Journal of Hazardous Materials 261 (2013) 491–499

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Organic matter humification in vermifiltration process for domestic sewage sludge treatment by excitation–emission matrix fluorescence and Fourier transform infrared spectroscopy

Xiaowei Li [a], Meiyan Xing [a,*], Jian Yang [a], Limin Zhao [b], Xiaohu Dai [a]

[a] State Key Laboratory of Pollution Control and Resources Reuse, The National Engineering Research Center for Urban Pollution Control, Key Laboratory of Yangtze River Water Environment, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China
[b] College of Civil Engineering and Architecture, Henan University, Kaifeng 475004, PR China

HIGHLIGHTS

- The VF was more efficient than the BF for sludge reduction and stabilization.
- An additional peak was found at EEWPs of 345/435 nm in ESVF1-HAL and ESVF2-HAL.
- Humification degree of organic matter was strengthened markedly in ESVF1 and ESVF2.
- The increase in height of vermifilter accelerated the organic matter humification.

ARTICLE INFO

Article history:
Received 1 May 2013
Received in revised form 14 July 2013
Accepted 31 July 2013
Available online 7 August 2013

Keywords:
Vermifiltration
Sludge reduction and stabilization
Humic acid
Excitation–emission (*Ex*/*Em*) matrix fluorescent spectra
Fourier transform infrared spectra

ABSTRACT

Performance of a conventional biofilter (BF) and two vermifilters (VFs, different heights) containing earthworms was investigated for domestic sewage sludge (DWS) treatment. Humic-acid like (HAL) fraction isolated from the influent sludge (IS) and effluent sludge of BF (ESBF) and VFs (ESVFs) were determined the elemental and functional composition, and structural characteristics using various analytical approaches. Results showed that performance of DWS treatment in the VFs was preferable to that in the BF. With respect to IS-HAL and ESBF-HAL, ESVFs-HAL had low C, H and N contents and C/O ratio, and high O, carboxyl and phenolic OH group contents, and C/N, C/H and *E4*/*E6* ratios, and large molecular weight. The excitation–emission (*Ex*/*Em*) matrix spectra revealed that an additional peak was found at *Ex*/*Em* wavelength pairs of 345/435 nm in ESVFs-HAL. Further, Fourier transform infrared spectra showed that vermifiltration led to the loss of aliphatic materials and carbohydrates, and the enrichment of carbonyl and phenolic OH groups in HAL fractions. Additionally, the increase in VF height seemed to accelerate humification degree of organic matter in the effluent sludge. In summary, vermifiltration is alternate technology for transformation of organic matter into humic substances, and thus improves quality of DWS as soil organic fertilizer.

1. Introduction

Sludge disposal of WWTPs is one of the major challenges of sustainable wastewater engineering [1], and the cost may be as high as 50–60% of the total operational costs of WWTPs [2,3]. Compared with other treatment processes used in DWS treatment, VF is a low-cost "bio-safe" technique, and thus is more suitable for wastewater and sludge treatment of WWTPs in developing countries [4–6].

Vermifiltration was firstly advocated by the late Prof. Jose Toha at the University of Chile [7,8], and processed wastewater and sewage sludge using earthworms, and their interactions with microorganisms. The process is widely used to treat municipal wastewater [9], domestic wastewater [10–14], and urban wastewater [15], and synchronous treatment of sewage and sludge [16]. Further, VF is found to have remarkable potential to stabilization

Abbreviations: ANOVA, analysis of variance; BF, biofilter; BOD_5, five day carbonaceous biochemical oxygen demand; COD, chemical oxygen demand; DWS, domestic sewage sludge; *E4*/*E6* ratio, ratio of absorbances at 465 nm and 665 nm; EEM, excitation–emission matrix; EEWPs, excitation/emission wavelength pairs; ES, effluent sludge; ESBF, effluent sludge of biofilter; ESBF-HAL, humic acid-like fraction extracted from effluent sludge of biofilter; ESVF-HAL, humic acid-like fraction extracted from effluent sludge of vermifilter; ESVF, effluent sludge of vermifilter; FRI, fluorescence regional integration; FT-IR, Fourier transform infrared; GFC, gel filtration chromatography; HAL, humic acid-like; IS, influent sludge; IS-HAL, humic acid-like fraction extracted from influent sludge; PEGs, polyethylene glycols; SEM, scanning electron microscopy; SFI, specific fluorescence intensity; SS, suspended solid; UV, ultraviolet; VF, vermifilter; VSS, volatile suspended solid; WWTPs, wastewater treatment plants.

* Corresponding author. Tel.: +86 021 65984275.
E-mail addresses: xingmeiyan@tongji.edu.cn, 84370169@qq.com (M. Xing).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.07.074

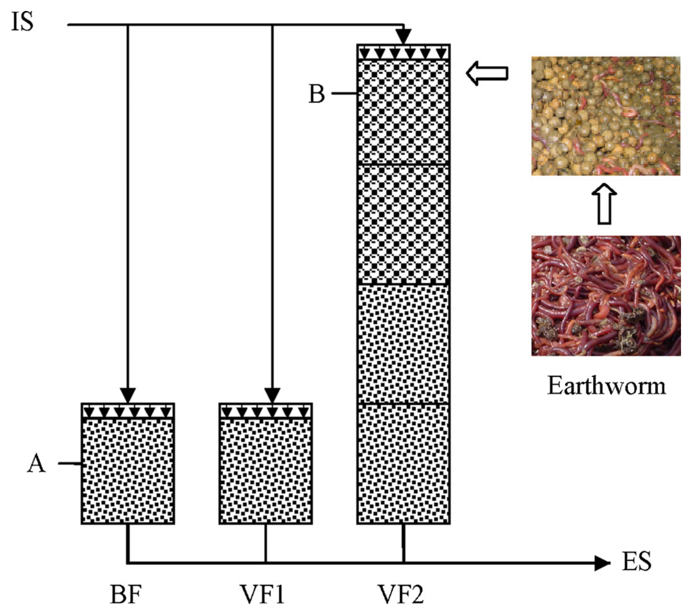

Fig. 1. Schematic diagram of three filter columns. BF, biofilter of 0.5 m height without earthworms; VF1, vermifilter of 0.5 m height with earthworms; VF2, vermifilter of 2 m with earthworms; IS, influent sludge; ES, effluent sludge; A, ceramic pellets of 6–9 mm in diameter; B, ceramic pellets of 10–13 mm in diameter.

and reduction of DWS [4,5,16–18]. Liu et al. [18] reported that VSS reduction of VF achieved the level of 40% sludge stabilization needed for anaerobic and aerobic digestion [19]. Additionally, the ES treated by VF and vermicast are also considered to be a good soil fertilizer or organic amendment [8]. However, there is little directly information about the feasibility of ESVF as soil organic fertilizer.

HAL fraction has an essential influence on the properties of soil and indirectly on the growth of plants [20]. Soil HAL fraction constitute an important source of macro and micronutrients for plants and microorganisms, contribute largely to the acid–base buffering capacity of soils, play an important role in metal speciation in soil, interact with organic xenobiotics, affect soil biological activity, and are able to bind mineral particles together promoting a good soil structure, and thereby improving aeration and moisture retention [21]. Thus, the amount and quality of HAL components in ESVF are considered as important indicators of its maturity and stability and a guarantee for a safe impact and successful performance in soil [22–25].

Previous studies have focused on treatment performance, the design parameters and factors influencing earthworms, organic matter distribution and transformation, microbial community and biofilm properties, and earthworm–microorganism interactions in vermifiltration systems [5,6,12–14,16–18,26]. To our knowledge, chemical features of HAL fractions isolated from ESVF have not previously been investigated.

Some advanced physico-chemical techniques are widely used to analyze the features of HAL fractions, such as UV, fluorescence, FT-IR and nuclear magnetic resonance (^{13}C) spectroscopy, thermal analysis and thermochemolysis–gas chromatography–mass spectrometry analysis and SEM [24,27–29]. However, few papers report molecular weight of the HAL fraction from DWS using GFC.

The objectives of this work are to investigate: (1) performance of VF of different height for reduction and stabilization of sewage sludge; and (2) compositional, functional and structural features of the HAL fractions isolated from effluent sludge in VF of different height using UV, GFC, EEM fluorescence and FT-IR spectroscopy. These results could be used to evaluate the feasibility of VF conversing sewage sludge from WWTPs to humified products, and the quality of the effluent sludge obtained as soil organic fertilizer.

2. Materials and methods

2.1. Experiment design and operation

Two cylindrical VFs and a conventional BF consisting of Perspex tubing (30 cm in diameter) were set up (Fig. 1) and assembled as previous described in Zhao et al. [4]. The heights of two VF columns (VF1 and VF2) were 0.5 m and 2.0 m, respectively, to clarify the effect of different height on sludge treatment. The columns were filled with ceramic pellets of 6–9 mm in diameter, while the upper half part of VF2 were filled with that of 10–13 mm in diameter. A layer of plastic fiber was placed on the top of the filter bed to avoid direct hydraulic influence on the earthworms and ensure an even influent distribution.

The VFs were inoculated with *Eisenia fetida* at an initial earthworm density of 32 g L^{-1} (fresh weight basis), while BF was set up without earthworms as the control of VF1. *E. fetida* was found to possess a high efficiency to treat organic wastes, and thus was chosen and widely used in vermifiltration [11]. The average weight of earthworm was 0.25–0.40 g per individual. The hydraulic loads of these filters were kept at 4 m d^{-1} during the experimental period. The IS of filter columns was taken from excess sludge of secondary sedimentation tank in the Quyang WWTP in Shanghai city, China. The chemical properties were water content (99.5%), pH (6.8–7.8), COD (9900–20000 mg L^{-1}), SS (4800–7500 mg L^{-1}), and VSS (65.4–74.7%). The IS was diluted to certain organic load of about 0.75 kg VSS m^{-3} d^{-1} by tap water, and then introduced to the filter columns through peristaltic pump.

2.2. Reduction and stabilization analysis

The influent and effluent samples were collected weekly for SS, VSS, COD, and BOD_5. COD was measured by a COD analyzer (NOVA 60, Merck, Germany). BOD_5 was measured using a WTW Oxitop IS 12 BOD analyzer. SS and VSS were analyzed according to the standard methods [30].

After four months of operation, three filter columns were tending toward stability for the SS and VSS removal. At this time, ESBF, ESVF1 and ESVF2 were collected for organic elemental analysis and