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**The biological treatment of synthetic fracking fluid in an extractive membrane bioreactor:
selective transport and biodegradation of hydrophobic and hydrophilic contaminants**

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Declaration of interest: none

Graphical abstract

Highlights

- Demonstrated transport and biodegradation of hydraulic fracturing wastewater components
- Characterized a microbial consortium capable of degrading all target compounds
- Extractive membrane bioreactor achieved successful remediation of organic contaminants
- Performance comparison revealed advantages of Hytrel™ over PDMS membranes

ABSTRACT

The biodegradation of selected organic constituents present in hydraulic fracturing wastewater were examined in an extractive membrane bioreactor (EMB) operating with Hytrel™ 3548 tubing. Synthetic hydraulic fracturing wastewater was generated via an extensive literature review and contained high concentrations (1000 mg L^{-1}) of a range compounds of varied hydrophobicity, viz. methyl ethyl ketone, benzene, phenol and acetic acid, as well as $30 - 120 \text{ g L}^{-1}$ of Cl^- at low pH. This hostile wastewater was circulated through the polymeric tubing, selectively transporting the organic compounds

through the membrane for biological degradation by an enriched bacterial consortium. 16S rDNA analysis revealed the presence of five dominant microbial strains including *Pseudomonas sp.*, *Comamonas sp.*, *Achromobacter sp.*, *Lysinibacillus sp.*, *Oxalobacter sp.* within the consortium. EMBs in batch operation achieved 99% removal of methyl ethyl ketone, benzene, and phenol after 72 hours and effectively removed acetic acid up to its ionization point. Continuous EMB operation provided 99% removal of benzene and phenol, 96% removal of methyl ethyl ketone, and 53% of acetic acid. The treatment of synthetic hydraulic fracturing fluid convincingly demonstrated the effectiveness of carefully selected amphiphilic polymers in EMBs for treating the hydrophilic and hydrophobic organic profile found in hydraulic fracturing wastewaters.

Keywords Hydraulic fracturing, extractive membrane bioreactors, flowback, produced water, biodegradation, transport through polymers

1. INTRODUCTION

Extraction of oil and gas resources have negatively impacted surface and subsurface water quality [1–5]. Unconventional methods such as high-volume hydraulic fracturing combine the processes of both directional drilling and the injection of high volumes of proprietary fluids to stimulate the flow of gas through subterranean rock reserves, approximately 1-5 km below the surface. During the fracturing

process, drilled wells are injected with large volumes of formation-dependent fluids containing water, proppant and chemical additives at pressures and temperatures up to 500 atm and 155°C [6], creating microfracture networks that increase the formation's permeability and thereby enhance gas recovery. The variability and heterogeneity of these fluids mixed with the interstitial water of the formation lead to complex wastewaters that return to the surface.

Upon dissipation of well pressure, water returns to the surface containing a mixture of fracturing fluid compounds and autochthonous organics from the formation. Hydraulic fracturing wastewater can be characterized into two classes, namely flowback and produced water. Flowback water is the water that returns to the surface of the well throughout the first few weeks after stimulation [7]. The remaining water that returns to the surface during the extended operation of the well is known as produced water. Similar to flowback water, produced water can contain constituents from the extant fracking fluid and organics contributed by the formation [8,9], however the composition can vary with time [10]. Additionally, transformation by-products due to extremes in temperature and pressure down hole are not uncommon [11–13], and can result in unpredictable wastewater profiles. However, both flowback and produced water can contain a heterogeneous profile consisting of high concentrations of aliphatic and aromatics organic compounds, naturally occurring radioactive materials (NORMs), total dissolved solids and metals [10,14–16], resulting in a lack of effective treatment strategies for these wastewaters.

Flowback and produced water, collectively referred to as hydraulic fracturing wastewater (HFW) is typically disposed of via deep well injection [17–19]. Both the practice of deep well injection for disposal and initial stimulation have been linked to seismic events increasing the risk of environmental contamination [20,21]. In contrast, other disposal strategies such as surface release and/or re-use require extensive treatment which can be difficult due to the high TDS (total dissolved solids), metal and xenobiotic presence in the water, limiting their applicability. Additionally, conventional biological treatment facilities are not equipped to handle these complex wastewater streams due to high volumes of influent wastewater and extremely toxic conditions [22]. Other technologies such ozonation, flocculation,

activated carbon absorption, and micro/ultra-filtration have been applied to the treatment of hydraulic fracturing wastewater but due to large energy and chemical footprint are often limited in application.

Extractive membrane bioreactors (EMBs) using tubular polymeric membranes have been suggested as a treatment strategy for complex wastewaters. Polymeric tubing employed in EMBs acts as a barrier to separate the hostile wastewater from a biotic system which metabolizes the xenobiotic species. EMBs operate under thermodynamically driven concentration gradients, selectively transporting organic constituents from the wastewater stream to the bioreactor through both partitioning and diffusive mechanisms. The additional presence of a biotic system promotes the continuous sequestration and metabolization of organic substrates, creating a constant driving force across the membrane. Early work on EMBs undertaken by Livingston [23,24] utilized silicone rubber (poly (dimethyl siloxane) or PDMS) tubing, however this was shown to be effective only under conditions of high solute hydrophobicity as PDMS is very hydrophobic by nature. Recent EMB studies continue along this same trend, utilizing only hydrophobic compounds, which are known to exhibit better partitioning behavior for hydrophobic PDMS membranes [25–28]. However, polymers which exhibit both hydrophilic and lipophilic properties may provide an alternative to PDMS tubing in the treatment of hydraulic fracturing wastewater which contains a variety of hydrophilic and hydrophobic organic compounds.

This study seeks to assess the ability of Hytrel™ 3548 tubing operating in an EMB to treat synthetic hydraulic fracturing wastewater containing a mix of contaminants of varied hydrophobicities. The acclimation and characterization of an enriched microbial consortia was undertaken to understand the effects of different co-substrates on microbial biodegradation within an EMB operating with Hytrel™ 3548. The EMB system was then operated in batch and continuous modes to characterize biodegradation performance.

2. MATERIALS AND METHODS

2.1 Chemicals and Polymers

All chemicals were purchased from Fisher Scientific (Ottawa, Ontario, Canada) or from Sigma Aldrich (Oakville, Ontario, Canada). Hytrel™ 3548, a polyether-polyester block copolymer with a low equilibrated water content of 5%, was generously provided by DuPont (Kingston, Ontario, Canada) in both tubing and granular form. Hytrel™ 3548 was selected because it does not transport ionic species [29]. The Hytrel™ 3548 tubing had inner and outer diameters of 5mm and 6mm, respectively and ovoid beads had dimensions of 5.5 mm x 3.5 mm. Polymers were washed in a 1:1 MeOH: DI solution for 24 hours at 400 rpm prior to use. Thereafter, five washing steps were conducted with DI water to remove any residual impurities and were set to air dry within a fume hood.

2.2 Synthetic Wastewater

A comprehensive literature review of quantitative peer-reviewed and industrial sources was compiled to determine consistency and/or variability of the organic constituents found in hydraulically fractured wells (Supplementary Information). Compounds comprising synthetic hydraulic fracturing wastewater (SHFW) were selected to be representative of the hydrophobic and hydrophilic organic profile found in flowback and produced waters. Selected compounds were present in >4 sources and were found in concentrations above 10 µg L⁻¹. Methyl ethyl ketone (M) was selected as a representative of hydrophilic ketone class molecules and as a proxy for acetone which is very volatile at 30°C. Benzene (B) was selected as a representative of the aromatic (benzene, toluene, ethylbenzene, xylene) class of compounds displaying moderate hydrophobicity. Phenol (P) was selected as a representative of semi-volatile, moderately hydrophilic compounds frequently found in petroleum wastewaters. Acetic acid (AA) was also selected due to its inherent presence in flowback and produced water at low pH's, and for its ability to dissociate under mildly acidic conditions. Properties of these representative compounds are presented in Table 1.

Additionally, to represent ranges in complexity of hydraulic fracturing wastewater, SFHW which refers to the collective composition of MBPAA (methyl ethyl ketone, benzene, phenol, acetic acid) and salts, contained either 30 g L⁻¹ chloride (~50 g L⁻¹ NaCl) or 120 g L⁻¹ chloride (200 g L⁻¹ NaCl).

2.3 Selective Enrichment

A microbial consortium capable of degrading the chosen compounds in synthetic hydraulic fracturing wastewater was selectively enriched. Contaminated soil and sludge samples used for the initial inoculation were obtained from PAH (polycyclic aromatic hydrocarbon) contaminated and tar sand deposits from Alberta, Canada as well as several previously isolated consortia capable of degrading a variety of organic compounds [30,31]. Enrichment was initialized by placing ≤5g of each soil sample and cryovial contents into a flask containing 100 mL of mineral media and low levels of substrates for microbial acclimatization. Mineral medium consisted of (in g L⁻¹): 7 (NH₄)₂SO₄, 0.75 MgSO₄•7H₂O, 6.6 K₂HPO₄, 8.42 KH₂PO₄, 0.05 Bacto-peptone and 1 mL L⁻¹ trace elements, in tap water. Trace element solution was prepared with (in g L⁻¹): 16.2 FeCl₃•6H₂O, 9.44 CaHPO₄, 0.15 CuSO₄•5H₂O, 12.3 disodium salt (EDTA), 0.3 MnSO₄, 0.06 ZnSO₄•7H₂O, 0.1 CoCl₂•6H₂O and 40 C₆H₈O₇ [30,32]. The enrichment was undertaken for 15 iterations, with 10% volume transfers added to a fresh 100 mL flask with increasing substrate concentrations. A successful consortium was considered to have been achieved once it was possible to consistently degrade 350 mg L⁻¹ MPBAA. The consortium was also demonstrated to be capable of metabolizing 2,4-xyleneol, acetone, and co-metabolizing pyridine. 16S rDNA metagenomic analysis using the Illumina MiSeq sequencing platform was performed by Metagenombio (Toronto, Ontario, Canada) to delineate the taxonomy of the organisms present within the final degrading culture.

2.4 Microbial Consumption of MPBAA

Inoculum was prepared from the previously developed microbial consortium in 100 mL mineral media in 250 mL air-tight flasks with 100 mg L⁻¹ of M, B, P and AA (present as acetate) at 30°C and 180 rpm for 24 hours to increase biomass concentrations. After incubation, a subsequent 10% volume (10 mL) was added independently to 3 air-tight, 250 mL Teflon septa sealed flasks to reach a starting biomass concentration of 75 mg L⁻¹. Each flask contained 100 mL of media containing of 100 mg L⁻¹ of each substrate (MBPAA) in equal concentrations. Samples were taken on an hourly basis until removal of all substrates had occurred. Separate single substrate degradation tests were conducted to determine the yield coefficient of the consortium for each substrate.

2.5 Partition Coefficient Determinations

Partition coefficients experiments (n=3) were performed as previously described [33] and were conducted to quantify the thermodynamic affinity of the target pollutants for Hytrel™ 3548. The partition coefficient for AA for Hytrel™ 3548 was conducted previously by [29]. PCs and other relevant solute properties can be seen in Table 1.

2.6 Membrane Bioreactor Setup

All experiments operating with polymeric tubing were conducted in a New Brunswick Scientific Bioflo III with a working volume of 3L at 30 ± 0.5°C and 320 rpm. A 7m length of Hytrel™ 3548 (corresponding surface area of 0.132 m²) was spirally wound around a stainless-steel mesh support with an open area fraction of 74% and placed within the reactor prior to operation.

2.7 Abiotic EMB Transport Tests

Abiotic transport tests were conducted to investigate the transient transport and distribution of the solutes (MBPAA) through the polymeric tubing in the absence of biological activity. Abiotic transport tests were undertaken in a New Brunswick Scientific Bioflo III in batch mode with a peristaltic pump recirculating 350 mL of synthetic wastewater through the tubing at 30 mL min^{-1} for 48 hours. The synthetic wastewater consisted of equal concentrations MBPAA at 1000 mg L^{-1} , at $\text{pH} \sim 2.80$.

2.8 EMB Biodegradation Tests

Biodegradation tests were conducted to determine the effectiveness of EMBs operated with Hytrel™ 3548 in treating fracking wastewater in both batch and continuous configurations at 320 rpm, 30°C with aeration at 0.25 vvm. Inoculum was added to 3L of mineral media within the reactor prior to operation.

In batch EMB experiments, a peristaltic pump recirculated 400mL (to account for additional sampling) of synthetic wastewater from and to a feed reservoir. Two batch experiments were conducted with synthetic wastewater containing either 30 g L^{-1} (BR1) or 120 g L^{-1} (BR2) Cl^- and 1000 mg L^{-1} MBPAA (each) at approximately $\text{pH} \sim 2.90$. The continuous EMB experiment (CR1) was undertaken with SFHW consisting of 1000 mg L^{-1} MBPAA (each) and 120 g L^{-1} chloride, at $\text{pH} \sim 2.90$. SFHW was continuously pumped from a sealed feed reservoir through the tubing and into a sealed collection reservoir at a flow rate of 0.28 mL min^{-1} (HRT ~ 8 hours) for 72 hours. The HRT was then increased from 8 hours to 12 hours (0.19 mL min^{-1}) and the system was then operated for an additional 24 hours.

2.9 Analytical Methods

Reactor samples were centrifuged for 10 min at 10,000 rpm and 5°C to prevent volatilization and subsequently filtered through $0.2\mu\text{m}$ nylon syringe filters prior to analysis.

Biomass concentration was determined using a BioChrom Ultraspec 3000 UV-VIS spectrophotometer at 600 nm (OD_{600}) and converted to cell dry weight via calibration curve.

Benzene and Methyl ethyl ketone were detected by gas chromatography using a Varian 450 equipped with a CP-8410 autoinjector, a Restek RTX 502.2 column (30m x 0.25 mm; 1.4 μ m) and a flame ionization detector. The carrier gas was hydrogen, flowing at 2.2 mL min⁻¹ with a 1:100 split ratio. Injection volume for aqueous samples was set to 0.4 μ L to prevent flashback. Nitrogen was used as the makeup gas, flowing at 25 mL min⁻¹. For both benzene and methyl ethyl ketone, oven programming was set to hold at 35°C for 1.5 min, ramping to 220°C at a rate of 40°C min⁻¹, with a final hold time of 1 min. The injector and detector were both set to 250°C, below the maximum threshold of the column.

Headspace analysis of volatile components were also analyzed by GC-FID via manual injection using a Hamilton 100 μ L syringe, equipped with a Chaney adapter. The syringe was heated to 30°C prior to sampling and injection to prevent condensation of sample within the syringe. External standards provided concentration determinations using phase 1:1 aqueous: air phase ratio, replicating the reactor vessel phase ratio.

Phenol was detected by HPLC equipped with a Varian Pursuit XRs C-18 column (5 μ ; 250 x 4.6mm) kept at 40°C with a 50:50 acetonitrile: water mobile phase and UV detection at 260 nm. Injection volume of aqueous samples was set to 10 μ L.

Both chloride and acetic acid were detected as previously described previously [29].

HytreI™ 3548 beads (5 grouped beads) were heated to 180°C and pressed to generate semi-translucent, thin films. Both attenuated total reflection infrared spectroscopy (FTIR-ATR) and contact angle determinations were performed on separately generated thin films. Attenuated total reflection infrared spectroscopy was performed on a Bruker Alpha spectrometer equipped with a platinum ATR accessory. All spectra (64 scans at a resolution of 4 cm⁻¹) were ratioed to the appropriate background

spectrum. Contact angle measurements (n=3) were performed on a Dataphysics OCA 15EC, with a micro syringe dispensing 5µL sessile droplets of DI water onto the membrane.

3. RESULTS AND DISCUSSION

3.1 MBPAA Consumption by Microbial Consortium

To demonstrate the effectiveness of the enriched microbial consortium, three independent batch biodegradation experiments were conducted with MBPAA at equal concentrations as shown in Fig. 1. After an initial acclimatization phase of ~ 1 hour, utilization of readily accessible substrates began, with AA, B and P being utilized simultaneously and completely, suggesting that each was metabolized as an independent carbon source, and this finding was confirmed by yield coefficient determinations (data not shown). In contrast, consumption of M began only once B and P reached <30% of their initial concentrations around hour 4, and complete removal of all substrates was achieved in 11 hours. These data suggest that the presence of B and P in the medium impart inhibitory effects on the metabolization of M as previously noted by Datta *et al.* [34,35].

The yield coefficients of this consortium are of similar magnitude to collected literature (Table 2) however AA showed a much higher yield coefficient in this study but aligns with the results of the MBPAA biodegradation study shown in Fig. 1. Characterization of the microbial consortium was further quantified through 16S rDNA taxonomic analysis, identifying the presence of 5 major microbial strains at the genus level (Fig. 2), namely *Pseudomonas sp.*, *Comamonas sp.*, *Achromobacter sp.*, *Lysinibacillus sp.*, and *Oxalobacter sp.*. This data was generated from 98.5% reads at the genus level.

3.2 Abiotic Transport of MBPAA

Transport tests were conducted to determine the efficacy of the EMB operation in sequestering and/or transporting the various MBPAA components over a 48-hour period. The EMB in this experiment was operated in batch configuration with recirculation of MBPAA through the polymer tubing. Concentrations of MBPAA in the tubing and reactor phases are shown in Fig. 3. Both B and P exhibited 99% and 90% transport from the tubing phase, respectively after 4 hours, due to the high affinity of the solutes for Hytrel™ 3548, as represented by their partition coefficients shown in Table 1. Additionally, Fig. 3 shows the transport of M and AA, exhibiting 91% and 48% removal from the tubing phase after 48 hours. The distribution of MBPAA within the system after the 48-hour abiotic transport test was determined by a mass balance and can be seen in Fig. 4, showing compounds with high PC's were primarily retained by the polymer, while lower PC-more hydrophilic compounds were transported through the polymer, and were present in the reactor in higher concentrations. As is the case in two-phase partitioning bioreactors, the polymer tubing acted as a buffer or reservoir for the organic compounds, by sequestering a significant fraction of the original solute mass within the polymer. This self-regulating process limits the inhibitory effects of the organic solutes while simultaneously permitting the re-release of compounds once the consortium has consumed the substrate in order to re-establish chemical equilibrium [31,33,36]. In the case of EMBs, both the sequestration and metabolization of organic substrates creates a continuous driving force across the membrane by maintaining a concentration gradient. Both Fig. 3 and Fig. 4 show the incomplete transport of AA from the tubing phase; the removal of ionizable compounds (acetic acid) is difficult due to the limited affinity of the target solute for the polymer phase, previously shown for low molecular weight organic acids [37].

Additionally, as AA is removed the pH of the wastewater rises in response. This results in the increasing dissociation of AA as the pH of the water rises closer to the target compound's pKa, as observed throughout the partitioning/removal process. Because dissociated forms of organic acids are not transported by Hytrel™ 3548 [29], the transport of AA decreases with increasing removal percentages

In both Fig. 3 and Fig. 4, compounds with lower PCs are sequestered less within the polymer and are present in the reactor phase at higher concentrations. B and P displayed the largest partition coefficients for Hytrel™ 3548, accumulating less in the reactor due to greater absorption by the polymeric membrane. M and AA showed >200 % increase in reactor aqueous concentrations compared to B and P. Higher PCs prevent accumulation and enhance removal rates through favourable solute-polymer interactions resulting in sequestration of the compound, potentially reducing the effects of solute inhibition [31,33], whereas lower partitioning compounds are transported through the tubing rather than sequestered. However, even at elevated concentrations of 1000 mg L⁻¹ MBPAA in SHFW the accumulation of compounds (Fig. 3) in the reactor are at concentrations that are easily degradable by the enriched microbial consortia (Fig. 1).

3.3 Biological EMB Operation

3.3.1 Batch EMB Operation (BR1)

Biodegradation tests were conducted with an EMB operating in batch configuration with recirculation to demonstrate the effectiveness of operating with Hytrel™ tubing subjected to the extreme conditions of hydraulic fracturing wastewater. Fig. 5(a) shows the transient transport/removal and associated cell concentration profile during the biodegradation of SHFW over 72 hours. Initial MBPAA concentrations were set to 1000 mg L⁻¹ each, with a pH ~ 2.90 (a pH substantially below the pKa of AA, thereby allowing transport through the polymer) and 30 g L⁻¹ chloride, replicating the extremes of pH and salinity found in hydraulic fracturing flowback and produced waters. Initially, rapid removal of B and P from the tubing-side fluid can be seen, resulting in 99% removal of both compounds within 24 hours, attributed to the rapid absorption of the solutes by Hytrel™ 3548, and to biodegradation of these solutes within the reactor. Additionally, the removal of B and P at 24 hours aligns with the predicted biomass growth of 203 mg L⁻¹ CDW based on previously determined yield coefficients, further indicating that no

M was degraded at this point. In contrast to B and P, M exhibited much slower transport (previously seen in Fig. 3), however 99% removal of M was achieved at the 72-hour mark. Although M accumulation was seen on the reactor side (Fig. 5(b)), likely due to co-substrate inhibition, removal of M from the wastewater stream was continuous throughout the experiment's duration. As seen in Fig. 5(b) once complete removal of B and P were achieved, biological removal of M in the reactor phase began, indicated by the decline in M reactor concentrations after 24 hours. Transport and biodegradation of AA was also observed throughout EMB operation, resulting in 58% removal after the 72-hour operational period (Fig. 5(a)). In addition to AA possessing a relatively modest PC (~ 1), during the operational period the initial pH of the SHFW rose from 2.90 to 4.83 (Fig. S3(a)) at the 72-hour mark, exceeding the pK_a of acetic acid, revealing that at 72 hours $>50\%$ of the AA in the wastewater was now present as acetate, which is not transported by Hytrel™ 3548 [29].

The prevention of salt transport by Hytrel™ 3548 tubing has been demonstrated previously [29,38], and similar results were obtained here (Fig. S2). Chloride concentrations were maintained within the tubing phase due to the limited ability of Hytrel™ 3548 to absorb water (5% equilibrated water content). Therefore, Hytrel™ 3548 effectively demonstrates the capacity for separating highly saline and low pH conditions from the biological system, which can significantly inhibit even halo-tolerant strains of microorganisms [39–41]. Finally, we note that the dissolved oxygen concentration within the reactor was maintained above 90% saturation throughout the duration of the experiment (data not shown), and this condition was maintained for all other biotic EMB experiments.

3.3.2 Batch EMB Operation (BR2)

Experiment BR2 was operated with an increased salt load ($120 \text{ g L}^{-1} \text{ Cl}^-$), replicating extreme conditions present in fracking wastewaters with chloride concentrations ranging from $\sim 1 \text{ g L}^{-1}$ – 200 g L^{-1}

[42,43]. Initial conditions were similar to BR1, set at 120 g L⁻¹ instead of 30 g L⁻¹ chloride. Improved removal rates were observed during the 72-hour operational period, as seen in Fig. 6(a). B and P exhibited rapid absorption and biodegradation achieving 99% removal of both compounds from the feed solution within 12 hours, correlated with continuous biomass growth. M showed significant removal rate improvements versus experiment BR1, achieving 99% removal in 48 hours, instead of 72 hours. Additionally, AA achieved 77% removal after 72 hours, compared to 58% with experiment BR1. AA removal correlated to the wastewater pH shift from 2.83 to 4.73 (Fig. S3(b)), consistent with BR1 (Fig. S3(a)).

Accumulation of M in the reactor phase for BR2 can be seen in Fig. 6(b), showing complete removal of M from the reactor after 12 hours, due to the complete removal and metabolization of B and P. Accumulation of M in all experiments is explained by the lower PC exhibited by M for Hytrel™ 3548 in addition to inhibition of biological removal by presence of B and P. Differences in permeability of representative compounds are attributed to differences in PCs, with higher PC's corresponding to increased permeabilities, as seen in the equation below.

$$P = PC \cdot D$$

Where, P is the permeability of a polymer, PC is the partition coefficient of a compound for a polymer and D is the diffusivity of a compound through the polymer.

However, in experiment BR2, increasing the salt concentration by 4x (from BR1) resulted in increased removal rates for all compounds, resulting in less accumulation of M in the reactor, as seen in experiment BR2 (Fig. 6(b)). These marked differences in removal rates between the BR1 and BR2 experiments can be attributed to the effect of increasingly hypersaline conditions in the wastewater stream, indicating that increased salt concentrations improved partitioning performance. This was observed during the removal of M, resulting in the greater partitioning performance of M for Hytrel™ 3548, improving the removal efficiency of M from 15 mg L⁻¹ h⁻¹ to 22 mg L⁻¹ h⁻¹. The basis of this performance

improvement has been attributed to hydration theory, stating that salts in solution will bind water molecules, inhibiting their solvation capacity thus increasing the activity of the non-electrolyte in solution resulting improved partitioning behavior [44,45].

3.3.3 Continuous EMB Operation (CR1)

An EMB operating with Hytrel™ 3548 tubing with a continuous feed of wastewater was operated with 1000 mg L⁻¹ MBPAA, 120 g L⁻¹ chloride at pH~2.90 at an HRT of 8 hours for 72 hours. Fig. 7(a) shows the continuous biodegradation of MBPAA from the SFHW and corresponding cell concentration profile. Initial rapid removal of the B and P was observed in Fig. 7(a), with B and P exhibiting 99% removal from the collected effluent within 5 hours. M exhibited 65% removal initially, attributed to solute partitioning into the polymer. Gradual M removal was observed thereafter, resulting in 90% removal of M after 72 hours of operation. In contrast, AA experienced gradual absorption showing 30% removal within 8 hours. These data revealed a plateau in AA removal, associated with the initial pH shifting in tubing close to acetic acid's pKa (Fig. S3(c)), resulting in the dissociation of AA to acetate, thereby limiting transport. which has been previously shown to have no affinity for Hytrel™ 3548 [29], and therefore is not transported. Once the AA concentration within the tubing had stabilized a pH decline was observed, leading to an increase in AA removal by 7% during the remaining 72 hours.

As seen in Fig. 7(b), M accumulated within the reactor phase during the entirety of the 72-hour operational period which was attributed to the constant influx of B and P, inhibiting the removal of M. Improvements in M removal were observed after hour 8, likely due to the maturation of the consortium and constant metabolization of B and P via increased biomass concentrations.

To improve removal rates the HRT of the wastewater was increased from 8 to 12 hours, for an additional 24-hour period after the 72-hour mark, as seen in Fig. 7(a). The higher HRT promoted the additional removal of both M and AA, with M removal increasing from 90% to 96% during the final 24-

hour period, whereas AA showed an increase in removal to 53% at a 12-hour HRT. Removal improvements are attributed to the higher HRT allowing for increased contact time between the solute and membrane permitting further diffusion of organics across the membrane in combination with the increase in biomass concentrations. Increasing the HRT of the system improves the transport performance of low partition coefficient compounds by increasing the contact time between the high solute concentration fluid phase and the transport membrane. The combined effect can be seen in Fig. 7(b), showing a decline M accumulation in the reactor decreases from 50 mg L⁻¹ at 72-hours to 6 mg L⁻¹ at 96-hours. Additionally, during this time, biofilm growth was observed along the first 30cm from the tubing inlet after 96 hours of operation (Supplemental Info).

3.4 Biofilm Formation

The continuous EMB experiment resulted in linear biomass growth throughout the 96-hour duration. After approximately 60 hours, the formation of a biofilm was observed on the inlet of the tubing, gradually decreasing in density from the inlet port until roughly 30 cm further along the tubing. As seen in Fig. 8, scanning electron microscopy captured the biofilm formation on the outside of the tubing, with no growth observed within the tubing. Observable biofilm growth on the inlet of the coiled tubing may be attributed to the rapid sorption of both B and P in this area due to the high affinity of both B and P for Hytrel™ 3548, combined with the slow-moving flow (HRT~8 and 12 hours) within the tubing. Absorption of both B and P may have been exploited by chemotactic bacteria to initiate film formation, such as flagellated *Pseudomonas sp.*, which are also required for the initial adhesion of the bacteria to a surface [47]. Several studies have observed chemotactic behavior in the presence of inanimate surfaces, whereby bacteria form biofilms on surface interfaces which desorb substrates in an effort to improve bioavailability of nutrients, inevitably resulting in increased degradation rates [48,49]. Additionally, quorum sensing by bacteria in aqueous or film microenvironments can impact the formation of biofilms, with multifactorial

inputs regulating gene expression in response to environmental conditions, such as: inducing chemotaxis, adhesion, motility and secretion and deposition of extracellular polysaccharides [50–52].

3.5 Performance Comparisons: New and Old

Conventionally, EMBs have been primarily operated with tubular PDMS (silicone rubber) membranes, however EMBs operating with Hytrel™ have introduced novelty into EMB systems showing some significant advantages over PDMS [36,53]. To date, studies using PDMS membranes have been conducted for only substantially hydrophobic compounds (e.g. 3-chloronitrobenzene, 1,2-dichloroethane), as PDMS is virtually impermeable to hydrophilic solutes and water. For example, several studies have determined that partitioning for phenol is negligible in PDMS or silicone oil [23,54,55]. A comparison of PCs for semi-hydrophilic and hydrophilic molecules for Hytrel™ and PDMS can be seen in Table 1, which shows minimal partitioning behavior for both M and P in PDMS. Additionally, sessile drop contact angle determinations (Fig. 9) reveal a significant difference in the hydrophilicity of Hytrel™ 3548 in comparison to PDMS, displaying an average contact angle of 70.3°, and by contrast, literature values for PDMS suggest a contact angle between 104° and 110°, respectively [56,57]. Therefore, EMBs operating with Hytrel™ 3548 have a significant advantage due to increased surface wettability, resulting in the ability of these EMBs to treat often neglected hydrophilic contaminants, which present high mobility and toxicity within aquatic environments [58].

The amphiphilic properties of Hytrel™ 3548 highlight its potential in the treatment of hydrophilic contaminants, displaying improved partitioning performance for hydrophilic compounds over PDMS, likely due to the ability of both water and hydrophilic organic molecules to hydrogen bond with the polymer soft segments. Ren *et al.*, in 2017 found that the maximal phenol removal capacity in an EMB operating in batch configuration with tubular PDMS (surface area ~ 0.142 m²) was 136.9 mg L⁻¹ d⁻¹ [59] and in comparison, the batch system in this study (surface area ~ 0.132 m²) showed a maximal removal

rate of $1018 \text{ mg L}^{-1} \text{ d}^{-1}$ for phenol (average of BR1 and BR2 experiments), a 743% increase. In another study, Freitas dos Santos and Livingston treated 1,2-dichloroethane (DCE) in an EMB under similar operating conditions (25% increase in membrane surface area), showing a maximal removal of 94.5% DCE, which yielded a 3x greater PC value than M [26]. By contrast, in experiment CR1 shown in this study, M exhibited a removal capacity of 96% under a similar operating time period, highlighting improved transport performance of Hytrel™ 3548 over PDMS for more hydrophilic compounds. These results, along with those from Livingston in 1993 suggest that PDMS affinity driven transport is the limiting factor for lower partitioning compounds, affecting mass flux across the membrane [23]. Therefore, removal of contaminants of varied hydrophobicities can be greatly enhanced by selecting a membrane with increased affinity for highly water-soluble compounds, while maintaining adequate separation of hostile wastewater environments from biotic systems.

4. CONCLUSION

This study demonstrated the effectiveness in both batch and continuous EMBs utilizing Hytrel™ 3548 tubing in the biological treatment of synthetic hydraulic fracturing wastewater. EMBs operating in both batch and continuous configuration exhibited excellent removal performance with an acclimated microbial consortium. Removal of 99% of M, B and P present in SHFW was observed within 72 hours while removal of AA was observed up to the ionization point. Furthermore, removal performance improvement was observed for batch EMBs under higher salt loading, improving overall organic removal rates, highlighting that system performance improves with higher salt loading. Additionally, continuous operation of EMB demonstrated the effectiveness of the system operating with a continuous influx of wastewater. The continuous EMB achieved 99% removal of B and P, 96% removal of M and 53% removal of AA after only 96 hours of operation. This study effectively demonstrates the performance of the amphiphilic properties of Hytrel™ 3548 in the treatment of both hydrophilic and hydrophobic organic contaminants present in hydraulic fracturing wastewaters.

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Fig. 1. Biodegradation of MBPAA by a microbial consortium in batch biodegradation experiments. Error bars represent standard deviation for $n=3$. $\diamond$ - M. $\ast$ - B. $\square$ - P. $\triangle$ - AA (buffered, present as acetate). $\bullet$ - Cell Dry weight. Yield coefficients of microbial consortia from single substrate degradation tests present in legend.

Fig. 2 16S rDNA taxonomic profile and relative abundance of enriched microbial consortium at the genus level

Fig. 3. Abiotic transport of MBPAA through Hytrel™ 3548. $\diamond$ - M concentration in reservoir. $\blacklozenge$ - M concentration in reactor aqueous phase. $\ast$ - B concentration in reservoir. $\blacksquare$ - B concentration in reactor aqueous phase. $\square$ - P concentration in reservoir. $\blacksquare$ - P concentration in reactor aqueous phase. $\triangle$ - AA concentration in reservoir. $\blacktriangle$ - AA (as acetate) concentration in reactor aqueous phase.

Fig. 4. Distribution of MBPAA in abiotic transport test after 48 hours.

Fig 5. Biological removal of MBPAA from SHFW (30 g L⁻¹ Cl⁻, pH~2.90) in experiment BR1, using Hytrel™ 3548 in EMB in batch operation with recirculation. (a) Transient removal of MBPAA from wastewater feed stream with corresponding biomass growth. (b) Accumulation of MBPAA in reactor's aqueous phase. ◇ - M in reservoir. ◆ - M in reactor. * - B in reservoir. ▣ - B in reactor. □ - P in reservoir. ■ - P in reactor. △ - AA in reservoir. ▲ - AA (as acetate) in reactor. ● - Cell Dry weight.

Fig 6. Biological removal of MBPAA from SHFW (120 g L⁻¹ Cl⁻, pH~2.83) in experiment BR2, using Hytrel™ 3548 in EMB in batch operation with recirculation. (a) Transient removal of MBPAA from wastewater feed stream with corresponding biomass growth. (b) Accumulation of MBPAA in reactor's aqueous phase. ◇ - M in reservoir. ◆ - M in reactor. ✱ - B in reservoir. ☒ - B in reactor. □ - P in reservoir. ■ - P in reactor. △ - AA in reservoir. ▲ - AA (as acetate) in reactor. ● - Cell Dry weight.

Fig 7. Biological removal of MBPAA from SHFW (120 g L⁻¹ Cl⁻, pH~2.83) experiment using Hytrel™ 3548 in EMB in continuous operation at HRTs of ~8 and ~12 hours. t=0 measurement taken from feed reservoir, with subsequent measurements taken from collection reservoir. (a) Transient removal of MBPAA from wastewater feed stream with corresponding biomass growth. (b) Accumulation of MBPAA in reactor's aqueous phase. ◊ - M in reservoir. ♦ - M in reactor. * - B in reservoir. ▣ - B in reactor. □ - P in reservoir. ■ - P in reactor. △ - AA in reservoir. ▲ - AA (as acetate) reactor. ● - Cell Dry weight.

Fig. 8. SEM images of biofilm growth on tubing inlet after 96 hours during continuous EMB operation. Biofilm growth was only present on the first 30cm of tubing. (a) Cross section of Hytrel™ 3548, visible film formation on outside of tubing. (b) Close up of inner face of tubing in a cross-sectional view, minor ridging due to slicing of tubing as seen on smooth surface. (c) Planar view of smooth inner tubing surface showing no film formation after 96 hours. (d) Planar view of the outer surface of the coiled tubing inlet after 96 hours, showing distinct topographic changes due to the presence of a biofilm.

Fig. 9. 5 μ L sessile drop of water on Hytrel™ 3548 pressed thin film, showing a contact angle of 70.3° (n=3), demonstrating this polymer's amphiphilic tendencies.

Table 1. Properties of compounds selected for SHFW.

Property	Methyl Ethyl Ketone	Benzene	Phenol	Acetic Acid
Structure
Formula	C ₄ H ₈ O	C ₆ H ₆	C ₆ H ₆ O	C ₂ H ₄ O ₂
CAS Number	78-93-3	71-43-2	108-95-2	64-19-7
Boiling Point (°C)	75.6	78.7	181.8	117.1
Density (kg m ⁻³)	805	876	1070	1050
Water Solubility (g L ⁻¹ , 25°C)	223	1.8	83	1000
Henry's Constant (atm m ³ mole ⁻¹)	5.69 x 10 ⁻⁵	5.33 x 10 ⁻³	1.53 x 10 ⁻⁶	2.856 x 10 ⁻⁶
LD ₅₀ oral, for rats (mg/kg)	2737	930	270	3310
pKa			9.99	4.76
Octanol-Water Partition Coefficient (Log-P)	0.29	2.13	1.46	-0.17
PDMS Partition Coefficients	0.4 [54]	90 [54]	0.8 [23], 0 [55]	
Partition Coefficient (Hytrel™ 3548)	4 ± 0.9	107 ± 3	56 ± 0.2	1 ± 0.1

Table 2. Yield coefficients obtained from degradation of MBPA components.

Compound	Y _{x/s}	Reference
MEK	1.02	This Study
	0.74	Kim and Sorial, 2010 [60]
	0.5	Datta and Philip, 2012 [61]
Benzene	0.83	This Study
	1.35	Littlejohns and Daugulis, 2008 [30]
	0.91	Hu <i>et al.</i> , 2015 [62]
	0.82	Nielson <i>et al.</i> , 2007 [63]
	1.2	Reardon <i>et al.</i> , 2000 [64]
Phenol	0.72	This Study
	0.67	Pripch and Daugulis, 2005 [65]
	0.7	
	0.81	
	0.8	Reardon <i>et al.</i> , 2000 [64]
Acetate	1.07	This Study
	0.65	Toretta <i>et al.</i> , 2014 [66]
	0.64	Strotman <i>et al.</i> , 1999 [67]