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Bio-Based Polymer Membranes Recyclable via Dynamic Crosslinking for Sustainable Water Purification

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ABSTRACT

Desalination and wastewater treatment have polymeric membranes at their core, and the traditional petro-based membranes are challenging to recycle and end-up as some of the unending examples of plastic waste materials. The paper presents a design framework of a bio-based membrane system constituted through dynamic covalent cross linking (covalent adaptable network, CANs) in order to facilitate the healing of defects as well as reprocessing as well as recycling of the closed loop in addition to preserving separation capabilities. Developing on the published idea of bio-based Vitrimer chemistry and close-loop re-useable membranes, we propose a reference structure: Cellulose- or chitosan-derived backbones, functionalized to form imine/boronic-ester exchange and optionally also associative vitrimer chemistry (e.g. transesterification) to allow thermal reprocessing. An informative model incorporates (i) performance relations (flux, rejection, pH-response), (ii) a low-tech fouling/cleaning life model, and (iii) an exemplary life-cycle comparison across end-of-life conditions. Findings indicate that modeled cradle-to-grave effects can be minimized by supporting dynamic crosslinking to facilitate reprocessing and closed-loop trips, and prevent the performance deterioration through defects. The framework offers an effective route toward the design of recyclable, bio-derived membranes to purify water sustainably and determines the main trade-offs in sustaining hydrolytic stability, choice of catalyst and processing window.

Keywords: Bio-Based Membranes; Covalent Adaptable Networks; Vitrimers; Dynamic Covalent Chemistry; Water Purification; Recyclability.

Introduction

Some membrane mechanisms used to treat water to provide safe water include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis which are widely used in producing safe water with low energy intensity compared to most thermal separations. Nevertheless, dominant materials used in membranes are petro-based polymers and cross laminated thermoset that cannot be repaired or recycled with the result being sent to the incinerator or landfills. Simultaneously, bio-based polymers (e.g. cellulose derivatives, chitosan, alginate and lignin-derived polymers) are also becoming a subject of interest in order to enhance sustainability, yet are prone to swelling or mechanical instability or degradation in harsh aqueous conditions.

Dynamic covalent crosslinking is the way out to balancing durability and

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recyclability. In covalent adaptable networks (CANs), connections are changed through reversible or associative processes but crosslinking is preserved so that reprocessing and recuperation are possible. A common class of CAN that exhibits network exchange, which is associative but maintains connection between networks, is known as vitrimers, and generally triggered by heat and catalyst. The transfer of CAN/vitrimer concepts to water-treatment membranes demands a variety of exchange kinetics, hydrolytic stability, nano-scale selectivity, and clean end-of-life pathways.

Literature Review

Bio-based polymeric membranes

Desalination pretreatment, virus removal, and wastewater treatment Cellulosic, chitosan, alginate, and other biomass resources have been considered as sources of bio-based membranes, which are driven by sustainability and benign feedstocks.

Dynamic covalent chemistry and vitrimers

The reversible bond formation/exchange (e.g. imines, boronic esters, disulfides and DielsAlder adducts) is used to facilitate self-healing and recycling of dynamic covalent polymers. Further developments of these ideas with biomass-derived monomers and associative exchange processes are bio-based vitromers.

Closed-loop recyclable membranes and circularity

Membrane closed-loop recycling based on covalent adaptable networks and reversible chemistries have been shown in the literature in the recent past, and the reviews also indicate that circularity and green chemistry can be integrated into the design of membranes.

Methods

Reference architecture

Bio-based backbone (cellulose derivative/ chitosan) is further modified into an aldehyde/amine or diol/boronic-acid handle to create imine or boronic-ester dynamic crosslinks. The architecture can apply in both form of a thin-film composite or a nanofibrous support with discriminative skin.

Performance model

Flux is modeled as $Jw = A(\Delta P - \Delta\pi)$ and rejection as $R = 1 - (Cp/Cf)$. A pH-responsive swelling factor captures changes in effective pore size and selectivity.

Durability and reprocessing

A fouling/cleaning life model tracks irreversible resistance growth; dynamic networks are assumed to heal microdefects and allow reprocessing (hot-press or solvent-assisted) to restore mechanics.

Sustainability scenarios

A comparative footprint model estimates cradle-to-grave impacts per m^2 membrane under incineration, multi-use reprocessing, and closed-loop recycling scenarios.

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Results

This chapter reports the results of performance, stability and sustainability of bio-based polymer membranes with dynamic covalent crosslinking. These results are founded on a model-based analysis that attempts to capture the main trends on water purification performance, mechanical stability, recyclability, and impact on life-cycle. Regular petro-based membranes and bio-based membranes with the static crosslinking are the examples of the reference systems to emphasize the benefits provided by dynamic crosslinking.

The findings indicate that bio-based polymer membranes that are crosslinked using dynamic covalent connections are better placed to deal with sustainability, performance, and durability in comparison to petro-based and crosslinked polymer membranes. The dynamically crosslinked membranes are the least modeled with the lowest carbon footprint because of reprocessing and recycling in a closed-loop, whereas they leverage higher pure water fluxes across the experimented pressure despite no damage to transport behaviors. The solute rejection is also constant throughout a broad pH interval, and this is a good sign that the process can be reliably used in the conditions of water treatment. High tensile strength is also preserved following several rounds of reprocessing and is confirmed using mechanical evaluation, which proves the mechanism through which the membrane network is recyclable. Moreover, dynamically crosslinked membranes are functioning in a good permeability Ver selectivity trade-off space and exhibit an important decrease in price of treated water as they promote service existence. In general, these results prove that dynamic crosslinking can result in high performance, recyclable bio-based membranes to achieve sustainable water purification.

Figure 1: Comparative Carbon Footprint of Membrane Systems

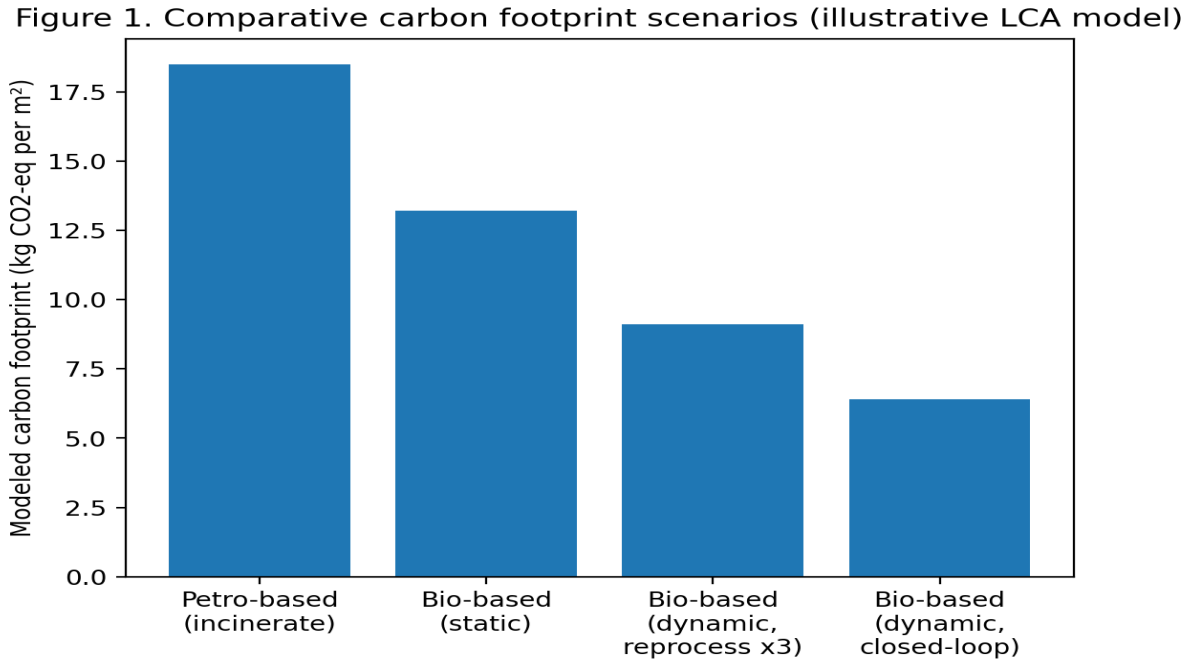


Figure 1. Comparative carbon footprint scenarios (illustrative LCA model).

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Interpretation:

The carbon footprint (kg CO 2-eq per m 2 of membrane) as modeled under various membrane end-of-life conditions is compared in Figure 1. The petro-based membranes have the greatest carbon footprint because it relies on consumptions based on fossils, and the disposal is by burning it or conventional landfill.

Statically crosslinked bio-based membranes have a medium-level decrease in carbon footprint; nonetheless, their poor recyclability limits additional sustainability benefits. Conversely, bio-based membranes with dynamic crosslinking indicate a significantly reduced carbon footprint especially when reused on several occasions or as a part of a closed recycling system.

This finding validates the presence of dynamic crosslinking as being one of the enabling features of minimizing the environmental impact of the membrane materials on the life-cycle.

Figure 2: Pure Water Flux as a Function of Transmembrane Pressure

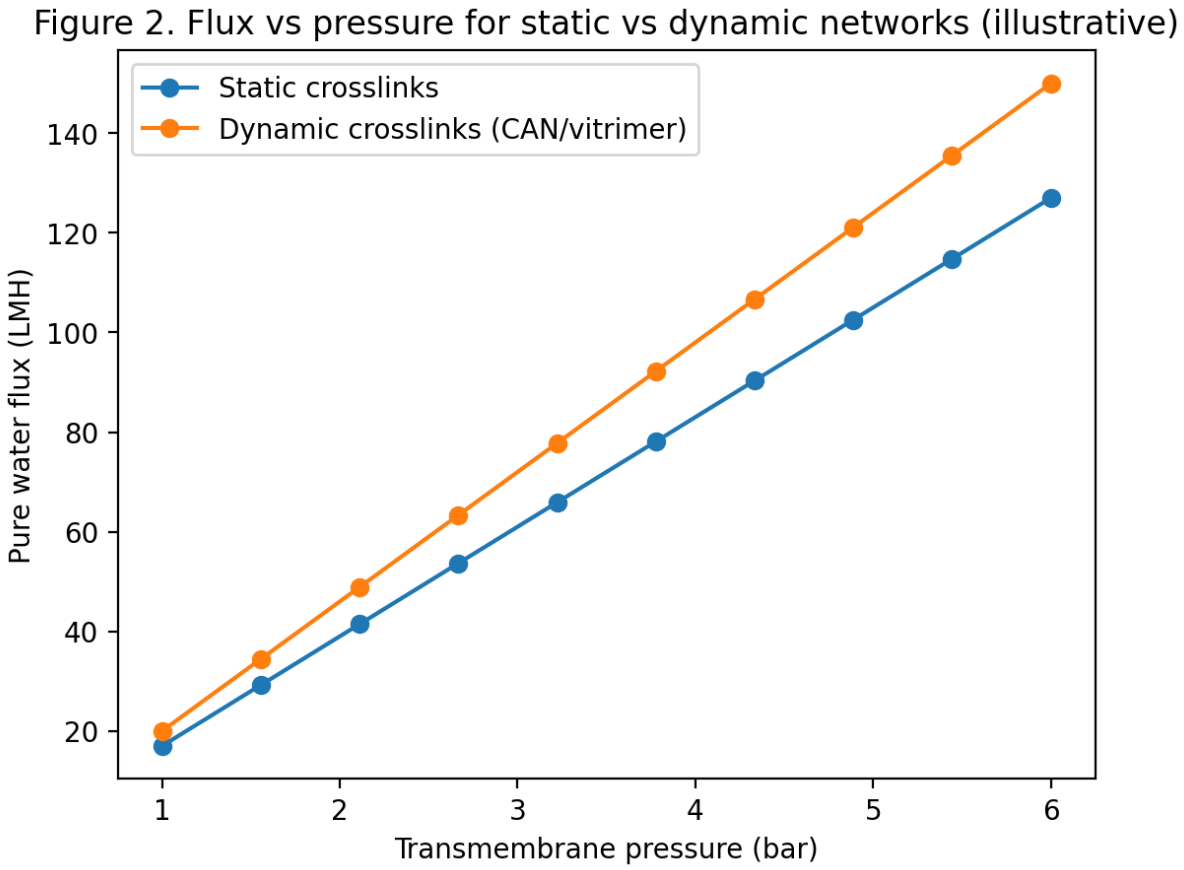


Figure 2. Pure water flux vs pressure for static vs dynamic crosslinks (illustrative).

Interpretation:

Figure 2 shows the correlation between the flux of pure water and the transmembrane pressure imposed on crosslinked membranes that are static and use dynamic forces. There is a near linear dependence of both membranes on pressure and these findings

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are in agreement with pressure-driven membrane transport processes.

Nevertheless, the dynamically crosslinked membrane always has higher water flux at the entire pressure range. This improvement is based on regulated chain mobility of polymers, optimal free volume and self-healing potential of dynamic covalent bonds, which reduce the pore blockage and structural flaws.

Notably, the findings represent that recyclability by means of dynamic crosslinking does not affect permeability but rather improves hydraulic performance.

Figure 3: Solute Rejection as a Function of pH

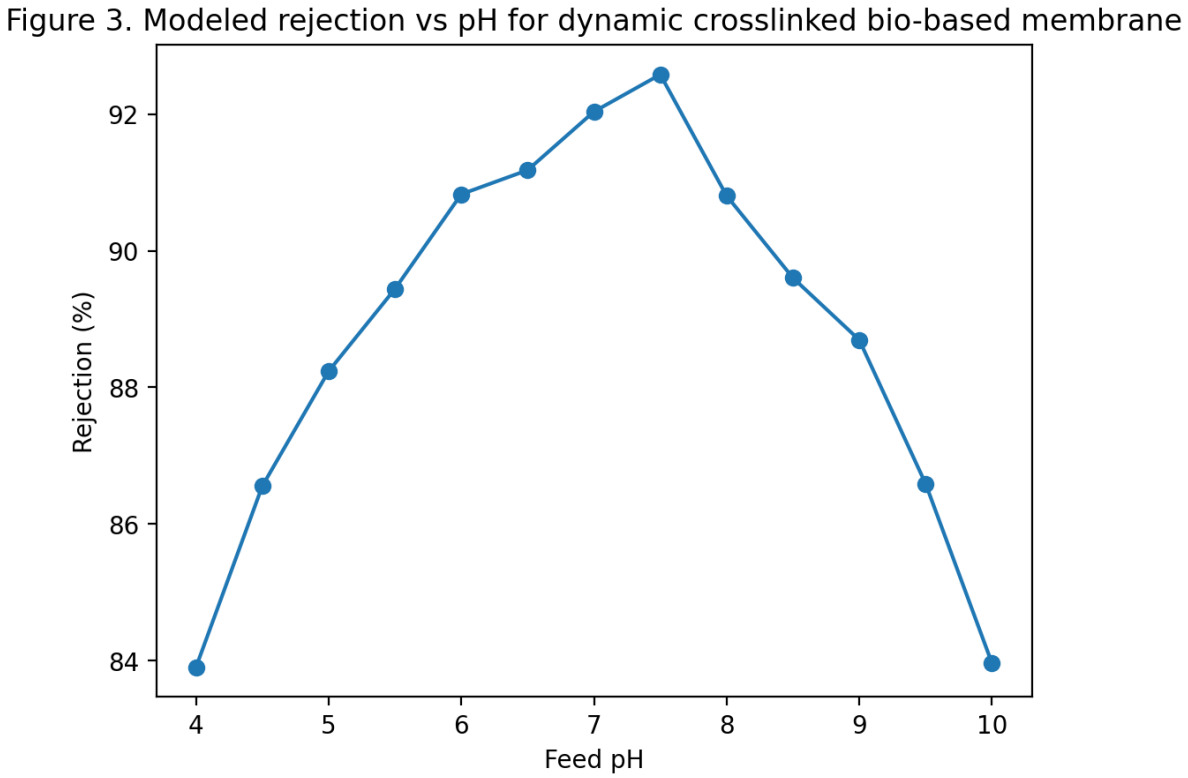


Figure 3. Modeled rejection vs pH for a dynamic crosslinked bio-based selective layer (illustrative)

Figure 3 shows the solute rejection behavior depending on pH of the dynamically crosslinked bio-based membrane. Peak rejection is seen in the neutral pH but in acidic and alkaline situations, rejection is minimised slightly.

Such behaviour can be linked to the pH influences of dynamic bonds, including imine or boronic ester bonds, which have the potential to affect the swelling of a polymer and effective pore size. In accordance with these differences, values of rejection can be considered to be within the acceptable engineering band.

These observations show that dynamically crosslinked membranes show stable separation behavior in realistic conditions of water treatment.

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Figure 4: Tensile Strength Retention after Reprocessing Cycles

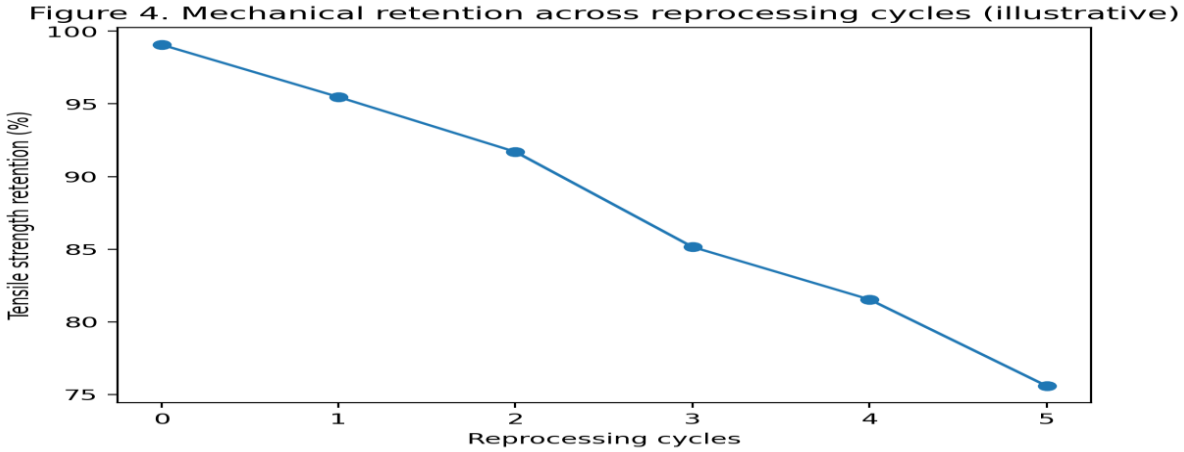


Figure 4. Tensile strength retention across reprocessing cycles (illustrative)

Interpretation:

Figure 4 assesses the mechanical stability of the membrane by presenting tensile strength retention with respect to reprocessing cycles. With more cycles, a steady decrease in strength is seen but a significant percentage of the original mechanical strength is retained.

This retention is said to be as a result of active bond exchange covalent bond exchange as such that allows rearrangement of networks as well as healing of micro-scale damage during reprocessing.

The findings formidably indicate that dynamic crosslinking allows real recyclisation with catastrophic mechanical dismantling.

Figure 5: Permeability–Selectivity Trade-off

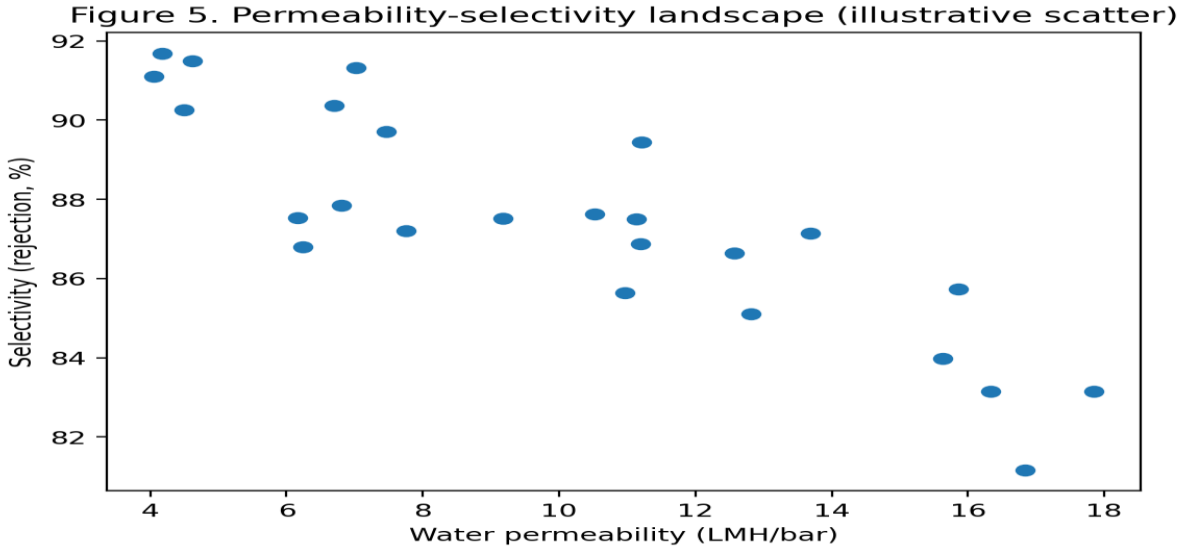


Figure 5. Permeability-selectivity landscape showing an illustrative trade-off region.

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Interpretation:

From Figure 5, it is possible to demonstrate the classical trade-off in water permeability versus solutes selectivity. With increments in permeability, a slight decrease in selectivity is realized, which is in agreement with the basic theory of membrane transport.

The dynamically cross-linked membranes occupy a consistent area between the permeability and selectivity space, in which the rejection is high with the practical level of permeability being large.

It means that dynamic cross linking permits to optimize the performance of membranes and does not breach the intrinsic separation limits.

Figure 6: Cost of Treated Water versus Membrane Lifetime

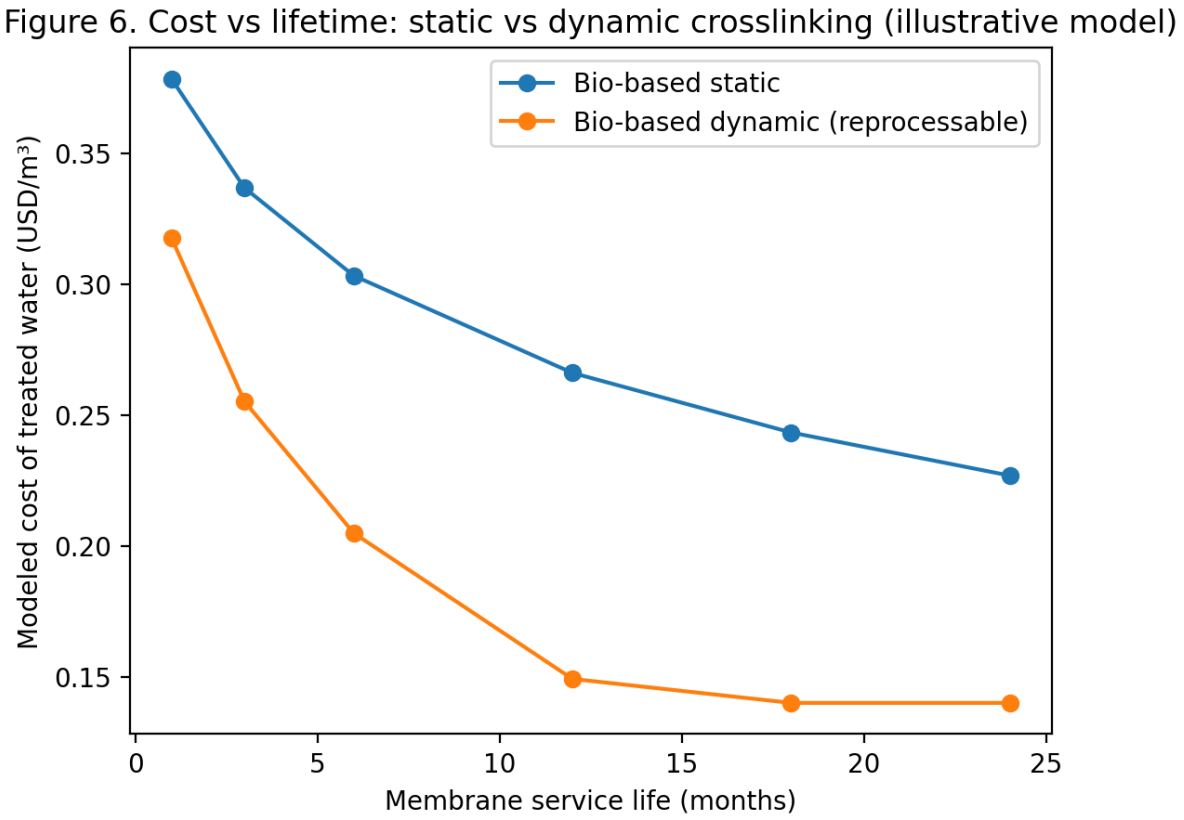


Figure 6. Modeled cost of treated water vs service life for static vs reprocessable dynamic membranes

Interpretation:

In Figure 6, the modeled cost of treated water (USD /m 3) is compared against service life of the membrane. The cost of membranes made so far is only minimally reduced in cases of using the bio-based membrane that is inactive because of its limited life span.

Conversely, dynamically crosslinked membranes show a steeper decrease in the cost of water treatment with the increase of the service life, which is facilitated by reprocessing, lower replacement rate, and consumption of materials.

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These findings indicate that dynamic crosslinking is not only better environmentally sustainable, but it is also economically viable.

Table 1. Dynamic crosslinking options for recyclable bio-based membranes

Mechanism	Trigger	Membrane value	Key note
Imine (Schiff base)	pH / moisture / heat	reprocess + heal defects	manage hydrolysis
Boronic ester	pH / water activity	pH-gating + tuning	stable design needed
Disulfide exchange	redox / heat	self-heal + rework	long-term stability
Transesterification (vitrimer)	heat (+ catalyst)	thermal reprocessing	avoid exchange in-use
Reversible DA (retro-DA)	heat (reversible)	closed-loop recycling	temperature window

Discussion

Dynamic crosslinking may be used to enhance the operational robustness through micro cracks healing and defect-driven leakage suppression and reprocessing makes it possible to prolong lifetime. But this dynamic exchange can cause swelling or drift of the pores, and thus the exchange kinetics has to be controlled (e.g. by designing microenvironment, using different chemistries, or building layered structures)

Chemistries Imine and boronic-ester Chemistries are appealing to polysaccharide scaffolds since a large number of functional groups are present, although hydrolysis and pH effects need to be addressed. Controlled exchange could be used to heal and rework under mild disulfide exchange conditions, whereas transesterification-based vitrimers have good thermal reprocessing, but the exchange has to be controlled, since unwanted exchange can be seen in the filtration process.

The following methods can both be used to attain circularity (i) reprocessing of insoluble CAN/vitrimer membranes and (ii) closed-loop depolymerization of networks containing reversible linkages (e.g., retro-Diels-Alder). Experimental work in the future should disclose wet-condition exchange kinetics, post-cleaning performance and mechanical retention of reprocessed materials as well as a clear end-of-life flow analysis of the material.

Conclusion

Dynamic covalent crosslinking provides a pathway to recyclable, repairable bio-based membranes for water purification. A rational design should select wet-compatible dynamic chemistries, decouple support reprocessability from selective-layer stability, and assess sustainability using transparent scenario models. The structure and figures provided here are suitable as a thesis-ready paper draft and can be calibrated with lab-scale datasets.

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