## Supplementary Materials

# Adsorption of Ciprofloxacin on Clay Minerals in Argentinian Santa Rosa-Corrientes Soils

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### Data Analysis methodology

The experimental results were analysed by fitting to four theoretical models: Freundlich, Langmuir, Temkin, and Dubinin Radushkevich (DR).

The Freundlich model supposes that the adsorption energy varies exponentially, assuming that the sites with the highest affinity for the adsorbate are the first to be occupied and the others are occupied later by using the equation:

$$q_e = K_F \cdot C_e^{1/n}$$

Where $K_F$ is the equilibrium constant and 1/n is a parameter related to the adsorption intensity.

The Langmuir model is, represented by the equation:

$$q_e = (q_{max}\ \alpha.C_e)/(1+\alpha.C_e)$$

Where the parameter $q_{max}$ (mg.g$^{-1}$) is a constant that denotes the maximum adsorption capacity, while the constant $\alpha = K_L$ (L mg$^{-1}$) defines the affinity of the adsorbate for the adsorbent. A characteristic of the Langmuir isotherm is to be able for determining a dimensionless constant called the equilibrium parameter ($R_L$), which explains the favorability of the adsorption process. It is defined by the following equation:

$$R_L = 1/(1+K_L.C_0)$$

where $C_0$ (mg.L$^{-1}$) is the initial adsorbate concentration. The $R_L$ can indicate that the shape of the isotherms is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Temkin model is expressed in the equation:

$$q_e = \beta\, lnK_T + \beta . lnC_e$$

Where $q_e$ is the amount of adsorbate at equilibrium (mg.g$^{-1}$); $C_e$ is the adsorbate concentration in equilibrium solution (mg.L$^{-1}$). β is a constant related to the heat of adsorption and is defined by the expression β = RT/b, b being the constant related to the heat of adsorption (J.mol$^{-1}$), T is the absolute temperature (K), R is the gas constant (8.314 J.mol$^{-1}$.K$^{-1}$), and $K_T$ is the Temkin isotherm constant (L.mg$^{-1}$).

The D-R model is expressed mathematically by the following equation:

$$lnq_e = lnq_{max} - K_{DR}.\varepsilon^2$$

where $q_e$ is the amount of adsorbate adsorbed per weight unit of adsorbent (mg g$^{-1}$), $q_{max}$ is the maximum adsorption capacity, $K_{DR}$ (mol$^2$ kJ$^{-2}$) is the constant to obtain the mean adsorption energy E (kJ.mol$^{-1}$), and ε is Polanyi's potential. ε and *E* are expressed by the following equations:

$$\varepsilon = R.T.ln\left(1 + \frac{1}{C_e}\right)$$

$$E = \sqrt{\frac{1}{2K_{DR}}}$$

## *Thermodynamic parameters*

The heterogeneous equilibrium can be represented with the apparent equilibrium constant $K_d$ defined by the equation:

$$K_d = \frac{q_e}{C_e}$$

, where $q_e$ is the concentration of the cipro adsorbed on the soil. The change in free energy indicates the degree of spontaneity of the process; more negative values reflect a greater sorption. Its variation can be expressed as a function of the change in enthalpy ΔH° (kJ $mol^{-1}$) and entropy ΔS° ($J.mol^{-1}K^{-1}$) with temperature:

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$$

, enthalpy and entropy changes come from the regression line of the apparent equilibrium constant at a function of temperature:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R\,T}$$

A negative value of ΔH° reflects that the process is exothermic, while negative values of ΔS° indicate a decrease in randomness at the solution-solid interface during sorption.

## Results

**Table S1**.- Experimental and calculated crystal lattice parameters of the crystal form with the cipro molecule as a neutral structure (distances in Å and angles in degrees).[a]

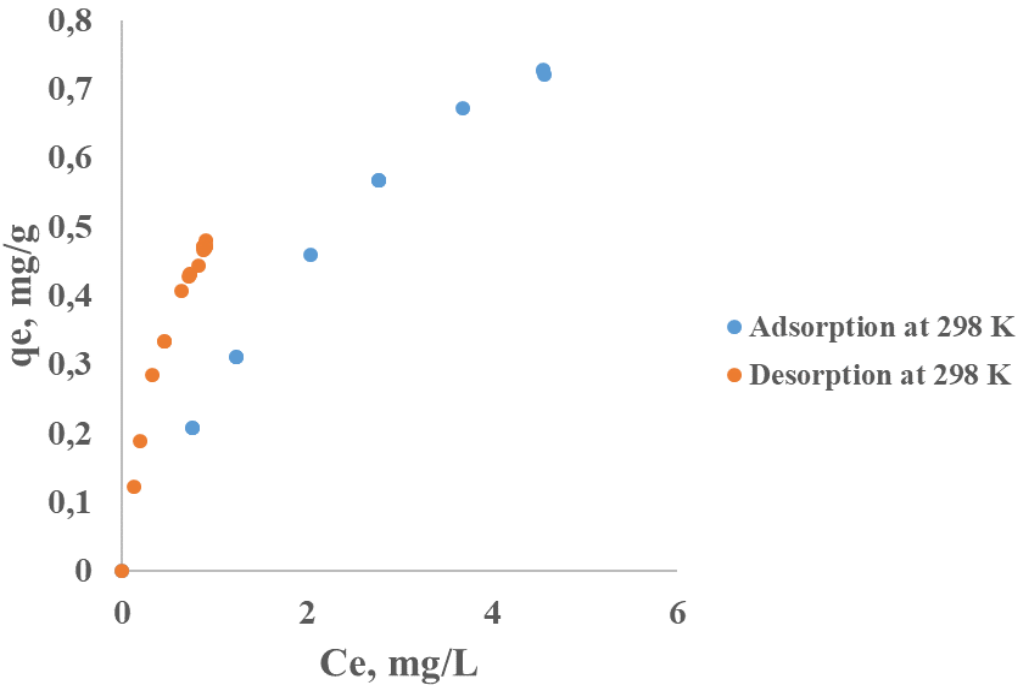
| Parameters | EXP | INTERFACE | INTERFACE_QEq | INTERFACE_ESP | CF | CF_QEq | CF_ESP |
|---|---|---|---|---|---|---|---|
| *a* | 8.06 | 7.47 | 7.61 | 8.08 | 8.18 | 7.72 | 7.23 |
| *b* | 9.73 | 10.22 | 9.80 | 9.85 | 9.45 | 9.99 | 10.02 |
| *c* | 10.32 | 10.98 | 10.85 | 10.42 | 10.58 | 10.42 | 11.53 |
| α | 99.9 | 102.1 | 106.0 | 97.9 | 105.0 | 107.0 | 106.4 |
| β | 104.5 | 103.6 | 96.1 | 108.8 | 97.9 | 97.1 | 99.9 |
| γ | 98.1 | 98.4 | 92.4 | 97.1 | 100.4 | 100.3 | 107.7 |

[a] EXP = experimental values; INTERFACE = calculated with the INTERFACE FF with net atomic charges assigned for the own FF, or by the QEq method, or as ESP charges calculated at DFT level; CF = calculated with the COMPASS FF.

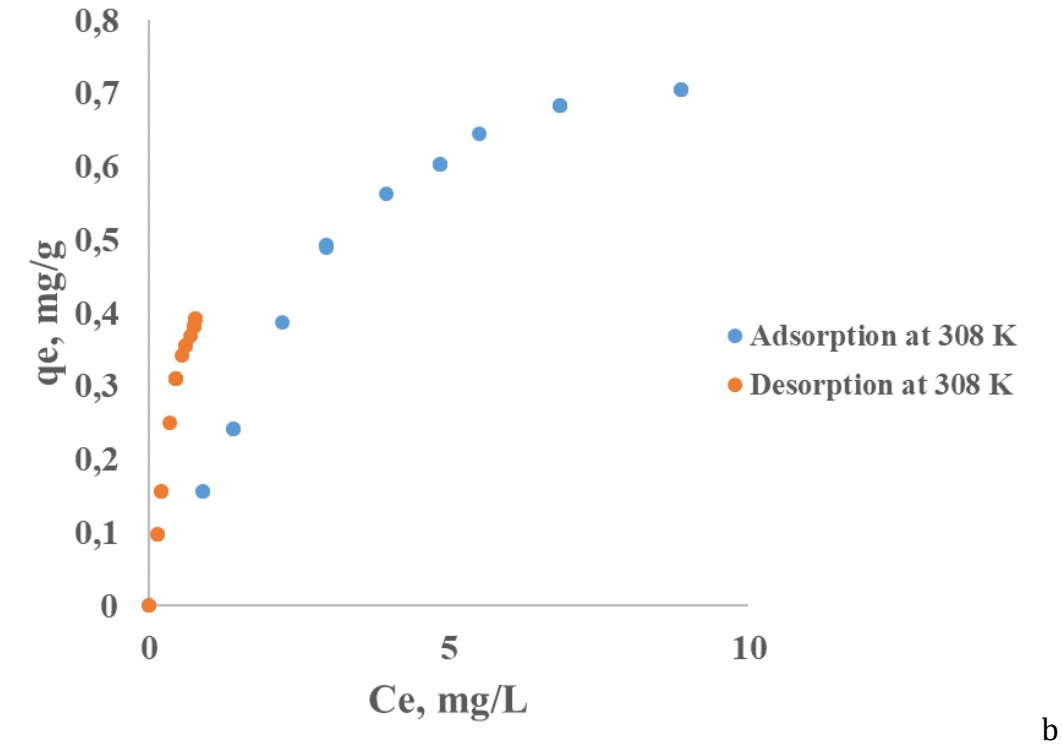
**Table S2**.- Experimental and calculated crystal lattice parameters of the crystal form with the zwitterionic cipro molecule (at 100 K) optimized with variable volume (distances in Å and angles in degrees).[a]

| Parameters | EXP | INTERFACE | INTERFACE_QEq | INTERFACE_ESP | CF | CF_QEq | CF_ESP |
|---|---|---|---|---|---|---|---|
| *a* | 7.89 | 8.31 | 8,71 | 8.32 | 7.96 | 8.60 | 8.12 |
| *b* | 8.50 | 8.03 | 8.62 | 8.38 | 8.12 | 8.66 | 8.33 |
| *c* | 10.75 | 11.39 | 10.31 | 10.87 | 11.30 | 10.02 | 10.63 |
| α | 87.4 | 94.0 | 88.9 | 89.6 | 91.2 | 88.9 | 89.8 |
| β | 84.5 | 93.0 | 82.8 | 86.2 | 91,6 | 81.1 | 81.6 |
| γ | 88.1 | 89.5 | 92.1 | 90.5 | 90.5 | 91.7 | 91.1 |

[a] EXP = experimental values; INTERFACE = calculated with the INTERFACE FF with net atomic charges assigned for the own FF, or by the QEq method, or as ESP charges calculated at DFT level; CF = calculated with the COMPASS FF.

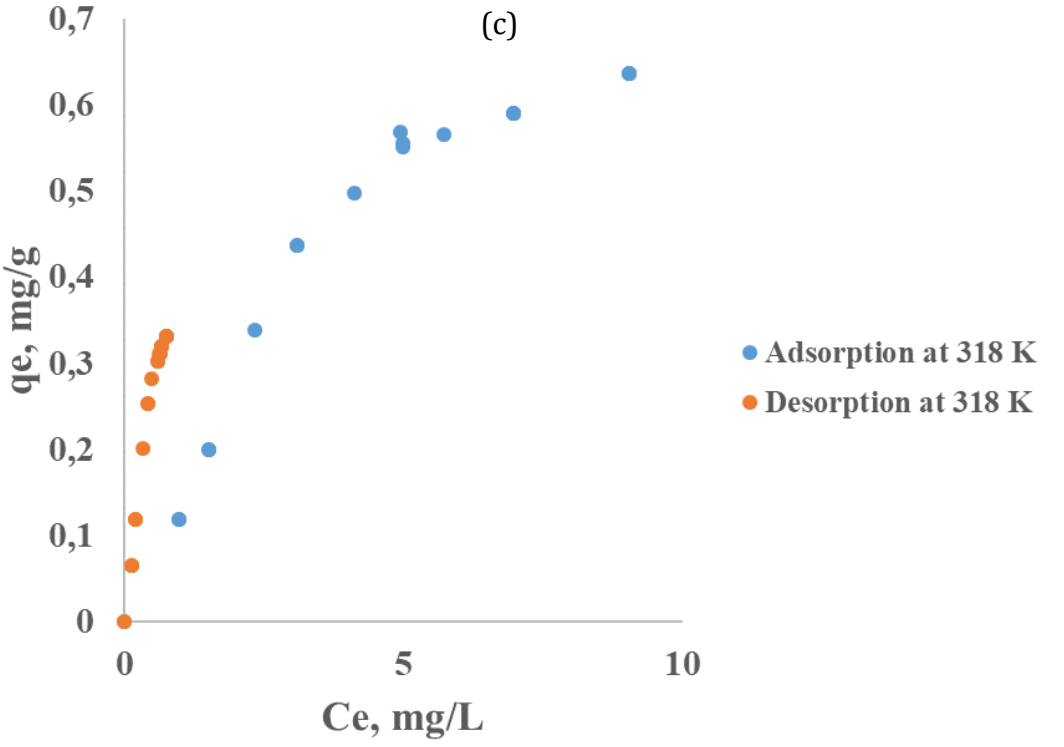



a




b

(c)




c

**Figure S1**.- Profiles of adsorption (blue line) / desorption (red line) isotherms of cipro in soils taken from 1-10 cm depth at 298 K (a), 308 K (b), and 318 K (c).