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Comments on "Efficient adsorption of Mn(II) by layered double hydroxides intercalated with diethylenetriaminepentaacetic acid and the mechanistic study. J. Environ. Sci. 85, 56–65"

In the paper entitled "Efficient adsorption of Mn(II) by layered double hydroxides intercalated with diethylenetriaminepentaacetic acid and the mechanistic study" in Journal of Environmental Sciences, volume 85, page 56–65, there were problems with mathematical notation and dimensional errors in the calculation for Giibbs free energy.

In Section 2.5: Adsorption isotherms and thermodynamics studies, authors calculated the Gibbs free energy change (ΔG^{o}) by using equation (8):

$$\Delta G = -R \times T \times \ln K_{ads} \quad (8)$$

where R (8.314 J/(mol·K)) is the gas constant, T (K) is the solution temperature, and K_{ads} is the equilibrium constant equal to the Langmuir equilibrium constant b. Their calculation results for thermodynamic parameters are listed in Table 3 (Huang et al., 2019).

We found that their calculation results for thermodynamic parameters were incorrect. In their paper, the Gibbs free energy change of adsorption is defined as $\Delta G = -R \times T \times \ln K_{ads}$, where K_{ads} is the adsorption equilibrium constant equal to the Langmuir equilibrium constant b (L/mg, shown in original Table 2, Huang et al., 2019). ΔG at different temperatures was calculated as follows:

At 293.15 K,

$$\begin{aligned}\Delta G &= -\mathrm{RTlnb}\\ &= -(8.314\ \mathrm{J/(mol\cdot K)}) \times (293.15\ \mathrm{K}) \times \ln(0.0129\ \mathrm{L/mg})\\ &= 10603(\mathrm{J/mol})\end{aligned}$$

At 303.15 K,

$$\begin{aligned}\Delta G &= -\mathrm{RTlnb}\\ &= -(8.314\ \mathrm{J/(mol\cdot K)}) \times (303.15\ \mathrm{K}) \times \ln(0.0176\ \mathrm{L/mg})\\ &= 10182(\mathrm{J/mol})\end{aligned}$$

Table 3 – Thermodynamic parameters for the adsorption of Mn(II) by LDHs-DTPA (the values of parameter b in the Langmuir model comes from Table 2, Huang et al., 2019).

Temperature (K)	b (L/mg)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
293.15	0.0129	−10.60	−20.34	−0.033
303.15	0.0176	−10.18		
313.15	0.0220	−9.94		

At 313.15 K,

$$\begin{aligned}\Delta G &= -\mathrm{RTlnb}\\ &= -(8.314\ \mathrm{J/(mol\cdot K)}) \times (313.15\ \mathrm{K}) \times \ln(0.0220\ \mathrm{L/mg})\\ &= 9937(\mathrm{J/mol})\end{aligned}$$

By comparing the calculated results with the data shown in Table 3 (Huang et al., 2019), we found that the absolute values of calculated results were equal to those in Table 3 but with opposite signs. The positive or negative of the Gibbs free energy change (ΔG) is the sign in determining the spontaneous tendency of adsorption reaction. The authors drew a conclusion that the adsorption processes were spontaneous in temperature range from 20 to 40 °C based on the negative values of ΔG. But according to the above tests, the values of ΔG calculated by the Langmuir equilibrium constant b should be positive, indicating that the Mn(II) adsorption by layered double hydroxides intercalated with diethylenetriaminepentaacetic acid is a non-spontaneous process.

There is also a mistake in dimensional principle. According to the Principle of chemical thermodynamics (IUPAC, 1993), the calculation of thermodynamic parameters must use the standard equilibrium constant (K°).

$$K^{\circ} = \exp(-\Delta G^{\circ}/RT)$$

where, ΔG° (J/mol) is standard free energy; R (J/(mol·K)) is gas constant,; and T (K) is temperature. K° is a dimensionless parameter. In the paper of Huang et al. (2019), the unit of K_{ads} (b) is L/mg, therefore, it is not the standard equilibrium constant K°, i.e., the K_{ads} (b) cannot be used for calculating the ΔG (MilonjiĆ, 2007; Zhou and Zhou, 2014).

1. The calculation method of the K° from the Langmuir model

In order to obtain the standard equilibrium constant K° (dimensionless), Zhou et al. (2012) reported a correct Langmuir model:

$$\theta = \frac{K^{\circ}\frac{C_e}{C^{\circ}}}{1 + K^{\circ}\frac{C_e}{C^{\circ}}} \quad (9)$$

where θ is the fraction of the surface covered at equilibrium, dimensionless. $\theta=q_e/q_m$, where, q_e is the equilibrium adsorption capacity of adsorbent, q_m is the maximum sorption capacity of adsorbent. C_e (mol/L) is the solute concentration at the equilibrium; C° (1 mol/L) is the molar concentration of the standard reference solution. The standard equilibrium constant K° (dimensionless) can be calculated by the modified Langmuir equation. It is worth noting that the solute concentration must use molar concentration, otherwise, the correct results cannot be obtained.

According to the modified Langmuir model, we calculated the thermodynamic parameters by using the data from Table 2 (Huang et al., 2019). The plot of $\ln K^\circ$ versus $1/T$ fitted a straight line (Fig. 1), and ΔH and ΔS were determined from the slope and intercept, respectively. The results of thermodynamic parameters are listed in Table 4 (Huang et al., 2019).

Comparing Tables 3 and 4, there are four significant differences before and after modification. (1) The values of ΔG become more negative with the increase in temperature. The value of ΔG indicates the degree of spontaneity of the adsorption process. The negative value shows that the adsorption process is favorable energetically (Zhao et al., 2011). (2) The adsorption enthalpy is positive which indicating that the adsorption is endothermic process (Wang et al., 2020). The result is consistent with the change of adsorption amount in the Langmuir model. (3) The adsorption entropy is positive but not negative. The positive ΔS value indicates that Mn(II) adsorption increases the disorder and randomness in the system (Tahir et al., 2016). (4) The unit of entropy is kJ/(mol·K) but not kJ/mol.

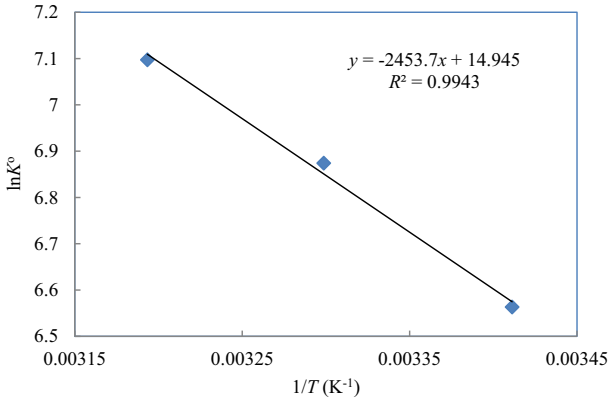

Fig. 1 – Linear plot of lnK° vs. 1/T for the adsorption of Mn(II) at 293.15, 303.15, 313.15 K.

Table 4 – Thermodynamic parameters for the adsorption of Mn(II) by LDHs-DTPA (The modified Langmuir model was used).

T (K)	B (L/mg)	B (L/mol)	K° (dimensionless)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
293.15	0.0129	708.7	708.7	−16.00	20.40	0.124
303.15	0.0176	966.9	966.9	−17.33		
313.15	0.0220	1208.66	1208.6	−18.48		

The atomic weight of manganese is 54.938 g/mol.

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