WATER RESEARCH 55 (2014) 323–334

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/watres

Fluorescent components of organic matter in wastewater: Efficacy and selectivity of the water treatment☆

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ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form
18 February 2014
Accepted 20 February 2014
Available online 2 March 2014

Keywords:
EEM
PARAFAC
Biological treatment
Filtration
Water quality
Microbial activity

ABSTRACT

Characterization of organic matter (OM) present in treated wastewater (TWW) after various treatment stages is important for optimizing wastewater recycling. The general aim of this research was to carry out a long-term examination of OM in wastewater along the treatment, by applying excitation-emission matrices (EEM) fluorescence spectroscopy and parallel factor analysis (PARAFAC). Fluorescent OM was examined in water samples obtained from four wastewater treatment plants (WWTPs) in Israel for 20 months. The PARAFAC analysis of EEMs of water samples from the four WWTPs yielded six components. The fluorescent components included proteinaceous tryptophan-like matter (C1), three humic-like components (C2–C4), a component (C5) that was characterized by excitation and emission with a distinct vibrational structure similar to that of pyrene and a component (C6) that was characterized by the excitation and emission spectra demonstrating two peaks where the appearance of two emission peaks was suggested to reflect the formation of an intra-molecular exyplex. The biological treatment strongly reduced the concentration of component C1 thus increasing the overall fraction of humic-like OM over the proteinaceous OM in the treated water. The fluorescence of component C1 could therefore be used as an indicator of the biological treatment efficacy. The concentration of the humic-like component C2 characterized by excitation and emission maxima at <240,305/422 nm, respectively, was also sensitive to biological treatment. The soil aquifer treatment was not effective in completely eliminating the fingerprints of the initial wastewater. The concentrations of the fluorescent components in wastewater after the biological treatment were only slightly affected by filtration (0.45 μm) of the samples. For water sampled prior to the biological treatment, the 0.45 μm filtration had the most pronounced effect on concentrations of the proteinaceous matter and component C6. Strong positive correlations were found between concentrations of component C1 and total carbon (TC) in wastewater samples from the WWTPs thus suggesting the proteinaceous fluorescence in wastewater as an indicator for TC reduction. Chemical oxygen demand (COD) and the fluorescein diacetate hydrolyzing activity (a measure for the total microbial

☆ Contribution of the Institute of Soil, Water and Environmental Sci, ARO, Bet Dagan, Israel (601/14 series).

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http://dx.doi.org/10.1016/j.watres.2014.02.040

activity) were strongly positively correlated with the concentrations of components C1–C3 thus suggesting the fluorescence of these components as indicators for reduction in COD and the total microbial activity in wastewater.

1. Introduction

Excitation-emission matrix (EEM) fluorescence spectroscopy is considered a useful tool for characterizing organic matter (OM) in various natural and engineered aquatic systems (Hudson et al., 2007; Henderson et al., 2009; Ishii and Boyer, 2012). Its potential to discriminate among various types of OM is based on differences in light emission following excitation by illumination of fluorophores present in aquatic OM (e.g., in humic and fulvic acids, proteinaceous material, pigments and various anthropogenic chemicals). A significant progress when using EEMs is obtained by applying Parallel Factor Analysis (PARAFAC; Stedmon et al., 2003; Stedmon and Bro, 2008) where the contribution of different fluorescent components to the total emission can be separated without additional assumptions regarding their excitation and emission spectra. Because of the physical nature of the excitation-emission process, the mathematical tri-linear PARAFAC model may deconvolute EEMs into chemically meaningful components (Andersen and Bro, 2003; Smilde et al., 2004). The PARAFAC analysis of EEMs enables the identification of the number of fluorescent components present, their excitation and emission spectra and concentration scores, thus providing a basis for quantitative analysis of changes in the composition of fluorescent matter in water samples.

Therefore, coupling of the EEM fluorescence spectroscopy with PARAFAC analysis can be useful for characterizing aquatic OM in different water treatment facilities, such as those for drinking water or wastewater. For instance, the EEM+PARAFAC methodology was used by Baghoth et al. (2011) to examine water along the process stages in two drinking water treatment facilities. Bieroza et al. (2011) compared the EEM+PARAFAC methodology with other data mining methods for characterizing OM properties and its removal from drinking water at sixteen water treatment facilities. Recently, a 32 month long monitoring program (EEM+PARAFAC) of raw and treated water (after coagulation-filtration) in a drinking water treatment plant was carried out by Sanchez et al. (2013), who commented on the scarce use of EEM fluorescence spectroscopy and PARAFAC in long-term studies of drinking water treatment facilities.

As distinct from water intended for drinking, wastewater (i.e., non-potable water originating from municipal sewage and industrial effluents) is typically characterized by high concentrations of diverse organic matter. Little work involving systematic long-term studies has been done with regard to EEM+PARAFAC analysis of wastewater along the different stages of water treatment processes. A detailed study of the distribution of fluorescent components in six municipal water recycling plants over 10–12 weeks has been carried out by Murphy et al. (2011). Yu et al. (2013) evaluated the removal efficacy of dissolved organic matter (DOM) at the wastewater treatment plant (WWTP) using the EEM+PARAFAC methodology and second derivative synchronous fluorescence; however, this study was based on just a one-day sampling from the multiple sites at the examined WWTP. Recently, a one month-long monitoring of fluorescence of municipal wastewater at various stages of treatments was carried by Bridgeman et al. (2013), however in this study a peak-picking analysis of the EEMs rather than the PARAFAC-based methodology was used.

The quality of the wastewater treatment may be important when the final product, treated wastewater (TWW), is intended for use in agriculture, e.g., for irrigation in arid and semi-arid regions experiencing a shortage in freshwater. For example, in Israel 78% of the produced TWW is used for agricultural purposes (http://www.mekorot.co.il; accessed in 7.11.2013). Under such circumstances, the TWW-originating DOM may affect soil properties (e.g., enhance clay dispersivity, induce water repellency, decrease aggregate stability and hydraulic conductivity) as well as the transport and fate of soil contaminants and their potential to pollute ground and surface water (Levy and Assouline, 2011; Gerstl and Graber, 2011).

It seems that monitoring the various stages of the treatment of wastewater would assist in determining whether and how the composition of the wastewater with respect to OM is indeed affected by the various levels of treatment. This information could contribute to the optimization of the wastewater recycling process. Therefore, it was deemed important to perform a longer-term examination of OM composition in wastewater from different sources along the treatment stages, by applying EEM fluorescence spectroscopy and the accompanying PARAFAC analysis. For that, we have examined fluorescent OM from four WWTPs and pursued the following specific goals: (1) to determine the major fluorescent OM components in different types of wastewater; (2) to evaluate whether the EEM+PARAFAC methodology may distinguish between TWWs from various WWTPs; (3) to examine the contribution of DOM components to the whole fluorescent OM in treated wastewater of varying quality, (4) to learn of the treatment efficacy and selectivity towards fluorescent OM components, and finally, (5) to examine possible relations between concentrations of fluorescent components in wastewater and common parameters used for characterizing the quality of water at different levels of purification.

2. Materials and methods

2.1. WWTPs and water sampling

Water samples were taken from four WWTPs in Israel between April 2010 and November 2011. The list of the WWTPs