SLOW DESORPTION BEHAVIOR OF ONE HIGHLY RESISTANT AROMATIC AMINE IN LAKE MACATAWA, MICHIGAN, USA, SEDIMENT

SHIHUA CHEN and MARIANNE C. NYMAN*
Department of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180, USA
(Received 10 January 2005; Accepted 2 June 2005)

Abstract—The desorption behavior of benzidine from Lake Macatawa (Holland, MI, USA) sediment was investigated in this study using batch solvent extraction method. Seven solvents were tested as the extracting reagents: Deionized water (DI), calcium chloride in DI (CaCl$_2$), sodium hydroxide in DI (NaOH), acetonitrile (ACN), a mixture of acetonitrile and ammonium acetate in DI (ACN-NH$_4$OAc), methanol (MeOH), and hydrochloric acid in DI (HCl). These solvents are proposed to react with sediment-associated benzidine by different mechanisms (e.g., cation exchange, hydrophobic partitioning, and covalent binding). Three sets of sorption isotherm experiments were conducted separately in these seven solvents with a 7-d, three-week, and two-month contact time. The results demonstrated nonlinear isotherms with Freundlich $1/n$ values varying from 0.25 to 0.52. The desorption behavior of benzidine in the solvents was evaluated after the sorption of benzidine onto the sediment with same contact times of 7 d, three weeks, and two months. A two-stage model subsequently was applied to simulate the experimental data. The rapidly desorbing rate constants were on the order of one to two per day for ACN, ACN-NH$_4$OAc, and NaOH solvents, and the slowly desorbing rate constants were on the order of $10^{-4}$ to $10^{-5}$d. Sequential desorption experiment demonstrated low total extraction efficiency of less than 40%. Both the observed sorption and desorption phenomena suggested that hysteresis and/or mass-transfer limited diffusion may result in the slow desorption behavior observed in this study.

Keywords—Benzidine  Sorption  Desorption  Solvents

INTRODUCTION

Concerns over aromatic amines, such as benzidine, exist because several of the aromatic amines already have been identified as highly toxic compounds. The exposure to them may result in serious health problems, such as cancer [1]. Although benzidine no longer is produced in the United States, benzidine-based dyes still are imported into the United States [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red zidine-based dyes still are imported into the United States although benzidine no longer is produced in the United States, may result in serious health problems, such as cancer [1]. Concerns over aromatic amines, such as benzidine, exist because several of the aromatic amines already have been identified as highly toxic compounds. The exposure to them may result in serious health problems, such as cancer [1]. Although benzidine no longer is produced in the United States, benzidine-based dyes still are imported into the United States [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red zidine-based dyes still are imported into the United States although benzidine no longer is produced in the United States, may result in serious health problems, such as cancer [1]. Concerns over aromatic amines, such as benzidine, exist because several of the aromatic amines already have been identified as highly toxic compounds. The exposure to them may result in serious health problems, such as cancer [1]. Although benzidine no longer is produced in the United States, benzidine-based dyes still are imported into the United States [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red [2]. Benzidine enters the environment by the reduction of benzidine-based dyes. For example, the reduction of Direct Red.
Sediment was sampled from the eastern basin of Lake Macatawa located in Holland (MI, USA) as the model lake. The primary contaminant of interest in this lake is 3,3′-dichlorobenzidine, released to the lake via a single permitted effluent diffuser, with a known point of introduction. Nyman et al. [34] studied the transport and transformation behavior of 3,3′-dichlorobenzidine and revealed that, during the 12-month incubation period, 3,3′-dichlorobenzidine disappeared slowly and benzidine, one of the major biodegradation products, together with an intermediate, 3-chlorobenzidine, were observed to accumulate over time. It is highly possible that benzidine would be degraded further in the engineered lake water-sediment systems. However, the sequestration of benzidine in sediments would influence the bioavailability significantly. The sequestered benzidine desorbs slowly and mostly is not available for the uptake by microorganisms in the water column.

The objectives of this study were to evaluate the long-term desorption behavior of benzidine in these engineered systems (e.g., various solvent-sediment batch reactors) and to determine the relative importance of the involved mechanisms by observing the sorption and desorption behavior of benzidine using an assortment of solvents. By conducting this study, better understanding of the sorption (and desorption) of aromatic amines in the suspended geosorbents would be gained.

MATERIALS AND METHODS

Chemicals

Benzidine was purchased from Sigma Chemical (St. Louis, MO, USA) with a reported purity over 95%. The selected physicochemical properties of benzidine are presented in Table 1. Acetonitrile ([ACN]; C$_2$H$_3$N, high-performance liquid chromatography [HPLC]-grade, 99.9%) and methanol ([MeOH]; HPLC-grade, 99.8%) were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Sodium hydroxide ([NaOH]; 98.6%), ammonium acetate ([NH$_4$OAc]; HPLC-grade, 99.1%), hydrochloric acid ([HCl]; technical-grade), calcium chloride dihydrate (CaCl$_2$·2H$_2$O), acetic acid (glacial, C$_2$H$_4$O$_2$, certified American Chemical Society plus), and sodium acetate (C$_2$H$_3$NaO$_2$, certified American Chemical Society fused) were all purchased from Fisher Scientific (Pittsburgh, PA, USA). All chemicals were used as received.

Sediment sample

Sediment was sampled from the eastern basin of Lake Macatawa located in Holland (MI, USA). The sediment sample was collected with a Ponar grab sampler. Lake water sample was collected below the water surface and then stored in amber glass bottles. Both sediment and lake water samples were chilled in ice during transportation and were kept in a refrigerator at 4°C until usage. The wetted sediment samples were dried in an oven at 100 ± 5°C for 48 h, broken up by mortar and pestle, and then further ground with a grinder due to the sediment sample’s cohesive structure.

It is possible that biodegradation may affect the loss of benzidine in the water-sediment systems as a function of time. However, Lee et al. [30] studied the sorption behavior of aniline and α-naphthylamine onto unsterilized and cobalt-irradiated soils and did not find apparent discrepancy between treated and untreated soils. Thereafter, they suggested that no further treatment needed to be taken to prevent the microbial activity from interfering with the sorption–desorption experiment. In addition, it is not likely to achieve biodegradation in these strong solvents used in this study. The data from our control experiment (not shown here) also proved the same hypothesis. Therefore, steps that would be taken to inhibit the biological activity seemed unnecessary in this study, and the addition of additional chemicals was avoided.

Solvent selection

Many methods have been reported in literature to measure the desorption kinetics, such as the batch method, the column method, and the gas-purge method [35]. In all these methods, clean deionized water (DI) was used and kept in contact with the preloaded sediment particles for hours or even longer. By diluting or replacing the aqueous phase with other clean DI, sorbed chemical should release continuously into the aqueous phase. This process could be repeated several times to get the satisfactory desorption results.

The batch method for the desorption experiment was used in this study. However, the desorption method in this study was different in terms of solvents used to perform the extraction. We proposed to study three sorption mechanisms: Electrostatic interaction (or cation exchange), hydrophobic partitioning, and covalent binding. To carry out this research objective, DI, 0.05 M of CaCl$_2$ in DI, 0.5 M of NaOH in DI, ACN, ACN-NH$_4$OAc (50:50 in volume of ACN:0.6 M NH$_4$OAc in DI), MeOH, and 0.1 M of HCl in DI were chosen as the extracting solvents. Among these solutions, CaCl$_2$ and HCl electrolyte solutions contain cations of Ca$^{2+}$ and H$^+$, respectively, which could be adsorbed to the negatively charged surface of the sediments and compete with protonated benzidine for the sorption sites [30]; MeOH, ACN, and ACN-NH$_4$OAc could penetrate to the natural organic matter or to mineral pores in the sediment matrix [36]; at the same time, NH$_4$OAc in the mixture also influences the cation exchange process [37]. Sodium hydroxide is believed to have the potential to hydrolyze the covalent bonds, which might be formed slowly with the carbonyl moiety groups in the sediments [38]. In each experiment set, DI was used as a control.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>IUPAC</th>
<th>CAS no.</th>
<th>Structure</th>
<th>MW (g/mol)</th>
<th>pK$_a$</th>
<th>Log $S_a$ (25°C) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzidine</td>
<td>4,4′-Diaminobiphenyl</td>
<td>92-87-5</td>
<td><img src="image" alt="Structure of Benzidine" /></td>
<td>184.2</td>
<td>3.3/4.3</td>
<td>1.34</td>
</tr>
</tbody>
</table>

* IUPAC = International Union of Pure and Applied Chemistry; CAS = Chemical Abstract Service; MW = molecular weight; pK$_a$ = acid dissociation constant; $S_a$ = octanol–water partition coefficient; $S_a$ = aqueous solubility. Data adapted from Lee et al. [30].
Batch sorption isotherm experiments

To conduct the sorption isotherm study, benzidine was dissolved in the following solvents: DI, CaCl$_2$ solution, NaOH solution, ACN, ACN-NH$_4$OAc, MeOH, and HCl solution. For each solvent, the dilution in-series method was employed to get the various benzidine concentrations needed for each of the isotherm experiments. Depending on the solubility of benzidine in each of the selected solvents, the concentration ranges for the solvents were different. For example, although the solubility of benzidine in MeOH is much higher than its aqueous solubility (400 mg/L as illustrated in Table 1), the solubility of benzidine in CaCl$_2$ solution is lower than the aqueous solubility. However, the solubility of benzidine in the selected solvents was not measured. Therefore, the benzidine concentration range in MeOH was 50 to 430 mg/L in this study, and in CaCl$_2$ solution the concentration range was 17.0 to 255.2 mg/L. The choice of the concentration range was to keep the concentration difference big enough to reduce the experimental error.

The batch experiments were conducted in 9-ml culture test tubes with Teflon$^{\circledR}$-lined screw caps in duplicate, following the similar procedure described by Lee et al. [30]. Each dried sediment sample (~1.3 g) was spiked with 5 ml of benzidine-water stock solution at 140 mg/L. The sample tube caps were sealed tightly with Parafilm$^{\circledR}$ (Neenah, WI, USA), which prevented the loss of liquid during the long-term experimental process. The sealed tubes then were wrapped in aluminum foil to minimize the possible effect of light (e.g., photodegradation of benzidine) during the duration of the experiment. The tubes were rotated end-over-end at a speed of 45 rpm for 7 d, three weeks, or two months at room temperature (i.e., 23.0 ± 0.5°C). After the preselected sorption contact time was reached, samples were centrifuged with IEC Centra GP8R from Thermo Electron (Franklin, MA, USA) at 1,350 g for 25 min to separate the solid and liquid phases. The supernatants were removed to the amber glass vials for HPLC analysis.

The empirical Freundlich isotherm model was employed to describe the sorption process, as shown in Equation 1

\[
q = K_q C^{1/n}
\]

where \(q\) is the sorbed benzidine concentration (mg/kg), \(C\) is the benzidine concentration in the solution phase (mg/L), \(K_q\) is the sorption affinity (mg/kg)/(L/mg)$^{1/n}$, and \(1/n\) is the non-linearity constant related to the energy distribution of the sorption sites. A unity of \(1/n\) indicates linear sorption and, therefore, equal sorption energies for all sediment sites [39].

Desorption experiments

Pre-equilibration. The methods of sample preparation were the same as those employed in the batch sorption isotherm experiments. The equilibration times taken for this pre-equilibration study were kept the same (i.e., 7 d, 3 weeks, and 2 months).

Solvent additions. After the preselected sorption contact time was reached, samples were centrifuged at 1,350 g for 25 min. The supernatants with an approximate volume of 3.8 ml were removed to the amber glass vials for HPLC analysis. The remaining water left in the sediment pore was about 1.2 ml, which carried approximately 0.6 μg of benzidine over to the sediments; this amount of benzidine was subtracted when performing the mass balance for the desorption processes. Five-milliliter aliquots of selected solvents (see Solvent selection for desorption section) then were added to the corresponding tubes and mixed with the condensed sediments by the vortex mixer. The same procedures were followed to seal, wrap, and rotate the samples as described above. At the designated times, the samples were centrifuged to separate the phases, and the benzidine concentrations in the solvents were measured by HPLC.

Sorbed benzidine concentrations \((q_0, \text{ mg/kg})\) for the desorption studies were calculated by assuming that the disappearance of mass in the solution corresponded to the same quantity presented in the sediment phase. Therefore, the following was used: \(q = (C_0 - C)/D_0\), where \(C_0\) and \(C\) are the initial and final concentrations in the solution (mg/L), respectively, and \(D_0\) is the sediment concentration (kg/L).

Sequential desorption with solvents. The sequential desorption experiment was conducted separately to perform the mass balance on the whole solvent-sediment system and to determine the overall desorption efficiency. Unlike the sacrificing method described above, the sequential desorption method kept using the same tube as the batch desorption reactor. The pre-equilibrated sediment with benzidine was extracted by one solvent for a selected time, the extract then was removed, and fresh solvent was added again to conduct the desorption. After one solvent was tested, another solvent was added to the tube following the same procedure. This desorption process for each solvent in this study was repeated three times, which lasted about 10 d with a duration of 0.25 d, 2.5 d, and 7 d for each of the three steps, respectively. All the extracts were analyzed by HPLC.

Desorption rate analysis

Cornelissen et al. [20] developed a model that divided the desorption process into three stages (i.e., the rapidly, slowly, and very slowly desorbing steps) to fit the desorption data for their study. However, the desorption process more often is described in the literature as biphasic, in which a rapid release of sorbate from the sorbent is continued by a much slower one, with one assumption that both steps follow first-order reaction rate kinetics. The equations are listed in Equations 2 and 3.

\[
\frac{dF_{\text{rap}}}{dt} = -K_{\text{rap}}F_{\text{rap}}
\]

\[
\frac{dF_{\text{slow}}}{dt} = -K_{\text{slow}}F_{\text{slow}}
\]

where \(F_{\text{rap}}\) and \(F_{\text{slow}}\) are the rapidly desorbing and slowly desorbing fractions in the sediment phase, respectively; \(K_{\text{rap}}\) and \(K_{\text{slow}}\) are the corresponding first-order rate constants (per day). Integrating Equations 2 and 3 will yield Equations 4 and 5, as follows:

\[
F_{\text{rap}} = F_{\text{rap},0} \times \exp(-K_{\text{rap}} \times t)
\]

\[
F_{\text{slow}} = F_{\text{slow},0} \times \exp(-K_{\text{slow}} \times t)
\]

where \(F_{\text{rap},0}\) and \(F_{\text{slow},0}\) represent the initial fractions before the desorption process starts. These initial fractions are subject to the constraint that the sum of them equals unity, which is shown in Equation 6.

\[
F_{\text{rap},0} + F_{\text{slow},0} = 1
\]

In addition, the total fraction of sorbate desorbed in the solution, which still is residing in the solid, is equal to unity at any time when the desorption is in progress, which is formulated in Equation 7.
where $F_{\text{sol}}$ stands for the total fraction of benzidine in the solution.

By fitting the experimental data to Equation 7 with the constraints of Equations 4 through 6, the values of fitting parameters of $F_{\text{sol}}$, $K_{\text{rap}}$, and $K_{\text{slow}}$ could be obtained by performing nonlinear least-squares regression with NLREG 6.3 (Brentwood, TN, USA).

**Analytical methods**

Benzidine concentrations in both aqueous and solvent phases were measured by Shimadzu (Columbia, MD, USA) HPLC equipped with an ultraviolet-visible detector (Shimadzu SPD-10A). This HPLC system consisted of an LC-10AD pump, an FCV-11AL solvent delivery system, an SCL-10A system control, and an SIL-10A autoinjector. The wavelength of the ultraviolet detector was set at 283 nm, at which the intensity of absorption for benzidine was found to be the highest. The chromatographic separations were achieved by using a reverse-phase Shimadzu Premier C18 column (150 x 4.6, 100–5; pH range: 2–8) coupled with a Supelco guard column packed with Spherisorb silica C1 (Alltech Services, Glen Dale, MD, USA). Acetonitrile and sodium acetate buffer (pH range: 4.7–4.9) were used as the mobile phase with a ratio of 25:75. The total flow rate was 1.0 ml/min with an operating pressure of 16.0 ± 0.2 M Pa. Ten microliters of sample was injected for each injection and every sample was measured in replicate. Under such conditions, the retention time ($t_R$) of benzidine was found to be 6.0 min. The concentrations of the unknown samples then were calculated based on the calibration curve obtained from the values of the external standards.

**RESULTS AND DISCUSSION**

**Lake Macataya sediment sample**

The sediment sample was classified as silty-clay type with silt and clay content more than 94%. The specific surface area was 19.32 m²/g and total pore volume was 6.86 x 10⁻⁴ m³/g. The pH of wet sediment sample was 7.1, which is more than pH units above the highest $pK_a$ value for benzidine (see Table 1). The organic carbon content was found to be approximately 12% for this sediment sample.

**Detection form of the benzidine molecule**

A quick experiment was set up to investigate if all the possible forms of benzidine in acidic solution (e.g., neutral, singly, and doubly protonated forms) could be detected readily by the HPLC. In this experiment, an exact amount of benzidine was spiked to make a solution concentration of 144 mg/L, and the system was well buffered at pH 4.88 with acidic acid and sodium acetate. The neutral fraction of benzidine in the solution was 78.7% based on the relationship between pH and $pK_a$. If only the neutral form in the solution was detected by HPLC, the concentration measured by HPLC should be about 78.7% of the initial spike. However, the experimental result illustrated that 95.2% of the initial input of benzidine was detected by HPLC. Considering the instrument error and experimental artifacts, it is reasonable to conclude that the measured concentration included both neutral and cationic forms of benzidine in the acidic solution. Similar results were obtained with another buffer solution at pH 2.44. Therefore, in this study, the concentrations given by HPLC were the total benzidine concentrations, if not mentioned otherwise.

**Batch sorption isotherm experiments**

The sorption isotherm experiments were conducted with three different equilibration times of 7 d, three weeks, and two months in the seven solvents. The data are plotted in Figure 1a to c. In all cases investigated, the quantitative comparisons between the various sorption isotherm constants became complicated. However, some trends still were evident in the observed sediment/solvent distribution data. The sorption affinity of benzidine in these different solvents approximately followed the order: HCl > DI > CaCl₂ > NaOH ≈ MeOH > ACN > ACN-NH₄OAc. The proton in the HCl solution would associate with the benzidine molecule to form the cationic species. The protonated benzidine had the potential to be sorbed quickly to the negatively charged surface of the sediment by electrostatic interaction. Therefore, this would explain why benzidine in the HCl solution had the highest affinity for sediment sites. It should be noted that, after mixing the 0.1 M of HCl with the sediments, some protons in the solution would react with the carbonates present in the sediments, thus lowering the amount of protons available for the association with benzidine molecules. The pH measurement showed that, after equilibrium, the final pH in the 0.1-M HCl solution with sediments increased to approximately five compared to the initial value of one. Even at this elevated pH, about 10% of the total benzidine still was in protonated form. The pH values in the other aqueous solvents remained stable over the time-course study. Second, benzidine molecules were highly hydrophobic, which accounted for the phenomena that benzidine in all the aqueous solutions (i.e., DI, CaCl₂, and NaOH) had higher affinity for sediment sites than that in the organic solvent phases (i.e., MeOH, ACN, and ACN-NH₄OAc). In contrast to ACN solvent itself, the addition of NH₄⁺ cation to ACN solvent decreased the affinity of benzidine molecules for sediment sites. This may be caused by the competition between benzidine and NH₄⁺ cation for the limited sorption sites. In general, the ln($K_I$) values were fairly stable for most of the solvents (i.e., HCl, DI, CaCl₂, NaOH, MeOH, and ACN-NH₄OAc) with different sorption times, and the maximum relative error was less than 8%. However, the ln($K_I$) values for ACN increased by about 25% when the contact time was extended from 7 d to two months.

All the sorption isotherms exhibited nonlinear behavior, with the 1/n-values varying from 0.25 to 0.52. For DI and the solvents of CaCl₂, ACN, ACN-NH₄OAc, and MeOH, the 1/n-values did not change significantly, with a maximum error of 20%, which was observed in the ACN-NH₄OAc solvent. However, these 1/n-values increased by 72 and 50% in the NaOH and HCl solutions, respectively, when the sorption time was extended from 7 d to two months. This observation might illustrate that the sediment sites with different sorption energies rearranged when the time-dependent reaction of NaOH and/or H⁺ molecules with the sorbed benzidine and/or benzidine in the liquid phase occurred.

**Desorption behavior in different solvents**

Three sets of desorption experiments were initiated, each having an equilibration time of 7 d, three weeks, or two months.
Fig. 1. Sorption isotherms in acetonitrile ([ACN]: □); acetonitrile-ammonium acetate ([ACN-NH₄OAc]: ○), 0.5 M of sodium hydroxide ([NaOH]: ▲); methanol ([MeOH]: ○); deionized water ([DI]: △); 0.1 M hydrochloric acid ([HCl]: ○) using (a) 7d, (b) three weeks, and (c) two months of equilibration time.

When contact time was three weeks or two months, the sorption of benzidine from the aqueous phase to the sediment phase reached equilibrium according to the sorption kinetics study. The subsequent desorption kinetics data are shown in Figures 3 and 4. In both experiments, the release of the sorbed benzidine to each solvent phase took place over time, and finally approached or nearly approached equilibrium for ACN and ACN-NH₄OAc solvents, revealing a biphasic desorption process in these solvents. Acetonitrile, ACN-NH₄OAc, and MeOH solvents could extract benzidine molecules from natural organic carbon or minerals in the sediment with ACN having the highest total extraction efficiency and MeOH having the lowest. This difference in total extraction efficiency between ACN and ACN-NH₄OAc can be explained by the data in Table 4. From the two data sets listed in Table 4, the rapidly desorbing fractions for ACN (0.09 for both 3-week and 2-month months. The results are given in Figures 2, 3, and 4, respectively, where the concentration of benzidine in the solvent (mg/L) is plotted against desorption time (day). The data demonstrate that a very small fraction of sorbed benzidine was desorbed to DI, the 0.05-M CaCl₂ solution, and the 0.1-M HCl solution. This phenomenon is attributed to the strong affinity of benzidine for the sediment matrix. Therefore, benzidine readily is adsorbed to the surface of the solid phase. In addition, benzidine is not desorbed easily due to its high hydrophobicity observed in DI, the 0.05-M CaCl₂ solution, and the 0.1-M HCl solution. In general, the desorption behavior of benzidine in DI, the 0.05-M CaCl₂ solution, and the 0.1-M HCl solution were very similar in all of the three desorption experiments conducted in this study, although these solvents may have different desorbing mechanisms. To make this observation clearer, the desorption percentage data for these three solvents are compared in Table 3. From the tabulated data, a very small fraction of sorbed benzidine was desorbed into DI, CaCl₂, and HCl solutions. It may imply that cation exchange process has insignificant effect on the benzidine desorption from the sediment. At normal or even elevated concentrations, these ions of Ca²⁺ and H⁺ (and very likely NH₄⁺) when present in ground and surface waters, have little impact on benzidine desorption.

Several other observations can be made by comparing Figure 2 with Figures 3 and 4. In Figure 2, the desorption behavior of benzidine in ACN, ACN-NH₄OAc, MeOH, and NaOH were quite different from that in Figures 3 and 4. The desorbed fraction of benzidine into these solvents increased over time, reached a peak, and then declined, as seen in Figure 2. One possible reason for this discrepancy was that, after 7 d of contact time, sorption equilibrium still was not reached. This also was proven by another set of sorption kinetics experiments conducted thereafter (see Fig. 5). The kinetics study revealed that 15 to 20 d was needed for the benzidine-water system to reach equilibrium; thereby, nearly 94% of the initial mass was adsorbed to the sediment phase. Therefore, most of the sorbed benzidine molecules were associated with the surface of the sediment and easily could be extracted by these solvents after 7 d of contact time. Benzidine concentration rose in the solution with the release of the loosely sorbed molecules from the sediment, and sorption process dominated again, leading to the decrease of the benzidine concentration in the liquid phases. Another possibility that the data might be flawed due to some unknown experimental error toward this observation was not excluded. In either case, further study is needed to clarify this phenomenon.
Slow desorption of benzidine

The concentration of benzidine in acetonitrile (ACN; □), acetonitrile-ammonium acetate ([ACN-NH4OAc]; ●), 0.5 M of sodium hydroxide ([NaOH]; ▼), methanol ([MeOH]; ○), deionized water ([DI]; △), 0.1 M of hydrochloric acid ([HCl]; ◆), 0.05 M of calcium chloride ([CaCl2]; ⊘) solvents from single extractions with different desorption times using samples that have been equilibrated for three weeks. Solid lines indicate the model fitting curves with 95% confidence interval. The goodness-of-fit \( r^2 \) and standard error are listed in Table 4.

Fig. 2. Concentration of benzidine in acetonitrile ([ACN]; □), acetonitrile-ammonium acetate ([ACN-NH4OAc]; ●), 0.5 M of sodium hydroxide ([NaOH]; ▼), methanol ([MeOH]; ○), deionized water ([DI]; △), 0.1 M of hydrochloric acid ([HCl]; ◆), 0.05 M of calcium chloride ([CaCl2]; ⊘) solvents from single extractions with different desorption times using samples that have been equilibrated for 7 d. Solid lines indicate the parametric trends.

Fig. 3. Concentrations of benzidine in acetonitrile ([ACN]; □), acetonitrile-ammonium acetate ([ACN-NH4OAc]; ●), 0.5 M of sodium hydroxide ([NaOH]; ▼), methanol ([MeOH]; ○), deionized water ([DI]; △), 0.1 M of hydrochloric acid ([HCl]; ◆), 0.05 M of calcium chloride ([CaCl2]; ⊘) solvents from single extractions with different desorption times using samples that have been equilibrated for three weeks. Solid lines indicate the model fitting curves with 95% confidence interval. The goodness-of-fit \( r^2 \) and standard error are listed in Table 4.

Table 2. Freundlich model parameters for various solvents with different equilibration times of 7 d, three weeks, and two months

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sorption time</th>
<th>( \frac{1}{n}^a )</th>
<th>Ln ( (K_f) ) (mg/kg)</th>
<th>( (L/mg)^{1/b} )</th>
<th>( r^2 )</th>
<th>No. of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>7 d</td>
<td>0.490 ± 0.031</td>
<td>6.402 ± 0.104</td>
<td>0.940</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.451 ± 0.032</td>
<td>6.593 ± 0.105</td>
<td>0.928</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.501 ± 0.033</td>
<td>6.441 ± 0.111</td>
<td>0.946</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>CaCl2</td>
<td>7 d</td>
<td>0.501 ± 0.029</td>
<td>6.258 ± 0.093</td>
<td>0.948</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.450 ± 0.030</td>
<td>6.516 ± 0.095</td>
<td>0.937</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.484 ± 0.031</td>
<td>6.403 ± 0.098</td>
<td>0.947</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>7 d</td>
<td>0.249 ± 0.020</td>
<td>5.591 ± 0.050</td>
<td>0.904</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.32 ± 0.015</td>
<td>5.511 ± 0.029</td>
<td>0.960</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.428 ± 0.011</td>
<td>5.643 ± 0.035</td>
<td>0.991</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>ACN</td>
<td>7 d</td>
<td>0.382 ± 0.010</td>
<td>4.992 ± 0.044</td>
<td>0.989</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.383 ± 0.016</td>
<td>5.417 ± 0.062</td>
<td>0.972</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.357 ± 0.009</td>
<td>6.237 ± 0.033</td>
<td>0.992</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>ACN-NH4OAc</td>
<td>7 d</td>
<td>0.413 ± 0.006</td>
<td>4.916 ± 0.023</td>
<td>0.997</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.432 ± 0.016</td>
<td>4.833 ± 0.067</td>
<td>0.979</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.516 ± 0.033</td>
<td>4.642 ± 0.150</td>
<td>0.946</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>7 d</td>
<td>0.373 ± 0.018</td>
<td>5.368 ± 0.072</td>
<td>0.963</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.355 ± 0.006</td>
<td>5.543 ± 0.025</td>
<td>0.995</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.412 ± 0.019</td>
<td>5.493 ± 0.087</td>
<td>0.972</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>7 d</td>
<td>0.345 ± 0.017</td>
<td>7.733 ± 0.052</td>
<td>0.964</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>three weeks</td>
<td>0.417 ± 0.017</td>
<td>7.550 ± 0.050</td>
<td>0.974</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>two months</td>
<td>0.523 ± 0.029</td>
<td>7.588 ± 0.045</td>
<td>0.958</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

\( *^a \frac{1}{n} \) = nonlinearity constant for Freundlich isotherm model; \( K_f \) = Freundlich coefficient; \( r^2 \) = correlation coefficient; DI = deionized water; CaCl2 = calcium chloride; NaOH = sodium hydroxide; ACN = acetonitrile; ACN-NH4OAc = acetonitrile-ammonium acetate solution; MeOH = methanol; HCl = hydrochloric acid.

The rapidly desorbing fraction will be released to the liquid phase very quickly, usually taking place within hours. After the rapidly desorbing fraction is depleted in the sediment matrix, the large amount of slowly desorbing fraction starts to desorb and the slow desorbing rate becomes very important for the accumulation of desorbed benzidine in the extract when desorption is extended to weeks or even months. In either of the experiments, the slow desorbing rate for ACN is 2 to 3.5 times faster than for ACN-NH4OAc. Therefore, ACN illustrated greater total extraction efficiency than ACN-NH4OAc did in this time course study. However, desorption of benzidine in MeOH did not exhibit the same pattern as that for ACN.

For the accumulation of desorbed benzidine in the extract when desorption and the slow desorbing rate becomes very important.

The large amount of slowly desorbing fraction starts to desorb and the rapidly desorbing fraction is depleted in the sediment matrix, the large amount of slowly desorbing fraction starts to desorb and the slow desorbing rate becomes very important for the accumulation of desorbed benzidine in the extract when desorption is extended to weeks or even months. In either of the experiments, the slow desorbing rate for ACN is 2 to 3.5 times faster than for ACN-NH4OAc. Therefore, ACN illustrated greater total extraction efficiency than ACN-NH4OAc did in this time course study. However, desorption of benzidine in MeOH did not exhibit the same pattern as that for ACN.

For the accumulation of desorbed benzidine in the extract when desorption and the slow desorbing rate becomes very important for the accumulation of desorbed benzidine in the extract when desorption is extended to weeks or even months. In either of the experiments, the slow desorbing rate for ACN is 2 to 3.5 times faster than for ACN-NH4OAc. Therefore, ACN illustrated greater total extraction efficiency than ACN-NH4OAc did in this time course study. However, desorption of benzidine in MeOH did not exhibit the same pattern as that for ACN.
Fig. 4. Concentrations of benzidine in acetonitrile ([ACN]; ▣), acetonitrile-ammonium acetate ([ACN-NH₄OAc]; ○), 0.5 M of sodium hydroxide ([NaOH]; ▲), methanol ([MeOH]; ●), deionized water ([DI]; △), 0.1 M of hydrochloric acid ([HCl]; ◊), 0.05 M of calcium chloride ([CaCl₂]; ♦) solvents from single extractions with different desorption times using samples that have been equilibrated for two months. Solid lines indicate the model fitting curves with 95% confidence interval. The goodness-of-fit ($r^2$) and standard errors are listed in Table 4.

Table 3. Desorption percentage (%) in the solvents with 7-d, three-week, and two-month contact times. Each value in Table 3 is the average value between duplicate measurements with differences of <10% between the duplicates.

<table>
<thead>
<tr>
<th>Sorption time</th>
<th>Desorption time (day)</th>
<th>DI*</th>
<th>CaCl₂</th>
<th>HCl</th>
<th>NaOH</th>
<th>ACN</th>
<th>ACN-NH₄OAc</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 d</td>
<td>1.79</td>
<td>0.078</td>
<td>0.076</td>
<td>0.002</td>
<td>1.824</td>
<td>5.824</td>
<td>4.318</td>
<td>3.154</td>
</tr>
<tr>
<td></td>
<td>4.63</td>
<td>0.060</td>
<td>0.130</td>
<td>0.000</td>
<td>3.278</td>
<td>10.517</td>
<td>6.956</td>
<td>4.156</td>
</tr>
<tr>
<td></td>
<td>9.66</td>
<td>0.362</td>
<td>0.087</td>
<td>0.000</td>
<td>3.354</td>
<td>6.879</td>
<td>4.503</td>
<td>2.947</td>
</tr>
<tr>
<td></td>
<td>27.47</td>
<td>0.000</td>
<td>0.047</td>
<td>0.000</td>
<td>2.306</td>
<td>3.568</td>
<td>2.233</td>
<td>1.508</td>
</tr>
<tr>
<td></td>
<td>29.60</td>
<td>0.042</td>
<td>0.069</td>
<td>0.000</td>
<td>1.710</td>
<td>3.315</td>
<td>3.054</td>
<td>1.260</td>
</tr>
<tr>
<td>Three weeks</td>
<td>0.97</td>
<td>0.110</td>
<td>0.170</td>
<td>0.036</td>
<td>4.595</td>
<td>7.805</td>
<td>6.361</td>
<td>3.984</td>
</tr>
<tr>
<td></td>
<td>3.16</td>
<td>0.153</td>
<td>0.194</td>
<td>0.059</td>
<td>5.544</td>
<td>8.599</td>
<td>6.779</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td>14.05</td>
<td>0.096</td>
<td>0.109</td>
<td>0.023</td>
<td>5.459</td>
<td>9.022</td>
<td>7.117</td>
<td>2.970</td>
</tr>
<tr>
<td></td>
<td>22.05</td>
<td>0.098</td>
<td>0.163</td>
<td>0.000</td>
<td>5.850</td>
<td>9.523</td>
<td>7.526</td>
<td>3.054</td>
</tr>
<tr>
<td></td>
<td>32.05</td>
<td>0.103</td>
<td>0.157</td>
<td>0.036</td>
<td>6.714</td>
<td>9.761</td>
<td>7.456</td>
<td>2.723</td>
</tr>
<tr>
<td></td>
<td>63.84</td>
<td>0.159</td>
<td>0.168</td>
<td>0.050</td>
<td>6.087</td>
<td>9.671</td>
<td>7.598</td>
<td>2.464</td>
</tr>
<tr>
<td></td>
<td>127.87</td>
<td>0.119</td>
<td>0.165</td>
<td>0.109</td>
<td>6.380</td>
<td>9.480</td>
<td>7.329</td>
<td>2.182</td>
</tr>
<tr>
<td>Two months</td>
<td>0.79</td>
<td>0.108</td>
<td>0.136</td>
<td>0.046</td>
<td>3.433</td>
<td>5.532</td>
<td>4.771</td>
<td>3.338</td>
</tr>
<tr>
<td></td>
<td>2.73</td>
<td>0.110</td>
<td>0.138</td>
<td>0.041</td>
<td>4.274</td>
<td>7.169</td>
<td>5.689</td>
<td>3.905</td>
</tr>
<tr>
<td></td>
<td>9.74</td>
<td>0.068</td>
<td>0.166</td>
<td>0.037</td>
<td>5.154</td>
<td>8.382</td>
<td>6.351</td>
<td>3.775</td>
</tr>
<tr>
<td></td>
<td>14.77</td>
<td>0.139</td>
<td>0.157</td>
<td>0.033</td>
<td>5.116</td>
<td>9.416</td>
<td>6.552</td>
<td>3.542</td>
</tr>
<tr>
<td></td>
<td>31.64</td>
<td>0.113</td>
<td>0.117</td>
<td>0.027</td>
<td>5.437</td>
<td>9.556</td>
<td>6.879</td>
<td>3.032</td>
</tr>
<tr>
<td></td>
<td>76.68</td>
<td>0.066</td>
<td>0.130</td>
<td>0.026</td>
<td>6.273</td>
<td>9.594</td>
<td>6.932</td>
<td>2.406</td>
</tr>
<tr>
<td></td>
<td>156.09</td>
<td>0.119</td>
<td>0.083</td>
<td>0.049</td>
<td>6.826</td>
<td>10.203</td>
<td>7.061</td>
<td>2.684</td>
</tr>
</tbody>
</table>

*DI = deionized water; CaCl₂ = calcium chloride; HCl = hydrochloric acid; NaOH = sodium hydroxide; ACN = acetonitrile; ACN-NH₄OAc = acetonitrile-ammonium acetate solution; MeOH = methanol.
was conducted. The amount of \textsuperscript{14}C-labeled aniline that could be recovered by treatment with 0.5 M of NaOH increased with time reaching a maximum of approximately 35% of the \textsuperscript{14}C-label associated with the sediment phase. They suggested the \textsuperscript{14}C-label measured in the base extract corresponded to the irreversible sorption of \textsuperscript{14}C-label to base-solubilized organic matter.

Desorption fractions

The rapidly and slowly desorbing fractions for the two data sets with three weeks and two months sorption times, \( F_{\text{rap}} \) and \( F_{\text{slow}} \), are tabulated in Table 4. Two major observations can be made based on the data in Table 4 and Figures 3 and 4. First, the model-fitted parameters \( F_{\text{rap}} \) and \( F_{\text{slow}} \) for NaOH (5%), ACN (9%), and ACN-NH\textsubscript{4}OAc (6 or 7%) are different when the sorption time is the same. This seems reasonable because the desorption mechanism for each solvent is supposed to be different. Second, the desorption fractions were not affected significantly by the longer sorption times. The initial fractions (e.g., \( F_{\text{rap},0} \) and \( F_{\text{slow},0} \)) for NaOH, ACN, and ACN-NH\textsubscript{4}OAc remained almost the same or showed only a very small decline when sorption time was extended from three weeks to two months. The similar trend could be obtained when comparing the overall desorption fractions of each solvent at different desorption times (see Table 3). For example, after about 32 d, the desorbed benzidine fractions were 9.8% (3-week sorption) and 9.6% (2-month sorption) for ACN, 7.5% (3-week sorption) and 6.9% (2-month sorption) for ACN-NH\textsubscript{4}OAc. Even when the whole desorption processes were stopped, which lasted for 128 d (3-week sorption) and 156 d (2-month sorption), the extraction efficiencies for ACN and ACN-NH\textsubscript{4}OAc remained nearly unchanged. The longer contact time of sorbents with the sorbate in our selected systems did not cause significantly the decrease of the rapidly desorbing fractions. The incubation time used in this study was not long enough to conclude that the reason for this might be insignificant aging effect. Even two months of contact time still is insufficient to trap large amounts of benzidine in the desorption-resistant sediment domains.

Desorption rate constants

The desorption rate constant (\( K \)) with three weeks and two months of sorption equilibration times were obtained by nonlinear least-squares regression and are presented in Table 4. The variables for the desorption experiment with 7 d of equilibration time were not reported here because of the observed nonequilibrium. In our study the rapid desorption rate constants were in the order of one to two per day, and the slow desorption rate constants were in the order of 0.1 to 1 \( \times \) \( 10^{-4} \) d. When the equilibrium time was increased from three weeks to two months, the rapidly desorbing rate constant (\( K_{\text{rap}} \)) for each solvent was about half as fast for most of the samples as that for the same solvent with the shorter equilibration time (i.e., 3 weeks of equilibration time). However, all the slowly desorbing rate constants (\( K_{\text{slow}} \)) increased with increasing sorption equilibrium times from three weeks to two months. The value of \( K_{\text{slow}} \) for NaOH with a two-month sorption time (1.47 \( \times \) \( 10^{-3} \) d) is 2.4 times that with a three-week sorption time (6.14 \( \times \) \( 10^{-3} \) d). Similarly, \( K_{\text{slow}} \) for ACN (1.27 \( \times \) \( 10^{-4} \) d) and ACN-NH\textsubscript{4}OAc (6.30 \( \times \) \( 10^{-5} \) d) for two-month sorption is 2.5 times and 1.8 times as fast as that with a three-week sorption time, respectively. The observed rate differences for each solvent may indicate that the sorbed benzidine became harder to desorb rapidly from the site in the sediment matrix as a function of time, with \( K_{\text{rap}} \) decreasing and \( K_{\text{slow}} \) increasing concurrently. This observation might be attributed to the aging effect: The longer contact time between sorbates and sediment matrix led to the deeper penetration of sorbate into the remote part of the sediment matrix [21].

Hulscher et al. [19], Cornelissen et al. [21], and Noort et al. [40] also studied the desorption kinetics of chlorobenzene, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in different sediments. They characterized the desorption process with rapid, slow, and very slow stages and found the rate constants for these three stages were about 0.05 to 0.50/h, 3 to 8 \( \times \) \( 10^{-3} \) /h, and 0.9 to 1.7 \( \times \) \( 10^{-4} \) /h, respectively. Compared to the rate constants found in this study, which are 1 to 2/d (0.04–0.08/h) for rapid desorption and 0.1 to 1 \( \times \) \( 10^{-4} \) /d (0.4–5 \( \times \) \( 10^{-4} \) /h) for slow desorption, the rapid desorption rate constants fall in the ranges of values reported in the literature, and the slow sorption rates are even slower than the very slow desorption rate termed in their study. This discrepancy might be explained by the fact that the models used in the individual studies have a different number of fitting parameters.

Mass-transfer–limited slow desorption

It is a common observation that a portion of the sorbed chemicals resist desorption for aromatic amines as well as for the other classes of hydrophobic organic compounds [19,41–

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Three weeks</th>
<th>Two months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate (1/d)</td>
<td>( K_{\text{rap}} )</td>
<td>( K_{\text{slow}} )</td>
</tr>
<tr>
<td>NaOH\textsuperscript{a}</td>
<td>1.62 ( \pm ) 0.43</td>
<td>(6.14 ( \pm ) 6.67)E-5</td>
</tr>
<tr>
<td>ACN-NH\textsubscript{4}OAc</td>
<td>2.30 ( \pm ) 0.41</td>
<td>(5.10 ( \pm ) 3.99)E-5</td>
</tr>
<tr>
<td></td>
<td>( F_{\text{rap},0} )</td>
<td>( F_{\text{slow},0} )</td>
</tr>
<tr>
<td>NaOH\textsuperscript{a}</td>
<td>0.05 ( \pm ) 0.004</td>
<td>0.09 ( \pm ) 0.002</td>
</tr>
<tr>
<td>ACN-NH\textsubscript{4}OAc</td>
<td>0.95 ( \pm ) 0.004</td>
<td>0.91 ( \pm ) 0.002</td>
</tr>
<tr>
<td></td>
<td>( r^2 )</td>
<td>( r^2 )</td>
</tr>
<tr>
<td>NaOH\textsuperscript{a}</td>
<td>0.73</td>
<td>0.75</td>
</tr>
<tr>
<td>ACN-NH\textsubscript{4}OAc</td>
<td>0.73</td>
<td>0.86</td>
</tr>
</tbody>
</table>

\( \text{NaOH} = \) sodium hydroxide; ACN = acetonitrile; ACN-NH\textsubscript{4}OAc = acetonitrile-ammonium acetate solution; \( K_{\text{rap}} \) = first-order rate constant for the rapidly desorbing fraction; \( K_{\text{slow}} \) = first-order rate constant for the slowly desorbing fraction; \( F_{\text{rap},0} \) = initial rapidly desorbing fraction; \( F_{\text{slow},0} \) = initial slowly desorbing fraction; \( r^2 \) = correlation coefficient.
43] and often is attributed to the mass-transfer–related mechanisms (rate-limiting diffusional processes) [11,32,44]. To reach all sorption sites, molecules must traverse through bulk liquid, film water, pore diffusion, and matrix diffusion. The mixing that takes place in most experiments makes both bulk diffusion and film diffusion less likely to be rate-limiting. Therefore, the pore and matrix diffusions are more likely the rate-limiting steps in the sorption processes. Desorption from the sediment follows the similar stages, only in the reverse directions as sorption. Weber et al. [11] proposed that pore diffusion within particles of that size (<1 mm) is fast compared to other diffusion processes. Therefore, the molecular diffusion into macromolecular organic carbon is the dominant process controlling the slow and irreversible binding of aniline. Pignatello [45] suggested that the slow release of HOCs (e.g., aliphatic hydrocarbons) resulted from the diffusion-limited desorption of molecules from remote regions in the sediment/solid matrix and that the mineral phase helped to shield the pollutant molecules from desorption. Fu et al. [25] and Kan et al. [43] studied the sorption and desorption of polycyclic aromatic hydrocarbons in surface sediments and found only 30 to 50% of sorbed pollutants could be desorbed. It was hypothesized in their study that the rate-limiting desorption hysteresis could be caused by some multistep process that promotes the soil aggregation and/or pore entrapment of contaminants in sediment organic matter.

In our sequential desorption experiment, the addition of solvents was in the order of DI, HCl, CaCl₂, NH₄OAc, ACN, MeOH, ACN-NH₂OAc, and NaOH (see Materials and Methods section). The preliminary results showed that, after this desorption process, only 30 to 38% of the initially spiked benzidine was desorbed from the sediment phase. It suggested that a large amount of sorbed benzidine (62–70%) resisted desorption. It seems logical that the diffusion processes and hysteresis would account for the slow desorption of benzidine in the sediments, although it is not possible to determine the relative contributions of these rate-limiting processes.

CONCLUSION

This study investigated the desorption behavior of benzidine in seven different solvents. Our observations revealed that it took about 15 to 20 d for the benzidine sorption to reach equilibrium with 94% of initial benzidine adsorbed onto sediment. Benzidine also had a strong affinity for sediment sites, which made it very difficult to desorb into DI, CaCl₂, and HCl solvents. Using a longer contact time did not improve the extraction efficiency in these three solutions. In ACN, NaOH, and ACN-NH₂OAc solvents, the release of sorbed benzidine exhibited a biphasic process, with a rapid increase of benzidine concentration in solution phase followed by a much slower increase until the establishment of equilibrium. The extraction efficiency for MeOH decreased over time, exhibiting a sorption process instead of a desorption process. The rapidly desorbing rates were on the order of one to two per day for NaOH, ACN, and ACN-NH₂OAc, and the slowly desorbing rates were on the order of 10⁻³ to 10⁻⁴/d with the assumption that both stages follow first-order kinetics. Consequently, the rapidly and slowly desorbed initial fractions (F_{fast,0} and F_{slow,0}) for each solvent were relatively constant in both experiments with three weeks and two months of sorption times, suggesting no apparent transition of sorbed benzidine (e.g., from soil organic matter–trapped benzidine to covalently bonded benzidine) during this time course study. Further evidence is needed still to confirm this observation.

Acknowledgement—The authors would like to thank the U.S. National Science Foundation for financial support in the form of a CAREER award (BES-0093191) to M.C. Nyman. The opinions in this paper do not necessarily reflect those of the sponsors. In addition, the authors also thank M. Zhou and Y. Yuan for their help with the preparation of some samples. Additionally, J. Harden is thanked for the sediment characterization data.

REFERENCES


