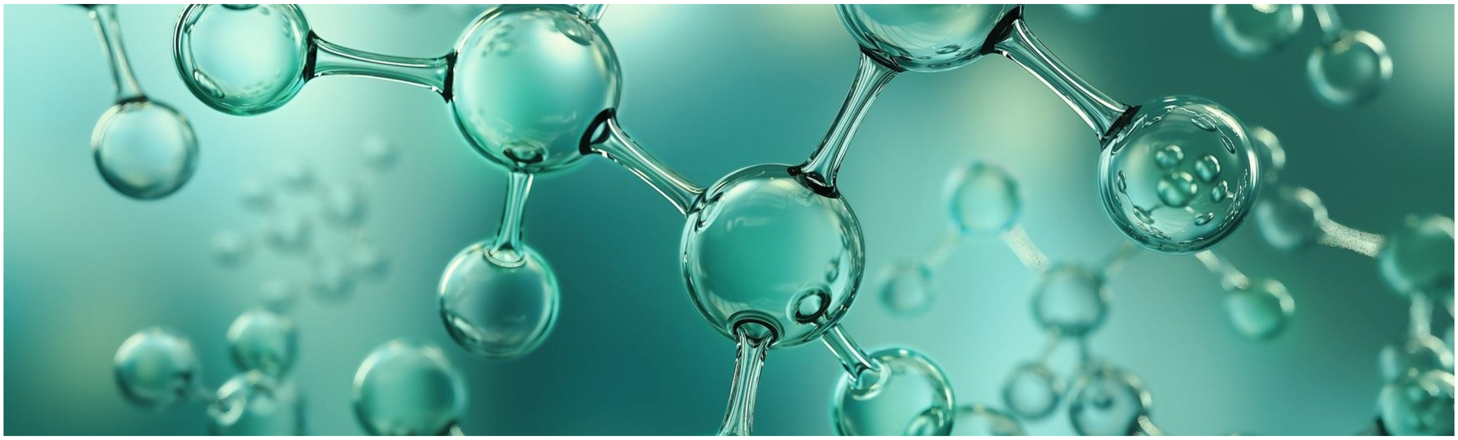

Written on 11 May 2026

3 minutes of reading

News

Fundamental Research

Thermodynamics/Molecular modeling

Surface, interface and materials science

The emergence of complex pollutants such as per- and polyfluoroalkyl substances (PFAS) in natural environments poses a major environmental and health challenge, and the associated new regulations require appropriate treatment methods. To this end, adsorption phenomena at the solid-liquid interface are critical to the development of rapid and selective filtration methods. That is because many pollution control processes involve a filtration step based on the adsorption of pollutants on porous grains, hence the need for a better understanding of adsorption phenomena.

Beyond traditional models and semi-empirical laws

The **amphiphilic nature of PFAS** (i.e., compounds with both hydrophobic and hydrophilic parts) causes them **to behave in complex ways when they are in solution and/or at a solid-liquid interface**. In particular, **aggregate formation** can be observed when their concentration exceeds the critical micelle concentration (CMC) [1]. The resulting **intermolecular interactions** between **adsorbed molecules** significantly alter the **adsorption isotherms**[1] and **kinetics**. Consequently, conventional models (e.g., Henry or Langmuir models[2]) that neglect these lateral interactions fail to account for the cooperative effects generated between molecules, particularly when the isotherms exhibit inflection points[3] [1,2]. Similarly, experimental adsorption kinetics often deviate from classical first-order laws, where the time evolution of the adsorbed amount is proportional to the deviation from the equilibrium adsorbed amount. It is for this reason that (semi-)empirical laws are frequently used to describe the experimental data obtained, without any knowledge of, or consideration for, the underlying adsorption mechanisms.

To address this issue, a PhD research project [3] proposes **modeling of the thermodynamic and kinetic aspects of adsorption** based on three key mechanisms:

- reservoir depletion (associated with a change in the concentration of pollutants in solution in the medium), which is significant in diluted systems,
- surface saturation (associated with the adsorbent's limited adsorption capacity)
- and lateral interactions between adsorbates [3].

Development of an adsorption model

Firstly, **a thermodynamic model incorporating two- and three-molecule interactions** was developed [Figure 1] in order to describe all the adsorption isotherms observed for amphiphilic molecules such as PFAS, as well as surfactants and certain antibiotics (L, S, and LS curves exhibiting 0, 1, or 2 changes in convexity). The **coupling between depletion and saturation**, in turn, leads to mixed-order kinetics[4], which explains the deviations observed experimentally compared to first-order kinetics. Finally, **the effects of cooperative interactions on kinetic parameters** are accounted for through adsorption and desorption constants (which depend on the amount adsorbed), affecting both the final equilibrium state and the time required to reach it.

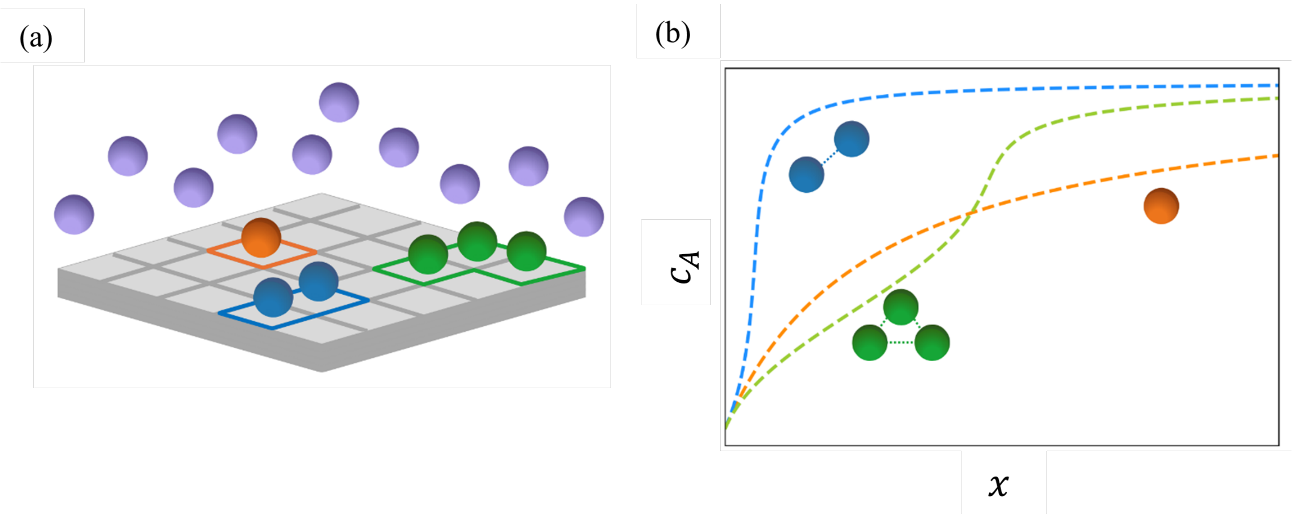

Figure 1 : (a) Lattice adsorption model [3]. Molecules available in solution (shown in purple) can adsorb as monomers (via interactions with the surface, shown in orange) or by forming aggregates (two- and/or three-body interactions, shown in blue and green, respectively).
(b) When adsorption is dominated by interactions between an adsorbate molecule and the surface, the adsorption isotherm has no inflection points [orange curve, (L)]. In contrast, when lateral interactions are present, the adsorption isotherm exhibits one [blue curve in (S)] or two [green curve in (LS)] inflection points. On the x-axis,x represents the molar fraction of the adsorbate in solution, and on the y-axis, cA represents the concentration adsorbed on the surface.

Extrapolation to highly diluted media

This adsorption model not only allows for a better interpretation of experimental measurements but also enables the extrapolation of results obtained at high concentrations to **highly diluted conditions** [Figure 2]. These new capabilities are particularly important for water treatment in natural environments, where pollutant concentrations are limited to a few ng/L, whereas with current technologies, it is extremely difficult to measure adsorption below a few µg/L [4].

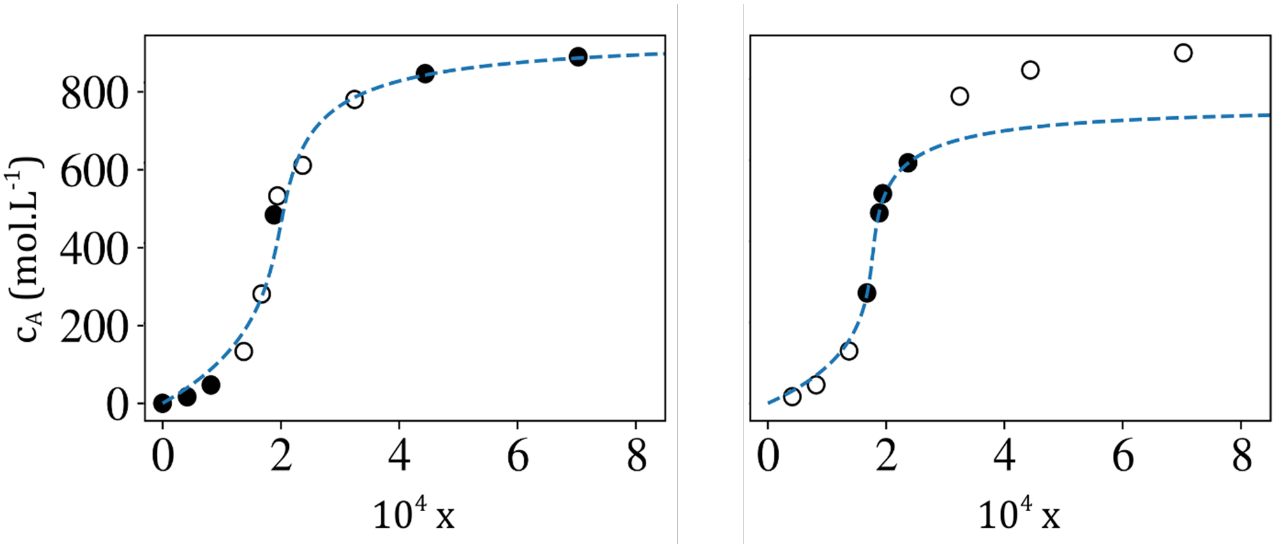

Figure 2 : Extrapolation of the adsorption isotherm for ciprofloxacin (an amphiphilic antibiotic) on a nanomagnetic surface [2, 4]. The black dots correspond to the experimental data used to fit the model, while the white dots represent the experimental data not used. The blue curve corresponds to the fitted model. (a) A uniform distribution of the data points used for the fit across the entire concentration range reduces the number of data points that need to be measured, while correctly reconstructing the adsorption isotherm in both the dilute and saturated regimes. (b) If the data points used for the fit are at intermediate concentrations, the model can estimate the adsorbed amount at very low concentrations but does not correctly predict the plateau.

Perspectives : évaluation et optimisation des filtres d’adsorption

En perspective, ce modèle pourrait être implémenté dans des simulations de type Lattice Boltzmann (méthode numérique pour la résolution d’équations de transport) afin de quantifier **l’impact sur le transport des adsorbats des isothermes spécifiques à un couple d’adsorbat-adsorbant**. A terme, cette avancée permettrait d’évaluer **la performance de filtres** basés sur l’adsorption et d’optimiser leur utilisation pour des composés spécifiques tels que les PFAS.

[1] In thermodynamics, a liquid-phase adsorption isotherm is the relationship, at constant temperature, between the adsorbed concentration c_A and the concentration of the adsorbate in the solution at equilibrium c_e. It should be noted that the adsorbed concentration c_A [in moles of adsorbate per unit volume of solid] is defined as the product of the adsorbed amount [in moles of adsorbate per unit mass of solid] and the density of the adsorbent solid [mass per unit volume of solid]

[2] In Henry's model, the adsorbed concentration is proportional to the solution concentration (linear relationship, where $c_A \sim c_e$), whereas the Langmuir model accounts for surface saturation, thus converging to a plateau (L-shaped curve).
[3] This change in convexity indicates an adsorption mechanism dominated by the formation of surface aggregates.
[4] i.e., the time variation of the adsorbed concentration $c_A(t)$ is a function of $c_A(t)$ and $c_A(t)^2$

References:

[1] Johnson, R. L., Anschutz, A. J., Smolen, J. M., Simcik, M. F., & Penn, R. L. (2007). ***The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces***. Journal of Chemical & Engineering Data, 52(4), 1165-1170.
>> DOI : https://doi.org/10.1021/je060285g

[2] Soares, S. F., Rocha, M. J., Ferro, M., Amorim, C. O., Amaral, J. S., Trindade, T., & Daniel-da-Silva, A. L. (2019). ***Magnetic nanosorbents with siliceous hybrid shells of alginic acid and carrageenan for removal of ciprofloxacin***. International journal of biological macromolecules, 139, 827-841.
>> DOI : https://doi.org/10.1016/j.ijbiomac.2019.08.030

[3] Ben Amor, N., Bauer, D., Braconnier, B., & Coasne, B. (2025). ***Adsorption Thermodynamics and Kinetics of Simple and Complex Fluids: Physical Modeling of Surface Saturation, Reservoir Depletion, Lateral Interactions, and Collective Effects.*** Langmuir, 42(1), 1348-1357.
>> DOI : https://doi.org/10.1021/acs.langmuir.5c05404

[4] Ben Amor, N., Braconnier, B., Coasne, B., Nieto-Draghi C., & Bauer, D. (2026). ***Reconstructing Adsorption Isotherms for Complex Molecules from Limited Data: A New Method Combining Extrapolation and Physics-based Modeling.*** Presented at the 2nd French and German conference on Adsorption. Article currently under Peer Review in Advanced Theory and Simulation.

Scientific contact: Daniela Bauer

A thermodynamic and kinetic adsorption model for more effective treatment of pollutants in solution
11 May 2026

Link to the web page :