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Chemical engineering and environmental challenges. Cyclic adsorption/reaction technologies: Materials and process together!

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Abstract

I start with a brief survey of paradigms in Chemical Engineering to highlight that in the early 70s my thesis advisor P. Le Goff already mentioned the strong link of chemical processes with Environment, Energy and Economy (Market). Then I move to my vision of ChE today summarized in ChE = M2P2E (Molecular, Materials, Process and Product Engineering). I describe how I built a research lab centered around Cyclic Adsorption/Reaction Processes focusing in adsorption technologies to help solving environmental problems. I stress the basic concepts of adsorption processes and the need to use proper diffusion models for intraparticle mass transfer instead of pseudo first order or second order kinetic models. I also consider that adsorbent metrics should be linked to the process where the material is used: materials and processes together!

In the last section I review some challenging areas where adsorption technologies are useful. Carbon Capture and Utilization involving Pressure Swing Adsorption to capture CO2 from flue gas in a pilot plant, 3D printed composite monoliths for Electric Swing Adsorption, and Utilization of CO2 to be transformed in methanol or Synthetic Natural Gas (SNG) (Power-to-Gas concept). I also address the general topic "Processing of diluted aqueous solutions" with special attention for the development of Simulated Moving Bed coupled with Expanded Bed Adsorption. Finally the integrated process to produce high-added valued compounds (vanillin and syringaldehyde) from Kraft lignin is shown as an example of Lignin valorization in pulp mill biorefinery.

1. Chemical engineering: past, present and future

In the early 70s during my doctoral work in Nancy, my advisor Prof. P. Le Goff [1] described Chemical Engineering (ChE) as an ensemble of separation and reaction processes to transform raw materials into useful products (Fig. 1). At that time we were living with the Second Paradigm of ChE – the Engineering Science movement represented by the book of Bird, Stewart and Lightfoot, “Transport Phenomena” published in 1960 [2]. The First Paradigm was around the concept of Unit Operation, a term coined by Arthur D. Little in 1915 [3]. It is interesting to note that in this “old” vision of ChE, Le Goff already emphasized the connections with Environment (waste generation and management), Energy and Market (Economy).

Later, in 1988, the Amundson report [4] although stressing the importance of core disciplines (Thermodynamics and kinetics, transport phenomena, reaction engineering, separation processes, process design and control, systems engineering) pointed out the relation of ChE with new frontier areas: Biotechnology and Biomedicine, Electronic, Photonic, and Recording Materials and Devices, Microstructured Materials, In-Situ Processing of Energy and Mineral Resources, Liquid Fuels for the Future, Responsible Management of Hazardous Substances, Surface and Interfacial Engineering Advanced Computational Methods and Process Control. A recent illustration of this last topic is the acquisition of PSE Ltd (a leading company on process modeling, simulation and optimization with the package gPROMS) by Siemens (a leading company in automation and control).

The Product Engineering perspective (Needs, Ideas, Selection of ideas, Manufacturing) already used in other Engineering areas and Management Schools [5] was pioneered in ChE by Cussler and Moggridge [6], Wesselingh [7] to name a few. Solke Bruin in his Inaugural lecture [8] at TU Eindhoven “Product-driven process engineering. The eternal triangle molecules, product, process” presented ChE as a lozenge with Transformations (reactions), Separations, Stabilizing and Structuring processes particularly relevant in the Food Engineering area. He also presented a “new” vision of ChE in the sense that chemical engineers need to address the whole chain - “To Make, To Service, To Care.”

My vision of ChE today is summarized in the formula ChE = M2P2E where “M” relates to Molecular and Materials Engineering and “P” relates to Process and Product Engineering (Fig. 2).
Molecular Engineering tools as Molecular Simulations will help more and more in the screening and design of adsorbents (MOFs, COFs, etc) for target processes and Computational Fluid Dynamics (CFD) will help in process design. Process Modeling and Simulation packages such as gPROMS are now used replacing homemade simulators and learning of numerical methods; this was predicted in the 90 s by the late Colin Mc Greavy (U. Leeds) when we were teaching a Chemical Reaction Engineering course at UFSC in Florianopolis.

2. Research in cyclic Adsorption/Reaction processes

2.1. Starting a research laboratory: MMM + K

When I started my lab at U. Porto in 1976 (now Laboratory of Separation and Reaction Engineering-LSRE) I had only one M (Man-humane resources) of the three MMM (Man, Money, Machines) needed according to old economists (Fig. 3).

However, I had some K (Knowledge) which helped me to start a research laboratory along with some principles:

i) If you don’t wish something, you will never get it,
ii) Keep eyes open to other areas (cross-fertilization),
iii) Accountability (publish research results),
iv) In research you can always do what you want; it can take longer because of lack of money, etc.
v) Researchers should leave their fingerprint in the lab,
v) Research can’t be done with absent people.

I started my lab with three PhD students, teaching assistants at the Department of ChE of U. Porto, working in topics involving Separation and Reaction Engineering related to Environment and Bioengineering.

i) removal of phenol from wastewater using polymeric adsorbent resins [10],
ii) denitrification of water in fluidized bed biological reactors [11],
iii) removal of heavy metals with complexing resins and adsorption/reaction processes [12].

I remember reading a comment by P. V. Danckwerts [13] on the use of chemical engineering principles. In his words: “I was reminded of this 15 or so years later when I sat in a committee concerned with sewage and water treatment. The suggestion that chemical engineering had some knowledge relevant to these processes, e.g., in the field of mass transfer, moved Civil engineers on the committee, who had always regarded the field as their own, to apoplexy”. I experienced the same reaction in a meeting in Porto...

2.2. Adsorption processes in fixed beds: the key results from De Vault equation

In many of these projects adsorption is the technology under study. I remember again P. Le Goff in his lectures saying:

"Any ChE problem including adsorption can be modeled by writing:

i) conservation equations (mass, energy, momentum balances),
ii) equilibrium law at the interface,
iii) kinetic laws of mass/heat transfer,
iv) boundary and initial conditions, and
v) optimization criterion.

I also tell my students that factors governing adsorption processes can be divided in first order factors (adsorption equilibrium isotherms) and second order factors (all leading to dispersive effects: kinetics of mass transfer, axial dispersion, etc.). The message is: equilibrium first and show a picture of I. Langmuir! (Fig. 4) [14].

I also say that to understand adsorption in fixed bed columns you must know De Vault equation developed in 1943 [15] from a “simplicissime” model based on equilibrium theory. Combining a mass balance in a bed volume element with the adsorption equilibrium isotherm \( \dot{q}_i = f(C_i) \) one can get:

\[
\dot{u}_C = \left( \frac{\partial f}{\partial C_i} \right) = \frac{u_i}{1 + \frac{1}{4} \left( \frac{C_i}{C_i} \right)}
\]

Don De Vault equation [1] shows that adsorption in fixed beds is a wave (concentration) propagation phenomenon; it also explains the effect of the nature of the adsorption equilibrium isotherm \( \dot{q}_i = f(C_i) \)
on the shape of the breakthrough curve. In the above equation \( u_i \) is the interstitial fluid velocity and \( \varepsilon \) is the bed porosity. De Vault equation says that the velocity of a concentration \( C_i \) depends on the slope of the adsorption equilibrium isotherm \( dq/dC_i \): if the isotherm is favorable the concentration front is compressive and will lead to a shock; if the isotherm is unfavorable it leads to a dispersive front (Fig. 5). To me this is the most important result to understand fixed bed adsorption: the concepts of compressive and dispersive waves as I learned from my thesis co-advisor Daniel Tondeur.

2.3. Adsorption equilibrium isotherms first!

So the first thing to do in adsorption process development is to measure adsorption equilibrium isotherms. For liquid/solid systems measurements are done by contacting different masses of adsorbent with a known volume of solution with initial concentration \( C_{i0} \). The average adsorbed concentration at any time is simply

\[
\langle q_i \rangle = \frac{V}{W} C_{i0} - \frac{V}{W} C_i(t)
\]

This is the operating line with slope \(-V/W\), which is simply the integrated mass balance and relates at any time the average adsorbed phase concentration and the fluid phase concentration. After sufficient time equilibrium is reached and a point of the adsorption equilibrium isotherm is obtained \((q_i, C_i)\). So with equilibrium and operating lines it is a simple exercise to understand the effect of initial concentration in liquid phase and the effect of adsorbent loading! Lots of experimental work and published papers could have been saved! Also the regeneration process can be easily understood with simple graphical schemes. (Fig. 6).

2.4. Kinetics of adsorption processes- it is time to use more realistic models and adsorbent metrics linked to processes!

Adsorption is a mass transfer operation between a fluid phase and a solid adsorbent phase. The driving force for the intraparticle mass transfer in the case of “homogeneous” adsorbents is \( q_i^* - \langle q_i \rangle \) where \( q_i^* \) is the adsorbent concentration at the interface in equilibrium with the fluid concentration at the interface \( C_i \).

The simplest kinetic law is the Linear Driving Force (LDF) model of Glueckauf [16]

\[
d\langle q_i \rangle/dt = k_b (q_i^* - \langle q_i \rangle)
\]

where \( k_b = 15D_b/\varepsilon_b^2 \). In a batch adsorption process \( q_i^* \) is changing with time unless the adsorbent particle is in an infinite bath. For porous adsorbent structures one can easily relate \( D_b \) with pore diffusion \( D_p \) at least for linear systems; for bidisperse adsorbent structures involving macropore diffusion and micropore (crystal) diffusion \( D_c \) adequate relations with \( D_h \) can be derived.

Other models are often used called pseudo-order models of first order, second order...It is time to describe adsorption using diffusion inside particles: LDF, Fick, Stefan-Maxwell! One of such pseudo-order models is Lagergreen model where the rate of adsorption is proportional to a distance to equilibrium \( q_i^* - \langle q_i \rangle \); I wrote a note on this “What’s wrong with Lagergreen pseudo first order model for adsorption kinetics? “[17].

Adsorption processes are Multi-scale problems both in space and
time ranging from nanometer scale (pore scale), micrometer scale (crystal), millimeter scale (adsorbent particle) up to the adsorption column scale (1-10 m) with time constants for convection, macropore diffusion, crystal diffusion, film mass transfer, etc. covering various orders of magnitude.

There is a growing interest in finding metrics for the screening of adsorbents. Everyone knows that a good adsorbent should have good adsorption capacity, fast adsorption kinetics, good selectivity, and good thermal, mechanical and chemical stability. However translating these properties in numbers is trickier. Metrics based on Working Capacity (WC), Adsorbent Figure of Merit (AFM), Capture Figure of Merit (CFM) etc. have been presented but in my opinion the metrics only make sense for a defined process in which the material will be used [18–20]. A good summary of adsorbent metrics can be found in reference [19]. The selectivity requirement for an adsorbent for Pressure Swing Adsorption (PSA) is not the same as that needed for use with Simulated Moving Bed (SMB) technology [21]. As Sircar said once “Each adsorbent must be “married” to a process that maximizes the potential” [22].

A comment on models should be made and as Einstein said: “Keep it simple but not simpler”. I have seen big failures in predictions of employment rates during the last financial crisis of 2008. Now we face tough times with COVID-19 staying at home and following the numbers of infected people in various countries. My colleague Manuel Alves prepared a plot in semi log scale of COVID-19 infections in India we were involved in the study of continuous electrocoagulation of fluoride containing wastewater [25]. This work was developed in parallel with EBA XPure) was developing a technology combining SMB and Expanded Bed Adsorption (EBA) [26,27]. One of the companies involved at that time XENDO (now BASF [24]). EBA is an interesting idea where the core-shell adsorbent particles expand nicely in a bed without the chaotic movement of particles thanks to properly designed particle size and density distribution allowing cell debris to pass through the bed whilst the solute (proteins) are retained by the adsorbent. In principle with EBA one doesn’t need previous solid/liquid separation; however some concerns remain with adsorbent capacity loss due to cell adhesion to the particle surface and dead volumes in the top of EBA columns are not good for SMB chromatographic separation [26,27].

Coming back to the modeling approach of adsorption processes I suggest:

- Start with simple models; obtain from such models information which remains valid for more complex models;
- The validity of a model is not just a result of a good fit; more important is the capability to predict the system behavior under conditions different from those used to get model parameters,
- Good results can only be obtained if the model well represents the reality and
- Use models to obtain useful design parameters and their dependence on operating conditions; use independent experiments if possible to get model parameters.

3. Some challenges: processing diluted aqueous solutions, carbon capture and utilization (CCU) and lignin valorization

There are societal challenges related to the need of clean air, water and soils and relevant topics as the processing of diluted aqueous solutions and valorization of biomass; in all these areas at some point adsorption technologies will be part of the solution.

3.1. Processing diluted aqueous solutions

Interestingly the first EU research project I got was on Environmental area “Purification of wastewaters by parametric pumping and ion exchange” [23]. Parametric pumping is a cyclic adsorption process involving two steps in a cycle: one step at lower temperature (say 20 °C) and other at higher temperature (say 60 °C) with flow reversal. So it is a temperature swing adsorption (TSA) with flow reversal. It can be useful in processing diluted aqueous solutions. We can recover a concentrated phenol solution in the top reservoir and a purified water in the bottom reservoir.

Processing of Diluted aqueous solutions is a topic relevant to industry and was addressed in the EU project PRODIAS coordinated by BASF [24]. One of the companies involved at that time XENDO (now XPure) were developing a technology combining SMB and Expanded Bed Adsorption (EBA) [25]. EBA is an interesting idea where the core-shell adsorbent particles expand nicely in a bed without the chaotic movement of particles thanks to properly designed particle size and density distribution allowing cell debris to pass through the bed whilst the solute (proteins) are retained by the adsorbent. In principle with EBA one doesn’t need previous solid/liquid separation; however some concerns remain with adsorbent capacity loss due to cell adhesion to the particle surface and dead volumes in the top of EBA columns are not good for SMB chromatographic separation [26,27].

The need for low-cost water treatment processes to remove fluoride, iron and arsenic is extremely important in some countries. In the framework of a project involved our lab, TU Munich and three Universities in India we were involved in the study of continuous electrocoagulation processes for fluoride removal [28,29].

3.2. Carbon capture and utilization

Some of these societal challenges are enormous as the Carbon Capture and Utilisation (CCU) to tackle Global Warming from Greenhouse Gases. I started my involvement with CO₂ capture in connection with the development of Sorption Enhanced Reaction Processes [30] to shift the equilibrium towards hydrogen production by coupling methane steam reforming with CO₂ sorption on hydrotalcites at high temperature [31]. Later I moved to capture of CO₂ from flue gases using various adsorbents such as 13X zeolites, carbon materials, binderless zeolites in different shapes (monoliths, beads, extrudates) using cyclic adsorption technologies as Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), Temperature Swing adsorption (TSA), Electric Swing Adsorption (ESA). All this work was developed in parallel with modeling and simulation with home-made packages for process simulation [32]. One of the PhD students working in this area was Zhen Liu who returned to ECUST in Shanghai, after a sandwich period at LSRE, and built a pilot plant (Fig. 8) to treat flue gas from a coal-fired power plant involving a 2-bed PSA and a 3-bed PSA under the guidance of Prof Yu Jianguo and Ping Li [33,34]. I was impressed with his achievement when I went to ECUST for his PhD defense.

Development of adsorbent processes is highly connected with...
materials development. The problems in the synthesis of new adsorbents is the scale-up from gr scale to kg scale and increase the productivity by using new reactors such as NETmix reactor [35]. Nevertheless at the end we get powder material and shaping is required to use the adsorbents in fixed bed columns. An example was the 3D printing of composite monolith of 13 X zeolite and activated carbon to be used in ESA operation for CO₂ capture [36].

The cost of CO₂ capture is still high and one option is storage. More interesting is the Utilization of CO₂ captured. Still there is a mismatch between the amounts of CO₂ to be captured and the potential use as reactant in current industrial processes. It is important to mention the transformation of CO₂ from geothermal power plant in methanol in Carbon Recycling International (Iceland) following the concept of methanol economy of Nobel Prize George Olah [37]. Another option is the use of adsorption/reaction cyclic process to make Synthetic Natural Gas (SNG) from CO₂. This is the Power-to-Gas concept; in a first step CO₂ from flue gas or other source is adsorbed over hydrotalcites (and concentrated) and in a second step hydrogen from water electrolysis powered by renewable energy (wind) is fed and methanation reaction occurs producing SNG [38,39]. This second step is the reactive regeneration of the adsorbent (Fig. 9).

This idea can be applied in pulp mills where the lime kiln is a source of CO₂ thus allowing its transformation in SNG which is needed in the plant.

3.3. Biorefineries and lignin valorization

Pulp mills are also nice examples of biorefineries. In Kraft processes lignin is removed from wood and the black liquor, after recovery of chemicals, is burned in boilers and therefore pulp mills are net producers of electricity injected in the grid. Typically for a pulp mill processing 1 million ton/year of wood, 250,000 ton/year of lignin are obtained. One may need to increase the capacity of the plant and be limited by the boiler capacity; in such case a fraction of the black liquor can be taken to produce chemicals such as vanillin or syringaldehyde depending on the wood source. In our lab, we developed an integrated process shown in Fig. 10 [40] involving first lignin oxidation followed by membrane separation of low molecular weight compounds from the degraded lignin, which can be sent to the boiler or used to make polyurethane foams. The permeate stream is sent to adsorption columns were a clear separation by families: acids, aldehydes, ketones is achieved (Fig. 11) [41]. Proper elution allows enriched fractions of the compounds of interest and finally extraction/crystallization processes lead to the final product (vanillin or syringaldehyde) [42]. There is room here to implement cyclic adsorption processes using some kind of multi-column technology.

A final word: Chemical Engineers combine expertise in chemistry, physics, mathematics and some in biology with an engineering thinking and are players in many frontier areas to develop Sustainable processes/products and help solving Environmental challenges. “Shaking the present. Shaping the future” is the motto of our lab.
Declaration of Competing Interest

No conflict of interests

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