

Discussion

Comment on “The removal of phenolic compounds from aqueous solutions by organophilic bentonite”

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Abstract

Quotation and calculation accuracy can play a key role in a scientific paper. This comment mainly presents the possible errors in an article by Akçay et al., including the questionable expression of Polanyi potential (ε) in the Dubinin–Radushkevich (DR) equation used by the authors and the discrepancies in adsorption thermodynamic parameters study.

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1. Introduction

Adsorption removal of contaminants from aqueous solutions using organo-clays has been studied by many researchers over the past few years. Recently, we read an article entitled “The removal of phenolic compounds from aqueous solutions by organophilic bentonite” by Mehmet Akçay and Gülten Akçay in *Journal of Hazardous Materials* [1], which studied the adsorption of *p*-chlorophenol (*p*-CP) and *p*-nitrophenol (*p*-NP) on dodecylammonium bentonite (DDAB). This study is definitely informative and useful to researchers interested in this field. However, it has come to our attention that several possible errors have been found in this article. We will discuss these issues subsequently.

2. Discussion

2.1. DR equation

In Section 3.2 “The Freundlich, Dubinin–Radushkevich and Langmuir equations”, the DR equation was used to model adsorption isotherms. As to the expression of Polanyi potential (ε) related to equilibrium concentration, the authors stated

that ε is “equal to $RT \exp(1/C_e)$ ”, namely:

$$\varepsilon = RT e^{1/C_e} \quad (1)$$

We would like to point out that the expression above is not correct, which is also rarely observed in previous literature. Akçay et al. cited two papers [2,3] as references about DR equation in their article; however, it is puzzling to find that neither form of ε in these two references is identical with that of ε used by the authors. Moreover, it should be noted that the ε expression used in the paper by Lin et al. [2] is also not correct, which was presented as:

$$\varepsilon = RT \ln \left(\frac{1}{C_e} \right) \quad (2)$$

This incorrect form probably derived from another paper by Krishna et al. [4], in which the wrong form of ε was used with no citation.

The DR equation is an adaptation of the earlier Polanyi potential theory of adsorption [5–7]. This theory for the volume filling of micropores, known as TVFM, is based on the idea that the mechanism for adsorption of gas molecules in micropores is that of pore filling rather than a layer-by-layer formation of a film on the walls of the pores. The commonly used equation forms are as follows:

$$q_e = q_m \exp(-\beta\varepsilon^2) \quad (3)$$

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$$\varepsilon = RT \ln \left(\frac{P_s}{P} \right) \quad (4)$$

where q_e and q_m are the sorbed amounts at equilibrium and saturation, respectively; β is a constant related to sorption free energy; P_s is the vapour pressure of the adsorbate; and P is the equilibrium pressure.

The DR equation was first used in the adsorption of gases and vapours by microporous solids such as active carbons, synthetic zeolites and dehydrated inorganic gels [8–10], in lesser extent for the adsorption of solutes from aqueous solutions. Aqueous solution application was initially proposed by Manes and Wohleber [11,12]. By analogy to the vapours, the Polanyi potential ε for solutes in aqueous solutions is defined as [13–15]:

$$\varepsilon = RT \ln \left(\frac{S_w}{C_e} \right) \quad (5)$$

where S_w is the solubility of the solute and C_e is the equilibrium solute concentration. This form is commonly called S model.

Another form, known as C model, has also been presented for determination of the Polanyi potential in aqueous solution application, in which ε is correlated to [16]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

This model seems to be used more and more widely during the recent years, especially in the adsorption removal of metal ions, dyes and other organic contaminants onto solids from aqueous solutions [3,17–23].

According to the linear form of Eq. (3), the slope of the plot of $\ln q_e$ versus ε^2 gives β and that of the intercept yields the sorption capacity q_m . It means that the incorrect form of ε will definitely result in wrong values of DR model parameters calculated by the authors. From a scientific point of view, it is suggested that the authors check their references carefully and cite the original papers to avoid possible errors.

Besides the Polanyi potential ε mentioned above, we would like to give some suggestions about the analysis of the sorption mean free energy E (equal to $(2\beta)^{-1/2}$ [24]). It is known that Freundlich and Langmuir isotherms could not reveal the adsorption mechanism. The purpose of applying equilibrium data to the DR model is mainly to clarify the adsorption type and evaluate the nature of interaction between sorbate and solid. Based on the theory of DR model, the sorption space in the vicinity of the solid surface is characterized by a series of equipotential surfaces having same sorption potential. The sorption mean free

energy is the energy required to transfer one mole of the sorbate from infinity in solution to the surface of solid. The magnitude of sorption mean free energy E is widely used for estimating the type of adsorption [25–28].

In Akçay and Akçay's article, the authors did not give further discussions about the adsorption type based on the magnitude of the sorption free energy, although they concluded that the DR isotherm provided the best correlation for the adsorption of *p*-CP and *p*-NP onto organophilic bentonite. Actually, according to the values of E given by the authors, the adsorption of *p*-NP onto DDAB could be classified as an ion exchange process ($E = 8\text{--}16$ kJ/mol) [29,30]; whereas the authors concluded in Section 4 that both of the two adsorption processes are of physical nature. Hence, we suggest that the authors recalculate the values of related parameters and add this analysis part to their study.

2.2. Thermodynamic parameters calculation

In Section 3.4, thermodynamic parameters, including the Gibbs free energy changes ΔG° , enthalpy changes ΔH° and entropy change ΔS° , were evaluated for the adsorption of *p*-CP and *p*-NP onto DDAB. However, some values given by the authors are questionable. The following equations were used for calculation:

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

when substituting Eq. (8) into Eq. (7), one obtains the well-known equation in chemical thermodynamics:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

According to the authors' calculation method, the values of ΔG° were calculated using Eq. (7), while the values of ΔH° and ΔS° were determined from the slope and intercept of the Van't Hoff plot of $\ln K_d$ versus $1/T$ (Eq. (8)). These results are displayed in Table 1. In order to verify these values, we substituted the values of ΔH° and ΔS° into Eq. (9), and then the values of ΔG° could also be obtained, which are listed in Table 1 for comparison. It is observed that the magnitude of ΔG° obtained in this way is abnormally larger than that calculated using Eq. (7) by Akçay et al.

We suppose that there may exist some errors in Akçay and Akçay's experimental procedures or data processing. The two methods are both widely used in thermodynamic studies

Table 1
Comparison of the values of ΔG° calculated using different equations

Phenolics	Temperature (K)	K_d	ΔG° (kJ/mol) ^a	ΔH° (kJ/mol)	ΔS° (kJ/molK)	ΔG° (kJ/mol) ^b
<i>p</i> -CP	298	2.72	-2.479			-65.514
	308	2.62	-2.466	-36.906	0.096	-66.474
<i>p</i> -NP	298	14.65	-6.651			-280.802
	308	15.45	-7.010	-46.276	0.787	-288.672

^a Calculated using Eq. (7) $\Delta G^\circ = -RT \ln K_d$.

^b Calculated using Eq. (9) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

[31–34], in fact. Fundamentally speaking, the results should be generally the same, no matter which one is adopted. However, the inconsistency of them revealing in this article is completely out of the range of reasonable experimental error. We also suggest the authors to check every step in their study carefully and provide a reasonable result of the thermodynamic parameters.

In addition, the expression of the equilibrium partition constant K_d was given by Akçay et al. as follows:

$$K_d = \frac{q_e}{C_e} V \quad (10)$$

The authors just simply mentioned that Eq. (10) was used to calculate the value of K_d , without explaining what the parameter V represents or citing any other papers for references. According to the definition of equilibrium constant, K_d is expressed as [35–37]:

$$K_d = \frac{a_s}{a_e} = \frac{v_e q_e}{v_e C_e} \quad (11)$$

where a_s is the activity of adsorbed sorbate, a_e is the activity of sorbate in solution at equilibrium, v_s is the activity coefficient of adsorbed sorbate and v_e is the activity coefficient of sorbate in solution at equilibrium. In the dilute range of the solutions, the ratio of activity coefficients was assumed to be unity. As the concentration of sorbate in the solution decreases and approaches zero, the activity coefficient v approaches to unity. Then Eq. (11) can be reduced to the following form:

$$\lim_{q_e \rightarrow 0} \frac{a_s}{a_e} = \frac{q_e}{C_e} = K_d \quad (12)$$

The value of K_d can be directly calculated using adsorption equilibrium experimental data. Also it can be obtained by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e using a graphic method proposed by Khan and Singh [38]. According to this method, regression straight lines are fitted through the data points by the least-squares method, and their intersection with the vertical axis gives the value of K_d . This method is now widely adopted in adsorption studies [35–37,39–42]. It seems that the expression of K_d in Akçay and Akçay's article might be cited from unclear resources or might be calculated in an incorrect way, which results in unwanted discrepancies eventually.

3. Conclusion

As a research paper, its contribution exists not only in the originality and creativity but also in its continuity and development for research that follows [43]. Especially, quotation and calculation accuracy can play a key role in scientific study. When secondary references are used without checking whether there are any mistakes in their sources, it may lead to quotation errors or even serious mistakes. In addition, enough attention should be paid to the data processing and analysis to insure one against potential mistakes. We suggest that the authors check back the whole of their article and rectify any possible errors.

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