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Adsorption of Pesticidal Compounds Bearing a Single Carboxyl Functional Group and Biogenic Amines by Humic Fraction-Immobilized Silica Gel

Cheng-Sheng Chen and Shushi Chen*

Department of Applied Chemistry, National Chiayi University, Chiayi 600, Republic of China

ABSTRACT: Fractions collected from humic acids under acidic and basic conditions were immobilized on silica gel and used as adsorbents for a variety of agricultural pesticide compounds bearing a single carboxyl functional group and biogenic amines in acetonitrile. Among these compounds examined under the same conditions, the percentage of adsorption varies considerably from 0 to almost 100%. The percentage is found to be highly related to the structure of the analyte and the type of functional group attached to it. The adsorption, better performed on adsorbent immobilized with the fraction collected under acidic conditions, is believed to result from the reversible interaction between the functional moieties of the analyte and humic acids (e.g., amino or carboxyl group of analyte vs carboxyl group of humic acids, etc.) as no adsorption is observed under the same conditions for analytes that are derivatives of alcohol, amide, and ester. Given the nature of the analyte, the time needed to reach the maximum percent of adsorption decreases as the amount of adsorbent is increased. Also, the longer the time that has elapsed, the higher the percentage of analyte adsorbed, thus indicating that the adsorption process is surface-oriented. Factors such as the acidic or basic origin of the additive in the liquid phase of the matrix also affect the percentage of analyte adsorbed.

KEYWORDS: *humic acid, silica gel, adsorption, pesticide, carboxyl group, additive, amino group, biogenic amine*

INTRODUCTION

Humic acid (HA) is derived by the microbial degradation of dead plant matter and can be found in soil nearly everywhere.[1] HA is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl, phenolate, and catechol groups, and sugar moieties, as shown in the top part of Figure 1. Because of its complex structure and presence of negative charges, it provides numerous benefits to crop production, including helping to improve structure in clay and compacted soils, thus enhancing water retention and drainage and thereby helping to increase seed germination rates and root penetration. HA also assists in transferring micronutrients from the soil to the plant. An additional benefit is fostering microflora populations in soils.[2]

The functional groups that contribute most to the negative surface charge and reactivity of humic substances are the phenolic and carboxyl groups, with pK_1 values near 4 and 8 for the protonations of the carboxyl and phenolate groups, respectively.[1] The measured pK values for a given sample are average values related to the constituent species as a result of the considerable overall similarities among individual humic acids.[3] Because of its negative charge density on the surface and the structure having a variety of components including quinone, phenol, catechol, and sugar moieties, the HA molecules may form a supramolecular structure held together by noncovalent forces, such as van der Waals force and $\pi-\pi$ and CH-π bonds.[4,5] To accomplish this action, the shape of HA is believed to be relatively flat in general.[4] In the case of fulvic acid, a molecule similar to HA but smaller in size, its structure is V-shaped with functional groups pointing outward after geometric optimization.[6] However, the shape of the molecule becomes flat if the carboxyl and phenolic groups are both ionized. Either way, the functional groups on the molecule are exposed; thus, they are fully accessible to micronutrients and ionized materials in water. As compared to a water molecule, acetonitrile is a poor proton acceptor and donor and, thus, causes no competition with the analyte for available interaction sites on the HA molecule.[7] The solvated proton has been described as behaving like a superacid in acetonitrile.[8] In light of that, the HA molecule is considered to be a suitable adsorbent for compounds containing carboxyl or amino groups in acetonitrile.

Applying HA to the removal of positively charged ions by forming the chelate complexes has been reported.[4] The formation of (chelate) complexes is an important aspect of the biological role of humic acids in regulating the bioavailability of metal ions.[5] Similarly, the separation and removal of humic acids, using ion-exchange resins through an ultrafiltration system or the fractionation technique on the formation of complexes, have also been documented.[9−11] However, the complexation of humic acids with organic compounds bearing a single functional group, such as the carboxyl or amino group, has not been reported thus far. Compounds with the carboxyl group are often used for pesticidal purposes in agriculture. For the sake of environmental protection, both the regulation and the adsorption of such pollutant compounds are necessary to prevent the contamination of underground water after use.

In contrast to carboxyl-containing compounds, biogenic amines, a group of low molecular weight organic bases, are known to be present in a wide variety of foods (fermented or

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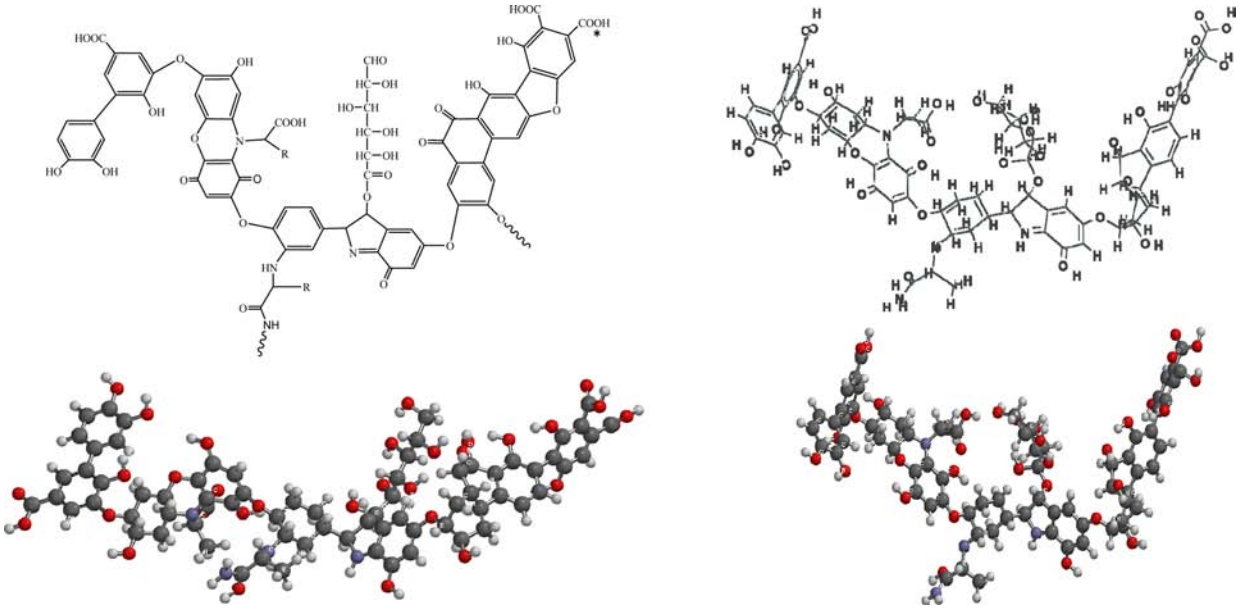

Figure 1. Simplified schematic drawing of the structure of a typical HA molecule (top left) and its corresponding 3D stick-and-ball model (bottom left) and the structural and 3D representations after energy minimization (top right and bottom right). Note that the HA molecule the theoretical calculation is based on is only one of the many reported HA molecules. It is not necessarily referred to the molecule in the humic fraction collected in this study.

nonfermented) and beverages, including wine and beer.[12−15] As a result of enzymatic action or the fermentation process, they are especially found in large quantities in protein-rich foods such as meat and fish.[16,17] Note that biogenic amines are compounds capable of making blood vessels contract or dilate. Therefore, their excessive intake may cause symptoms such as headache, nausea, hypertension, and even death in severe cases;[18,19] thus, the quantity of biogenic amines in foods is worthy of study and analysis, as it can serve as an indicator of food quality and its preservation. Among the methods available for analysis through separating biogenic amines as derivatives, a gradient HPLC system operated in the reversed-phase mode remains the one most preferred at the present time because of the complexity of their structure.[14,15,20−24]

In this work, liquid fractions of humic acids were collected under acidic and basic conditions, then dried, immobilized on silica gel, and used as the adsorbents for a variety of pesticidal compounds and biogenic amines bearing single carboxyl and amino functional groups, respectively, in acetonitrile. A mechanistic study based on the alterations in the structure and functional group of the analyte was conducted. These results were compared with the theoretical calculation results for further understanding of the adsorption process. Also, factors that affected the percentage of adsorption, such as the acidic or basic origin of the additive in the liquid phase, the amount of adsorbent used in the process, and the steric hindrance created by the analyte, were examined and rationalized to help explore the adsorption mechanism involved and thereby improve the adsorption efficiency.

■ EXPERIMENTAL PROCEDURES

Apparatus. An elemental analyzer, Elementar model vario EL III, was used to determine the carbon, hydrogen, sulfur, and nitrogen contents in the mass percent (wt %) of all solid phases examined in this study. The HPLC system used in this study was a Hitachi model L-7100 connected to a D-2500 Chromatopac data station and a UV detector. The detection wavelength was set at 260 nm for all measurements. A Hitachi spectrometer model U-3900 was used to acquire the UV spectra.

Chemicals. All chemicals used in this study, including the biogenic amines and organosilane reagent as linker, were purchased from Sigma (St. Louis, MO, USA) and Aldrich (Milwaukee, WI, USA) Chemical Co., respectively. The pesticide compounds used as analytes in the adsorption measurements were acquired from Chem Service, Inc. (West Chester, PA, USA). The silica gel (5 μm particle diameter, 100 Å porosity) used as the solid phase for the adsorption evaluation at ambient temperature, a production of Silicycle (Quebec City, QC, Canada), had a specific surface area of 400 m^2/g and was chemically modified according to the derivatization procedures reported previously.[25,26] The solvents, such as toluene, acetonitrile, methanol, triethylamine, methylene chloride, 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.

Immobilization of HA Fractions on Silica Gel. The liquid fractions collected from humic acids under acidic or basic conditions were dried under vacuum for 4 h before being added at a weight of about 0.15 g to 50 mL of dry DMF in a three-neck reactor. The temperature for the reaction was raised to 93 °C, and then the approximately equivalent number of moles of organosilane linker in 10 mL of dry DMF was added to the solution drop by drop over 2 h. Once this process was finished, the reaction was allowed to continue for 18 h. During the reaction, desiccated nitrogen gas was circulated in the reactor to maintain an inert (i.e., free from oxygen) dry environment. Finally, the silica gel was added to the reactor at 3.22 g for another 24 h of reaction. After the reaction, the functionalized silica gel, used as the solid phase, was collected and washed with DMF, methanol, toluene, acetonitrile, and distilled water several times before being dried under vacuum and sent to the Instruments Center at National Chung Hsing University for elemental analysis. The elemental analysis data in mass percent (wt %) for the fractions of humic acids evaluated in this study were then tabulated for the purposes of comparison and discussion in the following Results and Discussion.

Conditions for Adsorption Process. A weighted amount of solid phase (10 mg) was added to 100 μL of a 2.57×10^{-3} M solution of analyte for a controlled period of time. In each case, the solution was sampled for HPLC analysis both before and after the adsorption

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Table 1. Percentage of Adsorption for Pesticidal Compounds Containing a Single Carboxylic Group by Fractions Extracted from Humic Acids under Acidic and Basic Conditions after Their Immobilization on Silica Gel

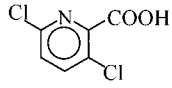
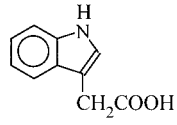
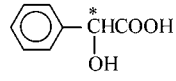
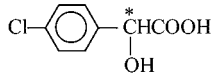
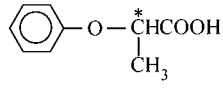
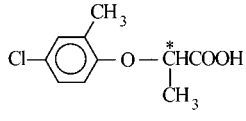
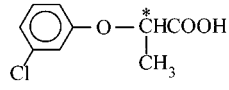
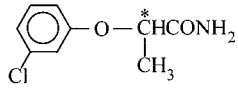
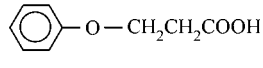
No	Compound (description)	Analyte Structure[a]	Extraction Conditions[b]	Percent Adsorption[c]	Mobile Phase[d]
1	3,6-Dichloropico-linic acid (Lontrel)		Basic Acidic	80.2±0.3 94.2±0.3/87.3±0.2	A
2	3-Indoleacetic acid (Heteroauxin)		Basic Acidic	41.8±0.3 52.2±0.3/89.0±0.4	A
3	Mandelic acid		Basic Acidic	n/a 65.1±0.2/93.1±0.6	A
4	*p*-Chloromandelic acid		Basic Acidic	60.5±0.4 75.6±0.1/77.0±0.5	B
5	2-Phenoxypropio-nic acid		Basic Acidic	n/a 64.6±0.3	A
6	2-(4-Chloro-2-methylphenoxy)pr-opionic acid (Mecoprop)		Basic Acidic	n/a 82.6±0.4	A
7	2-(3-Chlorophen oxy)propionic acid (Fruitone)		Basic Acidic	55.9±0.5 85.7±0.2	A
8	2-(3-Chlorophenox-y)propionamide		Basic Acidic	0 0	A
9	3-Phenoxypropio-nic acid		Basic Acidic	38.5±0.1 50.6±0.1/67.4±0.2	A

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Table 1. continued

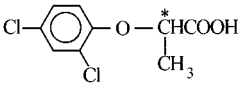
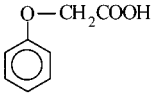
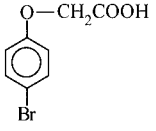
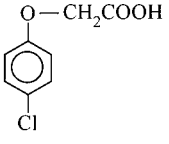
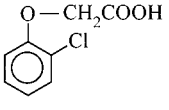
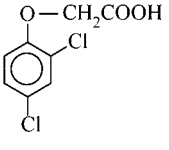
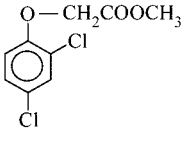
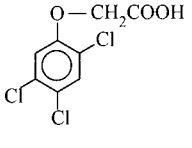
No	Compound (description)	Analyte Structure[a]	Extraction Conditions[b]	Percent Adsorption[c]	Mobile Phase[d]
10	2-(2,4-Dichlorophenoxy)propionic acid (Dichlorprop)		Basic Acidic	58.6±0.3 86.3±0.1	A
11	Phenoxyacetic acid (Phenylium)		Basic Acidic	51.3±0.2 80.6±0.4/87.5±0.1	B
12	*p*-Bromophenoxyacetic acid		Basic Acidic	n/a 85.2±0.1	B
13	*p*-Chlorophenoxyacetic acid (4-CPA)		Basic Acidic	69.9±0.3 83.4±0.4	B
14	*o*-Chlorophenoxyacetic acid		Basic Acidic	n/a 79.0±0.1	B
15	(2,4-Dichlorophenoxy)acetic acid (Weedar)		Basic Acidic	71.5±0.1 89.3±0.5	A
16	(2,4-Dichlorophenoxy)acetic acid methyl ester		Basic Acidic	0 0	A
17	(2,4,5-Trichlorophenoxy)acetic acid (Weedone)		Basic Acidic	80.2±0.3 ~100	A

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Table 1. continued

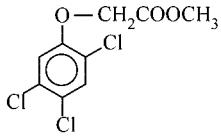
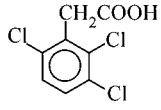
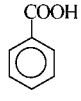
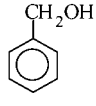
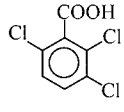
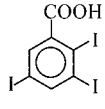
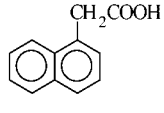
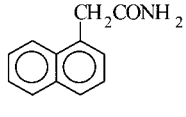
No	Compound (description)	Analyte Structure[a]	Extraction Conditions[b]	Percent Adsorption[c]	Mobile Phase[d]
18	2,4,5-Trichlorophenoxy)acetic acid methyl ester (2,4,5-T methyl ester)		Basic Acidic	0 0	A
19	2,3,6-Trichlorophenylacetic acid (Fenac)		Basic Acidic	n/a 64.4±0.1/31.2±0.2	A
20	Benzoic acid		Basic Acidic	n/a 64.3±0.2/77.7±0.1	A
21	Benzyl alcohol		Basic Acidic	0 0/4.9±0.1*	A
22	2,3,6-Trichlorobenzoic acid (2,3,6-TBA)		Basic Acidic	n/a 83.6±0.3/40.3±0.1	A
23	2,3,5-Triiodobenzoic acid (TIBA)		Basic Acidic	n/a 95.6±0.1/45.3±0.2	A
24	1-Naphthaleneacetic acid		Basic Acidic	35.8±0.4 48.0±0.6/81.1±0.2	B
25	1-Naphthaleneacetamide		Basic Acidic	0 0	B

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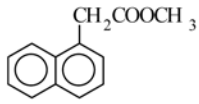
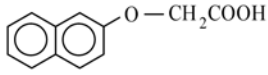
Table 1. continued

No	Compound (description)	Analyte Structure[a]	Extraction Conditions[b]	Percent Adsorption[c]	Mobile Phase[d]
26	Methyl-1-naphth -alene acetate		Basic	0	B
			Acidic	0	
27	2-Naphthoxyacetic acid		Basic	77.8±0.2	A
			Acidic	93.6±0.3	

[a]Some of the analytes are chiral. [b]Extracts from humic acids were obtained under either basic or acidic conditions, which corresponded to fraction 1 and fraction 2, respectively, in Table 3. [c]The symbol "n/a" indicates the data were not available at this moment for not carrying out the measurements. The data, right after the slash symbol "\" corresponding to the acidic conditions, were obtained with the addition of 5 μL of TEA to the liquid phase except for analyte 21, which was added at 10 μL. All of the reported percent adsorptions were measured over 3 h. The percentage of adsorption (%), an average of three measurements, was calculated on the basis of the difference in peak area of the analyte before and after the adsorption process was complete. The standard deviation was found to be <1% in all measurements. [d]The mobile phases were mixtures of organic solvent and acidified water with glacial acetic acid at a ratio of 250:3 by volume, (v/v), and were A, 70 (acetonitrile)/30, and B, 60 (methanol)/40, respectively.

process was completed during that specific period of time to calculate the percentage of adsorption by comparison. In the case of the biogenic amines, a derivatization process, as described previously, was carried out prior to the analysis.[24]

To study how the acidic or basic origin of the additive affected the adsorption of the analytes, an additive, such as glacial acetic acid or triethylamine in a volume ranging from 5 to 10 μL, was added to the aforementioned matrix containing the adsorbent and the analyte. The analysis was then performed immediately following the 3 h adsorption period.

Theoretical Calculation Using Spartan 10 Software. The theoretical calculation for the single-point energy was conducted on the basis of the semiempirical molecular orbital calculation method (PM3) using Spartan 10 software. The HA molecule, with a typical structure as shown in Figure 1, was first minimized in energy by changing the bond lengths and angles until a minimum energy structure was found prior to the calculations. Atoms of functional groups on both the humic acids and the analyte were simulated to interact with each other to determine the lowest formation energy (i.e., heat of formation).

RESULTS AND DISCUSSION

Fractions 1 and 2 from the humic acids were collected under acidic and basic conditions; they were then immobilized on silica gel and used as the adsorbents for a variety of pesticidal compounds and biogenic amines bearing single carboxyl and amino functional groups, respectively, in acetonitrile. The corresponding data, unreproducible with the untreated humic acids or under aqueous conditions, were tabulated along with the structure for all of the analytes examined in this study and the chromatographic conditions for adsorption determinations, as shown in Tables 1 and 2. A simplified schematic drawing of the structure of a typical HA molecule is illustrated in Figure 1 (top left). The corresponding 3D stick-and-ball model, the structural drawing and the 3D model after energy minimization are as represented in the bottom left, top right, and bottom right, respectively, of Figure 1. Figure 2 shows the adsorption of 2-naphthoxyacetic acid before and after the process involving the humic fraction extracted under acidic conditions. The percentage of adsorption was estimated to be 94% for a time period of 3 h. For the other compounds listed in Tables 1 and 2, the percentage of adsorption varied considerably from 0 to almost 100% measured under the same conditions and was found to be highly related to the structure of the analyte and the type of functional group attached to it. The adsorption, which was better on adsorbent immobilized with the fraction collected under acidic conditions, as shown in Figure 3, is believed to be a result of the interaction between the functional moieties of the analyte and the humic acids (i.e., amino or carboxyl group of analyte vs carboxyl group of humic acids, etc.) because no adsorption was observed for analytes that were the derivatives of alcohol, amide, and ester under the same conditions. A typical example was 2-(3-chlorophenoxy)-propionic acid versus 2-(3-chlorophenoxy)propionamide, and many others can be found in Table 1. Note that the only difference in structure of these two analytes lies in the functional group, that is, the carboxyl group versus the amide group. The $\pi-\pi$ interaction appears not to be involved in the adsorption process. Otherwise, the adsorption for these aforementioned derivatives of alcohol, amide, and ester, benzyl alcohol, and naphthalene-based analytes (e.g., compounds **25**, **26**, and **27** in Table 1) would have been observed under the same conditions. This proposed adsorption mechanism is consistent with the theoretical calculation results obtained with Spartan 10 software for the single-point energy, which indicated that the heat of formation between the carboxyl groups was lower than that for the interaction between other functional combinations (e.g., carboxyl vs hydroxyl groups, etc.). The lowest value was obtained as the carboxyl group with an asterisk on the HA molecule (as shown in Figure 1, top left) interacts with the carboxyl group of analytes (as listed in Table 1). Interestingly, the percentage of adsorption was significantly improved if the analyte was of an aromatic derivative with an electron-withdrawing group(s), such as halogen atom(s) (e.g., compounds **13**, **15**, **17** and others vs **11** in Table 1). Furthermore, more improvement was observed when the carboxyl group was near the aromatic moiety (e.g., compounds **22** and **23** vs **20** in Table 1). These results strongly suggest that

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Table 2. Percentage of Adsorption for Biogenic Amines by the Fraction of Humic Acids Extracted under Acidic Conditions

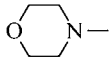
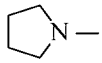
No	Compound	Analyte Structure[a]	Percent Adsorption[b]	Mobile Phase[c]
1	Ethanolamine	$HOCH_2CH_2NH-$	98.2±0.7	A
2	Methylamine	CH_3NH-	99.3±0.6	A
3	Morpholine		96.1±0.5	A
4	Isopropylamine	$(CH_3)_2CHNH-$	99.6±0.8	B
5	Propylamine	$CH_3CH_2CH_2NH-$	98.6±0.6	A
6	Pyrrolidine		97.8±0.9	A
7	Diethylamine	$(CH_3CH_2)_2N-$	~100	A
8	Isobutylamine	$(CH_3)_2CHCH_2NH-$	98.4±0.5	B
9	Butylamine	$CH_3CH_2CH_2CH_2NH-$	97.9±0.6	B

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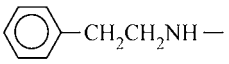
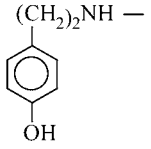
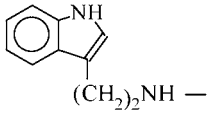
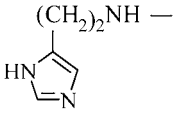
Table 2. continued

No	Compound	Analyte Structure[a]	Percent Adsorption[b]	Mobile Phase[c]
10	2-Phenylethylam -ine		~100	C
11	Pentamine	$CH_3CH_2CH_2CH_2CH_2NH-$	`100	C
12	Isopentamine	$(CH_3)_2CHCH_2CH_2NH-$	~100	C
13	Tyramine		~100	C
14	Tryptamine		~100	C
15	Histamine		~100	C

[a]The electrophilic derivatizing reagent is dansyl chloride. The derivatization reaction was carried out prior to the analysis.

[b]A nearly 100% adsorption was designated as the amount of analyte in the liquid phase beyond UV detection. [c]The mobile phases were mixtures of methanol and water at the following ratios by volume, (v/v): A, 50/50; B, 65:35; C, 70:30. The percentage of adsorption (%), an average of three measurements, was calculated on the basis of the difference in peak area of the analyte before and after the adsorption process was complete. The standard deviation was found to be <1% in all measurements.

the carboxyl group on molecules of humic fraction should be fully exposed and accessible to the large size analyte, which may cause the steric hindrance effect. Note that 2,3,5-triiodobenzoic acid, as shown in Table 1, was extremely large among the analytes examined in this study; however, the percentage of adsorption for a time period of 3 h was almost 100%.

Also, it was observed that the adsorption deteriorated as a result of the interference of a carboxylic interaction with another functional group (e.g., hydroxyl group) near the carboxyl group of the analyte. Typical examples include compounds **2**, **3**, and **4** in Table 1; the percentages of adsorption of these were unsatisfactory. In the case of the adsorption of biogenic amines under the same conditions, none of the aforementioned interference from the nearby functional group or hindrance effect was observed because the adsorption mechanism involved was believed to have been on the basis of the acid−base interaction and ion-pair formation in the acetonitrile.[7,8,27] This resulted in almost 100% adsorption for all of the reported biogenic amines, as shown in Table 2. Considering the nature of the analyte, the time required to reach the maximum percentage of adsorption decreased as the amount of adsorbent increased. The longer the elapsed time, the higher the percentage of analyte adsorbed as shown in Figure 4, all of which indicate that the adsorption process, in

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Figure 2. Chromatograms (top and bottom) showing the adsorption of 2-naphthoxyacetic acid before and after the process on the fraction of humic acids obtained under acidic conditions. The percentage of adsorption was estimated to be 94% for a time period of 3 h. Refer to Table 1 for chromatographic conditions and data.

Figure 3. Chromatograms (top and bottom) showing the adsorption of phenoxyacetic acid before and after the process on the fraction of humic acids obtained under basic conditions. The percentage of adsorption was estimated to be only 51% over 3 h. However, the percent adsorption was as high as 81% on the fraction of humic acids collected under acidic conditions over the same time period (refer to Table 1 for data).

the case of both pesticidal compounds and biogenic amines, was surface-oriented and similar to that in a previous study.[28] Except for the number of accessible interaction sites on the adsorbent, the viscosity of the liquid phase and the types of interactions between analyte and adsorbent are believed to affect the time required to reach the maximum percentage of adsorption.

Figure 5 shows the UV spectra for two fractions collected from humic acids dissolved in ultrapure water. As can be seen, these UV spectra were similar in profile in not having the absorption characteristics, although they were dark brown, brown, and light yellow in color for the samples from the top to the middle bottom of the figure. Besides, acidifying the fraction collected under alkaline conditions causes the precipitation. These unique features all led to the conclusion that the fraction collected under basic conditions (i.e., middle top curve for fraction 2) contained a composition not found in the fraction collected under acidic conditions (i.e., middle bottom for fraction 1). This difference in composition between fractions 1

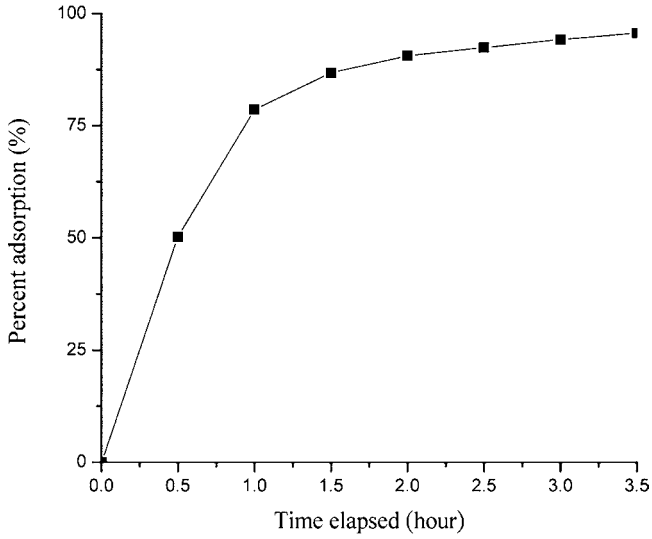

Figure 4. Percentage of adsorption of 3,6-dichloropicolinic acid, compound **1** in Table 1, over 3.5 h.

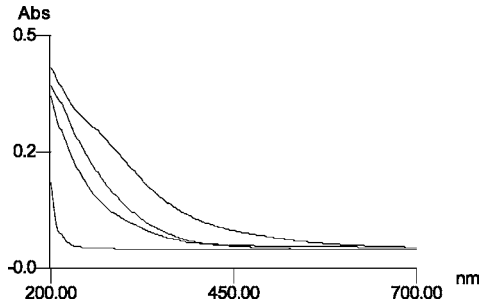

Figure 5. UV spectra for the humic acids (top) and the two fractions extracted from humic acids under acidic and basic conditions (middle top, middle bottom). Despite the difference in color, the spectrum profiles are quite similar in not having the absorption characteristics. The spectrum at the bottom shows the background signal generated by sodium borate, a salt present in the matrix. Note that UV spectra were recorded with samples containing the same mass percent for easy comparison.

and 2 and the original humic acids was further demonstrated by conducting an organic elemental composition analysis. The data are summarized in Table 3. Upon close examination, fraction 2 was found to have higher percentages of carbon and lower percentages of hydrogen and remained so even after being immobilized on silica gel. This indicated that the carbon

Table 3. Organic Elemental Compositions for Humic Acids and for Two Fractions Extracted from Humic Acids under Acidic and Basic Conditions

	organic elemental composition (%)			
sample[a]	C	H	N	S
humic acids	33.72	4.23	2.06	0
fraction 1	2.19	2.19	0.11	0
fraction 2	3.69	1.23	0.05	0
fraction 1 on silica gel	1.39	1.44	0.06	0
fraction 2 on silica gel	1.59	1.28	0.04	0

[a]The sodium salt of humic acids. Fractions 1 and 2 were collected from humic acids under acidic and basic conditions, respectively, and then immobilized on silica gel under the same conditions.

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in fraction 2 was likely in a state of a higher degree of aromaticity and condensation, as compared to fraction 1, which was believed to have more aliphatic-type carbons, or carbons functionalized with the hydroxyl group, or those as in the carboxyl group. In this case, the acidity and the concentration of the functional moiety containing oxygen, such as the phenolic OH and hydroxyl groups, were expected to be relatively high in fraction 1.[2,29] This could explain why better adsorption performance was obtained in general on adsorbent immobilized with the fraction collected under acidic conditions (i.e., fraction 1). The spectrum at the bottom of Figure 4 shows the background signal generated by sodium borate, a salt present in the matrix.

To further understand the adsorption mechanism involved and thereby improve the percentage of adsorption, an acidic or basic origin of additive, such as acetic acid or triethylamine, respectively, with a variety of volume combinations was administered to the liquid phase of the matrix containing the analyte before the adsorption measurement. The results for two selected analytes are summarized in Figure 6. As can be seen, the percentage of adsorption for these analytes in the presence of an additive of acidic origin, such as acetic acid in the matrix, dropped to zero in both cases. This dramatic change in percent adsorption clearly indicated that the acetic acid molecule, although smaller in size, was highly competent in interacting with the carboxyl groups on the humic acids, thus occupying the site responsible for the adsorption. On the other hand, the two analytes responded differently to an additive of the basic origin, such as triethylamine, insofar as the percentage of adsorption was concerned. It has been previously stated that the percentage of adsorption can be significantly improved without the additive in acetonitrile if the analyte is of an aromatic derivative with an electron-withdrawing group(s), such as halogen atom(s). Unfortunately, the negative effect on the percentage of adsorption for these types of analytes was observed in the presence of a tertiary amine, such as triethylamine, in the matrix. In the case of an analyte without an aromatic substitution, an improvement in the adsorption was, in general, obtained. However, when nontertiary amines, such as diisopropylamine or ethylamine, were added to the matrix as the basic origin of additive, the adsorption disappeared as in the case of added acetic acid for all of the analytes examined (results not shown). It was believed that the formation of the ion pair as a result of the acid−base reversible interaction in acetonitrile mentioned previously was responsible for the dramatic change. In acetonitrile, the dissociation constants of acids tend to be smaller than in water. Consequently, ion-pairing would occur to some extent. In contrast, free ions are expected to exist in water.[7,8] This is because the dielectric constant of acetonitrile is smaller (i.e., 36 vs 78). The relevant studies concerned with the interaction between the nitrogen element of amino or quaternary ammonium group and the matrix functionalized directly with the carboxyl group or bridged with the phosphate ion, however, in aqueous solution have been reported.[30−33] The force leading to adsorption with comparable efficiency was mainly electrostatic in nature, which fit the description above. Finally, this silica-modified adsorbent is recyclable because of its rapid and reversible sorption/desorption process. In light of that, the analyte could be concentrated through adsorption and then released to the solvent of known volume with acidic or basic additive added depending on the nature of analyte for the follow-up quantitative measurement. Currently, we are considering the possibility of concentrating the analyte through such an approach.

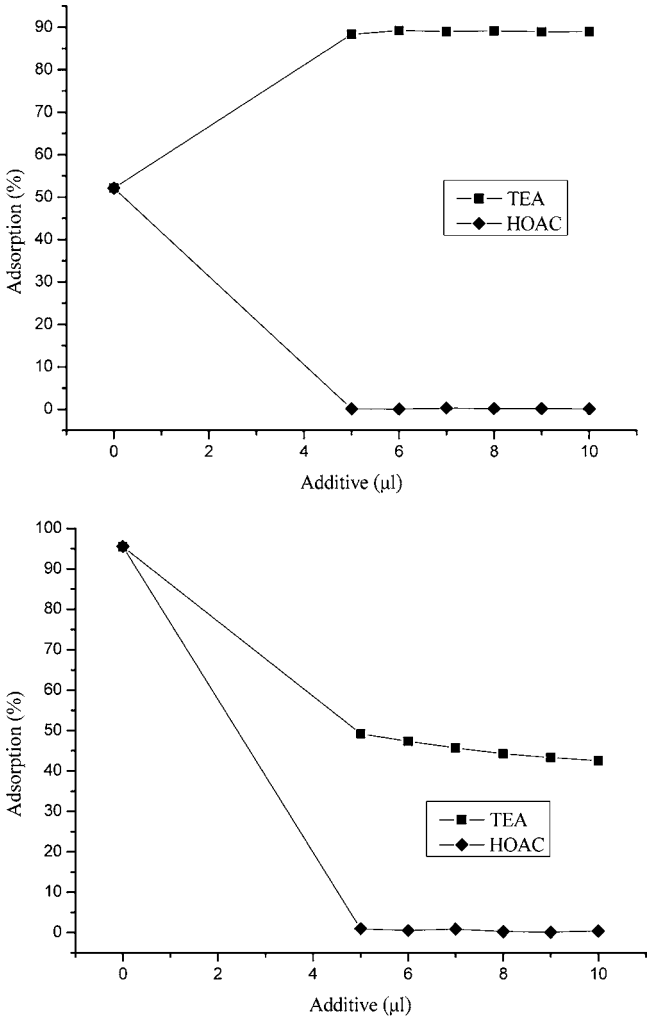

Figure 6. Effect of acidic or basic origin of the additive in the liquid phase of the matrix on the percentage of the analytes, 3-indoleacetic acid (top) and 2,3,5-triiodobenzoic acid (bottom), adsorbed on the solid phase. As can be seen, the effect of the acidic or basic origin of the additive on the adsorption was quite analyte-dependent.

AUTHOR INFORMATION

Corresponding Author

*E-mail: schenphd@mail.ncyu.edu.tw. Tel: 886 5 2717997. Fax: 886 5 2717901.

Notes

The authors declare no competing financial interest.

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