A Worksheet Based Model for Adsorption of Pollutants on Sorbents with Multiple Sites and Sorption Mechanisms

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Abstract*: Anthropogenic compounds as pharmaceuticals constitute potential pollutants as a result of their extensive use. In places were domestic water is treated and reused, eventually part of these chemicals would arrive to wastewater treatment plants, and from there be reused or released to nature. Thus, the need for a tool for the evaluation of the fate of such pollutants due to irrigation, rain, changes in water composition or different soil properties- is crucial. This study presents a worksheet based adsorption model that considers charged and neutral sites. Adsorption to charged sites is based on a Gouy-Chapman-Stern model, whereas amounts adsorbed on neutral sites are evaluated by a combination of Langmuir and partition mechanisms. Several sites of each kind, e.g., several clay minerals with different phisico-chemical parameters, might be considered simultaneously. Model results for metoclopramide, tetracycline and chlorpheniramine are presented. Very good fit between experimental and calculated values with a single set of adjustable parameters for each pollutant was observed. The versatility of the model combined with the fact that it is worksheet based, might make it a useful tool for environmental researchers*.

Keywords: Adsorption model, Gouy-Chapman-Stern model, Langmuir equation, partition mechanism, worksheet

1. Introduction

The awareness to the long term effects of chemicals released to the environment is increasing constantly. Anthropogenic compounds as medicines, pharmaceuticals, food constituents, surfactants, and several other organic molecules, constitute actually potential pollutants as a result of their extensive use. The source to such compounds might be industrial zones and factories, hospitals and clinics, and human domestic or veterinarian use. In countries were most the domestic water is treated and reused, eventually part of these chemicals would arrive to wastewater treatment plant. Even though their concentrations might be very low, some of those pollutants are not removed completely by treatment processes [1,2]. Thus, such chemicals might remain in the treated water that is used for irrigation, and the environmental significance of such remains should be considered.

According to that, there is a need for a tool for the evaluation of the fate of such pollutants due to irrigation, rain, changes in water composition or different soil properties. Such need will further increase with the vast introduction of desalinated water to the domestic water system, that might eventually reach wastewater treatment plants, changing broadly the hydrogeochemistry of the system [3,4].

Actually several models are used to evaluate adsorption/desorption of such pollutants to soil or other sorbents. In most cases those models are based on Freundlich or Langmuir adsorption equations [5-7]. One of the problems with such equations is that the coefficients are highly susceptible with the exact conditions of the system, as the concentration of the sorbent or even changes in the concentration of other solutes [8]. This study suggests the use of a worksheet based model that combines adsorption to charged sites according to a Gouy-Chapman-Stern electrostatic double layer model [9], with adsorption to neutral sites evaluated by an extended Langmuir equation which includes a partition mechanism ("Dual-mode model"- DMM) [10]. The actual version of the model can consider several types of both charged and neutral sites, in order to simulate contributions by different clay minerals and/or different types of other sorbents as organic matter, oxides, etc. The model was programmed using Microsoft "Excel" worksheet software, allowing any researcher to run evaluations based on experimental data specifically collected or even gathered from the literature. In this short communication we present as an example the detailed results on the adsorption of metoclopramide (an antiemetic drug) to several combinations of charged and neutral sites. Model results for tetracycline (an antibiotic) and chlorpheniramine (an antihistamine) are also presented. All calculations were performed with a single set of adjustable parameters for each pollutant.

2. Description of the Model

The concept of the model is to allow adsorption of adsorbates to two different types of adsorbing sites: (a) adsorption to charged sites based on a Gouy-Chapman-Stern model, which its equations are described extensively in the literature [11] (b) Sorption to neutral sites, evaluated by a Langmuir equation combined with a partition mechanism. This study assumes that the sorbent in case has a combination of charged and neutral sites, and the solution equilibrates with both types of "surfaces" simultaneously, by reacting with each surface separately (Fig.1). Around the charged sites a diffuse double layer effect is observed for charged species, whereas the equilibrium concentration of

each compound far enough from all adsorbing sites, is the same.

Such description is obviously a severe simplification of the system. In systems with several interacting species, real processes can only be described with models accounting for the specific chemical reactions between the matrix and the species in the solution [12]. Additional inaccuracies might arise from the fact that (a) equilibrium based models are limited, and kinetic rates might influence considerably [13], (b) the use of bulk sorbents data (as soils, for example) has failed in several occasions to predict reliably solute and contaminant behavior [14], and (c) charged sorbents do not conform to the essential assumptions of double layer models [15].
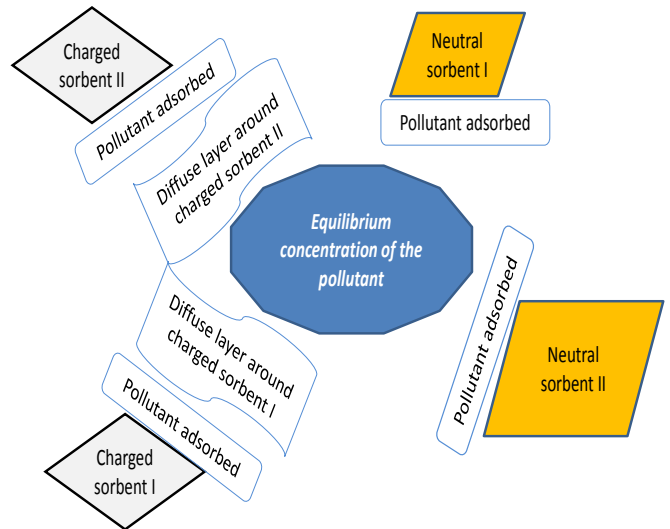

Figure 1: Scheme of the equilibrium between the pollutant concentration and several neutral and charged adsorbing sites.
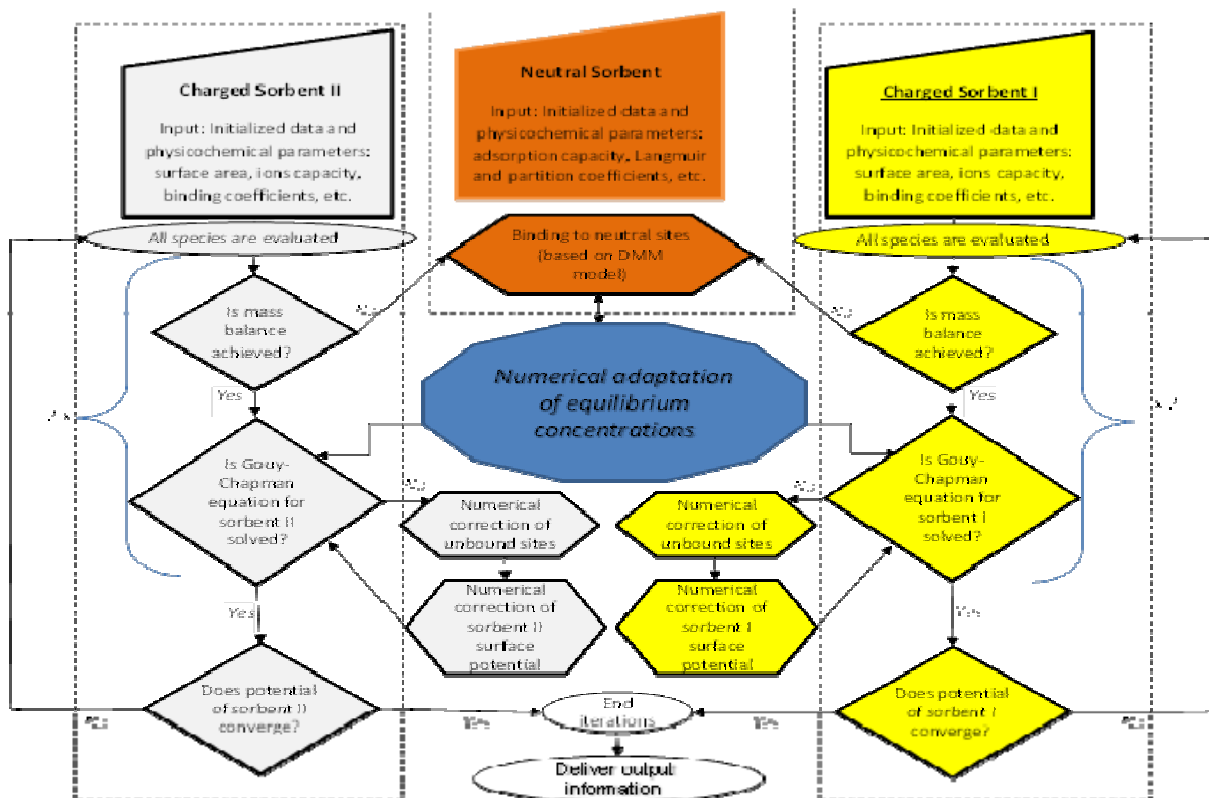

Figure 2: General scheme of the recursive calculation process

However any model attempting to deliver an estimate to such complex systems as pollutants in soil might be limited by the amount of adjustable parameters. Thus, if the simplifications assumed in this study might yield reasonable fit for the adsorption of a pollutant to a wide range of combinations of sorbents with a single set of adjustable parameters, it might achieve its modest goal.

Fig. 2 summarizes the recursive calculation procedure for a sample case were two different types of charged sites are present (for example- clay minerals and charged organic matter), together with one type of neutral site (for example, neutral organic matter).
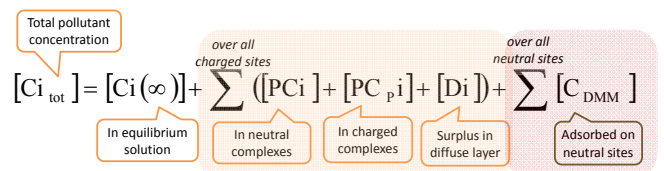

Figure 3: Schematic representation of the mass balance calculation for each sorbate

The stages needed for the recursive calculation can be summarized as follows:
1. Input data for the adsorbents is required.
2. For each type of sorbent its concentration in the suspension is needed. For charged sites, their specific

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surface area and cation or anion exchange capacity is also needed.

3. The charge and concentration of all adsorbates in the suspension
4. The interaction parameters between each of the adsorbates and the adsorbents are needed:
   a. For each charged sorbate:
   i. A binding coefficient for the formation of a non-charged complex on each charged site (K_{neut}).
   ii. A binding coefficient for the formation of a charged complex on each charged site ($K_{charged}$).
   b. In addition to that, for each sorbate (charged and neutral)
   i. A binding coefficient for the binding to each type of neutral sites by Langmuir mechanism (K_{Lang}).
   ii. A saturation value for each type of neutral sites (S_{max})
   iii. A sorbate's partition coefficient between each type of neutral site and the suspension (K_d).
5. The total amount of pollutant adsorbed would be the sum of the equilibrium concentration, species adsorbed to all sites, and the surplus in the diffused layers formed by charged sites. Thus, concentration of all species formed on the system are evaluated, and a mass balance calculation is performed taking in consideration all the possible "species" formed by each sorbate (Fig. 3)
6. If mass balance is fulfilled a numerical solution of the whole Gouy-Chapman equation – which combines Poisson's law and Boltzmann's distribution [16] - for each of the charged sorbents is seek. As described in Rytwo, 2004 [9], Gouy-Chapman equation yields an estimate of the actual value of the electrostatic potential of the surface of the sorbent. This potential is crucial for the calculation, since its causes repulsion and attraction of ions, influencing their binding. Gouy-Chapman equation is solved numerically for each type of charged sites considering all ions in the system, using the "goal seek" function of the worksheet software.

If the potential value obtained for all charged sites converges with value evaluated in previous iterations, the recursive process ends, and output is generated. Otherwise, the process goes back to stage 4.

3. Application of the Model

In order to demonstrate the use of the model, the adsorption of metoclopramide (MCP) to sorbents based on changing amounts of one type of charged and one type of neutral sites was evaluated, and is presented hereby.

3.1 Materials and Methods

To mimic charged sites SWy-2 montmorillonite was used, due to the vast database of binding coefficients based on Gouy-Chapman-Stern models of inorganic cations to that clay [9, 11, 17, 18]. SWy-2 was purchased from the Source Clay Repository of The Clay Minerals Society (Columbia, MO). Methoclopramide monohydrochloride, tetracycline hydrochloride, chlorpheniramine maleate, $CaCl_2$ and tetraphenylphosphonium chloride (TPP) were purchased from Sigma-Aldrich (Rehovot, Israel). To mimic neutral sites montmorillonite with 0.6 mmole TPP g^{-1} clay was

prepared (TPP-montmorillonite) following the procedure presented in Rytwo et al., 2007 [19]. Lack of charge at the sorbent was confirmed by electrokinetic surface measurements.

Pollutants adsorption to various combinations of organoclay and natural clay was examined. Adsorption experiments were performed as follow: into 15 ml plastic tubes with plastic screw caps distilled water, aliquots of each sorbents suspension, the tested pollutant and $CaCl_2$ solution were added. Pollutant concentrations ranged 0.01-0.4 mM, whereas $CaCl_2$ final concentration in all tubes was 5mM. The tubes were agitated for 48 hours to ensure equilibrium and then centrifuged at 14000 RPM for 30 min. Pollutant concentrations was determined in the supernatant by an HP 8452A UV-Visible spectrophotometer at 262nm ($\varepsilon=5600$ M^{-1} cm^{-1}), 310nm ($\varepsilon=11200$ M^{-1} cm^{-1}) and 272nm ($\varepsilon=15000$ M^{-1} cm^{-1}), for chlorpheniramine, metoclopramide and tetracycline, respectively. Amounts adsorbed were evaluated by mass balance. All adsorption experiments were conducted in triplicates at room temperature.

3.2 Evaluation of Binding Coefficients to Charged and Neutral Sites

In order to demonstrate parameters determination, description of the procedure for metoclopramide (MCP) is presented. An adsorption isotherm of MCP on SWy-2 montmorillonite mimicking charged sites was made, and model calculations in order to set the best fit with measured results were performed. Parameters for SWy-2 montmorillonite and Ca^{2+} were taken from literature [17]. Fig. 4 shows adsorption of MCP on 0.5 g L^{-1} montmorillonite, with three different binding coefficients for the formation of neutral complexes (K_{neut}). It can be assumed that MCP does not form charged complexes on montmorillonite, since it can be seen that reasonable fit can be made without the use of $K_{charged} \neq 0$. As not as in classical isotherms, x-axis values are not the concentration at equilibrium, but the amounts added- since this is indeed the real independent variable [8], whereas the equilibrium concentration is a consequence of the amount added in the experiment. Reasonable fit is obtained for K_{neut} ranging between 7000-15000.
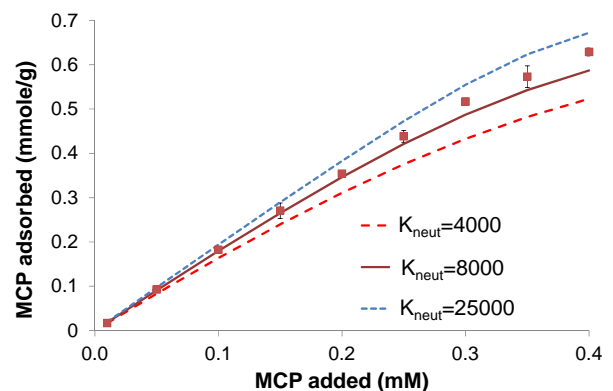
**Figure 4:** Adsorption experiment of metoclopramide (MCP) on 0.5 g L-1 SWy-2 montmorillonite. Points represent measured value, whereas lines are values calculated by the model using the coefficients detailed in the legend. In all calculations Kcharged=0.

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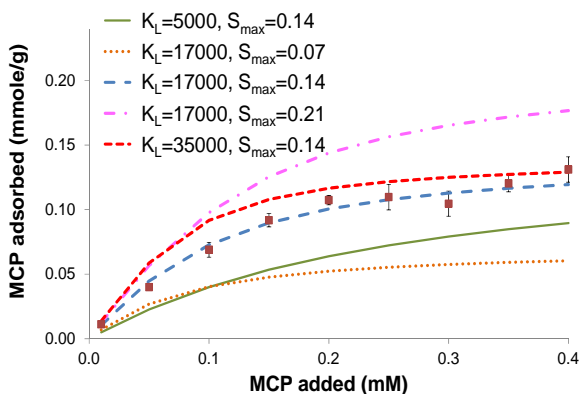
Figure 5: Adsorption experiment of metoclopramide (MCP) on 0.5 g L-1 TPP montmorillonite mimicking neutral sites. Points represent measured value, whereas lines are values calculated by the model using the coefficients detailed in the legend. In all calculations Kd=0.

A similar experiment was performed, by adding increasing amounts of MCP to a 0.5 g L^{-1} suspension of TPP montmorillonite mimicking neutral sites. Fig. 5 shows experimental value, and calculated adsorbed amounts with different combinations of Langmuir coefficient (K_L) and saturation adsorption (S_{max}). Very good fit is obtained for $K_L=17000$ and $S_{max}=0.14$ mmol/g without the need for a partition mechanism, thus $K_d=0$. Increasing K_L or S_{max} yields overestimates, whereas smaller values yield underestimates.
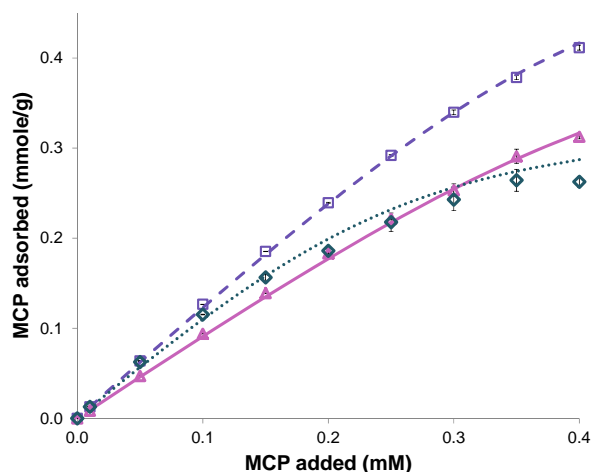
Figure 6: confirms that the same set of coefficients can be used for different amounts of sorbents, yielding a very good fit. Table 1 summarizes results evaluated for the three pollutants tested. It can be seen that as in the case of MCP, reasonable fit can be obtained for tetracycline and chlorpheniramine. In the case of tetracycline, the formation of charged complexes is required ($K_{charged}=100$), whereas in the case of chlorpheniramine, there is a need to consider also a partition mechanism on neutral sites ($K_d=100$).

Figure 6: Adsorption experiment of metoclopramide (MCP) on 0.5/0.25 g L-1 TPP montmorillonite/SWy-2 (rhombus and dotted line), 0.5/0.5 g L-1 TPP montmorillonite/SWy-2 (triangles and full line) and 0.25/0. 5 g L-1 TPP montmorillonite/SWy-2 (squares and dashed line). Points represent measured values, whereas lines exhibit values calculated by the model using coefficients in Table 1.

Table 1: Summary of model calculations for the adsorption of metoclopramide, tetracycline and chlopheniramine to sorbents combining variable amounts of neutral and charged sites. All calculations performed with the same set of adjustable parameters for each pollutant. R2 and RMSE between calculated and measured values are presented.

Pollutant	Coefficients for charged sites		Coefficients for neutral sites			Sites concentration (g L^{-1})		Fit measured to calculated	
	K_{neut}	$K_{charged}$	K_{Lang}	S_{max}	K_d	charged	neutral	RMSE (µM)	R^2
Tetracycline	1000	100	8000	0.8	0	0.50	0	20.7	0.997
						0.50	0.25	27.8	0.999
						0.50	0.50	24.0	0.991
						0.25	0.50	14.2	0.998
						0	0.50	12.2	0.998
Chlorpheniramine	3000	0	20000	0.18	100	0.50	0	58.1	0.997
						0.50	0.25	90.2	0.996
						0.50	0.50	27.2	0.994
						0.25	0.50	46.4	0.997
						0	0.50	14.0	0.997
Metoclopramide	8000	0	17000	0.14	0	0.50	0	10.4	0.998
						0.50	0.25	20.6	0.999
						0.50	0.50	34.8	0.990
						0.25	0.50	34.7	0.997
						0	0.50	29.4	0.999

4. Conclusions

The presented model can deliver -after determining a set of adjustable parameters- reasonable fit for the adsorption of pollutants even in variable amounts of combinations of different types of adsorbing sites. The ability to yield such fit can be valuable when predicting amounts of a pollutant sorbed on different soils or at different solution conditions. Additional work is ongoing in order to prepare a user-friendly version that might be delivered to researchers interested in using such model for their studies.

The authors will be glad to submit freely a version of the adsorption model and provide support in its use as long as the original manuscript is quoted.

5. Acknowledgment

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Author Profile

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