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Prediction of fixed-bed GAC filter consumption for complex VOC mixtures using a parsimonious competitive adsorption model and a single batch test

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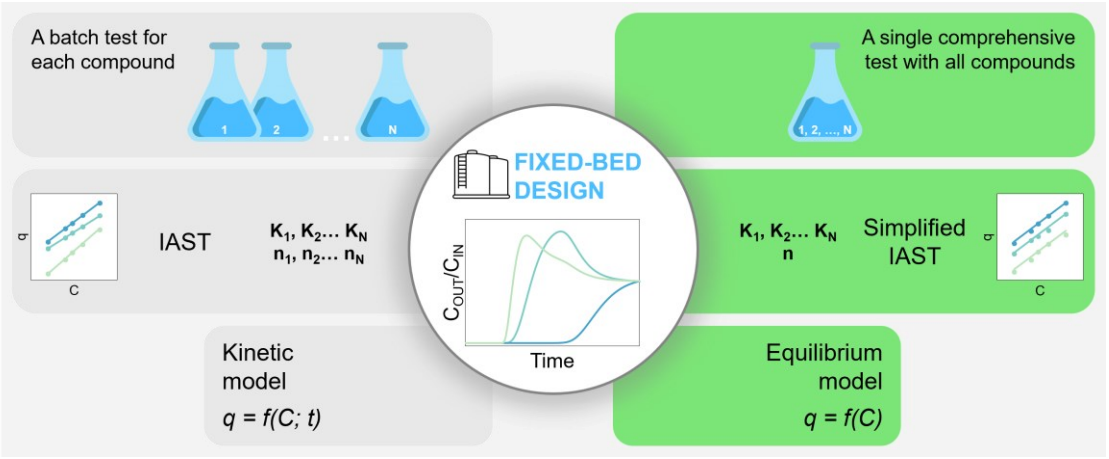
Abstract

The design of fixed-bed adsorbers for the treatment of drinking water and wastewater contaminated with complex mixtures of organics is a tedious procedure that requires detailed description – using a combination of experiments and modelling - of the individual and competitive adsorption behaviour of many dissolved species. To address the need for an experimental and modelling workflow that is both accurate and parsimonious, this study systematically evaluates the treatment of groundwater contaminated with 13 competing chlorinated hydrocarbons using a fixed-bed of granular activated carbon (GAC). Firstly, a single batch test, interpreted using a competitive Freundlich adsorption model, was demonstrated to be an effective alternative to multiple single-component tests for determining single-compound isotherm parameters. The isotherm parameters of the 13 chlorinated hydrocarbons were estimated from the batch test using both the Ideal Adsorbed Solution Theory (IAST) and the simplified IAST (SIAST) models, with the latter model emerging as more parsimonious and robust based on Akaike's information criterion. Then the experimental breakthrough and solid phase concentrations of the 13 compounds in a fixed-bed system were accurately predicted by implementing an equilibrium competitive adsorption transport model. The good agreement between the fixed-bed adsorption data and the competitive model confirmed and validated the whole approach. Compared to standard approaches based on mass balance considerations or rapid small-scale column tests, the proposed procedure enables quicker and easier scaling up of a multispecies sorption behaviour from a single batch test, thus reducing the experimental and modelling effort needed for the dimensioning of full-scale adsorbers for treating many-component mixtures of contaminants in aqueous matrices.

Graphical abstract



Highlights

- A single batch test can estimate adsorption isotherms for 13 chlorinated compounds.
- The SIAST model offers a simpler and robust alternative to IAST for GAC adsorbers.
- Competitive adsorption in fixed-beds is well-predicted by SIAST transport models.
- A new approach enables scaling-up multispecies adsorption from a single batch test.
- Workflow reduces efforts for designing full-scale adsorbers for water treatment.

Keywords

Competitive adsorption, Chlorinated hydrocarbons, Granular Activated Carbon, Simplified IAST, Akaike criterion, Damköhler number

1 Introduction

Chlorinated hydrocarbons find wide-ranging industrial application, as solvents for metal degreasing and dry cleaning processes, and in the production of pharmaceuticals, pesticides, paints, adhesives, and refrigerants [1–3]. However, many chlorinated hydrocarbons are toxic, and some are known carcinogens. The release of these compounds into the subsurface environment through accidental spill or inadequate disposal poses a serious health and environmental concern [3,4]. Chlorinated hydrocarbons are more dense and less viscous than water and have very low solubility in aqueous environments, where they create a separated oily phase. Following a spill, these non-aqueous phase liquids (NAPL) therefore migrate rapidly downward through the soil into porous aquifer systems and accumulate on top of lower hydraulic conductivity zones becoming a persistent source of groundwater contamination [5,6].

In the field of groundwater remediation, there is great interest in the development and application of in-situ remediation technologies (thermal treatment, chemical oxidation or reduction, surfactant cosolvent flushing, bioremediation, nanoremediation) that directly target NAPL sources in the subsurface. This is because contaminant source treatment is less expensive than management and maintenance of systems and processes for the treatment of contaminated water [7,8]. Notwithstanding, in-situ treatment of NAPL source zones is not always possible and many groundwater remediation projects continue to rely on the deployment of hydraulic containment barriers, necessitating ex-situ treatment of pumped water [9–11]. A so-called polishing stage of adsorption for the removal of dissolved chlorinated hydrocarbons and other recalcitrant compounds is a ubiquitous feature of ex-situ groundwater treatment plants. The principal types of adsorbents used in fixed-bed filters are granular activated carbon (GAC), granular ferric hydroxide [12], activated alumina [13,14], biochar [15], biosorbents [16,17], natural sorbent materials [18,19]. Among them, GAC filters combine relatively low cost [13] with exceptional efficacy in removing a spectrum of compounds, including disinfection byproducts [20,21], organic contaminants like chlorinated solvents [13] and pesticides [13,22], some heavy metals [23] like lead and mercury, as well as per- and polyfluoroalkyl substances (PFAS) [24–27]. Since adsorption is the final treatment step prior to water discharge, a custom design for fixed-bed filters should be applied rather than a generic approach to ensure compliance with required water quality standards. This tailored approach should adequately account for the specific composition of the contaminant mixture in the water to be treated. This is because the competition among different contaminants for the adsorption sites can in fact result in an unexpected early breakthrough of the contaminants with less affinity for GAC, a phenomenon that cannot be easily predicted by individually studying the adsorption behaviour of each single pollutant. In addition to the competition among various contaminants in water, the competitive effect of Natural Organic Matter (NOM) should also be considered, as it can lead to the premature elution of contaminants from the adsorption stage, particularly when present at elevated concentrations [28].

Knowledge of the breakthrough behaviour of the compound to be removed is a key aspect of fixed-bed adsorber design. To this end, various methodologies have been proposed, each varying in complexity and level of experimental effort involved. The typical approach employed by practitioners to predict contaminant breakthrough from GAC filters, which is based on mass balance considerations, evaluates the ratio between the maximum adsorbable mass of contaminant on the carbon bed and the contaminant mass flow entering the filter [14]. For a multi-species transport problem, the expected theoretical breakthrough time of the i-compound, $t_{BC,i}^{th}$, can therefore be estimated through the following equation:

$$t_{BC,i}^{th} = \frac{q_{IN,i}\, m_{GAC}}{C_{IN,i}\, Q} \tag{1.1}$$

where $C_{IN,i}$ is the average inlet concentration of the i-compound, $q_{IN,i}$ is the equilibrium adsorbent loading of the i-compound calculated with equation, m_{GAC} is the GAC mass in the fixed-bed adsorber, and Q is the flow rate. The calculation of $q_{IN,i}$ requires knowledge of the equilibrium adsorption

isotherm parameters for all contaminants present in the water, or at least for the pollutant with less affinity to GAC. These parameters can be either provided by the GAC supplier, found in the literature (generic values) or derived through case-specific batch adsorption experiments. Although this method requires very low experimental and modelling efforts, it considers only one single contaminant (no influence of competition), plug flow conditions (no effect of hydrodynamic dispersion), constant pollutant concentration in the inflow stream, and equilibrium sorption. Therefore, the breakthrough prediction may be inaccurate under certain conditions, especially when water contains a complex mixture of multiple contaminants, and the water composition is changing over time.

To overcome some of these limitations, methodologies based on scale-up of small-scale tests or mathematical modelling of contaminant breakthrough curves have been proposed. Scale-up methods consist in conducting a fixed-bed adsorption test at the laboratory scale using the actual contaminated water to predict the full-scale filter behaviour. This approach is attractive because a laboratory test is conducted in a fraction of time and with a lower volume of water compared to a pilot-scale test. Also, equilibrium (isotherm) and kinetic studies are not required, since the outcome of fixed-bed adsorption is directly observed rather than predicted. The rapid small-scale column (RSSC) test [29,30] is most commonly used to predict full-scale filter behaviour of different compounds. The method was used to predict the behaviour of two full-scale utilities using GAC for the removal of a mixture of endocrine disrupting chemicals, pharmaceuticals and personal care products from bench-scale tests [31]. In a different study the RSSC method was shown to be a powerful experimental alternative to modelling for the adsorption of arsenate onto granulated ferric hydroxide [32]. It has also been used to design fixed-bed tests to study PFAS and intermediate aromatic halogenated disinfection byproducts [21,33]. Scale-up methods like RSSC, however, fail to provide insight into the mechanisms underlying contaminant removal (e.g., competitive adsorption, mass transfer limitations) and lack the flexibility to accurately predict and extrapolate the pollutant mixture behaviour when the water composition differs significantly from that used in the laboratory tests [34]. This limitation may therefore lead to sub-optimal designs, especially in the presence of multiple contaminants [14,35]. Moreover, despite requiring less experimental effort than pilot-scale experiments, RSSC tests necessitate the collection and analysis of a large number of eluate samples at the column outlet to accurately characterize the breakthrough behaviour of the contaminant mixture. This results in increased costs and time compared to traditional batch sorption experiments used for isotherm determination. Such limitations often represent an obstacle for practitioners seeking to minimize experimental time, cost and complexity.

At the opposite end, mathematical models of contaminant flow and transport in beds of porous adsorbent particles can predict the breakthrough behaviour in its entirety from separately determined isotherm parameters, both in the case of single species and competitive multicomponent sorption. In contrast to purely experimental approaches (i.e. scale-up of small-scale tests), model-based methods have good prediction capability and can be used to simulate different operational scenarios and evaluate the influence of process parameters on contaminant breakthrough curves. Moreover, these models provide valuable insights into the nature of the adsorption mechanisms involved in contaminant removal. Therefore, once validated by experimental data, they can serve as a flexible and reliable tool for designing fixed-bed filtration systems.

Mathematical models of fixed bed adsorption vary widely in the degree of complexity and experimental effort needed for their calibration/validation. This variation depends on the assumptions made regarding the extent and origin of departure from thermodynamic equilibrium between the adsorbed and dissolved concentrations of the compounds [14,35]. For aqueous solutions containing chlorinated hydrocarbons in concentration levels typical of contaminated aquifers, the adsorption equilibrium is commonly described using a Freundlich isotherm, both for single-solute adsorption and for competitive multi-solute adsorption in the context of the Ideal Adsorber Solution Theory (IAST) [36–38]. These equilibrium models require two coefficients (the Freundlich isotherm parameters) for each solute in the contaminant mixture. These pairs of coefficients are determined experimentally through batch isotherm

tests conducted individually for each contaminant. When non-equilibrium effects arising from mass transfer limitations (e.g. film, pore and surface diffusion) [39] must also be considered, the model complexity increases significantly. This requires additional model parameters (e.g., a kinetic constant for each contaminant and each process) and more experiments (e.g., a kinetic sorption experiment for each contaminant). If the number of contaminants is relatively high, the experimental effort can become comparable to or even greater than that required for RSSC. Moreover, parameter identification issues may arise, since different processes (e.g. pore diffusion and surface diffusion) may act in parallel thus making more difficult the independent determination of the related coefficients.

Therefore, it is evident that the existing workflow for designing fixed-bed adsorption systems has significant limitations that present challenges when the water to be treated is contaminated with a complex mixture of pollutants. These limitations include low accuracy of breakthrough prediction (mass balance approach), insufficient flexibility and extrapolation capabilities (scale-up of small-scale tests), substantial experimental effort needed for implementation and validation (scale-up of small-scale tests and mathematical models), as well as implementation complexity and high number of involved parameters (mathematical models).

Given that industrially relevant streams often contain a multitude of contaminants (typically more than ten), maintaining experimental and modelling simplicity and parsimony in the design approach is not only a practical [28] but also a theoretical necessity [40,41]. To address these challenges, the present study proposes a parsimonious experimental-modelling workflow for fixed-bed adsorber design, which is schematically depicted in Fig. 1. The approach involves conducting a single multi-component batch isotherm test and applying a simplified competitive equilibrium (simplified IAST) [42] adsorption-transport model for accurate prediction of the contaminant breakthrough. The method was here applied to design an activated carbon filter for the treatment of a real groundwater contaminated with a mixture of 13 different chlorinated hydrocarbons and validated in the context of Akaike's information criterion. Comparison with the results of a laboratory-scale column test demonstrated the suitability of the approach and provided useful guidelines for model-based design of fixed-bed adsorption systems for the treatment of aqueous streams containing a large number of contaminants.

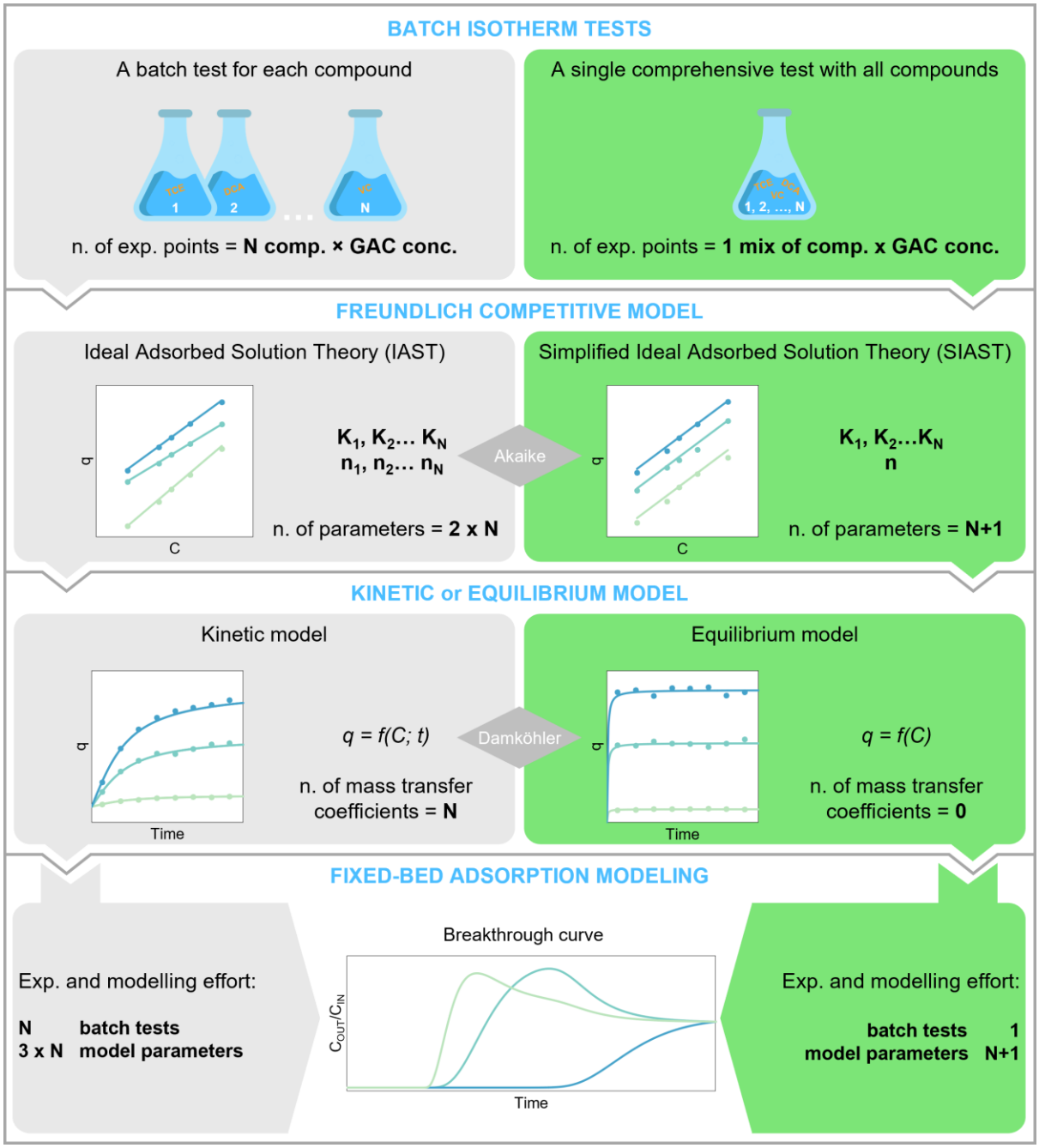


Fig. 1 – Workflow for fixed-bed adsorber design: comparison between a standard approach based on multiple batch tests and IAST competitive sorption modelling (grey) and the parsimonious experimental-modelling workflow proposed in this study (green).

2 Materials and methods

2.1 Groundwater

Groundwater samples were collected at an Italian contaminated site. They were extracted from a piezometer using a low-flow pump and stored in amber bottles without headspace in a laboratory refrigerator until use. Sodium azide was added to the bottles to a concentration of 50 mg L^{-1} to ensure abiotic conditions. During the sampling, groundwater was characterised by a temperature of 293 K, a pH of 7.8, an electric conductivity of 2288 µS cm^{-1} and a redox potential of 136 mV. A mixture of 13 different Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) was detected using the analysis method described in section 2.3. Specifically, five chlorinated ethylenes

were identified: trichloroethylene (TCE) at a concentration of 594 μg L^{-1}, the three isomers of dichloroethylene (1,1-DCE, c-1,2-DCE, and t-1,2-DCE) respectively at a concentration of 36, 17778, and 124 μg L^{-1}, and vinyl chloride (VC) at a concentration of 1683 μg L^{-1}. Four chlorinated ethanes were detected: 1,1,2,2-tetrachloroethane (TeCA) at a concentration of 117 μg L^{-1}, 1,1,2-trichloroethane (1,1,2-TCA) at a concentration of 676 μg L^{-1}, and the two isomers of dichloroethane (1,1-DCA and 1,2-DCA) respectively at a concentration of 152 and 3497 μg L^{-1}. Additionally, trichloromethane (TCM) was found at 2874 μg L^{-1}, dichloromethane (DCM) at 1109 μg L^{-1}, 1,2-dichloropropane (1,2-DCP) at 474 μg L^{-1} and a chlorinated ether (CE) at 3287 μg L^{-1}. The full list of the detected compounds and their average water concentration during the experimental period is provided in Table S1 of the Supplementary Information (SI). To assess the content of dissolved natural organic matter, which is known to be a strong competitor for adsorption in groundwater, the total dissolved organic carbon (TDOC) was measured and found to be 8.13 mg L^{-1}. However, it must be note that the carbon contribution deriving from all the VOCs and SVOCs present in the water was calculated to be equal to 8.21 mg L^{-1} (Table S2). For this reason, the NOM content, as well as its influence on the sorption dynamics, was considered negligible in this study.

2.2 Granular activated carbon

A commercial coal-based granular activated carbon (GAC), ORGANOSORB 10, was used in this study. The particle dimension ranges between 0.60 and 2.36 mm, the iodine index is 950 mg g^{-1}, and the BET surface area is 960 m^2 g^{-1}, as reported by the supplier. The measured bulk density is 647 kg m^{-3}.

2.3 VOC and SVOC analysis methods

VOCs and SVOCs were quantified in liquid samples through equilibrium headspace analysis using gas chromatography/mass spectroscopy (GC/MS). The EPA method 5021A (2014) + 8260D (2018), [43,44], was adopted for the VOC analysis. The method describes VOC determination by gas chromatography coupled with a mass spectrometer, with a static headspace (HS) extraction/preconcentration system. The instrument was equipped with a Rtx200 column (40 m, 0.18 mm ID, 0.4 μm, Restek). The EPA methods 3510C (1996) and 8270E (2018), [45,46], were adopted for the SVOC analysis using an instrument equipped with a Select PAH column. To assess adsorbed compounds, GAC samples were first immerged in 5 mL of carbon disulfide and sonicated. Subsequently, the organic extract was analysed for VOC and SVOC following the same protocol as for liquid samples.

2.4 Adsorption isotherms

2.4.1 Experimental determination of equilibrium data

A batch isotherm procedure was used to determine the equilibrium data. The GAC, at 11 different concentrations ranging from 0.5 to 20.0 g L^{-1}, was added to 40 mL vials, which were then filled headspace-free with groundwater containing VOCs and SVOCs. These vials were shaken for 24 h in a rotary shaker at a constant room temperature of 298 K. To establish the initial liquid concentration, blanks were run without any carbon dosage alongside the samples. After the 24-h shaking period, the GAC was allowed to settle and the VOC and SVOC concentrations in the liquid phase (C_i) were determined following the procedure described in section 2.3. The equilibrium adsorbed concentration for the i-compound was calculated using the following mass balance equation:

$$q_i = \frac{V}{m_{GAC}}\left(C_{0,i} - C_i\right) \tag{2.1}$$

where q_i is the equilibrium adsorbent loading for the i-compound (g g^{-1}), $C_{0,i}$ is the concentration in the blank for the i-compound (g L^{-1}), C_i is the equilibrium concentration in the liquid phase for the i-compound (g L^{-1}), V is the liquid volume (L), and m_{GAC} is the GAC mass dosed in the vial (g).

2.4.2 Modelling of equilibrium data

The Freundlich isotherm equation can be used to describe the adsorption on GAC of a single compound, i, in the absence of other adsorbing species:

$$q_i = K_i C_i^{n_i} \tag{2.2}$$

where K_i and n_i are the Freundlich isotherm parameters for the i-compound. The numerical values of the Freundlich parameters are determined by linear regression of the experimental data against Eq. (2.2).

The Ideal Adsorbed Solution Theory (IAST) is generally used to describe the adsorption on GAC of a compound in a multicomponent mixture. IAST was developed by Myers and Prausnitz (1965) [37] to describe competitive adsorption in the gas phase, and it was extended by Radke and Prausnitz (1972) [38] for multicomponent adsorption in liquid solutions. If each adsorbing species in the solution follows the Freundlich isotherm, then IAST yields the following equation for the adsorption of each compound at equilibrium [36]:

$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j} \left(\frac{n_i}{K_i} \sum_{j=1}^{N} \frac{q_j}{n_j} \right)^{\frac{1}{n_i}} \tag{2.3}$$

where K_i and n_i are again the single-compound isotherm parameters for each of the N compounds in the mixture. Furthermore, if the adsorption of each compound is described by the same value of the Freundlich exponent (n), a simplified form of IAST Eq. (2.3), hereafter referred to as the SIAST equation, is obtained [42]:

$$q_i = K_i^{\frac{1}{n}} C_i \left(\sum_{j=1}^{N} K_j^{\frac{1}{n}} C_j \right)^{n-1} \tag{2.4}$$

When K_i and n_i are available for all components, the IAST equation (or the SIAST equation if $n_i \approx n$ for all compounds) can be used to predict multicomponent adsorption equilibrium. The Freundlich parameters for each compound are derived through interpretation of single-component adsorption tests with Eq. (2.2). For a mixture of 13 components, this means performing 13 different single component batch tests to determine the 26 isotherm parameters necessary for the IAST model (13 couples of K_i and n_i) or the 14 needed for SIAST (13 K_i and only 1 n). To reduce the experimental effort, in this study the adsorption parameters of each component were determined by using a competitive model to fit the adsorption data obtained from only one multicomponent batch test (with all 13 contaminants in ones). The experimental equilibrium data obtained from the multicomponent batch test were fitted using a global least-squares fitting procedure where all isotherms were fitted at the same time. Specifically, for the IAST model, 26 fitting parameters were used (13 couples of K_i and n_i), while for the SIAT model, 14 parameters were used (13 K_i and only 1 n). The batch test was interpreted with both the IAST and the SIAST model to compare their accuracy, robustness and parsimony. To this purpose, the Akaike's information criterion (AIC) [41] was applied. The AIC is an index that balances model accuracy with complexity, favoring models that achieve a good fit with fewer parameters, and is defined as:

$$AIC = m \cdot \log\left(\frac{SSR}{m}\right) + 2P \tag{2.5}$$

where m is the sample size, P is the number of model parameters estimated from the data, and SSR is the sum of squared differences between observations and model predictions. Since the concentrations are of different orders of magnitude, the SSR is calculated using the base-10 logarithm of the concentrations. For relatively small sample sizes ($i.e., m/P < 40$) a corrected form of AIC is recommended:

$$AIC_c = AIC + \frac{2P(P+1)}{m-P-1} \quad (2.5)$$

According to the index definition, the model with the lowest AIC (or AIC_c) is to be preferred due to better balance between accuracy and complexity. While the Akaike's information criterion was used to compare different models, the coefficient of determination, r_i^2, was considered to evaluate the fitting quality between models and experimental data.

2.5 Fixed-bed adsorption

2.5.1 Experimental determination of breakthrough curves

A laboratory-scale fixed-bed adsorption test was conducted to treat groundwater contaminated with VOCs and SVOCs. The filter column had an internal diameter of 1.6 cm and was vertically wet-packed with 7.8 g of GAC to obtain a length of the reactive bed of 6 cm. A 25 L gas sampling bag was selected as the inlet groundwater reservoir to prevent volatilization losses due to headspace formation during the experiment. The water was pumped from the reservoir bag to the adsorption column with a peristaltic pump. Flow direction was from bottom to top and the average flow rate was 0.20 mL min^{-1}, corresponding to a Darcy velocity of 1.67×10^{-5} m s^{-1} and an Empty Bed Contact Time (EBCT) of 60 min. A total volume of 15.6 L of groundwater was treated in a timeframe of 55 days. The column effluent was collected in a tank placed on a laboratory scale and the weight of the treated water was registered over time to check for flow rate variations. The weight measurements of the outflow tank over time are reported in Figure S1 of SI.

Liquid samples at the column inlet and outlet were collected periodically during the test and analysed as described in section 2.3 to determine the VOC and SVOC concentrations. In this manner, the inlet concentration was monitored and the Breakthrough Curves (BCs) of the effluent compounds were obtained. The breakthrough time, $t_{BC,i}$, for the i-compound was determined as the time at which the ratio between the outflow concentration ($C_{OUT,i}$) and the inlet concentration ($C_{IN,i}$) of the i-compound reached the value of 0.5 ($C_{OUT,i}/C_{IN,i} = 0.5$). At the end of the test, the adsorption column was dissected, and the GAC bed was sampled at one-centimeter intervals along its length. Each sample was analyzed as described in section 2.3 to evaluate the equilibrium adsorbent loading of each compound and estimate the adsorbed profiles along the column.

The hydrodynamic parameters of the GAC bed, namely the effective porosity (ε) and dispersivity (α_x), were determined by modelling the BC of a conservative tracer (10 mM KBr) with the software MNMs 2024 (https://areeweb.polito.it/ricerca/groundwater/it/software/mnms/), which numerically solves the advective-dispersive transport equations [47–51]. The estimated effective porosity was 45%, while the dispersivity was 2.8 mm. The experimental and modelled tracer BC is reported in Figure S2 of SI.

2.5.2 Modelling and interpretation of breakthrough curves

The transport of adsorbable compounds in a one-dimensional porous medium was modelled by the following modified advection-dispersion equation, which assumes equilibrium interactions between the dissolved and adsorbed species in the context of the SIAST model:

$$\varepsilon \frac{\partial C_i}{\partial t} + \rho_b \frac{\partial}{\partial t}\left[K_i^{\frac{1}{n}} C_i \left(\sum_{j=1}^{N} K_j^{\frac{1}{n}} C_j \right)^{n-1} \right] + v_d \frac{\partial C_i}{\partial x} - \varepsilon D_x \frac{\partial^2 C_i}{\partial x^2} = 0 \quad (2.6)$$

where ε is the effective porosity of the porous medium, ρ_b is the bulk density of the porous medium, v_d is the Darcy velocity, D_x is the hydrodynamic dispersion coefficient calculated as $\alpha_x \frac{v_d}{\varepsilon}$, where α_x is the dispersivity. The appropriateness of the equilibrium assumption made in Eq. (2.6) was evaluated in terms of the Damköhler number, which represents the ratio of hydrodynamic residence time of retarded compound to the characteristic time for kinetically-limited sorption in the fixed-bed column, estimated as follows:

$$D_{a,i} = \frac{k_i^* (R_i - 1) \varepsilon L}{v_d} \quad (2.7)$$

where L is the column length, and R_i is the retardation coefficient for the i-compound given by:

$$R_i = 1 + \frac{\rho_b}{\varepsilon} n_i K_i C_{0,i}^{n_i - 1} \quad (2.8)$$

and k_i^* is the intraparticle mass transfer rate coefficient for the i-compound (s^{-1}) calculated with the empirical equation proposed by Worch (2008) [28]:

$$k_i^* = 0.00129 \sqrt{\frac{D_{L,i} C_{0,i}}{q_{0,i} r_p^2}} \quad (2.9)$$

where $D_{L,i}$ is the diffusion coefficient in free liquid ($m^2\ s^{-1}$), $C_{0,i}$ is the concentration in the inlet for the i-compound (mg L^{-1}), $q_{0,i}$ is the equilibrium adsorbent loading for the i-compound when the equilibrium concentration in water is $C_{0,i}$ (mg g^{-1}), calculated with Eq. (2.2), and r_p is the GAC particle radius (m). The diffusion coefficient in free liquid was evaluated using the Wilke-Chang equation [52]. In previous studies it was found that the assumption of local equilibrium can be made when the Damköhler number, $D_{a,i}$, is greater than 100 [53].

The fixed-bed adsorption column test was modelled using a Matlab code that numerically solves Eq. (2.6) using a finite difference approach to simulate the multicomponent competitive transport of contaminants with the SIAST adsorption model. The column test model was built following the geometry and operating conditions described in section 2.5.1. The column length was discretized into 30 segments ($\Delta x =$ 2.0 mm) and a total time of 55 days was simulated with a time discretization step of 120 s. The transport model was first run in direct mode to predict contaminant transport within the column, using known SIAST equilibrium parameters derived from interpretation of the batch test. Next, the code was applied in inverse mode to estimate the optimal SIAST parameters that best fitted the experimental column results. BCs and retention profiles of all the contaminants were simultaneously fitted using a global least-square approach with the Levenberg-Marquardt method.

3 Results and discussion

3.1 Interpretation of multicomponent adsorption isotherms

Equilibrium data, determined as described in section 2.4.1 using the groundwater sourced from an Italian contaminated site (see section 2.1) and GAC (see section 2.2), are depicted in Fig. 2 with markers. In this figure, the equilibrium liquid phase concentrations of each compound, C_i, are plotted on a log-log graph against their respective equilibrium adsorbent loadings, q_i. For easier data interpretation, the 13 VOCs and SVOCs identified in groundwater are categorised into three groups. The first group, Fig. 2A, consists of five chlorinated ethylenes: trichloroethylene (TCE), the three isomers of dichloroethylene (1,1-DCE, c-1,2-DCE, and t-1,2-DCE), and vinyl chloride (VC). The second group includes chlorinated ethanes, Fig. 2B, in detail 1,1,2,2-tetrachloroethane (TeCA), 1,1,2-trichloroethane (1,1,2-TCA), and the two isomers of dichloroethane (1,1-DCA and 1,2-DCA). The third class, Fig. 2C, is composed by trichloromethane (TCM), dichloromethane (DCM), 1,2-dichloropropane (1,2-DCP) and a chlorinated ether (CE).

The experimental data depicted in Fig. 2 shows a linear trend on a log-log scale graph, with similar slopes for all chlorinated hydrocarbons (CHs). This alignment suggests a uniform behaviour across the compounds and the possibility to apply a Freundlich model to describe the adsorption of these compounds onto GAC. According to the Freundlich model (Eq. (2.2)) and assuming independent sorption behaviour for the different species, the affinity of each contaminant with GAC – describing the tendency of the solute to adsorb on the carbon surface – is proportional to the intercept of the linear regression fitting the data on the log-log graph. Specifically, higher intercept values correspond to stronger affinities. In general, the affinity of a VOC or SVOC for GAC is proportional to the size of the molecule and to the number of carbon and chlorine atoms. Specifically, the higher the number of carbon and chlorine atoms, the stronger the affinity for the GAC [28]. The experimental data in Fig. 2 show that: i) among the chlorinated ethenes (Fig. 2A), TCE and c-1,2-DCE have potentially the greatest affinity for GAC; ii) TeCA, 1,1,2-TCA, and 1,2-DCA have similar affinity and higher than 1,1-DCA (Fig. 2B); iii) EC shows a great affinity for GAC, while DCM has a low one (Fig. 2C). However, it is important to note that these equilibrium data were derived from a single multicomponent test, and therefore the equilibrium concentrations are influenced not only by the individual compound affinity but also by the affinities and concentrations of other compounds present in the water. Under such conditions the sorption independence assumption does not hold and the standard Freundlich model does not allow to derive reliable individual affinity values.

For this reason, a competitive adsorption model must be used to interpret these equilibrium data and obtain the correct values of individual affinity. As described in section 2.4.2, the individual Freundlich parameters (K_i, n_i) for each compound were obtained from fitting of the equilibrium data of the multicomponent batch test using the IAST model. The model fitting and the Freundlich parameters obtained are shown respectively in Figure S3 and Table S3 of SI. A strong correlation between the IAST model and the experimental data can be observed in Figure S3, as confirmed by the coefficients of determination, r_i^2, which are all greater than 95% (Table S3). Among the chlorinated ethenes, TCE showed the highest value of K_i (2.48 (g g^{-1})/(g L^{-1})^n), while, contrary to what could have been inferred from the experimental equilibrium concentrations, c-1,2-DCE exhibited a K_i of 0.57 (g g^{-1})/(g L^{-1})^n, which is more than 4 times lower than TCE. The chlorinated ethene with the second highest K_i resulted instead to be t-1,2-DCE, with a value of 1.10 (g g^{-1})/(g L^{-1})^n. Finally, VC was the chlorinated ethene with the lowest K_i (0.18 (g g^{-1})/(g L^{-1})^n). Among the chlorinated ethanes, the compounds with a higher number of chlorines, namely TeCA and 1,1,2-TCA, showed higher K_i values, respectively 0.61 and 0.83 (g g^{-1})/(g L^{-1})^n. Smaller values, and similar among themselves, were instead found for 1,1-DCA (0.38 (g g^{-1})/(g L^{-1})^n) and 1,2-DCA (0.40 (g g^{-1})/(g L^{-1})^n). Lastly, for the third group, CE and 1,2-DCP had relatively high values of K_i, respectively 0.95 and 0.83 (g g^{-1})/(g L^{-1})^n, whereas DCM, similarly to CV, showed one of the lowest K_i values (0.22 (g g^{-1})/(g L^{-1})^n). While the values of K_i was found to vary

even by one order of magnitude, the Freundlich exponents, n_i, were relatively similar to each other, with an average value of 0.65.

Since both the slope of the experimental data in Fig. 2 and the Freundlich exponents determined with IAST (Table S3 of SI) showed to be relatively similar among the different CHs, fitting of the experimental equilibrium data with SIAST was also attempted. The SIAST model is a simplification of the IAST model where the adsorption of each compound is described by the same value of the Freundlich exponent (n). The graphical fitting of the experimental data and the Freundlich parameters obtained with the SIAST model are shown respectively in Fig. 2 and Table 1. A strong correlation between the SIAST model (dashed lines) and the experimental data (markers) is clearly visible in Fig. 2. This is confirmed by the coefficients of determination, r_i^2, which are all greater than 90%, except for DCM, which is equal to 79.4%, Table 1. The lower value of the DCM determination coefficient may be attributed to the characteristic curve inflection exhibited by the SIAST model at high liquid phase concentrations, typical of competitive models [36,54] but not followed by the DCM experimental data (Fig. 2C). However, it must be noted that, even though the SIAST model does not perfectly capture the shape of the DCM isotherm at high liquid equilibrium dissolved concentrations, it can still predict the corresponding values of equilibrium adsorbent loadings with a good degree of approximation. As expected, the K_i values estimated with SIAST were slightly different from those obtained with the IAST model. However, the same affinity trend was observed for the different contaminants. Among the chlorinated ethenes, TCE showed the highest value of K_i (2.02 (g g^{-1})/(g L^{-1})^n) and VC the lowest one (0.14 (g g^{-1})/(g L^{-1})^n). Regarding chlorinated ethanes, the heavier compounds, TeCA and 1,1,2-TCA, had higher values, whereas lower K_i were found for 1,1-DCA and 1,2-DCA. Lastly, DCM showed also in this case one of the lowest K_i values (0.10 (g g^{-1})/(g L^{-1})^n). A Freundlich exponent of 0.63 (one value for all contaminants) was predicted by the SIAST model, which is close to the IAST average of 0.65.

Overall, the IAST model enabled a more precise interpretation of the experimental data than SIAST, showing a slightly higher global coefficient of determination (99.6% for IAST and 98.8% for SIAST) and smaller SSR (0.81 for IAST and 1.08 for SIAST). However, the SIAT model performed better in terms of Akaike's information criterion (Table S4). The IAST AIC index, calculated considering all the 143 experimental data points (m) and the 26 parameters to be estimated (P), was, in fact, equal to -269. This value further increased to -257 by applying the corrected form of AIC (AIC_c), given that the ratio between m and P was less than 40. Lower AIC and AIC_c values, respectively equal to -275 and -272, were instead obtained for the SIAST model, mainly due to the smaller number of parameters to be estimated ($P = 14$) (Table S4). In conclusion, the SIAST model proved to be more robust than the IAST model in terms of Akaike's Information Criterion. It provided highly accurate predictions of the competitive sorption behaviour of the contaminant mixture while adopting a less complex and more parsimonious approach. For this reason, the SIAST model was selected as competitive sorption equilibrium model for the next steps of this study.

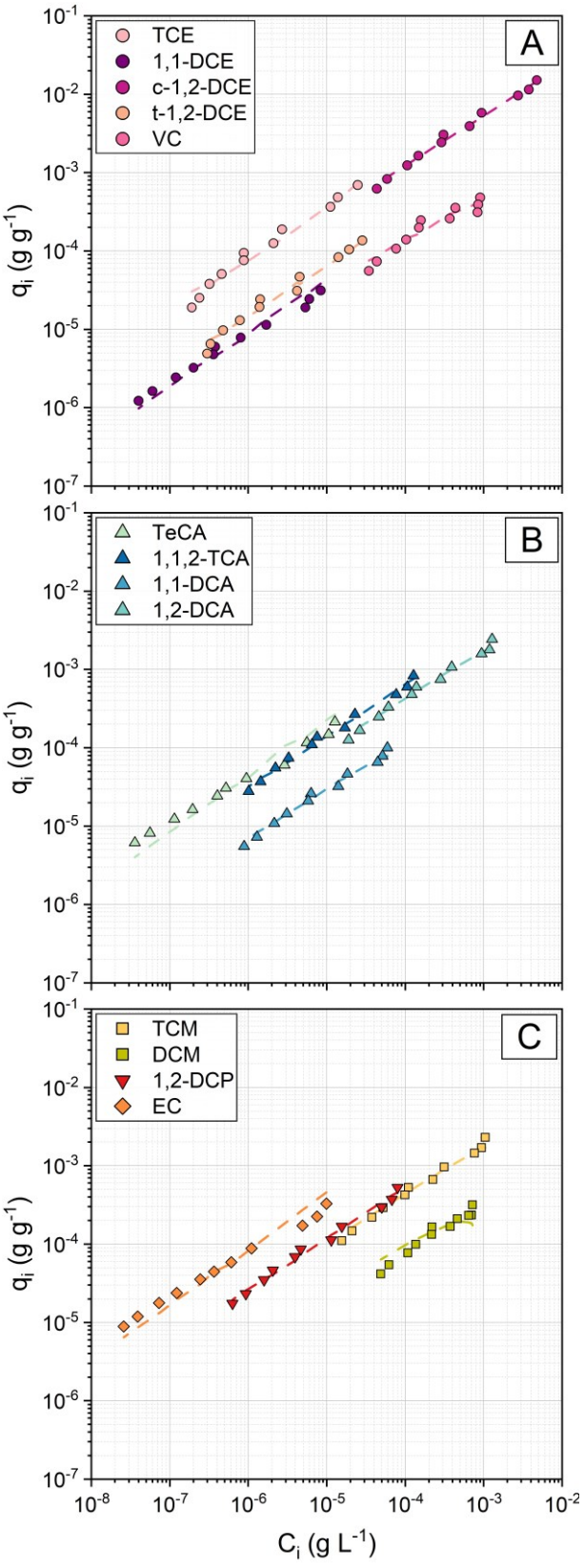


Fig. 2 – Log-log graph of the equilibrium concentrations in liquid phase for the i-compound, C_i, plotted against their respective equilibrium adsorbent loadings for the i-compound, q_i, for the 13 VOCs and SVOCs identified in groundwater during the competitive batch test. The experimental data from the batch test are depicted with markers, while the fitted SIAST model is represented with dashed lines.

The 13 compounds are classified in three groups: A) chlorinated ethenes, B) chlorinated ethanes, C) chlorinate methanes, propane, and ethers.

Table 1 – The Freundlich parameters (K_i, n) for each compound determined from fitting of the equilibrium data of the batch test with the SIAST model and the corresponding coefficients of determination, r_i^2.

Compound (acronym)	K_i (g g^{-1})/(g L^{-1})^n	n (-)	r_i^2 (%)
Trichloroethylene (TCE)	2.02	0.63	96.3
1,1-Dichloroethylene (1,1-DCE)	0.62	0.63	95.9
cis-1,2-Dichloroethylene (c-1,2-DCE)	0.49	0.63	99.2
trans-1,2-Dichloroethylene (t-1,2-DCE)	0.64	0.63	96.5
Vinyl chloride (VC)	0.14	0.63	90.1
1,1,2,2-Tetrachloroethane (TeCA)	1.62	0.63	92.5
1,1,2-Trichloroethane (1,1,2-TCA)	0.73	0.63	98.9
1,1-Dichloroethane (1,1-DCA)	0.29	0.63	98.3
1,2-Dichloroethane (1,2-DCA)	0.31	0.63	98.5
Trichloromethane (TCM)	0.33	0.63	98.2
Dichloromethane (DCM)	0.10	0.63	79.4
1,2-Dichloropropane (1,2-DCP)	0.72	0.63	98.6
Chlorinated Ether (CE)	2.68	0.63	93.6

3.2 On the validity of the assumption of equilibrium adsorption

The assumption of adsorption equilibrium during transport in a fixed-bed is justified only under conditions of sufficiently fast mass transfer. Such conditions prevail when the Damköhler number, given by equation (2.7), is greater than 100 [53]. To calculate the Damköhler number, the retardation coefficient, R_i, and the intraparticle mass transfer rate coefficient for the i-compound, k_i^*, were estimated for each compound using equation (2.8) and equation (2.9), respectively. The $EBCT$ was set equal to 60 min as in the fixed-bed adsorption test and the effective porosity, ε, was estimated from the tracer test equal to 0.45. The values of the intraparticle mass transfer rate coefficients, k_i^*, the retardation coefficients, R_i, and the corresponding Damköhler numbers, $D_{a,i}$ are reported in Table 2. The values of the diffusion coefficient in free liquid, $D_{L,i}$, are reported in SI, together with some details on the estimation procedure (Table S5).

The intraparticle mass transfer rate coefficients show the same order of magnitude for all the compounds, with a minimum of 1.31×10^{-5} s^{-1} for the TeCA and a maximum of 8.08×10^{-5} s^{-1} for the DCM. Variations of more than one order of magnitude were instead obtained for the retardation coefficients. The lowest and maximum values were respectively estimated for DCM (1133) and TeCA (42284). The resulting Damköhler numbers were all greater than 100. The lowest values were found for DCM (148) and VC (152), which indeed exhibit a lower affinity for activated carbon. These results implicate that the assumption of local equilibrium holds under the tested conditions [53], and the fixed-bed adsorption test can be interpreted using an equilibrium transport and adsorption model.

Table 2 – The intraparticle mass transfer rate coefficient, k_i^*, the retardation coefficients, R_i, and the Damköhler numbers, $D_{a,i}$, for each compound.

Compound	k_i^* (s^{-1})	R_i (-)	$D_{a,i}$ (-)
TCE	1.63×10^{-5}	28876	760
1,1-DCE	1.69×10^{-5}	25252	692
c-1,2-DCE	5.99×10^{-5}	1976	192
t-1,2-DCE	2.08×10^{-5}	16333	551
VC	7.08×10^{-5}	1325	152
TeCA	1.31×10^{-5}	42284	900
1,1,2-TCA	2.68×10^{-5}	9933	431
1,1-DCA	3.20×10^{-5}	6819	353
1,2-DCA	5.64×10^{-5}	2255	206
TCM	5.38×10^{-5}	2624	229
DCM	8.08×10^{-5}	1133	148
1,2-DCP	2.61×10^{-5}	11192	474
CE	1.63×10^{-5}	20244	560

3.3 Column test interpretation and modelling

The experimental results of the fixed-bed adsorption test are presented in Fig. 3 as markers. Fig. 3A, Fig. 3B, and Fig. 3C shows the breakthrough curves (BCs) of the 13 CHs, depicted as the evolution over time, expressed in number of pore volumes (PV), of the outlet concentration, $C_{OUT,i}$, normalized by the average inlet concentration, $C_{IN,i}$ (Table S1). As for the batch equilibrium data, the 13 CHs were categorised into three groups: A) chlorinated ethenes, B) chlorinated ethanes, C) others (TCM, DCM, 1,2-DCP, and EC). Additionally, Fig. 3D, Fig. 3E, and Fig. 3F depict the profiles of adsorbed concentration along the column length, reported as equilibrium adsorbent loading, q_i, normalized by the equilibrium adsorbent loading of the same compound at the column inlet, $q_{IN,i}$. Mass balance analysis, reported in Table S6 of SI, showed a good agreement between experimental BCs and adsorbed concentration profiles, with an average error of less than 10%. The graphs in Fig. 3A-F also show the breakthrough curves and concentration profiles (solid lines) predicted by the advection-dispersion-adsorption model in Eq. (2.6). This model explains the 1D transport of multiple compounds subject to competitive sorption onto a granular medium, assuming equilibrium interactions among liquid and solid phase and validity of the SIAST theory.

Focusing on the experimental data, VC and DCM were the contaminants that eluted first from the GAC column, showing a non-zero concentration after 680 PV. For both compounds, the BC presented a non-monotonic trend, with a concentration overshoot ($C_{OUT,i}/C_{IN,i} > 1$) right before reaching steady state conditions. This was particularly evident for VC, where the peak normalized concentration reached approximately 1.4. Such behaviour is typical in systems where multiple compounds compete for adsorption sites, with molecules having a higher affinity for GAC displacing those with lower affinity [14]. 1,1-DCA and 1,2-DCA were elute simultaneously, right after VC, followed by TCM, c-1,2-DCE, 1,1-DCE and t-1,2-DCE. At the end of the column test, after approximately 2900 PV, also 1,1,2-TCA and 1,2-DCP started eluting from the column with a concentration slightly above zero. No breakthrough was instead observed for TCE, TeCA and EC all over the test. The trend of the adsorbed concentration profiles at the end of the test (Fig. 3D-F) were in agreement with the BC results. In Fig. 3D, the equilibrium adsorbent load at the end of the column (5.5 cm) was greater than zero for all the chlorinated ethenes except TCE, whose advection front travelled only 1.5 cm from the column inlet. This is coherent with the BC data, which indicated that no traces of TCE were detected at the column outlet during the whole test. Regarding the chlorinated ethanes (Fig. 3E), 1,1-DCA and 1,2-DCA filled the whole

column, while 1,1,2-TCA and TeCA reached approximately 3.0 and 1.5 cm, respectively. As for the remaining compounds (Fig. 3F), the two chlorinated methanes (TCM and DCM) saturated the whole GAC column, whereas 1,2-DCP reached about half of the column length, and EC did not even saturate the first centimetre. It must be noted that also many concentration profiles, especially those of the compounds characterized by lower affinity with carbon, showed the non-monotonic shape typical of competitive transport phenomena. Moreover, the experimental data from the column test are consistent with the experimental isotherm from the batch test. Indeed, VC and DCM, which showed the lowest affinity for GAC, were the first compounds to be eluted from the GAC column and the most subject to competition effects. On the contrary, TCE, TeCA, 1,1,2-TCA, 1,2-DCP, and EC, which are characterized by a high affinity for the adsorbent material did not have sufficient time to elute from the column.

The transport model with competitive SIAST successfully predicted the elution behaviour of the various contaminants within the fixed-bed sorption filter, as evidenced by the good coefficient of determination of the global prediction, r^2, which resulted to be equal to 71.1% (Table S7). This result is particularly significant given that the Freundlich SIAST parameters used for the modelling prediction were determined directly from the interpretation of the multicomponent isotherm batch test described at paragraph 2.4 (Table 1). Thus, the parameter estimation, and therefore the forward prediction, was completely independent of the fixed-bed experiment results. More in detail, the model accurately predicted the elution order and time of VC and DCM, which were the first two compounds to exit from the GAC column. It also correctly anticipated the impact of competition on the shape of their breakthrough curves, although it overestimated the magnitude of the concentration peak. Also the elution of TCM and of the two dichloroethane isomers (1,1-DCA and 1,2-DCA) was properly caught by the model, whereas some discrepancies between the modelling prediction and the experimental data were observed for some chlorinated ethenes (1,1-DCE, c-1,2-DCE, and t-1,2-DCE). Finally, very good match was also achieved between the experimental adsorbed concentration profiles and the modelling prediction of the compounds that showed no breakthrough due to the high affinity for the GAC (i.e., TCE, 1,12-TCA, TeCA, 1,2-DCP, and EC).

The advection-dispersion-adsorption model in Eq. (2.6) was further applied to fit the experimental results of the fixed-bed test, aiming to determine the SIAST Freundlich parameters (K_i and n) through direct interpretation of the column experiment (inverse modelling). The parameters estimated from the column test were then compared with those obtained from the multicomponent isotherm batch test. The goal was to evaluate the potential error in predicting the contaminant breakthrough from a fixed-bed adsorption filter by directly extrapolating information from a simple and fast multicomponent batch test. The SIAST Freundlich parameters (K_i, n) estimated by fitting the fixed-bed adsorption test results are reported in Table S8, whereas Figure S4 shows the fitted BCs and concentration profiles. As clearly visible from the graphs, the agreement between the experimental data and the modelling prediction significantly improved, as also confirmed by the global coefficient of determination that increased from 71.1% (forward prediction) to 87.2% (inverse modelling) (Table S7). In particular, the fitted model better described the shape and magnitude of the VC and DCM BCs compared to the purely forward prediction. It also accurately reproduced the elution behaviour of TCM, 1,1-DCA and 1,2-DCA, as well as of 1,1-DCE, c-1,2-DCE, and t-1,2-DCE, which were not perfectly fitted by the forward model. No big differences were instead observed for the compounds with the greatest affinity for GAC, as they were already very well predicted by the forward model. In terms of parameters, a Freundlich exponent, n, of 0.65 was obtained from the column test interpretation (Table S8), which is close to the 0.63 estimated from the multicomponent batch experiment (Table 1). As for K_i, a parity plot, shown in Fig. 4, was built to highlight the differences the parameters estimated from the competitive batch test and those obtained from the transport experiment. The comparison reveals very good agreement, as the values are aligned with the parity plot bisector. Finally, using the new SIAST Freundlich parameters, equilibrium concentrations of the batch test were simulated to evaluate their deviation from the

experimental data. These results, shown in Figure S5, confirm a strong correlation of 97.2%, indicating that the model provides a good representation of the experimental data.

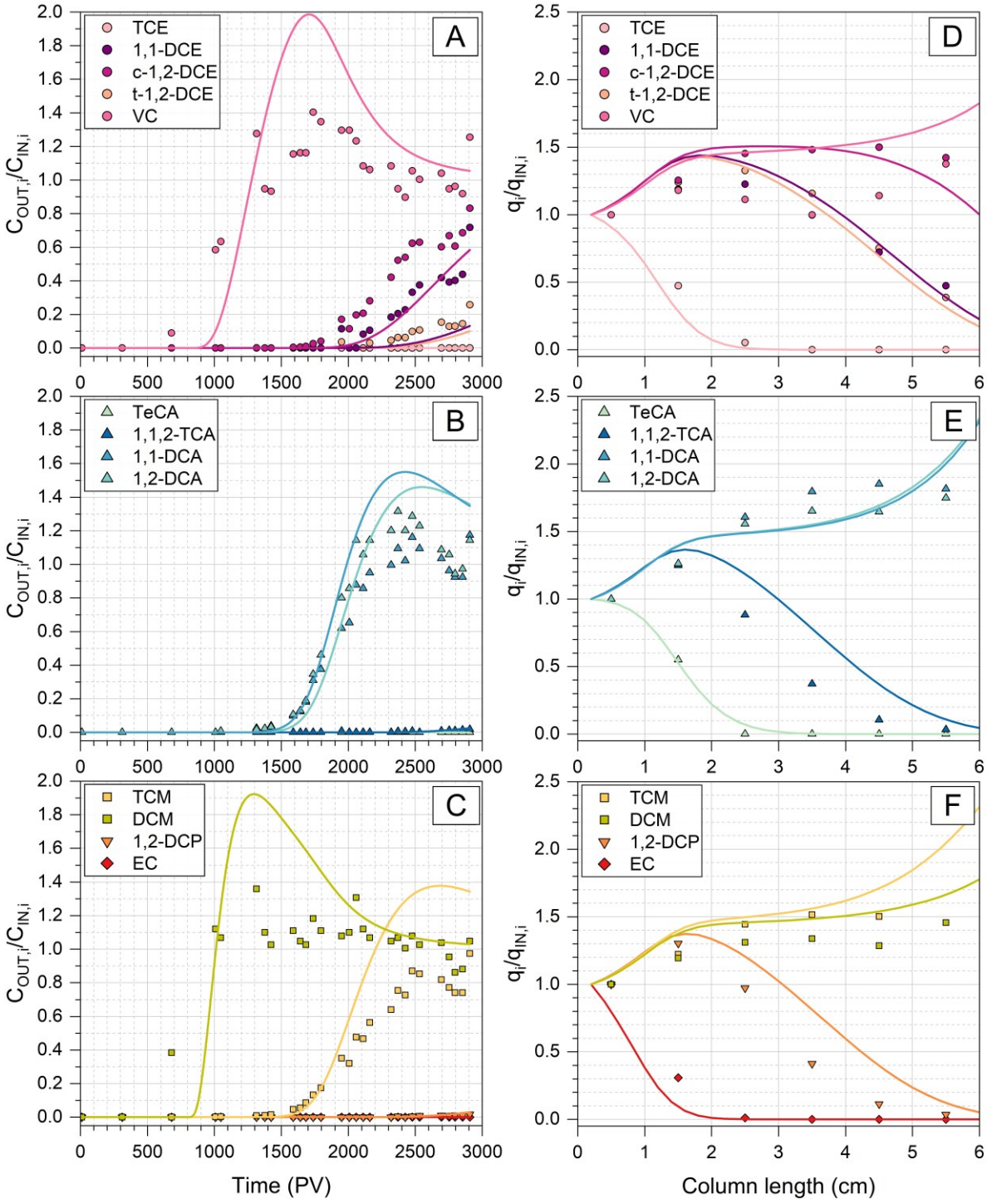


Fig. 3 – On the left, the breakthrough curves of the fixed-bed adsorption test for the 13 VOCs and SVOCs identified in groundwater as outlet concentration, $C_{OUT,i}$, normalized by the inlet concentration, $C_{IN,i}$ over time, expressed as pore volume (PV). On the right, the adsorbed concentration profiles expressed as equilibrium adsorbent load, q_i, normalized by the equilibrium adsorbent load at the column inlet, $q_{IN,i}$, in function of the column length. The experimental data, which were determined from the fixed-bed adsorption test, are depicted with markers; lines represent the forward prediction simulated with the SIAST-based competitive transport model using the Freundlich parameters estimated from the

multicomponent batch test. The 13 compounds are classified in three groups: A) chlorinated ethenes, B) chlorinated ethanes, C) chlorinate methanes, propane, and ethers.

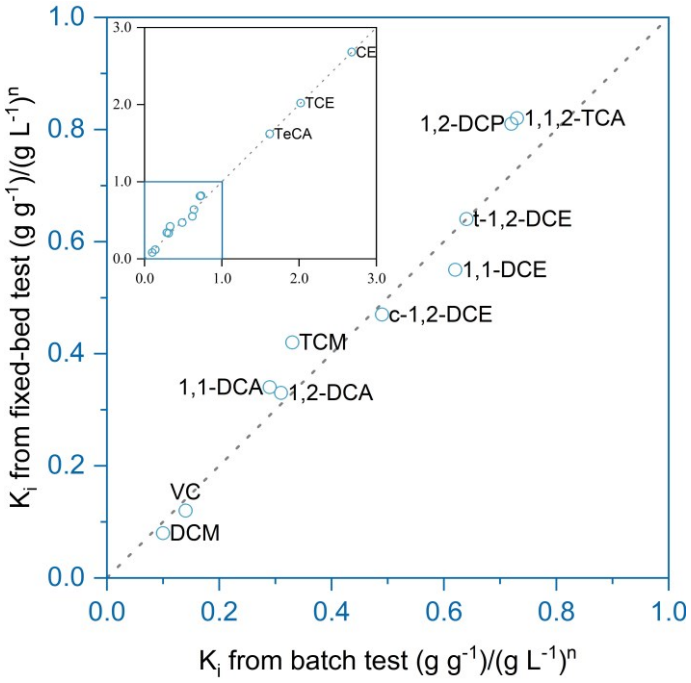


Fig. 4 – Parity plot between K_i Freundlich parameters estimated from batch and fixed-bed adsorption tests.

3.4 Prediction of fixed-bed GAC filter consumption

In water treatment plants, fixed-bed GAC filters have the role of protecting the final receptors or users of the purified water by ensuring that the concentration of all contaminants in the treated water is lower than the prescription limits. Therefore, as soon as the first contaminant starts eluting from the GAC filter, the carbon is considered exhausted and must be substituted or regenerated. Among the chlorinated compounds identified in the studied groundwater, dichloromethane (DCM) and vinyl chloride (VC) exhibited the lowest affinity for GAC. This was evidenced by their low K_i value. Consequently, DCM and VC were the first contaminants exiting the fixed-bed column, making them the primary compounds responsible for the exhaustion of the GAC. Therefore, assuming a hypothetical water treatment plant operates under the same hydro-chemical conditions as the fixed-bed test performed in this study, a reasonable estimation of the expected GAC exhaustion time can be obtained by directly up-scaling the experimental contaminant breakthrough time, t_{BC}. This experimentally predicted exhaustion time, determined as described in section 2.5.2, is equal to 732 PV for DCM and 941 PV for VC. Following the same approach, a modelling prediction of the expected GAC exhaustion time can be obtained also from the BCs simulated with the equilibrium SIAST adsorption-transport model. In the case of the forward simulation using the Freundlich parameters estimated from the batch test, a breakthrough time of 946 and 1149 PV can be predicted for DCM and CV, respectively (Fig. 3). This modelling result leads to a relatively small error in the prediction of the experimental exhaustion time, which is estimated of 30% for DCM and only 22% for VC. Such error becomes almost negligible when considering the results of the inverse fitting simulation (Figure S4), where the breakthrough times are practically identical to the experimental ones, i.e. 733 for DCM and 960 for VC.

However, it must be noted that fixed-bed column tests or competitive models are rarely employed in the design of a filtration stage because of their implementation complexity and high experimental effort required. More often, GAC consumption is therefore estimated through the mass balance approach described in Eq. (1.1). Such approach considers only the advective component of transport in porous

media (i.e. does not account for dispersivity) and is typically based on isotherm data derived from literature or provided by the activated carbon supplier (i.e. not site specific) [13,35]. Following this procedure, the expected exhaustion time for the GAC employed in this study was calculated using Freundlich parameters estimated from the batch test with the SIAST model for DCM and VC (Table 1). A breakthrough time of 1784 PV for DCM and 2140 PV for VC was predicted with this approach, resulting in an overestimation error of 144% for DCM and 127% for VC. The error further increased to 232% (2423 PV) for DCM and 136% (2219 PV) for VC when not site-specific Freundlich parameters were used, i.e. parameters estimated from isotherm experiments performed in synthetic water spiked with DCM (Figure S6) or VC (Figure S7) only and in absence of competitive sorption conditions.

The comparison of different methods for the estimation of the GAC exhaustion time highlighted the importance of using comprehensive approaches based on site-specific information for the robust design of fixed-bed adsorption filters. Methods that neglect the competitive sorption behaviour of complex mixture of contaminants, or the contribution of dispersion to the solute transport, can in fact lead to significant errors in the estimation of the GAC consumption. On the other hand, the parsimonious approach proposed in this work, based on a competitive advection-dispersion-adsorption transport model, where the SIAST parameters are estimated from one single multicomponent batch test, allowed to get a much more accurate estimation of the contaminant breakthrough time and, at the same time, limit the experimental effort compared to a full column experiment. The proposed approach was here applied to support the design of a fixed-bed adsorption filter for the treatment of groundwater contaminated with high concentrations of VOCs and SVOCs, which is a condition typical of contaminated industrial sites. Further studies should be conducted to validate this workflow also in other environmentally relevant conditions, such as for drinking water purification. This could be achieved by testing broader concentration ranges and evaluating the competitive effect of NOM.

4 Conclusions

Motivated by the need to simplify and improve the design of fixed-bed adsorption systems, which are still the most widely employed approaches for water and groundwater purification from organics (e.g. chlorinated solvents, hydrocarbons, PFAS, etc.), we have systematically investigated the treatment of groundwater contaminated with 13 different chlorinated hydrocarbons in a fixed bed of GAC. The results of the study led us to the development of a new workflow for the accurate and parsimonious model-based design of fixed-bed adsorbers. The following conclusions are supported by the data presented in this study:

- A single competitive batch test interpreted using a competitive adsorption model is a viable alternative to a multitude of single-component batch tests to determine single-compound isotherm parameters. Especially when a complex mixture of contaminants is present in water. In this study the Freundlich parameters of 13 chlorinated hydrocarbons were estimated using both the IAST and the simplified IAST model (SIAST). In the tested conditions, the SIAST model adequately represented the data and was more robust in terms of Akaike's information criterion.
- The Freundlich parameters, estimated from the competitive batch test using the SIAST model, lead to accurate prediction of the fixed-bed column test using a model that describes the transport of adsorbable compounds assuming equilibrium interactions between the dissolved and adsorbed species in the context of the SIAST model. The equilibrium hypothesis was validated using the Damköhler number, which can be estimated from the Freundlich parameters, compound concentrations, and fixed-bed operating conditions.
- The Freundlich parameters estimated from the competitive batch test using the SIAST model do not significantly deviate from those that would best fit the results of the fixed-bed column test. This confirms that the interpretation of a single multi-component isotherm test with a

competitive sorption model and the extrapolation of the results using a competitive adsorption transport model can ensure prediction capabilities comparable to laboratory column tests.

- The prediction made with the model, that uses the Freundlich parameters estimated from the competitive batch test, underestimates the GAC consumption by 22% to 30% if we consider the two compounds with less affinity to GAC (DCM and VC), but the error is an order of magnitude lower compared to that made with the theoretical breakthrough time method based on mass balance (from 136% to 232%).

In conclusion, the proposed workflow successfully overcomes the limitations of existing approaches for fixed-bed adsorber design. Firstly, it provides accurate predictions of experimental breakthrough, with much lower error than mass balance approaches typically employed by practitioners for GAC bed longevity estimations. Secondly, this method simplifies the experimental procedures compared to other model-based approaches by eliminating the need to perform multiple batch isotherm tests, as instead required for the application of competitive sorption transport models based on IAST. Moreover, the use of SIAST helps to reduce the model complexity by reducing the number of parameters, thus providing more robust predictions as confirmed by the Akaike's information criterion. Compared to fully experimental approaches, such as the scale-up of small-scale tests, the new workflow significantly reduces the experimental effort necessary for prediction of multicomponent breakthrough, both in terms of time and number of analyses needed for the experiments. Also, it offers much higher flexibility than scale-up methods, since the model allows to extrapolate results and test any working scenario, also with operational conditions different from those tested in the laboratory (e.g. variable contact time, contaminant inlet concentration, water composition, etc.). These findings have significant practical implications for the treatment of complex mixtures of contaminants in aqueous matrices, especially in the presence of organics with low affinity for carbon and very stringent concentration limits in water (e.g. groundwater contaminated with chlorinated solvents, light hydrocarbons, PFAS). In such cases it is in fact pivotal to be able to rely on robust, quick and inexpensive tools to support the design of sorbent beds and to guide the adaptive management of the filtration systems during operation under dynamically variable conditions.

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