Use of Bioremediation System to Regenerate Wastewater from Shale Gas Production.

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Abstract

This study addresses the growing environmental and health concerns arising from wastewater generated by the shale gas industry, focusing specifically on the toxic BTEX compounds. In response to the global energy crisis, shale gas extraction, primarily through hydraulic fracturing, has experienced exponential growth, leading to the production of contaminated effluents known as Flowback and Produced Water (FPW). Among its various contaminants, BTEX compounds stand out for their significant toxicity. The study investigates the potential of a Biological Membrane Bioreactor (BRM) with a halophilic bacterial consortium, providing a sustainable solution for FPW treatment. It develops a modelling framework to optimise the biological treatment process, specifically targeting the removal of BTEX compounds. The findings reveal that the BRM process effectively removes BTEX compounds, bringing them below Maximum Contaminant Levels (MCLs). Furthermore, the study highlights the superiority of external membranes over submerged membrane configurations, achieving maximum flows of 24.477 m³/s and 21.169 m³/s at an initial pressure of 1 Pa, while maintaining a consistent final pressure at 30 % for optimal performance. This integrated approach offers a biotechnological alternative to mitigate the environmental and health implications associated with shale gas extraction activities.

**Keywords**: shale gas, FPW, BTEX, BRM, optimization model.

* 1. Introduction

In recent years, there has been a global energy shortage and increasing energy demand worldwide, which has led to exploring unconventional natural gas sources from academia and industrial perspective. A promising alternative for highly energy-efficient gas is shale gas. Currently, shale gas production has been exponentially growing and it is expected to continue increasing and by 2040 shale gas and tight oil will supply 69 % of all-natural gas produced in the United States (Dou et al., 2021).

Shale gas extraction consists of hydraulic fracturing. When fracking a well, millions of litres of fresh water (7000–21,000 /well) are mixed with sand and chemicals and injected into the well at high pressure to break up the shale and release oil and gas, producing high volumes of polluted effluents (8–70 % of the injected water) (He et al., 2019). Flowback and Produced Water (FPW) encompass the water that resurfaces, known as flowback, and the water originating underground, termed produced water. Throughout different stages, the wastewater generated is collectively referred to as FPW.

FPW resulting from shale gas operations is known for its diverse composition, typically containing elevated concentrations of total dissolved solids (TDS), which encompass salts and metals, as well as hydrocarbons, organic compounds, production chemicals, and other substances. This composition varies significantly based on factors such as the shale play, well location, well depth, and other contributing factors (Dou et al., 2021). Based on Ma et al. (2023), among the myriad components found in FPW, toxic compounds like BTEX (benzene, toluene, ethylbenzene, and xylenes) are particularly concerning due to their documented toxicity. These compounds are frequently detected in FPW above regulatory limits, underscoring the environmental and health implications associated with shale gas extraction activities. Effective treatment is crucial, however it is technologically challenging.

Wastewater treatment involves four levels: pre-treatment and primary treatment for physical removal of suspended solids, oil, and grease; secondary treatment for ion removal with physical-chemical methods; and tertiary treatment for fracking reuse or surface discharge which require biological methods and membrane filtration (Dou et al., 2021).

Acharya et al. (2020), have shown the potential of using a biological membrane bioreactor (BRM) with a halophilic bacterial consortium. This biological process consists of an aerated tank containing conventional activated sludge fed with wastewater and an external or submersible micro or ultrafiltration membrane module for filtering the treated effluent. In high-salinity wastewaters, such as FPW, where bacterial flocculation is compromised, BRM can overcome the flocculation requirements and retain biomass in the reactor.  Noteworthy advantages of this system include the production of high-quality effluent suitable for reuse, a compact physical footprint, and a substantial reduction in excess sludge production.

This study focuses on the wastewater coming out of the shale gas industry operations, specifically addressing BTEX compounds. A literature review was undertaken to improve understanding and optimise the biological treatment of FPW. We develop a modelling framework to facilitate understanding of the use of a BRM for the removal of BTEX compounds. This integration seeks optimal operating conditions to maximise regenerated wastewater, providing a more sustainable alternative based on biotechnology for treating water extracted from shale gas.

* 1. Compounds of Concern

As reported by Ma et al. (2023), groundwater samples collected from spill-affected areas reveal elevated concentrations of BTEX compounds surpassing their Maximum Contaminant Levels (MCLs). Specifically, benzene exceeded the MCL in 90 %, toluene in 30 %, ethylbenzene in 12 %, and xylenes in 8 %. The regulatory Maximum Contaminant Levels (MCLs) for these BTEX compounds are set at 5, 1,000, 700, and 10,000 μg/litre (ppb) for benzene, toluene, ethylbenzene, and xylenes, respectively.

* 1. Methods
     1. BMR Configurations

Various BRM configurations offer flexibility in design, involving the placement of membranes either submerged in the bioreactor (BMS) or externally in a side-stream setup (BME). These variations induce shear stress, affecting the size of flocs, mass transfer resistance, bacterial access to pollutants, and altering apparent biokinetic parameters. Depending on the type of contaminant to be treated, the choice of BRM is influenced because the membrane's location can impact how filtration is applied and how flocculation formation is controlled (Sari et al., 2018).

* + 1. Mathematical Modelling

To enable the passage of filtrate through the membrane, a force must be exerted to drive fluids through it. The two most crucial transport mechanisms in BRM are diffusion and convection. The force used for membrane filtration in BRMs is a pressure gradient known as transmembrane pressure (TMP). Since flow and pressure are closely interconnected in the process, the series resistance model results from applying Darcy's law. According to the model, this relationship is expressed by the following equation:

|  |  |
| --- | --- |
|  | (1) |

Where represents the filtrate flux (/s), μ the filtrate viscosity (Pa · s), the operating pressure (Pa), the individual resistance component (), and total number of resistances considered in the system. Within the individual components of resistance, membrane resistance (), cake resistance (), or polarisation gel resistance () are typically considered, along with resistance due to pore blockage, whether reversible or irreversible (). In this case, μ from water was employed, if the removal of large compounds had already occurred. Additionally, it is assumed that the removal of BTEX does not have a significant impact on the filtrate's viscosity.

As reported by González-Hernández et al. (2013), depending on the chosen BRM configuration, distinct resistance types are associated with each, as outlined in Table 1. It is noteworthy that the values may, in some instances, indicate a range of validity. In our application, we specifically utilise an average value for to characterise the resistance within the system.

Table 1. Resistance values reported depending on the system utilised.

|  |  |  |
| --- | --- | --- |
| BRM type | Membrane type | Resistance () |
| BMS | Tubular, microfiltration (0.5 µm), ceramic | = 3-5, = 10, = 3-48 |
| BME | Tubular, microfiltration (0.05 µm), ceramic | = 3,6, = 29 |

Another way to generally describe the filtrate flow, according to McCabe et al. (2007), is through the relationship between the feed composition () and the permeate composition at an axial position (). Here, and refer to the molar fractions of the most permeable species, which is in a binary mixture. This depends on the relative permeabilities and and differences in partial pressure. This relationship is expressed by the following equation:

|  |  |
| --- | --- |
|  | (2)  (3) |

Where represents the feed pressure, the permeate pressure, the feed composition, and represents the permeate composition.

The relationship of absolute pressures is introduced into Eq. (2) and (3), making it possible to reduce the number of variables and eliminate :

|  |  |
| --- | --- |
|  | (4)  (5)  (6) |

On the other hand, the relationship of permeabilities for a binary mixture is the membrane selectivity α (also known as the ideal separation factor):

|  |  |
| --- | --- |
|  | (7) |

In this case, we are considering the relationship , as the impact of selectivity may be negligible compared to the effect of . However, in instances where ≠ 1, the model demonstrates flexibility in addressing these variable scenarios.

Diffusivities for solutes can be predicted using the Wilke-Chang correlation (Geankoplis, 2018):

|  |  |
| --- | --- |
|  | (8) |

Where is the molecular weight of solvent , in this case, water; is the viscosity of (Pa·s), is the molar volume of the solute at the boiling point (m³/kg mol), and for water.

Even though diffusivities calculated using Eq. 8 are for liquid phase, we are using this equation to estimate each element diffusion and using Eq. 7, estimate the multicomponent diffusion through the membrane. It is possible to estimate the molar volume for each BTEX compound based on its respective molecular formula at its normal boiling point. Simultaneously, the diffusivity coefficient of the ceramic membrane is influenced by various characteristics such as porosity, structure, and specific affinity for each compound. Therefore, an average was calculated using the values obtained by Kim et al. (2020). The resulting calculations are detailed in Table 2.

Table 2. calculated for each BTEX compound.

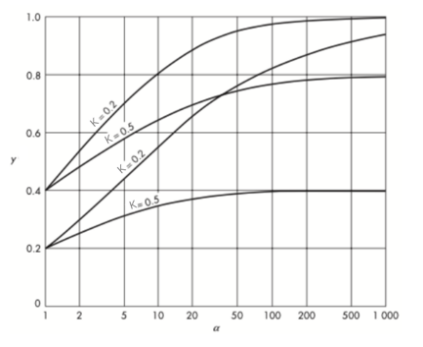
|  |  |  |  |
| --- | --- | --- | --- |
| Compound | Molar volume (m³/kg mol) | Diffusivity BTEX (\* | Diffusivity membrane (\*\* |
| Benzene | 0.24511 | 647,453.014 | 1.1 |
| Toluene | 0.27769 | 571,479.309 | 1.32 |
| Ethylbenzene | 0.30790 | 515,407.498 | 1.30 |
| Xylenes | 0.30790 | 515,407.498 | 1.29 |

\*Predicted using the Wilke-Chang correlation \*\*(Kim et al., 2020).

An increase in always leads to an increase in because the flow of increases while that of decreases; additionally, a decrease in increases , as shown in Fig 1. By reducing from 0.5 to 0.2, it is observed that, with a highly selective membrane, nearly pure permeate can be obtained for component . This suggests that a lower is more effective in obtaining permeate highly enriched in the desired component. Without loss of generality, we worked based on based on its wide operation range for both composition and membrane selectivity.

Therefore, by utilising the permeability ratio α and incorporating experimental data from literature curves, as shown in Fig. 1, we derived an empirical equation linked to the composition variable . Subsequently, we can calculate the permeate flow by considering the interplay of pressures, selectivity, and the composition of the feed, denoted as . This approach enables us to ascertain the volume of wastewater flow without BTEX contaminants.

|  |  |
| --- | --- |
|  | (9) |



* 1. Objective Function

In summary, the form of the nlp model BRM-BTEX is max () st (1-7), (9)*;*  ∈ ℝ are all variables .

Figure 1. Effects of selectivity (α, x-axis) and pressure

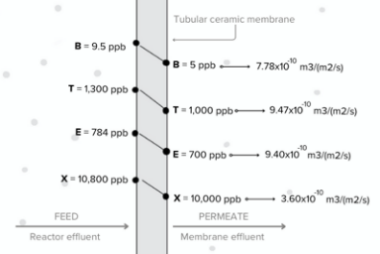
ratio (k´s iso-lines) on permeates composition (y-axis). (McCabe, et al., 2007)

* 1. Results and Discussion
  2. Operation Flux

The model results depict specific flows for each type of reactor considered in the filtration process, whether submerged membrane or external membrane, considering the associated resistances for each, and considering an initial operating pressure of 1 Pa. It was observed that the BME exhibits a superior maximum flow compared to the BMS, reaching values of 24.477 m³/s and 21.169 m³/s respectively. Similar findings were obtained by (Sari et al. (2018), where the choice of an external (side stream) membrane is supported by its comparable performance in deposit formation, superior efficiency at higher flow rates, and the positive influence of the slug flow regime in improving permeability compared to the BMS configuration. On the other hand, it was determined that the final pressure always tends to be 30 % of the initial pressure to optimise process performance. To validate this pressure relationship, a sensitivity analysis was conducted, varying initial operating pressures in increments of 0.01, 0.1, and 1, confirming the consistency and robustness of choosing BME as the preferred option in terms of flow through a porous medium, regardless of variations in magnitude under different operating conditions. These results are presented in Table 3.

* 1. Separation Efficiency

The permeate flow obtained for each BTEX component, considering the interplay of pressures (, selectivity and diffusivity of both the membrane and each BTEX compound (, as well as the feed composition (, is illustrated in Fig. 2. On the left side of the figure, the elevated initial concentrations of each BTEX compound found in the reactor effluent before entering the membrane (BME) are observed, while on the right side, their corresponding MCLs are depicted along with the required flow to achieve them. As can be observed, in all cases, there is a decrease in the concentration of the compounds: benzene (B), toluene (T), ethylbenzene (E), and xylene (X), demonstrating that with a BME their removal is possible at a relatively low total flow of 3.60x10^-9 m3/s, which has an impact on the required energy cost of the entire system. These results support those obtained by Mozo et al. (2021), where two types of BRMs based on crossflow and semi-dead-end filtration systems were experimentally used for the efficient removal of up to 90 - 99.9 % of hazardous aromatic compounds (BTEX and PAH) from wastewater.

Table 3. Flows at different initial pressure

for each type of BMR.

|  |  |  |  |
| --- | --- | --- | --- |
| Pressure (Pa) | | Permeate flow (m3/s) | |
| Initial | Final | BMS | BME |
| = 0.01 | = 0.003 | 0.212 | 0.245 |
| = 0.1 | = 0.03 | 2.117 | 2.448 |
| = 1 | = 0.3 | 21.169 | 24.477 |

Figure 2. Equilibrium concentrations and flows for BTEX compounds.

* 1. Conclusions

This study underscores the pressing environmental and health challenges posed by wastewater from the expanding shale gas industry, with a specific focus on the toxic BTEX compounds. The research reveals the promising potential of BRM with a halophilic bacterial consortium, presenting a sustainable solution for FPW treatment. The developed modelling framework demonstrates the efficacy of the BRM in removing BTEX compounds and aligning concentrations with MCLs. Furthermore, the study highlights the superiority of external membrane configurations over submerged counterparts, achieving optimal flows at an initial pressure of 1 Pa and maintaining a consistent final pressure at 30 %. This underscores the critical role of optimising energy-efficient processes, offering a biotechnological alternative that addresses the multifaceted challenges associated with shale gas extraction activities. This integrated approach not only enhances wastewater treatment efficiency but also contributes to achieving a sustainable balance between escalating energy demands and environmental responsibility, marking a significant step towards mitigating the environmental and health implications of the shale gas industry. As future work it is proposed to integrate this bioremediation wastewater model using the BRM system focused on the removal of BTEX compounds into a shale gas extraction model, as well as run experimental validation of the model.

References

Acharya, S. M., Chakraborty, R., & Tringe, S. G. (2020). Emerging Trends in Biological Treatment of Wastewater from Unconventional Oil and Gas Extraction.

Dou, Z., Liu, Y., Zhang, J., Xu, X., Zhang, W., & Zhu, J. (2021). Optimization of Well Factory Platform Mode Considering Optimal Allocation of Water Resources.

Geankoplis, C. J. (2018). Transport Process and Separation Process Principles. 5th. Pg. 448-449.

González-Hernández, Y., Zarragoitia-González, A., Jáuregui-Haza, U., Alliet, M., and Albasi, C. (2013).  Modelling and optimization of bioreactors with membranes for wastewater treatment.

He, M., Chen, W. J., Tian, L., Shao, B., & Lin, Y. (2019). Plant-microbial synergism: An effective approach for the remediation of shale-gas fracturing flowback and produced water..

Kim, I., Yoon, J., & Kim, S. D. (2020). Application of a solid ceramic membrane for monitoring volatile organic compounds in industrial wastewater.

Ma, L., Hurtado, A., Eguilior, S., & Llamas Borrajo, J. F. (2023). Acute and chronic risk assessment of BTEX in the return water of hydraulic fracturing operations in Marcellus Shale.

McCabe, W., Smith, J., & Harriot, P. (2007). *Operaciones Unitarias en Ingenieria Quimica Mcabe 7th. Pg. 925-935.*

Mozo, I., Stricot, M., Lesage, N., & Spérandio, M. (2021). Fate of hazardous aromatic substances in membrane bioreactors.

Sari Erkan, H., Bakaraki Turan, N., & Önkal Engin, G. (2018). Membrane Bioreactors for Wastewater Treatment.