

Adsorption and Desorption of Plasticizers with Humic-Fraction-Immobilized Silica Gel in Hexane: A Facile Approach to Pre-concentration

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ABSTRACT: Humic fraction (HF) collected under acidic conditions and used as an adsorbent for various phosphate-based plasticizers in hexane is immobilized on silica gel. Most plasticizer analytes examined in this study under the same conditions achieved adsorption percentages above 90% in 1 h based on the difference in peak area. The Fourier transform infrared (FTIR) spectroscopy results indicate that the interaction leading to the adsorptions between the functional moieties of the analyte and HF (e.g., the carboxylate group of analyte against the carboxyl group of HF) is specific, reversible, and dipole–dipole-oriented. Moreover, it is significantly enhanced by hexane. However, the π – π interaction (even hydrogen bonding in all cases) was either not as significant or absent in hexane and, therefore, contributed little or nothing to the percentage of adsorption. The interaction is highly affected by the acidic or basic origin of the additive introduced to the liquid phase of the matrix, and it is subject to the steric hindrance effect caused by the bulky alkyl groups attached to ether linkages and the relative position of the two ether bonds on the aromatic moiety of the analyte. The pre-concentration of the analyte and, thus, the recycle of the adsorbent can be achieved by adsorbing and, subsequently, desorbing it in a different solvent, such as acetonitrile. Furthermore, the adsorption process is surface-oriented because of its dependence upon both time and the amount of adsorbent.

KEYWORDS: Humic fraction, silica gel, adsorption/desorption, plasticizer, carboxylate group, dipole–dipole interaction

■ INTRODUCTION

Plasticizers are a group of substances used in plastics or other materials (e.g., cement, concrete, etc.) to impart fluidity (i.e., viscosity), plasticity (i.e., flexibility or softness), or other properties to the finished product by embedding themselves between the polymer chains. This effect spaces the chains apart (increasing the “free volume”), which significantly lowers the glass transition temperature for plastics, softens them, and increases flexibility.¹ The most commonly used plasticizers are in polyvinyl chloride (PVC) and other plastic applications, where good resistance to water and oils is required, which are esters of polycarboxylic acids (e.g., phthalate-based plasticizers) with linear or branched aliphatic alcohols of moderate chain length.^{2–6} *ortho*-Phthalate esters are a common choice in this category of plasticizers. However, substantial regulatory concerns were expressed over the safety of certain plasticizers; thus, the associated industries were pressured to shift to non-phthalates, especially in Europe. Several *ortho*-phthalates were classified as potential endocrine disruptors, and developmental toxicity was reported because of their transudation from the host material,^{7–9} which occurs because traditional plasticizers disperse host material particles through a mechanism of electrostatic repulsion in most scenarios.^{10,11} Therefore, safer plasticizers classified as the non-phthalates with better biodegradability, fewer biochemical effects, and resistance to ultraviolet (UV) and high temperature for particular applications are in development. At the same time, both the regulation and recovery of such pollutant compounds for environmental protection are necessary to prevent contaminating underground water following their use.¹² The analytical methods commonly used for determining phthalate-based plasticizers are chromatographic approaches, coupled to various detectors.^{13–19} Analytes have been pre-

concentrated through solvent extraction, with the use of an adsorbent to increase the signal intensity, and thus, facilitate the analysis in these studies.

Humic acid (HA), a complex mixture of numerous acids, is derived by the microbial degradation of dead plant matter and can be identified in soil nearly everywhere.²⁰ Because it contains various components (structurally), including quinone, phenol, catechol, and sugar moieties, numerical benefits, such as crop production and micronutrient transfer, exist and were proven experimentally and in the field.²¹ The application of HA for the removal of ions by forming chelate complexes has been shown.^{22,23} Similarly, the separation and removal of HA using ion-exchange resins through an ultrafiltration system or the fractionation technique on the formation of complexes under the same mechanism have been shown.^{24,25} Because of its complex structure and various functional components, such as carboxylate and phenolate groups, its adsorption-oriented application has been implemented in carboxyl-containing pesticides, biogenic amines in acetonitrile, and pesticides containing phosphorus in hexane.^{26,27} Adsorption is regarded as occurring mainly because of complexation, π – π stacking between humic fraction (HF) and analyte, acid–base type of interaction in the case of an amine, and enhanced dipole–dipole interaction in hexane.

In this study, the fraction of HA was collected under acidic conditions, immobilized on silica gel, and used as the adsorbent pre-concentrating material for various phthalate-based plasticizers in hexane. The variation in adsorption percentage was

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related to the steric hindrance effect caused by the bulky alkyl groups attached to ether linkages and the relative position of the two ether bonds on the aromatic moiety of the plasticizer analyte, which is discussed from a mechanistic perspective. Moreover, factors that affected the percentage of adsorption, such as the acidic or basic origin of the additive in the liquid phase and time elapsed during the adsorption process, were examined and rationalized to assist in the examination of the involved adsorption mechanism to improve the pre-concentrating efficiency by facilitating the adsorption/desorption process.

EXPERIMENTAL PROCEDURES

Apparatus. The high-performance liquid chromatography (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 detection wavelength in the adsorption evaluation was set at 260 nm for all measurements. The Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu model FTIR-8400 system with a resolution of 4 cm^{-1} . The silica gel was washed, dried, and pelleted with KBr after chemical modification for FTIR measurements. The FTIR spectra were obtained by scanning samples 10 times.

Chemicals. All chemicals used in this study, including the organosilane reagent as a linker in chemical immobilization reactions and plasticizer compounds, were purchased from Sigma (St. Louis, MO) and Aldrich (Milwaukee, WI), respectively. Silica gel ($5\text{ }\mu\text{m}$ particle diameter and $100\text{ }\text{\AA}$ porosity, with a specific surface area of $400\text{ m}^2/\text{g}$) was used as the supporting matrix of the solid phase during the adsorption evaluation at ambient temperatures and was obtained from Silicycle (Quebec City, Quebec, Canada). It was chemically modified with HF collected under acidic conditions before use as the adsorbent according to previously reported derivatization procedures.^{28,29} Solvents, such as toluene, acetonitrile, methanol, triethylamine, methylene chloride, hexane, and ethyl ether, were of HPLC grade and purchased from Fisher Scientific (Pittsburgh, PA) and Merck Taiwan, Ltd. (Taiwan, Republic of China). Filtered ($0.2\text{ }\mu\text{m}$) and distilled water were used for all instances of water use.

Conditions for Adsorption and Recovery Measurements. A weighted amount of solid-phase adsorbent (10 mg) was added to $100\text{ }\mu\text{L}$ of a $2.57 \times 10^{-3}\text{ M}$ analyte solution for a controlled period, as described previously.²⁶ The solution was sampled for HPLC analysis with a $15 \times 0.46\text{ cm}$ C_{18} column ($5\text{ }\mu\text{m}$ particle diameter) both before and after the adsorption process was complete for each measurement during a specific period to calculate and compare the adsorption percentages based on the difference in peak area. The measurement was repeated 3 times to obtain an average for all cases.


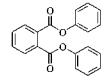
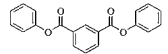
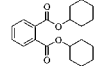
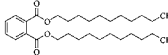
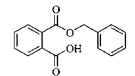
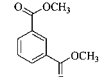
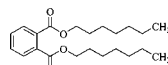
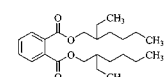
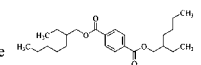
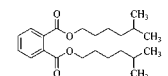
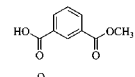
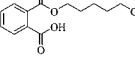
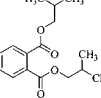
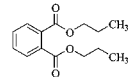
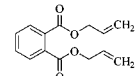
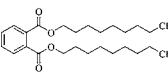
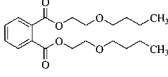
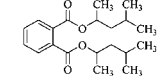
The recovery rate experiment was performed initially by decanting the liquid phase of the matrix to collect the adsorbent and washing it with fresh hexane several times immediately following completion of the adsorption process. The dried adsorbent was reimmersed in $100\text{ }\mu\text{L}$ of fresh HPLC-grade acetonitrile for 5 min to fully recover the adsorbed analyte. Thereafter, the solution was sampled for HPLC analysis, as previously indicated.

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 a volume ranging from 2.5 to $10\text{ }\mu\text{L}$ was added to the mentioned matrix containing the adsorbent and analyte. Thereafter, HPLC analysis was performed immediately following the 1 h adsorption period.

RESULTS AND DISCUSSION

The plasticizers shown in Table 1 are mainly *ortho*-phthalates, but several *meta*- and *para*-phthalates (i.e., isophthalates and terephthalates, respectively) and monoalkyl phthalates are also included for discussion purposes through a comparison of the factors affecting the adsorption percentages and the involved mechanism that leads to the adsorption. Table 1 shows the percentage of adsorption for all analytes examined in this study

Table 1. Percentage of Adsorption for Various Esters of Phthalic Acid with HF Extracted under the Acidic Conditions after Its Immobilization on the Silica Gel

No	Compound	Analyte Structure	Percent Adsorption/Recovery Rate (%) ^a	Mobile Phase ^b
1	Dimethyl terephthalate		98.5/99.8	A
2	Diphenyl phthalate		96.8/99.1	B
3	Diphenyl isophthalate		99.2/100.4	B
4	Dicyclohexyl phthalate		98.5	A
5	Diundecyl phthalate		~100	C
6	Monobenzyl phthalate		76.2*	B
7	Dimethyl isophthalate		98.8	A
8	Di-n-heptyl phthalate		98.7	C
9	Dioctyl phthalate		99.3/98.9	C
10	Dioctyl terephthalate		92.1	A
11	Diisoheptyl phthalate		98.5	C
12	Monomethyl isophthalate		53.9*	A
13	Monohexyl phthalate		49.1*	B
14	Diisobutyl phthalate		98.9	A
15	Dipropyl phthalate		~100/99.7	A
16	Diallyl phthalate		99.1	A
17	Dinonyl phthalate		~100	A
18	Bis(2-n-butoxyethyl) phthalate		~100	C
19	Bis(4-methyl-2-pentyl) phthalate		~100	C

^aThe reported percentage of adsorptions was measured over a time period of 1 h in hexane. The amount of HF-modified silica gel used as

Table 1. continued

the solid phase in each triplet adsorption measurement was 10 mg. The volume of liquid phase containing analyte is 100 μL . The asterisk indicated that the adsorption was carried out in acetonitrile. 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. The standard deviation was found to be less than 1% in all measurements. The recovery rate was calculated in the same manner.^b The mobile phase was (A) acetonitrile solvent of HPLC grade for most plasticizer analytes. Other mobile phases used in the measurement included (B) 490:10:1:1 and (C) 490:10:1:2 acetonitrile/methanol/acetic acid/triethylamine by volume (v/v/v/v).



Figure 1. Chromatograms showing the adsorption of diphenyl phthalate (compound 2 in Table 1) before (bottom) and after (center) the process was completed in hexane. The percentage of adsorption was estimated to be 96.8% for a time period of 1 h. However, the adsorption was not observed in acetonitrile, as shown in the chromatogram on the top. Refer to Table 1 for chromatographic conditions and recovery rate.

and the recovery rate for several selected analytes. The percentage of adsorption in hexane surpassed 90% in 1 h for all cases other than monoalkyl phthalates. However, the recovery rate obtained in acetonitrile for several selected analytes was higher. Typical chromatograms showing the adsorption of diphenyl phthalate (compound 2 in Table 1) in hexane and its subsequent desorption to recover the analyte in acetonitrile are

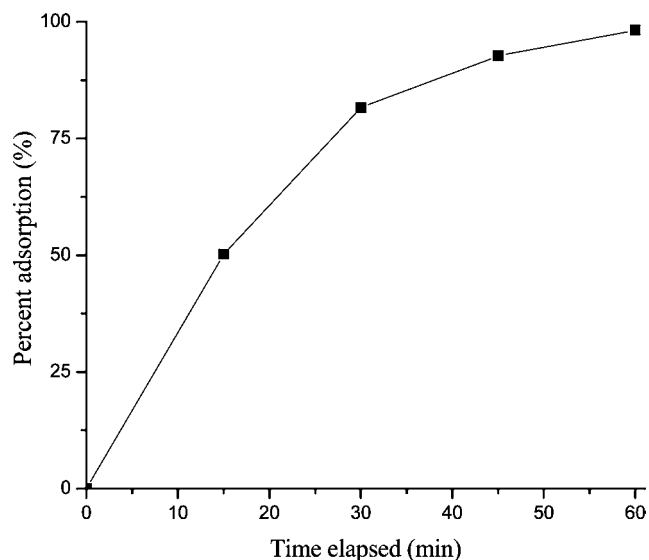


Figure 2. Effect of time elapsed during the adsorption process on the percentage of adsorption for dimethyl isophthalate in hexane. As seen, the adsorption process was nearly 95% complete in 45 min.

provided in Figure 1. The corresponding percentage of adsorption and the recovery rate were 96.8 and 99.1%, respectively, indicating that the adsorption process was highly specific and reversible. Figure 2 shows that a longer elapsed time indicates a higher percentage of adsorbed analyte. The results indicated that the time required to reach the maximum adsorption percentage may shorten as more adsorbent is used in the process (not shown). Furthermore, the low viscosity of hexane, a highly specific interaction resulting from the two functional carboxylate groups of analyte, and a significant interaction enhancement in hexane all contributed to the surface-oriented rapid adsorption, which was 80% complete in less than 40 min.^{25,26,30–33} None of these results was reproducible or observable when using other organic solvents, such as ether, or when performed in an aqueous environment.

The FTIR results shown in Figure 3 indicate that the enhanced dipole–dipole interaction between the analyte and HF-modified solid phase may have been the force responsible for the adsorption of the phthalate-based plasticizers in hexane. The most intense band corresponding to the frequency for the C–O stretching vibration at approximately 1125 cm^{-1} and a singlet absorption band for the C=O stretching vibration near the frequency of 1680 cm^{-1} , which was a doublet with the highest intensity in a previous study, were observed, which is the effect of a red shift attributed to the enhanced interaction.^{21,34–37} However, the frequency region became centered at 3500 cm^{-1} for a O–H vibration, which shifted to the blue end (blue shift). This indicated that the hydrogen bonding was not the dominant force that led to adsorption because these functional groups became freer in the HF-modified solid phase. The adsorbent used in the adsorption/desorption process evaluation for this study was recycled more than 20 times. This stable adsorption/desorption feature was impressive, which may be used as the material for the facile pre-concentration of phthalate-based plasticizers in hexane.

Three monoalkyl phthalates are shown in Table 1 to further discuss the type of interaction leading to the adsorption. The adsorption evaluation was performed in acetonitrile because these selected monoalkyl phthalates were insoluble in hexane.

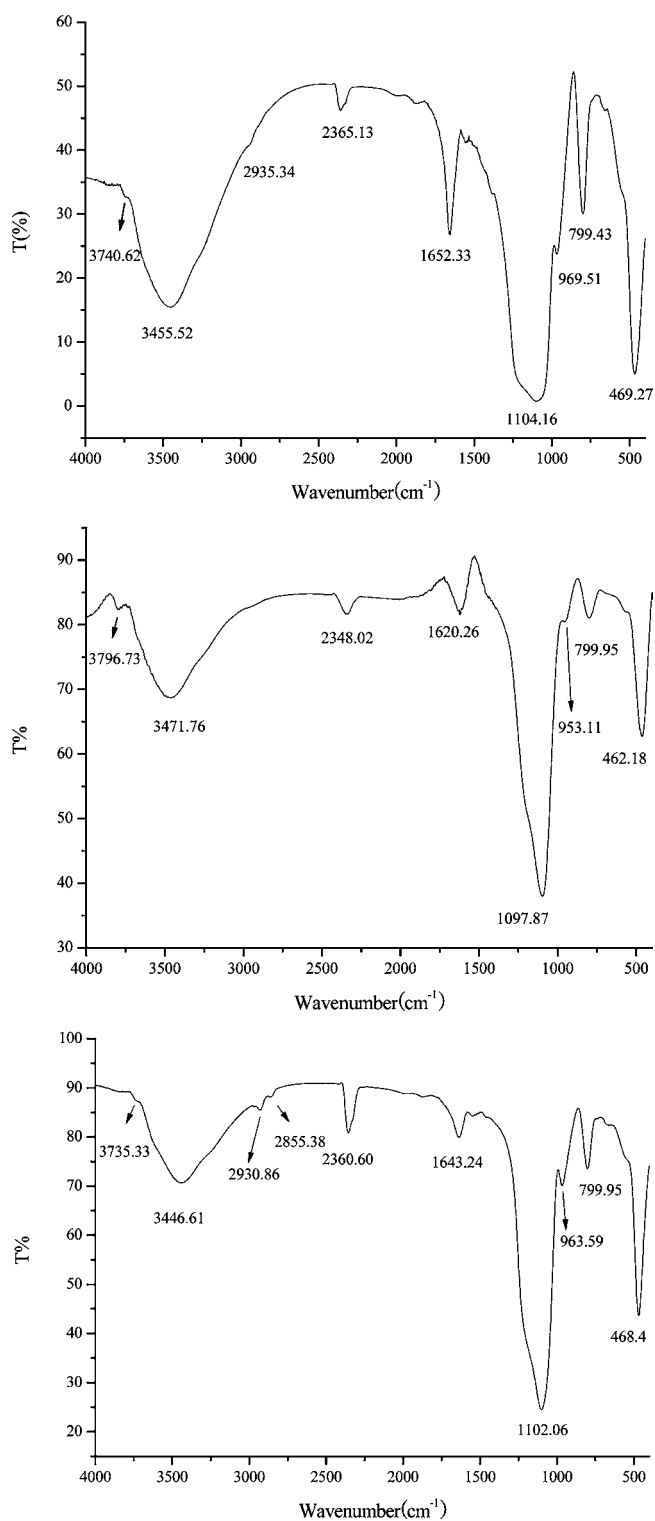


Figure 3. FTIR spectra for the adsorbent before (top) and after (center) the adsorption of diphenyl phthalate (compound 2 in Table 1) was complete in hexane. The spectrum on the bottom was for the adsorbent after being used repeatedly 20 times and was obtained by washing the adsorbent with HPLC-grade hexane and then acetonitrile to recover the adsorbed analyte.

The results were not as impressive because of the existing carboxylate group on the analyte. A study previously indicated that the interaction between carboxyl groups is the main force that leads to the adsorption of various carboxyl-containing

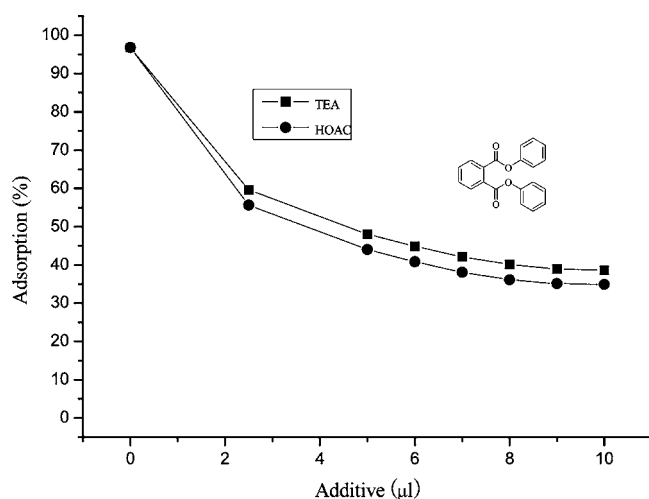


Figure 4. Effect of the acidic or basic origin of the additive in the liquid phase of the matrix on the percentage of adsorption for the diphenyl phthalate in hexane. As seen, the adsorption deteriorated dramatically in the presence of the additive.

pesticides on the HF-modified solid phase in acetonitrile.²⁶ No sign of hydrogen bonding was observed in the study, which explains why the adsorption for alcohols, amides, and esters was absent. Because the interaction enhancement in acetonitrile was not observed, the adsorption for all phthalate-based plasticizers examined in this study was absent in acetonitrile.

When closely examining the data in Table 1, several factors, such as the steric hindrance effect caused by the bulky alkyl group attached to an ether linkage, the relative position of these two ether bonds on the aromatic moiety of the analyte, and the acidic or basic origin of the additive, were considered to negatively affect the adsorption. Dioctyl terephthalate (compound 10 in Table 1) is a typical example in which the percent adsorption is significantly affected by two bulky octyl groups at the *para* position of the ring. These two factors have to exist simultaneously to have a profoundly negative effect on adsorption; otherwise, the individual effect is negligible, as occurred in compound 1. The only difference between these two compounds is in the bulkiness of the alkyl group attached to an ether linkage.

The adsorption mechanism may be examined optimally using an indirect approach by introducing additives, such as acetic acid or triethylamine, to the liquid phase to compete with the analyte for potential interaction sites on the solid phase; thus, any interaction related to the nature of polarity is affected, influencing the percentage of adsorption in a negative manner. Figure 4 shows the effect of the acidic or basic origin of the additive in the liquid phase on the percentage of adsorption for diphenyl phthalate in hexane. The percentage of analyte adsorption decreased in the presence of an additive of acidic or basic origin and leveled near 35% as the amount of additive in the liquid phase was increased to 10 μL because of the competition for interaction sites from the additive molecules. The π - π stacking interaction was described to be minor in strength during the adsorption of organophosphorus pesticides in hexane but was not negatively influenced by the presence of an additive of acidic or basic origin; thus, it was enhanced in hexane and is potentially responsible for the observed adsorption of diphenyl phthalate bearing two aromatic moieties when the volume of the additive was 10 μL.^{27,32-34} The results also explained why the adsorption

of all examined plasticizers disappeared in ether (e.g., *t*-butylmethyl ether).

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Notes

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