Article

Adsorption of Triazine Derivatives with Humic Fraction-Immobilized Silica Gel in Hexane: A Mechanistic Consideration

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ABSTRACT: A fraction of humic acid is collected under acidic conditions, then immobilized on silica gel and used as the adsorbent for various symmetrical triazine (s-triazine) derivatives in hexane. The enhanced hydrogen bonding between the analyte and humic fraction molecules, not the complexation interaction, is responsible for the adsorption observed in hexane, based on Fourier transform infrared (FTIR) spectroscopy results. The percentage of adsorption in hexane for all s-triazine derivatives reaches nearly 100% in 1 h, independent of the type, position, and size of the substituent on the aromatic nitrogen heterocyclic ring. Other factors leading to the variation of the percentage of adsorption include the type of liquid phase and the additive of acidic or basic origin present in the matrix.

KEYWORDS: humic acid, silica gel, adsorption mechanism, triazine, hydrogen bonding

■ INTRODUCTION

Melamine, a synthetic triazine compound and an organic base, is an important industrial chemical having been used as a component in various products since the late 1930s. Like cyanamide, it contains roughly 66% nitrogen (w/w) and provides fire-retardant properties when mixed with resins by releasing nitrogen gas upon burning or charring. In addition, melamine resin has been widely used in many other common applications, including durable tableware, worktops, whiteboards, fabrics, fertilizers, pigments, glues, etc.[1] Prior to being identified in foods as a protein replacement in the spring of 2007, melamine in pet food was linked to kidney failure in dogs and cats because it formed an insoluble precipitate in kidney tubules when co-ingested.[2−4] Since being added to fertilizers as a cheap nitrogen source to increase crop yields,[5,6] melamine has been found in almost every dairy product, processed food, and beverage through the food chain all over the world. However, this was thought in part to be a result of migration from plastic cups at high temperatures or packaging or processing equipment.[7]

Atrazine, simazine, and cyanazine (phased out in 2002) are other chemically similar triazines used worldwide as pre-emergent weed herbicides on animal feed crops in the United States.[4,8,9] Because some herbicides of this class are considered to be potential carcinogens and immunotoxins, their accurate analysis is essential to ascertain whether triazine residues are present in the food supply and the extent of human exposure.[10−17] The analysis of these triazine residues and other triazines of the same class, through GC- or LC-MS approaches, has been thoroughly described.[17−31] In some cases, analytes were enriched on graphitized black carbon, on molecularly imprinted polymer, or through different extraction processes with or without a medium, prior to CE or chromatographic analysis. Many studies concerned with the direct removal of triazine derivatives in the aqueous environment with the assistance of an adsorbent have also been conducted.[32−38] Although triazines are usually classified as bases in these studies, their strength is less than that of pyridine.

Humic acid (HA) is derived by microbial degradation of dead plant matter and can be identified in soil nearly everywhere with variable contents.[39] Because it is a complex mixture of numerous acids containing various components (structurally), such as quinone, phenol, catechol, and sugar moieties, numerical benefits, such as crop production and micronutrients transfer, exist in the laboratory and field.[40] The application of HA for the removal of ions by forming chelate complexes has been shown and has been proven to be an important biological aspect in regulating bioavailable metal ions.[41−43] Because of its complex structure including various functional components such as carboxylate and phenolate groups, its adsorption-oriented application has been implemented in carboxyl-containing pesticides and biogenic amines in acetonitrile, pesticides containing phosphorus, and phthalate-based plasticizers in hexane.[44−46] Adsorption is regarded as occurring mainly because of complexation between carboxyl groups of the humic fraction (HF) and analyte in acetonitrile and an acid-based type of interaction in the case of an amine. Dipole−dipole interaction and hydrogen bonding are responsible forces for the adsorption in hexane. Surprisingly, the $\pi-\pi$ stacking complexation is minor or absent in adsorption in all cases.

In this work, a fraction of humic acid was collected under acidic conditions, then immobilized on silica gel, and first used as the adsorbent for various triazine derivatives in hexane. The variation in percentage adsorption was independent of the structure of the analyte, but the presence of the secondary amino substituent on the s-triazine ring is highly related to the enhanced hydrogen bonding between the analyte and the humic fraction molecules in hexane and was discussed from a mechanistic perspective. In addition, factors that affect the percentage of adsorption, including the type of liquid phase and

Table 1. Percentage of Adsorption for Various Triazine Derivatives with Humic Fraction Extracted under the Acidic Conditions after Its Immobilization on Silica Gel
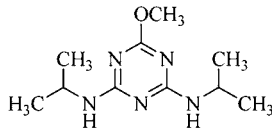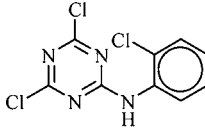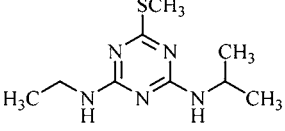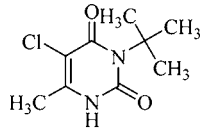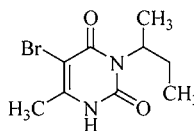
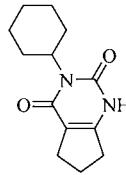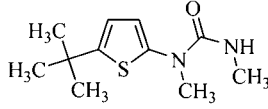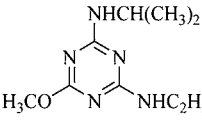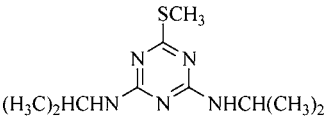| No	Compound[a]	Analyte Structure	Percent Adsorption(%)[b]	Mobile Phase[c]
1	Prometon		~100 /0	A
2	Anilazine		99.6 /0	B
3	Ametryne		~100 /0	A
4	Terbacil*		99.8 /9.2	A
5	Bromacil*		~100 /0	A
6	Lenacil*		~100 /0	A
7	Tebuthiuron*		~100 /0	A
8	Atraton		~100 /0	A
9	Prometryne		~100 /0	A

Table 1. continued

No	Compound[a]	Analyte Structure	Percent Adsorption(%)[b]	Mobile Phase[c]
10	Terbutryne		~100 /0	A
11	Metribuzin		~100 /0	B
12	Perthane[*]		42.4	B
13	Methoxychlor[*]		91.7	B
14	Terbumeton		~100 /0	A
15	Trietazine		99.5 /0	A
16	Procyazine		~100 /0	A
17	Atrazine		~100 /0	A
18	Simazine		~100 /0	A

Table 1. continued
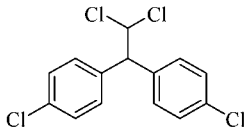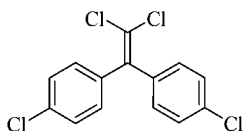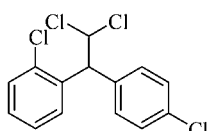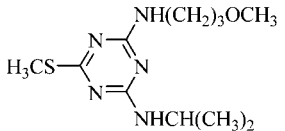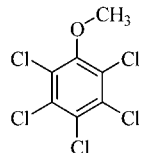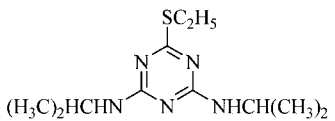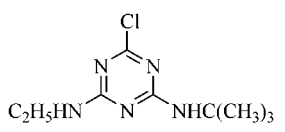
No	Compound[a]	Analyte Structure	Percent Adsorption(%)[b]	Mobile Phase[c]
19	p.p'-DDD*		37.3	B
20	p,p'-DDE*		6.2	B
21	o,p'-DDD*		37.8	B
22	Methoprotryne		~100 /0	A
23	Chlorothalonil*		94.5 /0	A
24	Pentachloroanisole*		93.5 /0	A
25	Dipropetryn		~100 /0	A
26	Terbuthylazine		~100 /0	A

Table 1. continued

No	Compound[a]	Analyte Structure	Percent Adsorption(%)[b]	Mobile Phase[c]
27	Propazine		~100 /0	A
28	Simetryn		~100 /0	A
29	Dichloran*		0	B
30	Aniline*		~100 /0	A
31	Benzylamine*		~100 /0	A

[a]Compounds with asterisks are not atrazine derivatives; however, they are included for discussion by comparison. The adsorption evaluation for dichloran (compound **29**) was in acetonitrile. [b]The reported percentage of adsorptions is measured over a time period of 1 h in hex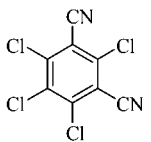ane (upper) and in diethyl ether (lower). The amount of humic acid modified silica gel used as the solid phase in each triplet adsorption measurement is 10 mg. The volume of liquid phase containing the analyte is 100 μL. [c]The mobile phases are (A) the acetonitrile solvent of HPLC grade used for most analyses and (B) 95:5 (acetonitrile/methanol) by volume (v/v).

an additive of acidic or basic origin, such as glacial acetic acid or triethylamine, were examined and rationalized to help explore the adsorption mechanism involved and, thus, improve the adsorption/desorption efficiency.

■ **EXPERIMENTAL PROCEDURES**

Apparatus. The HPLC system used in this study was a Hitachi model L-7100 coupled to a D-2500 Chromatopac data station and a UV detector. The mobile phase used in the adsorption evaluation was either acetonitrile or a solvent mixture of acetonitrile and methanol. The elution was isocratic on a C_{18} column (250 × 4.6 mm i.d.; 5 μm particle diameter) at a flow rate of 1.0 mL/min. The detection wavelength was set at 260 nm for all measurements. FTIR spectra were obtained by scanning samples 10 times on a Shimadzu model FTIR-8400 system at a resolution of 4 cm^{-1}. In FTIR measurements, the adsorbent was collected and then pelleted with KBr after being washed with fresh hexane and dried.

Chemicals. All chemicals employed in this study, including the organosilane reagent used as a linker in chemical immobilization reactions and the triazine derivatives and compounds used in discussing the adsorption mechanism, were purchased from Sigma (St. Louis, MO, USA) and Aldrich Chemical Co. (Milwaukee, WI, USA), respectively. The silica gel (5 μm particle diameter, 100 Å

porosity with a specific surface area of 400 m^2/g), used as the supporting matrix of the solid phase in the adsorption evaluation at ambient temperatures was a product of Silicycle (Quebec City, QC, Canada) and was chemically modified with a humic fraction collected under acidic conditions before being used as the adsorbent according to the derivatization procedures reported previously.[47,48] The solvents, such as toluene, acetonitrile, methanol, triethylamine, methylene chloride, hexane, and ethyl ether, were of HPLC grade and purchased from Fisher Scientific (Pittsburgh, PA, USA) and Merck Taiwan Ltd. (Taiwan, ROC). In all cases, filtered (0.2 μm) and distilled water was used.

Conditions for Adsorption and Recovery Measurements. A weighed amount of solid-phase adsorbent (10 mg) was added to a 100 μL of a 2.57 × 10^{-3} M standard solution of analyte, except for chlorothalonil (compound **23**) due to its low solubility in hexane, for a controlled period. In each measurement, the solution was sampled for HPLC analysis both before and after the adsorption process was completed, to calculate and compare the percentages of adsorption based on the difference in peak areas. The measurement was repeated three times to obtain an average in all cases. In this study, the adsorption was evaluated in the liquid phase of hexane, acetonitrile, and ethyl ether, respectively. The data were then used in the discussion of a mechanism involved in the adsorption process.

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The adsorbent was recovered by decanting the liquid phase of the matrix first and then sequentially washed with fresh hexane or acetonitrile several times. The adsorbent was dried before being used to acquire the FTIR spectrum.

To determine how the acidic or basic origin of the additive affected the adsorption of the analytes, an additive, such as glacial acetic acid or triethylamine of HPLC grade in a volume ranging from 2.5 to 10 μL, was added to the mentioned matrix containing the adsorbent and the analyte. The HPLC analysis was then performed immediately following the 1 or 3 h adsorption period.

■ RESULTS AND DISCUSSION

Compounds listed in Table 1 are mainly derivatives of s-triazine. However, several di- and triazines, amine-containing compounds and analogues of organochlorine compound DDT, are also included in Table 1 for the discussion of the mechanism involved in the adsorption process by comparison. To further understand the influence of the liquid phase on the adsorption, the percentage of adsorption for all analytes was evaluated in hexane, and in part in acetonitrile and ethyl ether, respectively; the corresponding data are provided in Table 1 as well for discussion. As can be seen, the percentage of adsorption shown in Table 1 reached nearly 100% over 1 h in hexane for all s-triazine derivatives that were examined. This clearly shows that the adsorption was a result of hydrogen bonding between the secondary amine groups of analyte and the carboxyl groups on the humic fraction molecules. These functional groups are able to act as the hydrogen-bond acceptor and/or donor and form hydrogen bonding afterward. In addition to $\pi-\pi$ complexation, hydrogen bonding, often described as an electrostatic dipole−dipole interaction, can be significantly enhanced in an aprotic solvent such as hexane.[49−51] This could be why the adsorption disappeared for all cases in ethyl ether under the same conditions, apparently indicating the formation of an ion pair resulting from the acid−base interaction mentioned previously between the analyte and the molecule in a humic fraction being absent.[44] Moreover, the adsorption of s-triazine derivatives in hexane was found to be totally independent of the type, position, and size of the derivative on the aromatic nitrogen heterocyclic ring. It is well-known that triazines are weaker bases than pyridine due to a resonance effect.[52] A similar discussion approach can also be applied to the compounds containing amine. In general, aromatic amines are much less basic than aliphatic amines due to the electron-withdrawing effect of the sp^2-hybridized carbons on the aromatic ring and to the resonance effect, as the lone-pair electrons on the nitrogen are partially delocalized into the π system of the benzene ring. These two factors would cause the electron pair on nitrogen to be less available for reaction with acid by pulling them toward the ring. This hypothesis can be further discussed and found supported by evaluating the adsorption of analytes, such as dichloran, aniline, and benzylamine (compounds **29**, **30**, and **31** in Table 1), and 2-phenylethylamine from a previous study in acetonitrile.[44] As shown in Figure 1, the percentage of adsorption for these analytes in acetonitrile improved as the amino group was moved away from the aromatic ring. In the case of dichloran, electrons pulled toward the aromatic ring were subject to an electron-withdrawing inductive effect from the electronegative chlorines and nitro group, resulting in a negative effect on the acid−base interaction by showing no adsorption. Except for dichloran (not soluble in hexane), the percentage of adsorption in hexane for aniline, benzylamine, and 2-phenylethylamine was nearly 100% in 1 h. These results indicate that the adsorption of
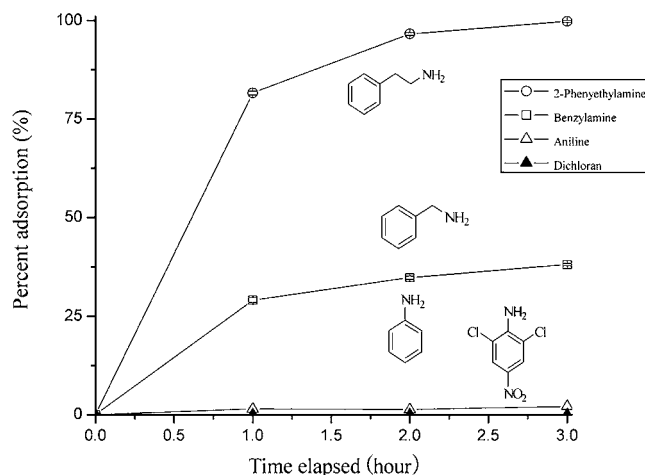

Figure 1. Effect of time elapsed during the adsorption process on the percentage of adsorption for dichloran, aniline, benzylamine, and 2-phenylethylamine in acetonitrile over a 3 h time period.

s-triazine derivatives on humic fraction-modified silica gel in hexanes was not mainly due to the nitrogen-containing aromatic heterocyclic ring.

Several analogues of the organochlorine compound DDT are included in Table 1, primarily for the purpose of exploring the type of interaction force leading to adsorption in hexane. The characteristics of the structure of these analytes (perthane, methoxychlor, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDD; compounds **12**, **13**, **19**, **20**, and **21** in Table 1) are free of any functional groups capable of forming dipole−dipole oriented interaction. Compound methoxychlor (compound **13** in Table 1) is an exception in having a methoxyl group acting as the hydrogen bond acceptor. Pentachloroanisole (compound **24** in Table 1) is the other compound not in the organochlorine category, however, having similar structural characteristics. As indicated in Table 1, a low percentage of adsorption was observed with analytes bearing only aromatic moiety, which was relatively acidic due to the electron-withdrawing nature of chlorine atoms. Note that an acidic π system of the benzene ring more readily forms complexation with the π system with no derivatives; thus, some adsorption is observed.[49] Almost no adsorption was observed for dichlorodiphenyldichloroethylene (*p,p'*-DDE, compound **20** in Table 1), a breakdown product of DDT and a potent androgen receptor antagonist, because the double bond that conjugated with the π system of the benzene ring in general may lower the overall energy of the molecule and increase the stability. Similarly, when the liquid phase of hexane was replaced with ethyl ether, no adsorption was measured for all examined triazine derivatives due to the competition for available binding sites on the solid phase for solvent molecules. Competition also can be observed by introducing additives such as acetic acid or triethylamine to the liquid phase. The percentage of adsorption was expected to deteriorate due to the additive molecule interference with the adsorption process, as shown in Figure 2. The rapid decrease in the percentage of adsorption strongly suggests that the interaction should be dipole−dipole in nature.

The aforementioned discussion on the interaction mechanism leading to the adsorption observed in hexane was highly supported by the FTIR results. To further explore the subject, three analytes were selected from different categories, including triazine, amine, and plasticizer, with characteristic structures
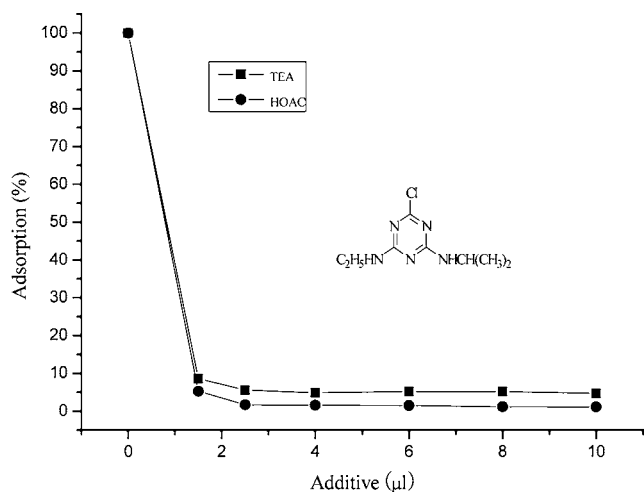
Figure 2. Effect of the acidic or basic origin of the additive in the liquid phase of the matrix on the percentage of adsorption for atrazine in hexane. As can be seen, the adsorption of analyte deteriorated dramatically due to competition from the additive molecules for the binding sites on the adsorbent.

capable of forming hydrogen bonding and dipole–dipole oriented interaction. Their corresponding FTIR spectra were acquired as the adsorption for these analytes was complete in hexane and acetonitrile, respectively. Upon closer examination of the data shown in Figure 3, a red shift and additional peaks were observed in the region of both C—O and C=O stretching vibrations for analytes prometon (bottom left) and tyramine (top right) as compared to those in the spectrum for the native adsorbent (top left). The peak centered at about 3500 cm^{-1} for O—H and N—H vibrations became broader to obscure the neighboring details, and several new peaks were observed in this region, indicating that an association between analyte and humic fraction molecules existed.[53] In the case of prometon, the distinguishable adsorption in the region of 2859–2930 cm^{-1} was from the C–H stretching vibrations of methyl and methylene groups on the analyte. Due to the low solubility of hexane, the adsorption of monobenzyl phthalate was carried out in acetonitrile with an interaction mechanism independent of hydrogen bonding.[44] The profile of the resulting FTIR spectrum (bottom right) was quite different. As can be seen, a red shift for both C—O and C=O stretching vibrations was observed as well. The significant blue shift in the region for O—H and N—H vibrations was in part contributed
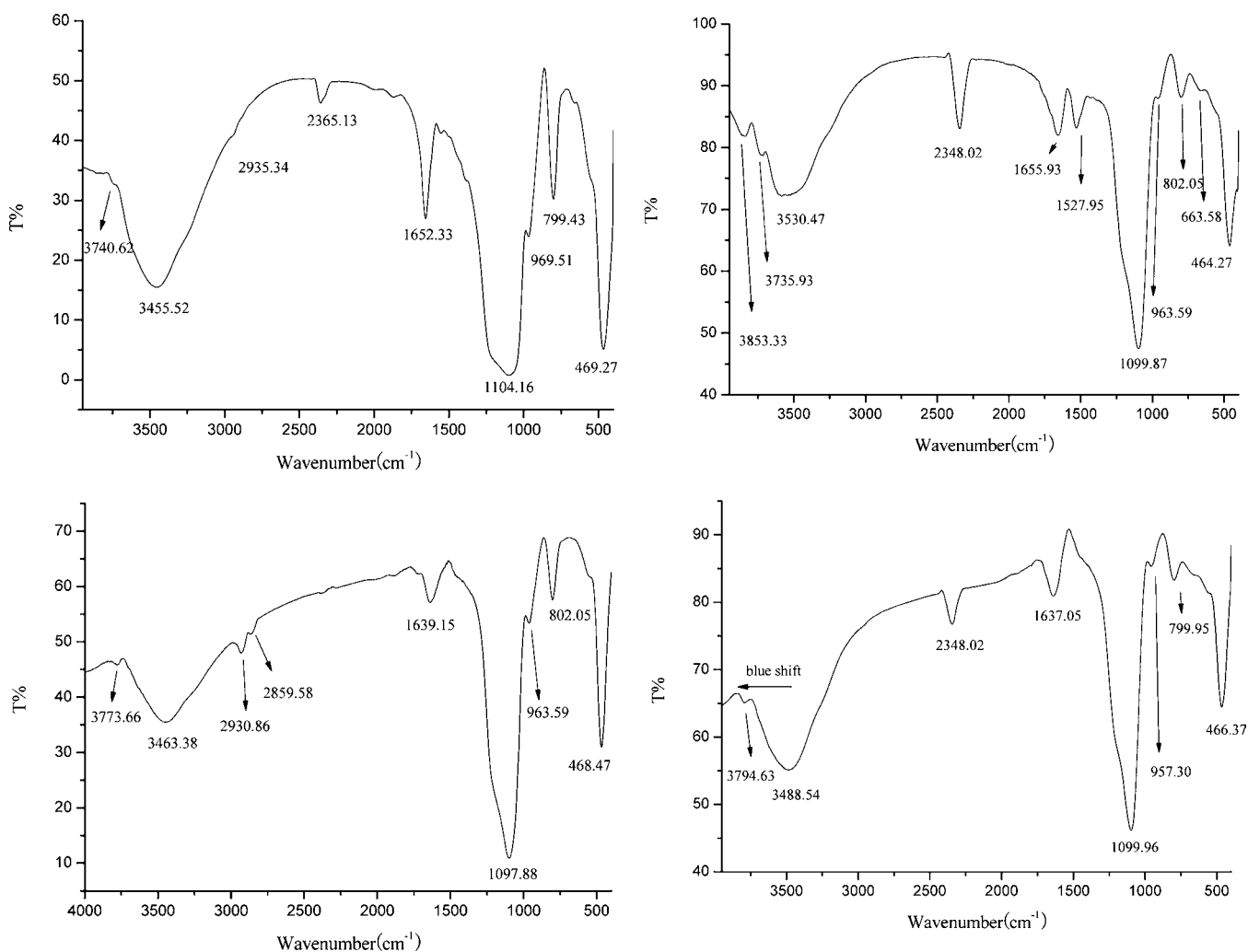

Figure 3. FTIR spectra for the analytes prometon (bottom left) and tyramine (top right) in hexane after the 1 h adsorption was complete. The spectrum for monobenzyl phthalate (bottom right) was obtained as the adsorption over 3 h time period in acetonitrile was complete. The spectrum (top left) for adsorbent was also acquired before the adsorption for comparison.

by the analyte from the one remaining carboxyl group not involved in the interaction in acetonitrile.

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Notes
The authors declare no competing financial interest.

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There was a change in the notations of positions for Figure 3 in the version of this paper published August 26, 2013. The correct version published August 30, 2013.

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