Sorption−Desorption of Imazamethabenz on Three Spanish Soils

Angel Cartón,[†] Tomás Isla,[†] and Javier Alvarez-Benedí*[,‡]

Departamento de Ingeniería Química, Universidad de Valladolid,
Prado de la Magdalena s/n, 47005 Valladolid, Spain, and Servicio de Investigación
Agraria, Junta de Castilla y León, Apdo 172, 47080 Valladolid, Spain

Methyl imazamethabenz (methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-4-yl)-*p*-toluate and *m*-toluate) is a weak acid herbicide used to control wild oats in cereal crops. This chemical has high soil persistence, which makes the study of the sorption−desorption processes of interest. Its kinetics and adsorption−desorption equilibria at different temperatures were determined in three agricultural soils using the batch equilibration technique. Kinetic profiles showed a two-step shape, with a fast initial adsorption until the first few hours followed by a slow adsorption during the rest of the whole range studied. Adsorption data conformed well to the Freundlich isotherm, with apparent increasing of adsorption with increasing of organic matter and clay content of the soils. The desorption process showed an important hysteresis phenomenon (i.e., nonreversible adsorption), which may affect imazamethabenz availability in soils.

Keywords: *Sorption; soil; imazamethabenz; hysteresis*

INTRODUCTION

Methyl imazamethabenz (IMZ) (methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-4-yl)-*p*-toluate and *m*-toluate) is an herbicide typically used to control wild oats weed on cereals farming, mainly on wheat crops. IMZ is a weak acid ($pK_a = 2.9$) applied as postemergence treatment of water solution at rates of 600 g (active ingredient)/ha (Tomlin, 1995).

Pesticides, when applied, are potential contaminants in a double way: Firstly, they can pollute the water table when transported through the soil (Davidson et al., 1983; Madhun and Freed, 1990; Sabatini, 1990). Degradation of pesticides may generate an additional problem if the degradation products are toxic or present a high mobility through the soil. Secondly, pesticides can alter the aptitude of soils for certain crops when they are retained. This second way of contamination can be important if a sensitive crop is cultivated in the next rotation.

The Servicio de Investigación Agraria (SIA) of the Junta de Castilla y León (Valladolid, Spain) detected appreciable concentration levels of IMZ 1 year after the application in cropland soils. Preliminary hypothesis included the possibility of high rates of application and a reduced degradation due to particular low mean temperatures during that year.

Shelton and Parkin (1991), among others, reported that bioavailability of a pesticide is a function of the sorption−desorption equilibria because sorbed material can only be metabolized after desorption, when it becomes dissolved in soil solution. Sorption of a solute on a soil depends not only on the compound itself but also on the soil characteristics. Several soil properties determine the retention degree of pesticides, such as the clay content and the organic matter (Singh et al., 1990; Barriuso et al., 1992). Additionally, as found with other weak acid herbicides (Comfort et al., 1992; Gan et al., 1994), soil pH can play an important role in determining

the mobility and availability of IMZ in the soil environment. The IMZ pK_a is 2.9; thus it is expected to be present in the anionic form at the ambient pH of the soils studied here (7.76−7.98).

The objective of this study was to determine the sorption and desorption equilibria of IMZ on three typical agricultural Spanish soils as a previous step for modeling purposes because estimates of sorption are needed to accurately model the persistence and mobility of IMZ in soils. The isotherms were determined at 5, 15, 25, and 35 °C, in accordance with typical temperatures in the area. A preliminary kinetics study was carried out to determine the time necessary to reach equilibrium. Desorption experiments were also of interest in this study to examine the persistence of this chemical in soils.

THEORY

Several authors (Gilchrist et al., 1993; Gamble and Khan, 1992) showed that solute adsorption on a soil can be described by second-order kinetics because, for adsorption to occur, a pesticide molecule has to encounter an unoccupied active site, while the desorption process is inherently described by first-order kinetics (a sorbed molecule has to dissociate into a free molecule and an unoccupied adsorption site). If the number of adsorption sites is assumed to be nonlimiting and constant through the adsorption process, the second-order kinetics become pseudo-first-order kinetics:

$$c = c_0 e^{-kt} \quad (1)$$

where c is the solution concentration, c_0 the initial solution concentration, k the kinetic constant, and t time.

Adsorption of pesticides is usually approximated by a two-step first-order kinetic model: fast initial adsorption followed by a second slow stage (Gilchrist et al., 1993; Hermosin et al., 1993). This can be explained by a double distribution of the adsorption sites: those which are readily accesible to the compound and those diffusionally conditioned, responsible for the second low-rate step.

There are many models used to represent adsorption equilibrium. The simplest and widest used are the

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linear, the Freundlich, and the Langmuir isotherms, represented by eqs 2.1, 2.2, and 2.3, respectively:

$$q = Kc \qquad (2.1)$$

$$q = Kc^{1/n} \qquad (2.2)$$

$$q = \frac{q_s Kc}{1 + Kc} \qquad (2.3)$$

where q is the soil pesticide concentration, c is the solution pesticide concentration, and K, q_s, and $1/n$ are parameters for each isotherm.

Hysteresis on sorption−desorption processes is a well-known phenomenon widely reported by many researchers. A failure in reaching the desorption equilibrium (Wauchope and Koskinen, 1983), other sorption mechanisms, or physical binding within the sorbent (McCloskey and Bayer, 1987; Horzempa and DiToro, 1983) have been suggested as mechanisms responsible for hysteresis. The hysteresis phenomenon in pesticides adsorption may be represented by several models. One of them was proposed by van Genuchten et al. (1974), who found that the ratio n_{des}/n_{ads} (where n_{ads} is the n parameter in the Freundlich equation for the adsorption process and n_{des} the same parameter for the desorption) was a function of the maximum adsorbed concentration (q_{max}):

$$\frac{n_{des}}{n_{ads}} = a + bq_{max}^c \qquad (3)$$

Parameters $a-c$ are then calculated by fitting the desorption data to this equation.

An alternative model was proposed by Gu et al. (1994). This model is a modification of the Langmuir isotherm which includes a correction factor $(c/c_{max})^h$ to account for nonequilibrium desorption hysteresis:

$$q = \frac{ke^{-2bq}q_s c}{ke^{-2bq}c + \left(\dfrac{c}{c_{max}}\right)^h} \qquad (4)$$

where c_{max} is the equilibrium adsorbate concentration after adsorption but before starting the desorption experiment and k, q_s, b, and h are parameters of the equation. The parameter h is a hysteresis coefficient, being $h = 0$ for complete reversibility and $h = 1$ if the process is not reversible.

MATERIALS AND METHODS

Pesticide. ASSERT (Cyanamid Ibérica, Madrid, Spain) was the commercial pesticide used in this research. Its active ingredient, IMZ, found in 30% (w/v) in the commercial pesticide, is formed by two isomers as shown in Figure 1: methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-*m*-toluate and methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-*p*-toluate. Other properties of IMZ, such as the octanol−water partition coefficient (66 and 35 for the meta- and para-isomers, respectively) and water solubility (857 and 1370 mg/kg for the meta- and para-isomers, respectively) can be found in Tomlin (1995).

Soils. Typical samples of agricultural soils used for cereals dry farming in Castilla y León, similar to those in which a problem of persistence of IMZ was detected, were collected by the SIA (Agronomy Research Center belonging to the local government). The selection of these soils did not respond to an exhaustive screening in order to cover the range of soil properties of the Spanish croplands, but they were selected between those soils which presented sugar-beet nascence
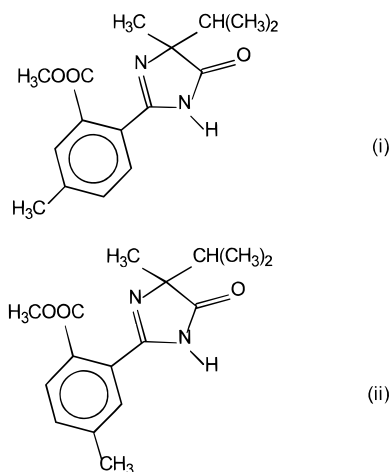

Figure 1. Structures of the two isomers of IMZ: (i) meta and (ii) para.

Table 1. Selected Chemical and Physical Properties of the Soils Used in This Study

soil	texture			% OM	pH
	% sand	% silt	% clay		
S	47.6	24.7	27.7	0.6	7.76
L	39.9	30.0	30.1	1.3	7.84
C	43.0	24.0	33.0	1.5	7.98

Table 2. Constants of the IMZ Adsorption Kinetics Fitted to a Two-Stage First-Order Model

soil, temp (°C)	first step		second step		SD
	c_0	$k (\times 10^{-6})$	c_0	$k (\times 10^{-6})$	
S, 25	11.8 (±0.2)	300 (±16)	10.3 (±0.3)	14 (±2)	0.214
C, 25	11.7 (±0.3)	500 (±20)	9.8 (±0.4)	20 (±2)	0.297
L, 25	11.7 (±0.3)	340 (±20)	9.9 (±0.3)	15 (±2)	0.219
S, 5	11.9 (±0.2)	1240 (±20)	10.7 (±0.4)	7 (±1)	0.241
C, 5	11.9 (±0.2)	1920 (±30)	10.5 (±0.2)	7 (±1)	0.231
L, 5	11.8 (±0.2)	1500 (±10)	10.6 (±0.3)	7 (±2)	0.178

problems after a 1 year rotation. They are a loamy sand (S) and a clay loamy sand (L) from Zamadueñas and clay loamy sand (C) from Villabañez. Soil samples from the top 15 cm were collected, air-dried, and passed through a 2 mm sieve. The texture and other characteristics of these soils are presented in Table 1.

Experimental Procedure. In all cases, a 0.01 N CaCl$_2$ matrix was used as solvent to prepare the herbicide solutions in order to maintain constant the ionic strength of the soil solution. Other effects of this salt are discussed by Koskinen and Cheng (1983). In addition, blanks with initial solution without soil were prepared to correct possible methodology errors. No degradation of herbicide was observed over all experiments.

The equilibration adsorption time was established after determination of the adsorption kinetics. These kinetic experiments were carried out in 100 mL flasks filled with 25 g of soil and 50 g of 12 ppm herbicide solution. The flasks were placed on a thermostatic bath controlled at the desired temperature (5, 15, 25, and 35 ± 0.1 °C) and magnetically stirred. After agitation of each sample over different periods of time ranging from 15 min to 2 days (0.25, 0.5, 1, 2, 4, 8, 16, 30, and 48 h), the flask content was passed to centrifuge tubes and centrifuged at 6000 rpm for 3 min. A fraction of the supernatant was filtered through a 0.45 mm filter and stored in vials in a refrigerator at 5 °C until analysis.

The adsorption isotherms were determined using the batch equilibration technique. Quantities of 5 g of soil and 10 g of pesticide solutions, ranging from 0.5 to 16 mg/L, were placed in centrifuge tubes and stirred during the pseudoequilibration time determined in the previous kinetic study. Then, the tubes were centrifuged, and a fraction of the supernatant was filtered through a 0.45 mm filter and collected for analysis.
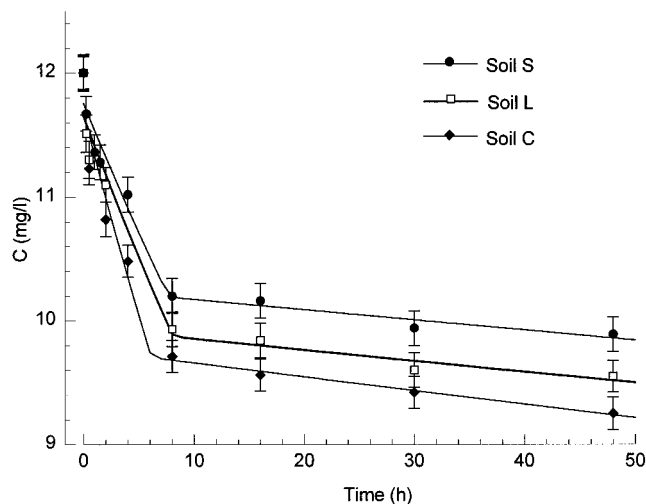
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Figure 2. Adsorption kinetics of IMZ at 25 °C, showing the two-step first-order kinetic fitting.

Desorption studies were conducted at the end of one-half of each adsorption stage by replacing a fraction of the clear supernatant liquid with 0.01 N CaCl$_2$ pesticide free solution. The initial pesticide solution concentration was diluted so that, after a new equilibration time, a fraction of the retained pesticide would be extracted from the soil, resulting in a new equilibration point. This operation was repeated four times for each desorption isotherm.

Analyticals. IMZ solution concentrations were determined by HPLC (Atienza et al., 1996), performed with a LCD Analytical 4100 series apparatus (LDC Analytical, Riviera Beach, FL): vacuum mobil phase degasifier, alternative pump CM4100, automatic injector, and UV detector SM4100. The column was a Waters Nova Pack C-18, 150 × 3.9 mm, 5 mm particle diameter. Working conditions were as follows: mobile phase, acetonitrile/water, 40/60; flux, 1 mL/min; injection volume, 20 mL; detector wavelength, 210 nm. Chromatographic data analysis was made using the LC-TALK software (LDC Analytical, Riviera Beach, FL). Standard solutions were prepared using 99.9% pure IMZ (Promochem, Wesel, Germany) in a 0.01 N CaCl$_2$ matrix. Calibration resulted in straight lines over the whole concentration range used (r^2 = 0.9999). The maximum LOD (estimated as three times the background noise) was 50 ppb (mg/kg) for the worse calibration (Miller and Miller, 1988). The standard solutions were replaced every week in order to avoid degradation phenomena.

RESULTS AND DISCUSSION

Kinetics. Kinetic experiments were conducted at two temperatures: 5 and 25 °C. The kinetic profiles of all soils suggest that IMZ adsorbs through two steps: an initial fast adsorption until the first few hours followed by a slower adsorption. The linearized form of eq 1 was used to fit the experimental data. Table 2 shows the fitted parameters. The experimental results at 25 °C and the fitted curves obtained are shown in Figure 2.

Pseudoequilibrium was assumed at the time for which an increase of 24 h in the adsorption time brought a significant decrease in the solution concentration of 0.1 mg/L or less. The decrease in the concentration in the second step at 25 °C was not significant, with 24 h taken as pseudoequilibration time because of laboratory convenience. The pseudoequilibrium time was taken as 48 h for adsorption at 5 °C. The fastest and greatest adsorption occurred in C-type soil, which is shown in Table 2 (kinetic constants) and Figure 2 (maximum adsorbed concentration), respectively. It is expected that this soil presents a greater number of adsorption sites than the other two soils, assuming that the number
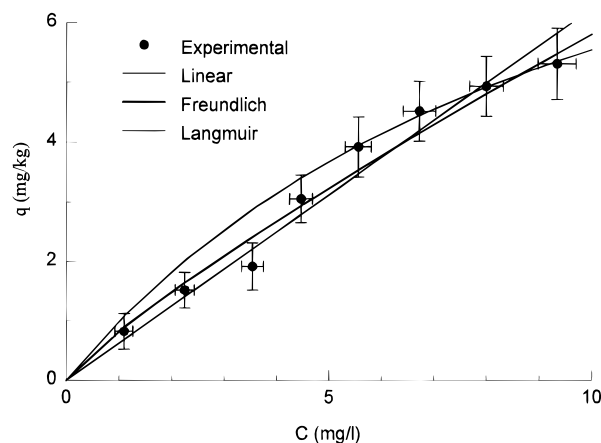

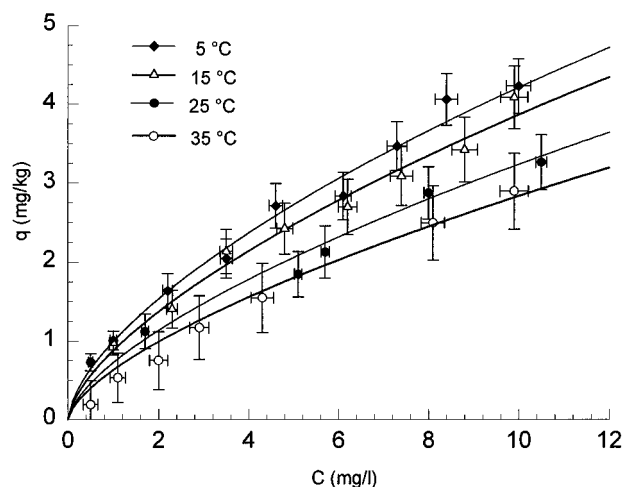**Figure 3.** Fitting of an IMZ adsorption isotherm to the linear, Langmuir, and Freundlich models.

Figure 4. Temperature effect on IMZ adsorption on S soil.

Table 3. Adsorption Isotherms of IMZ Fitted to the Freundlich Model

soil, temp (°C)	K	1/n	SD
S, 5	0.99 (±0.11)	0.63 (±0.05)	0.188
S, 15	0.88 (±0.08)	0.64 (±0.08)	0.160
S, 25	0.68 (±0.11)	0.65 (±0.09)	0.239
S, 35	0.53 (±0.09)	0.80 (±0.09)	0.259
C, 5	1.19 (±0.06)	0.72 (±0.02)	0.188
C, 15	0.83 (±0.07)	0.85 (±0.08)	0.195
C, 25	0.79 (±0.08)	0.82 (±0.08)	0.232
C, 35	0.70 (±0.08)	0.76 (±0.09)	0.230
L, 5	0.94 (±0.08)	0.67 (±0.13)	0.298
L, 15	0.83 (±0.11)	0.69 (±0.11)	0.321
L, 25	0.82 (±0.06)	0.67 (±0.05)	0.185
L, 35	0.66 (±0.09)	0.72 (±0.07)	0.207

of adsorption sites is proportional to the organic matter and the clay content of each soil.

Adsorption Isotherms. Equilibrium adsorption results were correlated through eqs 2. The isotherm coefficients were calculated by least-squares from the linearized form of these equations. In most cases, the Freundlich model led to the lowest errors. The Langmuir model represented less accurately the experimental data because its intrinsic tendency to an asymptotic value (represented by q_s) was not achieved in our experimental concentration range. The fitting through the linear isotherm led to mean errors between those found when the Freundlich and the Langmuir models were used. Table 3 shows the fitted parameters and the standard deviation. Figure 3 shows the differences in the fitting for the adsorption on the C soil at 25 °C.
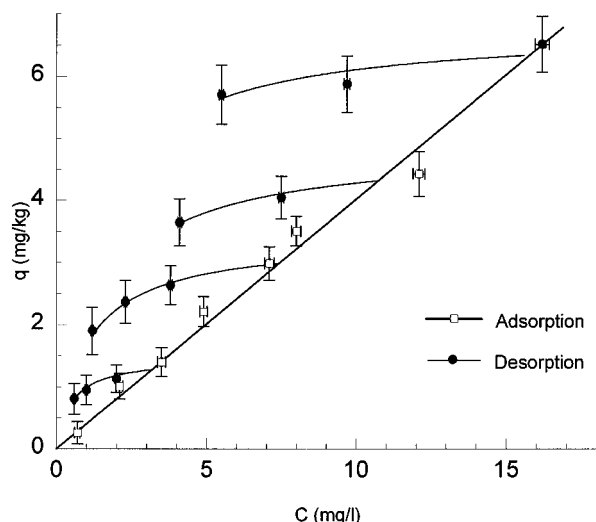
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Figure 5. Adsorption and desorption of IMZ on L soil showing the desorption hysteresis.

Table 4. Fitting of IMZ Desorption Isotherms to the Freundlich Model

no.	K	$1/n$	SD	n_{des}/n_{ads}
S 1	1.005 (±0.011)	0.061 (±0.007)	0.047	10.7
S 2	1.97 (±0.14)	0.08 (±0.07)	0.169	8.2
S 3	3.21 (±0.14)	0.03 (±0.03)	0.158	19.7
S 4	6.174 (±0.001)	0.017 (±0.001)	0.002	38.3
C 1	1.467 (±0.05)	0.08 (±0.03)	0.059	10.4
C 2	3.472 (±0.007)	0.052 (±0.002)	0.009	15.8
C 3	6.807 (±0.019)	0.036 (±0.002)	0.020	22.8
C 4	9.66 (±0.11)	0.036 (±0.007)	0.090	22.8
L 1	0.947 (±0.014)	0.302 (±0.017)	0.021	2.2
L 2	2.27 (±0.13)	0.12 (±0.04)	0.121	5.5
L 3	2.83 (±0.03)	0.180 (±0.004)	0.011	3.7
L 4	4.58 (±0.13)	0.12 (±0.03)	0.114	5.5

Table 5. Desorption Data Fitting to the Model of van Genuchten (1974)

soil	a	b	c
S	−0.066 (±0.005)	0.1654 (±0.0003)	−0.31015 (±0.00007)
C	0.022 (±0.002)	0.0978 (±0.0007)	−0.68016 (±0.00012)
L	0.211 (±0.006)	2.8747 (±0.0003)	−7.38155 (±0.00012)

Concerning the Freundlich isotherm, the K value is a relative measurement of the affinity of the adsorbent (soil) for the adsorbate (IMZ). The magnitude of the K values found for the adsorption of IMZ on the three soil types, ranging from 0.53 (±0.09) to 1.19 (±0.06), is indicative of an overall weak binding of this compound to the soil matrix. The biggest adsorption capacity at 5 °C was found for the C soil. The differences in adsorption capacity were not significant at the 95% confidence level at other temperatures. The $1/n$ parameter describes the degree of curvature of the isotherms. $1/n$ values approaching unity are indicative of an

availability of sorption sites not dependent with solution concentration. Values of $1/n < 1$ would indicate decreased adsorption of the herbicide as the adsorptive sites on the soil became occupied.

The adsorption of IMZ by soil increased as temperature decreased. This behavior is shown in Figure 4 for S soil. The adsorption constant K may be correlated to temperature through an expression given by eq 5:

$$\Delta H = -R \frac{d \ln K}{d \frac{1}{T}} \tag{5}$$

The isosteric heats of adsorption (ΔH) resulting from a fitting of ln K vs $1/T$ were −8.93 kJ mol^{-1} for C-type soil, −8.86 kJ mol^{-1} for L-type soil, and −8.05 kJ mol^{-1} for S-type soil. These values are consistent with those reported by Koskinen and Cheng (1983) and Madhun et al. (1986) for different herbicides, and they can be considered low-magnitude values, typical of adsorption involving enthropy-generating forces or electrostatic processes.

Desorption Processes. The desorption results were fitted to the linearized form of both Freundlich and Langmuir models. The lowest error is given by the Freundlich equation in most cases. As an example, Figure 5 shows the desorption curves, at 25 °C, for L-type soil. The magnitude of the hysteresis effect is easily appreciated from this figure. Table 4 shows the fitted parameters and the standard deviation. The n_{des}/n_{ads} values obtained for IMZ in this work are on a wide range (2.2−38.3), showing an important hysteresis effect. Hence, the IMZ mobility and availability in soil can be influenced by this phenomenon, and the hysteresis effect should be considered when solving the transport equation in solute transport models.

Desorption isotherms were also fitted to the models proposed by van Genuchten et al. (1974) and Gu et al. (1994). All the coefficients were calculated by least-squares. The results for these two models are registered in Tables 5 and 6, respectively. Found h values for eq 4 are within the range 0.07−1.000. These values indicate that the desorption process presents a high degree of irreversibility. This irreversibility is greater as the equilibrium starting point concentration is higher, hysteresis effect being minimized at low adsorption concentrations.

SUMMARY AND CONCLUSIONS

Kinetics experiments carried out in this work revealed that a time of 24 h is needed to reach pseudoequilibrium. Experimental data were fitted to a model of two steps of first-order kinetics. Adsorption conformed well with the Freundlich isotherm with $1/n$ ranging from

Table 6. Fitting of the Desorption Results to the Model of Gu et al. (1994)

no.	c_{max}	q_{max}	k	b	h
S 1	1.74 (±0.15)	1.1 (±0.2)	1.4 (±0.02)	−0.14 (±0.04)	0.85 (±0.04)
S 2	5.69 (±0.15)	2.1 (±0.3)	0.6 (±0.03)	−0.10 (±0.04)	0.59 (±0.13)
S 3	10.49 (±0.16)	3.3 (±0.3)	0.06 (±0.02)	−0.14 (±0.03)	1.00 (±0.07)
S 4	14.71 (±0.17)	6.5 (±0.3)	0.14 (±0.02)	−0.03 (±0.04)	0.07 (±0.02)
C 1	1.58 (±0.12)	1.5 (±0.2)	0.27 (±0.04)	−0.40 (±0.04)	1.00 (±0.03)
C 2	4.74 (±0.14)	3.7 (±0.2)	0.15 (±0.02)	−0.12 (±0.05)	0.99 (±0.12)
C 3	8.66 (±0.15)	7.4 (±0.2)	0.07 (±0.02)	−0.07 (±0.02)	1.00 (±0.02)
C 4	12.33 (±0.16)	10.6 (±0.2)	0.04 (±0.01)	−0.05 (±0.05)	1.000 (±0.004)
L 1	3.45 (±0.09)	1.4 (±0.2)	0.33 (±0.03)	−0.22 (±0.04)	0.72 (±0.02)
L 2	7.12 (±0.11)	2.9 (±0.2)	0.06 (±0.01)	−0.20 (±0.02)	1.00 (±0.01)
L 3	12.06 (±0.16)	4.4 (±0.2)	0.08 (±0.03)	−0.08 (±0.03)	0.86 (±0.05)
L 4	16.21 (±0.17)	6.5 (±0.2)	0.03 (±0.02)	−0.08 (±0.03)	0.99 (±0.04)

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0.63 (±0.05) to 0.85 (±0.08). Based on the K values, which ranged from 0.53 (±0.09) to 1.19 (±0.06), adsorption of IMZ suggests an overall weak binding. The resulting isosteric heats of adsorption were exothermic and relatively low, suggesting the involvement of low-energy (weak) mechanisms. Desorption presented remarkable hysteresis, with n_{des}/n_{ads} values ranging from 2.2 to 38.3. Hence, nonlinearity and nonsingularity of the sorption−desorption processes must be considered in predicting the environmental fate of this chemical.

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