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Note

Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewater with low-cost adsorbents

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Abstract

This note revisits the literature evaluating the thermodynamic parameters of adsorption equilibrium uptakes of heavy metals and dyes from water and wastewater streams using low-cost adsorbents derived from agricultural waste, industrial wastes, inorganic particulates, or some natural products. We highlighted the possible flaws in some adsorption studies when their thermodynamic parameters were assessed, since compensation effects during enthalpy and entropy evaluation were possibly overlooked.

Keywords: Adsorption; Thermodynamics; Heavy metal; Dye; Low-cost adsorbent; Equilibrium

1. Introduction

Heavy metals and dyes are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others; their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. Methods for removing metals or dyes from a water stream include adsorption, which is a highly effective and economical process provided the correct adsorbents are applied in an environment that favors adsorption. Activated carbon is the conventionally adopted adsorbent for removing metals and dyes from water. However, the high cost of activated carbon limits its use as an adsorbent in developing countries. The search for low-cost adsorbents, preferably derived from locally available waste materials, thus has become a main research focus [1,2]. To date, hundreds of studies on the use of low-cost adsorbents have been published. Brown et al. [3] reviewed the pretreatment methods used for modifying peat. Shukla et al. [4] reviewed the use of sawdust for removing unwanted materials from water. Babel and Kurniawan [5] reviewed the use of low-cost adsorbents for heavy metals uptake from contaminated water. Aksu [6] reviewed the use of bioadsorbents to remove organic matter from water.

Among the process parameters frequently investigated in the literature, temperature is shown to affect adsorption capacity [7–20]. When adsorption capacity increased with temperature, the process was claimed to be endothermic, and vice versa. The thermodynamic parameters present the essential parameters for subsequent engineering evaluation on the ultimate uptake of the adsorbents, and, hopefully, also provide insights to the adsorption mechanisms thus applied for further use in process modification and optimization.

2. Adsorption isotherm model

Most adsorption works adopt either the Langmuir or Freundlich isotherm (or both) for adsorption data correlation. The Langmuir isotherm is valid for dynamic equilibrium adsorption–desorption processes on completely homogeneous surfaces with negligible interaction between ad-

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sorbed molecules that exhibit the form

$$q_e = \frac{QbC_e}{1 + bC_e}, \tag{1}$$

where C_e denotes the equilibrium concentration in solution; q_e represents the amount adsorbed for unit mass of adsorbent; and Q and b are related to saturated monolayer adsorption capacity and the Langmuir constant, respectively.

The adsorption from the solution is much more complex than that from the gas phase. Blandamer and coworkers [21,22] showed that the adsorption equilibrium of adsorbate molecules j in aqueous solution to sites on the adsorbent originally occupied by water molecules could be presented as

$$j(\text{aq}) + \text{H}_2\text{O}(\text{ad}) \leftrightarrow j(\text{ad}) + \text{H}_2\text{O}(\text{aq}), \tag{2}$$

where “aq” and “ad” represent the aqueous state and the adsorbed state, respectively. The chemical potential of adsorbed molecules j can be stated in the form

$$\mu_j(\text{ad}) = \mu_j^0(\text{ad}) + RT\left[\ln(f(\theta))\right], \tag{3}$$

where f is a function of the degree of occupancy of the surface of the adsorbent, θ. Meanwhile, the chemical potential of adsorbate j in solution can be stated as

$$\mu_j(\text{aq}) = \mu_j^0(\text{aq}) + RT\left[\ln\left(\frac{C_e y_j(\text{aq})}{C_r}\right)\right], \tag{4}$$

where C_e and $y_j(\text{aq})$ are the solute molar concentration and the activity coefficient, respectively. $C_r = 1\ \text{mol}\,\text{l}^{-1}$. At equilibrium, $\mu_j(\text{ad}) = \mu_j(\text{aq})$; hence the standard Gibbs free energy change could be stated as

$$\begin{aligned}\Delta G^0 &= \mu_j(\text{ad}) - \mu_j^0(\text{aq}) \\ &= -RT\left[\ln\left(\frac{f(\theta)C_r}{C_e y_j(\text{aq})}\right)\right] = -RT\ln K_{\text{ad}},\end{aligned} \tag{5}$$

where K_{ad} is the adsorption equilibrium constant. If $f(\theta) = \theta/(1-\theta)$, Q is the saturated monolayer adsorption capacity, and the Langmuir constant b is K_{ad}, then

$$q_e = \frac{QbC_e}{(C_r/y_j(\text{aq})) + bC_e}. \tag{6}$$

It is hence apparent that Eq. (2) is a simplified case of Eq. (6) by setting $C_r/y_j(\text{aq}) = 1$. Restated, the solvation interaction term has been neglected by using Eq. (2) in low-cost adsorbent studies. Also, the ignorance of C_r means that the equilibrium constant b is not dimensionless in its evaluation.

3. Thermodynamics of adsorption equilibrium

With the changes in Gibbs free energy in Eq. (5), the isosteric heat of adsorption could be assessed as follows:

$$\Delta H^0 = R\frac{\mathrm{d}\ln K_{\text{ad}}}{\mathrm{d}(1/T)}. \tag{7}$$

Consequently, if the adsorption capability increases with temperature, $\Delta H^0 > 0$, the process is endothermic, or vice versa. Based on Eqs. (5) and (7), the entropy change of adsorption could be assessed as

$$\Delta S^0 = \left(-\frac{\Delta G^0}{T}\right) - \left(-\frac{\Delta H^0}{T}\right).$$

Some authors assessed their thermodynamic parameters of adsorption at three temperatures, 30, 40, and 50 °C [10,13–15,17,18,23–29]. Nevertheless, Table 1 lists the derived thermodynamic parameters obtained in the low-cost adsorbent studies. On the heavy metal side, the uptake of cadmium and nickel to ash [25] was noted to be endothermic, but a positive entropy change to achieve feasible adsorption. The adsorption of zinc [26] and of lead and chromium [28] on ash was demonstrated to be exothermic, with a negative entropy change that partially ‘retarded’ adsorption. On the dye adsorption, the uptake by red mud of rhodamine B, fast green, and methylene blue [18] was noted to be exothermic, but with a negative entropy change. The adsorption of basic red 9 on activated carbon or activated slag [17] was shown to be endothermic, with a corresponding positive entropy change.

4. Discussion

If the thermodynamic parameters were properly assessed, they could provide in-depth information regarding the inherent energy and structural changes after adsorption. For example, the following statement was made in an adsorption study using activated carbon and activated slag to adsorb basic red dye [17]: “The positive values of entropy show the increased randomness after the adsorption ....” Additionally, based on the same reasoning, a certain “orderliness” should be produced during the adsorption of Zn^{2+}, Cd^{2+}, and Pb^{2+} on ash [18], owing to their corresponding entropy changes being negative. Assuming this conclusion is true, then the origin of this produced orderliness should correlate with the ion radii, degree of solvation, surface energy of adsorbents, and so on, providing essential information regarding the underlying mechanisms.

Based on experiments over a wide range of temperature, the nature of hydrophobic effects had been re-examined [30]. Since the adjacent water molecules surrounding the hydrophobic molecule displayed some ‘orderliness’ (if not “iceberg”), the transfer of the hydrophobic molecules to an ‘oil-like’ pool must break down the water structure, thus increasing system randomness after micelle formation or protein unfolding. It is shown that the enthalpy and entropy changes for hydrophobic substance dissolution and protein unfolding process was a compensation process which gives a nearly constant Gibbs free energy change [31]. The ΔH^0 versus ΔS^0 plot would exhibit a linear character with the slope of a dimension of temperature, and is referred to as the so-called “compensation temperature” (T_C) [32,33]. Based

Table 1
Thermodynamic parameters collected in low-cost works

Ref.	Pollutant	Adsorbent	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
[9]	Cu^{2+}	Tree fern	+4.24	+0.0156
[12]	Crystal violet	Fly ash	+36.51	+209.64
	Basic fuchsin		+21.35	+173.83
[13]	Ethyl orange	Carbon slurry	−6.2	+74.2
	Mentanil yellow		−6.1	+71.7
	Acid blue		−5.8	+69.5
[14]	Chrysoidine B	Carbon slurry	−0.7	91.9
	Crystal violet		−2.0	88.9
	Meldola blue		−2.3	87.9
[15]	Basic red 9	AC (slurry)	+53.06	+264
[18]	Rhodamine B	Red mud	−67.1	−140.1
	Fast green		−84.6	−189.6
	Methylene blue		−31.0	−59.1
	Basic fuchsin		+21.35	+173.83
[19]	Mn^{2+}	Kaolinite	+36.73	+101
	Co^{2+}		+21.52	+54
	Ni^{2+}		+37.27	+107
	Cu^{2+}		+39.52	+117
[23]	Malachite green	Waste slurry	+10.87	+134
		Blast furnace slag	+18.70	+163
[24]	Pb^{2+}	Red mud	−85.94	−208
	Cr^{6+}		−78.50	−183
[25]	Cd^{2+}	Baggage fly ash	+11.74	+22.81
	Ni^{2+}		+15.41	+22.32
[26]	Zn^{2+}	Baggage fly ash	−76.83	−197.95
[27]	Cd^{2+}	Red mud	−85.94	−210
	Zn^{2+}		−78.5	−180
[28]	Pb^{2+}	Baggage fly ash	−11.44	−48.3
	Cr^{6+}		−14.24	−49.0
[34]	Pb^{2+}	China clay	−77.95	−238.46
		Wollastonite	−16.40	−47.92
[35]	Cr^{6+}	Bentonite	+5.62	+20
[36]	Sr^{2+}	Bentonite	+30.62	+140
[37]	Pb^{2+}	Lignin	+43.6	+230
	Zn^{2+}		+97.8	+430
[38]	Ni^{2+}	Orange peel	+53.89	+192.3
[39]	Pb^{2+}	Electric furnace slag	+24.15	+14.18
[40]	Cd^{2+}	Baggage	+9.08	+47
	Ni^{2+}		+13.64	+65
[41]	Zn^{2+}	Montmorillonite	+7.39	+6.39
	Cu^{2+}		+7.05	+9.09
[42]	Cr^{6+}	Barks	+89.835	Not given
[43]	Cr^{6+}	Leaves	+10.15	+43.96
[44]	Methylene blue	Fullers earth (FE) I	+158	+920
		FE II	+129	+1010
		FE III	+128	+1060
		FE IV	+127	+1080
[45]	Cu^{2+}	Blast furnace slag	+17.99	+108
	Ni^{2+}		+9.28	+91
[46]	Cd^{2+}	Blast furnace sludge	+12.04	+40
	Cr^{3+}		+21.59	+70
	Cu^{2+}		+16.40	+60
	Zn^{2+}		+30.87	+100
	Ni^{2+}		+28.26	+110
[47]	MB	Coconut shell fibers	+120.95	+292.1
	MO		+82.15	+168.9
[48]	Congo red	Coir pith	+7.705	+23.549

Note. The digits were rounded to a unified manner. Some numerical errors listed in literature were corrected in this table.

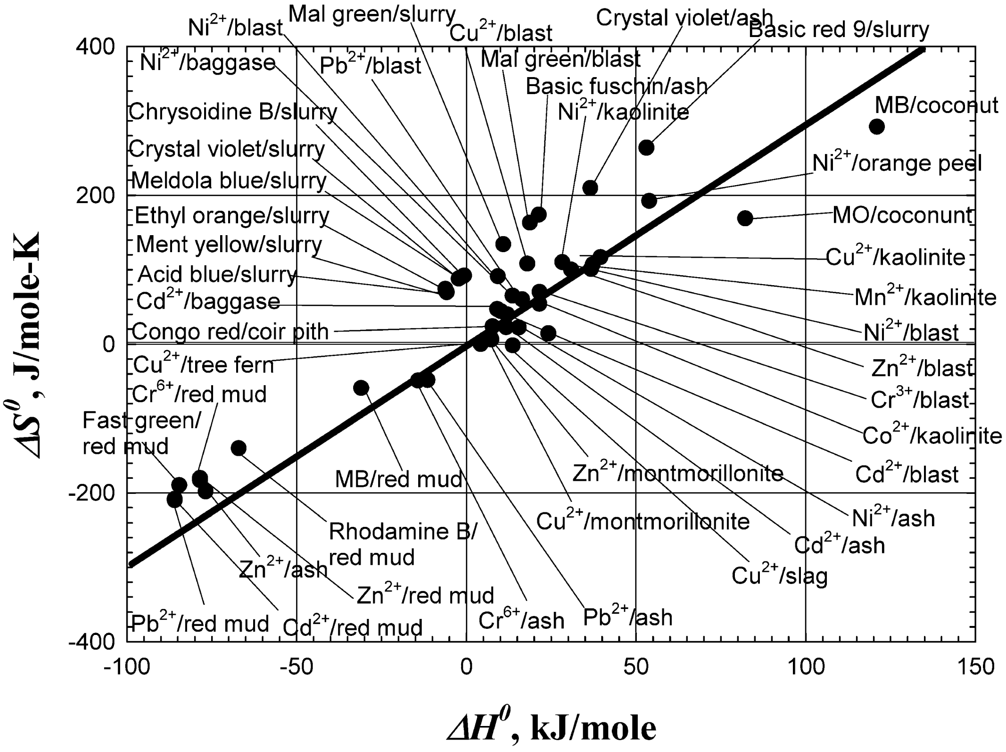

Fig. 1. The enthalpy–entropy compensation plot for low-cost adsorbent studies. Data listed in Table 1.

on the positive entropy change data listed in Table 1, some water structural break-down in the adsorption process can be expected.

Fig. 1 illustrates the thermodynamic data gathered in the low-cost works (Table 1). The figure displayed an apparent enthalpy–entropy compensation effect. The slope of this curve yields $1/T_C$, giving $T_C = 393$ K (120 °C). However, most adsorbates examined in the low-cost adsorbent studies are hydrophilic in nature. Since the thermodynamic parameters were evaluated from very different adsorbent/adsorbate combinations, it is not reasonable to note a universal correlation between the corresponding enthalpy change and entropy change following adsorption. An artifact is likely the cause for the noted enthalpy–entropy compensation phenomenon since both quantities were assessed through differentiation and subtraction of the same batch of adsorption isotherm data, but were derived from independent tests. Consequently, a large, positive ΔH^0 accompanied by a positive ΔS^0 and a negative ΔH^0 with a negative ΔS^0 all yield a nearly constant ΔG^0. The thermodynamic parameters reported in the open literature were thereby not at a rational basis for concluding whether the reported adsorption process is enthalpy or entropy driven. The higher "randomness" of the adsorbed surface/adsorbate system following adsorption proposed by Gupta et al. [17] is thereby highly contestable. Further studies should be conducted using an independent calorimetry test to confirm the reported thermodynamic parameters.

5. Conclusions

With adsorption isotherms, changes in Gibbs free energy, the isosteric heat of adsorption, and the changes in entropy could be assessed. However, an unlikely "enthalpy–entropy compensation" noted normally for transfer of hydrophobic substances between water and oil phases was observed when data from different sources were presented. Apparently such an occurrence is an artifact, indicating that the thermodynamic parameters reported in open literature may not be properly assessed. Caution should be paid to any conclusions thus drawn since the enthalpy and the entropy were not evaluated independently.

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