Synthesis of covalent organic polymers for removing CO2 and heavy metal ions with strong affinity

Ko, Dongah; Jakobsen, Mogens Havsteen; Hwang, Yuhoon; Yavuz, Cafer T.; Andersen, Henrik Rasmus

Published in:
Conference Proceeding. 8th Euro-Korean Conference on Science and Technology (EKC 2015)

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Conference Proceeding

(Preliminary Version, Final Version will be edited after the meeting*)

**N.B.* – Authors are invited to signal corrections in the mean time to improve this draft.

EKC 2015 제8회 유럽한국과학기술대회

Eighth Euro-Korean Conference on Science and Technology

Faculté de Médecine, Strasbourg, France, 22-24 July 2015

Engineering and Technology

Location: Room 209 (Building "Forum")
Date & Time: 2015-07-24 14:00-16:00
Session Chair: Prof. PARK, Chung Hae

14:00 - 14:20
Dr. LEE, Eungjang CELIA, University of Bordeaux *Aberration Corrected Direct Laser Writing on Silver-containing Phosphate Glass*

14:20 - 14:40
Mr. KIM, Sangyeob Department of Environmental Engineering and Water Technology, UNESCO-IHE Institute *Applicability of high pressure supersaturating oxygenation to MBRs wastewater treatment*

14:40 – 15:00
Ms. JANG, Jiyi KIST-Europe *Computational approaches for predicting toxicity of chemical mixtures*

15:00 – 15:20
Dr. KWAK, Sanghoon Verimag, University of Joseph Fourier *DESIGN OF ASYNCHRONOUS MSP430 MICROPROCESSOR*

15:20 – 15:40
Mr. OH, Hyondong Department of Aeronautical and Automotive Engineering, Loughborough University *Coordinated Standoff Tracking of Moving Ground Targets Using Unmanned Aerial Vehicles for Airborne Persistent Surveillance*

15:40 – 16:00
Mr. KIM, Yong-Ki Chungbuk National University *Recognition of Isolated Words Represented by Lip Image Streams using Dynamic Time Warping*

Poster Presentation

Dongah Ko
Department of Environmental Engineering, Technical University of Denmark

Synthesis of covalent organic polymers for removing CO_2 and heavy metal ions with strong affinity

Jihye Hwang
Department of chemical engineering, Norwegian University of Science and Technology

Optimization of absorber column

Eomji Park
Mechanical Engineering, Technische Universität Wien

Design Home-security robot based on OPRoS

Won Jong KIM
Department of Information Display and Advanced Display Research Center, Kyung Hee University

Cathodoluminescence Properties of Silicon Thin Films with Carbon Nanotube Electron Beam (C-beam) Exposure Technique

Minji Park
Environmental Safety Group, KIST Europe

EU CLP vs Korea GHS for Chemical Mixtures: A Solution for Korean Chemical Industry

Bongwoo Kwak
Automotive Components & Materials R&D Group, KITECH

Design of Wireless Power Transfer System with Hybrid of Inductive Coupling and Magnetic Resonance for Charging Electric Vehicle

Youngkuk Choi
Automotive Components & Materials R&D Group, KITECH

Design of Operational Drive System of Agricultural Unmanned Transportations

Jong Gwan Lim received the MS degree in biosystem engineering at KAIST (2006). He is a currently Ph.D candidate at the same university. His current research interests include Human-Robot Interaction (HRI), Machine Learning and Pattern Recognition.

Mi-Hye Kim received the Ph. D degree in mathematics from Chungbuk National University, (2001) She is currently a professor of department of computer engineering in the same university. Her research interests are mainly in the field of fuzzy theory & application, ubiquitous game and gesture recognition.

Synthesis of covalent organic polymers for removing CO_2 and heavy metal ions with strong affinity

Dongah Ko[1*], Mogens H. Jakobsen[2], Yuhoon Hwang[1], Cafer T. Yavuz[3], Henrik R. Andersen[1]
[1] *Department of Environmental Engineering, Technical University of Denmark, Miljoevej 113, 2800 Kgs. Lyngby, Denmark (doko@env.dtu.dk)*
[2] *Department of Micro- and Nano technology, Technical University of Denmark, Ørsteds Plads, 345B, 2800 Kgs. Lyngby, Demark*
[3] *Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea*

Abstract

Demand for functionalized adsorbent that contains not only high surface area but also selectivity and recyclability has been increased for several decades. Especially, growing environmental problems such as water pollution by heavy metal ions and global warming due to carbon dioxide concentration introduced various application possibilities of functionalized adsorbents for pollutant treatment. Since both carbon dioxide and heavy metal ions are non-degradable and stable compounds, those are difficult to be removed from polluted sites. Therefore, adsorption mechanism considered as a promise solution for removing those pollutants. Conventional technologies for both heavy metal ions and CO_2 treatment systems have encountered a number of limitations. In case of CO_2 treatment system, monoethanolamine (MEA) has been used for more than 60 years because of their low-cost with rapid reaction, however, insufficient CO_2 loading capacity and easy degradation of materials are still remained as a barrier [1]. Also, in the case of heavy metal ions treatment, activated carbon (AC) is commonly used for treatment due to its high porosity and low-cost, it has no functionality to uptake targeted pollutant selectively from heterogeneous circumstance. Besides, both MEA and AC regeneration process consumes considerable amount of energy, hence, used materials tend to be incinerated or thrown out rather than regenerated. Likewise, fulfilling only some conditions and ignoring others will lower the whole process efficiency during the treatment. Recently, porous polymers with various functionalities are suggested as a replacement of conventional methods to overcome several constrains. In this study, we designed functionalized covalent organic polymers (COPs) and synthesized it by bottom up methods to generate specific functionalities. By introducing functionalities into COPs we could enhance selectivity of adsorbent towards treatment target substances with sufficient surface area and porosity of adsorbent [2,3]. Surface area and porosity of functionalized COPs are analysed by Brunauer-Emmett-Teller (BET) surface area

method and scanning electron microscope (SEM) and functionalities are confirmed by elemental analysis (EA), Fourier transform infrared (IR), and Thermo-gravimetric analysis (TGA). CO_2 capacity, selectivity, isosteric heat of CO_2 adsorption was measured and calculated by BET, Idea Adsorbed Solution Theory (IAST) equation and Van't Hoff equation. Lastly, heavy metal removal amount, isotherm, and kinetic were measured by Inductive coupled plasma mass spectrometry (ICP-MS) and Atomic adsorption spectroscopy (AAS). Here, we present functionalized COPs, one for CO_2 adsorption that achieved sufficient CO_2 capacity with 61 of CO_2–N_2 selectivity owing to a nitrogen-rich structure and other for heavy metal ion treatment which carried sulfur functionality and achieved high selectivity towards heavy metals ions. All COPs showed thermal stability and low heat of adsorption which facilitating easy regeneration.

Keywords: *Covalent organic polymer, Functionalized adsorbent, Carbon dioxide capture, Heavy metal ions, Environment*

References

[1] Mohammad Songolzadeh, Mansooreh Soleimani, Maryam Takht Ravanchi, and Reza Songolzadeh, Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions, The Scientific World Journal, 2014, vol. 2014, 34

[2] Dongah Ko, Hasmukh A. Patel, Cafer T. Yavuz, 2015, Synthesis of Nanoporous 1,2,4-oxadiazole networks with high CO_2 capture capacity, Chem. Commun.,51, 2915-2917.

[3] Hasmukh A. Patel, Dongah Ko, Cafer T. Yavuz 2014, Nanoporous Benzoxazole Networks by Silylated Monomers, Their Exceptional Thermal Stability, and Carbon Dioxide Capture Capacity, Chem. Mater., 26 (23), pp 6729–6733.

Biography

Dongah Ko is PhD student in Technical University of Denmark. She finished her B.S degree in Environmental science department from Kyung Hee University. She received her Master's degree at the Graduate School of Energy, Environment, Water and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST) under supervision of Dr. Cafer T. Yavuz. In KAIST her research was focused on development of new covalent organic polymers for carbon dioxide capture. Currently, with same covalent organic polymers, she is working on heavy metal ion removal from polluted water under supervision of Dr. Henrik R. Andersen and Dr. Cafer T. Yavuz.

Optimization of absorber column

Jihye Hwang

Department of chemical engineering, Norwegian University of Science and Technology, Trondheim, Norway (jihye9996@gmail.com)

Abstract

Carbon dioxide is an important factor related to greenhouse gases and has a significant contribution to global warming. Therefore the importance of researching, optimizing and developing the concept of CO2 capture from flue has increased. To date, it exist three main approaches to capture CO2 generated from a primary fossil fuel (coal, natural gas or oil), biomass, or mixture of these fuels, and these are as follows; post-combustion, pre-

DTU Environment
Department of Environmental Engineering

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

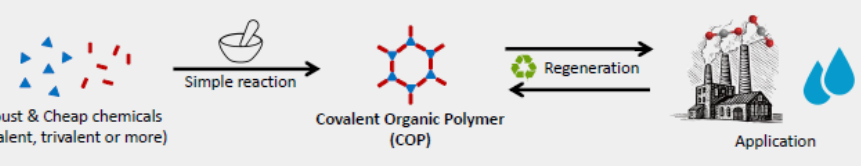
Dongah Ko[1], Yuhoon Hwang[1], Mogens H. Jakobsen[2], Cafer T. Yavuz[3], Henrik R. Andersen[1]

[1] Technical University of Denmark, Department of Environmental Engineering, Miljoevej 113, 2800 Lyngby, [2] Technical University of Denmark, Department of Micro- and Nanotechnology, Ørsteds Plads, Bygning 345B, 2800 Kgs. Lyngby, [3] Korea Advanced Institute of Science and Technology (KAIST), Graduate School of EEWS, Daejeon 305-701, Republic of Korea

doko@env.dtu.dk

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.

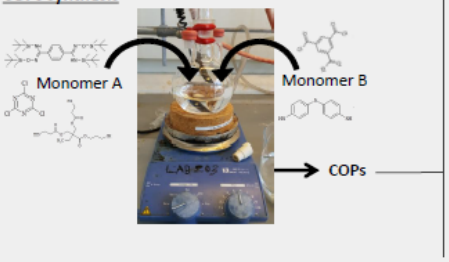
1. Covalent Organic Polymers (COPs)

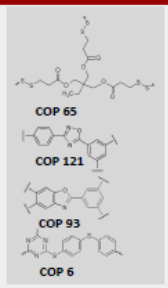


- ✓ Diversity
- ✓ Simple reaction
- ✓ Robust
- ✓ Low material cost
- ✓ Recyclability

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		

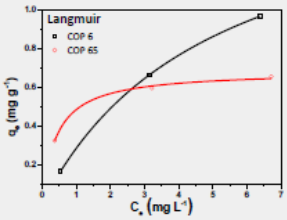
[1] Monoethanolamine
[2] Selectivity calculated by IAST calculation

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

4. Results and Discussion - Heavy metal ion removal

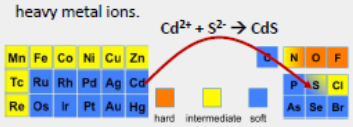
Cd^{2+} Initial concentration	COP 6[2]			COP 65[2]		
	0.7 ppm	4 ppm	7 ppm	0.7 ppm	4 ppm	7 ppm
BET surface area	7.300 m^2g^{-1}			0.001 m^2g^{-1}		
% removal[1] of Cd^{2+}	24%	18%	13%	48%	16%	9%
Langmuir maximum adsorption capacity	1.706 mg/g			0.695 mg/g		
R^2	0.9999			0.9995		

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



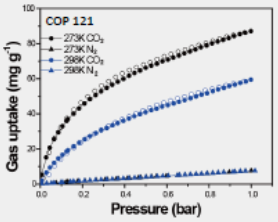
Langmuir adsorption isotherm

- ✓ Sulphur functionality have affinity onto heavy metal ions.



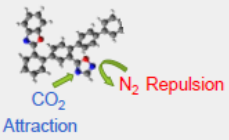
Hard-soft trends for acids

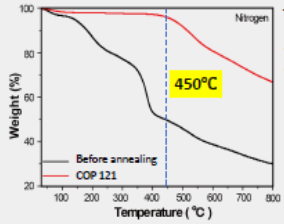
Hard-soft trends for bases



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*

5. Summary

Covalent Organic Polymers

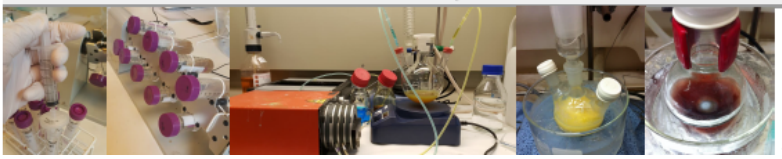
- ✓ Facilitate various functionalized COPs with simple reaction & mild condition.
- ✓ N atoms could enhance selectivity and capacity of CO_2.
- ✓ Sulphide gives strong affinity towards heavy metal ions.

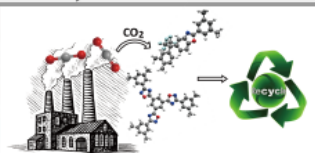
Performance

- ✓ 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.





KAIST