

High-Flux and Anti-Fouling Membrane Distillation Membrane with VOC Capture Ability Enabled by ZIF-8

Corresponding Author: Professor Bo Wang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The author has solved my doubts and recommends acceptance.

Reviewer #2

(Remarks to the Author)

In the present manuscript, an omniphobic ZIF-8 composite membrane was prepared, which could trap VOCs under vacuum through crystal phase transitions while reducing water vaporization enthalpy via linkage swing. While this manuscript has undergone revisions and shows substantial quality improvements, providing a wealth of valuable information for our readers, there are still some remaining issues. I recommend that the paper could be accepted after major revisions.

(1) Regarding the structural instability of ZIFs, the authors solely relied on ICP analysis to speculate the presence of defects and framework collapse, but lacked direct characterization evidence to substantiate these claims.

(2) In Figure 2d, as the ZIF-8 loading increases, both the hydrophobicity and wetting resistance of the membrane improve. Would further increasing the ZIF-8 loading continue to enhance its performance?

(3) The rapid increase in toluene concentration after 30 hours raises questions about the practical applicability of this membrane in VOC removal.

(4) While membrane regeneration relies on high-temperature desorption of VOCs, has the post-desorption treatment of these released compounds been adequately considered?

Reviewer #3

(Remarks to the Author)

This manuscript reports a work that fabricates a MOF-based membrane for membrane distillation. The novelty of this work is that the fabricated membrane is able to reduce the transport of volatile organic carbons (VOC) that constrains the use of MD for the treatment of complex wastewater. The membrane also has higher water flux than commercial membranes. My major concern is about the energy consumption of MD for desalination, even with the fabricated MOF membrane. The energy consumption of MD with MOF-based is ~3000 J/g, which is one order of magnitude higher than current thermal technologies for wastewater desalination. Therefore, the MOF membrane is unlikely to change the disadvantage of MD in terms of energy efficiency. Therefore, I suggest the authors focus on VOC removal and high water flux of the fabricated membrane rather than energy efficiency.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

Thanks for the responses from authors! Authors revised the manuscript in detail according to the comments of reviewers, and the quality of this paper was greatly improved. I recommended that this paper should be accepted for publication in your

journal.

Reviewer #3

(Remarks to the Author)

As this work does not reduce energy consumption of MD, the high flux seems to be one novelty. However, it is not accurate to claim high flux of 62 LMH in the abstract. To compare with other membranes, the flux needs to be normalized by the driving force. Therefore, LMH/bar needs to be reported rather than absolute value of flux. For the membranes in this work, ~60 LMH flux was achieved by a feed-side temperature of 70C, and a vacuum level of 85 kPa. This seems to be not a very high flux. For commercial MD membranes, the water flux is able to reach ~30 LMH at a temperature difference of 40C with ambient pressure. The authors need to look at the literature on the water permeability of MD under vacuum to justify that the water flux of their membrane is indeed better than commercial membranes.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

The authors have addressed my comment adequately. The work is now qualified for publication.

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Response to the reviewers' comments:

Reviewer#2:

1. *Regarding the structural instability of ZIFs, the authors solely relied on ICP analysis to speculate the presence of defects and framework collapse, but lacked direct characterization evidence to substantiate these claims.*

Our previous experiments have shown that the stability of ZIF-8 strongly depends on the synthesis method. Specifically, ZIF-8-2 and ZIF-8-3, which we used in MD membranes, exhibited good structural stability, whereas ZIF-8-1 demonstrated inferior stability.

To provide direct evidence of structural changes, we performed PXRD and SEM analyses of ZIF-8-1 after immersion in water at 70 °C for 10 days. The PXRD patterns showed distinct diffraction peaks corresponding to the (100), (002), (101), and (102) planes of ZnO, while SEM images revealed pronounced morphological changes (Figure R1). In contrast, the PXRD and SEM profiles of ZIF-8-2 and ZIF-8-3 remained largely unchanged under the same conditions (Figure R2).

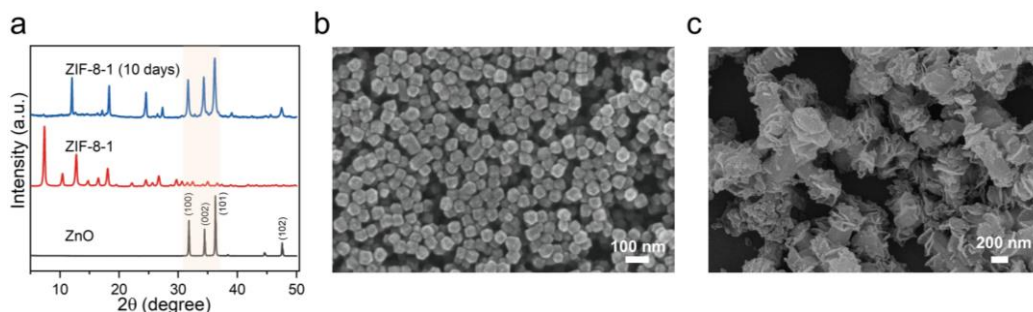


Figure R1. (a) PXRD patterns of ZnO, pristine ZIF-8-1, and ZIF-8-1 after 10 days of water immersion. (b) SEM image of pristine ZIF-8-1. (c) SEM image of ZIF-8-1 after 10 days of water immersion.

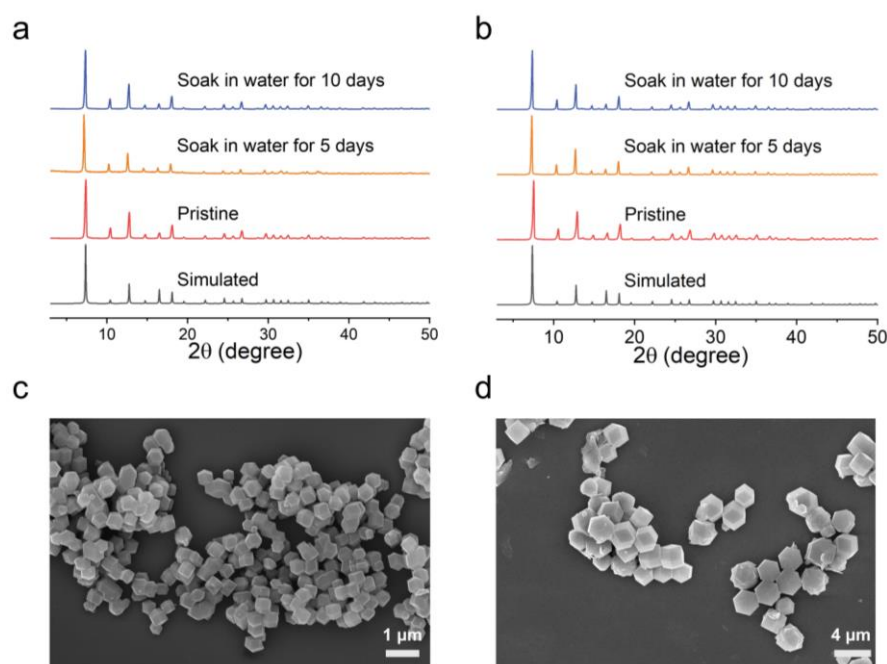


Figure R2. (a-b) PXRD patterns of ZIF-8-2 and ZIF-8-3 after immersion in water at 70 °C for 5 days and 10 days. (c-d) SEM images of ZIF-8-2 and ZIF-8-3 after 10 days of water immersion.

Compared with ZIF-8-2 and ZIF-8-3, ZIF-8-1 exhibited a significantly lower N/Zn ratio (3.67) than the theoretical value of 4, as revealed by elemental analysis and ICP measurements, indicating a higher density of coordination defects. In addition, its smaller particle size (~50 nm) leads to an increased surface area-to-volume ratio, further contributing to the formation of surface defects. These defects promote the competitive coordination of water molecules with Zn^{2+} and protonation of terminal 2-methylimidazole ligands, weakening Zn–N bonds. As a result, Zn^{2+} is released from the framework, and the supernatant pH increases from 7.4 to 8.9 over 10 days. Meanwhile, Zn^{2+} reacts with OH^- to form ZnO precipitates (*Chem. Commun.*, 2013, 49, 9140–9142; *J. Membr. Sci.*, 2015, 485, 103–111).

Accordingly, we have included the above results and discussions in the revised manuscript (Page 4) and SI (Supplementary Fig. 6).

2. In Figure 2d, as the ZIF-8 loading increases, both the hydrophobicity and wetting resistance of the membrane improve. Would further increasing the ZIF-8 loading

continue to enhance its performance?

Further loading beyond 92 wt% compromises the mechanical stability of the membrane, leading to crack formation and structural fragility. As a result, such membranes become unsuitable for MD. Therefore, 92 wt% represents an optimal balance between improved wetting resistance and sufficient mechanical integrity for practical operation.

3. *The rapid increase in toluene concentration after 30 hours raises questions about the practical applicability of this membrane in VOC removal.*

We appreciate the reviewer's concern regarding the observed rapid increase in toluene concentration after 30 hours. This result was obtained under a deliberately elevated feed concentration of 200 ppm, which was chosen to accelerate the adsorption process and evaluate the upper performance of the membrane. In practical applications such as shale gas wastewater treatment, typical VOC concentrations are significantly lower (10 ppm). Based on this practical concentration, our calculations indicate that the membrane can operate continuously for approximately 600 hours before requiring regeneration, corresponding to the treatment of 38,000 L of wastewater per square meter of membrane area. In addition, as detailed in our response to Comment 4, the adsorbed toluene can be readily desorbed using hot water vapor and concentrated to ~400 ppm, facilitating efficient post-treatment via biodegradation or advanced oxidation. These findings collectively support the membrane's feasibility and effectiveness for long-term VOC removal in practical settings.

Accordingly, we have included the above discussions in the revised manuscript (Page 8).

4. *While membrane regeneration relies on high-temperature desorption of VOCs, has the post-desorption treatment of these released compounds been adequately considered?*

Additional experiments revealed that a toluene-saturated ZIF-8 PE MMM-92%-FDTS membrane (~16 mg toluene adsorbed in a 3 cm² membrane) can be effectively regenerated by exposure to hot water vapor generated from 40 mL of water at 100 °C for approximately 30 min. This process resulted in nearly complete desorption of toluene. It indicates that the membrane can be rapidly regenerated using low-grade heat sources, such as industrial waste heat, with toluene concentrations increasing from 10 ppm in the original feed to ~400 ppm in the collected condensate. This concentrated condensate can then be subjected to appropriate post-treatment methods, such as biodegradation or advanced oxidation processes.

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In accordance with the suggestion, we have revised the manuscript to focus primarily on the membrane's high water flux and its effectiveness in VOC suppression during membrane distillation. We have minimized discussions related to energy efficiency, acknowledging that the energy consumption of membrane distillation (MD), even with the MOF-based membrane (~3000 J/g), remains higher

than that of existing thermal desalination technologies.

Response to Reviewer#3's Comments:

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As requested, we normalized our flux to transmembrane pressure and compared it with values reported in the literature. The resulting value was 71.8 LMH/bar, which ranks among the best reported for both polymeric and mixed matrix membranes used in VMD (Fig. R1). This value is significantly higher than those of commercial membranes, whether from published data (e.g., Immobilon-PS^Q PVDF, 19.7 LMH/bar [ACS Appl. Mater. Interfaces, 2018, 10, 13452]; VALQUA PTFE, 33.5 LMH/bar [Sep. Purif. Technol., 2023, 313, 123465]) or from our own tests on commercial membranes (e.g., ISEQ00010 PVDF, 26 LMH/bar).

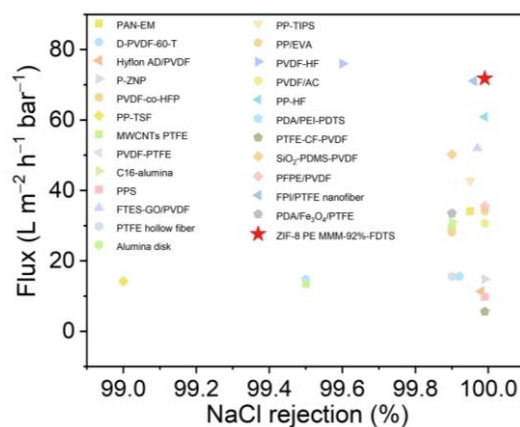


Fig. R1 Comparison of normalized water flux (LMH/bar) and salt rejection between the ZIF-8 PE MMM-92%-FDTS membrane and reported VMD membranes in literature.

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Responses to the Reviewers' Comments

Version 1

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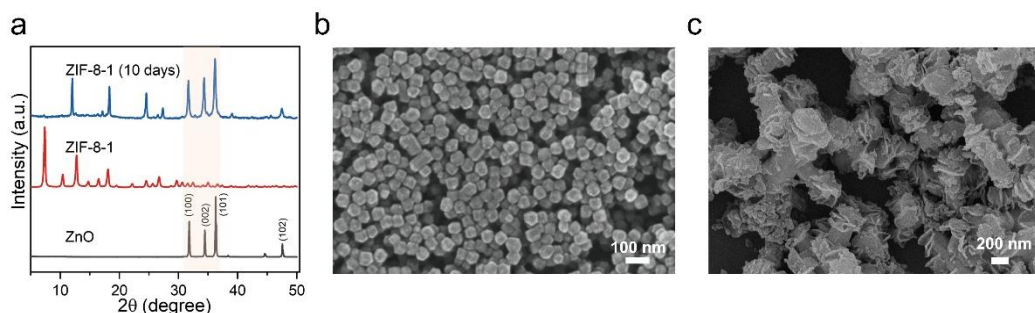


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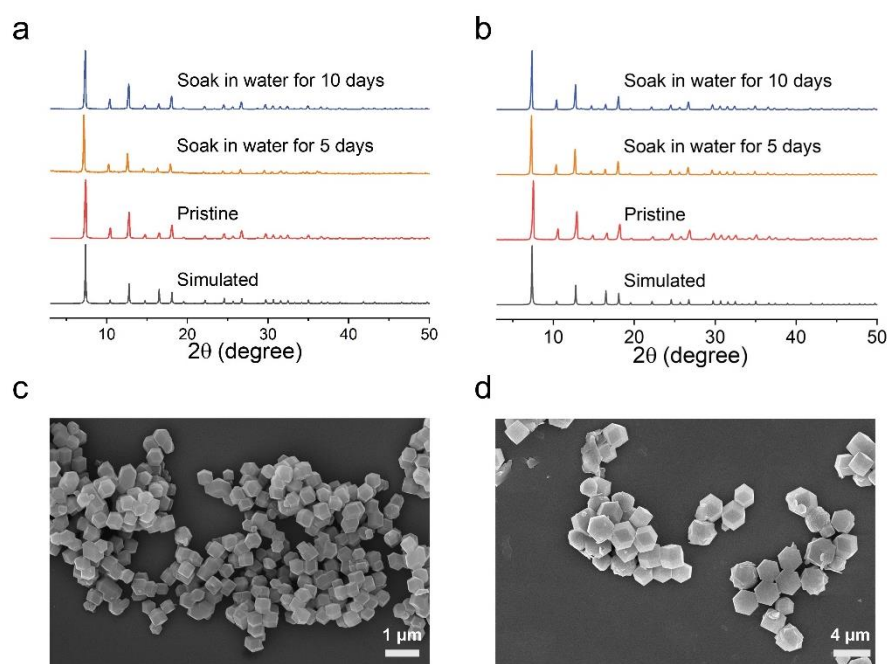


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Version 2

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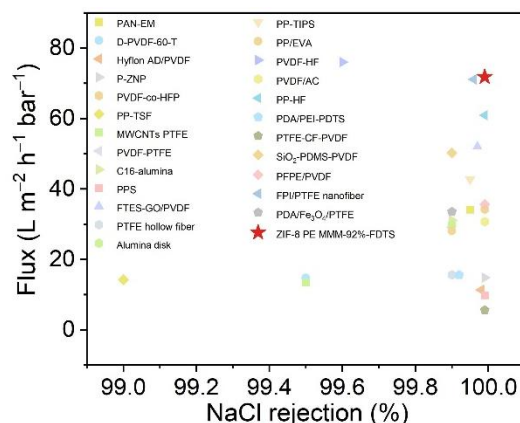


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Version 3

Response to Reviewer#3's Comments:

The authors have addressed my comment adequately. The work is now qualified for publication.

We thank the reviewer again for the valuable comments and feedback, which have helped to improve the manuscript.