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Comment on "Adsorption of uranium (VI) complexes with polymer-based spherical activated carbon", published by Y.-A. Boussouga *et al.* [Water Research 249 (2024) 120825]

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- Thermodynamic adsorption parameters

Abstract

Calculation of thermodynamic parameters of adsorption such as Gibbs free energy ΔG°_{ads} from experimentally determined adsorption data can be helpful for elucidation of sorption mechanisms. This approach includes the transformation of adsorption coefficients K_d or K_L into dimensionless standard adsorption constants K_{ads} [-]. The present comment reveals recently published misleading approaches and offers thermodynamically sound alternatives.

Recently, Boussouga *et al.* (2024) have published an article in Water Research on the adsorption of uranium complexes from aqueous solution on activated carbon spheres. It is a major aim of this study to elucidate the mechanism and the rate-limiting step of the adsorption process. For this purpose, the authors analyze their data in terms of kinetic and thermodynamic parameters. Thermodynamics of adsorption in aqueous suspension is a widely respected field, but rich in traps and pitfalls (e.g. Zhou and Zhou, 2014; Tran *et al.*, 2017; Zhou *et al.*, 2022). We think

that the approach applied in Boussouga *et al.* is erroneous and that the conclusions drawn are misleading. In order to avoid further confusion in this field, the article should be carefully reconsidered in Water Research, as follows.

First, we examine the applied thermodynamic approach. Boussouga *et al.* apply two common adsorption isotherm models – Langmuir and Freundlich model (Tran *et al.*, 2017; Atkins *et al.*, 2022) – for description of the experimental data. The authors derive thermodynamic parameters "comprising of Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) ... to identify whether the prevailing adsorption mechanism is physical or chemical" in nature. As a first step, the authors convert the experimental adsorption coefficient $K_{exp} = q_e/C_e$ [L/mg] into a dimensionless adsorption constant K_d [-] according to eq. 1. This conversion is necessary, because thermodynamic laws make use of sorption constants in the logarithmic format.

$$K_{\rm d} = q_{\rm e}/C_{\rm e} \cdot m_{\rm adsorbent}/V_{\rm solution} = K_{\rm exp} \cdot C_{\rm adsorbent} \qquad \text{with the units } [L/g] \cdot [g/L] = [-] \qquad (1)$$

 $q_{\rm e}$ [µg/g] and $C_{\rm e}$ [µg/L] are the uptake of the adsorbent and the dissolved concentration of the solute, respectively, under equilibrium conditions. $m_{\rm adsorbent}$ [g] and $V_{\rm solution}$ [L] are the mass of adsorbent and the volume of aqueous solution, respectively, used in the respective batch experiments. The procedure applied by Boussouga *et al.* eliminates the units in K_d , but is neither scientifically justified nor explained by the authors. $C_{\rm adsorbent}$ is an experimental parameter, which may vary from experiment to experiments. Using $C_{\rm adsorbent}$ for converting $K_{\rm exp}$ into K_d invalidates the general applicability of the adsorption coefficient. The value of K_d becomes arbitrary. Therefore, most thermodynamic considerations made in the article based upon these K_d values have to be put into question, in particular all values of ΔG° , one has to define the corresponding standard states. The authors do not define any standard state. In the SM part of

our Comment we suggest three scientifically founded methods for conversion of adsorption constants.

Results of the thermodynamic data treatment are summarized in Table 3 of the article. It is apparent that the K_d values presented there, irrespective of their arguable derivation, are numerically not compatible with the corresponding ΔG° values in the same table. Consider for example the first data line in Table 3 (data at 10 °C): $\Delta G^{\circ} = -R \cdot T \cdot \ln (K_d) = -8.314 \text{ J/(mol K)} \cdot 283$ K·ln (2) = -1.6 kJ/mol. This value is one order of magnitude different from $\Delta G^{\circ} = -(18 \pm 1)$ kJ/mol as given in Table 3. The inconsistency of the data in Table 3 poses a problem for the reader.

This does not prevent the authors from drawing mechanistic conclusions on the uranyl adsorption mechanism, such as " ΔG° were all negative ... suggested an energetically favorable and spontaneous physical adsorption". Here, we wish to point out that *a priori* spontaneity of adsorption cannot be derived from the sign of ΔG° . The driving force for adsorption comes from the distance between the actual system state and the equilibrium state. This means that spontaneous adsorption can indeed take place for $\Delta G^{\circ} \ge 0$. The criterion of spontaneity of a process is ΔG rather than ΔG° , as misleadingly interpreted by Boussouga *et al.*

The authors also interpret extensively the positive values of the change in standard adsorption entropy ΔS° in terms of adsorption mechanisms. We think that none of these deductions is robust, for two reasons: (i) the derived ΔS° values are erroneous (see below), and (ii) highly positive values of the adsorption entropy such as $\Delta S^{\circ} \approx 50$ J/(mol K), as presented in Table 3, result from solvation processes in the bulk phase rather than from surface processes. In other words: surface adsorption of dissolved species gives rise to reduction of their mobility, compared to the dissolved state, and hence tends to decrease the system entropy ($\Delta S^{\circ} < 0$) rather than to increase it. When the overall entropy change is strongly affected, or even dominated, by bulk phase effects, one does not learn much about surface steps from adsorption entropies.

Therefore, one is well advised to be cautious with mechanistic interpretation of entropy effects in terms of surface processes.

Supposed that the reader relies, for a moment, on the ΔG° and ΔH° values as given in Table 3, it follows that (at 10°C) $\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T = \{-(17 \pm 3) \text{ kJ/mol} + (18 \pm 3) \text{ kJ/mol}\}/283 \text{ K} = (3.5 \pm 21) \text{ J/(mol K)}$. The authors give $\Delta S^{\circ} = 48-54$ "kJ/mol" in Table 3. Obviously, the given units of ΔS° are wrong. But even when assuming ΔS° to be in the correct units of J/(mol K), the two values of ΔS° , 3.5 vs. about 50 J/(mol K), are not compatible. In summary, all entropy values and interpretations in Boussouga *et al.* are lacking a sound basis, in our view.

After a critical evaluation of the data treatment procedures in Boussouga *et al.*, it is also instructive to inspect the basis of this treatment: the experimental data themselves. A rough inspection of Figure 5 reveals, that the two diagrams A and C present significantly different temperature dependencies of uranyl adsorption. It is not possible for both temperature dependencies to be correct. A second hardly plausible set of experimental data is presented in Figure 2, where the uranium removal was investigated for various adsorbent dosages. Surprisingly, the remaining dissolved uranyl concentration C_e decreased only marginally when increasing the adsorbent dosage tenfold, from 1 to 10 g/L. We consider this data set to be inconsistent with the adsorption isotherms presented in Figure 4C. These examplarily addressed inconsistent data sets are not a minor issue: they are the core part of the study. Their inconsistency is demonstrated in quantitative terms in the attached SM part.

In summary, we address in this Comment a number of data inconsistencies, misleading approaches and other errors in the article of Boussouga *et al.* (2024), when deriving thermodynamic and kinetic parameters from experimental adsorption data. Because of the general importance of this topic, erroneous approaches should not remain undisputed in Water Research. As a positive contribution we offer several alternative approaches in the SM part attached to this Comment.

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Supplementary Material to the above Comment is available on line (see attached word file)

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