Comments on "Aqueous-phase methylene blue (MB) dye removal by mixture of eucalyptus bark (EB) biomass and kaolin clay (KC) adsorbents: kinetics, thermodynamics, and isotherm modeling"

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Jean-Claude BOLLINGER

Université de Limoges, Faculté des Sciences & Techniques, Groupement de Recherches Eau Sol Environnement (GRESE), 87060 Limoges, France

Corresponding author address: jean-claude.bollinger@unilim.fr (J.-C. Bollinger)

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To the Editor:
Recently, the above-named paper (hereafter named as ‘the original paper’) was published in this journal by Tan and Sen [1]. But, even though the objective of the paper pretends to be ambitious, some shortfalls limit the scientific value of this study. Indeed, due to a long-time experience in adsorption studies, either as author or as 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 [1], with pseudo-first order (the so-called Lagergren equation) and pseudo-second order kinetics equations (3) and (4), and also with Freundlich and Langmuir isotherm equations (9), (10) and (11). Indeed, several studies (among others: [2, 3, 4]) have demonstrated that non-linear regression is more appropriate to obtain parameters of kinetic models 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.
This is why Figures 7, 10, 11 and 12 should be deleted, and that the parameters given in Tables 1 and 4 should be recalculated under NLLS method, in order to correct the possible errors introduced by the application of wrong model equations.

An other point should be notified to the authors of the original paper: thermodynamic calculations have to be applied with due caution. Firstly, one should always remember that in the thermodynamic relationships such as equation (8) in [1], 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 of 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, this is too often forgotten; for recent discussions, read references [5, 6, 7].
In the specific case of MB adsorption, in order to calculate the (dimensionless) ‘thermodynamic’ Langmuir constant $K_L°$ for the adsorption process, the original authors can also make use of the equation:
$K_L° = K_L$ (L/mg) × 1,000 (mg/g) × M_{MB} (g/mol) × C° (mol/L)
(cited as equation (12) in reference [8]) where M_{MB} = 319.85 g/mol is the MB molar mass, and the factor 1,000 allows converting g to mg.

Several other confusions can alter the impact of the original study:
- the Lagergren pseudo-first order kinetic equation was not introduced in 1966 by the cited reference # 20 in [1], but as soon as 1898 what is detailed in a seminal paper by Ho [9]
- in equation (8), the solid-phase concentration at equilibrium q_e should of course be given in mg/g, not mg/L

- one cannot describe ΔG° as ‘the Gibb's energy change’ as printed just before equation (7), but it is ‘the Gibbs free energy’.

It is of course important to emphasize that this Letter to the Editor will not bring discredit upon the work by Tan and Sen [1]. The originally published article is really interesting and possesses substantial contribution to knowledge gap; however, some corrections should be conducted and published by the original authors. The present author hope 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 try to contribute to abolish the dissemination of undesirable and overlooked mistakes into the scientific literature, as detailed elsewhere [7].

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