



Research paper

ISOT_Calc: A versatile tool for parameter estimation in sorption isotherms

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ABSTRACT

Geochemists and soil chemists commonly use parametrized sorption data to assess transport and impact of pollutants in the environment. However, this evaluation is often hampered by a lack of detailed sorption data analysis, which implies further non-accurate transport modeling. To this end, we present a novel software tool to precisely analyze and interpret sorption isotherm data. Our developed tool, coded in Visual Basic for Applications (VBA), operates embedded within the Microsoft Excel™ environment. It consists of a user-defined function named ISOT_Calc, followed by a supplementary optimization Excel macro (Ref_GN_LM). The ISOT_Calc function estimates the solute equilibrium concentration in the aqueous and solid phases (C_e and q , respectively). Hence, it represents a very flexible way in the optimization of the sorption isotherm parameters, as it can be carried out over the residuals of q , C_e , or both simultaneously (i.e., orthogonal distance regression). The developed function includes the most usual sorption isotherm models, as predefined equations, as well as the possibility to easily introduce custom-defined ones. Regarding the Ref_GN_LM macro, it allows the parameter optimization by using a Levenberg-Marquardt modified Gauss-Newton iterative procedure. In order to evaluate the performance of the presented tool, both function and optimization macro have been applied to different sorption data examples described in the literature. Results showed that the optimization of the isotherm parameters was successfully achieved in all cases, indicating the robustness and reliability of the developed tool. Thus, the presented software tool, available to researchers and students for free, has proven to be a user-friendly and an interesting alternative to conventional fitting tools used in sorption data analysis.

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1. Introduction

Fate, reactivity and bioavailability of pollutants in the environment are mainly governed by sorption phenomena, which exemplify the transfer of a solute from a mobile phase (liquid or gaseous) to a sorbent solid phase. Thus, a detailed characterization of the sorption process is essential to evaluate pollutant transport and potential risk for the environment (Boxall et al., 2003; Kümmeler, 2004). Sorption behavior at different solute concentration levels is commonly assessed by constructing a sorption isotherm at equilibrium conditions. So the solute sorbed concentration (q) is represented as a function of the remaining aqueous concentration

(C_e). Accordingly, the slope of each point in a sorption isotherm stands for the solid-liquid distribution coefficient (K_d , Eq. (1)), which provides the solid retention magnitude at a given solute concentration (q or C_e):

$$K_d = \frac{q}{C_e} \quad (1)$$

Thus, the choice of an appropriate sorption isotherm is critical for accurate contaminant transport predictions (Hinz, 2001). Nevertheless, the sorption parametrization in most cases is often imprecise because of the complex nature of the sorbent (i.e., soil), along with a misuse of simple equations to attempt the data description. If the isotherm equation choice is inappropriate, inaccurate results will lead to underestimate or overestimate the potential adverse environmental effects. Eventually, this will negatively influence on the risk assessment studies needed for developing and implementing future regulations.

There are different equations which describe the sorption

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isotherms (Giles et al., 1974; Goldberg, 2005; Hinz, 2001; Kinniburgh, 1986; Limousin et al., 2007), being the Langmuir and Freundlich models the most used in the environmental sciences:

$$q = S_T \cdot \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

$$q = K_F \cdot C_e^N \quad (3)$$

In the Langmuir equation (Eq. (2)), S_T indicates the maximum sorption capacity, and K_L is the Langmuir affinity parameter. On the other hand, K_F and N stand for the Freundlich affinity parameter and the exponential unitless term (Eq. (3)), respectively. The determination of these parameters from the experimental data pairs C_e/q (usually obtained by batch equilibrium methods) is straightforward in the cited models, as the Eqs. (2) and (3) can be transformed to give linear functions that can be analyzed by ordinary least-squares (OLS), as:

$$\frac{1}{q} = \frac{1}{S_T} \cdot \frac{1 + K_L \cdot C_e}{K_L \cdot C_e} = \frac{1}{S_T} + \frac{1}{S_T \cdot K_L} \cdot \frac{1}{C_e} \quad (4)$$

$$\log(q) = \log(K_F) + N \cdot \log(C_e) \quad (5)$$

However, when three or more parameter isotherm equations are needed to describe data, the fitting of the model to experimental data requires the use of iterative non-linear least-squares methods (NLLS) (Ho et al., 2002). Furthermore, it is widely accepted that linearization of isotherm equations, when applicable, may lead to misleading results (Ho, 2004; Ho et al., 2005; Motulsky and Christopoulos, 2004). To date, there are several alternatives to conduct this data treatment. The possibilities range from specific programs, such as ISOFIT (Matott and Rabideau, 2008), to popular spreadsheets as MS-Excel – using the Solver add-in (Bolster and Hornberger, 2007) – or multipurpose statistical/mathematical packages; e.g., Origin (OriginLab Corp., Northampton, MA, USA), KaleidaGraph (Synergy Software, Reading, PA, USA), Matlab (Mathworks, Natick, MA, USA) or SigmaPlot (Systat Software Inc., San Jose, CA, USA) (Li et al., 2009; Sathishkumar et al., 2007; Xia and Pignatello, 2001).

In general, NLLS methods are based on the minimization of an objective function (U), which depends on a set of parameters to be optimized. U is defined as the sum of squared residual errors (e_i), obtained from the differences between an experimental magnitude (e.g., $q_{exp,i}$), and the corresponding values calculated on the basis of a guessed model (e.g., $q_{calc,i}$). For better results, the use of statistical weights (w_i) is recommended in the literature (Kinniburgh, 1986):

$$U = \sum_{i=1}^n w_i \cdot (e_i)^2 = \sum_{i=1}^n w_i \cdot (q_{exp,i} - q_{calc,i})^2 \quad (6)$$

where $q_{exp,i}$ and $q_{calc,i}$ indicate the experimental and calculated sorbed concentrations for each i data point, being n the number of data points. The $q_{calc,i}$ values are determined from the experimental (measured) equilibrium solute concentration in the liquid phase, the guessed isotherm type and the corresponding parameters. For instance, in the Freundlich isotherm (Eq. (3)), $q_{calc,i}$ takes the following form:

$$q_{calc,i} = K_F \cdot C_{exp,i}^N \quad (7)$$

In an iterative NLLS procedure, the system is solved when a minimum in the objective function is attained (U_{min}), providing the parameters that correspond to this U_{min} . To decide which type of isotherm best describes a given system, the user can try different isotherm equations, and apply different statistical tests over the results obtained. For example, the isotherm giving the lower

U_{min} could be considered as the best, although other factors should be taken into account, as the number of parameters to be optimized and their corresponding estimated standard deviations.

A different approach is proposed in this work, as we have developed a new function (ISOT_Calc) which calculates the theoretical solute equilibrium concentrations in the solid and liquid phases (q_T and $C_{e,T}$), for a given isotherm type (together with the corresponding parameters) and the experimental conditions (mass of sorbent, liquid phase volume and initial solute concentration). This is achieved by solving the mass-balance equation for each equilibrium point. Hence, the objective function to be minimized can be defined on the basis of residuals in C_e , q , or both simultaneously. The function has been developed as a user-defined function in the MS-Excel spreadsheet, and contains the most common isotherm models as predefined equations. Moreover, “custom isotherms” can also be introduced by the user. The optimization of the isotherm parameters can be carried out by using the Solver tool included in Excel, or by an Excel macro, also developed in this work (Ref_GN_LM), which is based on the iterative Gauss-Newton Levenberg-Marquardt optimization algorithm.

The described procedure has been successfully tested with several sorption data described in the literature. Specially, in the Excel versions corresponding to MS-Office 2007, 2010 and 2013 for MS-Windows, as well as MS-Office 2011 for Apple Mac OSX (Further details about the software, including requirements and availability can be found in [Supplementary material of the Appendix A](#)). The results have been compared with those given in the literature, as well with those obtained by the non-commercial program ISOFIT (Matott and Rabideau, 2008), and by the graphing/data analysis commercial program KaleidaGraph (Synergy Software).

2. Tool structure and mathematical background

2.1. Mass-balance solution

The main core of the developed implementation is an Excel user-defined function named “ISOT_Calc”, written in MS Visual Basic for Applications (VBA), as the optimization routine described below. It solves the mass-balance equations by a standard iterative Newton algorithm (Demidovich and Maron, 1981), which calculates the theoretical solute concentration in both solid and liquid phases (q_T and $C_{e,T}$, respectively) from a given isotherm equation, guessed parameters and experimental conditions.

For illustration purposes, we will consider the case of a system which describes a Freundlich-type isotherm. The initial experimental conditions in this system are: a volume of liquid phase (V), an initial solute concentration (C_0), and a sorbent mass (M_s). After equilibration, the remaining measured concentration in the liquid phase is $C_{e,exp}$. The sorbed concentration is calculated as:

$$q_{exp} = V \cdot \frac{C_0 - C_{e,exp}}{M_s} \quad (8)$$

On the other hand, the calculated mass-balance using the Freundlich model (Eq. (3)) can be written as:

$$V \cdot C_0 = V \cdot C_{e,T} + M_s \cdot q_T = V \cdot C_{e,T} + M_s \cdot K_F \cdot C_{e,T}^N \quad (9)$$

Where V , C_0 and M_s are the independent variables, with known values; K_F and N are the guessed parameter set of the model, and $C_{e,T}$ is the value to be calculated. This value can be determined by the iterative Newton method, defining a function which is equal to zero when the system is solved. This function, named F , is based on the difference between the experimental and calculated mass-balances:

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