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Synthesis of Covalent Organic Polymers for removing CO_2 and heavy metal ions with strong affinity

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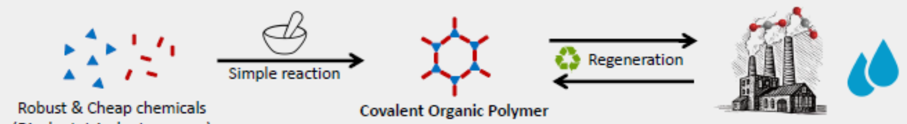
The demand for functionalized adsorbent that contains not only high surface area but also selectivity and recyclability has increased for several decades. Especially, growing environmental problems such as water pollution and global warming introduced various application possibilities of functionalized adsorbents for pollutant treatment. Our target contaminants are CO_2 and heavy metal ions and they are non-degradable, stable compounds. Hence, adsorption mechanism is considered as a promising solution for removing those pollutants. In this study, we developed several kinds of Covalent Organic Polymers (COPs) and applied them as a functionalized adsorbent for pollutant treatment systems.

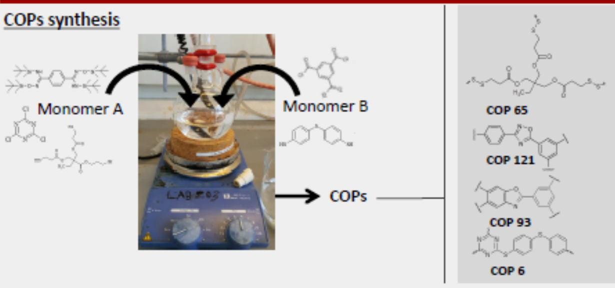
1. Covalent Organic Polymers (COPs)



- ✓ Diversity
- ✓ Simple reaction
- ✓ Robust
- ✓ Low material cost
- ✓ Recyclability

2. Experimental methods

COPs synthesis



Heavy metal ions removal

- Atomic Absorption Spectroscopy
- Sampling time: 10 min , 1 h, 3 h, 24 h, 48 h
- pH measure: Initial point, final point

CO_2 capture

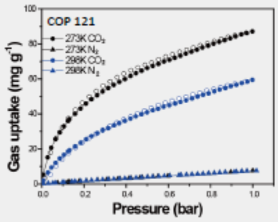
- BET instrument: volumetric type measurement
- Measurement conditions: ~ 1 bar, 273 K, 298 K
- Selectivity (N_2/CO_2): Ideal Adsorption Solution Theory (IAST) calculation

3. Result and Discussion - CO_2 capture

	MEA[1]	COP 121		COP 93		
	298K	273K	298K	273K	298K	323K
BET surface area	solution	24.5 m^2g^{-1}		605.8 m^2g^{-1}		
CO_2 uptake ($mg\ g^{-1}$)	60	87.1	59.4	139.6	91.1	60.7
N_2 uptake ($mg\ g^{-1}$)	NA	5.1	7.5	6.8	4.4	2.3
Selectivity[2]	NA	62	29	75.1	73.5	99.2
Thermal stability	110-130°C	up to 450°C		up to 550°C		

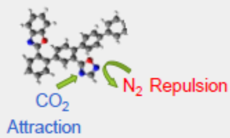
[1] Monoethanolamine
[2] Selectivity calculated by IAST calculation

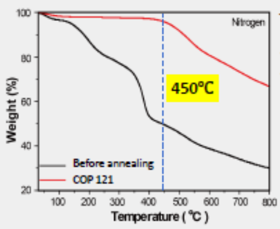
✓ In order to fill up 500 ml bottle with CO_2, 11 g of COP121 or only 7 g of COP 93 are needed.



Gas uptake capacity

✓ Nitrogen functionality can enhance the selectivity of the adsorbent.





Thermal stability

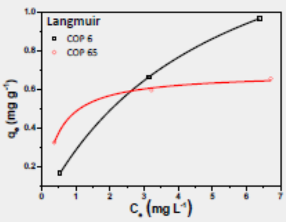
- ✓ Aromatic rings help on stabilization
- ✓ Safe regeneration by heat

1. Nanoporous Benzoxazole Networks by Silylated Monomers, their Exceptional Thermal Stability and Carbon Dioxide Capture Capacity, Chem. Mater., 26 (23), 6729–6733 (2014), H. A. Patel, D. Ko, C. T. Yavuz"
2. Synthesis of nanoporous 1,2,4-oxadiazole networks with high CO2 capture capacity, Chem. Commun., 51, 2915-2917 (2015), D. Ko, H. A. Patel, C. T. Yavuz"

4. Results and Discussion - Heavy metal ion removal

	COP 6[2]			COP 65[2]		
Cd^{2+} Initial concentration	0.7 ppm	4 ppm	7 ppm	0.7 ppm	4 ppm	7 ppm
BET surface area	7.300 m^2g^{-1}			0.001 m^2g^{-1}		
% removal[1] of Cd^{2+}	24%	18%	13%	48%	16%	9%
Langmuir maximum adsorption capacity	1.706 mg/g			0.695 mg/g		
R^2	0.9999			0.9995		

[1] % removal = $(C_i - C_e)/C_i \times 100$ C_i = initial concentration, C_e = equilibrium concentration
[2] Dose amount: 1g/L



Langmuir adsorption isotherm

✓ Sulphur functionality have affinity onto heavy metal ions.

$Cd^{2+} + S^{2-} \rightarrow CdS$

Hard-soft trends for acids

Hard-soft trends for bases

5. Summary

Covalent Organic Polymers

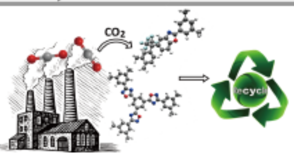
- ✓ Facilitate various functionalized COPs with simple reaction & mild condition.
- ✓ N atoms could enhance selectivity and capacity of CO_2.
- ✓ Sulphide gives strong affinity towards heavy metal ions.

Performance

- ✓ Achieved 139.6 $mg\ g^{-1}$ CO_2 capacity.
- ✓ High thermal stability up to 550°C.
- ✓ 99 times higher CO_2/N_2 selectivity .
- ✓ Cd^{2+} adsorption with high affinity

Application

- ✓ CO_2 adsorbent in factory stack.
- ✓ Gas molecular sieve.
- ✓ Storm, mine water treatment.
- ✓ Heavy metal polluted site treatment.



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