PERGAMON

Water Research 36 (2002) 1018–1024

WATER RESEARCH

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Application of a membrane bioreactor for treating explosives process wastewater

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Received 1 August 2000; accepted 2 May 2001

Abstract

A bench-scale anoxic membrane bioreactor (MBR) system, consisting of a bioreactor coupled to a ceramic cross-flow ultrafiltration module, was evaluated to treat a synthetic wastewater containing alkaline hydrolysis byproducts (hydrolysates) of RDX. The wastewater was formulated the same as hydrolysis wastewater and consisted of acetate, formate and formaldehyde as carbon sources and nitrite and nitrate electron acceptors. The MBR system removed 80–90% of the carbon sources, and approximately 90% of the stoichiometric amount of nitrate, 60% of nitrite. The reactor was also operated over a range of transmembrane pressure, temperature, suspended solids concentration, and organic loading rate to maximize treatment efficiency and permeate flux. Increasing the transmembrane pressure and temperature did not improve flux significantly. Increasing mixed liquor volatile suspended solids (MLVSS) concentration in the bioreactor decreased the permeate flux significantly. The maximum volumetric organic loading rate was 0.72 kg COD/m^3/day. The maximum food-to-mass ratio was 0.50 kg N/kg MLVSS/day and 1.82 kg COD/kg MLVSS/day. Membrane permeate was clear and essentially free of bacteria, as indicated by heterotrophic plate count. Permeate flux ranged between 0.15 and 2.0 m^3/m^2 day and was maintained by routine backwashing every three days. Backwashing with tap water containing chlorine bleach every fourth or fifth backwashing was able to restore membrane flux to its original value.

Keywords: Membrane bioreactor (MBR); Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); Hydrolysates; Ceramic tubular membrane; Acetate; Formate; Formaldehyde; Nitrate; Nitrite; Ultrafiltration

1. Introduction

The end of the cold war created a worldwide surplus of both conventional and nuclear weapons. The United States and other countries are destroying large quantities of weapons, which creates the need for safe and reliable disposal technologies for energetic materials and wastewaters associated with their processing. Among the high explosives that are manufactured and used in weapons, RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) is one of the most common, and is classified as a possible human carcinogen [1].

Previous work in our laboratory over the past four years has shown that RDX can be readily destroyed by alkaline hydrolysis in solution or on the surface of activated carbon [2]. The hydrolysis process produces concentrated wastewaters containing acetate, formaldehyde, formate, ammonia and nitrite. The resulting wastewater requires additional treatment, which can be accomplished in a packed-bed reactor. Using nitrite as the electron acceptor [3], over 90% of each organic carbon source was removed, and the results closely match the stoichiometry predicted by empirical redox equations.

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0043-1354/02/$ -see front matter
PII: S0043-1354(01)00284-6

This investigation extends the previous work using a membrane bioreactor. Membrane technology has attracted much attention from scientists and engineers in recent years as a new separation process in water and wastewater treatment. These separation processes have been applied to treat municipal and industrial wastewaters. Combining membranes with biological treatment is an attractive technique and has resulted in a new concept: *the membrane bioreactor* (MBR) [4]. The recent development of a new generation of more productive and less expensive ultrafiltration (UF) and microfiltration (MF) membranes make this possible. In the MBR, the entire biomass is confined within the system, providing both exact control of the residence time for the microorganisms in the reactor (solids retention time) and the disinfection of the effluent.

The objective of this study is to investigate the performance of a bench-scale continuous flow anoxic MBR system, consisting of a biological denitrification reactor coupled to a ceramic ultrafiltration membrane module, and its effectiveness in the degradation of RDX hydrolysate.

2. Methodology

2.1. Denitrifying culture

The reactor was started using an inoculum from a packed-bed reactor treating synthetic hydrolysate over a 2-year period [3]. The initial culture for the packed-bed reactor was obtained from an anaerobic digester at the Hyperion Wastewater Treatment Plant in El Segundo, California. These cultures were diluted with oxygen-free phosphate buffer, filtered, and incubated for 3 weeks in a minimal medium containing 0.2 g/L NH_4Cl, 0.1 g/L $MgCl_2 \cdot H_2O$, 0.04 g/L $CaCl_2 \cdot 2H_2O$, and 0.02 g/L Na_2SO_3. These cultures were also supplemented with RDX hydrolysates and trace mineral solution. The pH was maintained between 7.0 and 7.5, which is the optimum range for denitrification, by adding small amounts of 0.5 M H_3PO_4 daily to compensate pH increase from the denitrification and to provide phosphorus as a nutrient.

2.2. Feed composition

The feed solution was prepared using the ratio of 1.6 M NO_2^-, 1.5 M $HCOO^-$, 0.1 M CH_3COO^-, and 1.1 M HCHO, which is the same as RDX hydrolysates [2]. Nitrate (NO_3^-) was added to balance the electron acceptor and donor to allow all carbon and nitrogen to be removed. Using this approach, Zoh et al. [3] found that over 90% of each organic carbon source could be removed in a packed-bed, upflow reactor. The amount of each substrate can be calculated from balancing the empirical redox equation as follows:

$$(0.68NO_3^-) + 1.6NO_2^- + 1.5HCOO^- + 0.1CH_3COO^- + 1.1HCHO + 3.88H^+ \rightarrow 1.14N_2 + 2.8CO_2 + 3.94H_2O. \quad (1)$$

Table 1
Original composition of the synthetic hydrolysates of RDX wastewater

Compound	Concentration (mg C/L or mg N/L)	Concentration (mg COD/L)
Acetate	13.1	35.0
Formate	98.0	130.5
Formaldehyde	71.8	191.5
Total COD		357.0
Nitrite	122	
Nitrate	52	

The nitrate, shown in parenthesis, was added to balance electron acceptor and donor; no reduction in electron acceptor was anticipated for nitrogen uptake during cell synthesis. Using this stoichiometry, synthetic wastewater containing these compounds was prepared. Table 1 shows the concentration of each substrate and electron acceptor in terms of concentration as well as calculated COD. The MBR unit was operated with this ratio for about 3 months. The actual TOC of the solution was a little higher than the calculated amount, due to impurities in the formaldehyde and TOC of the make up water.

2.3. Experimental design of MBR unit

Fig. 1 shows the schematic diagram of the bench-scale MBR unit. This unit consists of a cross-flow zirconium tubular membrane with cut-off of 200 kDa (pore size: 0.02 μm) in a stainless steel housing (US Filter, Warrendale, PA). The ceramic membrane was 250 mm long, and had a 7 mm channel diameter. The total membrane surface area was 0.0055 m^2, and was operated over membrane pressures between 21 and 105 kPa.

The anoxic bioreactor consisted of a Plexiglas reactor with continuous stirring and an external jacket. A constant volume (1.2 L) of mixed liquor in the bioreactor was maintained using a liquid sensor situated on the surface of the mixed liquor. A Plexiglas cover was used to prevent aeration. The synthetic wastewater was maintained in two 5 L feed tanks; the carbon sources and nitrite were separated to avoid biological reaction. The feed solutions were pumped to the bioreactor and were controlled to maintain constant level in the bioreactor. Mixed liquor was pumped through the membrane tube and recycled back to the bioreactor. A pulsation dampener was used to avoid pressure peaks.

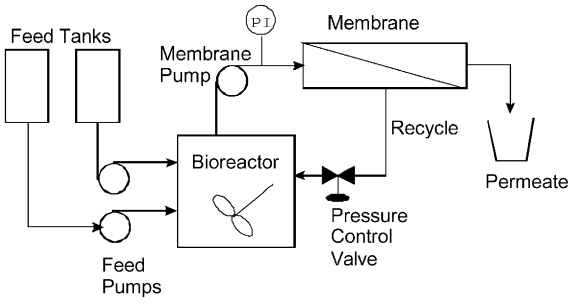

Fig. 1. Membrane bioreactor schematic diagram.

Permeate was collected from the membrane tube. A manually operated backpressure valve was adjusted to maintain the desired pressure. Four-way valves (not shown) were used to isolate the membrane for backwashing. The membrane was backwashed by pumping deionized water or 2% NaOCl solution followed by rinsing with deionized water. The backwashing procedure required approximately 30 min. Initial backwash water was returned to the reactor to recover biomass. When using NaOCl (2%), backwash water was collected and disposed. Except during backwashing, the entire system was covered and or flushed with nitrogen to prevent aeration.

2.4. Analytical methods

Formate ($HCOO^-$), nitrite (NO_2^-), and nitrate (NO_3^-) were analyzed using a Dionex Ion Chromatograph (basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity detector CDM-1). An Ion Pac AS9-SC analytical column (4 mm ID) was used with a subsequent suppressor column for the analysis. The mobile phase consisted of 0.75 mM $NaHCO_3$ and 2 mM Na_2CO_3 dissolved per 1L of milli-Q water. The eluent flow rate was set to 2 mL/min.

Formaldehyde (HCHO) was analyzed using a modification of the technique reported by Zoh et al. [3]. The reaction solution for formaldehyde was prepared by dissolving 0.5 g of 2,4-dinitrophenylhydrazine (DNPH) in 500 mL of 2 N hydrochloric acid and purified by shaking with 5 mL of chloroform. Formaldehyde in the sample was first allowed to react with DNPH in acidic solution in order to form 2,4-dinitrophenylhydrazone. Solid phase extraction (SPE, [5]) was used to concentrate the sample. The SPE columns were eluted with acetonitrile, and the solution was analyzed by HPLC. HPLC analysis was performed with a Hewlett Packard 1500 Series variable wavelength detector (Avondale, PA) equipped with an autosampler. An Adsorbosphere C-18 micron reversed-phase column (Alltech, Deerfield, IL) was used with a mobile phase consisting of 50% acetonitrile and 50% water (vol%) at a flow rate of 1.5 mL/min. An UV detector set to 254 nm was used to detect dinitrophenylhydrazone peak.

Finally, the MBR system was monitored with daily measurements of pH, dissolved oxygen (DO) and temperature. Chemical oxygen demand (COD), total organic carbon (TOC), suspended solids (SS) were measured on a weekly basis. All analyses were performed according to *Standard Methods* [6]. Permeate bacteria were counted using heterotrophic plate counts [7].

3. Results and discussion

3.1. Bioreactor performance

The reactor was operated for 60 days to reach steady state. Afterwards the concentration of each compound, COD, and TOC from the feed and the membrane permeate were measured in order to determine removal efficiency. As shown in Fig. 2, over 90% of formaldehyde, formate and nitrate were removed, however nitrite (NO_2^-) removal was about 55%. This lower removal of nitrite shows the impact of cell synthesis, and insufficient carbon exists to react with the electron acceptor. In the previous work with the packed-bed reactor [3], cell yield was estimated as 0.16 mg cells/mg COD or 0.31 mg cells/mg nitrogen. The unremoved nitrite suggests similar cell yields for this reactor system as well. The amount of nitrate added to the feed solution could be reduced to increase nitrogen removal.

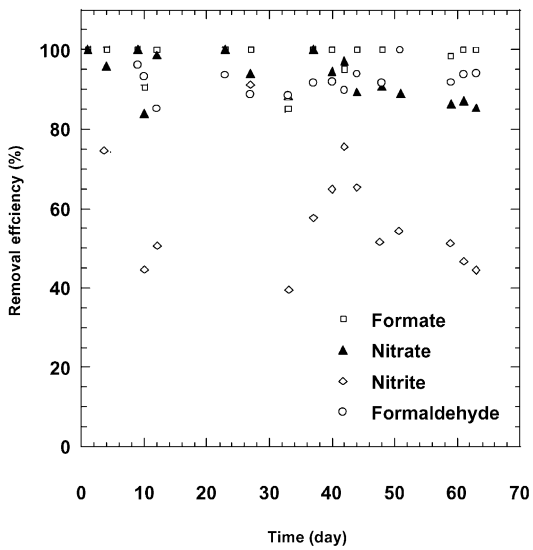

Fig. 2. Removal efficiency of each hydrolysate in the MBR.

Table 2
The MBR process performance for hydrolysates of RDX wastewater

	Feed	Permeate	Removal (%)
COD (mg/L)	357	10.5±3.0	97.2
TOC (mg/L)	205.0±10.0	5.0±1.5	97.6
SS (mg/L)		<5	
Turbidity (NTU)		<0.1	
pH	7.0±0.1	7.4±0.1	
NO_3^-–N (mg/L)	52	3.5	93.3
NO_2^-–N (mg/L)	122	55	55.0

Nitrite inhibition is another possibility. Beccari et al. [8] noted the inhibitory effects of nitrite in denitrifying systems, at concentrations well below those found in this study. Their results were for unacclimated systems, and are probably not applicable to this study; however, it is a question that should be considered when denitrifying in the presence of high nitrite concentration.

Table 2 shows the mean effluent concentrations and removal efficiency for COD, TOC, nitrate and nitrite. Over 97% of the COD and TOC were removed. The permeate was nearly free of suspended solids and the concentration was always less than 5 mg/L. The biomass concentration was stable and averaged 300 mg/L. No deliberate cell wasting was performed; cell loss through the membrane (almost negligible) and cell loss during backwashing were sufficient to stabilize the biomass concentration.

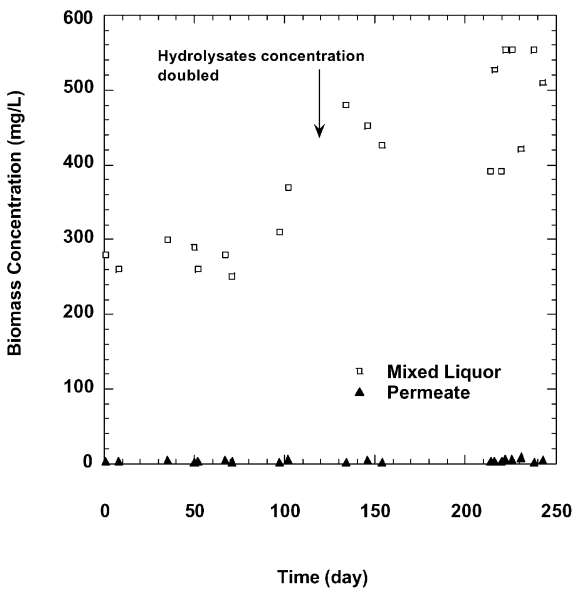

Fig. 3. Change in biomass concentration in the MBR.

The ability of the MBR to treat higher concentrations was also evaluated. At day 120 in Fig. 3, the feed concentrations were doubled. No observable decrease in removal efficiency occurred. The biomass concentration in the reactor increased from approximately 300 to 550 mg/L. The F/M ratio increased from 0.33 to 0.50 kg N/kg MLVSS/day, or 1.20 to 1.82 kg COD/kg MLVSS/day.

3.2. Membrane performance

In order to optimize the MBR design, it is important to know the relationships between the operating parameters and the MBR performance. Several factors may influence the physical performance of the membrane: transmembrane pressure, temperature, and suspended solids (biomass) concentration.

The impact of transmembrane pressure on the membrane flux was evaluated first. Fig. 4 shows a higher initial membrane flux at elevated pressure. The flux decreases rapidly over the next 10 min. After approximately 10 min, the flux is the same for all transmembrane pressures and gradually decreases in an almost linear fashion. Flux is essentially independent of transmembrane pressure after a short initial period (10–20 min).

Fig. 4 can be divided into two regions—*Period* I, where the flux decreases rapidly, and *Period* II, where the flux decreases slowly. The initial rapid decrease in flux is due to a rapid increase in foulant on the surface of the membrane. Thereafter the foulant becomes limited to a constant, steady-state value, and the changes in the

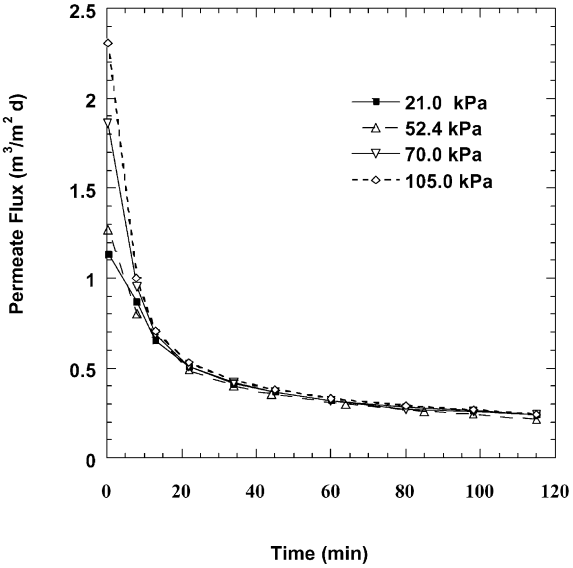

Fig. 4. Effect of transmembrane pressure on the permeate flux (MLVSS = 200–250 mg/L).

characteristics of the foulant are responsible for the long-term decline. There are two theories for these phenomena—pressure controlled model (concentration polarization), and mass transfer controlled model (film theory) [9]. Fig. 4 shows that, after 20 min, the flux is independent of transmembrane pressure; therefore, mass transfer is dominant in this system. Eq. (2) shows this mass transfer model (film theory)

$$J = \frac{D}{\delta}\ln\frac{C_G}{C_B} = k\ln\frac{C_G}{C_B}, \quad (2)$$

where J is the permeate flux and C_B is the bulk concentration of bacteria, C_G is the "gel" concentration at the membrane surface, D is the diffusion coefficient, and k is the mass transfer coefficient. While this model was derived for soluble species, it may be useful for predicting flux decline in the presence of biomass. Note in this model, there is no pressure term, and increase in transmembrane pressure does not increase flux. Based on this model, increasing the transmembrane pressure to increase the permeate flux will not increase flux.

The temperature dependence of the permeate flux was examined next. In general, higher temperatures should increase membrane flux. Cheryan [9] found that, as temperature increases, the beneficial effects (lower viscosity, higher diffusivity) result in a net increase in flux. However, the maximum temperature is limited in an MBR system, due to bacteria denaturation and other heat damage. To evaluate temperature effects, the steady-state flux 20 min after cleaning was measured in the range of 15–40°C (287–313 K). Fig. 5 shows only a small increase in limiting flux (from 0.22 to 0.27 $m^3/m^2/$day) when temperature was increased from 15°C to 40°C.

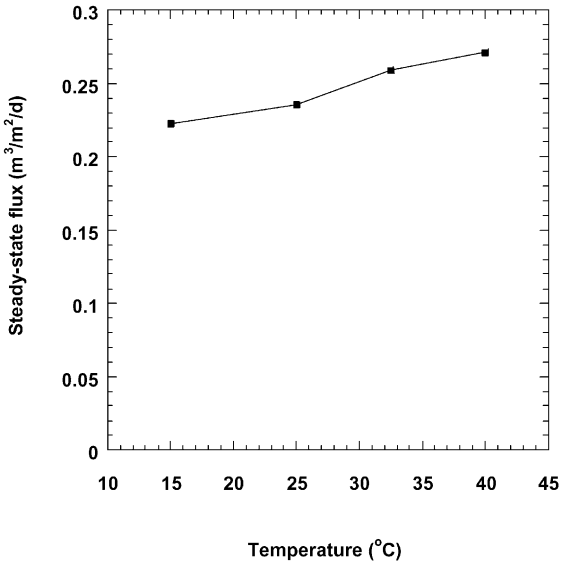

Fig. 5. Temperature dependence of flux (steady-state flux at $t = 20$ min).

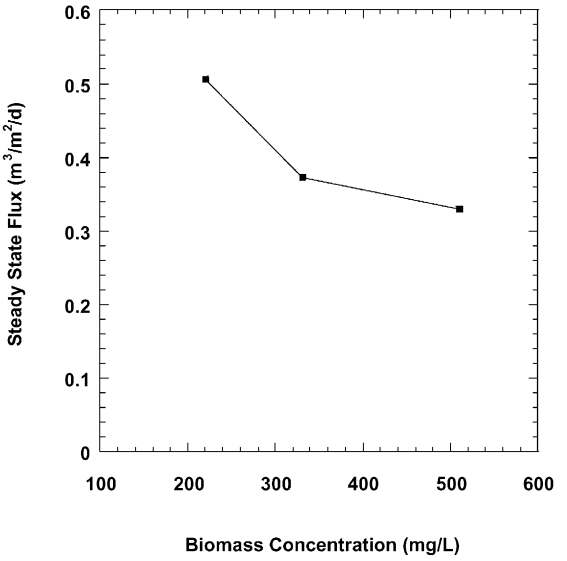

Fig. 6. The impact of biomass concentration on permeate flux.

The operation at higher feed concentration produced higher biomass, which provided an opportunity to observe membrane flux as a function of biomass concentration. The mass transfer model (Eq. (2)) suggests a strong flux dependence on biomass concentration in the mass transfer model. Fig. 6 shows a 40% reduction in flux when biomass concentration doubles. The increasing biomass concentration and decreasing flux suggest a trade-off between reactor volume and membrane surface area. An optimization could be performed, and is analogous to the trade-off between aeration tank volume and clarifier area in the activated sludge process.

3.3. Filtration performance

In order to check the filtration performance of MBR system, the permeate was analyzed using heterotrophic surface-plate counts. This is a quantitative method for the direct measurement of viable numbers of bacteria in a water environment [6]. After backwashing and cleaning with chlorine, no colonies were detected in permeate samples for the following 2–3 days. After 3 or 4 days, colonies began to appear. The test was repeated with the same results. The few colonies at the end of the cyclic run in the permeate probably came from the detachment of bacteria that are able to grow on the inner surface of the tubing or membrane housing.

3.4. Fouling of the membrane and cleaning method

Concentration polarization and the fouling of membranes are inherent problems in a membrane process. Maintaining a high crossflow velocity and high transmembrane pressure to improve flux without cleaning membranes can require excessive energy. Therefore, an efficient and optimum cleaning technique is required to make the process cost-effective.

Various methods have been proposed to reduce fouling [4]. Backwashing was selected because it was previously found to be effective in the cross-flow membranes [10,11]. Combinations of membrane washing with acids and bases were no more effective than ordinary backwashing. Periodic cleaning with NaOCl was also evaluated, and backwashing required more time.

Fig. 7 shows long-term flux change and cleaning cycle of the membrane. During a typical cycle (3–4 days), suspended solids accumulated on the membrane surface, and the permeation flux decreased to 7–15% of the initial value. At the end of the cycle, the permeation flux stabilized at about 0.10–0.15 m^3/m^2/day. Gander et al. [11] reported limiting membrane fluxes in the MBRs from 0.2 to 2.9 m^3/m^2/day depending on the membrane porosity. The porosity of our membrane was 0.02 μm, which corresponds to the lower range of their reported fluxes.

The large increases near 0 and 500 h are the result of backwashing with NaOCl. The new-membrane flux (about 2.5 m^3/m^2 day) was nearly restored by backwashing with 2% NaOCl. Backwashing with tap water recovered only 25–50% of original flux. We believe that the membrane flux could be continued indefinitely with this cleaning procedure. Cleaning with NaOCl or at extreme pH requires an inert membrane material such as a ceramic membrane. The alternating use of NaOCl and tap water provides a balance between an aggressive and more passive procedure. The periodic use of NaOCl insures that no long-term biomass buildup will occur.

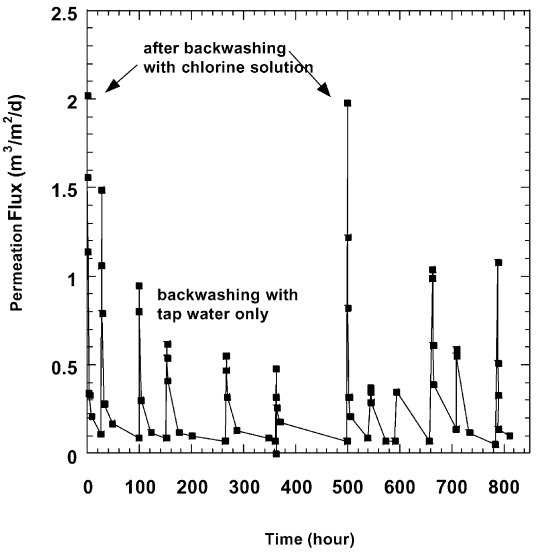

Fig. 7. Permeate flux as a function of time.

This study did not use a scaling wastewater, such as wastewaters that contain high concentrations of divalent cations. Therefore, the reduction in flux we observed was probably not caused by inorganic salt precipitation. Also cleaning at extreme pH values did not improve flux, which also suggests that salt precipitation was not the source of flux reduction. Flux reduction with a scaling wastewater may be greater than we observed.

3.5. Comparison of performance with packed-bed reactor (PBR) type

As mentioned previously, Zoh et al. [3] showed that the same RDX hydrolysates could be efficiently treated in an anoxic, packed-bed reactor (PBR). Both systems functioned well but the MBR system had slightly higher TOC removal. The PBR had higher nitrogen removal. These differences are relatively minor, but two important differences were noted. The MBR system effluent was essentially free of suspended solids (3.5 mg/L); the PBR system effluent averaged 55 mg/L TSS. The second difference is the need for a highly buffered wastewater with the PBR. It functioned as a plug flow reactor and buffering was required to avoid high effluent pH (effluent recycling may reduce this problem, but was not utilized).

Construction requirements are different for the two systems. While it is not possible to scale results from small-scale experiments, some observations can be made. The MBR system has greater maintenance requirements that the PBR system, and will need more moving equipment. A recirculation pump is required in addition to an influent pump. Also, the membrane operates at slightly elevated pressure, as compared to a PBR system. The PBR system does not require a high technology membrane—only column packing, which can be a manufactured packing material with high specific surface area, or natural materials such as crushed and graded stones. One hoped-for advantage of the MBR is portability. In applications such as hazardous waste cleanup, especially for spills, there is no time or need to build a permanent clean-up facility. An MBR, using smaller reactor volumes, and without heavy packing, might be small enough to place on a trailer and be transported to sites as needed. This comparison is not favorable for our case, since we were not able to obtain high biomass concentrations.

Biological denitrification is an attractive treatment option because it is one of the few processes for removing nitrate from water. It is also being evaluated

for drinking water denitrification; however, common denitrification process configurations (i.e., packed- or fluidized-bed reactors) are limited by the direct contact between the denitrifying microorganisms and the product water. Biomass must be removed from the product water by an additional treatment step. Membrane bioreactors may be promising alternatives for these treatment systems because they combine ultrafiltration or microfiltration with denitrification.

4. Conclusions

The membrane bioreactor system (MBR) effectively treated wastewater containing simulated RDX hydrolysates with high removal efficiencies. Approximately, 97.0% COD and 93.3% of nitrate, and 55% of nitrite were removed in the MBR. The MBR very efficiently separated the biomass from the effluent. The following specific conclusions are presented:

- Increasing transmembrane pressure did not increase permeate flux.
- Increasing temperature only marginally improved permeate flux.
- Increasing biomass concentration significantly decreased permeate flux.
- The maximum loading rate was 0.50 kg N/kg MLVSS/day or 1.82 kg COD/kg MLVSS/day with an F/M of 0.5 kg N/kg SS/day.
- Membrane backwashing alternating with tap water and tap water with free chlorine was required to maintain flux.
- The complete mixing aspects of the MBR provided pH stability not observed in a packed-bed reactor treating similar wastewater.

Acknowledgements

This research was partially supported by Lawrence Livermore National Laboratory. The authors are grateful for assistance and suggestions of Felipe Alatriste-Mondragon for guidance with heterotrophic plate counting, and Jeff Daniels and John Knezovich for their continuing support.

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