results of coking Plant E show that transformation was the major mechanism to remove LMW-MPAHs (59.9-77.3%), a large part of OPAHs, including anthraquinone, methylanthraquinone, and 9-fluorenone (46.7- 49.6%), and some NPAHs, including 2-nitrofluorene and 9-nitroanthrancene (52.9-59.1%). While adsorption by activated sludge mainly accounted for removing HMW-SPAHs (59.6-71.01%). The relatively high concentration of SPAH in excess sludge ($15000\mu g\cdot g^{-1}$) and treated effluent ($104\mu g\cdot L^{-1}$) are of great concern for their potential adverse environmental impacts. The estimated total LCR for different PAH and SPAH groups ranged between 3.2×10^{-4} and 1.7×10^{-1} in coking plant E and between 2.2×10^{-4} and 1.3×10^{-1} in central

WWTP. The LCR values of all target compounds except 3-NFlu and 7-Nitrobenzo[a]anthracene in the two coking WWTPs exceeded the cancer risk level recommended by the US EPA ($>10^{-6}$). Therefore, the cancer risk estimated by the current study is obviously unacceptable, and measures should be taken to control the pollution of PAHs and SPAHs in the ambient air.

Finally, we successfully established a screening method based on a GC×GC-MS to identify source-specific and previously unknown VOC and SVOC pollutants in coking plant E and central WWTP in Inner Mongolia, China. A total of 188 VOCs and VOCs, including 130 unknown pollutants, were identified. Most of the identified unknown VOCs and SVOCs are MPAHs (32 compounds), Benzene series (26 compounds), PAHs (25 compounds), and Phenols (including phenols, Nitro, and chlorinated phenols; 22 compounds). Other high groups mainly included NPAHs (12 compounds), OPAHs (11 compounds), alkanes (11 compounds), Polychloroethylenes (9 compounds), alkenes (8 compounds), and Polychloroethanes (8 compounds). There are 13 volatile compounds identified in the air of coking WWTPs without any previous knowledge of their existence in the wastewater or environment, some of which such as 1,2-benzenediamine, 2,4,6-trimethylbenzaldehyde, 2-formylphenoxyacetic acid, and 4-Bromo-1H-pyrazole, may pose immunomodulatory effects and might cause respiratory irritation, severe skin burns, and eye damage. Among 188 detected VOC and SVOC, 58 compounds were selected for quantitative analysis. The highest VOC and SVOC contents were found in the equalization basins of plant E and central WWTP (880.5 and 199.4 $\mu g \cdot m^{-3}$, respectively). In this study, the average values of total ozone formation potential (OFP) of coking plant E and central WWTP (716.3 and 191.7$\mu g \cdot m^{-3}$, respectively) was higher than the recommended value (100 $\mu g \cdot m^{-3}$). The result demonstrates that the coking WWTPs are a significant source of atmospheric VOCs and SVOCs.

Keywords: Coking wastewater, VOCs and SVOCs, Emission rate, Removal mechanism, Health risks.

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