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Separations Engineering: Advances in Adsorption

By Gennady Gor and Benoit Coasne

This themed issue of *Current Opinion in Chemical Engineering* is dedicated to recent advances in adsorption – especially in the context of fields relevant to chemical engineering. On this occasion, a series of 10 outstanding contributions, written by experts from both the academic and industrial worlds, have been gathered around key questions connected to adsorption phenomena in membrane and separation sciences, electrochemistry and energy conversion/storage, poromechanics and civil engineering, etc. All these contributions are short and focused mini-reviews – typically, about 2500 words – on the latest experimental and/or theoretical developments in emerging adsorption topics. About half of these mini-reviews deal with current advances in adsorption in chemical engineering fields: *Adsorption in Membrane Science, Coupling adsorption/mechanics; Adsorption and coadsorption processes at the industrial scale; Adsorption effects in electrochemistry; Adsorption-driven heat pumps/chillers*. The other half of these mini-reviews focus on advanced techniques to probe adsorption: *Spectroscopic tools for adsorption; Imaging techniques to probe adsorption; Probing adsorption using Nuclear Magnetic Resonance; Kinetic approaches for molecular modeling of adsorption; Free energy techniques for simulation of adsorption*. Each of these contributions focuses on some of the most important recently published work and emphasizes the significance of these advancements towards the overall progress of the field. The authors were also asked to focus on a few key advances based on the recent literature (within the past 2 to 5 years) rather than survey an entire field and to provide their critical assessment of these developments and future prospects. An additional key feature of the *Current Opinion journals* is to provide an annotation for each of the most interesting articles within the bibliography of the reviews.

Adsorption is a process of adhesion of atoms, molecules or ions in either gas or liquid phase, at the surface of solids or liquids. Most of the papers in this issue focus on physisorption, i.e. the process in which the adsorbed species do not form chemical bonds with the surface but only bind through physical forces (dispersion, electrostatic, etc.). Also the papers focus on adsorption on solid surfaces, and do not discuss adsorption on liquid phases. This however does not mean that chemisorption or adsorption on liquid surface is of lesser interest. The research of various aspects of adsorption is very broad, and this issue could have covered many more topics. We decided to limit them to those which have not been covered in recent review papers. There is a number of fields relevant to chemical engineering in which adsorption has recently emerged as a key ingredient. While in some applications adsorption effects have been recognized for a long time as important, there are over domains where they have been overlooked or only considered in a very effective fashion. This includes applications belonging to membrane science, poromechanics i.e. the field of mechanics of porous media which accounts for the coupling with the thermodynamics of confined fluids, gas or liquid adsorption in soft matter physics, phase transformation such as for heat pumps and chillers, etc. In fact, developments in these fields have often been done without specifically accounting for adsorption effects until recently. The present themed issue on *Advances in Adsorption* from *Current Opinion in Chemical Engineering* intends to highlight these recent developments. This is a timely issue as these efforts have been quite impressive in the last 10-20 years with significant breakthroughs reported – with or without direct technological transfer already made.

As indicated above, the mini-reviews in this themed issue subdivides into (1) five contributions focusing on advanced techniques to probe adsorption and (2) five contributions dealing with current advances in adsorption relevant to chemical engineering fields. In the two following paragraphs, we list and comment each of these mini-reviews.

Advanced techniques to probe adsorption • The paper by Ustinov presents an overview of the recent advances in development of kinetic Monte Carlo (kMC) method for application to modeling equilibrium phenomena [1]. As it is obvious from the name, the kMC method has been used for a number of years for modeling kinetics. However, in the recent years, it was shown to be a viable alternative to conventional (Metropolis) Monte Carlo to predict thermodynamic equilibrium, in particular adsorption equilibrium. This review outlines the main features of the method, and shows examples of application of this method for gas adsorption on solid surfaces. Importantly, the kMC method provides a straightforward way to calculate the Gibbs free energy, while performing simulations in the canonical ensemble • Another review focusing on free energy calculations – in the specific context of the flexibility of compliant MOF materials – is the work by Tanaka and Miyahara [2]. Such

advanced techniques, which are being more and more frequently used in modern research, allow going much beyond standard Monte Carlo and molecular dynamics simulations. This review shows how, under given thermodynamic conditions, the stability and the molecular mechanism responsible for MOF flexibility can be assessed using different thermodynamic integration schemes (using either the adsorption isotherm or the hydrostatic pressure as data to be integrated). Beyond the fundamental insights gained into the different flexibility modes of this class of porous materials, such advanced molecular simulation techniques are receiving increased attention to screen and predict *in silico* different materials for gas storage and separation applications.

- The review by Pini and Joss [3] discusses how imaging techniques applied to adsorption in microporous materials provide a mean to “*see the unseen*”. Recent progress made and on-going developments in this field aim at designing *in situ* techniques that probe transient and localized phenomena involved in porous adsorbents and catalysts. The review shows that, owing to the range of techniques available, involving microscopy, spectroscopy and tomography-based apparatuses, the rich and complex phenomena spanning several time and length scales can be monitored to gain insights into the adsorption but also the kinetics at play. With this respect, a strength of these methods, which can be applied to almost any system under static or kinetic conditions, is that they allow closing the gap by probing adsorption systems from the nanometer to the macroscopic scales.
- The review by the Allgeier’s group to some extent continues the possibilities to “*see the unseen*”, discussing the application of nuclear-magnetic resonance (NMR) relaxometry for probing the porous media [4]. Starting from the physics of NMR, the paper describes how the measured relaxation times of nuclear spins can be related to the surface chemistry and porosity. This relation makes NMR relaxometry a promising tool for characterization of range of various geological porous media (such as shales), as well as materials used in catalysis and gas separations.
- Tsyganenko et al discuss the process of controlled and selective desorption of molecules using resonance infrared laser [5]. The idea is based on direct excitation of vibrational states of adsorbed species. In this process only those adsorbed molecules whose vibrational frequency equals to the exciting radiation will be activated and desorbed from the surface. The review discusses the basic studies of these processes, highlighting potential applications for isotope separations, which have not been succeeded yet.

Current advances in adsorption relevant to chemical engineering fields

- Two reviews discuss the phenomena related to the coupling between adsorption and mechanics, approaching that from totally different perspectives, and discussing literature in different fields. The paper of Vandamme introduces the phenomenon of adsorption-induced deformation – appearance of stresses and strains due to adsorption of fluids in porous materials [6]. It proceeds with discussion of various theoretical approaches to predict those effects. Then the reciprocal effects are discussed: when materials are compliant, how this compliancy affects their adsorption properties. The review concludes with the discussion of specific challenges in theories of mechanics of adsorption: effects of pore morphology, pore-size distribution, anisotropy and non-linear responses.
- While also discussing the mechanics-adsorption coupling, the review by Weismüller [7] focuses mainly on electrosorption phenomenon. In this case instead of a gas or a liquid, described by its chemical potential, the adsorbing species is an electrolyte, described by the electric potential. The paper starts from the fundamental thermodynamic relations of the surface mechanics of electrodes, and proceeds to the overview of recent experimental measurements of electro-chemo-mechanical coupling, relating them to the calculations based on the density functional theory. The review also demonstrates the similarity between the mechanical effects of electrosorption and adsorption.
- The review by Julbe and coworkers focuses on the role of adsorption phenomena and surface reactions in the efficiency and control of membrane-based processes [8]. Such adsorption effects in this context are discussed by considering both gas-phase and liquid-phase separations for membranes ranging from inorganic to composite (i.e. organic/inorganic) membranes. In addition to reviewing the importance of adsorption for the design of separation processes using membranes, their contribution discusses other adsorption-related issues to be further explored: fouling phenomena, novel surface treatments and the possibility to use adsorption as a tool to characterize the microstructure of membranes and its evolution when used in real process conditions.
- The review by Pullumbi and coworkers deals with the important topic of gas separation using adsorption-based processes [9]. While these technologies are already in use for many processes such as purification, separation, etc., the authors have identified opportunities to further improve their efficiency and expand the scope of their applications. In particular, the role of numerical simulation aspects in boosting technological transfer towards the industrial world is highlighted. This includes research in the fields of multiscale modeling and simulation tools, process design and complex optimization, synthesis scale up/processing together with materials characterization

but also knowledge discovery in already existing databases • The review by Hastürk et al. focuses on the design of optimal adsorbents for adsorption heat transformation applications – either for cooling or heating processes. This important field of research keeps receiving very broad attention as it is a very promising environmentally friendly application [10]. In this contribution, after presenting the fundamentals of the thermodynamics of adsorption heat transformation, the authors adopt a material scientist point of view by considering different types of adsorbents. This includes samples as different as activated carbons, silica gels, zeolites and metal organic frameworks. Promising materials such as composite materials made of zeolites or silica gel with salts like LiCl or CaCl₂ are also envisaged owing to their large uptakes and transformation enthalpies.