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Petrochemical wastewater treatment and reuse by MBR: A pilot study for ethylene oxide/ethylene glycol and olefin units

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ABSTRACT

This study aims to investigate the technical feasibility of employing membrane bioreactor (MBR) as a practical approach for ethylene oxide/ethylene glycol (EO/EG) and olefin units wastewater treatment in a petrochemical complex. EO/EG unit wastewater mainly contains ethylene glycol and acetaldehyde and olefin unit wastewater includes benzene and ethyl benzene, with COD concentration of 1900 ± 900 mg/L and 900 ± 300 mg/L, respectively. Experimental studies of MBR pilot plants with volume of 2.5 m^3 were carried out during 6 months in different HRTs and various mixed ratios of EO/EG to olefin unit wastewater. Results revealed that using MBR, COD removal efficiency of 97.5% is accomplished in HRT of 13.5 h for EO/EG and 85% in HRT of 18 h for olefin wastewater. For the mixed ratio of 2/1 and in HRT of 18 and 24 h, COD removal efficiency of 93.5% and 96% was achieved, respectively. Membrane fouling was analyzed at different MLSS concentrations. The results at optimum MLSS of 8 g/L revealed that fouling resistance is mainly due to the membrane pore blocking, and cake and gel resistances contribute less to membrane fouling. Results indicated that MBR is a promising technology for treatment of high fluctuation toxic components in petrochemical wastewater.

Introduction

Increasing demand of water for industrial use and exhaustible water resources has brought up the issue of wastewater treatment and reuse for industrial applications in Middle East [1]. The special economic zone of Imam Khomeini port petrochemical complex in Iran also faces this challenge. Marun petrochemical complex as one of major companies in this zone contains various units including EO/EG, olefin and light and heavy poly ethylene. This company has attempted to provide a part of the required water through treatment of wastewater by a feasible technology.

Marun petrochemical complex wastewater mostly deals with the wastewater of EO/EG and olefin units. EO/EG unit wastewater is produced with a flow rate of 200 m^3/h. COD concentration of EO/EG unit wastewater is 1000 to 2800 mg/L and has high fluctuation due to operational changes. COD concentration of the wastewater is mostly due to the presence of ethylene glycol, yet it contains acetaldehyde and formaldehyde.

Ethylene glycol is a readily biodegradable compound with a half-life of approximately 3–3.5 days which can be removed from wastewater by activated sludge process [2–4]. Although most of aerobic microorganisms in common activated sludge systems are capable of treating light ethylene glycol, presence of aldehydes in concentrations of higher than 100 ppm would affect the activity of aerobic and anaerobic microorganisms in activated sludge negatively [5,6]. Different concentrations of acetaldehyde in wastewater with a COD of 1000 to 3000 ppm can be treated using highly-concentrated activated sludge with MLSS concentration of 4000 to 12,000 mg/L in a membrane bioreactor [7]. The olefin unit wastewater, with a flow rate of 100 m^3/h, has a COD concentration of 600 to 1200 mg/L after passing through an oil-water separator. Olefin unit wastewater with a COD/BOD ratio of four contains phenol, benzene, toluene, ethyl benzene, xylene, and poly-aromatic hydrocarbons (PAHs). Phenol, BTEX and PAHs are considered as hazardous contaminants in wastewater as they interrupt treatment process. This is due to the fact that they can only be removed by some microorganisms in activated sludge such

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as *Alcaligenese faecalis* and *Pseudomonas* [8,9]. Different studies have shown that a mixture of activated sludge microorganisms can be used in MBR for treatment of olefin unit wastewater [7,10]. However, different methods are suggested for the treatment of petrochemical industry wastewater and suitable methods are determined by considering wastewater characteristics, degree of contamination and financial aspect [11].

Membrane bioreactor (MBR) is one of the most promising technologies for wastewater treatment and water reuse [12]. MBR is a combination of activated sludge process and membrane technology and is widely used for wastewater treatment. High mixed liquor suspended solids (MLSS) concentration in this technology has made it a suitable choice for treatment of highly toxic wastewater such as petrochemical wastewater [13]. In addition to decelerating bacteria growth rate and decreasing production of excess sludge, high SRT in MBR leads to growth of sludge age which in turn improves MBR ability to tolerate toxic components [14,15]. In addition to the above-mentioned advantages, less required space and high-quality effluent have made MBR a promising technology for industrial wastewater treatment and reuse [16,17]. Also growth in design and application of MBR indicate its development for wastewater treatment purposes [18]. But MBR has also disadvantages such as membrane fouling [19], biological foaming [20] and high cost of investment [21]. It should be mentioned that MBRs with microfiltration membrane for water reuse, have noticeable amount of aerobic bacteria and coliphages which made ultrafiltration a better choice in some uses [22].

Several studies have shown the application of MBR in municipal wastewater treatment [21–24]. Literature also suggests application of MBR for wastewater treatment and water reuse in different industries including those producing wastewater containing heavy metals [25] and micro-contaminants [26], pharmaceutical industry [27], oil industry and refinery [28], and petrochemical industries [28–31]. Application of a membrane bioreactor results in high-quality water for different purposes. In case that the permeate from membrane bioreactor doesn't meet the criteria for recycling, polishing steps such as nanofiltration or RO would be required.

Min et al. investigated removal of acetaldehyde, butyraldehyde and vinyl acetate in a 10 L side-stream MBR with polyethersulphone tubular ultrafiltration membrane which has organic loading rate of 1.1 to 2.0 kgCOD/m^3/day and reported removal efficiency of more than 98% [32]. Application of membranes in petrochemical industries, have been investigated by Takht-Ravanchi et al. using MBRs with ultra- and microfiltration with pore sizes ranging from 0.05 to 0.4 μm in which RO is mostly used as a polishing step in industrial wastewater reuse [33]. Also Chung et al. used a MBR with polypropylene membrane for petrochemical wastewater treatment with a concentration of 400 mg/L phenol and observed a removal efficiency of 100% during 18 h [34]. In addition Galil et al. investigated treatment of a petrochemical wastewater containing BTEXs with COD concentration of 2000 to 4000 mg/L and flow rate of 500 L/day using a pilot-scale hollow fiber MBR and achieved effluent COD concentration of less than 50 mg/L [35].

In another study by Visvanathana et al. wastewater containing petrochemical contaminants is treated by MBR which lead to COD and BOD removal of 62–79% and 60–75%, respectively [36]. Qin et al. investigated a flat-sheet MBR with Chlorinated polyethylene microfiltration membranes and operating volume of 48 L in which 40% of its volume is anaerobic. They treated wastewater with COD concentration of 700 to 2000 mg/L at HRT of 19 h and achieved effluent with COD concentration of less than 50 mg/L [29]. Hassani et al. have reported COD removal efficiency of 75% in treatment of oil refinery wastewater with taking advantage of a side-stream hollow fiber MBR with operating volume of 20 L [37]. Also the removal efficiency of more than 98% was achieved by Dosta et al. in treatment of petrochemical wastewater with Phenol concentration of 12 mg/L and HRT of 0.45 day using a pilot-scale submerged flat-sheet MBR with operating volume of 8 m^3 [38].

Several investigations have been carried out to study treatment of petrochemical wastewater containing phenol and olefin using MBR [10,29,39]. High removal efficiency with different initial concentrations (47–500 mg/L) at HRTs of 1.5–7 days was achieved by MBR technology [36]. Despite high potential of MBR technology for industrial wastewater treatment, MBR plants have not been studied for the treatment of EO/EG unit, and a mixture of the wastewater of EO/EG and olefin units.

Since MBR efficiency and membrane fouling are highly dependent on feed characteristics and scale of operation [40–42], pilot-plant studies on wastewater are strongly recommended for industrial applications [39].

This article aims to investigate technical feasibility of MBR application for the wastewater treatment in Marun petrochemical complex EO/EG and olefin wastewater units. Regarding special characteristics of Marun petrochemical complex wastewater, this investigation as the first study is applicable in similar industries.

Experiments

The experiments were carried out in a pilot plant MBR located in Marun petrochemical complex, special economic zone of Imam Khomeini port petrochemical, Iran. The schematic diagram of the pilot plant is illustrated in Fig. 1. It consists of aeration and filtration tanks with a total volume of 2.5 m^3 and has flow rate of 139 to 333 L/h.

A flat-sheet membrane with an area of 10 m^2 was immersed in the filtration tank. The MBR module was supplied by Microdyn-Nadir BC10 which was equipped with polyethersulfone (PES) membrane with pore size of 0.04 μm. Activated sludge was acquired from a petrochemical wastewater treatment unit. The

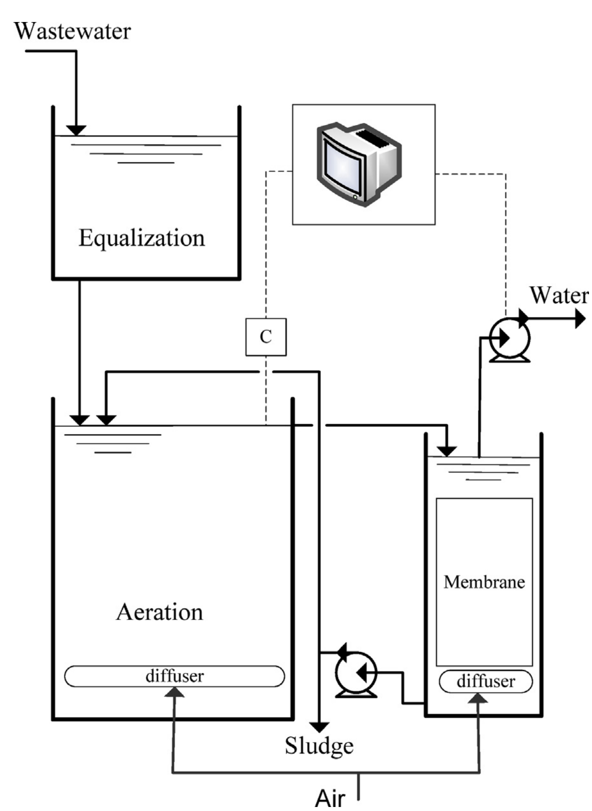

Fig. 1. Schematic diagram of the pilot plant.