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Letter to the Editor: Comments on “Adsorption of methylene blue and Cd(II) onto maleylated modified hydrochar from water”

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1 Letter to the Editor

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5 **Comments on “Adsorption of methylene blue and Cd(II) onto maleylated modified**
6 **hydrochar from water”**

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19 **Comments on “Adsorption of methylene blue and Cd(II) onto maleylated modified**
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23 *To the Editor:*

24

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

30

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

35
$$\text{Ln}(q_e - q_t) = \text{Ln}q_e - k_1t \quad (1)$$

36
$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2} \quad (2)$$

37 and also, with Langmuir and Freundlich isotherm equations as:

38
$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{K_L \cdot Q_0} \quad (3)$$

39
$$\text{Ln}q_e = \text{Ln}K_F + (1/n) \cdot \text{Ln}C_e \quad (4)$$

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

44 normality assumptions of standard least-squares. In this setting, non-linear method provides a
45 mathematically rigorous method for determining model parameter values; fortunately, we all have
46 now easy access to computer programs with non-linear least-squares (NLLS) adjustments, to be
47 applied in the present case in place of linear regression analyses. Moreover, it is also well known
48 that different linearization equations can result in different model parameters.
49 This is why I suggest that the parameters given in the original Tables 1 and 2 should be recalculated
50 under NLLS method. Then, the authors could compare their fitting results with these non-linear
51 ones and discuss the possible differences.

52

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

$$55 \Delta G^\circ = -RT \ln K_L \quad (5)$$

$$56 \ln K_L = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (6)$$

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

65 In the specific case of MB adsorption, one had to replace the Langmuir adsorption constant K_L by
66 calculating K_L° the (dimensionless) thermodynamic Langmuir constant for the adsorption process.

67 To do this, the original authors should use the equation:

$$68 K_L^\circ = K_L (\text{L/mg}) \times 1,000 (\text{mg/g}) \times M_{\text{MB}} (\text{g/mol}) \times C^\circ (\text{mol/L}) \quad (7)$$

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

$$72 \quad \Delta G^\circ = -RT \ln K_L^\circ \quad (8)$$

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

74

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

76 The term ‘heavy metal’, here attributed to Cadmium (6 appearances in the full text) is not really
77 appropriate, and one should commonly replace it by ‘trace element/metal’ or by ‘potentially toxic
78 element/metal’; for a useful reference on this subject, one can read the recent discussion by [Pourret
79 \(2018\)](#) and references therein. The old references to original [Langmuir \(1916\)](#) and [Freundlich
80 \(1906\)](#) papers are not appropriate nowadays: it is certainly better to cite a recent review on the
81 subject, for example [Tran et al. \(2017\)](#).

82 The fact that experimental data can be satisfactorily represented with a given model equation is not
83 any proof or any prediction of a given controlling step (kinetics) or of a given adsorption
84 mechanisms (isotherms, thermodynamics). For example, [Li et al. \(2019\)](#) stated in their subsection
85 3.3 ‘that the pseudo-2nd-order equation was better fitted to depict the MB and Cd(II) adsorption
86 onto CFHC than pseudo-1st order kinetic equation. This indicated the chemisorption was the
87 dominant adsorption mechanism’, but here the experimental data were only represented with
88 empirical mathematical models. Moreover, recently [Wang and Giammar \(2019\)](#) have drawn our
89 attention to the fact that in many cases the homogeneous surface diffusion model (HSDM) will give
90 better insight on the adsorption mechanism in spite of correct fitting with a PSO model. Similarly,
91 with reference to [Salvestrini et al. \(2014\)](#) the comments about the sign and the significance of the
92 thermodynamic parameters should be moderated. For example, [Li et al. \(2019\)](#) claimed in their

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

95

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

104

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