



Short Communication

Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters: Research updated



Yingju Chang^a, Juin-Yih Lai^b, Duu-Jong Lee^{a,b,c,*}

^a Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

^b R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan Christian University, Chungli, Taiwan

^c Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

HIGHLIGHTS

- Thermodynamic parameters reported in biosorption studies were assessed.
- The compensation effects noted for enthalpy–entropy data are an artifact.
- Confusion by use of arbitrarily adsorbate concentration is commented.
- No conclusion should be drawn based on unjustified thermodynamic parameters.

ARTICLE INFO

Article history:

Received 23 August 2016

Received in revised form 28 September 2016

Accepted 29 September 2016

Available online 1 October 2016

Keywords:

Adsorption

Thermodynamics

Heavy metal

Dye

Low-cost adsorbent

Equilibrium

ABSTRACT

The standard Gibbs free energy, enthalpy and entropy change data for adsorption equilibrium reported in biosorption literature during January 2013–May 2016 were listed. Since the studied biosorption systems are all near-equilibrium processes, the enthalpy and entropy change data evaluated by fitting temperature-dependent free energy data using van Hoff's equation reveal a compensation artifact. Additional confusion is introduced with arbitrarily chosen adsorbate concentration unit in bulk solution that added free energy change of mixing into the reported free energy and enthalpy change data. Different standard states may be chosen for properly describing biosorption processes; however, this makes the general comparison between data from different systems inappropriate. No conclusion should be drawn based on unjustified thermodynamic parameters reported in biosorption studies.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Adsorption removal technologies of heavy metals and dyes from wastewaters are highly efficient and affordable when the appropriate adsorbents are available (Fomina and Gadd, 2014). All aspects on biosorption processes, including its fundamentals (Li and Yu, 2014; Hung and Wang, 2014; Birungi and Chirwa, 2014; Shah et al., 2014), the development of new biosorbents (Abdolali et al., 2014a,b; Song et al., 2014; Dong et al., 2014), and the use of biosorbents for novel applications (Witek-Krowiak et al., 2014; Podstawczyk et al., 2014; Cobas et al., 2014), were studied. The search of low-cost, high performance adsorbents is the focus of contemporary research and development efforts.

Liu and Lee (2014) listed the biosorption studies since year 2006 till early 2013 on the removal of heavy metals and dyes from wastewaters. A total of 3741 biosorption papers were published since 2013 till the end of May 2016 based on Web of Science (WoS) search, with the top five country affiliations for corresponding authors being China, India, Iran, Turkey, and Pakistan (Table S1), and with the top five archive journals hosting these papers being Desalination and Water Treatment, Chemical Engineering Journal, Bioresource Technology, Environmental Science and Pollution Research and Journal of the Taiwan Institute of Chemical Engineers (Table S2). A total of 453 papers in the said 3741 biosorption papers evaluated the thermodynamic parameters, free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) under standard states based on a set of temperature-dependent equilibrium isotherm data and the use of van Hoff's equation (Table S3). Ramesh et al. (2005) identified the probable flaws in their collected adsorption studies and commented that all the thermodynamic

* Corresponding author at: Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan.

E-mail address: djlee@ntu.edu.tw (D.-J. Lee).

parameters reported in these papers should not be considered justified. Liu and Lee (2014) reviewed the biosorption studies up to early 2013 and noted identical flaws in their listed studies. This mini-review surveyed the current biosorption studies since 2013 and found that all the authors continuously reported unjustified thermodynamic parameters regardless of the possible flaws noted in the evaluation scheme.

2. Adsorption tests

In the studies listed in Table S3, the following metal ions were used as the adsorbate (As³⁺, Au³⁺, Ba²⁺, Cd²⁺, Ce³⁺, Co²⁺, Cr³⁺, Cr⁶⁺, Cs⁺, Cu²⁺, Eu³⁺, Fe³⁺, Gd³⁺, Hg²⁺, In³⁺, La³⁺, Li⁺, Mn²⁺, Ni²⁺, Pb²⁺, Pd²⁺, Re⁷⁺, Sb³⁺, Sm³⁺, Sr²⁺, Th⁴⁺, Tl⁺, U⁶⁺, Zn²⁺), with adsorption of Cu²⁺, Cr⁶⁺, and Pb²⁺ being related to environmental engineering field and ions such as Sr²⁺, Th⁴⁺, Tl⁺, U⁶⁺ affiliated to remediation of radioactive wastewaters. The Cu²⁺ is the most “popular” adsorbate in these adsorption studies. In dye adsorption studies, the following dyes were applied as the testing adsorbate (methylene blue (MB), acid blue-45, acid blue-80, amido black-10B, anthocyanins, azo coumarin dye, basic red-12, basic red-46, basic yellow-28, crystal violet, direct orange-26, direct yellow-50, reactive blue 5G, reactive dye yellow 145, red 23, reactive black 5, reactive red 120, reactive red 2, reactive dye ostazine black V-B, eriochrome black T, malachite green, Methyl orange, methyl violet, methylene blue, norbixin, remazol red RB-133, rhodamine B, safranin O, safranin T, sunset yellow), with the reactive dyes removal being the research focus and the MB being the most widely studied dyes in the biosorption studies.

Besides the synthesized adsorbent such as carbon nanotubes (CNTs), graphene and resin, most adsorbents adopted were derived from wastes and agricultural or natural products (acrylic acid grafted *Ficus carica* fiber, Banyan leave, chitin, sophora japonica pods powder lay, tannery waste, tunisian olive-waste cakes, walnut, neem bark, *Sargassum angustifolium*, *Acalypha hispida* leaf, anaerobic granular sludge, *Azadirachta indica*, Asphaltene, brown algae, gastropod shell dust, *Chlorella vulgaris*, coconut coir, cotton fiber, *Coriulus versicolor*, dried cactus, *Eichhornia crassipes*, extruded apple pomace, *Ficus auriculata* leaves, *Ficus carica* fibers, freeze dried apple pomace, porous sugarcane bagasse, palm tree leaves), and natural minerals (clean sand, diatomite, calcareous soil, canola biomass, carbonate rock, coal dust, coal fly, kaolinite clay, magnetic litchi peels (MLP), marble dust, natural pyrite, peanut husk, peat soil, red clay). These studies emphasized the merit of reusing waste as a resource for achieving the green targets of sustainable development of a modern society. Nonetheless, none of the said process found full-scale applications partly because the post-treatment of the used “green” adsorbents may not be green at all considering its high energy consumption, greenhouse gas emission and also the relatively high treatment costs. Furthermore, since these studies utilized very different adsorbent-adsorbate pair, no general correlation should be found when comparing their adsorption performance with simple parametric sets.

3. Thermodynamics parameters for adsorption equilibrium

3.1. Langmuir isotherm

The Langmuir isotherm model is widely applied to describe the adsorption isotherm data:

$$q_e = q_m \frac{K_{ad} C_e}{1 + K_{ad} C_e} \quad (1)$$

where K_{ad} is the equilibrium constant, C_e is the solute concentration in solution and q_e is the solute concentration on the adsorbent

surface, q_m is the maximum adsorption amount. Apparently the K_{ad} should be of unit $[1/C_e]$ in Eq. (1). Consider the exchange process of an adsorbate molecule $j(aq)$ at concentration of C_e in solution with a water molecule on the active site on adsorbent $H_2O(ad)$, and consider the adjacent solution-solvent layer at the adsorbate surface as a two-dimensional solute-solvent matrix (<http://www.le.ac.uk/chemistry/thermodynamics/pdfs/500/Topic0140.pdf>), the standard Gibbs free energy can be described as follows:

$$\Delta G^0 = \mu_j^0(ad) - \mu_j^0(aq) = -RT \ln K_{ad}, \quad (2)$$

where $\mu_j^0(ad)$ and $\mu_j^0(aq)$ are the chemical potentials based on their respective standard states. The chemical potentials at the studied states can be approximated based on the standard states as follows:

$$\mu_j(aq) = \mu_j^0(aq) + RT \ln \left[\frac{C_e \gamma_j}{C_r} \right] \quad (3a)$$

$$\mu_j(ad) = \mu_j^0(ad) + RT \ln [f(\theta)] \quad (3b)$$

where γ_j is the activity coefficient of solute, C_r is the standard state chosen for the solute, and the $f(\theta)$ is a function of surface coverage and temperature. One notes that when $\gamma_j = 1$, $C_e = C_r$ and $f(\theta) = 1$, $\mu_j(ad) = \mu_j^0(ad)$ and $\mu_j(aq) = \mu_j^0(aq)$.

Assuming that the n_0 solute molecules of individual weight w is added to a solution of volume V , and the n_d solute molecules is adsorbed by adsorbent with added mass W , then $C_e = (n_0 - n_d)/V$. Taking Langmuir model $f(\theta) = \theta/(1 - \theta)$, which follows the conventional Flory-Huggins form for polymer solution with $f(\theta) = 1$ at $\theta = 1/2$, and with $\theta = n_d/N_T = q_e/q_m$ where N_T is the number of total available active sites on the adsorbent surface, q_e and q_m are the adsorbed quantity and the maximum quantity per unit mass of adsorbent, the equilibrium constant K_{ad} can be stated as follows:

$$K_{ad} = \frac{C_r}{\gamma_j} \frac{q_e}{(q_m - q_e) C_e} \quad (4)$$

At limit of $\gamma_j = 1$, Eq. (4) is simplified to the following form:

$$q_e = q_m \frac{K_{ad}(C_e/C_r)}{1 + K_{ad}(C_e/C_r)} \quad (5)$$

The standard states for C_r should be chosen at the vicinity of the studied state for appropriately approximate the process. Clearly only if $C_r = 1$ in any adopted unit and the C_e follows the same unit Eq. (5) can be simplified to Eq. (1). Taking $C_r = 1$ mol/L at 25 °C, then Eq. (1) represents the adsorption process based on standard state with studied solute at 1 mol/L and 25 °C being reversibly adsorbed onto an adsorbate with 50% surface coverage. The question whether the use of Eq. (1) to describe the adsorption process with adsorbate at very low concentrations (for instance, with tests of a few hundred ppb) and adsorbent with low coverage (the use of fresh adsorbent for test) is valid remains unjustified.

3.2. Use of adsorbate unit

Based on Eq. (2), the free energy evaluated based on K_{ad} yielded with C_e reported at units other than mol/L would exhibit a difference attributable to the entropy change by mixing. Conversely, the units used for q_e have no effects on the equilibrium constants thus evaluated if the q_m data obtained in data fitting would be reported at the same unit as q_e . Different units for C_e (and for q_e) were applied to evaluate the parameters in Eq. (1), including C_e in mol/L and q_e in mg/g (Saleem et al., 1992), C_e in mg/L and q_e in mg/g (Wang et al., 2013), C_e in mol/L and q_e in mol/g (El-Bindary et al., 2014), C_e in μg/L and q_e in μg/g (Chen et al., 2016), both C_e and q_e in mg/L (Kamaraj and Vasudevan, 2016) and others. 84% of the cited papers in Table S3 reported their q_e data in mg/g and C_e data in mol/L, with the rest 28 papers were

Download English Version:

<https://daneshyari.com/en/article/4998023>

Download Persian Version:

<https://daneshyari.com/article/4998023>

[Daneshyari.com](https://daneshyari.com)