Modeling of chlorophenols competitive adsorption on soils by means of the ideal adsorbed solution theory

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Abstract

The adsorption of 3-chlorophenol (3-CP) and 3,5-dichlorophenol (3,5-CP) on two Italian soils was studied at 20 °C. Experiments on the pure components showed that 3,5-CP was more strongly adsorbed than 3-CP, and that the adsorption capacity could be related to the organic carbon fraction of the soil.

Competitive adsorption data were described by the fully predictive ideal adsorbed solution (IAS) theory. To this end, the Langmuir parameters determined from pure component adsorption data were used. Results showed that at low 3,5-CP concentration (up to 5–10 mM) the model describes satisfactorily the binary system behavior, whereas at higher concentrations predictions fail, suggesting that non ideality effects in the adsorbed phase should be accounted for.
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1. Introduction

Hazardous-waste risk assessment of contaminated sites is usually performed following a four-step procedure, accounting for (1) hazard identification, (2) exposure assessment, (3) toxicity assessment and (4) risk characterization [1]. The main source of uncertainties are included in exposure assessment, which requires the estimation of exposure concentrations for both on- and off-site receptors. These are usually determined by application of Fate and Transport models, that are written and solved for the possible contaminants pathways, including chemical release mechanisms (leaching and volatilization), chemical transformation and transport (subsurface or atmospheric transport). As far as our discussion is limited to subsurface migration of pollutants, Fate and Transport models usually introduce an empiric attenuation factor,

which accounts for adsorption, volatilization and biodegradation processes [2]. The exposure concentration is simply determined by multiplying this factor by the pollutant concentration in the contaminated site. In this approach, adsorption of contaminants on soils is described by simple linear models, i.e. by assuming a concentration-independent partition coefficient. Application of these models is limited to low concentrations, where a Henry-type adsorption isotherm may be appropriate. At higher concentrations, adsorption may be characterized by a strong non-linear behavior, which is not accounted for by a Henry-type equation. In addition, when more contaminants are present in the subsurface (this is very frequent in practice), they can compete for the available adsorption sites.

Since adsorption phenomena may alter natural and enhanced biodegradation rate of organic contaminants, and also affect the performance of biological treatment processes [3], there is a need to develop more refined models for pollutants adsorption. They should be capable of describing both

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Nomenclature

b_i	Langmuir coefficient of component i ($dm^3 \, mmol^{-1}$)
c_i	liquid phase concentration of component i ($mmol \, dm^{-3}$)
c_T	total concentration in the liquid phase ($mmol \, dm^{-3}$)
f_{oc}^*	minimum soil organic carbon content in which organic matter serves as primary sorbent (%)
G	Gibbs free energy ($kJ \, mol^{-1}$)
H_i	Henry constant of component i in the Langmuir equation ($dm^3 \, kg^{-1}$)
K_{ow}	octanol–water partition coefficient
N	number of components
Q_i	saturation capacity of component i in Langmuir isotherm ($mmol \, kg^{-1}$)
q_i	adsorbed amount of component i ($mmol \, kg^{-1}$)
q_T	total concentration in the adsorbed phase ($mmol \, kg^{-1}$)
S_a	soil surface area ($m^2 \, g^{-1}$)
T	temperature (K)
z_i	molar fraction of component i in the adsorbed phase
x_i	molar fraction of component i in the liquid phase

Greek letters

φ	relative mean square error between calculated and experimental data
Π	spreading pressure (atm)
μ_i^a	chemical potential of component i in the adsorbed phase ($J \, mol^{-1}$)
μ_i^l	chemical potential of component i in the liquid phase ($J \, mol^{-1}$)

Subscripts and superscripts

a	adsorbed phase
l	liquid phase
o	pure component
P	constant pressure
T	constant temperature

nonlinear adsorption of single components and competitive adsorption in multicomponent systems. Despite the number of proven models (Langmuir, Freundlich, bi-Langmuir, quadratic) for the description of single component adsorption of contaminants on real soils [4] and some experimental results on competitive adsorption [5], there is a lack of theoretical works addressing the problem of describing competitive adsorption in multicomponent mixtures of environmental interest. This is especially true for organic contaminants, whereas a good deal of papers is available, for instance, for metals.

The simplest, but often inadequate, approach to describe competitive adsorption is based on empiric combination of single component isotherms [6]. On the other hand, physically-grounded theories based on molecular thermodynamics have been developed in the chemical engineering field and applied to various systems of pharmaceutical and biochemical interests. All these models derive from the ideal adsorbed solution theory originally developed for gas mixtures by Myers and Prausnitz [7], later extended to nonideal adsorbed phases by Talu and Zwiebel [8], and applied to liquid phase systems by Migliorini et al. [9].

The aim of this work was to assess the possibility of applying molecular-thermodynamic models to describe the competitive adsorption of organic compounds on real soils. 3-Chlorophenol and 3,5-dichlorophenol were selected as model contaminants, since they are ubiquitous contaminants, and also because past experience in their use and determination was gathered in previous works [10–12]. Single component and binary adsorption data on two real soils collected near Rome (Italy) were obtained and used to test the results of a model based on the ideal adsorbed solution theory.

2. Molecular thermodynamics of adsorption

Adsorption of multicomponent mixtures can be described with increasing degree of complexity choosing different approaches [6]. Limiting our discussion to a two-component system, the competitive behavior of the two components can be accounted for using a bi-Langmuir adsorption isotherm:

$$q = \frac{H_1 c_1}{1 + b_1 c_1} + \frac{H_2 c_2}{1 + b_2 c_2} \tag{1}$$

where the coefficients H_i and b_i ($i = 1, 2$) are those obtained from single component isotherms. Unfortunately, this rather simple approach is limited to components characterized by the same saturation capacity, which case is truly very rare. To overcome this limitation more elaborated models, such as the ideal adsorbed solution (IAS) theory, need to be used.

2.1. The ideal adsorbed solution theory

This theory, developed by Myers and Prausnitz [7], can be derived from the general equilibrium criterion ($dG_{T,P} = 0$) applied to the distribution of solute i between the liquid and the adsorbed phases:

$$\mu_i^a = \mu_i^l \tag{2}$$

Radke and Prausnitz [13] and Migliorini et al. [9] showed that, if both phases can be assumed ideal, Eq. (2) can be written as:

$$c_i(\Pi, T, z_i) = c_i^0(\Pi, T) z_i \tag{3}$$

where Π is the spreading pressure, T is the temperature, c_i is the liquid-phase concentration, c_i^0 is the pure component liq-

uid concentration that would give rise to the same spreading pressure as the multicomponent mixture, and z_i is the mole fraction of i in the adsorbed phase.

The spreading pressure is defined as the difference between the interfacial tension of the solid–pure solvent interface and that of the solid–solution interface. Π is a property of the solution, and the Gibbs adsorption isotherm provides the following expression for it:

$$\Pi = \frac{RT}{A} \int_0^{c_i^0} q_i^0 \frac{dc_i^0}{c_i^0} \tag{4}$$

where A is the surface area and $q_i^0 = f_i(c_i^0)$ is the single component adsorption isotherm.

Provided that the mole fraction (x_i) and concentration (c_T) of a binary liquid mixture in equilibrium with the adsorbed phase are known, the equilibrium concentration of pure component 1, at the same spreading pressure and temperature as the mixture, can be readily calculated by equating the right hand side of Eq. (4) for the two components:

$$\int_0^{C_1^0} q_1^0 \frac{dc_1^0}{c_1^0} - \int_0^{C_2^0} q_2^0 \frac{dc_2^0}{c_2^0} = 0 \tag{5}$$

If both components obey the simple Langmuir isotherm, Eq. (5) becomes:

$$\frac{H_1}{b_1} \ln(1 + b_1 c_1^0) - \frac{H_2}{b_2} \ln(1 + b_2 c_2^0) = 0 \tag{6}$$

c_1^0 may be expressed in terms of c_2^0 by the stoichiometric relationship in the adsorbed phase $\left(\sum_{i=1}^N z_i = 1 \right)$, which yields:

$$c_1^0 = \frac{c_2^0 c_T x_1}{c_2^0 - c_T(1 - x_1)} \tag{7}$$

The mole fraction (z_i) and concentration (q_i) in the adsorbed phase are then easily obtained as:

$$z_i = \frac{c_1^0}{c_T x_i} \tag{8}$$

$$\frac{1}{q_T} = \sum_{i=1}^N \frac{z_i}{q_i^0} \tag{9}$$

$$q_i = z_i q_T \tag{10}$$

The main feature of the IAS model relies on being fully predictive, since pure component isotherms are the only information required to calculate the multicomponent equilibrium. Besides, the model is thermodynamically consistent. Nevertheless, its applicability may be limited by the underlying hypothesis of homogeneous and equally accessible adsorption sites.

Table 1
Composition of soil 1 and soil 2

Fraction (%)	Soil 1	Soil 2
Gravel	12.81	10.63
Sand	35.11	53.97
Silt	33.92	34.50
Clay	18.16	0.90

3. Materials and methods

3.1. Reagents

3-Chlorophenol (3-CP) and 3,5-dichlorophenol (3,5-DCP) (99% pure), methanol and ethanol (HPLC grade), used for standard mixtures preparation, and hydrochloric acid (37%) were all purchased from Carlo Erba (Milan, Italy); 2-bromophenol (purity >98%), used as internal standard, was purchased from Sigma–Aldrich (Steinheim, Germany).

3.2. Characterization of soil samples

The soils selected for the present study were collected in two different areas located near Rome (Italy). Namely, soil 1 was collected from the surface of a dismissed industrial area, whereas soil 2 was taken from a cave, situated in a volcanic area. Preliminary extraction tests indicated that phenols concentration in both soils was below the detection limit. The total organic carbon, measured following the Walkey-Black procedure [14], was 0.95% for soil 1, and 6.4% for soil 2. Both soils were air dried and passed through 2 mm sieve. The particle size distribution for soil fractions <2 mm, reported in Table 1, clearly indicates that soil 1 is characterized by much higher clay content than soil 2, which is mainly composed of sand and loam. The porosity values for the two soils, measured with a Helium Picnometer (Accu Pyc 1330, Micrometrics), are reported in Table 2. Finally, the pH, measured in a 0.1 M KCl slurry, was 6.6 for soil 1, and 6.4 for soil 2.

3.3. Batch adsorption tests

Adsorption equilibrium experiments were performed in 50 ml amber glass vials, kept under continuous agitation (400 rpm) on a multiposition magnetic stirrer, supplied by VELP Scientifica (Italy). Temperature was controlled to $20 \pm 1\,^\circ$C.

Single component tests were made by pouring 2.5 g of soil 1 or soil 2 into the vial, together with 12 ml of a 3-CP or 3,5-DCP solution (initial concentration: 0.3–25 mmol dm^{-3}).

Table 2
Bulk density (ρ_s), density (ρ_d) and porosity (N) of tested soils

	Soil 1	Soil 2
ρ_s (kg dm^{-3})	2.5735	2.3201
ρ_d (kg dm^{-3})	1.098	1.055
N (%)	57.34	54.52

Fig. 1. Experimental adsorption equilibrium data (●) and Langmuir isotherm (solid line) of (a) 3-CP and (b) 3,5-DCP on soil 1.
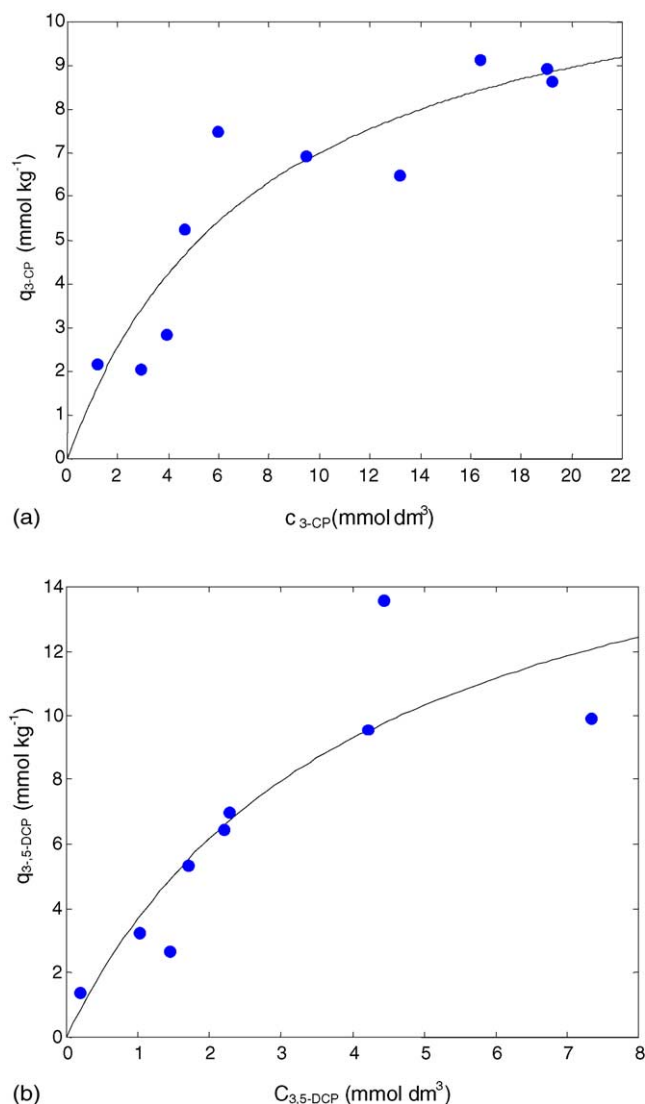

Fig. 2. Experimental adsorption equilibrium data (●) and Langmuir isotherm (solid line) of (a) 3-CP and (b) 3,5-DCP on soil 2.

The vials were stirred for 24 h in order to achieve equilibrium. Multicomponent adsorption tests were performed with the same procedure on 3-CP and 3,5-DCP solutions differing in initial molar composition and concentration. After 24 h, a sample of the soil slurry was withdrawn and centrifuged at 4000 rpm for 15 min in a PK 110 centrifuge supplied by ALC (Italy). The supernatant was then analyzed for 3-CP and/or 3,5-DCP, providing the 3-CP equilibrium concentration in the liquid phase. The 3-CP/3,5-DCP concentrations in the adsorbed phase were determined from the mass balance of each component in the liquid phase.

The pH of the soil slurries used for the adsorption equilibrium experiments was always near to that of the two soils, i.e. pH = 6–6.5. At these pH values, ionization of both 3-CP and 3,5-DCP can be considered negligible with respect to their adsorption behavior.
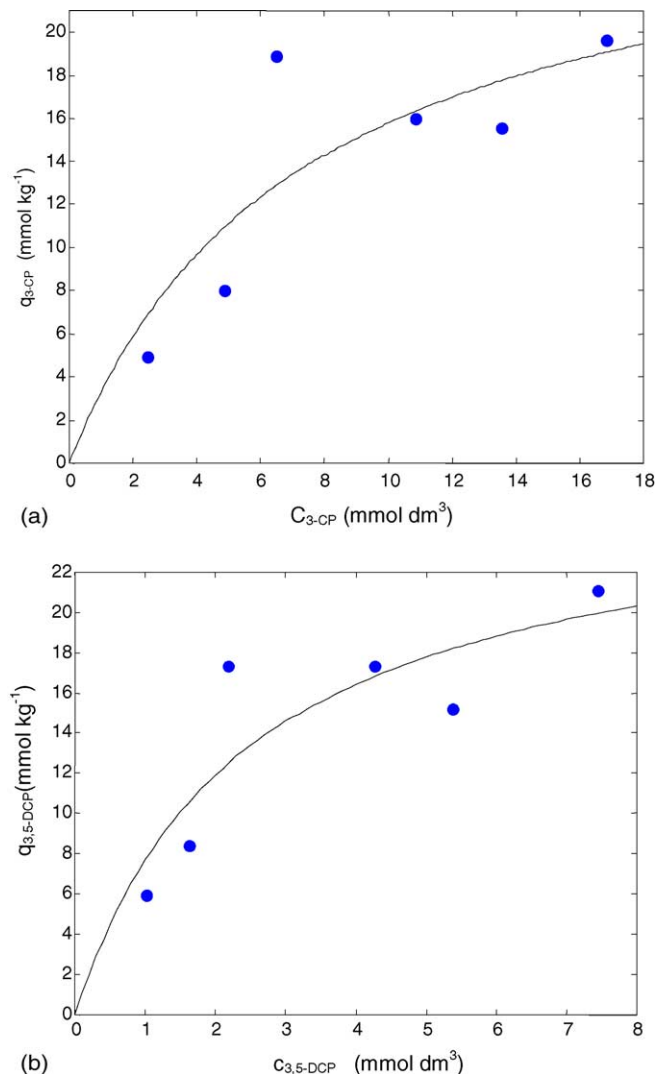
3.4. Extraction and analytical methods

Determination of 3-CP and 3,5-DCP in the supernatant was carried out by the solid phase microextraction (SPME) technique coupled to gas chromatography-flame ionization detection (GC-FID). SPME extraction was done using a manual 85 μm polyacrylate SPME device purchased from Su-

Table 3
Langmuir isotherm parameters obtained by fitting single component adsorption equilibrium data

	Soil 1		Soil 2	
	3-CP	3,5-DCP	3-CP	3,5-DCP
b (dm^3 mmol^{-1})	0.125	0.242	0.136	0.404
$Q = H/b$ (mmol kg^{-1})	12.697	18.84	27.411	26.588
$H = bQ$ (dm^3 kg^{-1})	1.587	4.559	3.728	10.741

pelco (Bellefonte, PA, USA). Namely, a 2 ml sample of supernatant was added to a 35 ml extraction glass used for the SPME extraction. The SPME content was then analyzed by means of GC-FID using an Autosystem XL gas chromatograph (Perkin-Elmer, Norwalk, CT) equipped with a 30 m × 0.25 μm i.d. BP5 capillary column (SGE, Ringwood, Australia). The 3-CP and/or 3,5-DCP concentrations were determined by the internal standard method as discussed in more details elsewhere [10].

4. Results and discussion

Single component equilibrium data of 3-CP and 3,5-DCP on the two soils are shown in Figs. 1 and 2. Data points were fitted to the Langmuir isotherm:

$$q = \frac{Hc}{1 + bc} \tag{11}$$

Fig. 3. Experimental adsorption equilibrium data of 3-CP ($\bullet$) and 3,5-DCP ($\blacksquare$) mixtures on soil 1 at different liquid phase molar compositions: (a) $x_{3\text{-}CP} = 0.12$; (b) $x_{3\text{-}CP} = 0.60$; (c) $x_{3\text{-}CP} = 0.70$ compared with IAS model predictions (solid lines).
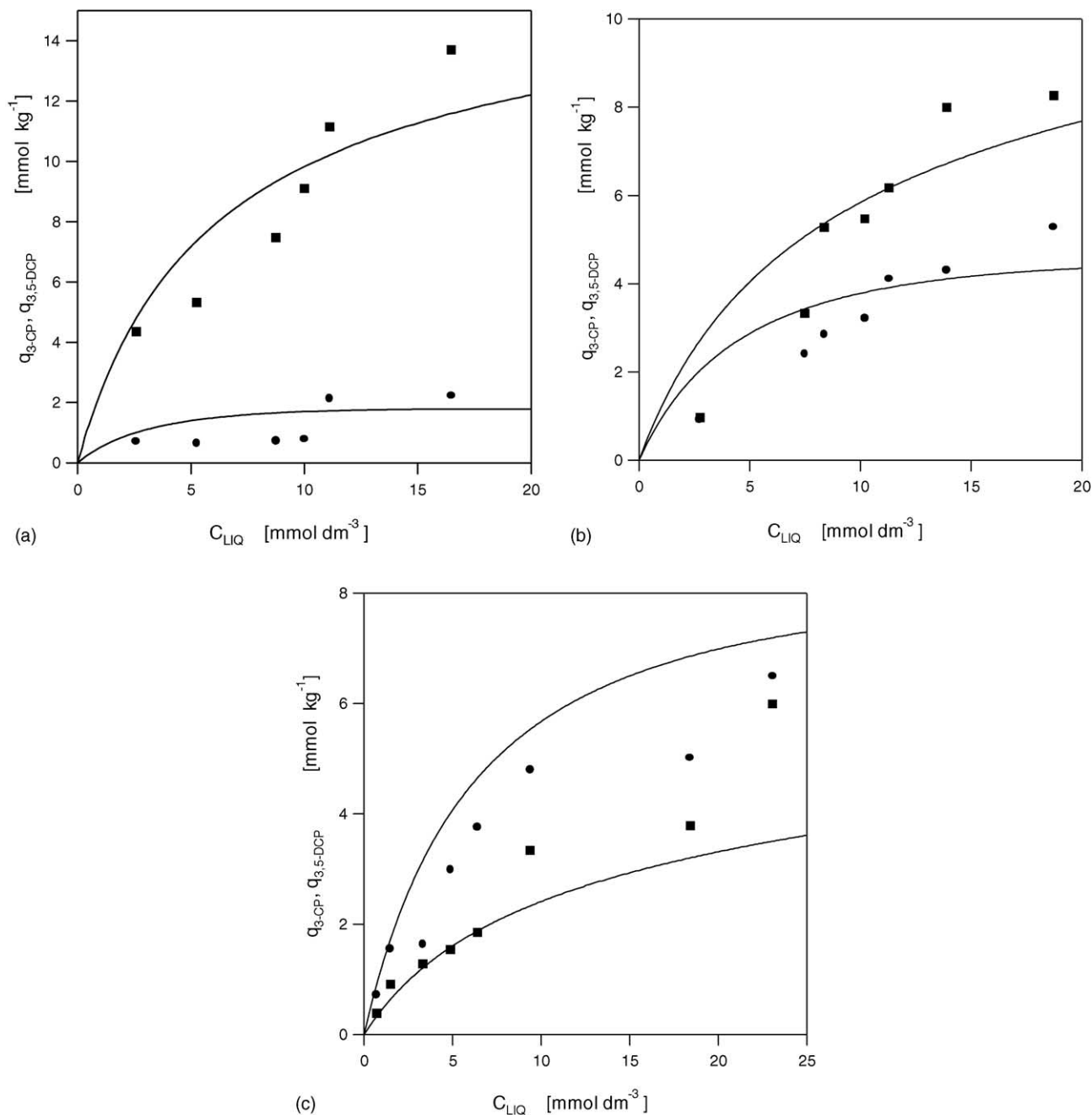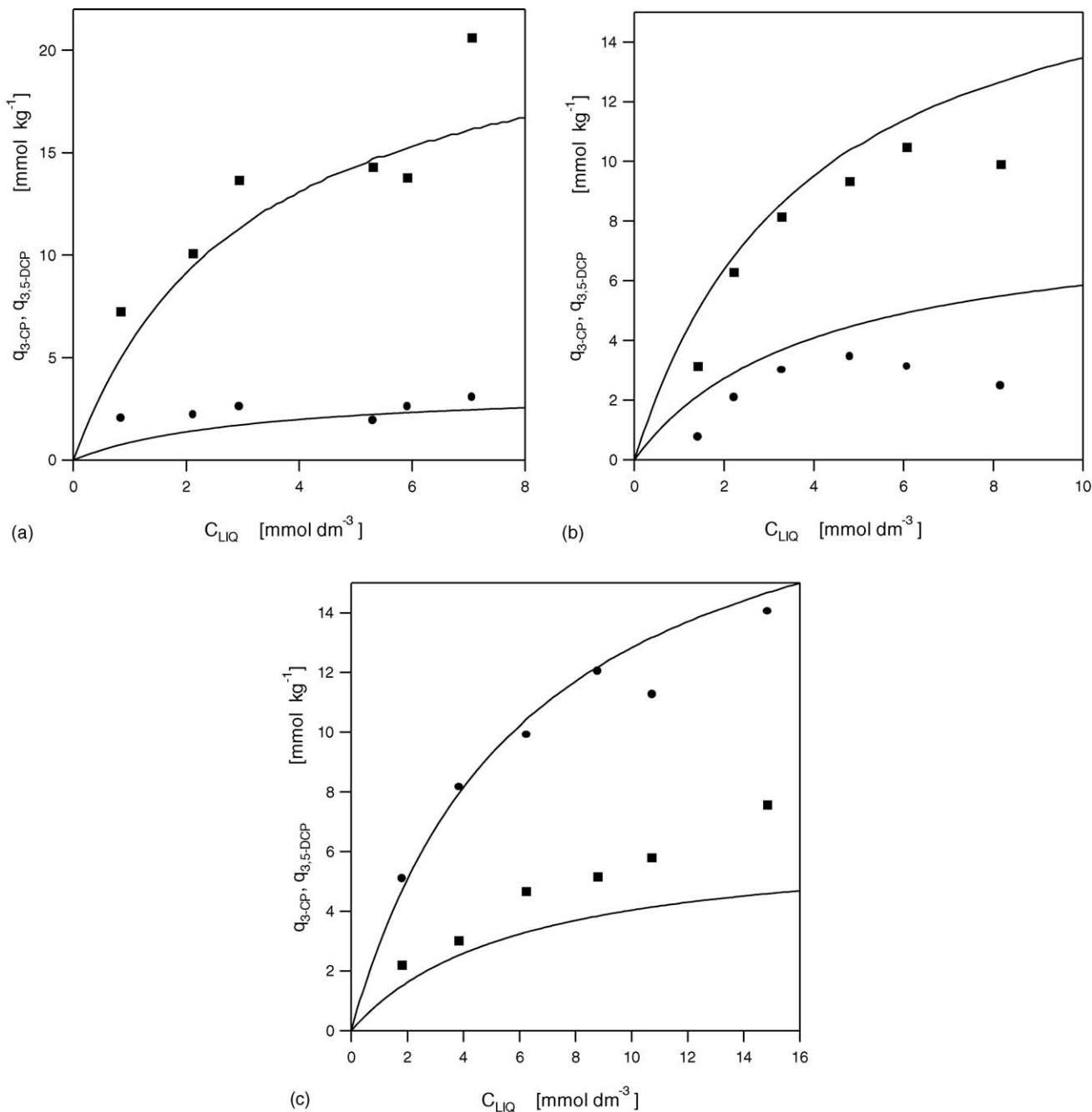
Fig. 4. Experimental adsorption equilibrium data of 3-CP (●) and 3,5-DCP (■) mixtures on soil 2 at different liquid phase molar compositions: (a) $x_{3\text{-CP}} = 0.15$; (b) $x_{3\text{-CP}} = 0.25$; (c) $x_{3\text{-CP}} = 0.90$ compared with IAS model predictions (solid lines).

Least-square estimation of the equilibrium parameters provided the values listed in Table 3.

The Henry constant accounts for the adsorption capacity of the soil at low to moderate concentrations. Accordingly, the following considerations can be made:

(a) 3,5-DCP is more strongly adsorbed than 3-CP on both soils, being the Henry constant larger for a three-fold factor;

(b) soil 2 exhibits a larger adsorption capacity, since the Henry constant is more than two times larger for both components.

The parameter Q, defined as the ratio between H and b, accounts for the adsorption capacity at equilibrium conditions. As can be seen, it is approximately the same for 3-CP and 3,5-DCP on each particular soil. Again, however, soil 2 shows much larger adsorption capacity. This difference could be, at

least partially, ascribed to the different organic carbon content of the two soils, since it is well known that the adsorption of organics on soils is directly related to the organic carbon fraction of the soil. For each soil, therefore, the minimum fraction of organic carbon in which organic matter serves as the primary sorbent was determined. This quantity can be calculated as [1]:

$$f_{oc}^* = \frac{S_a}{2(K_{ow})^{0.84}} \tag{12}$$

where S_a is the soil surface area and K_{ow} is the octanol–water partition coefficient for the contaminant of concern. Based on the soils texture given in Table 1, soil 1 may be classified as a loam ($S_a = 50$–$100\,\mathrm{m^2\,g^{-1}}$), whereas soil 2 as a sandy loam ($S_a = 10$–$40\,\mathrm{m^2\,g^{-1}}$). Accordingly, an average surface area of $75\,\mathrm{m^2\,g^{-1}}$ for soil 1, and $25\,\mathrm{m^2\,g^{-1}}$ for soil 2 were assumed. The K_{ow} data for 3-CP and 3,5-DCP were not available, and hence the values relative to 2-chlorophenol ($\log K_{ow} = 2.17$) and 2,4-dichlorophenol ($\log K_{ow} = 3.08$) were used. By using Eq. (12), the f_{oc}^* for 2-chlorophenol on soils 1 and 2 were equal to 0.56% and 0.19%, respectively, whereas the f_{oc}^* for 2,4-dichlorophenol were 0.1% and 0.03%, all values being well below the measured organic content (0.95% for soil 1 and 6.4% for soil 2). It can then be inferred that the organic matter serves as the primary sorbent of organics, for both soils, and that differences in their adsorption capacity follow the observed differences in their f_{oc}^* values.

The equilibrium data of 3-CP and 3,5-DCP binary mixtures for the two soils are reported in Figs. 3 and 4, along with predictions by the IAS theory. As described above, the IAS model only requires the knowledge of single component isotherms (in our case, the Langmuir parameters H and b). The adsorbed phase concentrations of each compound were calculated following the procedure outlined in Section 2.1. A comparison between experimental data and model predictions, performed at three different liquid compositions, is shown in Figs. 3 and 4.

To provide a quantitative assessment of the goodness of prediction the following quantity:

$$\varphi = \frac{\left[\sum_{i=1}^{N_p}((Z_1^{sp} - Z_1^{calc})/Z_1^{sp})^2 + \sum_{i=1}^{N_p}((q_{TOT}^{sp} - q_{TOT}^{calc})/q_{TOT}^{sp})^2\right]}{N_p} \tag{13}$$

was calculated, where N_p is the number of experimental data points. The following values were obtained: $\varphi = 0.159$ for soil 1, and $\varphi = 0.152$ for soil 2.

An analysis of the results shows that, when the 3-CP liquid concentration is low (i.e. below 5–10 mmol dm^3), the IAS model predicts quite satisfactorily the binary system behavior (Figs. 3a and 4a). At these conditions the adsorbed phase is mainly composed by 3,5-DCP and thus nonideality effects are likely to be negligible. On the contrary, IAS predictions fail when the 3-CP liquid concentration is higher (Figs. 3b, c and 4b, c). In these cases the adsorbed phase con-

tains both 3-CP and 3,5-DCP in comparable amounts, leading to increased nonideality effects that cannot be accounted for by an ideal and completely predictive model.

5. Conclusions

The competitive adsorption of chlorophenols on soils was described by means of a molecular thermodynamic model. The IAS theory was applied to predict the adsorptive behavior of 3-CP and 3,5-DCP binary mixtures. The only information used were the Langmuir parameters derived from single component adsorption isotherms. At low 3-CP concentrations the agreement between IAS predictions and experimental data was fairly satisfactory.

The approach used in this work may help in improving the accuracy of the adsorption routines of Fate and Transport models. Application of the IAS model could be helpful in describing competitive adsorption from single component adsorption data without the need of collecting binary data. Even if approximate, as clearly shown in this work, the IAS model represents a great advance with respect to the linear models that are usually used for Fate and Transport calculations. A possible improvement of the model results could be in principle achieved by accounting for non idealities in the adsorbed phase, but the model would in this way loose its predictive feature.

A further validation of the approach presented here could derive from extension of the proposed procedure to other compounds and possibly to multicomponent systems.

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