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Novel insights into anoxic/aerobic^1/aerobic^2 biological fluidized-bed system for coke wastewater treatment by fluorescence excitation–emission matrix spectra coupled with parallel factor analysis

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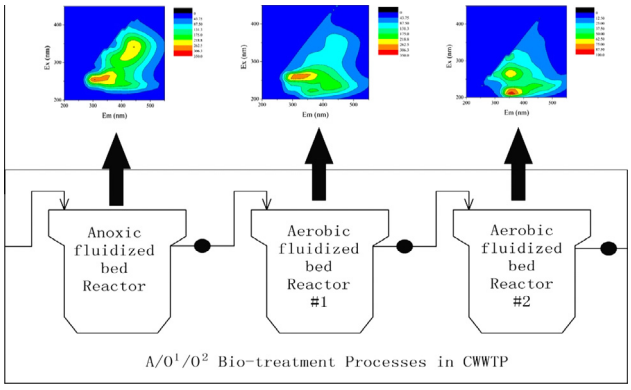
HIGHLIGHTS

- We developed a novel anoxic/aerobic^1/aerobic^2 process to treat coke wastewater.
- DOM in bio-treatment was characterized using EEM and PARAFAC.
- Correlations between contaminants and EEM components were investigated.
- EEM–PARAFAC can be used to monitor the performance of coke wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorescence spectroscopy coupled with parallel factor analysis (PARAFAC) was applied to investigate the contaminant removal efficiency and fluorescent characteristic variations in a full scale coke wastewater (CWW) treatment plant with a novel anoxic/aerobic^1/aerobic^2 (A/O^1/O^2) process, which combined with internal-loop fluidized-bed reactor. Routine monitoring results indicated that primary contaminants in CWW, such as phenols and free cyanide, were removed efficiently in A/O^1/O^2 process (removal efficiency reached 99% and 95%, respectively). Three-dimensional excitation–emission matrix fluorescence spectroscopy and PARAFAC identified three fluorescent components, including two humic-like fluorescence components (C1 and C3) and one protein-like component (C2). Principal component analysis revealed that C1 and C2 correlated with COD (correlation coefficient (r) = 0.782, $p < 0.01$ and $r = 0.921$, $p < 0.01$), respectively) and phenols ($r = 0.796$, $p < 0.01$ and $r = 0.914$, $p < 0.01$, respectively), suggesting that C1 and C2 might be associated with the predominating aromatic contaminants in CWW. C3 correlated with mixed liquor suspended solids ($r = 0.863$, $p < 0.01$) in fluidized-bed reactors, suggesting that it might represent the biological dissolved organic matter. In A/O^1/O^2 process, the fluorescence intensities of C1 and C2 consecutively decreased, indicating the degradation of aromatic contaminants. Correspondingly, the fluorescence intensity of C3 increased in aerobic^1 stage, suggesting an increase of biological dissolved organic matter.

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1. Introduction

460 Mt coke in China, important raw material for steelmaking, was yielded in 2012. Coke wastewater (CWW) is one of the harmful by-products of coke production, which contains considerable amounts of phenols, polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds (HCs), cyanide, and sulfide compounds. It has been reported that ~24.0 kt of phenols, ~0.7 kt of cyanide and 1.6 kt of benzo[a]pyrene were discharged from CWW in China in 2005 (NDRC, 2006). These compounds were recognized as carcinogenic, mutagenic and toxic contaminants, which were listed as US-EPA and EU priority pollutants (Angelino and Gennaro, 1997). Therefore, it was essential to efficiently remove these contaminants in CWW to reduce their hazard to aquatic organisms and humans.

The activated sludge process was indisputably the most frequently employed biological technique in CWW treatment plants (CWWTPs). In China, the existing CWWTPs mostly used anaerobic/anoxic/aerobic ($A^1/A^2/O$) bio-treatment process with continuously stirred reactors, since this combination was easily designed and operated (Wei et al., 2012). However, good performance in carbon and nitrogen removal was difficult to achieve because of toxic contaminants inhibition on various biological reactions (Staib and Lant, 2007). To solve this problem, worldwide researchers had focused on the development of efficient bio-treatment technique for CWW (Zhang et al., 1998; Maranon et al., 2008). However, most researches were conducted in bench or pilot scale, and only a few new developed techniques were applied in full-scale CWWTPs (Kim et al., 2009). Recently, the Chinese government issued stricter new standard for aqueous discharges of CWW (Ministry of Environmental Protection, 2012). Therefore, it was urgent to develop feasible higher efficient treatment process for Chinese CWWTPs. Based on $A^1/A^2/O$ process, our research group developed a novel anoxic/aerobic^1/aerobic^2 ($A/O^1/O^2$) internal-loop biological fluidized-bed system, which is now successfully applied in a full-scale CWWTP in south China (Zhang et al., 2010).

The phenols, PAHs and HCs in CWW were typical chromophoric dissolved organic matter (CDOM) (Zhang et al., 2013). Meanwhile, the microbial reactions in wastewater bio-treatments generated microbial CDOM (Li et al., 2008). These CDOM can be employed to distinguish the chemical composition of DOM (Hudson et al., 2007), and can provide useful information about the removal efficiency of contaminants. Excitation–emission matrix (EEM) fluorescence spectroscopy was an ideal method to qualitatively characterize CDOM, and the parallel factor analysis (PARAFAC) provided quantitative data about the individual CDOM components (Bro, 1997; Hua et al., 2010). Therefore, EEM–PARAFAC might have potential to rapidly and continuously monitor contaminant removal efficiency in CWWTPs.

To date, only a few researches used fluorescence spectra to describe the characteristic of CWW CDOM in laboratory or pilot scale tests (Zhao et al., 2009; Wei et al., 2012; Yang et al., 2013), but not in full scale CWWTPs. Therefore, this study aimed to describe the characteristics and behaviors of CDOM components in a full scale CWWTP with a novel $A/O^1/O^2$ fluidized-bed system. Qualitative analysis of CDOM was conducted using EEM–PARAFAC, and correlations between CDOM and routine parameters were investigated using statistical analysis.

2. Materials and methods

2.1. CWWTP and data set

The samples were collected from No. 1 Songshan CWWTP, which was located in Shaoguan Steel, Guangdong Province, China, with a designed treatment capacity of 1680 $m^3\ d^{-1}$. Table SM-1 in Supplementary Material (SM) presents the statistical monitoring variables of raw influent. The treatment of this CWWTP included three processes: pretreatment, bio-treatment and advanced treatment (Fig. 1). After pretreatment, the liquid effluent flowed into the bio-treatment processes. One $A/O^1/O^2$ system coupled with three internal-loop biological fluidized-beds in the volumes of 2360, 3280 and 2780 m^3 was applied (Table SM-2). The biological effluent then flowed through advanced treatment and the final effluent was discharged or reused. The water samples were collected from the influent of bio-treatment and the effluent of each stage in $A/O^1/O^2$, and then were stored in 2–4 °C prior to analysis. Sampling was conducted every 3 d from January 1, 2012 to December 31, 2012.

2.2. Analytical methods

The COD, NH_3, pH and MLSS were measured by online COD_{max}-Plus monitors (Hach, USA), by Amtax Compact analyzers (Hach, USA), by online GLI pH/ORP monitors (Hach, USA), and by online Solita SC monitors (Hach, USA), respectively. Other variables were determined at laboratory. Before analysis, the water samples were centrifuged and the supernatant was filtered with 0.7 μm GF/F filter and then 0.2 μm membrane filter (MFS, Japan) to obtain the extracted solution. The concentrations of phenols, sulfide and free cyanide were determined according to Standard Methods (APHA, 1998).

For EEM analysis, the extracted solution was diluted 10 times by ultra-pure water to a COD concentration in the range of 20–257 mg L^{-1}, and then the pH value of diluted solution was adjusted to 7.0 ± 0.1. EEM spectrograms of extracted solution were measured using a Cary Eclipse fluorescence analyzer (Varian Instruments, USA) with a 4 mL, 1 cm path length cuvette. The photomultiplier tubes voltage was set at 600 V, and the slits for both excitation and emission were 5 nm with scanning speed at 1200 nm min^{-1}. The fluorescence region 550 nm > Emission (Em) > 200 nm, 450 nm > Excitation (Ex) > 200 nm was set as the scan region with 5 nm intervals. Replicate scans were generally within 5% agreement in terms of intensity and within the slit width resolution in terms of peak location. Fluorescent intensity was calibrated in quinine sulfate equivalents (QSE), where 1 QSE is the maximum fluorescent intensity of 0.01 mg L^{-1} of quinine in 1 N H_2SO_4 at the Ex/Em = 350 nm/450 nm (Hoge et al., 1995). The Cary Eclipse analyzed samples in default ratio mode. The detailed information about spectra correction steps can be found in previous study (Yao et al., 2011).

2.3. PARAFAC

EEM spectrograms were combined into a 3-dimensional data array: 120 samples × 51 excitations × 71 emissions. Before analysis, the Raman scattering was removed by subtracting the pure water spectrogram from the sample spectrogram. Rayleigh scatter effects were removed from the data set by excluding any emission measurements made at wavelengths ⩽ excitation wavelength +5 nm, and at wavelengths ⩾ excitation wavelength +300 nm. Zero was added to the EEMs in the two triangle regions (emission wavelength ⩽ excitation wavelength +5 nm, and ⩾ excitation wavelength +300 nm) of the missing data (Yao et al., 2011). The PARAFAC analysis was conducted using MATLAB (MathWorksm, USA) to extract CDOM components from EEM fluorescence data. The algorithm used in this work is available from the N-way Toolbox for MATLAB at http://www.models.kvl.dk. After the PARAFAC model was established, core consistency diagnostic and split half analysis were used to validate the models. One sample was removed through comparing it to the others to determine whether