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Comments on "Adsorption of methylene blue and Cd(II) onto maleylated modified hydrochar from water"

To the Editor:

Recently, the above-cited paper (hereafter also named as 'the original paper') was published in this journal by Li *et al.* (2019). But even though the objective of the paper tends to be ambitious, some shortfalls limit the scientific value of this study. Indeed, due to a long-time experience in adsorption studies, both as an author and reviewer, I consider that several parts in the modeling methods and their subsequent discussions should be reconsidered.

In the scientific literature, some authors used the linear regression method to calculate the parameters of kinetic models and isotherm models; this is the case for the present original paper (Li *et al.*, 2019), where pseudo-first order (PFO) and pseudo-second order (PSO) kinetics equations are written as:

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2} \quad (2)$$

and also, with Langmuir and Freundlich isotherm equations as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{K_L \cdot Q_0} \quad (3)$$

$$\mathrm{Ln}q_e = \mathrm{Ln}K_F + (1/n).\mathrm{Ln}C_e \quad (4)$$

Indeed, several studies (among others: Badertscher and Pretsch, 2006; Barrow, 2008; Simonin, 2016) have demonstrated that non-linear regression is more appropriate to obtain parameters of kinetic and isotherm models than linear regression. This is because transformations of non-linear equations to linear forms implicitly alter their error structure and may also violate the error variance and

normality assumptions of standard least-squares. In this setting, non-linear method provides a mathematically rigorous method for determining model parameter values; fortunately, we all have now easy access to computer programs with non-linear least-squares (NLLS) adjustments, to be applied in the present case in place of linear regression analyses. Moreover, it is also well known that different linearization equations can result in different model parameters.

This is why I suggest that the parameters given in the original Tables 1 and 2 should be recalculated under NLLS method. Then, the authors could compare their fitting results with these non-linear ones and discuss the possible differences.

On an other hand, thermodynamic calculations have to be applied with due caution. Firstly, one should always remember that in the thermodynamic relationships given by Li *et al.* (2019) as:

$$\Delta G° = - RT \, \mathrm{Ln} K_L \quad (5)$$

$$\mathrm{Ln} K_L = (\Delta S°/R) - (\Delta H°/RT) \quad (6)$$

one can only take the logarithm of a dimensionless parameter! Moreover, when calculating the equilibrium constant, the only concentration unit should be mol/L (not mg/L or any other) to take the logarithm of the so-called ‘thermodynamic equilibrium constant’, whose (unitless) numerical value is then the same as that of the so-called practical constant from mol/L concentration units, taking into account the standard state $C°$ = 1 mol/L. Although this should be a well-known topic, it is too often forgotten; for recent discussions, one can read the following references: Salvestrini *et al.*, 2014; Zhou and Zhou, 2014; Tran *et al.*, 2017. Thus, the data given in original Table 4 have probably no real significance and they should be recalculated.

In the specific case of MB adsorption, one had to replace the Langmuir adsorption constant K_L by calculating $K_L°$ the (dimensionless) thermodynamic Langmuir constant for the adsorption process. To do this, the original authors should use the equation:

$$K_L° = K_L \text{ (L/mg)} \times 1{,}000 \text{ (mg/g)} \times M_{MB} \text{ (g/mol)} \times C° \text{ (mol/L)} \quad (7)$$

(cited as equation (12) in Mouni *et al.*, 2018) where M_{MB} = 319.85 g/mol is the MB molar mass, and the factor 1,000 allows converting g to mg. Then, they can calculate correct thermodynamic parameters according to the present equations (8) and (6):

$$\Delta G° = - RT \, \mathrm{Ln} K_L° \qquad (8)$$

and draw a new Figure S3 (as presented in the original Supplementary file).

Several other confusions can alter the impact of the original study, as detailed below.

The term ‘heavy metal’, here attributed to Cadmium (6 appearances in the full text) is not really appropriate, and one should commonly replace it by ‘trace element/metal’ or by ‘potentially toxic element/metal’; for a useful reference on this subject, one can read the recent discussion by Pourret (2018) and references therein. The old references to original Langmuir (1916) and Freundlich (1906) papers are not appropriate nowadays: it is certainly better to cite a recent review on the subject, for example Tran *et al.* (2017).

The fact that experimental data can be satisfactorily represented with a given model equation is not any proof or any prediction of a given controlling step (kinetics) or of a given adsorption mechanisms (isotherms, thermodynamics). For example, Li *et al*. (2019) stated in their subsection 3.3 ‘that the pseudo-2nd-order equation was better fitted to depict the MB and Cd(II) adsorption onto CFHC than pseudo-1st order kinetic equation. This indicated the chemisorption was the dominant adsorption mechanism’, but here the experimental data were only represented with empirical mathematical models. Moreover, recently Wang and Giammar (2019) have drawn our attention to the fact that in many cases the homogeneous surface diffusion model (HSDM) will give better insight on the adsorption mechanism in spite of correct fitting with a PSO model. Similarly, with reference to Salvestrini *et al.* (2014) the comments about the sign and the significance of the thermodynamic parameters should be moderated. For example, Li et al. (2019) claimed in their

subsection 3.5 a direct correlation between endothermic values and thermodynamic spontaneity; in fact, the species at equilibrium were not in their standard state (in the thermodynamic sense).

It is of course important to emphasize that this *Letter to the Editor* should not bring discredit upon the work by Li *et al.* (2019). The originally published article is really interesting and provides significant contribution to the scientific knowledge; however, as indicated above some corrections should be conducted and published by the original authors. The present author hopes that these comments will be read in the spirit in which they are intended; that is, constructive criticism to produce a better final scientific paper, and to avoid the dissemination of undesirable and overlooked mistakes into the scientific literature, as discussed for example in the recent critical review by Tran *et al.* (2017).

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