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Sorption of Aldrich Humic Acid to a test Aquifer
Material and Implications for Subsurface Remediation
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Sorption of Aldrich Humic Acid to a Test Aquifer Material

and Implications for Subsurface Remediation

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MANAGEMENT PERSPECTIVE

Title: Sorption of Aldrich Humic Acid to a Test Aquifer Material

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EC Priority/Issue:	This laboratory work was conducted at NWRI. It was funded by both PERD, Hydrocarbon Task, and Environment Canada under the Clean Environment (Toxic) Issue.
Current Status:	The work was conducted as part of a project for the development of a groundwater remediation method for the treatment of petroleum compounds in groundwater. A collaborative project funded by CRESTech (University of Waterloo) is evaluating the possibility of modeling the processes that occur when humic acids are used to remediate diesel fuel. In order to be successful the modeling effort requires data on the sorption of humic acid to aquifer solids, as provided in this paper.
Next Steps:	The results of this research will be compared to data generated in a multi-year pilot scale test (future publication) and will be used to validate the computer model generated at Waterloo, which will be marketed by Waterloo Hydrogeologic.

Abstract

Batch and column tests were conducted to investigate the sorption of aqueous Aldrich humic acid (HA) to Winter sand, a carbonate-rich model aquifer material. The batch tests indicated that over 148 days, up to 0.43 mg/g of HA was sorbed to the sand, following a Langmuir-type isotherm. Overall the sorption kinetics in concentrated HA batches (0.5 to 3 g/L) were relatively sluggish. Nonlinear regressions suggest that the bulk sorption process consists of a fast phase (typically > 50 % by 7 d) and a slow phase (approaching equilibrium by 148 d). The fast phase is apparently dominated by the initial surface-limited adsorption reaction, whereas the slow phase may be largely due to ongoing competitive exchange of dissolved and sorbed HA. A one day column test confirmed that sorption of aqueous HA by the sand is time-dependent, and provided better information on fast phase kinetics. The results of this study, particularly information on the extent of sorption and its sluggish kinetics at elevated HA concentrations, have important implications for the potential use of commercial HA solutions in subsurface remediation. In particular, the role that sorbed HA would play as a sink for hydrophobic contaminants will have to be considered.

Introduction

Some previous laboratory studies have tested the use of aqueous humic acids as carriers to increase the efficiency of the remediation of hydrophobic contaminants in the subsurface environment (1-9). Most of these tests have been conducted at the bench-scale. However, very little information is available on the sorption of commercial (i.e., available in bulk quantity) humic acids to soils and aquifer materials, and how this process would affect the potential use of these products in subsurface remediation. The batch and column tests reported in this paper have been conducted in order to provide basic information on the sorption of Aldrich humic acid (HA) by a model aquifer material, including an evaluation of the kinetics of the "bulk" sorption process.

Background. Information on the sorption of aqueous humic substances (HS) by soils and/or aquifer materials is largely limited to studies of natural HS conducted at relatively low dissolved concentrations (typically < 100 mg/L). These studies have indicated that the subsurface mobility of aqueous humic substances (HS) may be strongly affected by sorption to mineral/solid surfaces (10-20), particularly the sorption to positively charged surfaces of Fe and Al oxides (21-23). Only a few laboratory studies have been published on the dynamic transport of commercial humic substances such as Aldrich humic acid (1, 9) in the subsurface, or specifically on the sorption of these products to soil/aquifer materials (12, 24).

Based on studies of natural HS, the sorption of aqueous HS onto iron oxides decreases with increasing pH (10, 16), but is relatively unaffected by ionic strength in Na solutions (16, 25). In contrast, the sorption of HS to kaolinite is enhanced in Na solutions of higher ionic strength (25). HS sorption by oxides can be enhanced by the presence of divalent cations, such as Ca^{2+} and Mg^{2+} (10). The sorption of relatively polar and hydrophilic HS onto the surfaces of hydrous oxides (including colloids) may be dominantly by ligand exchange (11,16), a process that is very distinct from the sorption of strongly hydrophobic organics in soils and sediments, which bind largely to organic matter. In fact, large amounts of solid organic matter in soils may impede the sorption of aqueous HS (21). Positively charged mineral surfaces (e.g., aluminum and iron oxides) strongly sorb humic acid, accompanied by a

consumption of protons which suggests that a complexation reaction had occurred (26). In contrast, weaker sorption by negatively charged surfaces (e.g., silica, kaolinite) is not associated with consumption of protons (26).

Sorption of HS can reduce their mobility in the subsurface. In laboratory column studies, the sorption of aqueous HS onto aquifer material is generally time-dependent, with tailing of breakthrough curves over long periods (2, 13,14). This is in part due to preferential sorption of relatively hydrophobic "subcomponents" (13). Sorption of the HS often appears to be largely irreversible: desorption is very slow to negligible during dilution (13,16). Gu et al. (17) explained such behavior in terms of time-dependent adsorption and displacement processes between different organic components. In contrast, Avena and Koopal (24) found that the HS sorbed onto iron oxide surfaces could be rapidly desorbed (reversibly) by changing the pH.

Previous investigations have shown that sorption of HS onto mineral and sediment surfaces is nonlinear; the concentration of sorbed HS reaches a plateau at relatively high aqueous levels (11,14,16,23,25). For batch studies, this behavior has generally been modeled using the Langmuir model (11) or a modification of this equation (16). However, the use of a more complex model (14,19, 27) is required for simulation of dynamic sorption, in order to take into account time-dependency (i.e. non-equilibrium), competitive behavior (e.g., different molecular weight fractions of HA) and/or large differences in the kinetics of adsorption and desorption reactions.

Experimental Section

Batch tests. A number of studies have shown that the solids/solution ratio is a major control of the partitioning of a chemical species between aqueous and solid phases (28,29). In conventional batch tests, which have relatively high solution/solids ratios, the inferred partitioning coefficient may be overestimated, sometimes by several orders in magnitude. In this study, a "mini-well" batch technique was developed, in order to have a test solids/solution ratio close to actual subsurface (aquifer) conditions (Figure 1).

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For each batch, a cylindrical "mini-well" sampling tube was formed from a rectangular piece of 10 μm screen by crimping it lengthwise, then crimping one end shut. Each finished tube was ~ 1 cm in diameter and 5 to 8 cm in length. A large quantity (> 30 m³) of "Winter sand" had been purchased from a local aggregate supplier for a pilot-scale test (4-6). This carbonate-rich sediment (77 ± 2 weight % as CaCO₃) is composed mainly of medium to very coarse sand, granules and pebbles (> 99 % particles between 0.3 and 4.75 mm, see Table 1). Batches of Winter sand (400 to 700 g) were prepared using a sample splitting technique.

One to two liter volumes of 2 g/L and 3 g/L (nominal) Aldrich HA in Milli-Q water were prepared and portions were diluted to prepare standards and solutions at 1.5 g/L, 1 g/L, 0.5 g/L, 0.2 g/L and 0.1 g/L. For each concentration, duplicate batches were prepared, as well as duplicate "blanks" using Milli-Q water. Mason jars with lids were cleaned with a 2 % detergent solution (Contrad ®: VWR CanLab; in deionized water), rinsed with deionized water, dried and pre-weighed (with mini-screen). The following were placed in each jar and weighed: estimated solution to saturate a sand sample, sand sample with mini-well (middle of sand), and top-up solution to saturate the sand completely. The final ratios of sand to solution were 4 to 5 g/mL. The Mason jars were sealed to prevent evaporation, stored at 23 ± 2°C, and the batch solutions were sampled by glass mini-pipette from the mini-wells at 7, 14, 43, 94, 118 and 148 days. Their absorbance was analyzed by uv/vis spectrophotometer (Varian Model CARY3) at 500 nm. Then the samples were returned to the batches from which they were derived.

The aqueous Aldrich HA concentrations in the batch samples were determined by comparison to standard solutions. The absorbance of the HA standard solutions declined by approximately 0.4 AU (Figure 2) over the course of the experiment. The drop in absorbance over the first 50 - 100 days cannot be attributed to instrument drift alone, but might be due to one or more of the following: precipitation of fine, particulate phase HA (little observed), biodegradation (thought to be minimal), or ongoing abiotic alteration/reaction of the Aldrich humic acid in solution. The chemical alteration/reaction processes might include changes in the structures and sizes of aggregates of HA molecules over time. The standards were retained for all sampling episodes. Because aging has likely also affected the HA in batch solutions, no corrections for aging were applied.

Column Test. A stainless steel and glass "sediment" column (30) was used to examine the dynamics of sorption of Aldrich HA onto Winter sand. To avoid clogging, the fritted glass discs that were designed to provide water-permeable contact at each end of the sample being tested were replaced by stainless steel retainers made of 10 μm mesh screen and supporting components. The column was packed with split samples of Winter sand, and purged with Milli-Q. A Model A-30-S Eldex precision metering pump and stainless steel tubing (1/16" OD and 0.01" ID) were used to pump solutions through the column. The cylindrical sand column was 6 cm long and 7 cm in diameter.

An inline Spectra-Physics Model 8440 uv/vis detector was used to monitor HA breakthrough in the column effluent at 500 nm. Downgradient of the uv/vis detector, the effluent flowed upward in a 5 mL glass beaker past a bromide ion selective electrode (Cole Parmer, # 27502-04) that monitored the breakthrough of Br⁻ tracer. Data from both instruments was collected by a Campbell Scientific 21X Micrologger with a SM716 storage module. To minimize drift, a syringe pump (Cole Parmer 74900), with a 25 mL glass syringe was used for delivery of ionic strength adjuster solution (Orion ionplus) at a rate of 0.005 mL/min, to the eletrode reservoir. In the single column test reported here, the input solution (1000 mg/L KBr, 0.5 g/L Aldrich HA) was sparged with with N_2 (Grade 4.8) to minimize formation of CO_2 bubbles, and pumped through the column at a rate of 0.38 mL/min.

The raw absorbance data, as recorded in mV by the Micrologger, are reported, given that these values are assumed to be proportional to HA concentration (i.e., Beer's Law). A curve fitting program (GraphPad Prism ® Version 2.01, GraphPad Software Inc., San Diego, CA) was used to convert (by 3rd order polynomial fit) the bromide data from meter output (mV) to mg/L.

Results and Discussion

Batch Tests. The trends over 148 days in the concentrations of aqueous HA in the batches indicated that large quantities of HA were sorbed by the Winter sand (Figure 3). For the batches with relatively low initial Aldrich HA concentrations (0.1 and 0.2 g/L), nearly all (90 to 95 %) of the aqueous HA was sorbed by 7 d. For batches with

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higher initial HA concentrations (0.5 to 3 g/L), the bulk sorption process was more sluggish, approaching apparent equilibrium by 148 days (Figure 3). In more detail, the trends in concentrations indicated an initial fast sorption phase (typically > 50 % of total sorption), followed by a slow sorption phase. For nonlinear regression of these data, an empirical equation (1) was used, which incorporated both fast and slow (net) sorption components,

$$C_s = C_{max}(1-(F \times e^{-k_1 t} + (1-F) \times e^{-k_2 t})), \qquad \text{(Equation 1)}$$

where C_s is the sorbed concentration, C_{max} is the inferred maximum sorbed HA (final observed concentration), F is the fraction of fast sorption, k_1 is the apparent fast sorption kinetic coefficient, and k_2 is the apparent slow sorption coefficient. Equation 1 is essentially the "inverse" of one that has been applied to desorption test data (31). Note however that in the batch sorption tests reported here, the dissolved HA concentrations were not held constant. The application of Equation 1 to the batch test results should be viewed as an approximate, empirical fit, that provides some insight into the kinetics of the bulk sorption process, as a cumulative result of adsorption and desorption reactions, but is also effected by the rate of the aqueous transport process, mainly molecular diffusion. For the nonlinear regressions based on Equation 1, a curve-fitting program (CurveExpert Version 1.34) was used with no weighting of data. An example is shown in Figure 4. For various batch tests, the calculated values for F, k_1 and k_2 are shown in Table 2.

Based on the nonlinear regressions, the fast sorption parameters, F and k_1, decrease as the starting HA concentrations increase (Table 2). The fast sorption component is likely an initial adsorption-dominated phase (24). At higher dissolved HA concentrations, saturation of available surface sorption sites on the mineral surfaces was approached more rapidly. Thus, a smaller fraction of dissolved HA was sorbed over the first few days and a larger fraction of the dissolved HA was available for subsequent slow sorption by some other mechanism. This resulted in lower F and k_1 values.

The inferred kinetic parameter for slow sorption, k_2, was found to be consistent at ~ 0.02/day (Table 2). The fact that k_2 is virtually independent of the starting HA concentration suggests that, unlike the fast sorption process, the slow sorption process was not controlled by surface-saturation. The slow sorption component may be largely a competitive exchange of dissolved HA molecules or aggregates for sorbed HA (17,19,24). In essence, the slow sorption process may be a secondary net sorption process controlled largely by a reduction in the rate of desorption of HA over time, due to replacement of relatively loosely-held HA molecules (e.g., low molecular weight) by more tightly-held, high molecular weight HA at the sorption sites.

In line with previous studies, a Langmuir sorption isotherm for the final time step (148 days) can be constructed, using the data from all batch tests (Figure 5). This nonlinear isotherm follows Equation 2,

$$C_s = Q_{max} KC_w/(1+KC_w) \hspace{4cm} \text{(Equation 2)}$$

where C_w is the aqueous (dissolved) HA concentrations (g/L), Q_{max} is the saturation sorbed HA concentration (mg/g), and K is the fitted sorption parameter. For the fit shown in Figure 5, using CurveExpert 1.34, the parameters were as follows: Q_{max} = 0.423 mg/g, and K = 39.14 L/g. The Langmuir equation assumes a finite number of sorption sites are available, which become saturated with increasing solute (HA) levels. The high K value indicates that the aquifer material has particularly high affinity for the HA at lower concentrations.

Column Test. In agreement with the batch test results, the column test results indicated that, compared to the bromide tracer (Figure 6), the transport of the aqueous Aldrich HA was significantly retarded. The breakthrough of bromide was "complete" after approx. 400 min or 1.5 pore volumes, whereas the tailing of HA continued for more than 5 pore volumes.

Computer modeling of the column test data is not straight forward. The recently developed NOMADS model (20), which assumes competitive Langmuir-type sorption, and takes into account the different kinetics of adsorption and desorption reactions, would be well suited for simulation of the dynamic Aldrich HA sorption process. However,

the use of this model would require specific information on the kinetics of adsorption and desorption reactions for various molecular weight fractions of Aldrich HA to Winter sand, and such data are currently not available. Instead, a well-documented one dimensional solute transport computer model, CXTFIT (version 2.0; ref. 32) was used to simulate the bromide and HA breakthrough curves generated by the column test. Given that this model assumes that (ad)sorption is linear, and that the rates of adsorption and desorption are equal in magnitude, the CXTFIT simulation should be viewed as an approximation of the net (bulk) sorption process, yielding no insight into the complex details of the various component reactions.

Using CXTFIT, the bromide breakthrough curve could be matched assuming equilibrium and no retardation (Figure 6). A time delay of 20 minutes from exit of the column to detection of the bromide by the probe was assumed, based on earlier testing. The result of this simulation indicated an average linear velocity, v, of 0.023 cm/min, and that the dispersion coefficient, D, was 0.0023 cm^2/min.

For the HA breakthrough curve, a 10 minute time delay for detection was assumed, based on previous testing. As anticipated, based on the parameters (v and D) determined for Br, the breakthrough curve for the HA could not be closely simulated by CXTFIT in equilibrium (instantaneous sorption) mode. Thus, the two-site sorption, non-equilibrium sorption mode of CXTFIT was employed. In this type of simulation, all sorption is assumed to occur as linear adsorption, described by a single distribution coefficient, K_d, but only a fraction f of the sorption sites are assumed to be at equilibrium. For the remainder (1 - f), the sorption is assumed to follow first order kinetics. A good fit for the HA breakthrough was obtained (Figure 6), yielding the following parameters: retardation factor R = 2.01, dimensionless partitioning variable β = 0.572 and dimensionless mass transfer coefficient ω = 1.86,

where $R = 1 + \rho_b \times K_d / \theta$,

$\beta = (\theta + f \rho_b \times K_d) / (\theta + \rho_b \times K_d)$

$\omega = \alpha(1-\beta)RL/v$,

ρ_b is the bulk density,

θ is the volumetric water content or saturated porosity,

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α is the first-order kinetic rate coefficient,

and L is the characteristic length for dimensionless parameters, set to 6.0 (column length).

Given the flow rate (0.38 cc/min) and cross-sectional area of the column (38.5 cm^2), the water saturated porosity

(θ) for the test column was approximately 0.43. Based on column mass and volume data, the bulk density of the

Winter sand was determined to be approximately 1.6 g/cc. Using these values, the CXTFIT simulation yields K_d

(linear sorption) = 0.27 mL/g, f = 0.15 and α = 0.0082/min.

The low fraction of sorption sites "at equilibrium" in this simulation (f = 0.15 or 15 %) indicates that kinetic

sorption must be taken into account in subsequent applications and/or numerical modeling. This is consistent with

the batch test results as reported in the previous section.

The bulk sorption kinetic rate coefficient for the column test (0.0082/min or 0.05/h) is approximately two orders in

magnitude greater than that for the slow phase component in the batch tests (0.02/d). This comparison indicates

that the 1 day column test was unable to detect the relatively slow component of sorption observed in the long-term

(148 d) batch tests. This apparently is at least part of the reason for the lower apparent K_d value for the column

test (0.27 mL/g) compared to the partitioning (point K_d ~ 0.7 mL/g) at 0.5 g/L HA that can be inferred for the 148

d batch test isotherm. However, the column test gives better information about the kinetics of the initial "fast

phase" of sorption (27), given that the first measurements in the batch testing were at 7 d. In the CXTFIT

simulation reported here, the "fast sorption" phase is modeled as two components, instantaneous and time-

dependent (ad)sorption. Combined, the results of the batch and column data, which were collected at two different

time scales, suggest that there actually may be three main phases of sorption, based on bulk kinetics: very fast (i.e.,

nearly instantaneous), fast (approx. 0.05/h), and slow (~ 0.02/d).

Comparison to Earlier Tests. In the literature, sorption of HS to soils and aquifer materials is typically reported

per mass of organic C, rather than per total HA.. The Langmuir parameters for the batch test results of this study

can be restated in terms of organic carbon, given that Aldrich humic acid is 38.2 % C (33). The resulting

Langmuir parameters, based on nonlinear regression of the 148 d test data, are as follows: Q_{max} = 0.162 mg HA (as

organic C) per g Winter sand; K = 102.2 L/mg. The non-equilibrium 7 d sampling event data of this study yield the following apparent Langmuir coefficients: Q_{max} = 0.088 mg (organic C)/g and K = 45.0. A comparision of the 7 d and 148 d parameters indicates that the apparent sorption parameters were strongly dependent on the duration of the batch tests.

Previous batch tests of the sorption of Aldrich HA by soils and mineral surfaces (12, 14, 34) have typically been much shorter in duration (1 to 4 d), using agitation to mix dilute mixtures, where the solids/solution ratios were $\leq$ 0.15 g/mL (i.e., much lower than soil/aquifer conditions). Given these factors, it is difficult to make a direct comparison of the sorption parameters reported in this study with those of previous studies. Previously reported batch tests of Aldrich HA in suspensions of kaolinite (34), clay-rich soil (35) and Ca-bentonite (12) indicated Langmuir-type sorption, with stronger affinity of Aldrich HA and solids compared to this study (148 d isotherm): by ~ 1 order in magnitude (OIM) for kaolinite, by ~ 2 OIM for clay-rich soil, by ~ 3 OIM for Ca-bentonite. These stronger affinity results in earlier tests were probably due mainly to the larger specific surface areas of the fine-grained solids, and the lower solids/solution ratios (0.002 g/mL for ref. 34; 0.15 g/mL for ref. 35; < 0.13 g/mL for ref. 12, compared to 4 - 5 g/mL in this study).

Jardine et al. (14) conducted 50 h batch tests of the sorption of dissolved natural organic matter (NOM) to an aquifer material. Similar to this study, these authors reported Langmuir and kinetic parameters. Their Langmuir parameters (Q_{max} = 0.245 mg (organic C)/g solids, K = 0.14 L/mg or 1400 L/g) indicated greater affinity than this study. As above, the greater affinity was likely due to the finer texture of their aquifer material (9.5% clay) and their lower solids-solution ratio (< 0.15 g/mL). Their reported rates of "slow" sorption, based on these batch tests, were – 0.05 to 0.1/h, similar to the "slow" rate of sorption observed in our column study (0.0082/min or ~ 0.05/h). It is probable that the short duration of the batch testing by Jardine et al. affected both the extent of sorption observed and the apparent kinetic parameters.

In addition to their batch tests, Jardine et al. (14) conducted column tests, using the same aquifer material and low levels of NOM (5 to 30 mg/L as carbon). To simulate their results, they used an earlier version (1.0) of CXTFIT,

as well as two other non-equilibrium, two-site sorption programs, DISPER and SOTS. The latter two programs assumed nonlinear sorption; SOTS allowed different rate coefficients for sorption and desorption. Jardine et al. found that closeness of fits to observed data were often similar for the three models, and they inferred that the observed tailing of HA breakthrough was mainly due to time-dependent sorption, rather than nonlinearity. They concluded that two-site, multi-kinetic models that assume linear isotherms may be adequate for describing subsurface transport of humic substances. This is in agreement with our finding, that CXTFIT provided reasonable simulations of the sorption of Aldrich HA to Winter sand.

Using Aldrich HA and a column of sandy aquifer material, Abdul et al. (1) conducted a 9 h sorption test, followed by desorption. They reported a linear partitioning coefficient K_d (their K_p) of 0.71 mL/g at an aqueous HA concentration of 29 mg/L (as organic C). This is much lower than the partitioning (apparent K_d of 4.18 mL/g) based on our 148 d Langmuir isotherm for this concentration of Aldrich HA (as organic C) and Winter sand, but similar to the partitioning (1.72 mL/g) indicated by our apparent (non-equilibrium) 7 d Langmuir isotherm. These comparisons reinforce our conclusion that apparent sorption parameters for HA in aquifers/soils are largely controlled by the duration of the test, whether in a batch or column.

Totsche et al. (19) studied the breakthrough of low levels (11 to 20 mg/L as C) of aqueous NOM (soil-derived) in columns containing two soil materials at pH 4.5. They observed incomplete breakthrough, approximately 30 % of influent NOM appeared in the effluent, even after 25 pore volumes. This very high retention of NOM (largely HS) by the soils may be a reflection of both the low pH and the low dissolved NOM concentration in their tests. Previous testing by Jardine et al. (21) indicated a maximum sorption of NOM to two soils at pH ~ 4.5. As indicated in our batch tests (Figure 5) and similar previous studies, the transport of aqueous HS in soils/aquifers may be severely retarded at low aqueous concentrations, given the steep slope of the Langmuir isotherm at these levels.

Implications of Results for Subsurface Remediation. The results of this study indicate that if a commercial humic acid is added to water for use in subsurface remediation, a substantial fraction will become sorbed to

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soil/aquifer solids. If high concentrations of aqueous HA are used, the kinetics of this sorption will be relatively sluggish, requiring weeks or more to reach approximate equilibrium. For computer simulation of the subsurface transport of aqueous HA, the sorption kinetics will have to be taken into account. Given typical remediation schedules (weeks to years), the kinetics indicated by long-term testing (e.g., 148 d batch tests) are required. In contrast, the distinction of various "early" phases of sorption (i.e., very fast and fast), as indicated by conventional 1-2 d batch and column tests, may be superfluous for modeling of pilot and field-scale applications.

Given the steep slope of the Langmuir isotherm at low Aldrich HA concentrations (e.g., < 0.1 g/L), the transport and breakthrough of dilute Aldrich HA solutions in field applications would be severely retarded. In such a scenario, the mobilization of contaminants might actually be retarded by the addition of HA to groundwater (19), at least temporarily. At increasingly higher levels of aqueous Aldrich HA (> 0.1 g/L), the breakthrough of HA would become more rapid, given the fact that a finite amount of surface sites are available for sorption of the aqueous HA.

If a concentrated solution of a commercial humic acid is used in subsurface remediation, the fraction that becomes sorbed will ultimately become an important sink for hydrophobic contaminants. This could compromise the mobilization of contaminants in the aqueous HA solutions to some extent. On the positive side, in the post-treatment phase, after the "spent" HA carrier solutions have been extracted, the sorbed humics would increase the organic content (f_{oc}) of the soil/aquifer material and would retard the further migration of the dissolved contaminant. Combined with in-situ bioremediation (natural or enhanced), this might result in a substantial reduction in the rate(s) at which residual NAPL and/or sorbed contaminants are released from the zone of contamination.

This study reports tests with one commercial humic acid and one model aquifer material. In its favour, there is a considerable amount of information on the chemical properties of Aldrich HA, but this product is relatively expensive (~ $20.00 US per kg: 1999 quote). Thus, it would be useful to test other, less expensive commercial humic acid products. Further data are also required on how variations in the composition of aquifer materials

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(e.g., grain size distribution, mineralogy, organic carbon content) and aqueous chemical parameters (e.g., ionic strength, pH, temperature) affect the sorption of commercial humic acids in the subsurface. These tests should be of appropriate duration (several weeks or longer), and should employ solids/solution ratios similar to subsurface conditions, as in the batch tests reported in this study.

ACKNOWLEDGEMENTS

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Table 1 - Particle size distribution of "Winter sand", as reported by the supplier.

Particle Size (mm) by Sieve	Weight %
> 4.75	0
2.36 - 4.75	25.3
1.18 - 2.36	34.7
0.60 - 1.18	30.0
0.30 - 0.60	9.0
0.15 - 0.30	0.5
0.075 - 0.15	0.2
<0.075	0.3

Table 2. Parameters obtained for nonlinear regressions (Equation 1) of selected batch test data.

Initial aqueous HA conc. (g/L)	F	k_1	k_2	r^2
0.5 (I)	0.89	0.58/day	0.023/day	0.994
0.5 (II)	0.84	0.64/day	0.032/day	0.992
1 (I)	0.81	0.43/day	0.022/day	0.996
1 (II)	0.83	0.48/day	0.024/day	0.998
2 (I)	0.56	0.34/day	0.018/day	0.986
2 (II)	0.64	0.35/day	0.019/day	0.990

Figure 1. Illustration of batch test apparatus.
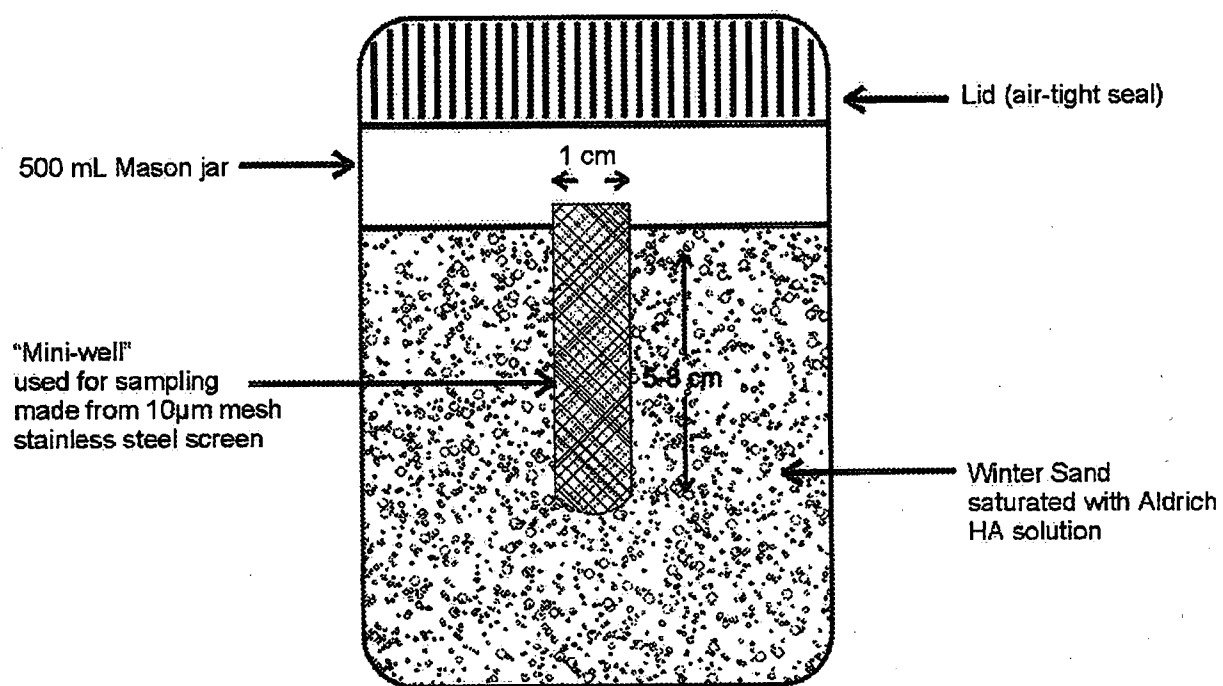
Figure 2. Changes in absorbance of 1 g/L Aldrich HA standard.
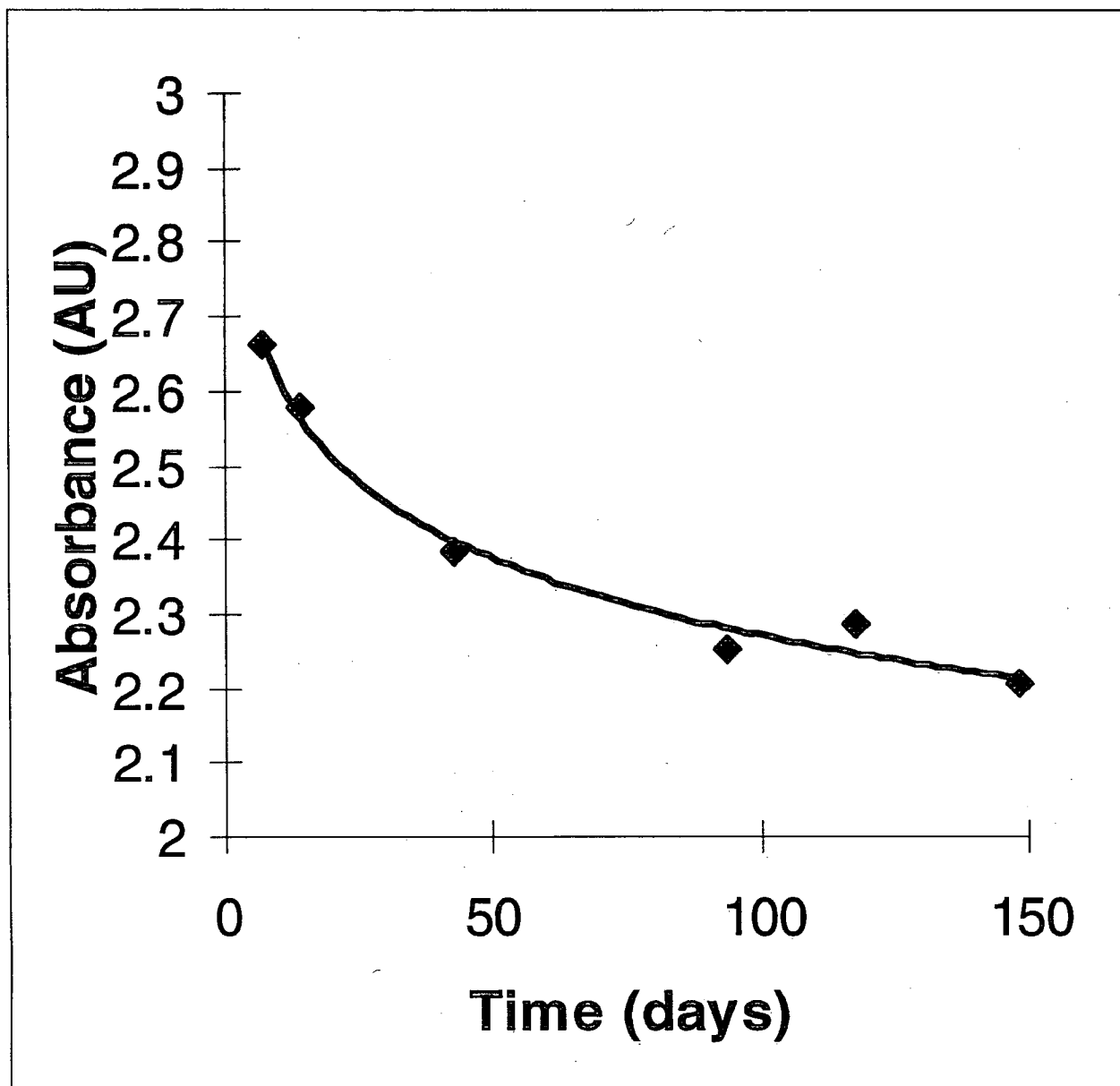
Figure 3. Declines in aqueous Aldrich HA over time in batches (initially 0.5 to 2 g/L HA). Note that each batch is represented by a unique symbol.
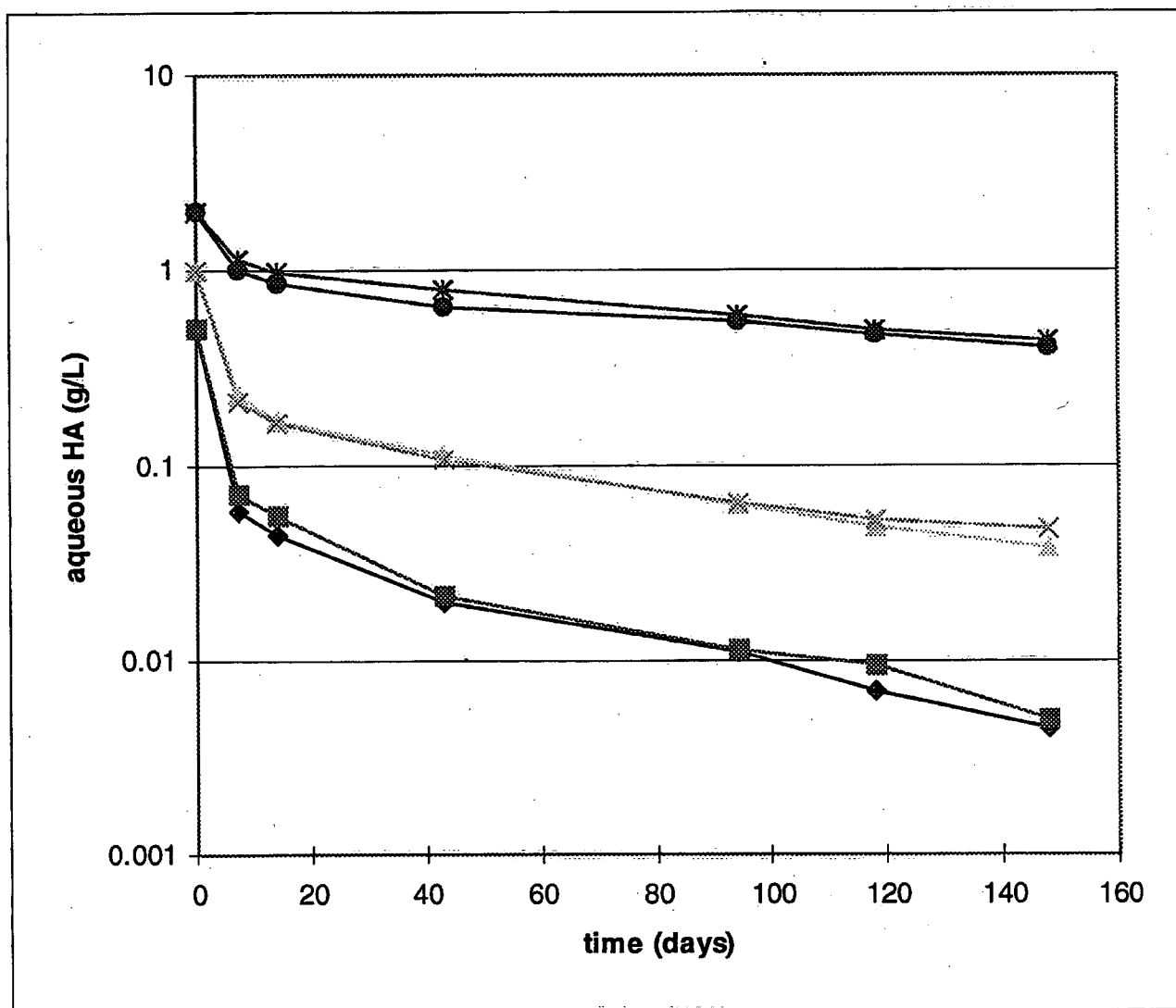
Figure 4. Example of a nonlinear regression of batch test data using Equation 1. In this case, the initial aqueous

HA was 1 g/L (nominal).
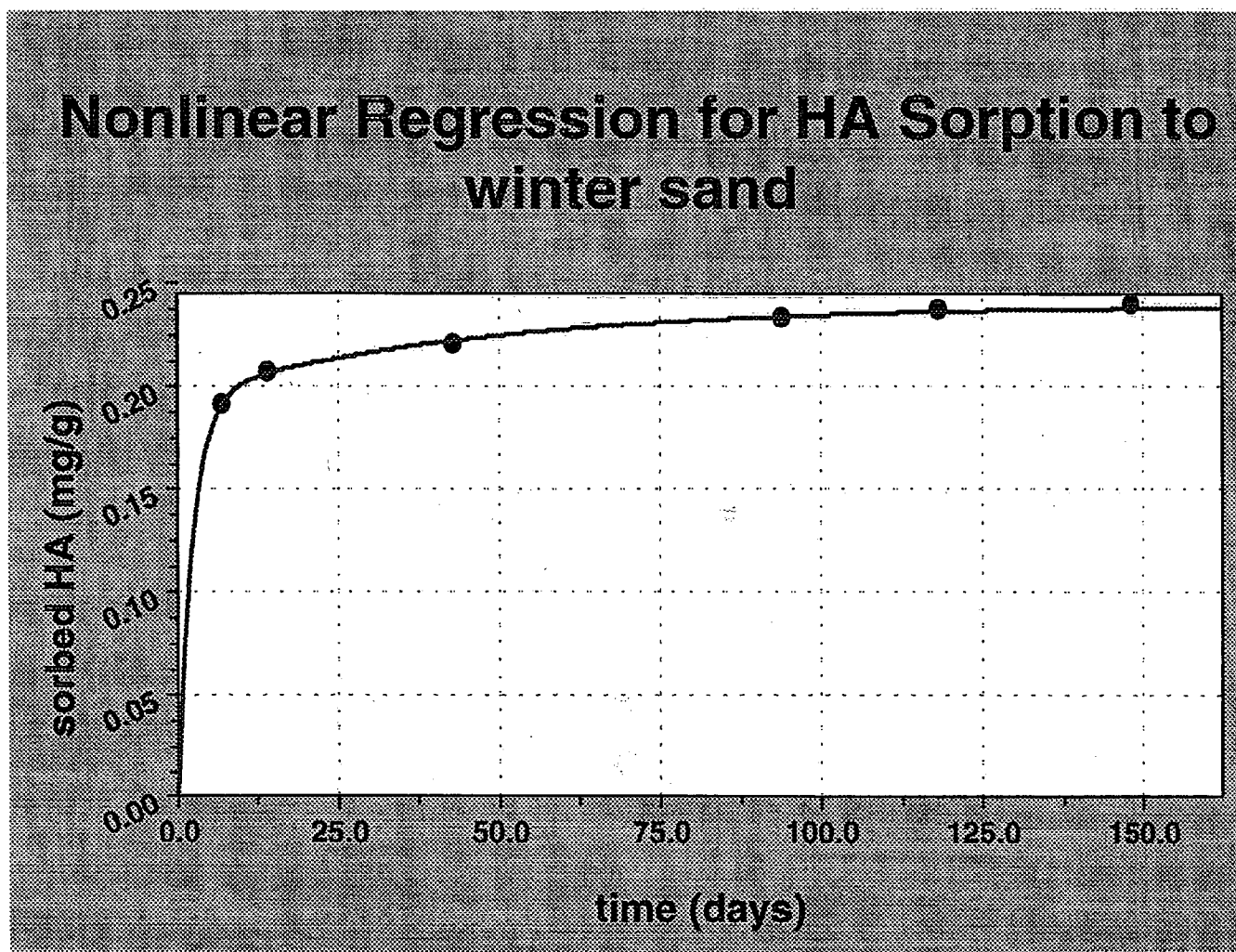
Figure 5. Langmuir isotherm for the sorption of Aldrich HA to Winter sand at 148 d.

For this fit, the Langmuir parameters are as follows: $Q_{max} = 0.423$, K = 39.14.
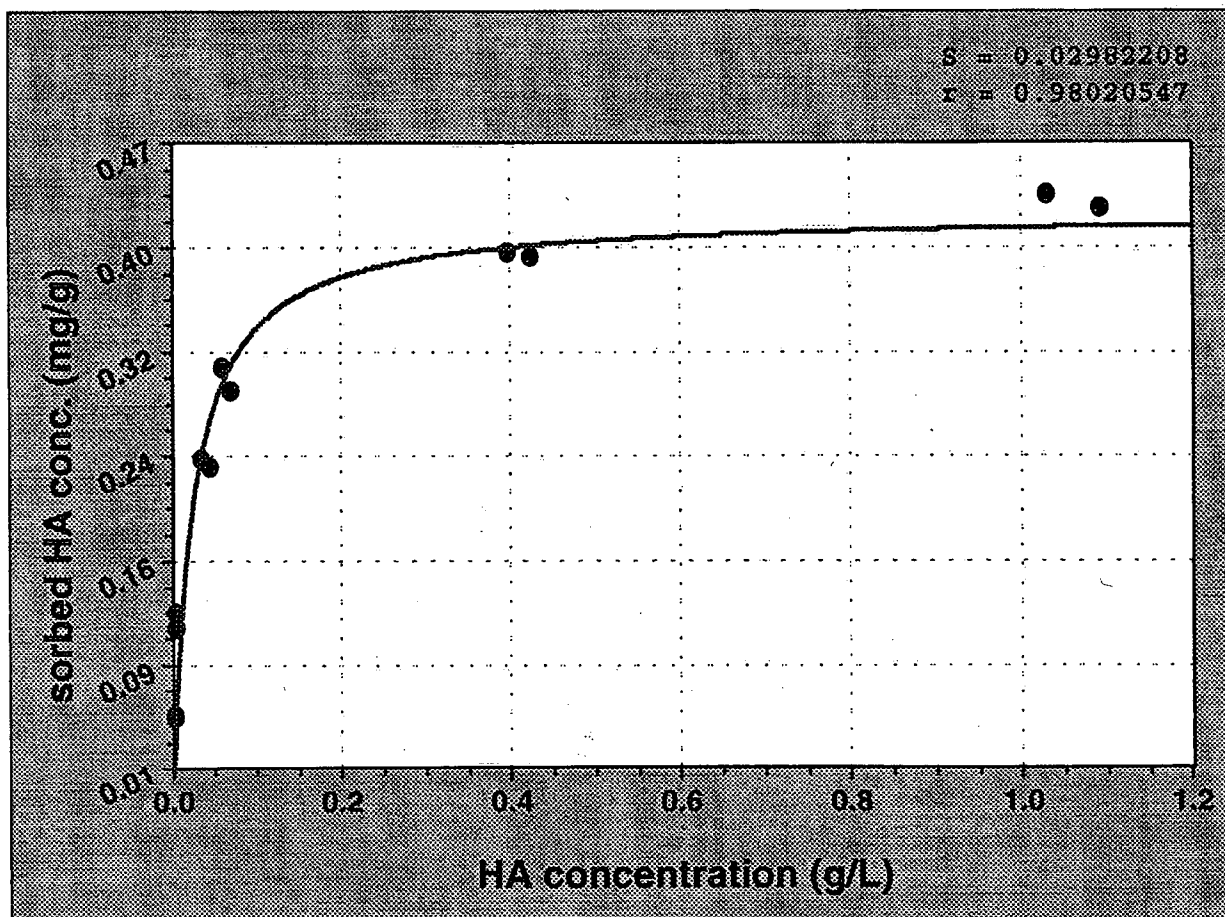
Figure 6. Observed and simulated (CXTFIT) breakthrough curves for Br and Aldrich HA, column test.