Waste Management 78 (2018) 911–916

Contents lists available at ScienceDirect

Waste Management

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

Fate of pharmaceutically active compounds in sewage sludge during anaerobic digestions integrated with enzymes and physicochemical treatments

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ARTICLE INFO

Article history:
Received 12 February 2018
Revised 27 June 2018
Accepted 7 July 2018

Keywords:
Mesophilic condition
Thermophilic condition
Enzymolysis
Ultrasonic irradiation
Sludge retention time

ABSTRACT

The removal of 4 typical pharmaceutically active compounds (PhACs) in sewage sludge, i.e. diclofenac (DCF), clofibric acid (CFA), carbamazepine (CBM), and triclosan (TCS), was evaluated during 3 integrated processes of anaerobic digestions (ADs). The integrated processes included ADs integrated with mixed enzymolyses (MEADs), ADs integrated with mixed enzymolyses together with ultrasonic irradiation pre-treatment (MEUADs), and ADs integrated with mixed enzymolyses together with mechanical rotary disc post-treatment (MEADRDs). The SRTs were set at 15 d. Gas chromatography-mass spectrometry (GC/MS) following solid-phase extraction was used to analyze and detect the target compounds. Under the mesophilic condition, the highest removal during MEAD and MEUAD was 67.6% and 77.1% of CFA, and 78.1% of CBZ during MEADRD. There was little differences between the removals of 4 PhACs during MEADRD, and all the removal rates were higher than 70%. Especially the removal of DCF increased from 40.6% during MEAD to 71.7% during MEADRD. The overall removal during MEADRD was highest with the increase by about 20.9% from that during MEAD. The highest removal during MEAD, MEUAD and MEADRD was 81.1%, 70.7% and 71.8%, respectively, of CFA under the thermophilic condition. MEADRD could realize the highest overall removal, up to 69.4% with the increase by 11.0% compared with MEUAD. The results showed that the integrated process, MEADRD, under both mesophilic and thermophilic condition was suitable for the effective removal of PhACs, and MEADRD under the mesophilic condition was a preferable choice from the energy-saving perspective.

1. Introduction

Pharmaceutically active compounds (PhACs) as emerging pollutants have caused growing concerns about their possible threats to the aquatic environment and human health from both the public and the scientists in recent years. The main categories of PhACs found in the aquatic environment are antibiotics, pain killers, muscle relaxants, and hormonal drugs (Acuña et al., 2015; Mathon et al., 2016). Usually these chemicals can finally enter into the environment via the discharge of sewage effluent as well as wastewater and waste from drug manufacturing plants and hospitals, sludge disposal, the discard of private households and landfills (Li, 2014).

Many investigations have also revealed that the removal of PhACs by the conventional wastewater treatment processes (flocculation, sedimentation, and activated sludge treatment) is limited (Martin et al., 2015; Mathon et al., 2016; Pilli et al., 2016; Santos et al., 2007). Therefore, common technologies used for water and wastewater treatment, based on either filtrations or biological treatment (such as activated sludge) are not suitable for the removal of these complex polar molecules, PhACs. The compounds would not be completely removed during sewage treatment, and consequently be discharged into the receiving streams (Cabrita et al., 2010; Martin et al., 2012; Mestre et al., 2009). Thus, it is not surprising that a number of the widely used prescription pharmaceuticals have been detected ubiquitously in the aquatic environment, mostly in the levels from ng/L to μg/L. Therefore, complementary treatment procedures such as membrane filtration and the adsorption of activated carbons are often recommended to be used in conjunction with the traditional processes (Deegan et al., 2011). Besides, there have been sewage treatment processes targeting at the removal of pharmaceuticals and their metabolites as well in recent years since the mere disappearance of the parent compounds cannot be considered as a certain sign of their

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https://doi.org/10.1016/j.wasman.2018.07.018
0956-053X/

complete removal, but possibly as an indication of biotransformation at an unknown degree (Deegan et al., 2011).

The occurrence of PhACs in the solid samples such as sewage sludge has been less reported. This fact could be due to the lack of reliable analytical methods for their determination in these complex samples. Their detection, even in trace amounts, has been enabled in recent years with the development of very sensitive analytical techniques. Sewage sludge is generated as a by-product in sewage treatment plants (STPs) (Martin et al., 2015). It is reported that 53% of sewage sludge generated in the European Union (Maeng et al., 2011) has been used in agriculture directly or after composting. Agricultural utilization does not only represent the cheapest option for the sludge disposal, but also provide a useful fertilizer (due to organic, nitrogen and phosphorus content in sewage sludge) and a soil conditioner material (e.g. for restoring disturbed or derelict land or improving humus content and water holding capacity of arid sandy soils) (Martin et al., 2015). However, the emerging pollutants, PhACs in sewage sludge should also be taken care because of their pseudo-persistence, their continuous discharge to the environment and their potential ecotoxicological effects (Camacho-Munoz et al., 2012; Rodil et al., 2012).

With the extensions of sewage treatment volume and the increasingly stringent requirements of treatment, the treatment and disposal of sewage sludge are becoming more and more emergent (Hospido et al., 2010). Therefore, it is of great interest to investigate the fate and effective removal of PhACs in the sewage sludge treatment before the release of sewage sludge into the environment through agricultural use and other land disposals (Zhou et al., 2015a). Only a few studies reported the occurrence of these compounds alongside the sludge stabilization treatment, mostly anaerobic digestions (ADs) (Martin et al., 2015). The removal rates of these pharmaceuticals varied in a considerable range. The ADs with the individual pre-treatments or post-treatments including mechanical, chemical and biological methods to enhance the removal of PhACs in sewage sludge were also reported by our group (Zhou et al., 2017). The combinations of ADs with ultrasonic irradiation, mechanical rotary disc treatment and enzymolyses, respectively, could improve the performances of the removal by about 10% in general. Ultrasonic irradiation pre-treatment might be most effective to enhance the removal of PhACs during ADs while enzymolyses performed not well as the enzymes were harsh to surroundings, and needed long time to adapt the environment. Therefore, there will still be the room for the improvement on the removal during ADs through their integration with two or more different treatment methods.

In this work, the behavior and fate of 4 typical PhACs in sewage sludge were evaluated during ADs integrated with mixed enzymes together with physicochemical methods based on the previous study conducted by our group mentioned above. The objectives of this study were to explore the performances of integrated AD processes on the removal of PhACs in sewage sludge, and to further manifest the more suitable and preferable one. The sludge retention times (SRTs) were set at 15 d. The target PhACs consisted of anti-inflammatory painkiller diclofenac (DCF), lipid regulating agent clofibric acid (CFA), epilepsy drug carbamazepine (CBM), and broad-spectrum antibacterial agent triclosan (TCS).

2. Materials and methods

2.1. Chemicals and materials

The reference standards of CFA, TCS, CBZ and DCF were bought from ANPEL Co., Ltd (Shanghai, China) with the purity of over 99%. They were dissolved in methanol to 1.0 g/L and stored at −18 °C in the dark. Before use, fresh working solutions were prepared at set concentrations from stock solutions with appropriate dilution, and stored at 4 °C in the dark. The enzymes used in this study were papain and lysozyme. They were of analytical grade, and bought in Sigma-Aldrich (USA). Other chemicals such as methanol, acetone, methyltert-butylether (MTBE), dichloromethane and n-Hexane were of HPLC grade, and all were purchased from ANPEL Co., Ltd (Shanghai, China). Potassium sodium tartrate tetrahydrate, hexaammonium heptamolybdate tetrahydrate, L-Ascorbic acid, sodium hydroxide, potassium antimony tartrate hemihydrate, potassium peroxydisulfate, ammonia solution, and hydrochloric acid were all provided from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and COD reagents from HACH Company (USA). They all were of analytical grade. The derivatization reaction reagent, N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was of the purity of 99.5%, and purchased from Sigma-Aldrich (USA). Ultrapure water was prepared with a Milli-Q Water Purification System (Millipore, Massachusetts, USA).

C8 Cartridges (6 cc/200 mg) for solid-phase extraction (SPE) were supplied by Supelco (USA). Vacuum suction filter was purchased from Tianjin Laboratory Equipment Co., Ltd (China). GF/B Glass fiber filters (Φ 0.22 μm) were bought from Whatmans, USA. Termovap Sample Concentrator (DC-24) for drying with nitrogen stream was supplied by ANPEL Co., Ltd (Shanghai, China).

2.2. Experimental procedure

The AD tests were conducted in the two parallel oval-shaped anaerobic digesters made of stainless steel with total volume of 25 L, and working volume of 20 L each. The detailed description about the digesters could be found in the literature (Zhou et al., 2017). Sewage sludge was collected from the sludge circulation lines of the biological treatment units of a STP located in east district of Shanghai, China, and then thickened with settling to the MLSS 7–8 g/L, and stored at 4 °C until use. The conventional indicators of the sludge were as follows: COD 16,000.0 mg/L, NH_3-N 65.0 mg/L, TP 90.6 mg/L, VSS 3200.0 mg/L, and pH 7.5–8.0. The original concentrations of CFA, TCS, DCF, and CBZ in the sludge were 27.8, 58.5, 114.2, 74.6 ng/L, respectively. The sludge for the tests was spiked using pipette with 4 target compounds to reach 7.5 μg/L each.

The digesters should go through the start-up stage successfully before tests. The procedure for the start-up could be found in the literature (Zhou et al., 2015b). Following the start-up, the digesters were fed with the previously spiked sludge. Before its feeding, the sludge was placed in a water bath to raise its temperature to that of the corresponding ADs, and continuously stirred for 2 h to obtain homogeneity. SRTs of mesophilic anaerobic digestion (MAD) and thermophilic anaerobic digestion (TAD) were set at 15 d based on the previous results (Zhou et al., 2017). The whole tests were conducted with three kinds of integrated processes, i.e. ADs integrated with mixed enzymolyses (MEADs), ADs integrated with mixed enzymolyses together with ultrasonic irradiation pre-treatment (MEUADs), and ADs integrated with mixed enzymolyses together with mechanical rotary disc post-treatment (MEADRDs). ADs would firstly run for 2–3 SRTs to be stabilized when a test began. The conventional indicators were also monitored for the confirmation of stabilization.

According to Zhou et al. (2017), papain and lysozyme were selected due to the better removal of PhACs, and the tests were carried out based on their mass ratio of 1:1 and the whole dosage of 30 mg/g TS. The mixed enzymes were added to the spiked sludge before its feeding into the digesters. Because of the low amount of the enzymes, the stability of the system was not affected (Damrongsakkul et al., 2008; Homaei, 2015; Pan et al., 2016). This study was the first one exploring the effective removal of target PhACs by MEADs.