

Liquid phase sorption-desorption hysteresis appears time-independent: how meaningful are equilibrium models?

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The sorption of chemical compounds by diverse materials is one of the major processes affecting the environmental fate of chemicals and the efficacy of remediation technologies. There is an understandable intention to explain the sorption data in terms of equilibrium models and, if possible, provide molecular-level interpretations. However, desorption hysteresis is often reported for various chemicals sorbed from liquid phases by soils, sediments and multiple geosorbents, whereas sorption/desorption kinetics seem to be completed. Therefore, an important question is whether equilibrium sorption models are meaningful and useful when time-independent desorption hysteresis occurs. This contribution discusses and models the scenarios where time-independent desorption hysteresis appears, following sorption from solution. All the scenarios are based on considering coupling between sorption sites and "gates" controlling the site accessibility and undergoing opening/closure, depending on solute concentration [1]. These scenarios consider that sorbed molecules may (1) be physically entrapped during desorption and become prevented from exchange with the environment; (2) bind irreversibly to sorbent matrix such that the sorption sites capable of irreversible binding are "paradoxically" (but in an explained way) not fully occupied in the presence of non-zero concentrations of solutes; (3) interact with a non-relaxed sorbent state formed during desorption such that free sorbate exchange with the environment takes place. Scenario (2) leads to the case when using equilibrium models for sorption isotherms is formally possible but fundamentally flawed. In all three scenarios, experimental desorption isotherms are more suitable for modeling the environmental fate of chemicals and using equilibrium models than the sorption isotherms. The significance of obtaining sorption-desorption-resorption isotherms for understanding whether equilibrium models are applicable is reinstated. The lack of coincidence between desorption and resorption isotherms would demonstrate that equilibrium models are hardly applicable to any of the branches. In that case, a deeper understanding of irreversible processes and sorption/desorption kinetics mechanisms should be sought.

[1] Borisover, M. (2023), *Adsorption*, <https://doi.org/10.1007/s10450-023-00380-4>.