Bioresource Technology 214 (2016) 259–265

Contents lists available at ScienceDirect

Bioresource Technology

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

Biosorption of effluent organic matter onto magnetic biochar composite: Behavior of fluorescent components and their binding properties

Dong Wei [a], Huu Hao Ngo [b], Wenshan Guo [b], Weiying Xu [a], Yongfang Zhang [a], Bin Du [a,*], Qin Wei [c]

[a] *School of Resources and Environment, University of Jinan, Jinan 250022, PR China*
[b] *School of Civil and Environmental Engineering, University of Technology Sydney, Broadway, NSW 2007, Australia*
[c] *Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, PR China*

HIGHLIGHTS

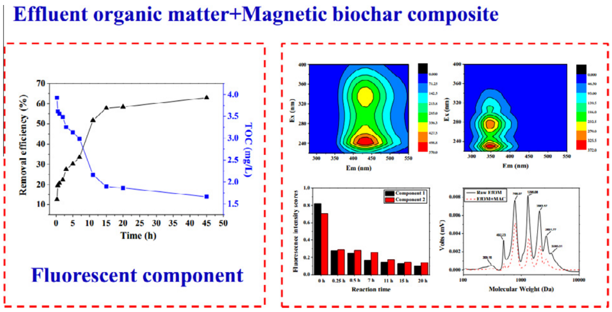
- MBC was successfully prepared, characterized and applied for treating EfOM.
- Fluorescent components of EfOM were identified by using EEM–PARAFAC.
- Fluorescence quenching order of EfOM onto MBC was obtained from 2D-COS.
- The majority of EfOM in terms of MW were removed with different degrees.

ARTICLE INFO

Article history:
Received 16 February 2016
Received in revised form 22 April 2016
Accepted 23 April 2016
Available online 26 April 2016

Keywords:
Effluent organic matter (EfOM)
Excitation–emission matrix (EEM)
Parallel factor analysis (PARAFAC)
Two-dimensional correlation spectroscopy (2D-COS)
Synchronous fluorescence spectroscopy

GRAPHICAL ABSTRACT



ABSTRACT

Effluent organic matter (EfOM) is of great concern as one of main sources of organic pollutants from biologically treated wastewater, which is harmful to the quality of receiving waters. In present study, magnetic biochar composite (MBC) was successfully prepared, characterizated and applied to EfOM treatment. The interaction between EfOM and MBC was explored by a combination of excitation–emission matrix (EEM), parallel factor analysis (PARAFAC), synchronous fluorescence, two-dimensional correlation spectroscopy (2D-COS), and molecular weight distribution. Result implied that two fluorescence components were derived from EEM–PARAFAC, and their relative fluorescence intensity scores expressed decreased trend. Moreover, fluorescence quenching of EfOM with increased MBC took place sequentially in the following order: protein-like fraction < fulvic-like and humic-like fractions. Molecular weight distribution suggested that MBC had different uptake ability to various size ranges of EfOM. The obtained results could provide a potential application of fluorescence spectroscopy for EfOM treatment assessment.

1. Introduction

Recently, effluent organic matter (EfOM) originating from wastewater treatment plant (WWTP) is of significant concern since it negatively affects the quality of effluent (Henderson et al., 2011). The main components of EfOM are consisting of dissolved natural organic matter, refractory compounds, residual degradable substrate, intermediates, soluble microbial products, and trace harmful chemicals (Barker and Stuckey, 1999). The production of EfOM in biological wastewater treatment are greatly influenced by many operational stress conditions, such as hydraulic shock loads, low pH, nutrient deficiency, and presence of toxic compounds etc (Jarusutthirak and Amy, 2007). It is generally accepted that the deep treatment of EfOM is not only beneficial to meet the strict disposal standards but also an essential strategy for making

---

* Corresponding author.
E-mail address: dubin61@gmail.com (B. Du).

http://dx.doi.org/10.1016/j.biortech.2016.04.109
0960-8524/© 2016 Elsevier Ltd. All rights reserved.

better reuse of limited water resource. Therefore, various effectiveness of specific EfOM treating processes have been developed in recent years, including flocculation, ion exchange, sorption, biofiltration, advanced oxidation, and membrane processes (Shon et al., 2006).

Among all above-mentioned methods, sorption is considered as a promising choice for EfOM removal effectively from WWTP effluents aiming at decreasing the pollution of receiving water bodies (Zietzschmann et al., 2014). Biochar, as one of typical kind of low-cost sorbents, has been successfully applied for removing potential organic and inorganic pollutants because of its free availability and high sorption capacity. However, one challenge of the application of biochar is the difficulty to separate and recover it from aqueous solution except by high speed centrifugation or filtration, which means high of operational complexity together with a large amount of energy consumption (Ren et al., 2013). To solve this problem, functionalized magnetic materials have been developed in the field of wastewater treatment to overcome the recovery of adsorbents from treated aqueous solution (Jin et al., 2015). Compared with conventional separation methods, the advantage of magnetic nanoparticles is easy to combine with magnetic field to achieve rapid magnetic separation (Mohan et al., 2011). Therefore, it is expected that the combination use of biochar and magnetic separation would have a well prospect in advanced treatment of EfOM in practical application.

Since the components of EfOM are complicated, many analytical methods have been developed and applied to reveal the EfOM removal mechanism during advanced treatment process, including ultraviolet/visible spectrometry (UV/Vis), fluorescence spectroscopy, Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) etc (Michael et al., 2015). Fluorescence spectroscopy, including three-dimensional excitation–emission matrix (3D-EEM) and synchronous fluorescence, has been extensively utilized for characterization the chemical composition, concentration, distribution and dynamics of samples in water and wastewater due to its rapid, selective and sensitive (Ni et al., 2010; Yu et al., 2013). In particular, detailed investigations have been reported on the utilization of parallel factor analysis (PARAFAC) as an effective multivariate data analysis method to deconvolute complex EEMs into independent fluorescent components which represent groups of similar fluorophores (Ishii and Boyer, 2012). Recent research also has demonstrated that two dimensional correlation spectroscopy (2D-COS) could resolve overlapped peaks problem of one-dimensional synchronous fluorescence by extending spectral intensity trends over a second dimension, and thus provide insightful information about the relative directions and sequential orders of structural variations (Xu and Jiang, 2013). Since a significant typical fluorescent components present in aquatic EfOM (e.g. humic and fulvic acids, and proteinaceous material) (Esparza-Soto et al., 2011; Yu et al., 2015), it is of a particular interest for providing a basis of fluorescence analysis and multivariate calibration method as a powerful tool to characterize the binding property of EfOM during sorption process. However, there is still a lack of thorough examination towards this point.

Based on the above discussion, the objective of this study was to investigate the feasibility of EfOM sorption onto magnetic biochar composite (MBC) from wastewater. For this purpose, MBC was synthesized, characterized and applied for EfOM removal in view of sorption contact time, adsorption kinetics and adsorption isotherm. A combined use of 3D-EEM, PARAFAC, synchronous fluorescence, 2D-COS, and molecular weight distribution were employed to elucidate the interaction between EfOM and MBC. The obtained results could provide insightful information to select, design and optimize the WWTP effluent treatment facilities by considering the point of spectroscopy characterization.

2. Materials and methods

2.1. Effluent organic matter sample

EfOM sample was collected from the secondary settling tank of a municipal WWTP in Jinan, Shandong province, China. The WWTP was treated by using Anaerobic–Anoxic–Oxic (A^2/O) activated sludge process with a treatment capacity of 20,000 m^3/day. The sample was filtered through a 0.45 nm filter, and next stored at 4 °C until use. Total organic carbon (TOC) of the collected EfOM sample is typically around 9.0 mg/L with pH at about 7.5.

2.2. Synthesis of magnetic biochar composite

Biochar was carbonized by using shell as raw material. MBC was prepared by using co-precipitation method (Mohan et al., 2011), and the detailed procedure was as follows: Firstly, 50 g biochar was suspended in a beaker with 500 mL of deionized water. Then, 18 g $FeCl_3$ and 20 g $FeSO_4$ were sequentially added to another beaker with 1500 mL of deionized water and stirred until they were dissolved completely. Next, both solutions were mixed and stirred at 60–70 °C for 20 min. Thereafter, 10M-NaOH (aqueous) was added drop wise into the mixed suspension until the pH was 10–11. After mixing for 1 h, the suspension was aged at room temperature for 24 h and filtered. The remaining solid particles were repeatedly washed with deionized water followed by ethanol. Finally, the prepared MBC was dried at 50 °C for 12 h in a hot air oven.

2.3. Batch sorption experiment

For sorption kinetic experiment, about 30 mg of MBC was added into a 150 mL conical flask containing 50 mL EfOM solution and 50 mL deionized water (TOC about 4.5 mg/L). The initial pH value of the mixed solution was adjusted to 7.0 by using 0.1 mol/L HCl or NaOH. The samples were taken at different time intervals in the range of 0–45 h and analyzed for their TOC concentrations. TOC was selected as a surrogate parameter because it was wildly used for the quantification of EfOM (Michael et al., 2015). The sorption isotherm was carried out with EfOM varied different initial TOC concentrations (3.5–9 mg/L) onto MBC (10 mg) at pH 7.0 for 48 h to ensure equilibrium.

2.4. EEM–PARAFAC

As for the adsorption capacity analysis for batch kinetic experiment, the suspensions were measured to obtain a time-dependent 3D-EEM. 3D-EEM of excitation wavelength were subsequently scanned from 200 to 400 at 10 nm increments by varying the emission wavelength from 280 to 550 nm at 0.5 nm increments, respectively. A 290 nm emission cutoff filter was used in scanning to eliminate second order Raleigh light scattering. The scanning speed was set at 1200 nm/min for all the fluorescence measurements. PARAFAC was performed to interpret the EEM fluorescence data ($n = 9$). PARAFAC analysis was conducted using MATLAB 7.6 (Mathworks, Natick, MA, USA) with the N-way toolbox (Andersson and Bro, 2000). Prior to modeling, first-order Rayleigh and Raman light scattering in EEM data was removed by using interpolation method (Bahram et al., 2006).

2.5. Synchronous fluorescence spectra and 2D-COS

Before the binding test, 100 mL EfOM sample with initial TOC about 4.5 mg/L was added into each erlenmeyer flask by varying different MBC concentration from 50 to 450 mg/L at pH 7.0 for