Journal of Membrane Science 511 (2016) 228–237

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Treatment of textile wastewater using sequential sulfate-reducing anaerobic and sulfide-oxidizing aerobic membrane bioreactors

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ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form
19 March 2016
Accepted 21 March 2016
Available online 28 March 2016

Keywords:
Anaerobic membrane bioreactor
Sulfate reduction
Textile wastewater
Color removal
Membrane fouling

ABSTRACT

This study aims at evaluating the performance of sequential sulfate-reducing anaerobic and sulfide-oxidizing aerobic membrane bioreactors (MBRs) for the treatment of synthetic textile wastewater. The process performance was evaluated under varying concentrations of COD (1000–2000 mg/L), NaCl (500–1000 mg/L), and sulfate (500–1500 mg/L), but keeping dye (Remazol Brilliant Violet 5R) concentration constant at 200 mg/L. In sulfate reducing anaerobic MBR (AnMBR), COD removal efficiency remained between 80% and 85%. The sulfate reduction efficiency was directly related with COD/sulfate ratio. Almost complete decolorization was attained in the AnMBR, whereas slight recolorization was observed in the AeMBR due to autooxidation of aromatic amines. EDS analyses illustrated that cake layer in AnMBR contained much higher amounts of S, Fe and Cu due to formation of metal–sulfide precipitates, whereas Ca and P were the major inorganic elements in AeMBR. In the cake layers of both MBRs, high molecular weight soluble organics were observed by gel permeation chromatographic analyses together with the identification of proteins and polysaccharides by the FT-IR analyses. Capillary suction time, specific resistance to filtration and supernatant filterability tests illustrated that AnMBR sludge had less filterability and stable operation was possible with a flux of around 5 LMH.

1. Introduction

In textile industry, water is primarily utilized during the dyeing and finishing operations. The textile industry may be accepted as one of the most polluting industrial sectors considering both volume and composition of wastewater generated [1]. Over one million-ton of dye is produced annually and around 50% of the produced dye is used in textile industries [2]. Azo dyes are the most widely used class of dyes with word market share of 60–70% [1,3] and around 20–50% of the applied dyes remain in the aqueous phase in dyeing operation, leading to colorization of the effluent stream. In addition to dyes, several auxiliary chemicals are used in the dying process and the produced wastewater is quite complex and variable in characteristics [4,5]. The composition of textile wastewater depends very much on the process, coloring matters, dyestuffs and the accompanying chemicals. The release of dye containing effluents into the environment is undesirable due to serious potential environmental problems linked with the dyes and their breakdown products, i.e. aesthetic deterioration and the carcinogenic nature of aromatic amines generated as by-products of anaerobic azo-dye biodegradation [6].

Although aerobic treatment of azo dyes is quite difficult due to its recalcitrant nature and toxicity to microorganisms [7], under anaerobic conditions azo dyes are used as electron acceptors and are readily cleaved generating aromatic amines [6–8]. Contrary to the azo-dyes, aromatic amines are generally stable under anaerobic conditions whereas they are aerobically biodegradable [6,8,9].

Membrane bioreactor (MBR) technology combines the activated sludge process with membrane filtration process. With the use of micro- or ultra-filtration membranes (pore size: 0.05–0.4 μm), complete physical retention of microorganisms are achieved [10]. Therefore, in the past two decades, remarkable progress has been achieved on the MBR technology all over the world and become attractive option for the treatment and reuse of industrial and municipal wastewaters.

Although anaerobic bioreactors are more efficient for color removal, aerobic MBR has been generally used in several lab and pilot scale studies [11] and limited number of studies are available in the literature on the textile wastewater treatment using anaerobic MBR (AnMBR) [7,8,12]. In our previous studies [7,8], we have illustrated that anaerobic MBR (AnMBR) can be successfully used for the treatment of textile wastewater. Even at high salinity conditions, AnMBR showed high efficiency and aerobic MBR (AeMBR) following the AnMBR was responsible for the effluent

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http://dx.doi.org/10.1016/j.memsci.2016.03.044
0376-7388/

polishing as well as aromatic amine degradation [8]. Textile wastewaters generally have high conductivities, even up to 9 mS/cm, due to high concentrations of NaCl and some other inorganics added to increase the dye fixation by fabric [13]. Additionally, sulfate concentration in the textile wastewater may reach to very high levels as sulfate is added to the dye bath for ionic strength adjustment [14]. Sulfate concentration may also increase due to sulfuric acid use for the neutralization of alkaline textile wastewater before biological treatment. In the presence of sulfate, sulfate reducing conditions will develop, which completely changes microbial community and affects the color removal performance [14,15]. Additionally, sulfide formed under sulfate reducing conditions should be further oxidized biologically. In the literature, there are limited number of studies on the treatment of textile wastewater using AnMBRs [7,8] and sulfidogenic MBRs. To the best of our knowledge, there is no study on the treatment of textile wastewater using sequential sulfate-reducing anaerobic and sulfide-oxidizing aerobic MBRs. Hence, this study aims at evaluating the efficiency of sequential sulfate reducing and sulfide oxidizing MBRs for the treatment of synthetic textile dye wastewater under varying operational conditions. Also, a special emphasis have been given for the investigation of fouling in the MBRs as the presence of sulfide may completely change the fouling characteristics due to possible metal–sulfide precipitate formation in the bioreactors.

2. Materials and methods

2.1. Membrane bioreactors

Sequential AnMBR and AeMBR (Fig. S1, Supplementary materials) were used throughout the study. Both reactors were made of plexiglass. AnMBR had the dimensions of $11 \times 14 \times 37$ cm with total and working volumes of around 5.7 L and 4 L, respectively. AeMBR had the dimensions of $8 \times 14 \times 38$ cm with total and working volumes of 4.3 L and 2.5 L, respectively. The reactors were operated in sequential mode, i.e., the effluent of AnMBR was fed to the AeMBR (Fig. S1, Supplementary materials).

The detailed information on the MBRs is provided in our previous publication [8]. Flat sheet microfiltration polyethersulfone (PES) membranes with 0.45 μm pore size were mounted into modules such that the total effective area of membrane surface was 0.01 m^2 for each module. In both MBRs, the gas flow rate was kept similar at 1 $m^3/(m^2$ membrane area h) to physically scour the cake layer developed on the membrane surface. In the AnMBR, biogas recirculation was used to scour the cake layer as illustrated in Fig. S1 (Supplementary material). The AeMBR was aerated continuously with the rate of 1 $m^3/(m^2$ membrane area h) both to physically scour the cake layer on the membrane and to supply the oxygen required for biological activity. Oxygen concentration in the AeMBR was always above 3 mg/L, which illustrated that the air supplied for cake scouring was sufficient to supply the required oxygen for aerobic growth. The volume of biogas produced in the AnMBR was measured continuously using water displacement method.

Intermittent filtration cycle, i.e. 5 min suction followed by 1 min relaxation (non-suction), was adopted in both MBRs to alleviate cake formation on the membrane surface.

2.2. Operating conditions of MBRs

The sequential AnMBR and AeMBR were fed with synthetic wastewater (Table S1, Supplementary materials), which contained glucose as an organic carbon source, inorganic nutrients required for growth, and Remazol Brilliant Violet 5R (RBV-5R) as a model dye compound.

Table 1
Operating conditions of the MBRs.

Parameters	Periods (Days)			
	I (1–42)	II (43–91)	III (92–125)	IV (126–237)
COD (mg/L)	1000	1000	1000	2000
SO_4^{2-} (mg/L)	500	1000	1500	1000
NaCl (mg/L)	1000	1000	1000	500
	Anaerobic MBR			
Flux (LMH)	4.69 ± 0.96	4.54 ± 0.59	4.93 ± 0.40	4.35 ± 0.61
HRT (Day)	1.98 ± 0.88	1.92 ± 0.34	1.74 ± 0.18	2.0 ± 0.35
	Aerobic MBR			
Flux (LMH)	7.95 ± 1.04	8.21 ± 0.74	8.26 ± 0.88	8.91 ± 1.23
HRT (Day)	1.45 ± 0.42	1.30 ± 0.1	1.30 ± 0.14	1.22 ± 0.20

Throughout the study, dye (RBV-5R) concentration was kept at 200 mg/L. NaCl was also added to the synthetic wastewater in order to simulate the high conductivity values in the textile wastewaters. NaCl concentration was kept at 1000 mg/L in the first three periods and decreased to 500 mg/L in the last period (Table 1). In the first three periods, sulfate concentration was increased steadily from 500 mg/L to 1500 mg/L and decreased to 1000 mg/L in the last period. COD concentration was kept at 1000 mg/L in the first three periods and then increased to 2000 mg/L in the last period. Hence, COD/sulfate ratio was changed between 0.67 and 2.0 (Table 1).

As given in reaction (1), the theoretical COD/sulfate ratio required to completely oxidize COD and reduce sulfate is 0.67 if the biomass production is ignored [16].

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (1)$$

However, the electron flow from COD oxidation to sulfate reduction generally averaged 75–85% as the rest of the COD may be utilized for growth [16–19]. Therefore, the COD/sulfate ratio required by sulfate reducing bacteria for complete COD and sulfate removal ranges between 0.8 and 1.0.

Both AnMBR and AeMBR were previously operated under varying operational conditions for more than 410 days in our previous studies [7,8]. Hence, anaerobic and aerobic biomass had already been well acclimated to the wastewater and the operational conditions.

In the AnMBR, the hydraulic retention time (HRT) and flux were 1.75–2.0 days and 4.35–5.0 L/(m^2 h) (LMH), respectively. In the AeMBR, the HRT and flux values were 1.2–1.5 days and 8–9 LMH, respectively (Table 1).

From both MBRs, sludge was only drawn for the analytical purposes, hence sludge retention time (SRT) was considered as infinite.

COD, sulfate, pH, conductivity, and color were regularly measured in the influent. Permeate, and mixed liquor of the MBRs were sampled regularly for the determination of COD, sulfate, sulfide, azo dye, alkalinity, extracellular polymeric substances (EPS) and soluble microbial product (SMP) concentrations. In MBRs, pH, and transmembrane pressure (TMP) values were also measured online. Additionally, oxygen concentration and oxidation–reduction potential (ORP) were measured online in AeMBR and AnMBR, respectively.

2.3. Membrane cleaning

Operation of the MBRs was stopped and the fouled membrane