JOURNAL OF ENVIRONMENTAL SCIENCES XX (2018) XXX–XXX

Available online at www.sciencedirect.com

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ENVIRONMENTAL
SCIENCES

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Spectroscopic study on transformations of dissolved organic matter in coal-to-liquids wastewater under integrated chemical oxidation and biological treatment process

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ARTICLE INFO

Article history:
Received 26 January 2018
Revised 6 April 2018
Accepted 8 April 2018
Available online xxxx

Keywords:
Coal-to-liquids wastewater
Spectroscopic analysis
Dissolved organic matter fractionation
UV–visible spectrum
Excitation–emission matrix parallel factor analysis (EEM-PARAFAC)

ABSTRACT

A large amount of wastewater containing various toxic organic contaminants is produced during coal pyrolysis. In this study, several spectroscopic methods were used to monitor the transformation of organic pollutants during an integrated chemical oxidation and biological process. The results showed that the hydrophobic acid fraction increased after Fenton oxidation, which was likely due to the production of small-molecule organic acids. Soluble microbial products were generated during biological treatment processes, which were degraded after ozonation; meanwhile, the hydrophilic base and acid components increased. Ultraviolet–visible spectroscopic analysis indicated that peaks at the absorption wavelengths of 280 and 254 nm, which are associated with aromatic substances, were detected in the raw water. The aromatic substances were gradually removed, becoming undetectable after biological aeration filter (BAF) treatment. Fourier transform infrared spectroscopy analysis revealed that the functional groups of phenols; benzene, toluene, ethylbenzene, and xylene (BTEX); aromatic hydrocarbons; aliphatic acids; aldehydes; and esters were present in raw wastewater. The organic substances were oxidized into small molecules after Fenton treatment. Aromatic hydrocarbons were effectively removed through bioadsorption and biodegradation after BAF process. Biodegradable organic matter was reduced and finally became undetectable after anoxic–oxic treatment in combination with a membrane bioreactor. Four fluorescent components were fractionated and obtained *via* excitation–emission matrix parallel factor analysis (EEM-PARAFAC). Dissolved organic matter fractionation in conjunction with EEM-PARAFAC was able to monitor more precisely the evolution of characteristic organic contaminants. It was concluded that the integrated treatment process was effective in removing the characteristic organic contaminants in coal-to-liquids wastewater.

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https://doi.org/10.1016/j.jes.2018.04.006

Introduction

With the gradual consumption of petroleum resources, much attention has been paid to the coal liquefaction industry worldwide (Huang and Yuan, 2015; Wei and Shi, 2015). Coal-to-liquid (CTL) is a strategic industry for replacing petroleum resources, and thus a measure that can safeguard Chinese energy security. Beyond that, the coal liquefaction industry is not only important for realizing clean and efficient utilization of coal, but also is necessary for improving the quality of fuel oil. Optimization of the production technology of coal-to-oil can promote the transformation and upgrading of the coal industry and help solve the problems regarding coal production capacity and related issues.

The rapid development of the CTL industry in China has brought extensive attention to the treatment of effluent produced *via* coal liquefaction. CTL processes generate a large amount of wastewater, which characteristically has a high organic concentration and low biodegradability. The chemical oxygen demand (COD) of this wastewater is generally around 9000–10,000 mg/L. In addition, CTL wastewater is very complex in its chemical composition of organic matter and contains many toxic and bioresistant organic substances, such as hydrocarbons, aldehydes, phenols, and benzenes.

The characteristics of the dissolved organic matter (DOM) in wastewater affect the treatability and process options for the wastewater (Jiang et al., 2017). Because of the complex constituents of DOM in CTL wastewater, traditional biological processes alone are unable to purify wastewater effectively, so combined physicochemical and biological processes are always used for such wastewater (Yue et al., 2015; Sahu et al., 2017). Actually, integrated processes have been established and operated for many years in China for CTL wastewater treatment. In particular, desulfurization, dephenolization, and deamination pretreatments are conducted first for separation of sulfide ions, phenols, and ammonium, respectively (Hou et al., 2014; C.Q. Han et al., 2010; H.J. Han et al., 2010). After that, Fenton oxidization is used to detoxify the wastewater and improve its biodegradability (Peng et al., 2016), and then the wastewater is treated further *via* an efficient biological aeration filter (BAF). To remove the residual organic matter in the wastewater, an integrated ozonation preoxidation and anoxic–oxic (A/O) process is applied (Nawrocki and Kasprzyk-Hordern, 2010; Barker and Stuckey, 1999; Deng et al., 2017). Finally, the A/O effluent is treated in depth by a membrane bioreactor (MBR) for water reclamation.

At present, most of the CTL wastewater in China conforms to the emission standard after such treatment, but the effluent might contain some toxic substances at trace concentrations. Few studies have focused on the monitoring and evaluation of these trace toxic organic pollutants in CTL wastewater treatment (Lu et al., 2006), yet most of these substances have carcinogenic, teratogenic, and mutagenic effects and pose a great threat to ecological security and human health. In addition, it has been difficult to observe the changes undergone by organic pollutants during the actual treatment of CTL wastewater. Therefore, it was necessary to find a simple and effective method to monitor the characterization of the changes in organic pollutants during CTL wastewater treatment processes.

Spectroscopic methods have been widely used for characterization of dissolved organic contaminants in wastewaters from different industrial sources. Li et al. (2017) investigated the migration and transformation of organic compounds in wastewater from physicochemical treatment processes by using different spectroscopic methods. They applied ultraviolet absorbance (UVA) and fluorescence techniques to assess the formation of biodegradable dissolved organic carbon (BDOC) and bromate during ozonation and suggested that measurement of UVA was able to assess the formation of BDOC and bromate. They employed LED ultraviolet (UV) fluorescence sensors to monitor DOM online to predict the formation potential of disinfection by-products (DBPs) during water disinfection treatment. It was found that both protein-like and humic-like fluorescence can be excited by UV_{280} LED and then detected *via* photodiodes combined with light filters (350 ± 15 nm and 440 ± 30 nm, respectively) and that the UVA at 280 nm can substitute for the UVA at 254 nm for online monitoring of DOM and for predicting DBP formation potential (Li et al., 2016). Fluorescence analysis combined with parallel factor analysis (PARAFAC) is widely used to predict the transformation of typical DOM in water treatment processes or in aquatic environments. Li studied the changes in DOM during municipal wastewater treatment using fluorescence analysis and PARAFAC (Li et al., 2014). In addition, Osburn et al. (2012) combined excitation–emission matrix (EEM) fluorescence and PARAFAC analysis to model base-extracted particulate organic matter (POM) and DOM compositions in the Neuse River Estuary (NRE). It was demonstrated that four PARAFAC components (C1–C3 and C6) were derived from terrestrial sources to the NRE, one component (C4) was enriched in the POM and in surface sediment pore water DOM, and one component (C5) was related to recent autochthonous production. Sgroi et al. (2017) used EEM and different data processing methods, including peak-picking methods, Fourier transform infrared (FT-IR) analysis, and PARAFAC, to evaluate their suitability for producing effective surrogate pollutant indices. Use of a convenient and sensitive fluorescence analytical technique as a monitoring tool could quickly reveal the removal and conversion of organic compounds in different water bodies.

As mentioned above, CTL wastewater contains different kinds of harmful organic contaminants, but few studies have focused on the transformation of these pollutants at the molecular level throughout the wastewater treatment process. In this study, we combined the methods of UV spectroscopy, FT-IR spectroscopy, and EEM fluorescence spectroscopy to systematically investigate the molecular structure and transformation of organic components during an integrated treatment process for CTL wastewater. In addition, gas chromatography–mass spectrometry (GC–MS) was conducted to analyze the variation of organic matter in CTL wastewater and verify the accuracy of the spectroscopic analysis (Appendix A Fig. S9 and Table S1). The objective of this study was to gain insight into the transformation mechanisms of organic pollutants in different wastewater treatment stages and to evaluate the operating efficiency of the integrated process for CTL wastewater treatment.

Please cite this article as: Peng, S., et al., Spectroscopic study on transformations of dissolved organic matter in coal-to-liquids wastewater under integrated chemical oxidation and biological ..., J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2018.04.006