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 ExcelTM 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

25 usual sorption isotherm models, as predefined equations, as well as the possibility to easily
26 introduce custom-defined ones. Regarding the Ref_GN_LM macro, it allows the parameter
27 optimization by using a Levenberg-Marquardt modified Gauss-Newton iterative procedure. In
28 order to evaluate the performance of the presented tool, both function and optimization macro
29 have been applied to different sorption data examples described in the literature. Results showed
30 that the optimization of the isotherm parameters was successfully achieved in all cases,
31 indicating the robustness and reliability of the developed tool. Thus, the presented software tool,
32 available to researchers and students for free, has proven to be a user-friendly and an interesting
33 alternative to conventional fitting tools used in sorption data analysis.

34 **Keywords**

35 Sorption; Isotherm parameters; Nonlinear Least-squares; Excel; Orthogonal Distance
36 Regression; Levenberg-Marquardt

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50 1. Introduction

51 Fate, reactivity and bioavailability of pollutants in the environment are mainly governed by
52 sorption phenomena, which exemplify the transfer of a solute from a mobile phase (liquid or
53 gaseous) to a sorbent solid phase. Thus, a detailed characterization of the sorption process is
54 essential to evaluate pollutant transport and potential risk for the environment (Boxall et al.,
55 2003; Kümmerer, 2004). Sorption behavior at different solute concentration levels is commonly
56 assessed by constructing a sorption isotherm at equilibrium conditions. So the solute sorbed
57 concentration (q) is represented as a function of the remaining aqueous concentration (C_e).
58 Accordingly, the slope of each point in a sorption isotherm stands for the solid-liquid
59 distribution coefficient (K_d , Eq. 1), which provides the solid retention magnitude at a given
60 solute concentration (q or C_e):

$$61 \quad K_d = \frac{q}{C_e} \quad (1)$$

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

69 There are different equations which describe the sorption isotherms (Giles et al., 1974;
70 Goldberg, 2005; Hinz, 2001; Kinniburgh, 1986; Limousin et al., 2007), being the Langmuir and
71 Freundlich models the most used in the environmental sciences:

$$72 \quad q = S_T \cdot \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

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

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 Eq. 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 literature⁴:

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

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:

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

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

$$147 \quad V \cdot C_0 = V \cdot C_{e,T} + M_s \cdot q_T = V \cdot C_{e,T} + M_s \cdot K_F \cdot C_{e,T}^N \quad (9)$$

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

$$153 \quad F = V \cdot C_0 - (V \cdot C_{e,T} + M_s \cdot K_F \cdot C_{e,T}^N) \quad (10)$$

154 This equation is solved by successive approximations of $C_{e,T}$, being the value in the $n+1$
 155 iteration calculated from the previous one and the corresponding values of the F function and its
 156 derivative with respect to $C_{e,T}$. However, in order to avoid negative concentration values in the
 157 iterative process, the derivatives are taken respect to $\ln(C_{e,T})$. In this way, the value computed in
 158 the $n+1$ iteration is obtained as:

$$159 \quad \ln(C_{e,T,n+1}) = \ln(C_{e,T,n}) - \frac{F_{(n)}}{F'_{\ln(n)}} \quad (11)$$

160 Where $F'_{\ln}$ indicates the derivative of the F function with respect to $\ln(C_{e,T})$. The exponential
 161 form of Eq. 11 gives the new value for $C_{e,T}$, which is always positive:

$$162 \quad C_{e,T,n+1} = \exp\{\ln(C_{e,T,n})\} = \frac{C_{e,T,n}}{\exp\{F_{(n)}/F'_{\ln(n)}\}} \quad (12)$$

163 As the developed function contains several isotherm types, the procedure uses numerical
 164 differentiation in order to maintain a reasonable length code. The iterative process ends when
 165 the difference between experimental and calculated mass-balances is lower than a tolerance
 166 limit; which has been established as $\leq 0.001\%$ relative difference. This takes about 4-10

167 iterations for each data point. The initial value used to start the iterative process is the total
168 concentration of the solute. This feature allows simulating theoretical isotherms without the
169 knowledge of the experimental solution equilibrium concentration ($C_{e,exp}$).

170 The developed function includes 11 predefined models corresponding to the most common
171 isotherms used in solid-liquid equilibrium studies (Czinkota et al., 2002; Goldberg, 2005; Hinz,
172 2001; Kinniburgh, 1986; Xia and Pignatello, 2001). Table A1, given in the Appendix A, shows
173 the predefined models together with the corresponding number of parameters. Moreover, we
174 have included the possibility to enter directly a user-defined isotherm (type 0) in a cell of the
175 spreadsheet. This is achieved by the inclusion of a parser runtime subroutine in the VBA code
176 (Volpi, 2003), by substitution of the literal cell text into the corresponding numerical values.
177 Regarding isotherm parameters, they must be written as "P(1), P(2),...", and the solute
178 concentration in liquid phase as "Ce". For example, a Freundlich isotherm introduced as user-
179 defined would take the form: "P(1)*Ce^P(2)" (without the quotation marks).

180 The algorithm described returns the expected $C_{e,T}$ as the primary result, along with q_T as an
181 intermediate calculation (see Eq. 9). In the Excel spreadsheet, both results can be easily
182 retrieved by using the 'Index' function. For example, a call to the function as
183 "`=INDEX(ISOT_Calc(B16:D16;$C$8:$C$9;11;$C$6),1)`" will return $C_{e,T}$. Nevertheless, if the
184 last number (the index) is changed from 1 to 2, the function will return q_T . The other terms in
185 the user function are:

- 186 • B16:D16; standing for cells containing the C_0 , V , M_s , respectively.
- 187 • \$C\$8:\$C\$9; representing the parameter set of the guessed isotherm model.
- 188 • 5; meaning the guessed isotherm equation. In this case corresponds to the Freundlich
189 model (Eq. 3).
- 190 • \$C\$6; corresponding to a "dummy" cell, used only in custom isotherms (type 0)

191 As ISOT_Calc requires a considerable amount of data input, a dialog box (developed using the
192 built-in VBA InputBox function) has been added to assists users (see Fig. 1).

193

194 **2.2. Optimization procedure**

195 One of the functions developed in this work consists of an optimization routine written as a
196 macro (named ref_ GN_LM), based on the Levenberg-Marquardt modification of the Gauss-
197 Newton iterative algorithm (Johnson and Faunt, 1992). In each iteration, the isotherm
198 parameters are shifted according with the expression:

$$199 \quad \{J^T J + \lambda \text{diag}(J^T J)\} \Delta P = J^T \text{Err} \quad (13)$$

200 Where J stands for the Jacobian matrix that contains, calculated by numerical differentiation,
201 the partial derivatives of the errors with respect to the parameters. ΔP is the vector containing
202 the shifts of parameters, λ is the Marquardt parameter and Err indicates a vector containing the
203 residual errors. The starting value for λ is set to 10, and it is decreased 10-fold each successful
204 iteration when the optimization process converges; if not, λ is set equal to the number of
205 consecutive non-convergence iterations. This procedure stops when the relative difference in the
206 objective function (e.g., Eq. 6) between two consecutive iterative cycles is less than 0.1% and
207 the Marquardt parameter is lower than 0.01. In any case, the maximum number of iterations is
208 limited to 20. To maintain similar magnitude orders of parameters during the refinement
209 procedure, they are changed internally to their corresponding natural logarithms. In addition,
210 this also avoids the possibility to obtain negative values. The routine allows estimating the
211 errors in the parameters from the residuals and the shifting matrix (Johnson, 2000).

212 Although this corresponds to a standard optimization procedure, this work also provides a
213 unique definition of the residuals regarding other procedures described in the introduction
214 section. As noted previously, the mass balance procedure calculates the data pairs ($C_{e,T}$ and q_T)
215 for each equilibrium point from the experimental conditions and guessed isotherm parameters.

216 This allows defining the residual errors in C_e , q , or distance (d) between the calculated and
 217 experimental points:

$$218 \quad \Delta C_{e,i} = C_{e,\text{exp},i} - C_{e,T,i} \quad \Delta q_i = q_{\text{exp},i} - q_{T,i} \quad (14)$$

$$219 \quad d_i = \sqrt{(C_{e,\text{exp},i} - C_{e,T,i})^2 + (q_{\text{exp},i} - q_{T,i})^2} = \sqrt{(\Delta C_i)^2 + (\Delta q_i)^2} \quad (15)$$

220 Differences in the definition of the errors are shown in Fig. 2. This figure represents a
 221 hypothetical isotherm with its experimental data points (symbolized as diamonds), together with
 222 a solid line which stands for the ISOT_Calc function calculated points from the Freundlich
 223 equation (Eq. 3). One data point is detailed in the zoomed in section, indicating the errors in q
 224 and C_e (Eq. 14) and the d distance between an experimental and a circle-shaped calculated point
 225 (Eq. 15). Additionally, Fig. 2 also shows the error (Δq_i) obtained by a conventional procedure
 226 (e.g., using the Freundlich model in Eq. 6).

227 Although the errors are calculated as described, the objective functions to be minimized in the
 228 optimization procedure use weighting factors to allow all data points to be equally significant.
 229 This is particularly interesting when dealing with pollutant sorption onto natural sorbents. As
 230 most environmentally relevant concentrations fall within the trace levels, accurate modeling in
 231 the lower region of the isotherm is crucial. Thus, the objective functions for minimization of the
 232 errors in C_e and q are calculated from the corresponding relative errors. This is equivalent to use
 233 weighting factors equal to the inverse of the squared measured values (e.g., $w_i = 1/(C_{e,\text{exp},i})^2$ or
 234 $w_i = 1/(q_{\text{exp},i})^2$):

$$235 \quad U_{C_e} = \sum_{i=1}^n \frac{1}{C_{e,\text{exp},i}^2} \Delta C_{e,i}^2 = \sum_{i=1}^n \left(\frac{\Delta C_{e,i}}{C_{e,\text{exp},i}} \right)^2 \quad (16)$$

$$236 \quad U_q = \sum_{i=1}^n \frac{1}{q_{\text{exp},i}^2} \Delta q_i^2 = \sum_{i=1}^n \left(\frac{\Delta q_i}{q_{\text{exp},i}} \right)^2 \quad (17)$$

On the other hand, the definition of residual errors as the distance between experimental and theoretical points allows an easy implementation of the orthogonal distance regression. This possibility, pointed by Poch and Villaescusa (2012), has been satisfactorily applied to theoretical Langmuir isotherms for determining the isotherm parameters. In fact, in a “classical” procedure for modeling sorption data, it is assumed that C_e is the independent variable (error-free), and the isotherm parameters are calculated in order to minimize the errors in the dependent variable (q). The orthogonal distance regression takes into account the errors in both variables (C_e and q), and the weighted objective function (U_d) to be minimized is defined as a combination of Eq. 16 and 17:

$$U_d = \sum_{i=1}^n \left\{ \left(\frac{\Delta C_{e,i}}{C_{e,\text{exp},i}} \right)^2 + \left(\frac{\Delta q_i}{q_{\text{exp},i}} \right)^2 \right\} \quad (18)$$

As the $C_{e,T,i}$ and $q_{T,i}$ values are directly obtained using the ISOT_Calc function, the calculation of the different objective functions (Eq. 16 to 18) is straightforward. Table A2 shows a possible arrangement of a worksheet, indicating the experimental data, the calculated $C_{e,T,i}$ and $q_{T,i}$ values and the individual errors.

The optimization of the isotherm parameters is an easy task using the macro ref_GN_LM. Once started, it requires the residual errors ($\Delta C_e / C_e$, for example), the parameters to be optimized, and a starting cell to print the results. The results include the final values of the parameters together with their estimated standard deviations –the standard deviation (SD) and relative standard deviation (RSD), respectively–. Moreover, they will also contain other statistical parameters, such as the sum of weighted squared residuals (Eq. 16, 17 or 18), the mean weighted square error (MWSE) and the root mean square error (RMSE):

$$MWSE = U / (n - p) \quad RMSE = \sqrt{MWSE} \quad (19)$$

Where p indicates the number of parameters refined and n stands for the number of experimental points. All these statistical values taken together, along with the estimated errors

261 in the isotherm parameters, are very useful to decide which isotherm equation fits better to a set
262 of experimental data points.

263 The use of the Solver function in the Excel spreadsheet allows another possible optimization of
264 the isotherm parameters. In this case, the user defines a cell containing the value of the objective
265 function (value to be minimized, corresponding to the sum of squared errors) and the parameters
266 to optimize. Although the results obtained are similar to those obtained with ref_GN_LM
267 macro, this latter is significantly faster. Moreover, as Solver function does not provide the
268 estimated errors of the optimized parameters, they should be calculated using another routine;
269 e.g., Solvstat for Excel (Billo, 2001).

270

271 **3. Results and discussion**

272 To test the calculation procedures, we have applied the described routines to determine the
273 isotherm parameters in several sorption examples found in the literature. In order to be able to
274 compare results, we have calculated the corresponding parameters by using the different
275 optimization possibilities included in the ISOT_Calc/Ref_GN_LM procedure (i.e., minimizing
276 U_{Ce} , U_q and U_d ; as described in Eqs. 16-18), and also by using the ISOFIT (Matott and
277 Rabideau, 2008) and KaleidaGraph (Synergy Software) programs. Both ISOFIT and
278 KaleidaGraph minimize the squared differences between q_{exp} and q_{calc} , this latter calculated after
279 the proposed isotherm equation and the experimental C_e values. To get comparable results, we
280 have used similar weighting factors ($w_i=1/(q_{exp,i})^2$) in both programs.

281 The first tested system (System I) corresponds to the sorption of tetracycline onto a natural
282 loamy soil (Teixidó et al., 2012). The 16 experimental data points are shown on the left side of
283 Fig. 3. The shape of the isotherm suggests a Langmuir-type isotherm, as indicated in the
284 reference. Results are given in Table 1 (as System I). They include the parameters for the tested
285 isotherm equations in each calculation mode, together with their estimated errors (SD values)
286 and MWSE values. In each case, the MWSE for the Freundlich model is 2-3 times higher than

those corresponding to the Langmuir model, clearly confirming that this latter is a better model for describing the data. It should also be noted that the MWSE values depend on the calculation procedure. For instance, ISOT_Calc uses a different residual definition (as indicated in Eq. 14 and 15) than KaleidaGraph and ISOFIT. In agreement with the obtained error values, the good fit of the Langmuir model to experimental data is also shown on left side of Fig. 3, where both experimental and calculated isotherms are plotted. In addition, the right side of this figure also depicts an acceptable distribution of the errors ($\Delta C_e/C_e$ and $\Delta q/q$, as squares and triangles, respectively) obtained when the objective function is U_d . As it can be noticed by the reader, this figure allows an easy identification of the outliers or the worst fitted experimental points.

The second system (System II) deals with a 10-experimental point data set that has been taken from Kinniburgh (1986). It describes the sorption of Zn(II) ions onto ferrihydrite (an iron hydrous oxide gel). Although the sorption data were firstly attributed to a Langmuir-type isotherm by the authors, Matott and Rabideau (2008) showed that the Freundlich equation gave better fitting results (9-times lower sum of squared residuals). Other tested isotherm models with three parameters (Toth, Polanyi, etc.) were also evaluated in this work. They lowered the objective function, but in a lesser extension. Thus, we have compared the Langmuir and Freundlich models on this data set. In all calculations (using ISOFIT, KaleidaGraph and the different ISOT_Calc/Ref_GN_LM modes), the MWSE values obtained for the Freundlich model were about 7-9 times lower than in the Langmuir model (see “System II”, in Table 1).

Regarding the third studied system (System III), this describes the sorption of trichloromethane onto a soil with a high content of natural organic matter (Xia and Pignatello, 2001). The authors tested several isotherm models (Freundlich, Dual Mode –DMM– and Polanyi-Manes) to fit the 107 experimental data points. Although the Polanyi-Manes model gave a lower MWSE value than the obtained with the DMM (0.0051 and 0.0070, respectively), it was considered not appropriate to explain the experimental data. Otherwise, it can also be argued that the small difference in MWSE is attributed to a higher number of adjustable parameters (4 and 3 used in the Polanyi-Manes model and DMM, respectively). Besides, although more adjustable

parameters sometimes may achieve better data fittings, it is recommended use simpler isotherm equations (i.e., with lesser number of parameter equations). Thus, we have compared the results obtained with the Freundlich and Dual Mode models. In the original article, the isotherm parameters were determined either using the linearized form of the Freundlich model (as in Eq. 5) or NLLS regression in the DMM case. In this latter case, the objective function was equivalent to the indicated in Eq. 6, being $w_i = (1/q_{exp})^2$. Results for system III are also presented in Table 1. Although different calculation procedures have been used, the calculated isotherm parameters are very similar, both for the Freundlich model and DMM (i.e., differences lie near the estimated errors of the parameters). In all cases, the MWSE values for DMM were about the half of the corresponding obtained for the Freundlich model, in agreement with the results given by Xia and Pignatello (2001).

As exemplified by Table 1, good fittings have been successfully achieved in the three examples. Nevertheless, we have also conducted a test to evaluate the ability of the optimization procedure in system III. Although the corresponding parameters for the DMM isotherm are already known $-K_D=10.6$, $S^0=13.3$ and $b=1.3$ – we have introduced deliberately bad starting values; such as 1000, 1, 0.001 and combinations of them. Table 2 lists the parameter sets used as initial values and the optimized values obtained using the different objective functions. It also includes the number of iterations needed to achieve the final values. Results show that despite the wide range of initial estimates, the final values are very similar (for each objective function), being the differences within their estimated SD. This visibly indicates the robustness against bad estimates of the optimization procedure.

4. Conclusions

The combination of the ISOT_Calc/Ref_GN_LM (developed as function and macro for MS-Excel, respectively) has proven to be a useful tool in the evaluation of the isotherm parameters from sorption data. The function ISOT_Calc enables MS-Excel to calculate the theoretical equilibrium concentrations in the liquid and solid phases ($C_{e,T}$ and q_T) for a guessed isotherm

equation (together with its parameters), at the given experimental conditions (V , M_s and C_0). This feature can be used for two different purposes; the main is for the optimization of the isotherm parameters (fitting the model to experimental data), but it can also be used for isotherm simulation. The developed function includes as predefined models the most common used isotherms. Moreover, user-defined isotherms can also be easily applied.

Regarding the developed macro Ref_GN_LM, it allows refining the isotherm parameters. This optimization can be carried out over the residuals defined in either C_e or q , or a combination of both as well. This allows minimizing the orthogonal distance between the calculated and experimental data pairs, taking into account the errors in both variables. Hence, this procedure represents a good alternative to the commonly used regression methods, in which the minimization is carried out only over the sorbed concentration (q). The implementation of this macro, based on the Levenberg-Marquardt procedure, has proven to be robust and reliable. Although the optimization could also be carried out using the MS-Excel Solver tool, the routine described here is faster. On the other hand, Ref_GN_LM is an independent macro, allowing the refinement of the parameters of other functions, as a stand-alone NLLS regression method.

One of the main features of the ISOT_Calc/Ref_GN_LM procedure is its integration in the Excel spreadsheet. This means that sorption data analysis and graphical interpretation (e.g., editing or plotting of experimental data and calculated results) are easy tasks, even for low-level computer users. As Microsoft Excel is one of the most academia and industry popular spreadsheets, additional license fees for other fitting programs can also avoided. Additionally, other useful plots to identify best isotherm model to describe the data can be simply obtained, comparing the experimental and calculated K_d values or the residuals plot. For instance, this latter plot allows testing if residuals are randomly distributed or if systematic errors exist.

All the above mentioned capabilities make the ISOT_Calc/Ref_GN_LM a versatile tool in the study of sorption isotherms. The comparison between different models is straightforward, as it can be attained with statistical parameters (MWSE or RMSE) and visual inspection of

366 experimental/calculated isotherms or residual distribution plots. All these options taken together
367 have proven to be remarkably interesting in assessing sorption in complex scenarios (e.g.,
368 natural soils). Finally, the results obtained when applying our developed procedure to literature
369 data are virtually the same as published, and those obtained with well-established programs
370 such as ISOFIT and KaleidaGraph.

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378 **APPENDIX A. SUPPLEMENTARY MATERIAL**

379 Further details associated with the present work can be found in the appendix A file. This
380 Supplementary material includes: a software description (including requirements and
381 availability); a list of the predefined isotherms in the ISOT_Calc function; and a suggested
382 example of isotherm data and calculations.

383 **APPENDIX B. SUPPLEMENTARY MATERIAL**

384 Appendix B includes an easy-to-follow tutorial video (length: 9 min, 35 sec) showing how to
385 use the ISOT_Calc/Ref_GN_LM procedure. Specially, this video details how to fit experimental
386 data using predefined isotherm equations and user-defined isotherm equations. This material is
387 available free of charge via the Internet.

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- 390 Billo, E.J., 2001. Excel for Chemists: a Comprehensive Guide, 2nd edn. Wiley-VCH, New
391 York, NY, 760 pp.
- 392 Bolster, C.H., Hornberger, G.M., 2007. On the use of linearized Langmuir equations. Soil
393 Science Society of America Journal 71, 1796-1806. doi:10.2136/ssa2006.0304
- 394 Boxall, A.B., Kolpin, D.W., Halling-Sorensen, B., Tolls, J., 2003. Are veterinary medicines
395 causing environmental risks? Environmental Science & Technology 37, 286A–294A. doi:
396 10.1021/es032519b
- 397 Czinkota, I., Foldenyi, R., Lengyel, Z., Marton, A., 2002. Adsorption of propisochlor on soils
398 and soil components equation for multi-step isotherms. Chemosphere 48, 725-731.
399 doi:S0045-6535(02)00139-X
- 400 Demidovich, B.P., Maron, I.A., 1981. Computational Mathematics, 3rd print. edn. Mir,
401 Moscow, 688 pp.
- 402 Giles, C.H., Smith, D., Huitson, A., 1974. General treatment and classification of solute
403 adsorption-isotherm. 1. Theoretical . Journal of Colloid and Interface Science 47, 755-765.
404 doi:10.1016/0021-9797(74)90252-5
- 405 Goldberg, S., 2005. Equations and models describing adsorption processes in soils, in:
406 Tabatabai, M.A, Sparks, D.L. (Eds), Chemical processes in soils. Soil Science Society of
407 America, Madison, pp. 489-517.
- 408 Hinz, C., 2001. Description of sorption data with isotherm equations. Geoderma 102, 405-406.
409 doi:10.1016/S0016-7061(00)00071-9
- 410 Ho, Y.S., 2004. Selection of optimum sorption isotherm. Carbon 42, 2115-2116.
411 doi:10.1016/j.carbon.2004.03.019
- 412 Ho, Y.S., Chiu, W.T., Wang, C.C., 2005. Regression analysis for the sorption isotherms of basic
413 dyes on sugarcane dust. Bioresource Technology 96, 1285–1291.
414 doi:10.1016/j.biortech.2004.10.021
- 415 Ho, Y.S., Porter, J.F., McKay, G., 2002. Equilibrium isotherm studies for the sorption of
416 divalent metal ions onto peat: Copper, nickel and lead single component systems. Water,
417 Air, & Soil Pollution 141, 1–33. doi:10.1023/a:1021304828010
- 418 Johnson, M.L., 2000. Parameter correlations while curve fitting. Methods in Enzymology 321,
419 424–446. doi:S0076-6879(00)21207-X
- 420 Johnson, M.L., Faunt, L.M., 1992. Parameter estimation by least-squares methods. Methods in
421 Enzymology 210, 1–37. doi:0076-6879(92)10003-V
- 422 Kinniburgh, D.G., 1986. General purpose adsorption isotherms. Environmental Science &
423 Technology 20, 895–904. DOI: 10.1021/es00151a008
- 424 Kümmerer, K., 2004. Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks,
425 2nd edn. Springer-Verlag, New York, NY, 528 pp.

- 426 Li, R., Wen, B., Zhang, S., Pei, Z., Shan, X., 2009. Influence of organic amendments on the
427 sorption of pentachlorophenol on soils. *Journal of Environmental Sciences* 21, 474–480.
428 doi:10.1016/S1001-0742(08)62294-9
- 429 Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthes, V., Krimissa, M., 2007. Sorption
430 isotherms: A review on physical bases, modeling and measurement. *Applied*
431 *Geochemistry* 22, 249–275. doi:10.1016/j.apgeochem.2006.09.010
- 432 Matott, L.S., Rabideau, A.J., 2008. ISOFIT - A program for fitting sorption isotherms to
433 experimental data. *Environmental Modelling & Software* 23, 670–676.
434 doi:10.1016/j.envsoft.2007.08.005
- 435 Motulsky, H., Christopoulos, A., 2004. *Fitting Models to Biological Data using Linear and*
436 *Nonlinear Regression: a Practical Guide to Curve Fitting*. Oxford University Press, New
437 York, NY, 352 pp.
- 438 Poch, J., Villaescusa, I., 2012. Orthogonal Distance Regression: A Good Alternative to Least
439 Squares for Modeling Sorption Data. *Journal of Chemical and Engineering Data* 57, 490–
440 499. doi:10.1021/jc201070u
- 441 Sathishkumar, M., Binupriya, A.R., Vijayaraghavan, K., Yun, S.-I., 2007. Two and three-
442 parameter isothermal modeling for liquid-phase sorption of Procion Blue H-B by inactive
443 mycelial biomass of *Panus fulvus*. *Journal of Chemical Technology and Biotechnology* 82,
444 389–398. doi:10.1002/jctb.1682
- 445 Synergy Software. http://www.synergy.com/wordpress_650164087/kaleidagraph/
446 (accessed Dec 2015).
- 447 Teixidó, M., Granados, M., Prat, M.D., Beltrán, J.L., 2012. Sorption of tetracyclines onto
448 natural soils: data analysis and prediction. *Environmental Science and Pollution Research*
449 19, 3087–3095. doi:10.1007/s11356-012-0954-5
- 450 Volpi, L., 2003. Runtime Math Formulas Evaluation in Excel.
451 http://digilander.libero.it/foxes/mathparser/Run_Time_%20Math_Formula_%20Excel.htm
452 (accessed Dec 2015).
- 453 Xia, G., Pignatello, J.J., 2001. Detailed sorption isotherms of polar and apolar compounds in a
454 high-organic soil. *Environmental Science & Technology* 35, 84–94.
455 doi: 10.1021/es001320l

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Figure captions:

Fig. 1. Dialog box to enter experimental values and isotherm equation in ISOT_Calc.

Fig. 2. Definition of errors in experimental data.

Fig. 3. Left: Sorption isotherm of tetracycline onto a loamy soil. The solid line stands for the Langmuir model fit. Data from Teixidó et al. (2012). Right: Distribution of residuals from the relative errors in C_e (squares) and q (triangles).

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485 **Fig. 3.** Left: Sorption isotherm of tetracycline onto a loamy soil. The solid line stands for the
 486 Langmuir model fit. Data from Teixidó et al. (2012). Right: Distribution of residuals from the
 487 relative errors in C_e (squares) and q (triangles).

Table 1. Isotherm parameters for Systems I, II and III. The estimated standard deviations are given between parentheses.

Parameter	Langmuir model			Freundlich model			Dual Mode model (DMM)			
	S_T	K_L	$MWSE$ ($\times 10^{-4}$)	K_F	N	$MWSE$ ($\times 10^{-4}$)	K_D	S^o	b	$MWSE$ ($\times 10^{-4}$)
System I										
Lit. values ^a	693(27)	3.5(0.3)	23	828(36)	0.71(0.03)	61	-	-	-	-
ISOFIT ^b	690(31)	3.5(0.2)	22	817(39)	0.71(0.02)	65	-	-	-	-
KaleidaGraph ^b	690(32)	3.5(0.2)	22	817(40)	0.71(0.02)	65	-	-	-	-
ISOT_Calc ^c	730(26)	3.2(0.2)	9	849(46)	0.72(0.02)	93	-	-	-	-
ISOT_Calc ^d	757(25)	3.0(0.2)	0.05	775(30)	0.68(0.02)	0.1	-	-	-	-
ISOT_Calc ^e	729(22)	3.3(0.2)	39	848(43)	0.72(0.02)	94	-	-	-	-
System II										
Lit. values ^f	7.98	3.10								
ISOFIT ^b	8.1(0.7)	3.0(0.4)	40	8.5(0.1)	0.682(0.009)	6	-	-	-	-
KaleidaGraph ^b	8.1(0.7)	3.0(0.4)	40	8.5(0.1)	0.682(0.009)	6	-	-	-	-
ISOT_Calc ^c	8.0(0.7)	3.1(0.4)	18	8.5(0.2)	0.687(0.009)	2	-	-	-	-
ISOT_Calc ^d	8.8(0.6)	2.6(0.3)	6	8.4(0.1)	0.677(0.010)	1	-	-	-	-
ISOT_Calc ^e	8.2(0.6)	2.9(0.3)	25	8.5(0.2)	0.684(0.009)	3	-	-	-	-
System III										
Lit. values ^g	-	-	-	18.6(0.2)	0.921(0.002)	134	10.6(0.2)	13.3(1.4)	1.3(0.2)	70
ISOFIT ^b	-	-	-	18.3(0.2)	0.920(0.002)	129	10.6(0.1)	13.3(1.4)	1.3(0.2)	69
KaleidaGraph ^b	-	-	-	18.3(0.2)	0.920(0.002)	131	10.6(0.1)	13.2(1.4)	1.3(0.2)	72
ISOT_Calc ^c	-	-	-	18.9(0.2)	0.916(0.002)	14	10.9(0.2)	10.1(1.0)	1.8(0.2)	9
ISOT_Calc ^d	-	-	-	18.1(0.3)	0.924(0.003)	62	10.6(0.1)	14.8(1.6)	1.2(0.2)	31
ISOT_Calc ^e	-	-	-	18.5(0.3)	0.921(0.002)	79	10.7(0.1)	13.6(1.4)	1.3(0.2)	41

^a: from Teixidó et al. (2012)
^b: calculated using Eq. 6, where $w_i = (1/(q_{exp,i}))^2$
^c: calculated using Eq. 16, ^d: calculated using Eq. 17 and ^e: calculated using Eq. 18
^f: from Kinninburg (1986)
^g: from Xia and Pignatello (2001)

Table 2. Comparison of the optimized isotherm parameters in system III using different initial values (DMM sorption isotherm).

Starting values			Final values after parameter optimization											
			Objective function: U_{Ce}				Objective function: U_q				Objective function: U_d			
K_D	S^0	b	K_D	S^0	b	Nit ^a	K_D	S^0	b	Nit ^a	K_D	S^0	b	Nit ^a
0.001	0.001	0.001	10.93	10.26	1.77	9	10.60	15.09	1.14	10	10.65	13.58	1.30	10
1	1	1	10.94	10.12	1.80	7	10.60	14.80	1.16	7	10.65	13.31	1.33	7
1000	1000	1000	10.93	10.27	1.77	9	10.60	15.10	1.13	8	10.65	13.58	1.30	9
1000	1	1	10.94	10.12	1.80	10	10.60	14.86	1.16	11	10.65	13.31	1.33	10
1	1000	1	10.93	10.28	1.77	9	10.60	15.09	1.14	9	10.64	13.66	1.29	9
1	1	1000	10.94	10.13	1.80	8	10.60	14.86	1.16	8	10.65	13.42	1.32	9
1	0.001	0.001	10.94	10.13	1.80	9	10.60	15.08	1.14	11	10.65	13.57	1.30	12
0.001	1	0.001	10.93	10.26	1.77	10	10.60	15.15	1.13	9	10.64	13.64	1.29	10
0.001	0.001	1	10.93	10.28	1.77	9	10.60	15.11	1.13	9	10.65	13.40	1.32	10

^a: number of iterations until convergence