Bioresource Technology 266 (2018) 75–81

Contents lists available at ScienceDirect

Bioresource Technology

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

Post-treatment of anaerobic membrane bioreactor (AnMBR) effluent using activated carbon

Do Thi Mai[a,b], Chinagarn Kunacheva[b], David C. Stuckey[b,c,*]

[a] Interdisciplinary Graduate School, Nanyang Technological University, Singapore 639798, Singapore
[b] Nanyang Environment & Water Research Institute, Advanced Environmental Biotechnology Centre, Nanyang Technological University, Singapore 637141, Singapore
[c] Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom

ARTICLE INFO

Keywords:
Activated carbon
Soluble microbial products (SMPs)
Anaerobic membrane bioreactor (AnMBR)
Effluent
Ciprofloxacin

ABSTRACT

Anaerobic membrane bioreactors (AnMBR) are very effective for wastewater treatment, however, with the antibiotic ciprofloxacin (CIP) (0–4.7 mg CIP/L) in the feed their performance decreases, the characteristics of the effluent changes, and further treatment is needed to recycle or discharge the treated effluent. Batch experiments using six activated carbons to treat AnMBR effluents resulting from the treatment of a synthetic wastewater containing ciprofloxacin were carried out at 35 °C. 22–82% COD was removed at a dose of 1 g activated carbon/L, while size characterization showed the 13.4 kDa and < 1 kDa fractions were the most difficult to adsorb, while CIP was often removed with high efficiencies of mainly 100%. Significant removal of VFAs also occurred, up to 100%, and this contributed greatly to COD removal. Nitrogen containing compounds and phenols showed the highest removal (~100%), whereas other groups such as esters, alkanes, and alkenes showed lower removal efficiency.

1. Introduction

Anaerobic membrane bioreactors (AnMBR) often result in high COD removals in wastewater treatment, and have many advantages over conventional aerobic systems, including the production of biogas (methane) that can reduce the energy demands of treatment, low sludge production (~10–30% of aerobic systems), and high loading rates with smaller footprints (Seghezzo et al., 1998). The AnMBR reactor can achieve as high as 99% chemical oxygen demand (COD) removal (Bailey et al., 1994); however, under non-favourable conditions, such as low hydraulic retention time (HRT), psychrophilic temperature, etc., lower performance was observed (Hu and Stuckey, 2006; Smith et al., 2015).

In our recent study, the addition of ciprofloxacin (CIP) to an AnMBR feed resulted in the reduction of methane production and COD removal (Mai et al., 2018). Furthermore, the AnMBR showed even lower COD removals when the feed contained high concentrations of CIP (4.7 mg CIP/L), with the COD removal reduced from > 95% with the no and low-CIP concentrations (< 1.5 mg/L) reactor, to only 78 ± 13% with the high CIP concentration (4.7 mg/L); this led to a higher COD in the effluent (111 ± 63 mg COD/L (Mai and Stuckey, in preparation). The effluent during this period did not satisfy the discharge regulations of several regions such as Singapore, Japan and Europe, with regulations ranging from 60 to 125 mg COD/L (Japan, 2015; Legislation, 1994; Singapore, 2017). Volatile fatty acids (VFAs), and some low molecular weight (MW) soluble microbial products (SMPs) such as aromatic and nitrogen containing compounds (N-compounds) increased under high concentrations of CIP; p-cresol was present at 49 μg/L in the effluent. More aromatic compounds were also found in an aerobic membrane bioreactor (MBR) when exposed to pharmaceuticals (Zhang et al., 2016). The presence of phenolic and indolic compounds, which have been shown to be carcinogenic (Nowak and Libudzisz, 2006), may also cause adverse effects to ecosystems and human health if they are discharged to the environment. In addition, disinfection by-products (DBPs) can be produced from SMPs which could cause risks to human health as some of those products are genotoxic, mutagenic and/or carcinogenic (Richardson et al., 2007). Moreover, DBPs produced from N-compounds, which were produced under CIP exposure (Mai et al., 2018), were more toxic than carbon-containing DBPs (Plewa et al., 2007). Another concern are various pharmaceuticals in sewage which were not completely removed in the WWTP and are discharged to the environment (Kümmerer, 2009; Michael et al., 2013), even by an MBR or AnMBR (Michael et al., 2013; Xiao et al., 2017), which are very effective treatment processes. The presence of pharmaceuticals in the aquatic environment may have a potential impact on ecosystems and human health (Heberer, 2002; Kümmerer, 2003). Hence, the effective

* Corresponding author at: Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom.
E-mail address: d.stuckey@imperial.ac.uk (D.C. Stuckey).

https://doi.org/10.1016/j.biortech.2018.06.063
Received 17 April 2018; Received in revised form 19 June 2018; Accepted 20 June 2018
Available online 21 June 2018
0960-8524/

post-treatment of AnMBR effluents is needed to satisfy the discharge and the recycling standards, as well as to remove potentially toxic compounds such as phenol and N-compounds present as SMPs in the effluent, and remaining antibiotics (eg. CIP). This is important as interest in wastewater recycling is increasing due to the lack of fresh water.

For the post-treatment of AnMBR effluents, adsorption by powdered activated carbon (PAC) was investigated as one of the most efficient treatment methods for removing traces of organic solutes (Trzcinski et al., 2011; Vyrides et al., 2010). PAC and granular activated carbon (GAC) had the highest COD removals of 84% and 80%, respectively, exceeding ultrafiltration membranes (1 kDa), coagulation-flocculation and polymeric adsorbents which had COD removals ranging from 75% to 32% (Trzcinski et al., 2011). Comparing PAC with other biological methods such as aerobic, or anaerobic, or combining these types of biomass with PAC, Vyrides et al. (2010) obtained similar results to PAC alone, and removed 80% of the dissolved organic carbon (DOC). The adsorption of activated carbon is high due to its porous structure, with a large surface area (500–1500 m^2/g), and numerous internal pores and functional surface groups. Due to this, activated carbon can adsorb various solutes that are known to be present in water, including organics such as phenol and phenolic compounds (Dąbrowski et al., 2005), volatile organics (Chiang et al., 2002), pharmaceuticals (Rakić et al., 2015) and metal ions like lead, copper, zinc, chromium and cyanide (Monser and Adhoum, 2002). However, activated carbon adsorption does not remove all organic compounds, and Gur-Rezniket al. (2008) showed that about 24% of the dissolved organic matter was non-adsorbable, being mainly hydrophilic and transphilic compounds, although the exact composition of these compounds is unknown due to analytical challenges. Also, high MW organics in anaerobic effluent were showed more adsorbable than low MW compounds (Barker et al., 1999; Trzcinski et al., 2011; Vyrides et al., 2010). The < 1 kDa fraction was only 70% removed by PAC, while higher fractions showed higher removal efficiencies of 90–100% (Vyrides et al., 2010). Until now the identification of these compounds in wastewater and which are removed or left by adsorption, was limited due to the inadequacy of existing analytical methods. However, using recent developments in analytical techniques to measure low MW SMPs (< 580 Dalton) (Kunacheva et al., 2017a), for the first time we can truly understand what these compounds are, and how they are adsorbed, or not.

Therefore, the aim of this study was to investigate the removal of organic compounds in AnMBR effluents treating a synthetic wastewater containing CIP using different activated carbons. We used both conventional Size Exclusion Chromatography (SEC), and the analysis of specific compounds including VFAs and low MW SMPs (< 580 Dalton) to understand which solutes adsorption removes, and what are not removed. In addition, we physically characterised different activated carbons which contributed to understanding how the adsorption of natural organic compounds occurred. Based on these insights, the choice of a suitable type or types of activated carbon for different effluent characteristics, especially AnMBR effluents, can be made to minimise effluent COD.

2. Material and methods

2.1. AnMBR configuration

The configuration of the AnMBR was identical to previous studies (Ketheesan et al., 2016; Kunacheva et al., 2017b). In brief, the reactor had a working volume of 3.2 L with a flat sheet membrane with a total surface area of 0.11 m^2, and an average pore size of 0.2 µm, was submerged in the reactor. The AnMBR was inoculated with anaerobic sludge from a municipal wastewater treatment plant (WWTP- Ulu Pandan Water Reclamation Plant, Singapore) with the total suspended solids (TSS) of 6 g/L. The reactor was in a water bath to control the temperature at 35 ± 1 °C, and the solids retention time (SRT) was kept at 300 days. The synthetic feed (~500 mg COD/L) was based on that used by (Ketheesan et al., 2016), and was comprised of glucose, meat extract, peptone, $NaHCO_3$, K_2HPO_4, and trace metals. Operation of the reactor, and CIP addition were scheduled as shown in Table 1.

Table 1
Operation of reactor.

Phase	Operating time (days-cumulative)	HRT (h)	CIP in influent (mg/L)	COD feed (mg COD/L)
Phase I	44 (44)	12	0	485 ± 22
Phase II	44 (88)	6	0	487 ± 31
Phase III	41 (129)	6	0.5 ± 0.1	490 ± 28
Phase IV	11 (140)	6	1.5 ± 0.1	512 ± 21
Phase V	93 (233)	6	4.7 ± 0.7	490 ± 22
Phase VI	45 (278)	6	0	485 ± 20

AnMBR effluent was sampled during reactor operation in Phases II, IV, VI. In Phase V, two sample effluents were taken at days 248 and 263 due to the significant differences in the VFAs and SMP composition/concentration over time in this Phase. Effluent samples were denoted as EFF-I, EFF-II, EFF-III and EFF-IV corresponding with Phases II, V, and 2 effluent samples in phase VI, respectively. No effluent samples were analysed in depth in Phases I, III and IV as they all had similar characteristics in terms of COD, SMP composition, VFA accumulation, and SEC. Despite this, in phase VI where the AnMBR was operated for a long time at high CIP concentrations of 4.7 mg CIP/L, a significant difference in a number of parameters in the initial and later periods was observed; therefore, two samples at the start and end of Phase VI were taken for analysis. In brief, the four effluent samples had COD concentrations of 9, 238, 56 and 24 mg/L, respectively. EFF-I and EFF-IV contained no VFAs, while EFF-II contained 162 mg/L acetic acid and 81 mg/L propionic acid, and EFF-III contained 29 mg/L and 5 mg/L of acetic acid and propionic acid, respectively. All the effluent samples were filtered through 0.45 µm for COD and SMP analysis, while further filtration through 0.2 µm for VFA, CIP and size distribution were performed.

2.2. Experimental set up

AnMBR effluent (1 L) and activated carbon (1 g) were added to 1000 mL glass bottles for the adsorption experiment, and stirred at 500 rpm at 25 °C for 24 h. The samples were then settled for 10 mins and filtered through 0.45 µm to separate the liquid; all samples were then stored at 4 °C and analysed within 10 days.

An initial kinetic study of one activated carbon (SA2) was then conducted to see how fast adsorption occurred; SA2 was chosen based on its middle range characteristics of activated carbons shown in Table 2. The experiments were conducted in 160 mL glass bottles containing 100 mL of AnMBR supernatant taken during Phase II, with 2 g AC/L. The kinetics were modelled using either a Pseudo-first order (Eq. (1)) or Pseudo-second order (Eq. (2)) expression;

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \quad (1)$$

Table 2
Characteristics of activated carbons tested.

Carbon types	Denotation	B.E.T surface area (m^2/g)	Pore volume (cc/g)	Pore radius (Å)	Particle size
Filtrasorb 300 D	FD	884	0.04	16.33	d_{85} = 2.36 mm
NRS EA 0.5–1.5	NRS	768	0.18	18.13	d_{98} = 0.5 mm
Hydrodarco C	HYD	370	0.28	20.20	d_{99} = 150 µm
SAE2	SA2	619	0.26	18.19	d_{95} = 150 µm
WP-AO	WP	761	0.10	18.14	d_{80} = 75 µm
SAE Super	SAS	1021	0.33	18.00	d_{97} = 150 µm