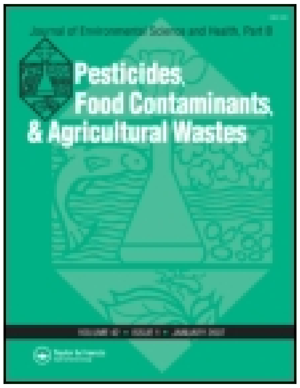

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Effects of temperature on sorption-desorption processes of imidacloprid in soils of Croatian coastal regions

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Sorption-desorption behavior of imidacloprid in six soils collected from five coastal regions in Croatia at 20, 30 and 40°C was investigated using batch equilibrium technique. Isothermal data were applied to Freundlich, Langmuir and Temkin equations, and the thermodynamic parameters ΔH°, ΔG°, ΔS° were calculated. The sorption isotherm curves were non-linear and may be classified as L-type, suggesting a relatively high sorption capacity for imidacloprid. Our results showed that the K_F^{sor} values decreased for all the tested soils as the temperature increased, indicating that the temperature strongly influences the sorption. Values of ΔG° were negative (-4.65 to -2.00 kJ/mol) indicating that at all experimental temperatures the interactions of imidacloprid with soils were spontaneous processes. The negative and small ΔH° values (-19.79 to -8.89 kJ/mol) were in the range of weak forces, such as H-bonds, consistent with interactions and partitioning of the imidacloprid molecules into soil organic matter. The ΔS° values followed the range of -57.12 to -14.51 J/molK, suggesting that imidacloprid molecules lose entropy during transition from the solution phase to soil surface. It was found that imidacloprid desorption from soil was concentration and temperature-dependent, i.e. at lower imidacloprid concentrations and temperature, lower desorption percentage occurred. Desorption studies revealed that hysteretic behavior under different temperature treatments existed, and it was more pronounced at 20°C in the soils with higher OC content. The study results emphasize the importance of thermodynamic parameters in controlling soil pesticide mobility in different geographical locations, seasons and greenhouse conditions.

Keywords: Sorption, desorption, imidacloprid, Croatian olive orchard, temperature, hysteresis phenomena.

Introduction

Pesticides, despite the difficulties they are causing through their toxicity to non-target species, as well as the possibility of their accumulation in the tissues,[1] are effective chemicals to control various pests, mainly when other alternative methods are not successful and available. One such relatively new and potent chemical with low soil persistence and high insecticidal activity at very low application rates is the nitromethylene insecticide imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine, IMI)], one of the most widely used in the world. The favorable selective toxicity of IMI to insects *versus* mammals is attributed to differences in its binding affinity to the nicotinic acetylcholine receptor (nAChR), making it safer for insect control than other neurotoxins (particularly organophosphates)[2] and enabling its diverse use in soil, seed, and foliar treatment among different crops,[3] as well as in non-agricultural practices.[4]

In Croatian coastal regions, IMI is increasingly being used in olive-growing areas as an effective means of olive fruit fly infestation control. Although used at low dose rates, it is usually applied more than once during the growing season.[5] Thus, intensive use of IMI, in addition to its high water solubility (510 mg/L, 20°C),[4] may cause severe contamination of aquifers and thus drinking water, which is consistent with the USEPA statement regarding IMI's potential to leach to groundwater.[6] Contamination by IMI has been reported in groundwater aquifers and surface water[7–11] and this finding has led to the study of its behavior in soils.

Since the pesticide residues are an important source of pollution both in soils and surface or groundwaters, it is necessary to carry out basic studies on the main processes governing the transport of such compounds, their sorption-desorption and mobility. Among the various physico-chemical processes that can predict the fate and environmental risks of pesticides in the soil/water environment, sorption is one of the most important processes which controls all other processes such as their movement, persistence, and degradation.[12] Sorption of IMI by soils of

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various kinds, as well as on the certain individual soil fractions and other substrates has been widely studied with a conclusion that the main physical and chemical factors governing these processes are the presence of organic and/or inorganic colloids.[13–19] On the other hand, desorption of IMI is also critical in determining the availability to the target species, its behavior in runoff stream and in groundwater pollution. Desorption governs the release of pesticides from the soil and several studies have reported irreversible sorption and the occurrence of hysteretic phenomena; less desorption than predicted by adsorption isotherms.[16,19–21] The degree of irreversibility of the sorption plays a significant role in determining the mobility of pesticide in the soil.[22]

Sorption-desorption processes are highly dependent on soil characteristics, including texture, organic carbon content (OC), cation exchange capacity (CEC) and pH. One often omitted, but crucial, parameter in sorption-desorption reactions which intensively affects retention and release of pesticides is temperature.[23] The effect of temperature is of special importance in greenhouses, where higher temperatures are used for cultivation.[9,16,20,23] Therefore, changes in the sorption capacity and intensity with temperature should be included in transport and pesticide leaching models, in order to be able to predict the true extent of mobility and the risk of water contamination by pesticide.[24,25]

According to the sorption theory, sorption decreases with an increase in temperature and pesticide molecules sorbed on a surface tend to desorb with the temperature rise. It suggests weak sorption interaction between soil surface and pesticide molecule, which supports physical sorption. To gain further insight into the sorption process and its mechanism, knowledge of thermodynamic data is necessary. The thermodynamic data can predict the final state of the pesticide molecule in the soil system from an initial nonequilibrium state[26,27] and give improved insight on the molecular interactions between pesticide molecule and different constituents of the soil. For example, Adhikari and Singh[28] reported that the sorption process can be better expressed by the evaluation of the ΔG° change corresponding to the transfer of pesticide from bulk solution into the appropriate site of the organic matter or clay mineral lattice. Similarly, they also reported that an understanding of the change in ΔH° and ΔS° helps in determining the ΔG° change and disorders occurred during the sorption process.

Literature data concerning the temperature effect on the sorption and the desorption behavior of IMI, as well as the one regarding the sorption thermodynamic parameters are limited, although temperature is an important parameter influencing the equilibrium and rate of sorption and desorption. Therefore, in the present study, the effect of temperature on the sorption and desorption behavior of IMI was investigated in six Croatian soils at different temperatures using batch experiments. The objective of this study was to illustrate the sorption-desorption processes and thermodynamic characteristics of IMI at different temperatures, and to elucidate the underlying sorption-desorption mechanism related to the transport and fate of IMI under laboratory conditions that could be useful to predict its behavior in the environment.

Materials and methods

Chemicals

Analytical IMI at purity 99.9% was obtained from Riedel-de Haën (Germany). All other chemicals used were of analytical grade, except acetonitrile which was of HPLC grade (J.T. Baker, Holland). Sodium pyrophosphate, sulphuric acid, potassium dichromate, sodium hydroxide, sodium acetate and calcium chloride were purchased from Kemika (Croatia), while ammonium acetate and mercury chloride were from Alkaloid (Macedonia). Stock standard IMI solution (1 g/L) was prepared by dissolving the required amount of IMI in the HPLC-grade acetonitrile and stored at 4°C. Dilutions were prepared with aqueous calcium chloride solution (0.01 M) to achieve the desired final concentrations.

Soils

Due to the intensity of olive production, the soils were sampled from five coastal regions of Croatia (Istria, Kvarner, North, Central and South Dalmatia), defined by Universal Transverse Mercator (UTM) system coordinates as follows: 44°41′19″ N, 14°45′11″ W (Pag, soil S1), 44°08′17″ N, 15°36′04″ W (Zadar, soil S2), 43°21′03″ N, 16°44′34″ W (Brač, soil S3), 45°18′02″ N, 13°37′13″ W (Istria, soil S4), 42°37′31″ N, 18°11′06″ W (Dubrovnik, soil S5) and 45°21′24″ N, 14°37′43″ W (Krk, soil S6). All soils used in the study were collected from the A horizon at depths of 0–30 cm following the standard methodology of soil sampling,[29] air-dried for 24 hours, ground (porcelain mortar + rubber pestle) and passed through a 2-mm sieve prior to use. They were selected on the basis of their texture (mechanical composition), pH values, OC content and CEC. The soils have never been treated with IMI, as verified by analyzing its residues in the soil. Physicochemical properties of the tested soils are given in Table 1.

The mechanical composition of the soil samples was determined by the "pipet method".[30] Soil sample pH values were measured in a soil + deionized water and in a soil + 0.01 M calcium chloride suspension (1:2.5, soil:solution ratio). The MP 220 laboratory pH meter (Metler Toledo, Germany) was used for pH determination in aqueous phase. Hydrolytic acidity (HA) was determined by the Kappen method,[31] CEC was measured using ammonium replacement,[32] while Na, K, Mg and Ca were analyzed by Atomic Absorption Spectrophotometer (Perkin Elmer Analyst, USA). The OC content of the soils was determined spectrophotometrically (Cary 100 Bio WINUV, Varian,

Table 1. Physico-chemical characterization of the experimental soils.

Soil	*Location*	*Textural classes*	*Clay (%)*	*pH*^{a}	*CEC*^{b} *(cmol/kg)*	*HA*^{c} *(cmol/kg)*	*OC*^{d} *(%)*	$C_{ox\ Ha}{}^{e}$ *(%)*	$C_{ox\ Fa}{}^{f}$ *(%)*
S1	Pag	clay loam	37.02	6.42 (± 0.11)	34.19 (± 0.99)	5.65 (± 0.45)	3.61 (± 0.01)	1.37 (± 0.02)	0.48 (± 0.04)
S2	Zadar	sandy loam	7.02	6.66 (± 0.04)	14.01 (± 0.63)	1.93 (± 0.23)	1.06 (± 0.02)	0.30 (± 0.01)	0.10 (± 0.02)
S3	Brač	loam	16.72	7.13 (± 0.01)	25.67 (± 0.74)	2.98 (± 0.90)	2.06 (± 0.03)	0.70 (± 0.06)	0.24 (± 0.03)
S4	Istria	clay	62.02	4.34 (± 0.09)	105.59 (± 3.02)	94.01 (± 2.90)	1.60 (± 0.03)	0.53 (± 0.05)	0.19 (± 0.04)
S5	Dubrovnik	sandy loam	11.62	6.74 (± 0.06)	28.02 (± 0.46)	4.17 (± 0.91)	2.87 (± 0.02)	1.10 (± 0.07)	0.38 (± 0.02)
S6	Krk	clay	42.72	6.69 (± 0.02)	49.16 (± 0.31)	16.21 (± 0.09)	4.74 (± 0.03)	1.85 (± 0.05)	0.65 (± 0.06)

[a] measured in soil + 0.01 M calcium chloride mixture (1 + 2.5 by weight)
[b] cation exchange capacity
[c] hydrolitic acidity
[d] organic carbon content
[e] carbon of humic acids
[f] carbon of fulvic acids

Australia) by dichromate method.[33] In addition, carbon of humic ($C_{ox\ HA}$) and fulvic acids ($C_{ox\ FA}$) were determined after alkaline extraction of samples with a mixture of 0.1 M sodium pyrophosphate and sodium hydroxide according to the classical method of Kononová and Belčiková.[34] The total carbon ($C_{ox\ TOT}$) and $C_{ox\ HA}$ were determined spectrophotometrically, while $C_{ox\ FA}$ was determined by difference between $C_{ox\ TOT}$ and $C_{ox\ HA.}$

Sorption-desorption kinetics experiments

To determine the sorption and desorption equilibrium time batch sorption and desorption kinetics experiments were carried out in 50-mL polypropylene centrifuge tubes at initial IMI concentrations of 2.5, 5 and 10 mg/L at 20(±1)°C. All of the kinetics experiments were performed in triplicate sets of tubes containing 5.0 g of soil and 25 mL of different initial IMI concentrations prepared in the background of 0.01 M calcium chloride and 100 mg/L mercury chloride solution from stock IMI solution. Calcium chloride solution was used as a background electrolyte in order to minimize ionic strength changes and to promote flocculation. Mercury chloride was added to the pesticide solution as a biocide to prevent any microbial activity during the sorption experiment. The suspensions were shaken (150 rpm) on a rotary agitator (Unimax 1010, Heidolph, Germany) in the dark at temperature of experiment. After distinct time intervals, the tubes were centrifuged at 4000 rpm for 30 min (BR4i Multifunction, Thermo Electron Corporation, France), filtered through a polypropylene hydrophilic filter of 0.45 μm (Whatman, Puradisc 25 TF, USA), and 1 mL of the supernatant liquid was used for high performance liquid chromatography (HPLC) analysis. The quantity of IMI sorbed at time t (h), q_t (mg/kg), was deduced from the mass difference between initial ($t = 0$ h) and final solution concentration taken at time t (h).

Sorption-desorption equilibrium experiments

In the present study, the IMI sorption by soils was quantified using the standard batch equilibrium method.[34] The predetermined mass of each soil (5 g), in triplicate, was equilibrated with 25 mL of aqueous solutions of IMI by shaking in a rotary agitator at three temperatures 20(±1), 30(±1) and 40(±1)°C for 48 h to achieve equilibrium. The equilibrium time was determined according to the sorption kinetics study and previous studies of the IMI sorption.[5,36] Initial pesticide solutions, in the concentration range of 0.1, 0.25, 0.5, 1, 2.5, 5, and 10 mg/L, were prepared in the same way as in the kinetics experiment. Equilibrium phases were separated by centrifugation (4000 rpm) for 30 min at temperature of experiment. After filtration through a polypropylene hydrophilic filter of 0.45 μm the aqueous phase was analyzed by HPLC. Blank experiments were performed using the same experimental procedure but without added soil to check for possible losses due to the volatilization and sorption of IMI to the centrifuge tubes or the filters. However, such losses in the blank experiments were less than 3.4% of the initial solute concentrations and therefore indicated no correction was required. Control samples, containing no IMI, only soil, 0.01 M calcium chloride and mercury chloride solution, were used for each series of experiments. The amount of IMI sorbed by soil after equilibration was calculated from the difference between the initial and equilibrium solution concentration using Equation 1:

$$q_e^{sor} = (\gamma_i - \gamma_e)\frac{V}{m} \tag{1}$$

where q_e^{sor} is the amount of IMI sorbed at equilibrium (mg/kg), m is the mass of the soil (kg), γ_i and γ_e are the initial and equilibrium concentration of IMI (mg/L), respectively, V is the volume of the solution (L) from which sorption occurs.

Desorption experiments were conducted immediately after the sorption experiments with the same concentrations of IMI. After completing the sorption process, the supernatant (25 mL) was removed and replaced with the same volume of 0.01 M solution of calcium chloride. New suspensions were shaken with a rotary agitator for 24 h to achieve equilibrium and then centrifuged under the conditions described previously to separate the liquid phase for analysis. This procedure was repeated five times for each soil sample. The amount of IMI remaining sorbed by the soil was calculated as the difference between the initial sorbed and the desorbed amount according to Equation 2:

$$q_e^{des} = \left(\gamma_e^{sor} - \gamma_e^{des}\right)\frac{V}{m} \tag{2}$$

where q_e^{des} is the amount of IMI remaining sorbed by the soil (mg/kg), γ_e^{sor} is the equilibrium sorption concentration of IMI (mg/L) and γ_e^{des} is the equilibrium desorption concentration of IMI (mg/L). The percentage of IMI desorbed was calculated as follows (Equation 3):

$$P^{des} = \frac{\sum_{a=1}^{5} q_e^{des}}{q_e^{sor}} \times 100 \tag{3}$$

Analytical methods

The concentration of IMI was analyzed by HPLC using a Thermo Separation Products (Spectra System, USA) equipped with a UV/VIS detector. All analyses were performed on a Supelco reverse phase C_{18} column (150 mm length, 46 mm ID, 5 μm particle size). The mobile phase of acetonitrile and water (1:4, v/v) was used under isocratic conditions at a flow rate of 1.2 mL/min. IMI was analyzed at 270 nm wavelength. The injection volume and the column temperature were 20 μL and 25°C, respectively. Under these conditions the retention time of IMI was 4.3 min.

Calibration curve of IMI was linear from 0.05 to 10 mg/L with a regression coefficient of $R^2 = 0.9996$ (six calibration points, in triplicate). The detection limit of IMI was 0.001 mg/L and the lower limit of quantification (LOQ) was 0.005 mg/L. The mean recovery was 93.2% with a relative standard deviation lower than 5%.

Theory/calculation

In order to explain the sorption-desorption behavior of IMI in the tested soils, Freundlich, Langmuir and Temkin nonlinear equilibrium models were studied.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of sorption over the surface and it is represented using the Equation 4:

$$q_e^{sor/des} = K_F^{sor/des}\gamma_e^{1/n} \tag{4}$$

where $q_e^{sor/des}$ is the amount of IMI sorbed per unit mass of the soil (mg/kg), γ_e is the equilibrium IMI concentration in solution (mg/L), $K_F^{sor/des}$ is the Freundlich distribution coefficient (coefficient of sorption-desorption capacity)(mg/kg)(mg/L)$^{1/n}$), *1/n* is the Freundlich exponent (coefficient of nonlinearity), usually in the range $0 < 1/n \leq 1$.

Basic assumptions of Langmuir's theory are that: 1) the sorption takes place at specific homogeneous sites within the sorbent, and 2) sorption rate is proportional to the uncovered surface, while desorption rate is proportional to the surface, which is already covered with a monomolecular layer. The Langmuir sorption-desorption isotherm can be represented by Equation 5:

$$q_e^{sor/des} = \frac{q_{max}^{sor/des} K_L^{sor/des}\gamma_e}{1 + K_L^{sor/des}\gamma_e} \tag{5}$$

where $q_{max}^{sor/des}$ is the maximum amount of sorbed IMI per unit mass of soil (mg/kg) to form a monolayer, $K_L^{sor/des}$ is the constant which depends on the enthalpy of sorption.

The Temkin isotherm takes into the account sorbent-sorbate interactions, and assumes that: 1) the heat of sorption of all the molecules in the layer decreases linearly with coverage due to sorbent-sorbate interactions, and 2) the sorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin sorption-desorption isotherm can be represented by Equation 6:

$$q_e^{sor/des} = \frac{RT}{b} ln\left(K_T^{sor/des}\gamma_e\right) \tag{6}$$

where $B_1 = RT/b$ is a constant that determines the characteristics of the sorption-desorption energy, and $K_T^{sor/des}$ is equilibrium binding constant (corresponding to the maximum binding energy) (L/mg).

The conformity of sorption and desorption experimental data to different equilibrium isotherm models is presented by the coefficient of determination (R^2) and the standard error of estimate (SEE). SEE provides a measure of agreement between the calculated and observed values and is defined as Equation 7:

$$\text{SEE} = \sqrt{\frac{\sum (q_m - q_e)^2}{n-2}} \tag{7}$$

where q_m and q_e are the measured and calculated IMI's sorption amount, respectively, and n is the number of measurements.

The contribution of organic matter to the sorption capacity can be quantified by the associated organic carbon partition coefficient (K_{OC}), represented as Equation 8:

$$K_{OC} = \frac{K_F^{sor}}{f_{OC}} \times 100 \tag{8}$$

where f_{OC} is the amount of the OC content per unit mass of soil (mg/kg). The coefficient K_{OC} and the ΔG° are related by the Equation 9:

$$\Delta G^0_{OC} = -RT \, ln \, K_{OC} \quad (9)$$

where ΔG°_{OC} is the organic matter normalized free energy change of sorption (kJ/mol), T is the absolute temperature (K), R is the universal gas constant (8.314 J/molK).

The thermodynamic parameters such as ΔG°, ΔH°, isosteric enthalpy (ΔH) and ΔS° provide additional information regarding energetic changes involved during the temperature-dependent sorption. The ΔG° was calculated using the Equation 10:

$$\Delta G^0 = -RT \, ln \, K_O \quad (10)$$

where K_o is the thermodynamic equilibrium constant. Values of K_o were determined by plotting ln (q_e^{sor}/γ_e) versus q_e and extrapolating the linear plot to zero q_e. The ΔH° and ΔS° changes were calculated using the slope and intercept of the linear Van't Hoff equation, respectively, using the Equation 11:

$$ln K_0 = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \quad (11)$$

The molar isosteric enthalpy (ΔH) is the standard enthalpy of sorption at a fixed surface coverage indicating the difference in binding energies between the sorbent and the sorbate. ΔH can be calculated using the Clausius-Clapeyron equation (Equation 12):

$$\Delta H = R\frac{d(ln\gamma_e)}{d(1/T)} \quad (12)$$

The other parameters which can be calculated from the experimental data are the activation energy (E_a) and sticking probability (S^*), which may provide further support for the involvement of physical sorption mechanism in the sorption of IMI on the tested soils. They were calculated using a modified Arrhenius equation (Equation 13):

$$S^* = (1-\theta)exp\left(-\frac{E_a}{RT}\right) \quad (13)$$

where θ is surface coverage, which is calculated by Equation 14:

$$\theta = \left(1 - \frac{\gamma_e}{\gamma_0}\right) \quad (14)$$

where γ_0 and γ_e are the initial and equilibrium IMI concentrations, respectively. The S^* indicates the measure of the potential of a sorbate to remain on the sorbent indefinitely, its value lies in the range $0 < S^* < 1$ and is dependent on the temperature of the system.

The extent of the sorption-desorption hysteresis can be quantified for each pair of sorption and desorption isotherms using the hysteresis coefficient H.[20] This coefficient is calculated using Freundlich exponents (coefficient of nonlinearity, *1/n*) estimated from the sorption and desorption isotherms and it can be expressed by Equation 15:

$$H = \frac{1/n_{des}}{1/n_{sor}} \times 100 \quad (15)$$

where $1/n_{sor}$ and $1/n_{des}$ are Freundlich exponents for sorption and desorption, respectively.

Statistical analysis

Sorption and desorption data were collected as an average of three replicates and the standard deviation was calculated and used as error bars to discriminate differences among isotherms. Variances among temperature treatments were analyzed by calculating P-values associated with one-way ANOVA test with *post hoc* comparison (Tukey HSD test). The results were considered statistically significant at $P < 0.05$. The data were analyzed using Software Statistica® software package Version 7.0 and Wolfram Research Mathematica® software package Version 7.0.

Results and discussion

Sorption-desorption kinetics of imidacloprid in soils

Sorption-desorption kinetics of IMI on the selected Croatian soils were studied at 20(±1) °C using the various initial IMI concentrations (2.5, 5 and 10 mg/L) in order to estimate the time needed to achieve the sorption and desorption equilibrium. The graphs obtained are shown in an example of the soil S6 in Figures 1a and 1b. The IMI sorption and its desorption kinetics were found to be a two-step process. In the initial and rapid sorption step 39–74% of the added IMI was sorbed within 3 h depending on the initial IMI concentration. The second step was slower, tending to reach final equilibrium at 48 h of reaction. Capri et al.[5] and Nemeth-Konda et al.[36] studied the sorption of IMI and they found that insecticide was removed from the solution within the first hour of the 24 h sorption experiment. The rapid initial sorption of IMI is a surface phenomenon. The vacant sites in the soil particles were filled up rapidly in the initial stages and followed a linear variation. This is followed by a slow migration and diffusion of the pesticide molecule (the rate of sorption decreased drastically and reached the steady state) into the structure of the organic matter matrix and mineral structure.[37] The same trend was observed by Capri et al.[5] while studying the sorption of IMI on Italian, Spanish and Greek soils. From the results it is clear that the sorption of IMI in soils is rapid in the initial period and the amount of insecticide participating in the long-term behavior is insignificant compared to that participating in the preliminary phase of rapid sorption. Due to the irreversibility of IMI's sorption,[19] a longer period of desorption process was needed. After the first desorption step (24 h), only 7 to 17% of the total sorbed amount of

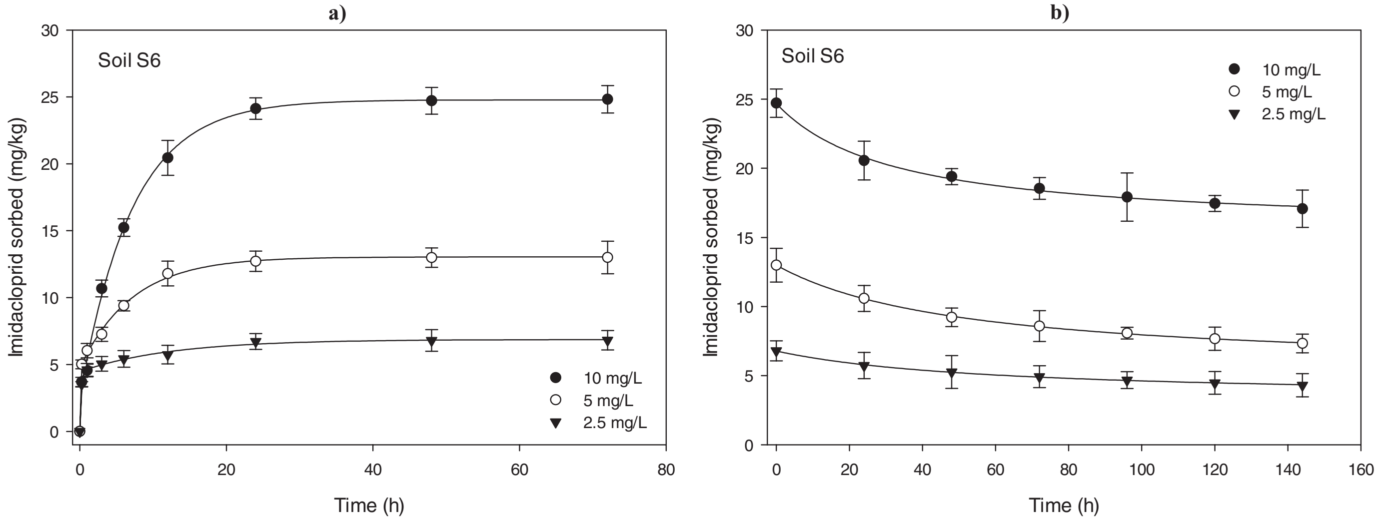

Fig. 1. Effect of contact time and initial imidacloprid concentration on kinetic of a) sorption and b) desorption processes of imidacloprid in soil S6 (initial imidacloprid concentration in solution: 2.5, 5 and 10 mg/L; temperature 20°C).

IMI was desorbed, depending on the initial IMI concentration. The percentage of IMI desorption increased as the equilibration periods prolonged, and after 144 h of equilibration time it was between 13 and 31%. Similar trends were observed in all tested soils.

Sorption of imidacloprid by soils at different temperatures

In order to find a mathematical model that best describes the sorption processes of IMI in the tested soils, three nonlinear equilibrium models were used: Freundlich's (Equation 4), Langmuir's (Equation 5) and Temkin's (Equation 6). The R^2 and the SEE were used to assess the adequacy of the equilibrium models (Table 2). According to the R^2 values, the Freundlich model fitted better the experimental data ($R^2 > 0.997$) than the Langmuir ($R^2 > 0.912$) and Temkin model ($R^2 > 0.800$). However, the SEE values of the Freundlich and Langmuir equations were much lower than those of Temkin equation. This suggested that the Freundlich isotherm model gave the most adequate explanation of the sorption equilibrium process of IMI at 20, 30 and 40°C, thus it was chosen for the description of all temperature equilibrium experiments.

The sorption Freundlich isotherms of IMI at investigated temperatures are presented in Figure 2, where the sorbed amount of IMI uptake by the soils (mg/kg) was plotted against the equilibrium concentration in water (mg/L). As it can be seen from the results presented in Figure 2, the sorption isotherms corresponding to the sorption of IMI show a decreased slope in the initial portion of the curves and may be classified as L-type[38] at all investigated temperatures. This indicates that tested soils have a medium affinity for IMI and that no strong competition from the solvent for sorption sites occurs. The curves in this case do not tend to define a plateau, belonging to the subgroup III of the Giles classification. Therefore, it seems reasonable to suppose that in this case a complete monolayer of IMI molecules covering the sorbents surface is not formed. Likewise, the L-isotherms are characteristic for the microporous and energy heterogeneous sorbent, and they may indicate that beside organic matter, clay fraction of the soil also contributes to the IMI's sorption. This shape of isotherms has been previously reported for IMI sorption. [17, 19, 39]

As shown in Table 2, the K_F^{sor} values decreased for all the tested soils as the temperature increased from 20 to 40°C, indicating that the temperature strongly influences the sorption. Therefore, from isotherms of the tested soils it is evident that an increase of 10°C decreased K_F^{sor} values from 1.16 to 1.44 fold, while increasing temperature of 20°C decreased K_F^{sor} values from 1.40 to 1.99 fold. These values are comparable with the results of Fernandez-Bayo et al.[16] and Zahor[40] who reported 1.5–1.8 fold and 1.2 fold decrease in the sorption of IMI by soil when temperature increased from 15 to 25°C and from 25 to 55°C, respectively. In order to elucidate the effect of temperature treatment on the sorption of IMI by tested soils, analysis of Variance (ANOVA) was used. Correlation analysis of pooled data ($n = 18$) was carried out at temperatures of 20, 30 and 40°C for all tested soils, indicating that the IMI sorption significantly depended on the temperature level ($P < 0.05$). The effect of temperature can be explained on the basis of the IMI solubility (510 mg/L at 20°C). [4] At higher temperatures IMI solubility increases, showing lower tendency to get sorbed by the tested soils.[41] Other investigators also concluded that the aqueous activity coefficient is a major factor controlling the extent of sorption of organic pollutants in soils as a function of temperature. [42] In addition, increasing temperature can perhaps change the "character of humic substances" in the soil matrix, such as the sorption to mineral and surface area that influences IMI

Table 2. Evaluated parameters with standard deviation, standard error of estimate (SEE) and determination coefficients (R^2) for imidacloprid sorption by experimental soils using Freundlich, Langmuir and Temkin models at different temperature conditions (20, 30 and 40°C).

		Freundlich isotherm				*Langmuir isotherm*				*Temkin isotherm*			
Soil	*Temperature* (°*C*)	K_F $(mg/kg)/(mg/L)^{1/n}$	*1/n*	R^2	*SEE*	K_L (L/mg)	q_m (mg/kg)	R^2	*SEE*	K_T (L/mg)	B_l	R^2	*SEE*
S1	20	4.92 (± 0.03)	0.918 (± 0.005)	0.999	0.018	0.080 (± 0.006)	71.94 (± 2.49)	0.920	0.008	9.08 (± 0.34)	4.20 (± 0.16)	0.787	4.121
	30	3.92 (± 0.05)	0.915 (± 0.002)	0.998	0.029	0.083 (± 0.004)	64.52 (± 2.15)	0.941	0.009	8.03 (± 0.45)	3.74 (± 0.21)	0.802	3.467
	40	3.17 (± 0.05)	0.913 (± 0.004)	0.999	0.011	0.088 (± 0.009)	59.62 (± 2.09)	0.814	0.018	7.71 (± 0.27)	3.50 (± 0.24)	0.770	3.591
S2	20	2.92 (± 0.04)	0.888 (± 0.007)	0.998	0.035	0.101 (± 0.010)	35.59 (± 1.83)	0.980	0.011	7.55 (± 0.28)	2.87 (± 0.29)	0.823	2.510
	30	2.03 (± 0.02)	0.887 (± 0.003)	0.996	0.047	0.117 (± 0.013)	26.88 (± 1.63)	0.955	0.025	6.65 (± 0.34)	2.21 (± 0.17)	0.840	1.801
	40	1.47 (± 0.06)	0.818 (± 0.003)	0.995	0.053	0.148 (± 0.011)	14.16 (± 1.23)	0.954	0.052	6.86 (± 0.48)	1.57 (± 0.19)	0.850	1.246
S3	20	3.87 (± 0.06)	0.915 (± 0.002)	0.996	0.018	0.075 (± 0.009)	60.24 (± 1.47)	0.929	0.011	8.08 (± 0.24)	3.63 (± 0.20)	0.789	3.540
	30	2.82 (± 0.04)	0.913 (± 0.004)	0.998	0.035	0.079 (± 0.005)	44.64 (± 1.29)	0.944	0.015	7.12 (± 0.29)	2.94 (± 0.26)	0.816	2.602
	40	2.08 (± 0.04)	0.897 (± 0.002)	0.999	0.014	0.086 (± 0.007)	39.26 (± 1.37)	0.752	0.033	6.67 (± 0.21)	2.75 (± 0.17)	0.764	2.851
S4	20	3.57 (± 0.04)	0.912 (± 0.001)	0.993	0.023	0.073 (± 0.008)	56.81 (± 2.13)	0.941	0.011	7.80 (± 0.31)	3.46 (± 0.20)	0.798	3.268
	30	2.56 (± 0.03)	0.897 (± 0.003)	0.998	0.034	0.077 (± 0.006)	38.76 (± 1.88)	0.973	0.012	6.98 (± 0.18)	2.72 (± 0.24)	0.819	2.394
	40	1.98 (± 0.02)	0.893 (± 0.002)	0.999	0.022	0.082 (± 0.010)	34.01 (± 0.93)	0.839	0.038	6.64 (± 0.34)	2.41 (± 0.16)	0.782	2.391
S5	20	4.43 (± 0.04)	0.893 (± 0.004)	0.997	0.024	0.099 (± 0.011)	54.35 (± 2.46)	0.950	0.009	8.89 (± 0.35)	3.83 (± 0.19)	0.798	3.664
	30	3.69 (± 0.03)	0.884 (± 0.003)	0.996	0.049	0.109 (± 0.013)	42.37 (± 2.31)	0.944	0.014	8.33 (± 0.21)	3.41 (± 0.15)	0.834	2.869
	40	3.16 (± 0.04)	0.884 (± 0.003)	0.998	0.021	0.113 (± 0.009)	36.95 (± 2.27)	0.923	0.016	7.84 (± 0.28)	3.27 (± 0.22)	0.794	3.141
S6	20	5.74 (± 0.04)	0.919 (± 0.003)	0.999	0.012	0.078 (± 0.008)	85.47 (± 3.15)	0.895	0.008	9.80 (± 0.39)	4.58 (± 0.14)	0.776	4.649
	30	4.94 (± 0.04)	0.916 (± 0.004)	0.996	0.024	0.084 (± 0.007)	68.97 (± 2.93)	0.962	0.006	9.11 (± 0.43)	4.19 (± 0.32)	0.794	4.027
	40	4.11 (± 0.03)	0.908 (± 0.005)	0.994	0.020	0.085 (± 0.006)	62.50 (± 3.11)	0.808	0.018	8.79 (± 0.36)	3.92 (± 0.26)	0.770	4.073

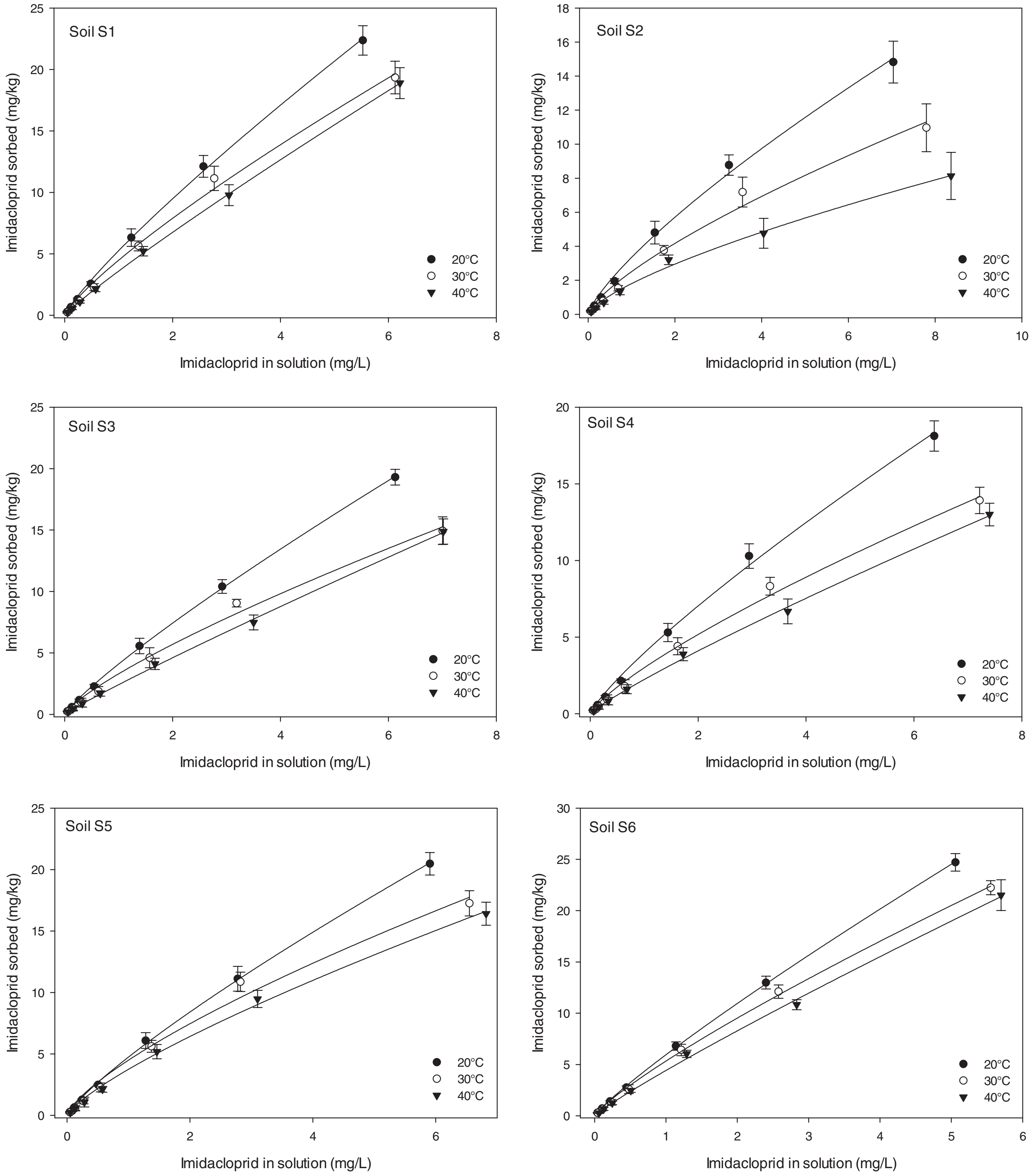

Fig. 2. Sorption isotherms plots of imidacloprid for experimental soils at different temperature conditions (20, 30 and 40°C) represent by Freundlich model. Values are means ± standard deviations. Symbols represent the experimental data, while lines represent the theoretical curves described by the Freundlich model.

Table 3. Values of organic carbon partition coefficient (K_{OC}) and organic matter normalized free energy change of sorption (ΔG°_{OC}) for imidacloprid in experimental soils at different temperature conditions (20, 30 and 40°C).

	20°C		*30°C*		*40°C*	
Soil	K_{OC} *(kg/L)*	ΔG°_{OC} *(kJ/mol)*	K_{OC} *(kg/L)*	ΔG°_{OC} *(kJ/mol)*	K_{OC} *(kg/L)*	ΔG°_{OC} *(kJ/mol)*
S1	136.13 (± 0.55)	−11.98	108.43 (± 1.55)	−11.81	87.71 (± 1.01)	−11.65
S2	274.16 (± 2.55)	−13.68	190.99 (± 5.64)	−13.24	138.21 (± 2.68)	−12.83
S3	187.82 (± 1.48)	−12.76	136.72 (± 3.36)	−12.40	101.00 (± 1.11)	−12.02
S4	223.33 (± 2.05)	−13.18	160.01 (± 1.38)	−12.79	123.91 (± 1.15)	−12.55
S5	154.33 (± 1.16)	−12.28	128.60 (± 1.96)	−12.24	110.06 (± 0.63)	−12.24
S6	121.07 (± 1.30)	−11.69	102.11 (± 0.94)	−11.66	86.76 (± 0.59)	−11.73
Mean	182.81 (± 57.99)		137.81 (± 33.30)		107.94 (± 20.40)	

sorption. This suggested that temperature may influence the structure of organic matter and the characteristics of the sorbates. The influence of the humic substances on the IMI sorption was discussed in more details in our previous article.[19]

In our study, the sorption isotherm *1/n* values were below unity (*1/n* < 1) (Table 2), indicating that the initial slope of the isotherm was non-linear with respect to the concentration in the aqueous phase. The Freundlich exponent *1/n* is related to the sorption site energy distribution, as well as to heterogeneous organic matter domain, where the lover *1/n* values indicate a more heterogeneous sorption site energy distribution. As shown in Table 2, *1/n* decreased with an increase of temperature from 20 to 40°C. Deviations from the linear function at temperatures of 20, 30 and 40°C ranged from 8.1% (soil S6) to 11.2% (soil S2), 8.4% (soil S6) to 11.6% (soil S5), and 7.7% (soil S1) to 18.2% (soil S2), respectively.

The organic carbon partition coefficient, K_{OC} (Equation 8) usually expresses the hydrophobicity of the pesticide and may be used to estimate migration and predict behavior of an organic pesticide in the environment. The values of K_{OC} decreased with increasing temperature, illustrating that high temperature was not favorable for sorption. According to the mobility classification of pesticides,[43] IMI can be categorized as having a medium mobility (K_{OC} = 150 – 500 L/kg) at 20°C,[4] showing less tendency to be sorbed by the examined soils. With a temperature increase from 20 to 40°C, K_{OC} decreased from 182.81 to 107.94 L/kg (Table 3), and at higher temperatures IMI can be categorized as a high mobility pesticide (K_{OC} = 50–150 L/kg). Increased temperature will lead to a higher IMI solubility and thus lower sorption coefficient K_{OC}.[23] Kong et al.[41] reported that the water solubility of IMI increases by a factor of 14, with a temperature increase from 30 to 76°C. Thus, the release rates of the contaminants and their leachable concentrations will likely be further reduced in a cold climate.

The values of organic matter normalized free energy change for IMI sorption, ΔG°_{OC}, were in the range of −13.68 to −11.69, −13.24 to −11.66, and −12.83 to −11.73 kJ/mol, at 20, 30 and 40°C, respectively (Table 3). Similar results (ΔG°_{OC}ranged from −13.61 to −11.83 kJ/mol) were observed by Liu et al.[17] who studied the sorption behavior of IMI in China soils. The negative values of ΔG°_{OC}indicated that the sorption of IMI on the tested soil samples is a spontaneous process and physical in nature. In such cases, it can be inferred that there is a continuous partitioning of IMI into soil organic matter.[44] The ΔG°_{OC}values for IMI sorption under the effect of different temperatures indicated that the sorption coefficients decreased as the temperature increased and they were in the order 20°C > 30°C > 40°C.

Estimation of sorption thermodynamic parameters

The values of the thermodynamic parameters (ΔG°, ΔH° and ΔS°) for IMI sorption are presented in Table 4 and

Table 4. Various thermodynamic parameters obtained for imidacloprid sorption by experimental soils at different temperature conditions (20, 30 and 40°C).

	20°C		*30°C*		*40°C*							
Soil	*Ln* K_o	ΔG° *(kJ/mol)*	*Ln* K_o	ΔG° *(kJ/mol)*	*Ln* K_o	ΔG° *(kJ/mol)*	ΔH° *(kJ/mol)*	ΔS° *(J/molK)*	R^2	E_a *(kJ/mol)*	S^*	R^2
S1	1.76	−4.28	1.53	−3.84	1.41	−3.68	−13.15	−30.39	0.967	−4.95	0.472	0.929
S2	1.28	−3.13	0.91	−2.29	0.77	−2.00	−19.79	−57.12	0.946	−6.98	0.559	0.997
S3	1.51	−3.69	1.20	−3.01	1.04	−2.72	−18.02	−49.08	0.967	−5.67	0.517	0.871
S4	1.43	−3.50	1.12	−2.83	0.97	−2.53	−17.73	−48.77	0.967	−6.26	0.524	0.929
S5	1.70	−4.15	1.54	−3.87	1.42	−3.69	−10.90	−23.09	0.993	−4.39	0.512	0.929
S6	1.91	−4.65	1.77	−4.46	1.68	−4.37	−8.89	−14.51	0.989	−4.90	0.433	0.963

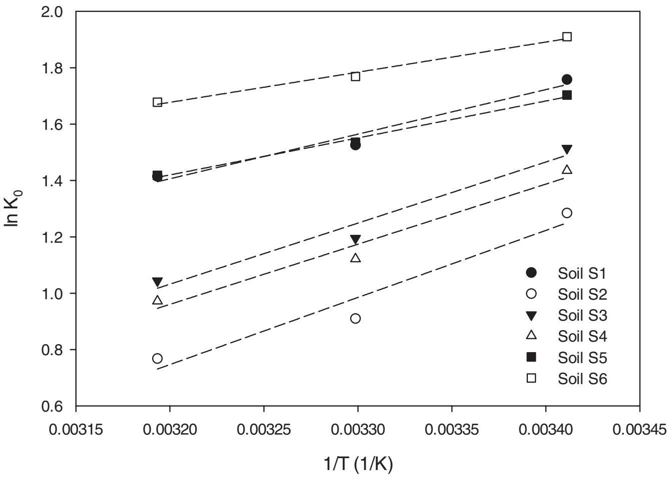

Fig. 3. Plot of ln K_o versus $1/T$ to evaluate of enthalpy (ΔH°) and entropy (ΔS°) for imidacloprid sorption by experimental soils.

Table 5. Isosteric enthalpy of sorption (ΔH) in relation to the initial imidacloprid concentrations (γ; 1, 2.5, 5 and 10 mg/L) at different temperature conditions (20, 30 and 40°C).

		Initial concentration, γ (mg/L)			
Soil	*Isosteric enthalpy (kJ/mol)*	*10*	*5*	*2.5*	*1*
S1	ΔH	−4.51	−6.44	−6.31	−6.40
	R^2	0.855	0.993	0.985	0.97
S2	ΔH	−6.63	−8.39	−7.25	−7.16
	R^2	0.992	0.988	0.969	0.960
S3	ΔH	−5.25	−6.93	−7.21	−7.34
	R^2	0.777	0.998	0.969	0.955
S4	ΔH	−5.72	−8.36	−6.86	−6.74
	R^2	0.885	0.996	0.975	0.967
S5	ΔH	−3.82	−4.18	−5.13	−5.10
	R^2	0.733	0.843	0.993	0.994
S6	ΔH	−4.57	−6.28	−4.74	−4.84
	R^2	0.914	0.990	0.999	0.997

Figure 3. Changes in ΔG° may be used as a measure of the extent of the driving force of the reaction. The ΔG° values ranged from −4.65 to −2.00 kJ/mol (Table 4), depending on the temperature of the experiment. The thermodynamic treatment of the sorption data shows that ΔG° values were negative and decreased with temperature rise, indicating that the sorption of IMI by the soils was spontaneous with a high preference to the soil surface. Variation of ΔG° values with temperature may be due to the increase in the degree of freedom of sorbed IMI molecules, which enhances desorption rather than sorption at higher temperatures.[45] The magnitude of ΔG° also showed that the sorption of IMI takes place via physical processes involving weak forces of attraction, [23] primarily by dissolution-like partition of IMI into soil organic matter.[44]

The absolute ΔH° values of sorption can give improved insight on the molecular interactions between IMI molecules and soil functional groups. Physical sorption enthalpy in the range of 4 to 8 kJ/mol indicates existence of van der Waals interactions, whereas in the range of 8 to 40 kJ/mol H-bonds are the main interactions.[46,47] The ΔH° values associated to chemical sorption are usually higher than 40 kJ/mol. IMI molecule has functional groups that are able to form both types of interactions, H-bonds and Van der Waals interactions. The presence of -NO_2 group in the IMI molecule will result in increasing the overall polarity in the way that more polar molecule is likely to move closer to the charged surfaces increasing the likelihood of Van der Waals interaction. In our study the ΔH° of sorption had negative value and was in the range of −19.79 to −8.89 kJ/mol. The exotermic nature of the sorption processes show that these processes are energetically stable, and that the sorption occurred through a bonding mechanism. Our results for ΔH° sorption were in the range of weak forces. Hence, the IMI's sorption may be due to the H-bonding and Van der Waals forces. [42] The ΔH° magnitude can also help to explain the binding strength between IMI and soil functional groups, the higher value of ΔH° shows stronger binding. Results of our study indicate that the interactions between IMI and the studied soils were stronger at lower temperature.

The values of isosteric enthalpy of sorption, ΔH (Table 5) depended on the initial concentration of IMI and were in the following range of −6.63 to −3.82, −8.39 to −4.18, −7.21 to −4.74 and −7.34 to −4.84 kJ/mol for 10, 5, 2.5 and 1 mg/L, respectively. The values of ΔH sorption expressed as a function of sorbed IMI amount were almost the same in all the tested soils, supporting our inference regarding the mechanism of sorption. These values are relatively small and are of the order which is consistent with a physical type of the sorption.[23]

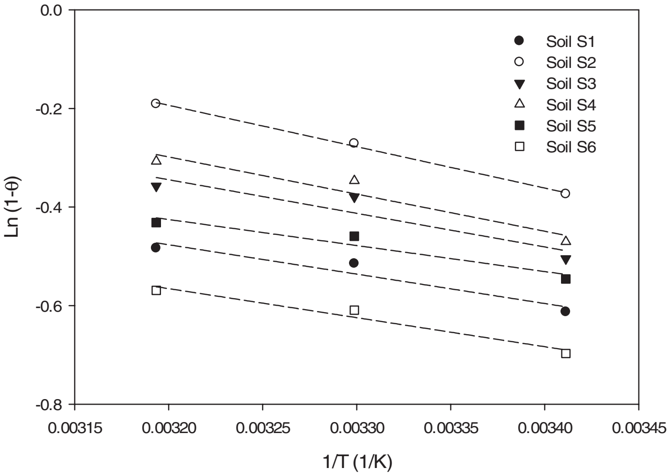

Fig. 4. Plot of ln (1-θ) versus $1/T$ to evaluate energy of activation (E_a) and sticking probability (S^*) for imidacloprid sorption by experimental soils.

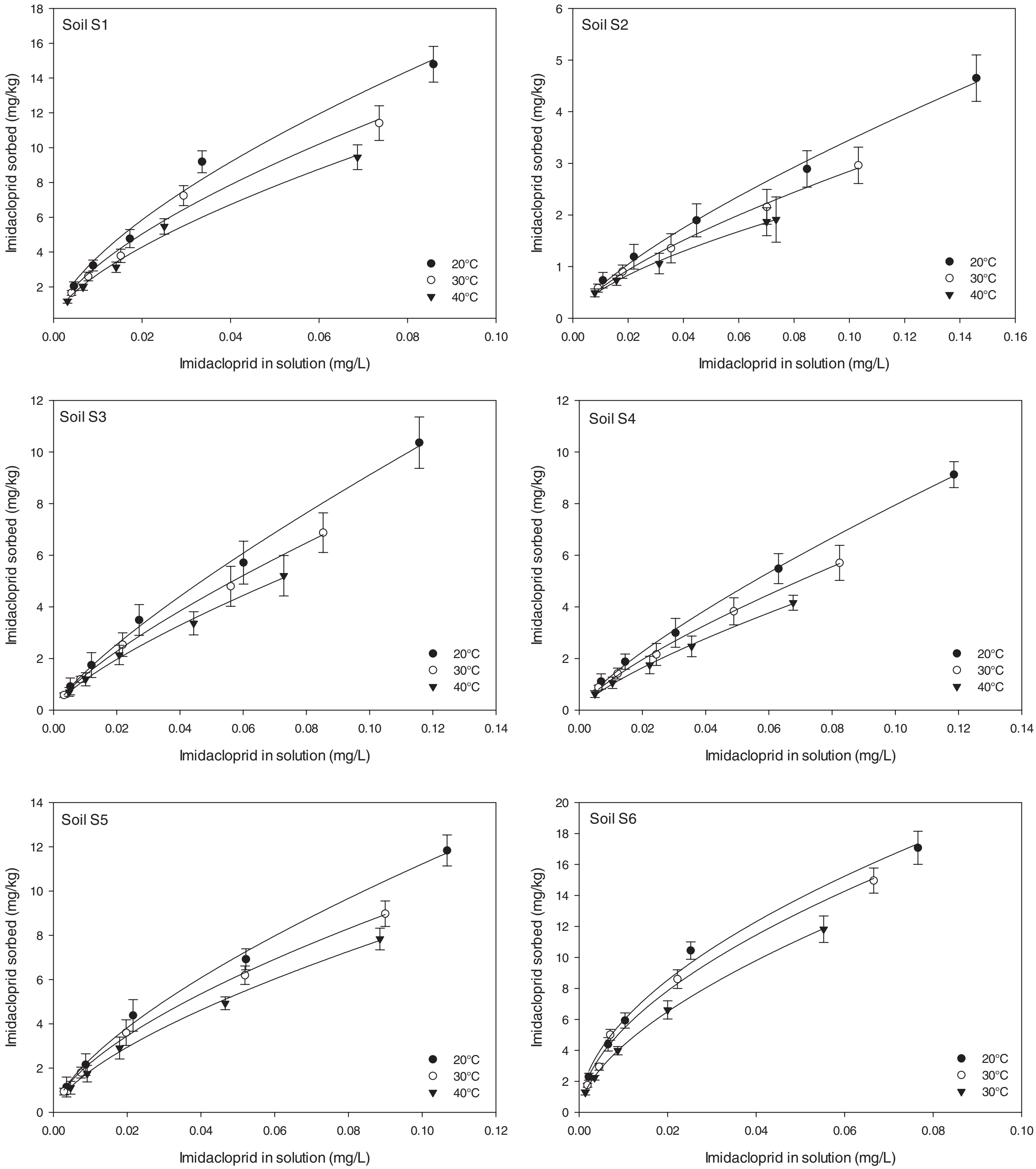

Fig. 5. Desorption isotherms of imidacloprid for experimental soils at different temperature conditions (20, 30 and 40°C) represent by Freundlich model. Values are means ± standard deviations. Symbols represent the experimental data, while lines represent the theoretical curves described by the Freundlich model.

The negative values of ΔS° (in the range of -57.12 to -14.51 J/molK) suggest the decreased randomness at the soil-solution interface during sorption of IMI on soil particles. During the sorption process, solute IMI molecules lose entropy during transition from the solution phase to solid surfaces and such a loss is greater than the translational entropy gained by sorbed solvent IMI molecules.

Furthermore, in order to further support the claim that physical sorption is the predominant mechanism of IMI binding, the values of activation energy (E_a) and sticking probability (S^*) were determined on the basis of experimental data and are presented in Table 4. The values of E_a and S^* are estimated from the plot of ln $(1-\theta)$ against 1/T, where intercept and slope of the plot are represented as ln S^* and E_a/R, respectively (Fig. 4). As we can see from the Table 4, the E_a values were negative, indicating that the sorption process is exothermic in nature and lower temperatures favor sorption of IMI by the tested soils. The relatively low magnitude of our experimental data of E_a (-6.98 to -4.39 kJ/mol) suggested that the sorption was a diffusion-controlled process and physical in nature, as E_a for physical sorption must be low (10–28 kJ/mol).[48] The values of S^* for the sorption of IMI by soils was less than one, (Table 4), indicating that probability of IMI to stick on surface of soil is high as $S^* \ll 1$.

Desorption of imidacloprid from soils at different temperatures

The isotherms for the IMI desorption in tested soils at three temperatures, 20, 30, and 40°C are presented in Figure 5. As can be seen from the plots, the isotherms for the low concentrations of IMI were similar to the sorption isotherms, while for the higher concentrations isotherms varied significantly. Similar results were observed by Fernandez-Bayo et al.[16] and Papiernik et al.[21] who studied the desorption behavior of IMI in Spain and USA soils. Desorption data are also shown in Table 6, where the desorbed amount was expressed as a percentage of the total amount of IMI sorbed. For example, when desorption was measured from the equilibrium point of the sorption isotherm corresponding to the initial IMI concentration of 10 mg/L, 68.64, 73.27 and 76.88% of the sorbed IMI desorbed from the soil S2 in six steps at 20, 30 and 40°C, respectively. The lowest

Table 6. The sorbed amount and desorbed percentage of imidacloprid at experimental soils in relation to the initial concentration level (γ; 1, 2.5, 5 and 10 mg/L) at different temperature conditions (20, 30 and 40°C).

		20°C		*30°C*		*40°C*	
Soil	*Initial concentration, γ (mg/L)*	*Sorbed amount^a (mg/kg)*	*Desorbed amount^b (%)*	*Sorbed amount^a (mg/kg)*	*Desorbed amount^b (%)*	*Sorbed amount^a (mg/kg)*	*Desorbed amount^b (%)*
S1	10	22.37	33.87	19.34	40.48	18.90	49.95
S2		14.83	68.64	10.97	73.27	8.13	76.88
S3		19.30	46.31	14.95	53.87	14.88	64.93
S4		18.12	49.64	13.92	58.93	13.00	67.92
S5		20.48	42.22	17.26	47.94	17.41	54.94
S6		24.71	30.91	22.24	32.75	21.52	45.07
S1	5	12.12	24.14	11.15	34.91	9.77	43.90
S2		8.77	67.03	7.19	69.86	4.76	59.68
S3		10.40	45.07	9.05	46.99	7.48	54.87
S4		10.29	46.72	8.32	53.88	6.68	62.99
S5		11.12	37.77	9.17	32.43	9.48	47.89
S6		12.99	19.62	12.11	28.99	10.84	38.91
S1	2.5	6.32	24.47	5.65	32.82	5.22	39.81
S2		4.81	60.53	3.76	63.73	3.21	66.69
S3		5.57	37.23	4.61	44.78	4.11	47.76
S4		5.30	43.50	4.41	50.77	3.89	54.95
S5		6.09	28.14	5.62	36.00	5.19	43.81
S6		6.80	12.79	6.42	21.98	6.03	33.97
S1	1	2.58	23.26	2.29	29.94	2.13	36.45
S2		1.96	55.10	1.53	59.56	1.33	69.07
S3		2.27	32.16	1.88	39.70	1.70	42.15
S4		2.15	38.60	1.79	47.44	1.60	48.87
S5		2.48	25.00	2.27	30.52	2.12	38.10
S6		2.76	12.32	2.60	20.07	2.46	25.31

[a] sorbed amount of IMI after 48 h sorption process

[b] desorbed amount of IMI after 144 h desorption process

Table 7. Hysteresis coefficients (*H*) and estimated parameters with standard deviation and determination coefficients (R^2) for imidacloprid desorption from experimental soils using Freundlich model at different temperature conditions (20, 30 and 40°C).

	20°C				30°C				40°C			
Soil	K_F (mg/kg)/(mg/L)$^{1/n}$	$1/n$	R^2	H	K_F (mg/kg)/(mg/L)$^{1/n}$	$1/n$	R^2	H	K_F (mg/kg)/(mg/L)$^{1/n}$	$1/n$	R^2	H
S1	86.68 (± 0.63)	0.697 (± 0.017)	0.9884	0.759	70.81 (± 0.65)	0.682 (± 0.003)	0.9864	0.746	63.07 (± 0.09)	0.691 (± 0.008)	0.9910	0.749
S2	15.96 (± 0.13)	0.681 (± 0.005)	0.9940	0.813	11.86 (± 0.20)	0.641 (± 0.006)	0.9920	0.723	8.69 (± 0.07)	0.595 (± 0.005)	0.9861	0.728
S3	56.38 (± 0.29)	0.786 (± 0.011)	0.9950	0.859	45.34 (± 0.25)	0.763 (± 0.006)	0.9974	0.836	36.78 (± 0.07)	0.746 (± 0.005)	0.9945	0.831
S4	37.99 (± 0.22)	0.711 (± 0.002)	0.9906	0.779	29.58 (± 0.26)	0.689 (± 0.004)	0.9907	0.768	25.93 (± 0.11)	0.702 (± 0.009)	0.9967	0.786
S5	60.01 (± 0.13)	0.703 (± 0.003)	0.9888	0.787	47.08 (± 0.10)	0.668 (± 0.005)	0.9918	0.755	41.72 (± 0.06)	0.676 (± 0.004)	0.9926	0.765
S6	84.39 (± 0.55)	0.566 (± 0.003)	0.9860	0.656	79.49 (± 0.37)	0.600 (± 0.020)	0.9875	0.655	69.05 (± 0.12)	0.607 (± 0.004)	0.9880	0.669

percentage of IMI desorption was achieved in the soil S6 for all initial IMI concentrations at temperatures investigated. These findings indicate that a significant hysteresis occurred in the sorption-desorption of IMI, i.e. the great fraction of IMI was resistant to desorption even after 6 days of contact time between soil and IMI molecule.

The desorption Freundlich distribution coefficient values (K_F^{des}) for the tested soils at all temperatures investigated were higher than the sorption values (K_F^{sor}), while opposite trend was observed for desorption coefficient of nonlinearity ($1/n$) (Table 7). As shown in Table 7, the temperature effect caused a decrease in the value K_F^{des} from 1.06 to 1.35 fold and from 1.22 to 1.84 fold, with increasing temperature of 10, and 20°C, respectively, indicating that the temperature strongly influence the desorption. The statistical analysis of Variance (ANOVA) confirmed that the amount of IMI desorbed was significantly affected by the different levels of temperature in all tested soils ($P < 0.05$).

In our study, $1/n$ constants decreased with increasing temperature, with deviations from the linear function ranging from 21.4% (soil S3) to 43.4% (soil S6), 23.7% (soil S3) to 40% (soil S6), and 25.4% (soil S3) to 40.5% (soil S2) at temperatures of 20, 30 and 40°C, respectively.

In order to eliminate the discrepancies between sorption and desorption isotherms hysteresis coefficient H was calculated, and the respective values for the tested soils at all studied temperatures are presented in Table 7. Hysteresis is manifested by increasing differences between the slopes of sorption and desorption isotherms.[19,49,50] Conceptually, the lack of similarities between the sorption and desorption isotherms is a result of binding of the organic matter and mineral particles, especially clay minerals.[51] When the value of H is lower, sorption-desorption hysteresis is more pronounced with higher nonlinearity, so the desorption rate is slower in relation to the sorption rate. This is possible because the high clay and organic matter content in the soils cause a higher sorption capacity. In Table 7, we can see that hysteretic behavior under different temperature treatments of sorption-desorption processes existed, and it was more pronounced at 20°C in the soils with higher OC content, particularly humic acids. In all tested soils, desorption increased with increasing initial concentration of IMI, indicating the decreasing trend of H with increasing equilibrium concentration. It means that at higher equilibrium concentration, sorbed molecules of IMI were desorbed more easily compared to a lower concentration.

Conclusion

This study focused on the investigation sorption-desorption processes of IMI in soils of Croatian coastal regions, as a function of temperature using a batch technique. The experimental data revealed that the sorption and desorption isotherms of IMI in the tested soils were nonlinear and L-type at all temperatures investigated, indicating a decrease in specific sorption sites when IMI concentration in solution increases. Pseudo sorption and desorption equilibrium were reached within 24 and 144 h, respectively, and these times were chosen as the equilibrium time for obtaining the sorption isotherms. According to the sorption modeling data, the Freundlich model was found to be the best approach for the sorption equilibrium data description at investigated temperatures. Values of K_o decreased with temperature, confirming that the IMI had a low preference for sorption at high temperature. The results of temperature effect and thermodynamic parameters confirmed that the sorption process is exothermic in nature. Values of ΔG° were negative and decreased with the temperature rise, indicating the spontaneous and feasible process of IMI sorption on the studied soils, whereas the negative values of ΔS° showed the decreased randomness at the solid-liquid interface during IMI sorption onto soil particles. Low values of ΔH° corresponded to the weak forces, such as H-bonds, consistent with interactions and partitioning of the IMI molecules into soil organic matter. In all soils, a higher sorption capacity was observed at lower temperatures, indicating that the percentage of desorbed IMI amount increased as the temperature rise. The results pointed to the significant deviation of desorption experimental data from the sorption data, indicating that the sorption and desorption were distinctly different processes in these soils. It can be assumed that the desorption process appeared to be the result of a complex, time-dependent interplay of several chemical and physical processes and irreversible binding of IMI to the soil surfaces, leading to hysteresis.

The study results emphasize the need for controlled IMI usage, especially in soils with low humus content (Zadar and Istria soil), while IMI's application at high temperatures and greenhouse conditions should be strictly controlled for reasons of its greater mobility in soil, and thus a greater risk for environmental and groundwater pollution. Further research, aided also with the actual field data, will be directed to investigate the IMI's binding mechanisms itself in order to better understand the causes for hysteretic phenomena. Education of agricultural chemicals applicators, as a result of these studies, is necessary to avoid the potential occurrence of IMI in the environment.

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