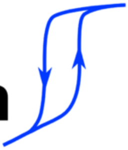
PhD Seminar

Adsorption



September 29-30, 2022

ERLANGEN TVT

FAU
Friedrich-Alexander-Universität

DESIGN OF PARTICULATE PRODUCTS

DECHEMA

DAY 1

Thursday, September 29th

Arrival & Get-together $13^{00} – 13^{20}$

Opening $13^{20} – 13^{30}$

Prof. Dr. Matthias Thommes

Carola Schlumberger

Session I – Thermodynamics of Adsorption $13^{30} – 15^{00}$

Hounfodji Jean Wilfried

Max Planck Institute, Magdeburg

Title: Adsorption of most common drug residues from hospital wastewater on vermiculite exchanged with magnesium: a DFT study

Fiedler Marius

Institute of Process Systems Engineering / Institute of Thermal Separation Processes, Hamburg

Title: A molecular dynamics approach to predict adsorption isotherms

Eder Simon

Institute of Separation Science and Technology, FAU Erlangen-Nürnberg

Title: Aspects of Gas Storage: Effect of Confinement on supercritical Isotherms

Session II – Gas Phase Adsorption $15^{30} – 17^{00}$

Al-Awaad Haidar
Thermodynamics & Mathematical Physics Unit, Faculty of Engineering, University of Mons
Title: Two-stage of VPSA Process for Capturing CO2 from Flue Gases Using Metal-organic Framework

Gehrke Laura
Thermal Process Engineering, University of Duisburg-Essen
Title: Adsorption of heterocycles on silica alumina gels

Lairana Lima Duarte
Fraunhofer Institute for Material and Beam Technology, IWS Dresden
Title: Evaluation of MOF coatings for water adsorption properties

Bus departure to TVT, FAU Erlangen-Nürnberg 17^{30}

Laboratory Tour at TVT, FAU Erlangen-Nürnberg $17^{45} – 18^{45}$

Dinner at Mein Lieber Schwan, Erlangen 19^{00}

DAY 2

Friday, September 30th

Session III – Gas Phase Adsorption $9^{00} – 10^{00}$

Roßmann Philip

Erlangen Center for Interface Research and Catalysis, FAU Erlangen-Nürnberg

Title: Separation of n-butane and 1-butene mixtures on ZIF-8 and silicalite-1

Ali Usman

Institute of Physical Chemistry, JLU Giessen

Title: Physisorption Studies of hydrothermally tuned-mesoporous silica monoliths

Session IV – Novel Adsorbents and their Characterization $10^{30} – 12^{30}$

Liu Guanhong

École National Superior de Chimie de Rennes

Title: Enhanced thermal activation of peroxymonosulfate by activated carbon for efficient removal of perfluorooctanoic acid

Söllner Jakob

Institute of Separation Science and Technology, FAU Erlangen-Nürnberg

Title: Network analysis of disordered, mesoporous materials using physisorption hysteresis

Guggenberger Patrick

Institute of Inorganic Chemistry – functional Materials, University Vienna

Title: Application of N_2 physisorption at cryogenic temperatures in current materials science research projects

Dr. Raval Niravkumar

Laboratoire Environnement Dynamiques Territoires Montagnes, Université Savoie Mont Blanc

Title: Fabrication of chitosan-based carbons for the eco-efficient removal of emerging contaminants from the wastewater

Lunch Break 12^{30} – 13^{30}

Session V – Liquid Phase Adsorption and Chromatography 13^{30} – 15^{00}

Heiduk Caroline

Institute for Chemical and Thermal Process Engineering, TU Braunschweig

Title: Determination of adsorption isotherms in self-packed columns using the extended Elution by Characteristic Point method

Zarai Somayeh

Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg

Title: Determination of adsorption isotherm parameters using frontal analysis

Carola Schlumberger

Institute of Separation Science and Technology, FAU Erlangen-Nürnberg

Title: Adsorption and nanoporous materials characterization in the liquid phase: Novel methodologies based on NMR relaxometry

Closing 15^{00} – 15^{15}

DAY 1

Thursday, September 29th

Arrival % Get-together 13^{00} – 13^{20}
Opening 13^{20} – 13^{30}
Prof. Dr. Matthias Thommes
Carola Schlumberger

Session I – Thermodynamics of Adsorption

Adsorption of most common drug residues from hospital wastewater on vermiculite exchanged with magnesium: a DFT study 13^{30} – 14^{00}
Hounfodji Jean Wilfried

A molecular dynamics approach to predict adsorption isotherms 14^{00} – 14^{30}
Fiedler Marius

Aspects of Gas Storage: Effect of Confinement on supercritical Isotherms 14^{30} – 15^{00}
Eder Simon

Break

Title: Adsorption of most common drug residues from hospital wastewater on vermiculite exchanged with magnesium: a DFT study

Jean Wilfried Hounfodji[1]*, Wilfried G. Kanhounnon*[1]*, Gaston Kpotin*[1]*, Juliette Lainé*[2]*,*
Guy S. Atohoun[1]*, Michael Badawi*[2]*, Yann Foucaud*[2]
[1]*Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire (LACTHESMO) Université d'Abomey-Calavi, Bénin*
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Over the past decades, the easier access to healthcare and the growing standard of living have conducted to an increasing use of pharmaceutical products, which residues accumulate in the environment to the point of becoming a major concern for the scientific community and for public authorities [1]. These contaminants are known to disturb the metabolism of organisms but can also induce the proliferation of bacterial strains and, therefore, their resistance to antibiotics. Thus, the poor or, in some cases, the absence of wastewater treatment for the removal of pharmaceutical products entails a serious concern for the environment. In this work, vermiculite clay mineral, represents a possible and effective option for the removal of micropollutants by adsorption. Here, we investigate the adsorption of aspirin, paracetamol, ibuprofen, diazepam, diclofenac, and carbamazepine, on the hydrated surface of vermiculite exchanged with magnesium by means of density functional theory (DFT) calculations and thermodynamic calculations [2]. We demonstrate that diclofenac exhibits the highest affinity for the vermiculite surface, followed by paracetamol, ibuprofen, aspirin, carbamazepine, and diazepam. The adsorptions are all exothermic with no risk of toxic by-products generation. Furthermore, heating the vermiculite to 360 K should be sufficient to desorb the pollutant and, consequently, regenerate the adsorbent.

References

1. Hernando, M.; Mezcua, M.; Fernandezalba, A.; Barcelo, D. Environmental Risk Assessment of Pharmaceutical Residues in Wastewater Effluents, Surface Waters and Sediments. *Talanta* **2006**, *69*, 334–342, doi:10.1016/j.talanta.2005.09.037.

2. Li, B.; Liu, S.; Guo, J.; Zhang, L. Interaction between Low Rank Coal and Kaolinite Particles: A DFT Simulation. *Applied Surface Science* **2018**, *456*, 215–220, doi:10.1016/j.apsusc.2018.06.121.

A molecular dynamics approach to predict protein adsorption isotherms

Marius Fiedler[1], Thomas Waluga[1], Sven Jakobtorweihen[1], Irina Smirnova[1]
[1] Hamburg University of Technology, Hamburg, Germany

An increasing number of pharmaceuticals are biopharmaceuticals. In 2020 up to 31,4 % of the turnover of pharmaceutical industry in Germany where made with biopharmaceuticals, most of them as peptides or proteins [1]. In general the downstream processing makes up to 70 % of the production cost, with ion-exchange chromatography as one of the most important processes. Therefore, a high optimization potential lies in these processes, and a good comprehension is needed for an economic production.

Molecular simulations have been used numerous times for the evaluations of adsorption. However, most of the research focuses on qualitative interactions of single molecules to an adsorbent or a wall. Free energy calculations can be used to get statistical data from interactions of one single molecule and other interaction partners. This method has been used for multiple systems in the past and it has been shown that bulk properties can be calculated from this statistical analysis [2]. In a prove of concept it has been shown that Molecular Dynamic simulations can be used to calculate whole adsorption isotherms [3]. However, due to high computational demand some simplification had to be done, which highly effect the accuracy of the calculation. Due to progress in the parallelization of the calculations and higher computational resources it is possible to overcome these limitations. In addition, experimental data are needed for an accurate set-up of the simulation system and to verify the results of the simulations.

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[2] D. Markthaler, S. Jakobtorweihen, N. Hansen, *Living J. Comput. Mol. Sci.* **2019**, *1* (1). DOI: 10.33011/livecoms.1.2.11073.

[3] S. Jakobtorweihen, J. Heuer, T. Waluga, *J. Chromatogr. A*. **2020**, *1620*, 460940. DOI: 10.1016/j.chroma.2020.460940.

Aspects of Gas Storage: Effect of Confinement on supercritical Isotherms

*Simon Eder, Matthias Thommes**
Institute of Separation Science and Technology
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During the last decades, major progress was made concerning the understanding of subcritical, low pressure adsorption of fluids like nitrogen and argon at their boiling temperature in nanoporous materials. It was here possible to understand how structural properties affect the shape of the adsorption isotherms, leading to new methods that are now commonly used for characterization.

However, within the context of gas storage applications, supercritical high pressure gas adsorption is important. High-pressure adsorption experiments introduce several complexities, both in terms of collecting isotherm data and interpreting the results. A key feature is here that the experimentally determined surface excess adsorption isotherm may exhibits a characteristic maximum at certain pressure. For a given temperature and adsorptive/adsorbent system, the surface excess maximum (and the corresponding (absolute) adsorbed amount) is related to the storage capacity of the adsorbent. However, there is still a lack of understanding how key textural properties such as surface area, pore size, pore volume and pore network characteristics affect the shape of supercritical high pressure adsorption isotherms and here in particular the position of the surface excess maximum.

In order to address this open questions we have a performed a systematic experimental study assessing the effect of pore size/structure on the supercritical adsorption isotherms of pure fluids such as C2H2, CO2 and H2 over a wide range of temperatures and pressures (from well above the bulk critical point to the near-critical region) on a series of model materials exhibit well defined pore sizes, i.e. ordered micro- and mesoporous materials such as zeolites, mesoporous molecular sieves (e.g., KIT-6, MCM-41 silica) and a hierarchically structured mesoporous NaY-zeolite. One key result of our experiments is that we find a clear correlation between the pressure of the surface excess maximum (at a given temperature) and pore size. This was further investigated by performing complimentary molecular simulation studies. Our results allow one to explore in detail important structure-property relationships and allowed us to derive a tool for predicting gas storage properties of nanoporous materials at given thermodynamic conditions based on their textural properties. Within this context we have recently also expanded our studies to MOFs and ZIFs.

Session II – Gas Phase Adsorption

Two-stage of VPSA Process for Capturing CO2 from Flue Gases Using Metal-organic Framework **Al-Awaad Haidar**	15^{30} – 16^{00}
Adsorption of heterocycles on silica alumina gels **Gehrke Laura**	16^{00} – 16^{30}
Evaluation of MOF coatings for water adsorption properties **Lairana Lima Duarte**	16^{30} – 17^{00}
Break	
Bus to laboratory	17^{30}
Laboratory Tour at TVT, FAU Erlangen-Nürnberg	17^{45} – 18^{45}
Bus to restaurant	18^{45}
Dinner	19^{00}

Investigation of catalytic COS formation on oxidic adsorbents

S. Pfeifer[1], C. Pasel[1], C. Bläkerl[1], T. Eckardt[2], D. Bathen[1,3]
[1]University of Duisburg-Essen, Chair of Thermal Process Engineering,
Duisburg/Germany
[2]BASF Catalysts Germany GmbH, Nienburg/Germany
[3]Institute of Energy & Environmental Engineering (IUTA),
Duisburg/Germany

The main component of natural gas is methane. Besides that, trace amounts of sulfur-containing components, carbon dioxide and higher hydrocarbons can be also included. The raw gas must be purified to fulfill pipeline standards and high purity specifications of the final product, such as Liquefied Natural Gas (LNG). An industrially common method for this purpose is the fixed-bed adsorption technology using cyclic temperature swing adsorption processes (TSA). In these processes toxic and corrosive sulfur components such as H2S, COS, CH3SH and C2H5SH can be removed. Due to the good regenerability, oxidic adsorbents are used. During the desorption phase of the fixed-bed, COS-formation may occur due to a catalytic reaction of H2S and CO2. After desorption, the treated purge-gas is recombined with the raw gas and returned to the process. However, no reduction of the COS-concentration is achieved by the treatment, so that the COS undesirably enters the product gas stream as a polluting component. For the design and optimization of such processes a deep knowledge of the adsorption behavior of the components to be separated and the COS formation is required. Furthermore, the adsorption properties of the adsorbents used must be well known. The aim of this research project is to systematically investigate the adsorption and desorption behavior and the catalytic activity of commercial and newly developed adsorbents.

For this purpose, experiments are performed in a fixed-bed adsorption unit with process temperatures between 25 °C and 200 °C. By using mass balances, the equilibrium loads are determined from the measured outlet concentrations. A comparison of the adsorption behavior of the respective components and the total amount of COS formed allows conclusions to be drawn both about the adsorption mechanisms occurring and about the selectivity and catalytic activity of the adsorbent. In the presentation first results of the COS-formation will be presented and discussed.

Two-stage of VPSA Process for Capturing CO_2 from Flue Gases Using Metal-organic Framework

Haidar AL-AWAAD[1], Guy DE WEIRELD[1]
[1] *Thermodynamics & Mathematical Physics Unit, Faculty of Engineering,*
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The anthropogenic emissions of greenhouse gases to the earth's atmosphere have been recognized as responsible sources of global warming. Roughly, over 60 % of global warming impacts are relevant to the emissions of carbon dioxide into the atmosphere [1]. In this study, an adsorption process is proposed whereas the vacuum pressure swing adsorption (VPSA) process is implemented for the reduction of CO_2 emissions from both power plants and energy-intensive industries. The VPSA technology seems to be an effective method for separating CO_2 from flue gases with less energy consumption. Al-MOF MIL-160 [$Al(OH)(O_2C-C_4H_2O-CO_2)$] is selected as an adsorbent because it exhibited: water stability, ultra-microporosity, potential interacting sites, and good selectivity to capture CO_2 from post-combustion conditions [2]. Hence, a two-stage (first one to increase the concentration, the second one for purification) VPSA process composed of two columns in each stage was designed. A six-step Skarstrom cycle including pressure equalization steps in each stage was employed, and the impacts of various operation parameters were studied. The overall process performance of the two-stage VPSA process resulted in a CO_2 purity of 95.01% and a CO_2 recovery of 90.04% with CO_2 productivity of 0.1165 gCO_2/gads.h. The total energy consumptions were 937.95 kJ/kgCO_2. Therefore, the targets of 95% CO_2 purity, and 90% CO_2 recovery are met in accordance with the requirements of the U.S. Department of Energy (DOE).

References:

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Adsorption of heterocycles on silica-alumina gels

<u>L. Gehrke</u>[1], C. Bläker[1], C. Pasel[1], D. Bathen[1,2]
[1]University of Duisburg-Essen, Duisburg/ Germany
[2]Institute of Energy and Environmental Technology e. V. (IUTA), Duisburg/ Germany

As the adsorption of heterocycles has been studied insufficiently up to now, five-atom molecular rings where one carbon atom is either replaced by nitrogen, oxygen or sulfur are used in this study. While cyclopentane forms dispersion and induction interactions, depending on the heteroatom, additional types of interactions can occur and thus influence adsorption. Using a sensor gas calorimeter, the adsorption on two silica-alumina-gels is investigated by simultaneously measuring adsorption isotherms and heats of adsorption.

The slope and curvature of adsorption isotherms provide qualitative information about the strength of interactions. Additionally, the energy levels in the load-dependent heat of adsorption allow a quantitative energetic characterization of different adsorption sites. By comparing adsorption isotherms and load-dependent heats of adsorption, the influence of the heteroatoms on the nature and strength of the interactions can be determined. Based on the results and the properties of adsorbents and adsorptives, individual adsorption sites may be identified and assigned to certain interactions.

References

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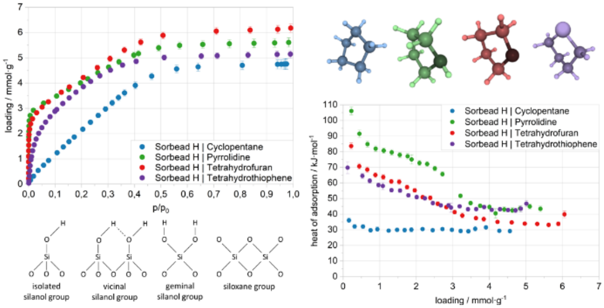
Graphical Abstract



Evaluation of MOF coatings for water adsorption processes

Lairana Lima Duarte[1], Elke Schade[1], Steffen Hausdorf[2], Jens Friedrich[1],
Stefan Kaskel[1,2]
[1]Fraunhofer IWS, Dresden, Germany
[2]Dresden University of Technology, Dresden, Germany

Humidity control is essential for many applications, e.g., storing and fabricating moisture-sensitive products, adjusting buildings' indoor atmosphere, and even inside a car. Maintaining adequate humidity levels protects electronic components, avoids rusting, prevents respiratory issues, and suppresses mold proliferation. Moreover, high relative humidity inside a car causes fogging, blocking the driver's vision. Thus, indoor humidity control is a matter of maintenance, health, and safety.

Considering the recent and forecasted rise in the electric vehicles market, technologies dedicated to improving battery usage are welcomed. In comparison to condensation, which is the most widely used method to control moisture levels, water adsorption systems have the potential to reduce energy consumption. The adsorbent passively adsorbs water, removing it from the ambient air. The cyclic operation of an adsorbent-based system requires desorption, which can be done with a minor energetic input. Metal-organic frameworks that are hydrolytically stable, present high uptakes at moderate relative pressures, require low temperatures for regeneration, and can be produced in large quantities by green synthesis using inexpensive linkers are strong candidates for such an application.

This work evaluates the influence of different binders on Al-Fumarate and MIL-100(Fe) coatings, using aluminum as a substrate, according to their mechanical, chemical, and physical properties. The samples were characterized by tape test, drop test, N2 isotherms at 77 K, thermogravimetric analysis, infrared spectroscopy, and scanning electron microscopy (SEM). Moreover, their water adsorption properties were accessed by water isotherms at 298 K, breakthrough experiments, and stability over cycles. Surface pre-treatment and binder concentration showed a strong influence on coating adhesion. Samples' exposure to saturated water vapor atmosphere affected the coating quality. Two mechanically resistant formulations were identified for both MOFs, with a reduction in BET surface area of 18.5% and 59.8%.

DAY 2

Friday, September 30th

Session III – Gas Phase Adsorption

Separation of n-butane and 1-butene mixtures on ZIF-8 and silicalite-1 **Roßmann Philip**	$9^{00} – 9^{30}$
Physisorption Studies of hydrothermally tuned-mesoporous silica monoliths **Ali Usman**	$9^{30} - 10^{00}$

Break

Separation of *n*-butane and 1-butene mixtures on ZIF-8 and silicalite-1

Philip Kazys Roßmann and Martin Hartmann, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen Center for Interface Research and Catalysis (ECRC)

Separation processes in the industry consume approximately 10 % of the globally produced energy. About 80 % of all separation processes are thermal separations [1]. Porous materials, viz. zeolites and zeolite-imidazolate frameworks (ZIFs) are potential candidates for an alternative separation process. Therefore, we expanded the olefin- paraffin separation from light olefins [2,3] to C4 hydrocarbons, namely *n*-butane and 1- butene using ZIF-8 and silicalite-1. In this work, a steam-assisted method for synthesizing ZIF-8, with high specific surface BET area is described. In breakthrough experiments both materials reveal a rare paraffin-selective adsorption behavior.

Synthesis and Characterization

ZIF-8 was synthesized by a steam-assisted method. The metal precursor zinc oxid nanoparticles (0.200 g, 2.44 mmol) and the ligand 2-methylimidazole (0.611 g, 7.37 mmol) were placed and mixed in a 10 mL Teflon crucible. Deionized water (2.0 mL) was added at the bottom of the Teflon liner of a 45 mL Parr autoclave; this way the crucible was not in contact with water. The crystallization was carried out for 24 h at 120 °C. The obtained solid recovered by centrifugation yielded 0.52 g powder. Silicalite-1 nano particles were synthesized following the procedures Song et al. [4], with a molar ratio of 25 Si : 9 TPAOH : 0.16 NaOH : 495 H2O. The powder XRD pattern reveal pure phases. The specific BET surface area - determined by N2 sorption - amounts to 1800 m2/g for ZIF-8 and 163 m2/g for silicalite-1.

One component adsorption isotherms

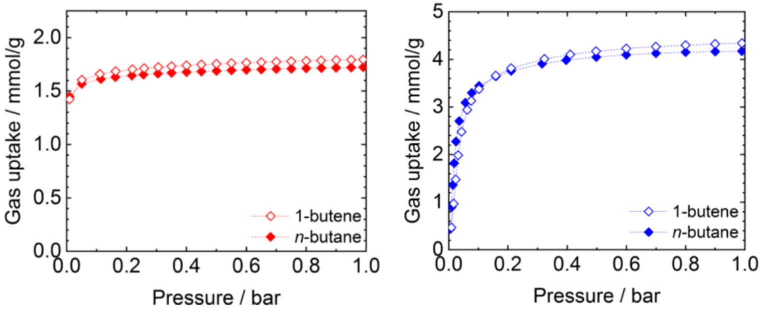


Figure 1: Single component adsorption isotherms of n-butane and 1-butene on ZIF-8 (left) and Silicalite-1 (right)

Fig 1. shows the *n*-butane and 1-butene adsorption isotherms of ZIF-8 and silicalite-1 at a pressure of 0.1 MPa and a temperature of 30 °C. ZIF-8 shows to a loading of 15 molecules *n*-butane and 16 molecules 1-butene per unit cell. For silicalite-1, the loading is 9.8 and 10 molecules per unit cell for *n*-butane and 1-butene, respectively.

Breakthrough experiments

In the next step, the adsorbent powders were shaped with methyl cellulose as binder [5]. For the breakthrough experiments, the extrudates were place into a column (V = 0.33 cm3) and studied at a total pressure of 1013 hPa and a temperature of 30 °C. Figure 2 displays the breakthrough curve of ZIF-8 and silicalite-1. For both adsorbents, 1-butene breaks through first and is displaced by *n*-butane resulting in a roll-up. The loading of *n*-butane is higher than the 1-butene loading. The boiling point of 1-butene (-6.2 °C) is lower than of *n*-butane (-0.5 °C); because of the lack of any specific adsorbate/adsorbent interactions between the olefin and the porous material, *n*-butane is preferably retained by the non-polar framework.

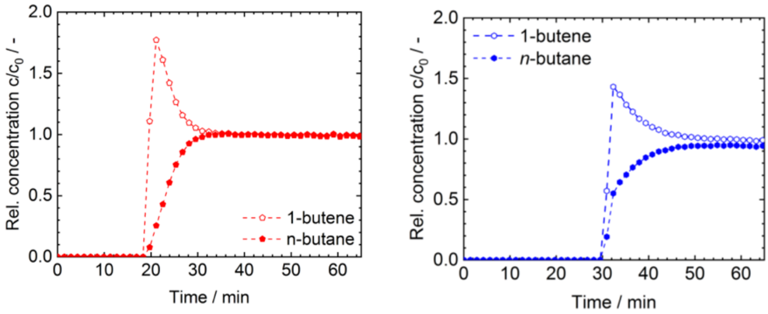


Figure 2: Breakthrough curve of an equimolar n-butane /1-butene mixture on ZIF-8 (left) and silicalite-1 (right). Measurement parameters: mZIF-8 = 0.2 g, V = 1.2 cmN3/min, T = 20 °C

Literature

[1] B. R. Pimentel, A. Parulkar, E.-K. Zhou, N. A. Brunelli, and R. P. Lively, ChemSusChem, vol. 7, no. 12, Art. no. 12, 2014.

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Physisorption studies about tuning of mesoporosity in silica monoliths controlled by hydrothermal treatment

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Hierarchical silica monoliths with macro-mesopores have high potential as support for catalysis and adsorbents with fine efficiency and productivity for a number of applications. In this study, we performed detail physisorption studies of mesoporosity in silica monoliths treated at various hydrothermal temperatures. Basic aim of this study was to investigate the possibility of controlled tuning of mesoporosity and understanding the connectivity of mesopores in silica monoliths by using series of hydrothermal treatments. We systematically increased the temperature from 80°C to 95°C by varying 3°C and 95°C to 110°C by varying 5°C. Comparative studies by two different adsorbents (Ar87K and N277K) confirmed the pore blocking at lower hydrothermal temperature and open mesoporous system at higher temperature with increase in mesopore size. Adsorption and desorption hysteresis scans further explored the type of connectivity in mesoporous silica monoliths that somehow reflects the data from BET pore size distribution of different adsorbents. This study successfully concluded that the lower hydrothermal temperature leads to pore blocking in mesopores space, but there is no cavitation found in silica monoliths and higher hydrothermal temperature leads towards open mesopores space, but overall pore volume remains same. A systematic increase in pore size distribution with orderly increase of temperature confirmed the controlled tuning of mesopore space over wide range of hydrothermal temperatures. By every 3°C increase in temperature leads to an increase of by 1 nm in average pore size distribution till 95°C. The higher temperature from 95°C to 110°C leads to open mesoporous system with a lower surface area.

Session IV – Novel Adsorbents and their Characterization

Enhanced thermal activation of peroxymonosulfate by activated carbon for efficient removal of perfluorooctanoic acid. **Liu Guanhong**	10^{30} – 11^{00}
Network analysis of disordered, mesoporous materials using physisorption hysteresis **Söllner Jakob**	11^{00} – 11^{30}
Application of N2 physisorption at cryogenic temperatures in current materials science research projects **Guggenberger Patrick**	11^{30} – 12^{00}
Fabrication of chitosan-based carbons for the eco-efficient removal of emerging contaminants from the wastewater **Dr. Raval Niravkumar**	12^{00} – 12^{30}

Lunch Break

Direct and efficient reduction of perfluorooctanoic acid using bimetallic catalyst supported on carbon

Guanhong Liu[a,b], Meiyun Feng[a], Muhammad Tayyab[c], Jianqiu Gong[c],
Mingyang Yang[d], Kuangfei Lin[a]*
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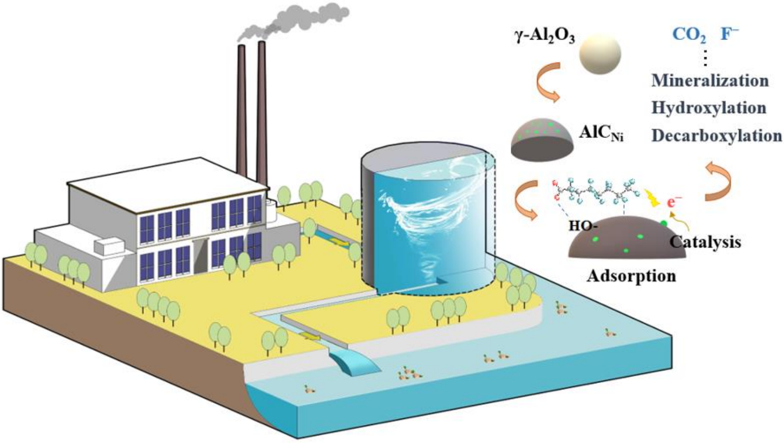
[b]Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR-UMR 6226, F-35000, Rennes, France.
[c]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, China
[d]School of Architecture and the Built Environment, Delft University of Technology, Delft, The Netherlands

A variety of metal elements have exhibited strong reductive and dehalogenative capabilities for the removal of persistent organic pollutants, owing to electron transfer or electron-hole activation through various methods. Herein, a bimetallic C_{Ni}-Al_2O_3 structure (AlC_{Ni}) was successfully synthesized to simultaneously function as sorbent and catalyst in the reduction of perfluoroalkyl carboxylic acids (PFOA) polluted wastewater. The physicochemical properties of AlC_{Ni} was comprehensively characterized by TEM, SEM, Raman, FTIR, XPS, and BET. Then, in the batch experiment, using a reaction period of 3h, 98 % of PFOA was removed by AlC_{Ni} through a mechanochemical stirring method and 70.43 % of fluorine ions was released from PFOA anchored onto the surface of AlC_{Ni}. Both thermocatalysis and photocatalysis technologies were incorporated and compared when utilized in tandem with AlC_{Ni} to mitigate the PFOA. In addition, peroxymonosulfate (PMS) and sodium sulfite (Na_2SO_3) were also integrated into experiments, separately, as a strong oxidant and reductant to improve the degradation effect of PFOA. However, the degradation efficiency of both were lower than that of AlC_{Ni}, even when assisted by elevated temperatures and ultraviolet irradiation. The feasibility of employing AlC_{Ni} for PFOA degradation was further investigated at various temperature and pH conditions. The data obtained from HPLC-MS/MS, TOC, and IC with multiple characterizations of AlC_{Ni}/PFOA, proposed the predominant degradation pathways comprising adsorption, defluorination-hydroxylation, and decarboxylation. This study provides a valuable remediation method without utilizing chemical agents and special activation for PFOA by AlC_{Ni}, which can be suitable for large-scale sewage treatment applications.

Key words: Perfluorooctanoic acid; Bimetallic catalyst; Electron transfer; Mechanical reduction



Network analysis of disordered, mesoporous materials using physisorption hysteresis

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Physisorption characterization of porous materials is a widespread tool to obtain textural parameters like surface area, pore size and volume, which can be used to understand the performance of materials in their application. Network properties of porous materials are rarely investigated, even though highly influencing their behaviour. In this work, we develop and apply a network model based on site percolation to adsorption – desorption hysteresis and corresponding desorption scanning curves. The intrinsic thermodynamic part of the hysteresis is accounted for by using dedicated NLDFT kernels. We therefore were able to obtain statistical network parameters yielding information about connectivity and access to macroporosity for vycor glas, controlled pore glass as well as sintered particles. This model provides a statistical framework for desorption percolation which is meant to be included into more extensive work following.

Application of N_2 physisorption at cryogenic temperatures in current materials science research projects

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Gas adsorption is a powerful technique which allows determining a variety of material properties like pore volume, pore size (distribution), pore shape, pore connectivity, and surface area. Therefore, three current research projects will be presented which have recently been published by our group. In all of them, nitrogen physisorption performed at 77K played a major role in ascertaining and comparing the textural properties of the prepared novel mesoporous materials and allowed to verify the success of synthetic steps e.g. the removal of templates and the accessibility of pores after materials functionalization. Firstly, a project covering the synthesis of hollow mesoporous silica particles (HMSP) with catalytically active amino groups on the internal shell wall and its application as a size-exclusive catalyst will be presented.[1] In the second project, targeting the removal of organic dies in wastewater, the adsorption performance and capacity of a covalent organic framework (COF) were boosted by precisely controlling the thickness of COF deposit layers on graphene oxide substrate, allowing a fast diffusion of dye molecules through the macropores and avoided the typical issue of micropore blocking.[2] Finally, a project focusing on the synthesis and characterization of hyper-cross-linked polymers (HCPs), which were made from the self-condensation of benzyl methyl ethers with p-toluenesulfonic (*p*-TSA) acid as a reusable polymerization catalyst, will be presented.[3]

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Fabrication of chitosan-based carbons for the eco-efficient removal of emerging contaminants from the wastewater

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As the contaminants of emerging concern (CECs) are usually present at ppb/ppt level in water bodies, it's always been difficult for the wastewater treatment plants to completely decontaminate the water from such micropollutants that may further pave the way to design new adsorbents for easy application at the treatment plants. Hence, this study focuses on the fabrication of spherical shaped carbons from chitosan (C-CS), CS impregnated graphene oxide (C-CSG) and CSG-doped Fe_3O_4 nanoparticles (C-CSGF) by chemical (2.5 M NaOH for 2 h) and physical (pyrolyzed at 800 °C for 1 h) activation to produce a highly porous adsorbent materials suitable for the efficient removal of CECs. The carbon beads were characterized (with BET, SEM and TEM) and utilized for the removal of multiple CECs (i.e., Bisphenol A (BPA), Carbofuran (CBF), Carbamazepine (CBZ), Diclofenac (DCF), Dimethoate (DMA) and Imidacloprid (ICP)). Characterization results showed that the obtained surface area was 776, 540 and 372 $m^2 g^{-1}$ for C-CS, C-CSG and C-CSGF beads, respectively and all the carbon bead samples presented a multi-scale porosity. C-CSGF beads provided the best adsorption capacities for all the ECs removal ($\geq 60\%$) at pH 7.0 within 240 min contact time. The study indicates the development of an effective material that can be implemented to prepare new adsorbents using CS at a large-scale for ECs polluted wastewater treatment. Further research is required to study the degradation of ECs affecting public health with metal-doped carbons (i.e., C-CSGF), which has potential to break down the targeted analytes.

Keywords: Chitosan, Graphene oxide, Magnetic nanoparticles, Emerging contaminants, adsorption-degradation.

Session V – Liquid Phase Adsorption and Chromatography

Determination of adsorption isotherms in self-packed columns using the extended Elution by Characteristic Point method 13^{30} – 14^{00}
Heiduk Caroline

Determination of adsorption isotherm parameters using frontal analysis 14^{00} – 14^{30}
Zarai Somayeh

Adsorption and nanoporous materials characterization in the liquid phase: Novel methodologies based on NMR relaxometry 14^{30} – 15^{00}
Schlumberger Carola

Summary

Determination of adsorption isotherms in self-packed columns using the extended Elution by Characteristic Point method

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Zeolites can be produced in a wide variety. Especially their pore geometry can be adjusted in a defined range for a highly selective adsorption of molecules depending on the molecule size and flexibility. Knowledge of the isotherms is important in selecting a suitable adsorbent and for the subsequent process design. Since sugars differ significantly in price and availability, all methods for determining these isotherms have specific advantages and disadvantages.

Static batch experiments are state of the art for low-cost sugars. However, the calculation of the loading requires the difference between two concentrations determined by HPLC, which is subject to uncertainties. Even with small relative errors, this causes a large scatter in the determined loading. Furthermore, the real loading must be calculated by considering the solvent adsorption which leads to further uncertainty.

For very expensive adsorptives, the dynamic Elution by Characteristic Point (ECP) method is recommended, as it theoretically provides complete isotherms with a single measurement. However, this method is based on the ideal chromatography model and therefore, requires a high number of theoretical plates $N_t \geq 2000$ [1]. This is not always achievable, especially for adsorbents that were not developed for chromatographic purposes. A solution was found to overcome this problem by the application of the ECP method with self-packed columns [2]. However, a remaining challenge is suitably packing of the zeolites in the column. An uneven packing with occurring short-circuit flows and dead zones cause measurement errors.

Therefore, isotherms for the adsorption of saccharides on zeolite HBEA150 extrudates from water are currently determined by ECP and compared with results from batch experiments. The limitations of the extended ECP method are being investigated with regard to reproducibility at different volume flows and column geometries.

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Determination of adsorption isotherm parameters using frontal analysis

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Preparative chromatography plays a crucial role as a separation process for the purification of valuable compounds. In order to design and optimize the chromatographic separation processes, the knowledge of the adsorption isotherms is essential. The isotherms can be determined using various experimental techniques. In general, the isotherm parameters are experimentally determined in a single component system, and the adsorption behaviors in multi-component system are estimated by applying extended multi-component isotherm models. Therefore, it is recommended to measure a few competitive equilibrium data to check the accuracy of the competitive models. Frontal analysis (FA), which is one of the frequently applied methods for measuring adsorption equilibria, is applicable to measure adsorption isotherms of single-component to competitive multi-component systems [1].

In this work, the adsorption behaviours of two different component systems, cycloketones and methoxybenzenes, have been investigated using FA. The isotherm model parameters measured in single-component systems were applied to describe the competitive adsorption behaviors of ternary mixtures.

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Adsorption and nanoporous materials characterization in the liquid phase: Novel methodologies based on NMR relaxometry

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In the past, major progress concerning the textural characterization of porous materials in the gas/dry state has been made [1]. The main drawback of these methods stems from their inability to test wet materials (i.e., in presence of the liquid/mobile phase), thus providing no direct information concerning the state of the nanoporous materials immersed in a liquid phase. This is particularly important for functionalised nanoporous materials, where the interaction of surface functional groups with the chosen liquid may affect the effective surface area and pore characteristics for separation processes. Hence, for the optimization of processes in the liquid phase (e.g., liquid chromatography) characterization only based on gas adsorption and liquid intrusion techniques (e.g., mercury porosimetry) is not sufficient. However, far fewer advances have been made in assessing textural properties in the liquid phase.

One of the important challenges is a reliable and fast assessment of surface area. For this, the application of NMR relaxation measurements has recently received a lot of attention [2-5]. This method is based on the fact that the relaxation signal of a liquid in contact with a surface behaves differently from that of the bulk phase (or “free” liquid). Hence, a material with a high surface area in suspension has a shorter relaxation time, as more fluid is bound to the surface. Despite the fact that the application of NMR relaxometry for textural characterization of various material types (including silicas, titania, carbons and even metal-organic framework materials (MOFs)) has been reported in the literature, a rigorous and systematic validation of the method utilizing materials with true surface area benchmark data has not yet been reported.

In this work, the surface area of nonporous and mesoporous silica model adsorbent materials as well as nanoporous carbon blacks immersed in a liquid phase is investigated by methodologies based on NMR relaxometry and compared with benchmark adsorption data by applying procedures based on argon (87 K) adsorption. We further investigate the effect of confinement and pore network characteristics on NMR relaxation and consequently on a reliable assessment of surface area, but also explore the potential of NMR relaxation for pore size analysis.

Our results strongly indicate the huge potential of NMR relaxometry for advancing textural characterization in the liquid phase. Further development of this technique will in combination with other techniques such as inverse size exclusion chromatography (ISEC), conductivity measurements, electroacoustics [6] contribute to the development of a novel experimental tool box for textural characterization in the liquid phase.

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