Chemosphere 206 (2018) 750–758

Contents lists available at ScienceDirect

Chemosphere

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

Performance and methane fermentation characteristics of a pilot scale anaerobic membrane bioreactor (AnMBR) for treating pharmaceutical wastewater containing m-cresol (MC) and iso-propyl alcohol (IPA)

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HIGHLIGHTS

- Pharmaceutical wastewater can be effectively remedied in the AnMBR system.
- The average total removal efficiency of MC and IPA were 95% and 96%, respectively.
- HRT has been observed to be important factors for effective AnMBR process.
- The main VFA were found to be acetic acid, propionic acid, butyric acid.
- AnMBR was composed of an IC anaerobic reactor and membrane module.

ARTICLE INFO

Article history:
Received 28 January 2018
Received in revised form
9 April 2018
Accepted 2 May 2018
Available online 11 May 2018

Handling Editor: A. Adalberto Noyola

Keywords:
Anaerobic membrane bioreactor (AnMBR)
Iso-propyl alcohol (IPA)
M-cresol (MC)
Hydraulic retention time (HRT)
Methanogen community

ABSTRACT

In this study, a pilot scale anaerobic membrane bioreactor (AnMBR) was operated for 80 days to treat pharmaceutical wastewater containing m-cresol (MC) and iso-propyl alcohol (IPA). The aim of the study is to investigate the performance and methane fermentation characteristics of AnMBR at different hydraulic retention time (HRT) (48, 36, 24, 18 and 12 h). The average total removal efficiencies of MC and IPA were 95%, 96% during the 80 days, which demonstrated that the AnMBR system performed well in the MC and IPA removal. The major volatile fatty acid (VFA) was found to be acetic acid, propionic acid, butyric acid, besides, the VFA accumulated apparently when HRT decreased to 12 h. The decrease of HRT led to an increase of relative abundance of methanosarcina from 13 to 33% and a decrease in biogas yield from 0.19 to 0.05 $L/gCOD_{removal}$. The biogas production was found to increase dramatically at HRT of 36 h. The trend of methane content kept stable at this stage with the average value of 78.5% which higher than other HRTs. The investigation of methanogen community showed that *methanosarcinaceae* was always dominant acetoclastic methanogens and *methanomicrobiales* was the dominant hydrogen utilizers throughout the operational period. When the HRT dropped to 12 h, the growth of the *methanosarcinaceae* and *methanomicrobiales* was observed, the amount of the *methanosarcinaceae* and *methanomicrobiales* sharply increased. After the overall research, HRT of 36 h was chosen as the most suitable operating condition due to the comprehensively preferable performance and more economical.

1. Introduction

Pharmaceutical wastewater is mainly generated by chemical-synthetic industries, the components are complicated because of the high chemical oxygen demand (COD), toxicity and a low biochemical oxygen demand (BOD)/COD ratio (Kasprzyjk-Horden et al., 2008; Sreekanth et al., 2009). In some chemical synthesis

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https://doi.org/10.1016/j.chemosphere.2018.05.008
0045-6535/

pharmaceutical industries, m-cresol (MC) and iso-propyl alcohol (IPA) are used as the solvent in the productive process of β-lactam, steroids, vitamins, cephalosporins and intermediates and so on. For instance, in the production of cephazolin which the 7-Phenglacetamido-3-chloromethyl-3-cephem-4-carboxylic acid *p*-methoxybenzyl ester (GCLE) was employed as raw materials, GCLE will react to generate GTDE, then through the reaction of cracking, crystallization in the production of ATDA where need to add MC. The IPA is added in the process of cafazolin acid salt formatting cefazolin sodium. As a result, pharmaceutical wastewater containing solvent of MC and IPA is produced from theses pharmaceutical industries.

This wastewater has the characteristics of highly corrosive, toxicity and carcinogenicity (ATSDR, 1992a; Jiang et al., 2006; Bai et al., 2007). Once the pollutants were inhaled or absorbed by the skin, it may lead to the damage of liver and kidney (Andersen, 2006; Leclercq et al., 2014), headaches, dizziness, eye irritation even induce cancer (John Kennedy et al., 2007; Tu et al., 2012; Rossitza, 2015). It not only affects human health, but also shows the impact on biological survival. In addition, cresols (including o-cresol, MC and p-cresol) which are listed as priority pollutants by US Environmental Protection Agency (EPA) (Chen et al., 2017a), are major toxic pollutants in phenolic compounds (Surkatti and El-Naas, 2014a). Numerous IPA exposures have been reported in the medical and medico-legal literature and sometimes result in fatal outcomes (Alexander et al., 1982; Kelner and Bailey, 1983; Gaulier et al., 2011; Palmiere et al., 2012). Therefore, it is urgently to treat pharmaceutical wastewater containing MC and IPA by appropriate and efficient technologies (Klavarioti et al., 2009).

Currently, multiple studies have reported that MC and IPA can be treated by carbon adsorption (Viraraghavan, 1998; Schmotzer et al., 2002; Shen, 2002; Sun and Chen, 2014), ion exchange (Surkatti and El-Naas, 2014b; Choi et al., 2016a) and chemical oxidation (Du et al., 2012) and biological methods (ATSDR, 1992b). However, physical and chemical processes have some defections. Adsorption is only used to treat low concentration MC wastewater (less than 200 mg/L) and the high cost of activated carbon is discovered comparing with biological methods (Ahmaruzzaman, 2008; Lin and Juang, 2009; Chen et al., 2017b). The ion exchange method can be used to treat MC wastewater with a concentration of 100–600 mg/L (Bai, 2016). Chemical oxidation, a destructive treatment, cannot recycle cresols and reuse oxidants and it even has relative higher operating cost (Zhou et al., 2017). Biological treatments are the practical and favored approach compared to physical and chemical processes since its cost-effectiveness, high efficiency and safety.

Historically, anaerobic process is the most common biological technology for the treatment of pharmaceutical wastewater or high-strength wastewaters as it requires no oxygen, reduces biomass yield and low-energy consumption compared to aerobic process (Ng et al., 2015a). Chelliapan et al. (2011) reported that a unique up-flow anaerobic stage reactor (UASR) was employed to treat pharmaceutical wastewater, indicating the removal efficiency of COD was 45% with an organic loading rate (OLR) of 3.7 kgCOD/($m^3 \cdot d$). Chelliapan and Golar (2011) employed an upflow anaerobic fixed bed reactor could effectively remove 60–70% of the COD with an OLR of 1.5–4.6 kgCOD/($m^3 \cdot d$) in the antibiotic solvent pharmaceutical wastewater. Li et al. (2015) used an upflow anaerobic sludge blanket (UASB) to treat chemical synthesis-based pharmaceutical wastewater containing rich organic sulfur compounds and sulfate, the COD removal decreased nearly 70% under condition of OLR of 8 kgCOD/($m^3 \cdot d$). Furthermore, there are a few anaerobic processes applied in the treatment of MC and IPA wastewater, to authors' knowledge. However, the traditional anaerobic process is incapable of achieving the complete separation of hydraulic retention time (HRT) and sludge retention time (SRT), resulting in the loss of anaerobic sludge from the reactor and poor effluent quality. Based on this, it should be drew attention to provide an effective wastewater treatment technology which have many advantages than other anaerobic bioreactor to solve the above issue and study the related reactor performance.

AnMBR is a kind of wastewater treatment technology which combines membrane separation and anaerobic bioreactor. The microorganisms are completely blocked in the bioreactor by membrane module to achieve the separation of HRT and SRT, ensuring the high concentration of sludge, and then the reactor could obtain effective organic contaminants removal and resistance of impact loads. AnMBR offers many other advantages over traditional anaerobic processes, such as smaller footprints, longer SRT, shorten HRT, less sludge production, in which brought better effluent qualities and the rapid start-up of biological processes (Visvanathan et al., 2000; Yigit et al., 2008; Wang et al., 2010). Recently, the feasibility of AnMBR in treating high-strength wastewater containing refractory contaminants has been verified by lots of studies. As Zayen et al. (2010), an AnMBR was used to treat landfill leachate could achieved a COD removal up to 90% at OLR of 6.27 kgCOD/($m^3 \cdot d$). Galib et al. (2016) reported that the AnMBR achieved COD removal efficiency of 88–95% with OLR increased from 0.4 to 3.2 kgCOD/($m^3 \cdot d$) for the treatment of meat-processing wastewater. Although many AnMBRs were applied in the treatment of industrial and pharmaceutical pollutants, there was rarely attention on the treatment of solvent wastewater, especially containing the deleterious MC and IPA which were used largely. Moreover, the overall performance and suitable operating condition of reactor should be researched to give reliable and economic reference in the future wastewater treatment of pharmaceutical solvents.

Accordingly, the objective of this paper was to investigate the performance and methane fermentation characteristics at different HRTs (48, 36, 24, 18 and 12 h) by applying a pilot-scale AnMBR. The reactor was composed of an internal circulation (IC) anaerobic reactor as the anaerobic pretreatment process which has superior removal efficiency compared with the technology of continuous stirred tank reactor (CSTR) as bioreactor in the traditional AnMBR, and membrane module as the anaerobic post-treatment process for the treatment of the IC reactor effluent. The ability of removal MC and IPA pollutants, VFA and terminal fermentation products, bicarbonate alkalinity, biogas production, methane content, as well as the methanogenic community was studied in this paper. Then the most appropriate HRT was discussed mainly based on MC and IPA removal and methane content, the ratio of permeate VFA and bicarbonate alkalinity.

2. Materials and methods

2.1. Experimental apparatus

A schematic diagram of pilot-scale anaerobic process was shown in Fig. 1. The system combined an anaerobic internal circulation (IC) and membrane modules. Detailed parameters of the IC system used in this research were listed as follows: height 1.5 m, internal diameter 2.5 m, providing a working volume of approximately 4.4 m^3. The membrane module was hollow fiber curtain membrane made of polyvinylidene fluoride (PVDF) (HT-MBR-20-PVDF, Hangzhou Haotian Membrane Technology Co., Ltd., China) with a pore size of 0.22 μm. There are four membrane components; each membrane has area of 7 m^2 with a total area of 28 m^2. In fact, there are 20 m^2 of membrane area which are able to meet the experimental needs according to the designed membrane flux. So when a membrane is under backwashing, the other three can work