Comment

Comment on “Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solution: A critical review, published by Tran et al. [Water Research 120, 2017, 88–116]”

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Correct treatment of adsorption thermodynamics requires consistent handling of adsorption isotherms and the corresponding sorption coefficients. The present comment points to some inconsistencies and misunderstandings in a recent review article.

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Tran et al. (2017) addressed the issue of an increasing number of scientific publications containing inconsistent concepts. With respect to the expected broad attention of such a review, we take the liberty to re-consider some of the author’s suggestions and procedures in order to avoid new inconsistencies. Specifically, we see a need for clarifications in chapter 7: Adsorption thermodynamics.

The key question in this chapter is how to handle correctly the sorption constant Kc in the fundamental equation ln Kc = −ΔG°/RT = −ΔH°/RT + ΔS°/R (eq. (71) in the review article) in order to derive meaningful thermodynamic parameters from measured adsorption data. Usually, adsorption constants have a certain dimension, e.g. L/mmol for the Langmuir sorption constant Kc. However, Kc in eq. (71) has to be dimensionless. Using K-values with dimensions is mathematically incorrect and gives arbitrary values for ΔG° and ΔS°. In order to solve this problem, Tran et al. suggest eq. (76), which defines Kc = SA/(Sv × [A]) = e^{ΔG°/RT} wherein SA (in mmol/m²) are the adsorbate species bound to surface sites, Sv (in mmol/m²) are the vacant surface sites on the surface of an adsorbent, and [A] (in mg/L) is the concentration of adsorbate A in solution at equilibrium. With these definitions eq. (76) is erroneous: Kc has the dimension of a reciprocal concentration rather than being dimensionless. This initial error makes it hard for the reader to follow all the subsequent considerations and derivations in this chapter. Later on the authors suggest: “Kc can be easily obtained as dimensionless parameter by multiplying Ks by 55.5 and then by 1000”, i.e. Kc = 55.5 × 1000 × Ks (eq. 79). From a mathematical point of view eq. (79) is also incorrect because one cannot convert a dimensional constant (Ks) into a dimensionless constant (Kc) just by multiplication with one or several numbers. The value 55,500 is equal to the molar concentration of H2O in pure water (in mmoles/L), so that eq. (79) should be correctly written as: Kc = 55,500 mmol/L × Ks (for Ks in L/mmole). However, what is the rationale for this procedure? It is based on the assumption of a ‘substitutional adsorption’ (Zhou and Zhou, 2014) according to Aq + SH2O_ads ↔ A_ads + H2O_trw where H2O is replaced from the adsorption site (S) by the adsorbate A. The adsorbent has no vacant sites (Sv) in this model. Instead, H2O plays the role as an active adsorbate (Fig. 1). Whether such an interpretation of water as competing adsorbate is appropriate for hydrophobic surfaces (e.g. poly(tetrafluoroethene)) may be questionable.

The message of this consideration is as follows: it would be helpful for the reader if the authors were to elucidate the model and assumptions behind the applied mathematical procedure. We refer the reader to the paper of Zhou and Zhou (2014) where this was done in a profound way.

In the next subchapter (7.3.), the derivation of Kc from Freundlich isotherm constants KF (in mg/g)/(mg/L)n is considered. This conversion is performed by eq. (88) Kc = KF × p_{water}/1000 × (10^n/p_{water})^{(1−n)/n} wherein p_{water} is the density of pure water (in g/mL). An inspection of this equation reveals that it is inconsistent with the definition of the Freundlich equation in this review q_e = KF × C_e^n (eq. (56)) with n as exponent of C_e, whereas in the source article of eq. (88) of Ghosal and Gupta (2015) 1/n was used. Both definitions can be found in the literature, but they should not be used inconsistently.

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within a single article. Apart from the mathematical issue (‘elimination’ of units), such a formal conversion does not provide an answer to the following question: what is the physical or chemical meaning of thermodynamic parameters derived from an empirical isotherm equation, such as the Freundlich equation? The Freundlich equation describes non-linear adsorption isotherms on an empirical basis. If one considers a distribution of non-uniform adsorption sites, such as is normally the case in most adsorbents, what is the meaning of the calculated thermodynamic parameters? Which kind of adsorption site averaging is involved? We think that the Freundlich constant cannot be attributed to any particular sorption affinity as is the case for the Langmuir constant for uniform sorption sites, and the significance of thermodynamic parameters derived from the Freundlich constant is per se questionable.

In the next subchapter 7.4., the equilibrium constant $K_C$ is derived from partition coefficients $K_D = a_d/a_s$ (eq. 92) “where $a_s$ is the activity of the adsorbate adsorbed onto the adsorbent, $a_d$ is the activity of the adsorbate in solution at equilibrium”. There are two possibilities for misinterpretation in this approach. Firstly, the term ‘partitioning’ is most frequently used for solute distribution between two volume phases rather than for surface adsorption. Secondly, a partition equilibrium is established when the activities of a solute or sorbate are equal in the two corresponding states, e.g. adsorbed and dissolved. This is the case if the two activities are related to the same standard state. According to eq. (92), this condition would lead to $K_p = 1.0$ in all cases by definition because $K_p$ represents the equilibrium state, which is certainly not meant by the authors. The first possible misunderstanding results from an unclear definition: the authors use $a_s = \gamma_s \times C_s$ with $C_s$ in mg/L. This is a volume-based definition of the adsorbed adsorbate concentration. Unfortunately, the authors do not specify which volume is referred to. The reader has the choice between two reference volumes: that of the water phase and that of the adsorbent phase. Until that point in the article, the adsorbent had never been used in volume units. At that point, however, the amount of adsorbent in terms of L is the only correct measure. $C_s$ is the adsorbed adsorbate concentration in moles per L adsorbent and $C_d$ is the freely dissolved adsorbate concentration in moles per L water. Without these annotations it might be hard for the reader to follow the presented line of derivations.

In summary, we fully agree with the final statement of Tran et al.: “In scientific publications, the correct use of technical terms and accurate calculations are essential.” We value their work and are sure that they agree that this also applies to critical reviews.

**United reference**

Tran et al., 2016.

**References**


