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Treatment of chemical synthesis-based pharmaceutical wastewater in an ozonation-anaerobic membrane bioreactor (AnMBR) system

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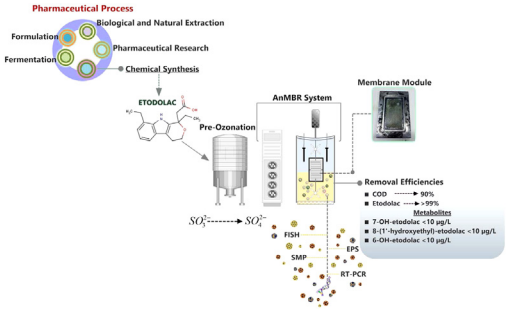
HIGHLIGHTS

- AnMBR was successfully operated up to 7500 mg/L of COD with 85–90% of COD removal.
- Pre–ozonation process was applied to raw wastewater because of sulfite inhibition.
- Pre–ozonation was effective to obtain high Etodolac removal efficiency up to 99%.
- The pre-ozonation-AnMBR system was provided the efficient operation conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, treatability of etodolac chemical synthesis wastewater from the pharmaceutical industry was investigated in a hybrid ozonation-Anaerobic Membrane Bioreactor (AnMBR) system. The AnMBR was successfully operated up to 7500 mg/L of chemical oxygen demand (COD), but sulfite inhibition occurred at this loading. A pre-ozonation process was applied to overcome the problem of sulfite inhibition resulted from raw wastewater by decreasing the sulfite concentration through oxidation to sulphate. Furthermore, it was shown that this process was also effective obtaining high etodolac removal efficiencies up to 99%. Approximately 90% COD removal efficiency was achieved by the combined system. Extracellular polymeric substance (EPS) decreased in the conditions of long sludge retention time (SRT), hydraulic retention time (HRT) and low organic loading rate (OLR) values. Therefore, the granule size also decreased during the entire operation. Real-time polymerase chain reaction (Q-PCR) and fluorescent in situ hybridization (FISH) analyses revealed that high sulfite concentration affected the microbial population in the order of methanogens, acedogens and sulphate reducing bacteria (SRB).

1. Introduction

In recent years, pharmaceutical wastewater has become a serious source of water pollution with the rapid development of the pharmaceutical industry. Wastewaters in a pharmaceutical industry generally originate from the chemical synthesis and formulation of the drugs. The chemical synthesis-based pharmaceutical wastewaters have high chemical oxygen demand (COD), total suspended solids (TSS) value and a wide pH range of pH (1–11), due to various organic and inorganic constituents including solvents, additives, catalysts and reactants [1,2]. In addition, water consumption and wastewater generation in the chemical synthesis process are larger than in other pharmaceutical manufacturing

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processes. Some pharmaceutical active compounds were added to the priority pollutant list of the European Union Water Framework Directive in 2014. In this context, it should be focused on the removal of the active compounds in each pharmaceutical wastewater in addition to organic matter.

Pharmaceutical wastewater has traditionally been treated using physico-chemical and biological processes. However, biological processes such as anaerobic and aerobic systems are still the favoured options for the pharmaceutical wastewater due to the cost-effectiveness of the latter treatment [3]. Especially, anaerobic treatment processes are preferred because of high COD concentration and low biodegradability of the components of this wastewater [4–12]. Previous studies have reported several anaerobic treatment processes such as the up-flow anaerobic sludge blanket (UASB), two-phase anaerobic digestion system-MBR hybrid system, hybrid reactor combining UASB-anaerobic filter, and anaerobic continuous stirred tank reactor (CSTR) for the treatment of chemical synthesis-based pharmaceutical wastewater [1,9,13–14]. However, anaerobic treatment has limitations in its use to provide better effluent quality, efficiency and reliability due to the washout of microorganisms in the high biomass concentrations. In recent years, anaerobic membrane bioreactors (AnMBRs) have received considerable attention because of lower energy requirement, high effluent quality, a small footprint, low sludge production and prevention of methanogens washout, regardless its settling and granulation properties [15–17]. AnMBRs can also play a key role in energy generation due to their capacity to produce methane from the utilisation of a large fraction of organics in wastewaters [18,19].

In the literature, only a few papers have reported the treatment of pharmaceutical wastewater using the AnMBR process. Dutta et al. [20] investigated removal of pharmaceuticals and organic matter from municipal wastewater using a two-stage anaerobic fluidized bioreactor. An anaerobic fluidized membrane bioreactor was used as a second stage treatment process and granular activated carbon (GAC) was added to the system for the control of membrane fouling. Ng et al. [17] investigated the treatment of chemical synthesis-based pharmaceutical wastewater using a laboratory-scale anaerobic bioentrapped membrane reactor and AnMBR coupled external membrane modules. The membrane fouling was evaluated by EPS and soluble microbial product (SMP) results. Monsalvo et al. [21] focused on the removal of trace organics from a synthetic wastewater containing pharmaceuticals, endocrine disruptors, personal care products and pesticides by AnMBR. McCurry et al. [22] investigated removal of disinfection byproduct precursors and pharmaceuticals in an anaerobic fluidized membrane bioreactor. GAC was added to the reactor in order to improve the removal of the pharmaceuticals. Some toxic compounds such as metals, ammonia, phenol, formaldehyde, sulfide and sulfite are inhibitory to anaerobic bacteria. High sulfite concentration in the raw wastewater exerts a strong acute inhibitory effect on anaerobic bacteria [23]. Sulfite causes a lag phase of different length in methane production. In order to prevent the inhibition by sulfite, it is necessary to avoid any accumulation of sulfite in the process [24]. If only sulfite removal is desired, electrocoagulation/electroflotation or oxidation could be applied [25,26]. Treatment alternatives for pharmaceutical wastewater are very limited because they are not usually designed by considering their characteristics having a wide and different content although some treatment options are available as shown in the studies cited above. Hence, it is necessary to develop a compact treatment system of pharmaceutical wastewater with reduced footprint and effective efficiency by considering and overcoming the sulfite inhibition. Ozonation could be used to prevent sulfite inhibition by decreasing the sulfite concentration through oxidation to sulphate. Furthermore, ozonation ensures increase in biodegradability and micropollutant removal [27]. In this context, ozonation is selected as pre-treatment method.

The aim of this study was to research the feasibility of AnMBR for the treatment of chemical synthesis-based pharmaceutical wastewater. A pre-ozonation process was applied to the raw wastewater in order to reduce the sulfite concentration. The combined pre-ozonation-AnMBR system provided efficient operating conditions. An evaluation of microbial diversity was performed considering the populations of acidogenic, methanogenic and (sulphate reducing bacteria) SRB, which depended on the change in the OLR. In addition, real-time polymerase chain reaction (Q-PCR) and fluorescent in situ hybridization (FISH) analyses were carried out to determine the microbial population in the AnMBR.

2. Experimental

2.1. AnMBR and ozonation system

The anaerobic reactor system used in the study was purchased from Electrolab, United Kingdom (FerMac 320 bioreactor fermenter). The system was modified by submerged flat-sheet and hollow-fiber membrane modules and used as an AnMBR (completely mixed reactor at a stirring rate of 150 rpm). The flat-sheet microfiltration membrane (polyethersulfone-PES) with a pore size of 0.05 μm was purchased from Microdyn-Nadir GmbH. The nominal pore size of the hollow-fiber microfiltration membrane (Polipropilen-PP) purchased from Zena Company was also 0.05 μm. The effective surface area of 66 cm^2 was the same for both membrane types. The reactor was made of quartz glass and was equipped with 1 pH probe, 1 thermometer, 1 level sensor, 4 internal pumps (feeding, acid-base dosing and foam), a temperature jacket and a mixer. The reactor has an inside diameter of 160 cm and a height of 320 cm with a total volume of 6.4 L and a working volume of 4 L. The permeates were drawn through the membranes by a peristalitic pump (Watsom Marlow) and recorded by a computer via a PLC card and an RS 232 line. Cake formation and fouling on the membrane surface were minimized by periodic sparging with nitrogen gas from a nitrogen generator (UHP Nitrogen Generator Model: NG2081 HC). CH_4 was determined by ABB, Advance Optima AO 2020, Switzerland, gas analyzer equipped with thermomagnetic and infrared photometers. The transmembrane pressure was kept constant at 200 mbar throughout all the experiments.

The ozonation experiments were conducted in a lab-scale venturi-injection system. Ozone was generated by an ozone generator (Degremont Technologies) capable of producing 4 g/h ozone. Atmospheric oxygen was used to produce ozone, which was introduced by venturi injection into the reactor. The reactor was a 5 L cylinder made of stainless steel. The circulation loop had a volume of 2 L. The pump was used to circulate the wastewater in the reactor. The temperature of the contactor was controlled by a water bath at 35 °C. In the pre-ozonation experiments, 2 g/h ozone was applied to the wastewater by venturi injection for a period of 60 min. The combined ozonation-AnMBR system is shown in Fig. 1.

2.2. Experimental procedure and reactor operation stages

The chemical synthesis pharmaceutical wastewater was obtained from the etodolac manufacturing tanks of a pharmaceutical factory, located in Gebze, Turkey. The AnMBR reactor was inoculated with granuler sludge from an up-flow anaerobic sludge blanket reactor treating wastewater of a beer industry. The reactor was operated at a pH of 7, temperature of 35 °C, reactor volume of 4 L and infinite SRT. The sludge samples were taken from the reactor only for analysis purposes.