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A novel application of anaerobic bio-entrapped membrane reactor for the treatment of chemical synthesis-based pharmaceutical wastewater

Kok Kwang Ng, Xueqing Shi, Melvin Kai Yin Tang, How Yong Ng *

Centre for Water Research, Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, Singapore 117576, Singapore

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ABSTRACT

Pharmaceutical wastewaters are mainly generated by chemical-synthetic industries and usually contain high chemical oxygen demand (COD) and toxicity. A novel lab-scale anaerobic bio-entrapped membrane reactor (AnBEMR) packed with bio-ball carriers was constructed and compared with an anaerobic membrane bioreactor (AnMBR). The aims of this study are to investigate the treatment performances and evaluate the stability of the membrane filtration of the AnBEMR and AnMBR under the conditions of a high organic loading rate (OLR), ranging from 8.0 to 36.7 kgCOD/m^3 d, and high total dissolved solids (TDS), ranging from 18,411 to 25,925 mg/L, in the treatment of chemical synthetic-based pharmaceutical wastewater. Four different hydraulic retention times (HRTs) of 10.6, 14.1, 21.3, and 42.6 h were studied. Total COD (TCOD) removal efficiency of the AnBEMR ranged from 36.7% to 50.8% at an OLR of 8.7 ± 0.7 kgCOD/m^3 d, while the highest OLR (34.0 ± 2.7 kgCOD/m^3 d) only led to TCOD removal efficiency of 10.1–20.7%. The AnBEMR achieved approximately 5–10% higher TCOD removal efficiency than the AnMBR. The influences of HRT and TDS (salinity) were also studied. The results show an increase of trans-membrane pressure (TMP) with decreasing HRT in both MBRs, where extracellular polymeric substances (EPS), soluble microbial products (SMP) and suspended biomass concentration were significantly higher at the shortest HRT of 10.6 h, resulting in faster membrane fouling. Membrane fouling was improved in the AnBEMR (i.e., longer membrane filtration operating periods) due to the production of lower concentrations of EPS and SMP (protein and carbohydrate contents). Proteins, rather than carbohydrates, were the major component of EPS and SMP in both reactors. The study concludes that the application of the AnBEMR could achieve better treatment performance and reduced membrane fouling by producing lesser EPS, SMP, and suspended biomass concentration.

1. Introduction

Pharmaceutical wastewater is one of the most significant gateways for emerging pollutants to enter water bodies, particularly with the rapid growth of the pharmaceutical industry and associated human needs. Pharmaceutical wastewater is categorized as high-strength wastewater because it typically contains high concentration of chemical oxygen demand (COD), ammonia, suspended solids or heavy metal; sometimes, shock loading will also happen to the biological system. Pharmaceutical wastewater also contains a variety of organic and inorganic constituents, including spent solvents, catalysts, reactants and small amounts of intermediate products [1–3]. Large volumes of complex and obstinate composition wastewaters, along with biological substances, cleaning agents and disinfectants are simultaneously produced that might pose potential threats, such as endocrine disruption and have severe side effects on the aquatic environment [4]. Even though pharmaceutical wastewater may contain diverse refractory organic materials that cannot easily be degraded, the anaerobic process of biological treatment is still a practical and favored approach for high strength and organically polluted wastewater, as the aerobic process requires high-energy consumption and creates foaming.

Anaerobic treatment for pharmaceutical wastewater has been performed using several modern technologies, such as the up-flow anaerobic sludge blanket (UASB) [3,5,6] up-flow anaerobic biofilter process (UABP) [7] and fixed-film reactor (FFR) [8]. Oktem et al. [5] reported that the hybrid UASB could effectively remove 72% of the COD in the chemical synthetic-based pharmaceutical wastewater at an organic loading rate (OLR) of 8 kgCOD/m^3 d. Chen et al. [6] also demonstrated the use of UASB in the treatment of pharmaceutical

* Corresponding author. Tel.: +65 6516 4777; fax: +65 6774 4202.
E-mail address: howyongng@nus.edu.sg (H.Y. Ng).

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Nomenclature

AnBEMR	anaerobic bio-entrapped membrane reactor
AnMBR	anaerobic membrane bioreactor
BSA	bovine serum albumin
Ca^{2+}	calcium
Cl^-	chlorides
CH_4	methane
COD	chemical oxygen demand (mg/L)
EPS	extracellular polymeric substances (mg/L)
EPSc	extracellular polymeric substances (carbohydrate) (mg/L)
EPSp	extracellular polymeric substances (protein) (mg/L)
F^-	fluoride
F/M	food-to-microorganism ratio
FFR	fixed-film reactor
HRT	hydraulic retention time (h)
K^+	potassium
MBR	membrane bioreactor
MLSS	mixed liquor suspended solids (mg/L)
MLVSS	mixed liquor volatile suspended solids (mg/L)
Na^+	sodium
$NaHCO_3$	sodium bicarbonate
NaOCl	sodium hypochlorite
NH_3–N	ammonia nitrogen (mg/L)
OLR	organic loading rate (kgCOD/m^3 d)
PDVF	polyvinylidene fluoride
PO_4^{3-}	phosphate
SMP	soluble microbial products (mg/L)
SMPc	soluble microbial products (carbohydrate) (mg/L)
SMPp	soluble microbial products (protein) (mg/L)
SO_4^-	sulphates
SRT	sludge retention time (day)
TCOD	total chemical oxygen demand (mg/L)
TDS	total dissolved solids (mg/L)
TMP	trans-membrane pressure (kPa)
TN	total nitrogen (mg/L)
TOC	total organic carbon (mg/L)
TSS	total suspended solids (mg/L)
UABP	up-flow anaerobic biofilter process
UAF	up-flow anaerobic filter
UASB	up-flow anaerobic sludge blanket
UF	ultrafiltration
VSS	volatile suspended solids (mg/L)

wastewater containing 6-Aminopenicillanic acid and amoxicillin. The OLR were varied from 12.6 to 21.0 kgCOD/m^3 d and the average COD reduction was 52.2%. The performance of an UABP treatment of pharmaceutical wastewater was investigated by Chen et al. [7], and showed that a COD removal of 70–93% was achieved in the anaerobic system at a hydraulic retention time (HRT) of 2–20 d. Nevertheless, the washing out of anaerobes and retention of the high biomass concentrations in the system are still crucial concerns for the anaerobic treatment process. Therefore, the development of the anaerobic membrane bioreactor (AnMBR) provides a promising solution, since the AnMBR combines the advantages of the anaerobic process with the production of solid-free effluent and complete retention of biomass by membrane filtration [9–11]. Recently, specific studies have reported that the applications of AnMBR for the treatment of different high-strength wastewaters could achieve satisfactory COD removal and biogas yield. The results of these studies are summarized in Table 1. However, study on AnMBR for treatment of chemical synthesis-based pharmaceutical wastewater for organic removal, system performance, operation parameters and membrane fouling has yet to be reported.

Although the AnMBR offers many advantages over modern anaerobic processes such as combined unit operation that incorporates solids removal and organics reduction in one reactor, membrane fouling is still a major concern, especially with the high biomass concentration in the AnMBR. In view of this concern, the anaerobic bio-entrapped membrane reactor (AnBEMR) has been developed as an alternative to the AnMBR. The application of the anaerobic entrapped biomass process has not been researched as previous investigations of the entrapped biomass technique only focused on the aerobic biological processes [18–20] and aerobic MBRs [21,22]. The entrapped biomass technique was developed for various types of wastewater treatment in order to achieve high simultaneous removal of carbon and nitrogen within a single through-put process, and with an intention to handle high loads of dissolved organics, low suspended biomass concentration and development of slow-growing bacteria to tackle complex organic compounds [18,19]. In recent years, several researchers have reported that the entrapped biomass technique coupled with the membrane could reduce membrane fouling due to lower production of abundant soluble organics and lower suspended biomass concentration in the system [20–22].

The main objective of this study is to study a conventional AnMBR and a novel AnBEMR with entrapped biomass in the reactor for the treatment of chemical synthetic-based pharmaceutical wastewater, with the objective of evaluating the treatment performance at different OLRs and membrane fouling behaviour. As the AnBEMR membrane fouling may not be similar to that of the AnMBR, the extracellular polymeric substances (EPS) and/or soluble microbial products (SMP) and their characteristics during membrane fouling were also investigated.

2. Experimental methods

2.1. Experimental setup

Two lab-scale anaerobic membrane bioreactors (an AnMBR and an AnBEMR), each with a total effective working volume of 10-L, were simultaneously investigated for organic removal and membrane fouling behaviour for the treatment of chemical synthetic-based pharmaceutical wastewater. More specifically, each AnMBR consisted of a 5-L completely mixed anaerobic reactor coupled with a 5-L membrane tank, in which a polyvinylidene fluoride (PDVF) GE hollow fiber ultrafiltration (UF) membrane module (GE-LS1) was installed (Fig. 1). The hollow fiber membrane module had an effective filtration area of 0.047 m^2 and nominal pore size of 0.04 μm; each hollow fiber had a length of 220 mm with an outer diameter of 1.9 mm and an internal diameter of 0.8 mm. The membrane tank (5-L) was a circular column with a height of 75 cm, internal diameter of 12 cm and wall thickness of 3 mm, and was made of acrylic. The design of having the membrane unit external to the anaerobic reactor allowed the ease of membrane cleaning and replacement while maintaining a strictly anaerobic environment in the anaerobic reactor.

As shown in Fig. 1, peristaltic pumps were used to feed influent into the anaerobic reactor, recycle mixed liquid from the anaerobic reactor to the membrane tank, and withdraw permeate from the membrane module. The excess mixed liquor in the membrane tank was recirculated back into the anaerobic reactor by gravity. A magnetic stirrer was used to achieve homogeneous mixing in the anaerobic reactor. Level sensors were installed in the anaerobic reactors and membrane tanks to control the input of influent and