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Effect of Temperature and Soil pH on the Sorption of Ibuprofen in Agricultural Soil

Edgar HILLER[1] *and Martin ŠEBESTA*[2]

[1]*Department of Geochemistry, Faculty of Natural Sciences and* [2]*Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovak Republic*

**Corresponding author: hiller@fns.uniba.sk*

Abstract

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Besides many natural factors, soil pH and temperature can have significant effects on the sorption of pharmaceuticals in soils. This is the first study, which aimed to evaluate the effect of soil pH and temperature on the sorption of ibuprofen in soil. Sorption–desorption experiments at 20°C indicated weak retention of ibuprofen in the soil. Sorption of ibuprofen in the soil was affected by both temperature and pH with the latter showing much greater effect. The extent of ibuprofen sorption increased with decreasing pH mainly due to the change of ibuprofen speciation from negatively charged ions at high pH to the neutral form at low pH. At pH 4, the distribution coefficient K_d was 1.30 l/kg, whereas at pH 8, it was only 0.42 l/kg. When temperature increased, the sorption of ibuprofen decreased, showing that its sorption was exothermic.

Keywords: human pharmaceuticals; mobility; retention; soil; thermodynamics

Recently, human pharmaceuticals, including ibuprofen, have been a subject of many studies that describe their occurrence in the environment (Monteiro & Boxall 2010), effects on living organisms (Fent *et al.* 2006), and physico-chemical processes like sorption, transport, and microbial degradation (Yamamoto *et al.* 2009; Revitt *et al.* 2015). Ibuprofen (2-[4-(2-methylpropyl)phenyl]propanoic acid) is a human drug widely used all over the world. It belongs to non-steroidal, anti-inflammatory drugs (NSAID) and is used in the treatment of rheumatic disorders, pain, and fever (Mestre *et al.* 2007). Previous research showed that ibuprofen was not completely eliminated in wastewater treatment plants with the removal efficiency range from 13 to 99% (Verlicchi *et al.* 2012). Therefore, it may enter the surface waters, and subsequently stream sediments and groundwaters. Ibuprofen occurs in surface waters and sediments at concentrations reaching up to tens of mg/l and hundreds of mg/kg, respectively (Carmona *et al.* 2014). Moreover, the occurrence of ibuprofen in agricultural soils, even at a depth of 30 cm, indicates that its main source is the irrigation of fields with treated wastewaters (Oppel *et al.* 2004) and the application of sewage sludges (Karnjanapiboonwong *et al.* 2011). The results of Karnjanapiboonwong *et al.* (2011), who identified ibuprofen in soils at a depth of 30 cm, indicate that this drug is mobile and persistent, and may leach into groundwaters. This is in line with low sorption of ibuprofen in soils with reported Freundlich sorption coefficient (K_F) values between 0.10 to 3.42 $\text{mg}^{(1-1/n)}\cdot\text{l}^{1/n}/\text{kg}$ (González-Naranjo *et al.* 2013; Durán-Álvarez *et al.* 2014; Estevez *et al.* 2014) and with its moderate soil persistence under aerobic conditions (Xu *et al.* 2009a), which may be prolonged under anaerobic conditions (Lin & Gan 2011). Ibuprofen sorption in soils is correlated positively with organic carbon content (Xu *et al.* 2009a; Estevez *et al.* 2014) and clay content (González-Naranjo *et al.* 2013). However, to our best knowledge, there is no study which would investigate the effect of other soil properties on the sorption of ibuprofen like soil pH and temperature. Particularly, the role of temperature in the sorption of pharmaceuticals in soils is neglected, although the temperature of surface soils from temperate climatic regions may range from 5°C to 30°C (Pokladníková *et al.* 2008). Additionally, it is known that soil pH has profound impact on the sorption of ionizable pharmaceuticals (i.e. organic acids and bases) in soils (Schaffer *et al.* 2012; Schaffer & Licha 2015).

The main objective of this study is to determine whether soil pH and temperature have any effect on the sorption of ibuprofen in soil. To meet the objective, sorption of ibuprofen was determined at four temperatures (at 5, 10, 20, and 30°C), and six pH values (pH 4.0, 4.5, 5.76 (natural soil pH), 6.0, 7.0, and 8.0) at a temperature of 20°C. In addition, desorption of ibuprofen from soil to water at a temperature of 20°C was also measured in order to assess the propensity of ibuprofen to be leached from the soil.

MATERIAL AND METHODS

Soil and sorbate. The soil was collected from an agricultural field in the southern part of the Borská lowland (SW Slovakia) near the village of Lozorno. The soil sample was taken from A horizon at a depth of 0–20 cm. It belongs to the eutric Haplic Arenosol soil type. Prior to experiments, the soil was air-dried, passed through a 2 mm sieve, and mixed. The physico-chemical properties of the soil are given in Table 1. Total organic carbon content (OC) was measured by dichromate oxidation (Nelson & Sommers 1996). Humic and fulvic acids (C_{HA} and C_{FA}, respectively) were determined according to the method by Sims and Haby (1971). Soil pH was measured in soil–water suspension at soil to water ratio of 1 : 2.5 (wt/wt). Particle size distribution was determined by the pipette method and calcium carbonate content ($CaCO_3$) was measured using a volumetric device (Jackson 1958). Cation exchange capacity (CEC) was determined with 1 M ammonium acetate at pH 7.

Ibuprofen of analytical grade (99.8%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The stock solution of ibuprofen (~20.0 mg/l) was prepared in 0.01 mol/l $CaCl_2$ and 100 mg/l NaN_3 aqueous solution. Sodium azide was used to prevent microbial degradation of ibuprofen in sorption–desorption experiments of this study although Vulava *et al.* (2016) demonstrated that ibuprofen was not degraded during a 7-day sorption experiment. This stock solution was diluted to obtain solutions at five initial concentrations of ibuprofen (~1.0, 5.0, 10.0, 15.0, and 20.0 mg/l). Initial ibuprofen concentrations for sorption experiments in this study fall within the concentration range commonly applied in other studies (Estevez *et al.* 2014; Vulava *et al.* 2016).

Sorption experiments. Soil (3 g) and 5 ml of ibuprofen solution were added in 10-ml glass tubes and shaken at end-over-end shaker for 48 h in the dark at 20 ± 1°C. The control samples for each ibuprofen concentration without soil were also prepared to account for its possible losses. At equilibrium, the suspensions were centrifuged at 3000× *g* for 15 min to obtain clear supernatants. Preliminary experiments have shown that a shaking period of 48 h is sufficient for the attainment of sorption equilibrium (data not shown).

Desorption of ibuprofen was determined immediately after sorption with the highest initial concentration of ibuprofen (20 mg/l). After the removal of 3.0 ml of the supernatant, the same volume of fresh background solution containing no ibuprofen was added and the tube was shaken for 48 h, and then centrifuged. Four desorption cycles were performed.

Sorption isotherms of ibuprofen at different temperatures (5, 10, 20, and 30°C) were determined by the same procedure as described above. Constant

Table 1. Basic physico-chemical properties of the soil

Property	Value
Particle size distribution	
Sand (%)	85.5
Silt (%)	13.9
Clay (%)	0.60
pH	5.76
OC (%)	0.48
C_{HA} (%)	0.11
C_{FA} (%)	0.12
$CaCO_3$ (%)	0.20
CEC (cmol/kg)	6.83
Clay minerals	
Illite/chlorite Kaolinite	

OC – total organic carbon content; C_{HA} and C_{FA} – humic acid and fulvic acid carbon content, respectively; CEC – cation exchange capacity temperature was maintained using a thermostatic chamber with adjustable temperature. The effect of pH on ibuprofen sorption was measured at one initial concentration of 1.0 mg/l and at a temperature of 20°C. Soil pH was maintained during the experiment by adding concentrated HCl or 10 M NaOH aqueous solution. The following soil pH values were selected: 4.0, 4.5, 5.76 (the original soil pH), 6.0, 7.0, and 8.0. All experiments were done in triplicate.

Determination of ibuprofen. The ibuprofen analysis was performed by direct injection of clear supernatants into the High Performance Liquid Chromatography system (model HP 1050; Hewlett Packard, Waldbronn, Germany). Ibuprofen was detected by fluorescence detector at an emission and excitation wavelength of 310 nm and 232 nm, respectively. A mixture of acetonitrile with methanol at a ratio of 1 : 1 by volume was used as the mobile phase under isocratic elution regime. The analytical column used was LiChrospher (125 × 4 mm i.d., 5 μm) and the flow rate of mobile phase was 1.0 ml/min at 30°C. Under these chromatographic conditions, the detection limit was 0.50 mg/l with an extended measurement uncertainty of 10% R.

Data analysis. The amount of ibuprofen sorbed by soil was calculated using the equation:

$$S = \frac{(C_0 - C) \times V}{m} \qquad (1)$$

where:

S – sorbed amount of ibuprofen in soil (mg/kg)

C_0 – initial concentration of ibuprofen in solution (mg/l)

C – equilibrium concentration of ibuprofen in solution (mg/l)

V – volume of solution (l)

m – weight of soil (kg)

The amount of ibuprofen desorbed from soil in each desorption cycle was determined by the equation:

$$S_\mathrm{d} = \left[C_\mathrm{d} - \left(C \times \frac{V - V_r}{V}\right)\right] \times \frac{V}{m} \qquad (2)$$

where:

S_d – desorbed amount of ibuprofen (mg/kg)

C_d – concentration of desorbed ibuprofen in solution (mg/l)

C – remaining concentration of ibuprofen at the end of each desorption cycle (mg/l)

V_r – replaced volume of aqueous solution in each desorption cycle (l)

The sum of desorbed amounts of ibuprofen in four cycles gives its total desorbed amount from the soil.

The sorption and desorption data were fitted with both the Freundlich (in logarithmic form) and linear sorption isotherms:

$$\log S = \log K_\mathrm{Fd} + 1/n_\mathrm{d} \times \log C \qquad (3)$$

$$S = K_\mathrm{dlin} \times C \qquad (4)$$

where:

K_F – Freundlich sorption coefficient ($\mathrm{mg}^{(1-1/n)} \cdot \mathrm{l}^{1/n}/\mathrm{kg}$)

$1/n$ – Freundlich exponent

K_dlin – linear distribution coefficient (l/kg)

Symbols $1/n_\mathrm{d}$ and K_Fd refer to desorption, whereas K_F and $1/n$ to sorption. The ratio between $1/n_\mathrm{d}$ and $1/n$ was used to calculate the desorption hysteresis index (HI). Organic carbon distribution coefficient (K_oc) was calculated as:

$$K_\mathrm{oc} = (K_\mathrm{dlin}/\mathrm{OC}) \times 100 \qquad (5)$$

where:

OC – total soil organic carbon content (%)

In the case of experiments focused on the effect of pH, only single initial concentration of ibuprofen was used, therefore, the sorption of ibuprofen was described as:

$$K_\mathrm{d} = \frac{S}{C} \qquad (6)$$

where:

K_d – distribution coefficient (l/kg)

Thermodynamic parameters associated with the sorption process were calculated from K_dlin measured as a function of temperature. Using the following equations, the enthalpy (ΔH; J/mol), entropy (ΔS; J/K×mol), and Gibbs free energy change (ΔG; J/mol) were determined:

$$\ln K_\mathrm{dlin} = \frac{\Delta S}{R} - \frac{\Delta H}{R}\left(\frac{1}{T}\right) \qquad (7)$$

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

where:

R – gas constant (8.314 J/K·mol)

T – thermodynamic temperature (K)

If the enthalpy and the entropy of sorption is independent of temperature, then a plot of $\ln K_\mathrm{dlin}$ vs $1/T$ is linear according to the van't Hoff equation (Nordstrom & Munoz 1994).

Parameters fitted with both the Freundlich and linear sorption equations were determined by regression using the statistical software GraphPad Prism 6.

RESULTS AND DISCUSSION

Sorption and desorption of ibuprofen at 20°C. Sorption–desorption isotherm of ibuprofen in the soil is shown in Figure 1 and the corresponding parameters are listed in Table 2. As the measured sorption isotherm was essentially linear with 1/*n* value close to 1, it fitted also well to the linear sorption isotherm. The K_{dlin} value of 0.79 l/kg is similar to those reported in the literature (Xu *et al.* 2009a). Lower K_d values were obtained by Estevez *et al.* (2014) in agricultural soils of volcanic origin whereas higher ones determined Xu *et al.* (2009a), mainly in soils with elevated contents of soil organic carbon and clay fraction (Table 3). Based on the low K_{dlin} and K_F values it is concluded that the sorption of ibuprofen in the soil was relatively weak when only ~30% of ibuprofen was sorbed under the experimental conditions. Moreover, the K_{oc} value was equal to 165 l/kg. This K_{oc} value is consistent with those reported in some previous studies (Table 3) but a variability in K_{oc} values for ibuprofen exists likely due to different chemical properties of soil organic matter, contribution of soil minerals to overall sorption, and pH-dependent ibuprofen speciation in solution (Yamamoto *et al.* 2009; Schaffer & Licha 2015).

The desorption isotherm of ibuprofen was highly non-linear (Figure 1) with $1/n_d$ value of 0.32. The calculated value of HI was 0.32, indicating that desorption of ibuprofen was not complete; a part of ibuprofen was not desorbed from the soil. Indeed, approximately 54% of the total sorbed amount of ibuprofen was extracted from the soil after four desorption cycles. Generally, there is a lack of studies on the desorption of ibuprofen in soils. However, scarce studies documented that ibuprofen was mobile in soils with medium to high tendency for leaching to natural waters (Xu *et al.* 2009b; Durán-Álvarez *et al.* 2014) when more than 50% of the total sorbed drug was desorbed.

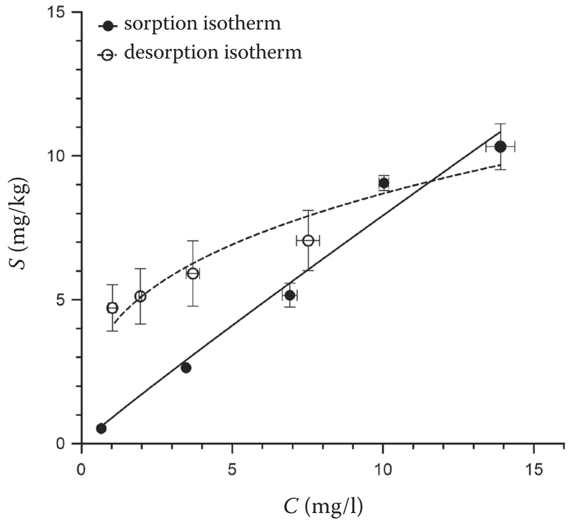

Figure 1. Sorption and desorption isotherm of ibuprofen for the soil sample at pH = 5.76 and 20°C; error bars represent standard deviation (*n* = 3); lines represent the Freundlich equation fit

Effect of soil pH on ibuprofen sorption. Final pH values of the soil suspensions after sorption were similar to the initial pH values adjusted by the

Table 2. Values of sorption and desorption parameters for ibuprofen in the test soil (mean and 95% confidence interval in parentheses)

Temperature (°C)	$\log K_F$ ($mg^{(1-1/n)}.l^{1/n}/kg$)	1/*n*	R^2	K_{dlin} (l/kg)	R^2
Sorption					
5	0.067 (0.032–0.102)	0.895 (0.852–0.939)	0.994	0.887 (0.831–0.942)	0.958
10	0.030 (–0.020–0.080)	0.910 (0.848–0.971)	0.987	0.838 (0.771–0.905)	0.931
20	–0.102 (–0.141–(–0.063))	0.999 (0.951–1.050)	0.994	0.790 (0.743–0.837)	0.966
30	–0.202 (–0.293–(–0.110))	0.974 (0.866–1.080)	0.967	0.597 (0.530–0.663)	0.885
Desorption					
	$\log K_{Fd}$ ($mg^{(1-1/n)}.l^{1/n}/kg$)	$1/n_d$	R^2		
20	0.604 (0.535–0.673)	0.323 (0.225–0.420)	0.797		

K_F and K_{Fd} – Freundlich sorption and desorption coefficients, respectively; 1/*n* and $1/n_d$ – Freundlich exponent for sorption and desorption, respectively; K_{dlin} – linear distribution coefficient

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Table 3. Range of initial ibuprofen concentrations (C_0), main soil/sediment properties (OC – organic carbon content, clay – clay content, pH) and the sorption parameters for ibuprofen (K_F – Freundlich sorption coefficient, $1/n$ – Freundlich exponent, K_{dlin} – linear distribution coefficient, K_{oc} – organic carbon distribution coefficient) obtained in this study and previous research studies

C_0 (mg/l)	K_F	Unit for K_F	$1/n$	K_{dlin} (l/kg)	K_{oc} (l/kg)	OC (%)	Clay (%)	pH	References
0.5–10	0.27–3.42	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	1.03–1.51	0.56–3.71	87–129	0.44–3.16	3.60–42.5	7.06–7.54	Xu *et al.* (2009a)
0.02–0.1	na	na	na	0.09–0.91	18–120	0.08–2.20	na	5.70–6.70	Yamamoto *et al.* (2009)
1.0×10^{-5}–0.01	1.18–3.05	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	0.82–0.99	na	na	0.80–2.60	7.30–17.8	25.0–48.0	Durán-Álvarez *et al.* (2014)
0.5–10	1.05–2.26	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	0.76–1.08	1.40–1.56	140–238	0.87–1.74	12.5–17.5	7.63–8.01	González-Naranjo *et al.* (2013)
1.0–200	0.10–0.70	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	0.70–0.90	0.04–0.52	10–32	0.39–2.33	14.9–28.0	7.90–8.50	Estevez *et al.* (2014)
0.1–20	1.48–259	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	0.64–1.02	1.72–45.5	192–989	0.40–9.00	6.00–20.0	4.50–6.50	Vulava *et al.* (2016)
1.0–20	0.79	$mg^{(1-1/n)} \cdot l^{1/n}/kg$	1.00	0.79	165	0.48	0.60	5.76	present study

na – not available

addition of HCl or NaOH, and were within 0.1 pH unit or less. The values of K_d were found to be 1.30, 1.22, 0.80, 0.81, 0.40, and 0.42 l/kg for soil pH values of 4.00, 4.50, 5.76, 6.00, 7.00, and 8.00, respectively. Figure 2 shows the speciation of ibuprofen and its K_d values as a function of pH. As could be seen from Figure 2, the sorption of ibuprofen strongly depended on the soil pH. The values of K_d decreased with increasing pH up to pH 7, and then remained constant. The shift in ibuprofen sorption with changing pH is mainly due to two factors associated with ionizable nature of the drug and charge characteristics of soil organic matter and minerals. Ibuprofen is a weak organic acid with dissociation constant pK_a value of 4.91 (Babić *et al.* 2007), meaning that it occurs mostly as conjugate acid (i.e. neutral molecule) in solution under acidic conditions (pH < pK_a) and its anionic form prevails at pH values higher than pK_a (Figure 2). It is expected that during sorption of ibuprofen at lower pH values, the soil surface would have the low net negative charge density because soil organic matter and minerals are only partially ionized at acidic pH. Therefore, electrostatic repulsion is minor at these solution pH values, and sorption of ibuprofen is promoted by attractive hydrogen bonds through its carboxylic group and hydrophobic interactions between the apolar core of ibuprofen molecule and the soil organic matter. At pH values greater than the pK_a of ibuprofen, the adsorbate occurs increasingly as carboxylate anion. Simultaneously,

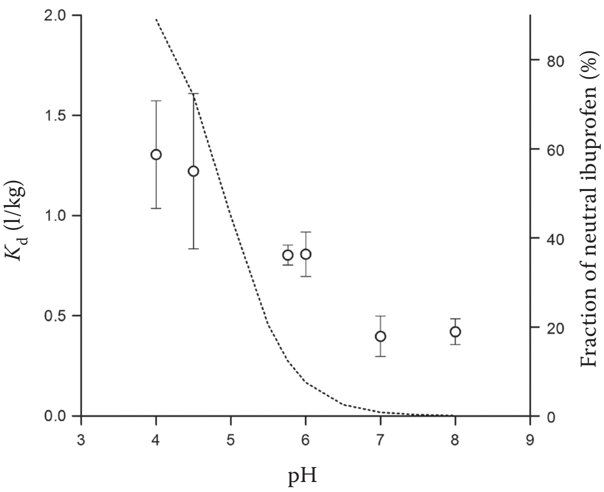

Figure 2. Dependence of distribution coefficient (K_d) on the soil pH (white circles with error bars) and fraction of neutral ibuprofen molecules vs pH (dotted line); fraction of neutral ibuprofen was calculated using the equation: $\alpha = 1/1 + 10^{(pH - pKa)}$; error bars represent standard deviation ($n = 3$)

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organic and mineral components of the soil become increasingly negatively charged as pH rises because most of soil components have the values of point of zero charge less than 5 (Kosmulski 2009). Due to the deprotonation of both ibuprofen molecules and soil surfaces at higher pH, electrostatic repulsion of carboxylate anions from negatively charged soil surfaces prevails, and sorption of ibuprofen by soil decreases sharply. No data exist about the sorption of ibuprofen in soil as a function of pH but the results of this study are consistent with those obtained by Behera *et al.* (2012) using montmorillonite, kaolinite, and goethite as adsorbents of ibuprofen at different pH values. They observed dramatic reduction in ibuprofen sorption by all three minerals with increasing pH. Inverse relationships between the sorption and the soil pH are also common for other acidic pharmaceuticals like naproxen (Schaffer *et al.* 2012) and sulfamethoxazole (Kodešová *et al.* 2015). An additional explanation of the decreased sorption of ibuprofen in soil at higher pH is that ibuprofen anions are more soluble and hydrophilic than their neutral counterparts (octanol-water partition coefficient $\log K_{\mathrm{ow}}$ = 4.91 for the neutral ibuprofen vs 1.39 for the ibuprofen anion; Kerns *et al.* (2003)), supressing its sorption interactions with natural solids.

Effect of temperature on ibuprofen sorption. The sorption isotherms for ibuprofen at four temperatures are shown in Figure 3 and the fitted sorption parameters are given in Table 2. The values of K_F were 1.17, 1.07, 0.79, and 0.63 $\mathrm{mg}^{(1-1/n)} \cdot \mathrm{l}^{1/n}/\mathrm{kg}$ at 5, 10, 20, and 30°C, respectively, and decreased with increasing temperature. The Freundlich exponent $1/n$ was not significantly different from one at temperatures of 20 and 30°C, however at lower temperatures, it deviated slightly from one. Nevertheless, the sorption isotherms of ibuprofen fitted well to the linear sorption isotherm (Table 2) and K_{dlin} values ranged from 0.60 l/kg at 30°C to 0.89 l/kg at 5°C. Significant differences in K_{dlin} values ($P < 0.05$; Tukey's *post hoc* test) were found between all temperatures with the exception of the difference between 5°C and 10°C. The reduction of ibuprofen sorption with increasing temperature and ΔH value of –10.43 kJ/mol show that it is an exothermic process. The effect of temperature can be explained in part by the water solubility of ibuprofen, which is 21 mg/l at 25°C (Yalkowsky & He 2003). Ibuprofen solubility in water depends on the temperature, and it increases at higher temperatures (Yalkowsky & He 2003), which in turn may reduce sorption affinity of ibuprofen for soils, as confirmed previously for other ionizable organic chemicals (Biggar & Cheung 1973; Koskinen & Cheng 1983). The magnitude of ΔH falls into the range of weak forces such as physical adsorption and van der Waals forces (Chiou 2002), which agrees well with low sorption potential of ibuprofen in the soil (see above). The presence of –COOH group leads to an increase of its overall polarity, thus increasing the likehood of van der Walls interaction with charged soil surfaces, whereas benzene ring with aliphatic chain allows ibuprofen molecule to bind with soil organic matter through physical sorption. The values of ΔG ranged from +0.21 to +1.16 kJ/mol and increased with temperature, indicating that the sorption of ibuprofen in the soil was not spontaneous. According to Antunes *et al.* (2012), this may be due to repulsion between the soil surface and ibuprofen that are both negatively charged at soil pH of 5.76. Positive values of ΔG were also found for the soil sorption of negatively charged pharmaceutical, sulfisoxazole (Maszkowska *et al.* 2014). The negative value of ΔS (–0.038 kJ/K·mol) suggests a decrease of randomness at the soil–solution interface during ibuprofen sorption in soil. Negative entropies for the sorption result mostly from the fact that the loss of entropy during transition of sorbate molecules from the aqueous solution is higher than the gain of entropy due to the loss of structured water molecules surrounding the sorbate. The observed

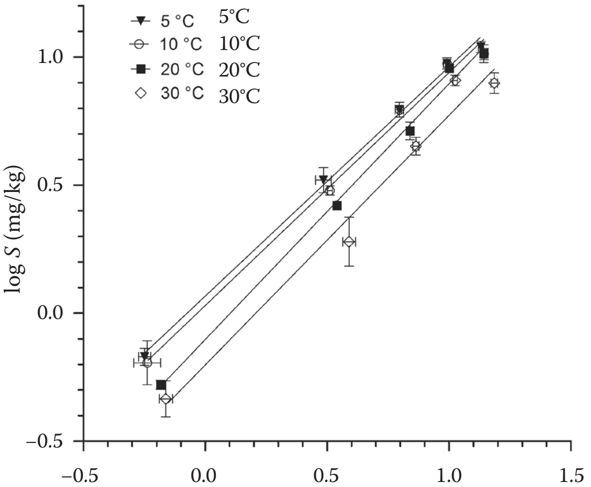

Figure 3. Sorption isotherms of ibuprofen for the soil sample at pH = 5.76 as a function of temperature; error bars represent standard deviation (n = 3); lines represent the Freundlich equation fit

temperature-dependent sorption of ibuprofen in soil was comparable with that for propranolol, carrying positive charge (Maszkowska *et al.* 2014), and anionic picloram (Biggar & Cheung 1973).

CONCLUSION

The sorption of ibuprofen in soil was shown to be pH- and temperature-dependent. The effect of soil pH on ibuprofen sorption was more pronounced than that of temperature. The sorption of the test compound in soil decreased with increasing pH from 4.0 up to 8.0 and the same held for the temperature effect, indicating that the sorption of ibuprofen in soil was exothermic with an enthalpy change of –10.43 kJ per mol. The results indicate that the addition of lime to soils, which is a common practice to increase soil pH, is not favourable from environmental point of view because it may cause an increase of mobility of ibuprofen and other hazardous organic compounds that behave as organic acids. Similarly, natural or synthetic fertilizers contain ammonium nitrogen, which also increases soil pH, and thus the mobility of acidic pharmaceutical compounds in soils.

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