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Variations in toxicity of semi-coking wastewater treatment processes and their toxicity prediction

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ABSTRACT

Chemical analyses and bioassays using *Vibrio fischeri* and *Daphnia magna* were conducted to evaluate comprehensively the variation of biotoxicity caused by contaminants in wastewater from a semi-coking wastewater treatment plant (WWTP). Pretreatment units (including an oil-water separator, a phenols extraction tower, an ammonia stripping tower, and a regulation tank) followed by treatment units (including anaerobic–oxic treatment units, coagulation-sedimentation treatment units, and an active carbon adsorption column) were employed in the semi-coking WWTP. Five benzenes, 11 phenols, and five polycyclic aromatic hydrocarbons (PAHs) were investigated as the dominant contaminants in semi-coking wastewater. Because of residual extractant, the phenols extraction process increased acute toxicity to *V. fischeri* and immobilization and lethal toxicity to *D. magna*. The acute toxicity of pretreated wastewater to *V. fischeri* was still higher than that of raw semi-coking wastewater, even though 90.0% of benzenes, 94.8% of phenols, and 81.0% of PAHs were removed. After wastewater pretreatment, phenols and PAHs were mainly removed by anaerobic-oxic and coagulation-sedimentation treatment processes respectively, and a subsequent active carbon adsorption process further reduced the concentrations of all target chemicals to below detection limits. An effective biotoxicity reduction was found during the coagulation-sedimentation and active carbon adsorption treatment processes. The concentration addition model can be applied for toxicity prediction of wastewater from the semi-coking WWTP. The deviation between the measured and predicted toxicity results may result from the effects of compounds not detectable by instrumental analyses, the synergistic effect of detected contaminants, or possible transformation products.

1. Introduction

Coal production in China rose from 1107.6 million tonnes oil equivalent in 2004 to 1844.6 million tonnes oil equivalent in 2014 (46.9% of global coal production), accompanied by an increase of wastewater produced from coal carbonization (BP, 2015). The wastewater from coal carbonization generally contains a high concentration of toxic organic chemicals, e.g., phenols, polycyclic aromatic hydrocarbons (PAHs), and benzenes, and may pose a potential ecological risk to the aquatic environment (Li et al., 2003; Marañón et al., 2008; Liu et al., 2016a; Zhang et al., 2013). Han et al. (2011) measured the toxic effects of coking wastewater on *Zea mays* L., suggesting that it affected the growth, fresh biomass, and cell division, and showed genotoxicity via an obvious increase of micronucleus frequency in root tips. The genotoxicity of coking wastewater was further verified using *Vicia faba* and *Hordeum vulgare* root tips (Dong and Zhang, 2010). Biotoxicity of coking wastewater was also investigated by using various aquatic organisms from different trophic levels, such as luminescent bacteria, algae, crustaceans, and fish embryos (Zhao et al., 2009a, 2014; Zhu et al., 2013).

The wastewater from coal carbonization was divided into two categories: the semi-coking wastewater produced from the middle- (700–800 °C) and low- (500–600 °C) temperature carbonization processes and the coking wastewater produced from the high-temperature carbonization process (950–1050 °C). The semi-coking and coking wastewater exhibit similar properties, but the concentrations of con-

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taminants, such as PAHs, phenols, etc., in semi-coking wastewater are typically higher than the levels in coking wastewater (Wang et al., 2014; Liu et al., 2016b). Semi-coke production is an emerging industry. The treatment, discharge, and environmental impact of semi-coking wastewater have become a difficult issue because of its complexity, heterogeneity, and toxicity. Therefore, it is necessary to comprehensively study the removal of contaminants and the variation of biotoxicity in the semi-coking wastewater treatment processes using chemical analyses and bioassays to ensure ecological safety.

The biotoxicity of a mixture is dependent on the species, concentration, toxicity, and interaction of contaminants in water (Villa et al., 2012; Tian et al., 2012; Escher et al., 2013). Accurate prediction of the toxicity of actual wastewater based on the concentrations and toxicity of detected compounds is complicated due to the potential synergism and antagonism. Nevertheless, it has been concluded that as the number of components in the mixture increase, the synergistic or antagonistic effects will weaken to the additive effects if the added component cannot yield a much stronger joint effect with an existing component (Tian et al., 2012). This facilitates the toxicity prediction for actual water samples, because the joint toxicity of a mixture with additive effects could be predicted by concentration addition (CA), independent action (IA), two-step prediction, etc. Many researchers have shown that the CA model is typically more rational because it can provide reliable estimates of the toxicity of a broad range of mixtures composed of various chemicals, especially for the mixtures with unspecific mechanisms of action (Altenburger et al., 2003; Arrhenius et al., 2004; Zhou et al., 2010). However, the predictability of CA for semi-coking wastewater with a high concentration of contaminants has not been demonstrated.

The objective of the present study was to evaluate the treatment performance of a semi-coking wastewater treatment plant (WWTP) employing anaerobic-oxic (A/O) biological treatment combined with coagulation and adsorption treatment using chemical analyses, to investigate the variation of biotoxicity during treatment processes using the bioluminescence inhibition assay, and the immobilization and lethality assay with *D. magna*, and to analyze the predictability of CA for semi-coking wastewater. The work will contribute to understanding the removal of contaminants and the potential biotoxicity during semi-coking wastewater treatment processes, and will demonstrates the validity of its toxicity prediction.

2. Materials and methods

2.1. Semi-coking WWTP and sampling

Wastewater from a semi-coking WWTP located in Yulin, Shaanxi Province, China, with an average treatment capacity of 3000–5000 m^3/d was studied. The WWTP applied a series of pretreatment and treatment processes, as shown in Fig. 1. The pretreatment units included an oil-water separator, a phenols extraction tower, an ammonia stripping tower, and a regulation tank. In the phenols extraction tower, the extractant (mixture of tributyl phosphate and kerosene) and wastewater were mixed in the proportion 1:7, and the extraction time was 20 min. The effluent from the phenols extraction tower was pumped into the ammonia stripping tower after adjustment of the pH to 11, and the air was blown into the wastewater in the ammonia stripping tower to recover the ammonia. The treatment units included A/O treatment, a coagulation-sedimentation unit, and an active carbon adsorption column. After pretreatment, the wastewater was directed to the A/O treatment unit with a hydraulic retention time (HRT) of 20 h. The effluent of the biological treatment processes was passed through the coagulation-sedimentation unit, containing polymeric ferric sulfate as coagulant and semi-coke as coagulant aid, followed by an active carbon adsorption column for further treatment. The effluent of the semi-coking WWTP was reused for coal carbonization in the semi-coke plant. Sampling locations along the wastewater treatment processes are shown in Fig. 1. The collected samples were immediately transferred from the site to the laboratory at 4 °C and then stored in a refrigerator.

2.2. Sample extraction and chemical analyses

Individual standard solutions of five benzenes, benzene, toluene, ethylenzene, cumene, and styrene, and five PAHs, naphthalene, acenaphthylene, fluorene, phenanthrene, and fluoranthene, were purchased from o2si smart solutions (USA). The phenols standard solution containing 11 compounds, i.e., phenol, 2-chlorophenol, o-cresol, 2-nitrophenol, 2,4-dimethylphenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 4-nitrophenol, 2,3,4,6-tetrachlorophenol, 2-methyl-4,6-dinitrophenol and pentachlorophenol, were obtained from Sigma–Aldrich (USA).

Before extraction, the water samples were filtered through 0.8 glass-fiber filters to remove suspended particulates. Sodium chloride was added to the extracting sample to improve recovery rate, to avoid emulsification and to shorten the separation time of the aquatic and organic phases. First, 10% NaOH was added to adjust the pH≥12. Basic and neutral organic compounds were extracted with dichloromethane using an ultrasonic vibrating device, and then the aqueous and organic phases were separated using a centrifuge. Secondly, sulfuric acid was added to the aquatic phase to adjust the pH≤2. Acid organic compounds were extracted similarly to the basic and neutral organic compound extraction. The two parts of the organic phase were mixed, and anhydrous sodium sulfate was added to remove the water. The volume of extract was concentrated to 1.8 mL using a rotary evaporator.

The determination of target compounds was carried out by Agilent GC-2014 gas chromatography (USA) equipped with a DB-5MS capillary column (30 m×0.25 mm×0.25 μm) and flame ionization detector. The detailed instrument conditions for the different categories of chemicals are as follows. The injection port temperature was maintained at 250 °C. Nitrogen was the carrier gas at a flow rate of 1.0 mL/min. For the benzenes, the column temperature was programmed from 60 °C for 2 min and then increased by 8 °C/min to 150 °C for 1 min, and the split ratio was 20:1. For the phenols, the column temperature was programmed from 80 °C for 2 min and then increased by 8 °C/min to 300 °C for 5 min, and the split ratio was 10:1. For the PAHs, the column temperature was programmed from 60 °C for 2 min and increased by 10 °C/min to 250 °C, and then increased by 5 °C/min to 310 °C for 5 min. The split ratio was 10:1.

After filtering the water samples collected from the different treatment units, conventional indices including total phosphorus (TP), total nitrogen (TN), NO_3^--N, NO_2^--N, NH_4^+-N, chemical oxygen demand (COD), and total organic carbon (TOC) were measured according to the Water and Wastewater Analytical Methods to evaluate the performance of the semi-coking WWTP (SEPA, 2006).

2.3. Bioassays

2.3.1. Bioluminescence inhibition assay with Vibrio fischeri

The acute toxicity test using luminescent bacteria is the most widely used method for monitoring environmental pollution because of its high throughput and sensitivity, cost effectiveness, and simple operation. The intensity reduction of the luminescence emitted by the marine bacteria *V. fischeri* is used to quantify the toxicity of pollutants. *V. fischeri* was purchased from the China Center of Industrial Culture Collection and was used for toxicity test (15 min exposure), according to a modified ISO 11348 (2008) procedure. Briefly, 100 μL of bacterial suspension prepared from logarithmically growing bacteria was exposed to 100 μL of the testing sample in a cell of the microplate for 15 min. Based on the result of the preliminary test, the testing sample was diluted into a series of different concentrations (as percentages). Three replicates were performed for each concentration. The relative