Computational Screening & Design of Alkylamine-Functionalized Polymer Sorbents

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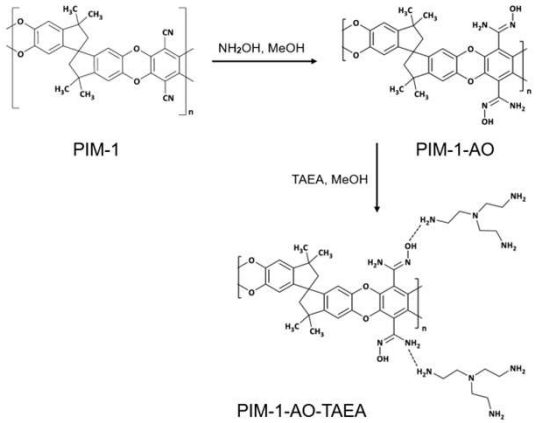
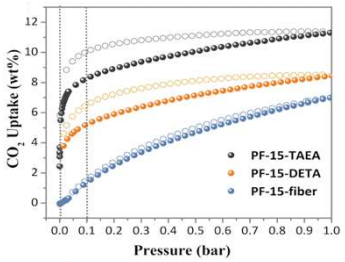
Motivation from Recent Experiment Work[1,2]



PIM-1 polymer fibers (PF-15) functionalized with amidoxime (AO) and aminated with TAEA (Tris(2-aminoethyl)amine) or DETA (Diethylenetriamine)

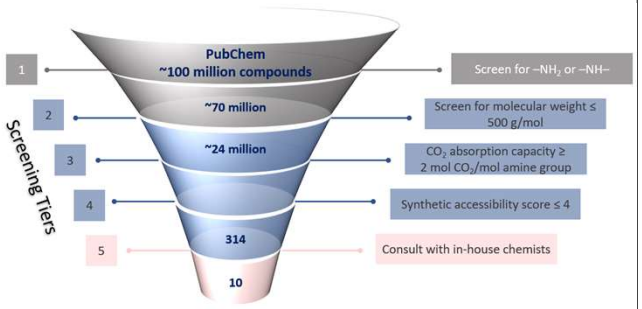


The CO_2 uptake of the aminated-functionalized polymer is greater than that of the corresponding non-aminated polymer system

Finding Better Polymer-Amine Sorbents using Computational Tools

- A better combination of polymer-amine could exist that will have even higher CO_2 uptake
  - Millions of amines are available in literature and the PubChem database
  - Similarly, other porous polymers could perform better than PIM-1
- This project seeks to screen and design a better polymer-amine sorbent, understand CO_2 uptake process by the sorbent at a molecular level, and investigate the effects of water in CO_2 capture, such as CO_2 overall mass transfer and CO_2 uptake.

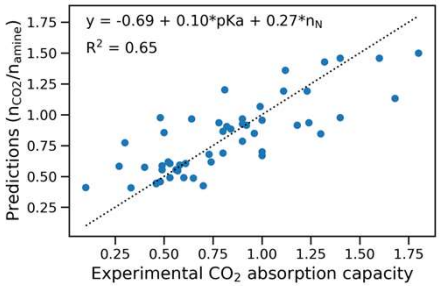
Screening of Amines



~100 million compounds available in PubChem database screened to select 10 high-performance amines for CO_2 capture

CO_2 Absorption Capacity Prediction

- A regression model was fitted to correlate CO_2 absorption of 54 primary and secondary amines with pKa and amine count
- The model's accuracy is satisfactory for screening applications
- This model was employed to predict the CO_2 absorption capacity of millions of amines in the PubChem database



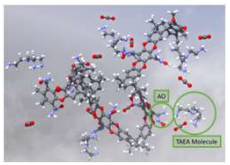
Parity plot for predicted versus experimental CO_2 absorption capacity of primary and secondary amine molecules

Screening of Polymers

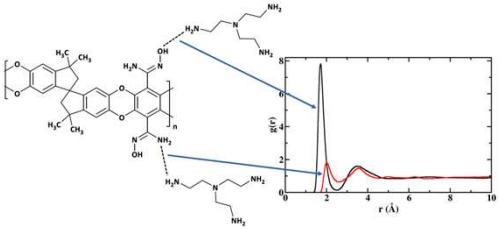
- Systematic literature survey was conducted for porous polymers
- A promising porous polymer PIM-EA-TB having surface area greater than PIM-1 has been identified based on synthesizability criteria

Computational Testing of Polymer-Amine Sorbents

- Tools/methodologies are being developed to test the polymer-amine combination



Snapshot of a simulation showing PIM-1-AO, TAEA and CO_2 molecules



Radial distribution function (g(r)) indicates stronger TAEA hydrogen bonding with -OH over -NH2 in PIM-1-AO

Effect of water on diffusion of CO_2 molecules inside the sorbent

PIM-1-AO-TAEA-CO_2 system	Density (g/cc)	Self-diffusion coefficient (10^{-5} cm^2/s)	
		TAEA	CO_2
Water not present	1.173 ± 0.004	0.00052 ± 0.0001	0.025 ± 0.003
Water present (8% weight)	1.171 ± 0.006	0.00074 ± 0.0001	0.038 ± 0.007

Water's hydrogen bonds with PIM-1-AO and TAEA molecules slightly enhanced CO_2 diffusion

Conclusions

- Ten amines and two polymers were identified for further study
- Computational tools are being developed to test the polymer-amine sorbents
- Future work will mainly focus on
  - Relationship between the amine structure and CO_2 loading and/or the reaction kinetics of CO_2 uptake
  - Understanding the role of water in the CO_2 capture process
  - Comparing computational estimates for CO_2 loading performance ranking and investigation of amine-polymer stability

References

1. Miles, A., Wilfong, W. C., Hopkinson, D., & Sekizkardes, A. K. (2020). Alkylamine Incorporation in Amidoxime Functionalized Polymers of Intrinsic Microporosity for Gas Capture and Separation. *Energy Technology*, *8*(10), 2000419.
2. Sekizkardes, A.; Kusuma, V.; Culp, J.; Muldoon, P.; Hoffman, J.; Hopkinson, D. Single Polymer Sorbent Fibers for High Performance and Rapid Direct Air Capture. *ChemRxiv* 2022.

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