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Characterization of effluent organic matter from different coking wastewater treatment plants

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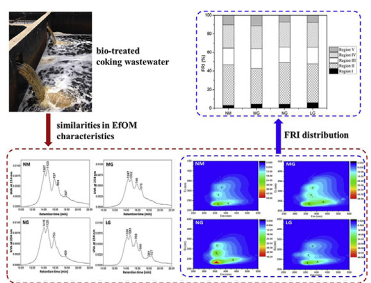
HIGHLIGHTS

- Effluents from four coking WTPs of typical design were sampled to characterize EfOM.
- Predominant species in all samples were hydrophobic compounds with high SUVA values.
- Molecular weights of the sampled EfOM were mainly in the range 500–1500 Da.
- Aromatic compounds accounted for a large proportion of the sampled EfOM.

GRAPHICAL ABSTRACT



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ABSTRACT

Effluent organic matter (EfOM) in bio-treated wastewater generally has negative impacts on advanced wastewater treatment processes. Thus, a comprehensive characterization of EfOM would help determine feasibility of wastewater treatment. The aim of this work was to characterize EfOM originating from four coking wastewater treatment plants (WTPs) in China, using specific UV absorbance (SUVA), EfOM fractionation, size exclusion chromatography, and excitation-emission matrix (EEM) fluorescence spectroscopy. It was found that the predominant species in all the EfOM samples were hydrophobic compounds with high SUVA values. The molecular weight (MW) distribution of the sampled EfOM was in the range of 300–1500 Da, and stronger UV absorbance was observed in the high MW (> 500 Da) region. The EEM fluorescence spectra showed that aromatic compounds accounted for a large proportion of the sampled EfOM based on the fluorescence regional integration technique. The abovementioned analysis highlights the similarities in the characteristics of the EfOM originating from different coking WTPs, regardless of treatment plant design. Meanwhile, significant differences between the characteristics of the EfOM in coking wastewater and municipal wastewater were observed.

1. Introduction

Organic matters in aquatic systems are comprised of a variety of complex compounds derived from terrestrial, aquatic, and anthropogenic sources. Wastewater effluent is an important source of these compounds. Effluent organic matter (EfOM) in bio-treated wastewater has attracted increasing attention due to the steady increase in its quantity as a result of rapid modernization (Cai and Lin, 2016; Hofman-Caris et al., 2017). The discharge of such effluents contributes significantly to the heterogeneous mixture of organic matter in the receiving waters. Indirect wastewater reuse

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often occurs when these waters that receive EfOM serve as sources of drinking water supply, and this could adversely affect human health (Kim et al., 2014). Therefore, advanced wastewater treatment has been recognized as a critical step for mitigating EfOM damage to aquatic ecosystems and providing water that is safe for common usage. Unfortunately, advanced treatment processes, such as coagulation and membrane processes, often fail to achieve optimal performance due to the adverse influences of EfOM. For example, an increase in coagulant dosage was required to reach ideal removal efficiency while poor floc formation was observed (Shon et al., 2005b; Nam et al., 2008). Membrane treatment processes are generally compromised by intensive fouling, which reduces separation efficiency dramatically (Filloux et al., 2012; Kim and Dempsey, 2013). Furthermore, substantial amounts of disinfection byproducts (DBPs) were generated upon chlorination (Zhao et al., 2006). Therefore, the first step in mitigating the adverse effects of EfOM is understanding its characteristics well enough to establish an appropriate technology for its advanced treatment.

EfOM is usually described as a combination of natural organic matters (NOMs), soluble microbial products (SMPs), and synthetic organic compounds (SOCs) (Shon et al., 2006). NOMs mainly originate from plants or other terrestrial sources (Leenheer and Croue, 2003). SMPs are complex organic compounds released through substrate metabolism, as well as by decay of biomass during biological treatment processes (Barker and Stuckey, 1999). SOCs are generated from the production and use of synthetic organic compounds (Shon et al., 2006). Most of EfOM is present as dissolved organic matter (DOM), which is difficult to remove. Since EfOM compromises water quality and complicates water treatment, it remains a focus of research in this field.

Due to the heterogeneous nature of EfOM, bulk parameters are often proposed for its characterization, such as dissolved organic carbon (DOC), light absorption, hydrophilicity/hydrophobicity, fluorescence, aromaticity, and functional groups (Jarusutthirak and Amy, 2007; Quaranta et al., 2012; Puspita et al., 2015). Although many researchers have studied EfOM in bio-treated municipal wastewater (BTMW) extensively (Filloux et al., 2012; Quaranta et al., 2012; Audenaert et al., 2013), there are only a few studies on EfOM in industrial wastewater. The composition of EfOM in industrial wastewater is more complex than that in BTMW, and depends on the industry classification, raw material used, production processes, and wastewater treatment technology applied. Coking wastewater is a typical industrial organic wastewater that has attracted much attention because the pollution it causes is difficult to deal with. Coking wastewater is generated during the high-temperature carbonization of raw coal (Wei et al., 2012). It contains considerable amounts of toxic and refractory organic compounds, resulting in poor removal performance using traditional biological treatment processes (Yu et al., 2016). As one of the major coke producers, China is facing great challenges in dealing with the pollution caused by coking wastewater. According to statistics, chemical oxygen demand (COD) of discharges from coking plants accounted for 1.26% of the total industrial COD discharged in China (EPA of China, 2010). Therefore, to meet increasingly stringent emission standards, or even for its reclamation, it is imperative to characterize EfOM in detail so that advanced treatment processes for effective removal of EfOM from bio-treated coking wastewater (BTCW) can be optimized.

In the current study, effluent samples were collected from four wastewater treatment plants (WTPs) at different coking plants of typical designs in China for comprehensive characterization of EfOM. These coking plants had different geographical locations, coal feed sources, and processing scale. This resulted in different treatment schemes for each WTP, which could induce differences in the EfOM characteristics. The aim of this research was to establish the ranges of the characteristic parameters of EfOM from different coking WTPs, and simultaneously, compare these to the characteristic values of EfOM in BTMW. To this end, specific UV absorbance (SUVA), EfOM fractionation, size exclusion chromatography (SEC), and excitation-mission matrix (EEM) fluorescence spectra were employed. It is anticipated that this paper will provide referential values for the design and application of advanced treatment processes for effective removal of EfOM from BTCW.

2. Experimental methods

2.1. Materials

The chemicals used in this study were all of reagent grade. For the fractionation of EfOM, styrene-divinylbenzene macroporous resin XAD-4 and acrylic ester macroporous resin XAD-8 were purchased from the Dow Chemical Company (USA). Prior to use, all the resins were purified using the Soxhlet extraction method. Potassium hydrogen phthalate (KHP) and poly (sodium-styrenesulfonate) (PSS) were purchased from Sigma-Aldrich (USA). The deionized water used, was obtained from a Milli-Q water purification system (Milli-Q Academic, Millipore, USA).

2.2. Treatment plants and effluent collection

The effluent samples were collected from the discharge point of the WTP of each coking plant. These were the Neimeng Coking Company, Ltd. (NM, Inner Mongolia, China), Maanshan Iron & Steel Group Corp. (MG, Anhui, China), Nanjing Iron & Steel Group Corp. (NG, Jiangsu, China), and Liuzhou Iron & Steel Group Corp. (LG, Guangxi, China). The location of each coking plant is marked in Fig. S1, and detailed information about the operation of each coking WTP is summarized in Table S1. The samples were stored in a refrigerator (4 °C) for character analysis within seven days. The samples typically had a tan color and an unpleasant odor. The major water quality parameters are shown in Table 1.

2.3. Characterization methods

Prior to chemical analysis, all samples were filtered using 0.45 μm membranes. The filters were pre-rinsed with 200 mL of deionized water and then 50 mL of wastewater sample before use. The filtered samples were then used for 5-day biochemical oxygen demand (BOD_5), COD, DOC, SUVA, EfOM fractionation, SEC, and EEM fluorescence spectra analyses.

2.3.1. General characterization

Physical and chemical parameters of the samples were investigated in accordance with the National Standard Methods in China (EPA of China, 2002). DOC content was determined with a Shimadzu TOC analyzer (TOC-L, Shimadzu, Japan) based on the Non-Purgeable Organic Carbon measurement procedure and KHP was used as a standard. Each sample was measured three times to get an average value, and the standard deviation was <5%. UV absorbance measurements were recorded using an UV–vis spectrophotometer (T6, Persee, China) with 1 cm-long quartz cells. The specific UV absorbance (SUVA) index, defined as the ratio of the UV absorbance at 254 nm (UV_{254}) to the DOC concentration, was applied to estimate the aromaticity of EfOM.

2.3.2. EfOM fractionation

The EfOM fractionation procedure used here was developed by Malcolm and Maccarthy (1992). On the basis of the hydrophilic-hydrophobic properties of organic matter, EfOM was separated into four different fractions using XAD-4 and XAD-8 resins. These