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Considering membrane sequencing batch reactors for the biological treatment of petroleum refinery wastewaters

Seyedramin Pajoumshariati, Nasim Zare, Babak Bonakdarpour*

Department of Chemical Engineering, Amirkabir University of Technology, Tehran 15875, Iran

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ABSTRACT

In the present study a membrane sequencing batch reactor (MSBR) was assessed for treatment of petroleum refinery wastewater (PRW). Mean COD, O & G and TPH removal efficiencies of 80%, 82% and 93.4% respectively – achieved during more than three-month operation of the MSBR with real PRW of varying composition – attested to the robustness of the MSBR system for treatment of PRW. The MSBR system was also able to withstand and recover from a toxic shock loading applied during part of its operation. GC/MS analysis revealed that the majority of the organic constituents of the PRW were eliminated as a result of MSBR treatment whereas a minority were only partially biodegraded. The effect of the application of relaxation – a hydraulic membrane cleaning method that has been extensively studied in MBRs but not in MSBRs – on membrane fouling was both quantified and characterised. The finding of the present work showed that, compared to the use of air scouring alone, relaxation results in a significant drop in the rate of membrane fouling in MSBRS and affects the way mixed liquor physicochemical properties influence membrane fouling. Also, the membrane fouling layer at the end of MSBR operation was visually and chemically characterised.

1. Introduction

Petroleum refinery is an example of an industrial facility which produces a wastewater containing a range of mainly hydrocarbon compounds, some of which can cause serious problems if released into the environment [1]. It also uses a lot of process water [2]. For this reason, prior to disposal or reuse, petroleum refinery wastewater (PRW) is subjected to a series of physical, chemical and biological treatments.

The traditional process combination used industrially in the treatment of PRW is gravity separation followed by air flotation and biological treatment (usually the activated sludge process) [3]. Oil, grease and the heavier hydrocarbons as well as the colloidal substances are usually removed by the physicochemical pre-treatment processes, whereas the main function of the biological treatment unit is the removal of dissolved organics, which are mainly the lighter hydrocarbons, and include several highly toxic components [4]. Sequencing batch reactors (SBR) are bioreactor designs that have been employed as alternative to activated sludge processes (ASP) for treatment of PRW on an industrial scale [5,6]. One disadvantage reported for both the ASP and SBR process is the fairly high suspended solids in their effluent which is caused by the limited efficiency of the associated sedimentation process [5,6]. This in turn will result in a fairly low MLVSS in the bioreactor causing a low rate of biological biodegradation of pollutants in the PRW. Another serious disadvantage is the high sensitivity of these biological processes to toxic shock loading, which is an inevitable phenomenon during the operation of a typical petroleum refinery. Galil et al. reported that toxic shock loading of activated sludge process used for treatment of PRW on an industrial scale caused by sudden discharge of phenolic waste seriously impaired bioflocculation of the activated sludge eventually resulting in complete inhibition of the biological process [7].

In order to remedy the disadvantages associated with biological treatment of PRWs non-biological alternative processes such as advanced oxidation have been considered for the treatment of PRW [8]. Alternatively, the chemical coagulation process that usually precedes the biological process is replaced with a more advanced process such as electrocoagulation [9]. However, these processes suffer from high costs and there is fairly low experience with them on an industrial scale.

Another approach has been the incorporation of a physical or chemical process after the biological unit. A particularly successful examples of the former have been hybrid biological-membrane processes. A prominent example of these processes is membrane bioreactors (MBRs). These are modified activated sludge processes in which the sedimentation unit is replaced by an internal or external

* Corresponding author.
E-mail address: babakb@aut.ac.ir (B. Bonakdarpour).

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membrane unit. The use of MBRs for the treatment of PRWs has been considered by a number of researchers [4,10–13].

An alternative technology to MBRs which has been considered for the treatment of a variety of wastewaters [14–17] – but not real PRW – is membrane sequencing batch reactors (MSBRs). MSBRs are sequencing batch reactors (SBRs) in which the settling phase of the operation is replaced by pumping the effluent through micro- or ultra-filtration unit which is either immersed inside the SBR or connected to it. MSBR has various advantages over both SBRs and MBRs. Compared to SBRs, MSBRs: 1) provide higher treatment quality due to complete biomass retention [18]; 2) can yield higher solid retention times (SRTs) which will result in enhancement of nutrient removal [19]; and 3) due to the elimination of the settling phase are more compact. Compared to continuous systems like MBRs, they provide several advantages such as: 1) process flexibility as the process variables can be easily adjusted to suit changing wastewater characteristics; 2) ability to perform simultaneous nitrification-denitrification; 3) simpler construction and less chance of the development of filamentous bulking as a result of the MSBR's inherent feast-famine regime [5]. They, however, share the MBRs disadvantages associated with membrane fouling and the consequent need for membrane cleaning and replacement.

The assessment of the suitability of any new biological process for treatment of real PRW must take into account the robustness of the biological process, its sensitivity to toxic shock loading –and in the case of membrane based biological processes such as MSBR - the rate and nature of membrane fouling during operation with wastewater of variable composition. Robustness means that removal performance of the proposed biological process must be relatively unaffected by daily changes in the chemical composition of the PRW; this is important because during normal operation of a petroleum refinery the composition of PRW changes from one day to the next. Problems with operation of some units of a petroleum refinery or routine washing or maintenance do occur from time to time leading to a pronounced but temporary increase in the concentration of one or more toxic chemical constituent of PRW such as phenol or furfural resulting in toxic shock loading of the biological process. Another characteristic, therefore, of a suitable biological process for treatment of real PRW is that it must be fairly insensitive to toxic shock loading or be only transiently affected by it.

The membrane fouling characteristic of MSBRs is another important consideration in assessment of their suitability for treating real PRW. Membrane fouling characteristics for a variety of wastewaters and operating conditions have been extensively studied for MBRs [20–22] and revealed the complex interrelationship between operating parameters, wastewater chemical composition and membrane fouling. However, there are much fewer reported studies on the membrane fouling characteristics of MSBRs and none concerning real PRWs. There is therefore a vital need for data concerning membrane fouling in MSBRs especially when these reactors are operated with real industrial wastewaters – like PRW – which contain potentially toxic components.

The success of a membrane based biological process – from the point of view of membrane fouling – in the treatment of an industrial wastewater depends on the efficacy of the membrane cleaning protocol or strategy employed. One of the methods that reportedly results in decrease in fouling rate in MBRs is relaxation. Relaxation is defined as temporary cessation of the permeate withdrawal whilst the air flow is scouring the membrane [23].

Relaxation, however, is more effective in the removal of reversible than irreversible fouling [24]. Backwashing, which is an alternative hydraulic method of membrane cleaning, is more effective in removal of irreversible fouling compared to relaxation and has been studied as a method of fouling mitigation in a MSBR treating a synthetic wastewater containing 4-chlorophenol [18]. However, compared to backwashing, relaxation has the advantage of less energy consumption and no permeate loss [25,26]. Furthermore, back washing is not applicable for most commercial flat sheet membranes [26]. The effect of relaxation has been extensively studied and optimised for MBR systems [24–26]. Given the difference between the mode of permeate removal in MSBRs and MBRs the effect of relaxation on membrane fouling rate and mechanism in MSBRs also needs to be studied. Relaxation has been employed in some MSBR studies as a method of membrane fouling retardation [27–29]. McAdam et al. found that in short term filtration studies in a MSBR, the application of relaxation resulted in a decrease in the rate of rise of TMP [27]. However, to the knowledge of the authors no systematic study has been carried out on the effect of relaxation on membrane fouling in MSBR systems especially during long term operation in the presence of actively growing biomass.

The aim of the present study was the assessment of the suitability of MSBR system for treatment of real PRW. For this purpose, MSBR was operated for more than three months with real PRW of varying composition and its removal performance as well as membrane fouling rate and characteristics were determined. In the case of the former, especial attention was paid to the robustness of the MSBR system and its response to toxic shock loads. Membrane fouling characterisation was mainly focused on the quantification as well as characterisation of the effect of relaxation on membrane fouling in MSBRs.

2. Materials and methods

2.1. Experimental setup and operating conditions

A mixture of activated sludge collected from two biological wastewater treatment plants (one treating the wastewater from Tehran Petroleum Refinery and the other treating the kitchen wastes of the main Petroleum Ministry building in Tehran using an MBR) was used to inoculate the MSBR. This was done to impart diversity to the microbial population in the activated sludge inoculum. Microscopic observations of inoculum confirmed the presence of diverse protozoan populations in the activated sludge. A MSBR fully controlled by computer using the Labview software was used, the details of which has been presented in our previous work [30]. The membrane module used in this study was a submerged flat sheet membrane module (Kubota, Japan) with a pore size of 0.4 µm and effective area of 0.11 m^2. The MSBR with the volume of 10 L was aerated continuously at the rate of 10 L min^{-1} ($SAD_{membrane}$: 5.45(m^3 m^{-2} h^{-1})) through a tubular diffuser (2 mm holes with 2 cm pitch) located beneath the module to scour the membrane on both sides. The MSBR was operated for a period in excess of three months at fixed SRT, HRT, total cycle time and volume exchange ratio (VER) of 20 days, 8 h, 4 h and 0.5 respectively, and a temperature of 27 ± 1 °C. The cycle time was composed of a filling (11 min), a reaction (149 min) and a withdrawl/idle (80 min) phase. Aeration was performed throughout the MSBR cycle.

Chemical cleaning was performed according to the recommendation of the manufacturer with 1% (V/V) sodium hypochlorite (NaClO) followed by 1% (W/V) oxalic acid. Physical cleaning was performed by flushing the membrane with tap water to remove the sludge cake from the membrane surface. Membrane filtration flux of 50 LMH has been applied through the experiment. If the water flux of the cleaned membrane was less than the initial value, chemical cleaning was implemented.

Effluent of the dissolved air flotation (DAF) unit from Tehran Petroleum Refinery was fed to the MSBR. Before entering the MSBR, the PRW feed was supplemented with NH_4Cl (46.736 mg/l), KH_2PO_4 (10.738 mg/l), $CaCl_2{\cdot}2H_2O$ (0.01 mg/l), $MgSO_4{\cdot}7H_2O$ (0.005 mg/l) and $FeCl_3{\cdot}6H_2O$ (0.071 mg/l) as sources of macro- and micro-nutrients and $NaHCO_3$ (200 mg/l) as buffer for pH adjustment. It should be pointed out that the PRW also consisted of the human wastewater of the Tehran Petroleum Refinery.

In the present study, the MSBR was operated under two different regimes of membrane cleaning: In the first regime (days 0–30) only air scouring was employed, whereas during the second regime (day 30