Comments & Replies

Comments on "Adsorption Equilibrium and Kinetics of Reactive Black 5 and Reactive Red 239 in Aqueous Solution onto Surfactant-Modified Zeolite" (Karadag, D.; Turan, M.; Akgul, E.; Tok, S.; Faki, A. *J. Chem. Eng. Data* 2007, *52*, 1615−1620)

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Most recently, Karadag et al. published a paper about adsorption of two anionic dyes, RB5 and RR239, from aqueous solution onto CTAB-zeolite.[1] In their report, it has been shown that the treatment of a mineral zeolite with CTAB and therefore modification of the zeolite surface has a drastic effect on adsorption of the mentioned anionic dyes. The effect of initial concentration, contact time, temperature, and pH has been investigated. Their study includes both equilibrium and kinetic data. Although the aim of their study is interesting, there are several important and basic comments on both the kinetics and equilibrium studies of their report.

(1) Kinetic Studies

The reported rate constant values, k, of the pseudo-second-order model in Tables 4 and 5 for RR239 and RB5 at initial dye concentration, C_0, of (60, 90, 120, and 150) $\text{mg}\cdot\text{L}^{-1}$ are (1.288, 1.073, 1.048, and 2.096) $\text{kg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ and (0.040, 0.134, 0.195, and 0.108) $\text{kg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, respectively. It is clear that there is not any trend in the k values by increasing the initial concentration of dye. Recently, it was shown theoretically by Azizian[2] that the adsorption rate constant of a pseudo-second-order model is a complex function of the initial concentration of solute. Although the theoretical derivation shows a complex function between k and C_0, it does not mean that there is not any trend in the k values by increasing C_0. Therefore, on the basis of a theoretical point of view, there should be a change with a trend in the k values by changing C_0 but maybe not a simple change like a linear form. For example, recently we showed experimentally that k decreases with an increase of C_0 but not in a linear form.[3] This pattern was also reported by Crini et al.[4] Therefore, on the basis of the above explanations, it seems that the reported k values by Karadag et al.[1] are doubtful because the trend of change of k with C_0 is meaningless.

They also reported the measured equilibrium amount of adsorbate, q_e, in Table 4 for RR239. For $C_0 = 150\ \text{mg}\cdot\text{L}^{-1}$ and pH = 5, by increasing temperature from (25 to 30) °C, q_e decreases sharply from (15.663 to 6.720) $\text{mg}\cdot\text{g}^{-1}$, but by further increasing the temperature to (35 and 40) °C, q_e decreases only partially to (6.510 and 6.175) $\text{mg}\cdot\text{g}^{-1}$, respectively.[1] Unfortunately, there is not any explanation in relation to these strange effects of temperature in their manuscript. In my opinion, these data are doubtful; otherwise it will be interesting for the authors explain it. The same strange pattern is reported in Table 5 for RB5 ($C_0 = 150\ \text{mg}\cdot\text{L}^{-1}$, pH = 5) where for temperatures of (25, 30, 35, and 40) °C the q_e values are (6.666, 2.975, 2.666, and 2.332) $\text{mg}\cdot\text{g}^{-1}$, respectively.

The pseudo-second-order model has been used for kinetic modeling of experimental data by the authors, and the calculated values of q_e by this model were listed in Tables 4 and 5. As can be seen in these tables, the agreement between experimental and calculated q_e values at temperatures (30, 35, and 40) °C are very poor, and in all cases the difference between experimental and calculated values is more than 100 % (for example $q_e = 6.720\ \text{mg}\cdot\text{g}^{-1}$ and $q_{e,\text{calcd}} = 15.526\ \text{mg}\cdot\text{g}^{-1}$, Table 4). Therefore, if the reported data in Tables 4 and 5 are correct, then it can be concluded that modeling their kinetic data with a pseudo-second-order model is not suitable. Although there is not any agreement between the reported experimental and calculated q_e values, surprisingly the authors wrote that *"The pseudo-second-order kinetic model agrees very well with the dynamic behavior for the adsorption of dyes RR239 and RB5 onto CTAB-zeolite under several different dye concentrations, temperatures, and pH values"*.[1]

As presented in Figure 4 for adsorption kinetics of RR239 at each concentration, there are six experimental data points, but as presented in the Supporting Information (Figure S5), only five experimental data have been used for fitting of experimental data to the pseudo-second-order model (t/q vs t plot). There is not any explanation in their text or any scientific reason for deleting one of the experimental data in Figure S5.

In my recent publication, it has been shown that for modeling of adsorption kinetics the q_t data at the initial period of adsorption are very important and the absence of initial q_t data can lead to incorrect kinetic modeling.[5] In Figures 4 and 5, and at each concentration, among the six kinetic data, q_t, five of them are very close to the equilibrium value, q_e.[1] In my opinion, these data are not sufficient for kinetic modeling, and for correct modeling, they have to measure and apply the initial q_t data (q_t data at $t < 2$ min for their systems) as well.

(2) Equilibrium Studies

As presented in Figures S1, S2, S3, and S4 (in Supporting Information), the authors used four experimental equilibrium data for fitting with the Langmuir model and five experimental equilibrium data with the Freundlich model and then compared the results of fitting (Table 2). On the fourth page of the manuscript, they wrote that "*the Freundlich model exhibited a slightly better fit than the Langmuir model*".[1] For comparison of fitting of two different models, the same experimental data

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(including the same number of experimental data points) should be used. So, in my opinion, their comparison for fitting of the Langmuir and Freundlich models is not correct.

Although for fitting of experimental data with the Langmuir model a nonlinear fitting method is the best,[6–8] the following linear form of the Langmuir isotherm

$$C_e/q_e = C_e/q_{max} + (1/q_{max}K_L) \tag{1}$$

is better for fitting than the following linear equation[7,8] that has been used by Karadag et al.[1]

$$1/q_e = 1/q_{max} + (1/q_{max}K_L)(1/C_e) \tag{2}$$

So it is recommended to apply nonlinear fitting or at least eq 1 instead of eq 2.

On the fifth page of their manuscript, they defined the equilibrium constant, $K_c = C_{Ae}/C_e$, and on the same page they wrote "*The* $q_{e,calcd}$ *values of the pseudo-second-order model in Tables 4 and 5 were used to obtain* C_{Ae} *and* C_e". The main question here is why they used the $q_{e,calcd}$ values of the pseudo-second-order model for calculation of C_{Ae} and C_e when the experimental q_e data were available? Also, since the agreement between the experimental q_e and calculated $q_{e,calcd}$ is very poor (see Tables 4 and 5), all of the obtained thermodynamic parameters (Table 6) are doubtful.

In closing, I believe that in the Karadag et al. report[1] both the equilibrium and kinetics experimental data are not sufficient for correct and good modeling, and they have to repeat their experiments several times (to reduce errors) with a higher number of data points and reanalyze their data.

Literature Cited

(1) Karadag, D.; Turan, M.; Akgul, E.; Tok, S.; Faki, A. Adsorption Equilibrium and Kinetics of Reactive Black 5 and Reactive Red 239 in Aqueous Solution onto Surfactant-Modified Zeolite. *J. Chem. Eng. Data* **2007**, *52*, 1615−1620.

(2) Azizian, S. Kinetic Models of Sorption: a Theoretical Analysis. *J. Colloid Interface Sci.* **2004**, *276*, 47.

(3) Azizian, S.; Yahyaei, B. Adsorption of 18-Crown-6 from Aqueous Solution on Granular Activated Carbon: a Kinetic Modeling Study. *J. Colloid Interface Sci.* **2006**, *299*, 112.

(4) Crini, G.; Peindy, H. N.; Gimbert, F.; Robert, C. Removal of C.I. Basic Green 4 (Malachite green) from Aqueous Solutions by Adsorption Using Cyclodextrin-based Adsorbent: Kinetic and Equilibrium Studies. *Sep. Purif. Technol.* **2007**, *53*, 97.

(5) Azizian, S. A Novel and Simple Method for Finding the Heterogeneity of Adsorbents on the Basis of Adsorption Kinetic Data. *J. Colloid Interface Sci.* **2006**, *302*, 76.

(6) Persoff, P.; Thomas, J. F. Estimating Michaelis-Menten or Langmuir Isotherm Constants by Weighted Nonlinear Least-Squares. *Soil Sci. Soc. Am. J.* **1998**, *52*, 886.

(7) Kumar, K. V.; Sivanesan, S. Isotherms for Malachite Green onto Rubber Wood (Hevea Brasiliensis) Sawdust: Comparison of Linear and Non-Linear Methods. *Dyes Pigments* **2007**, *72*, 124.

(8) Azizian, S.; Haerifar, M.; Basiri-Parsa, J. Extended Geometric Method: a Simple Approach to Derive Adsorption Rate Constants of Langmuir-Freundlich Kinetics. *Chemosphere* **2007**, *68*, 2040.

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