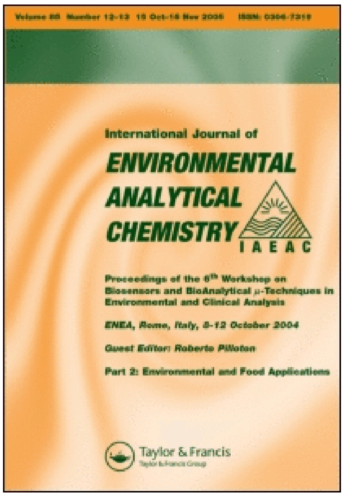

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An Investigation on the Concentration Efficiencies of Some Macroreticular and Ambersorb Resins Using Radio-Labelled Organic Contaminants Commonly Encountered in Water

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AN INVESTIGATION ON THE CONCENTRATION EFFICIENCIES OF SOME MACRORETICULAR AND AMBERSORB RESINS USING RADIO-LABELLED ORGANIC CONTAMINANTS COMMONLY ENCOUNTERED IN WATER*

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The extraction efficiencies of the three commercially available Ambersorb®, carbonaceous, polymeric resins, XE-340, XE-347 and XE-348 were evaluated for their use as sorbents for environmental pollutants using four model, radio-labelled water-borne organic contaminants. Their accumulation behaviour was compared with that of the thoroughly-studied Amberlite®, macroreticular XAD-2 (hydrophobic) and XAD-7 (hydrophilic) resins. These model compounds were desorbed from the resins using known volumes of commonly-used solvents to select the solvent for a particular resin(s). In this preliminary study, at $<4\,\mu g/L$ concentrations of the labelled compounds in aqueous solution (pH 5.78), the order of extraction efficiency of the resins was found to be XAD-2 > XAD-7 > XE-340 ≫ XE-347 ≫ XE-348 for organics. Several inherent impurities originally present in the carbonaceous resins were desorbed by solvents during elution. These resins therefore required exhaustive soxhlet purification prior to use. Most of the impurities were identified by gas chromatography/mass spectrometry.

KEY WORDS: XE-Ambersorb resins, solid adsorbents, XE-340, XE-347, XE-348, XAD-Amberlite resins, XAD-2, XAD-7, radio-labelled compounds, lindane, fluorene, di-2-ethylhexyl phthalate, 2,4-dichlorophenol, resin impurities, trace organics, water, fortification.

INTRODUCTION

Statistical inferences[1] correlating increased incidence of human cancer with water-borne organic contaminants have been reported. Several reviews[2-7] reporting the concerns over these implications and the necessity to generate a database

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for mutagenic testing in order to evaluate the long-term health effects, environmental impacts and other related risks have been published. These reviews have clearly pointed out the mandatory requirement for pre-concentration of these trace level organics from treated waters for their determination, identification, characterization and biological testing, since most of these organic contaminants, owing to their solubility characteristics, are invariably present at sub-microgram per litre levels and are not removed by the water treatment facilities. Jolley[8], Jolley and Suffet[9] and Kopfler,[10,11] have discussed the merits of the different, enrichment techniques currently available for low-level water-borne organics. Various other methods of concentration procedures for environmental organic pollutants have already been documented.[12,13]

The most widely-used method of accumulative sampling for trace levels of organics in aqueous matrices for the purposes of analysis and biological testing comprises the adsorption on solid sorbents. Since the advent of the Amberlite® macroreticular XAD resins, pre-concentration of these organics using other solid sorbents such as activated carbons, silanized siliceous materials, etc., has been discouraged in favour of polymeric XAD resins. These resins offer a convenient and relatively inexpensive means of scavenging and accumulating environmental contaminants especially from large volumes of water samples. The distinct advantages of these XAD resins are their physical and chemical stability compared to activated carbon and the facile desorption of the sorbates to permit column regeneration.

The literature is replete with information regarding XAD resins used individually or comparatively for trapping from aqueous media low-levels of a variety of organic chemicals, covering a range of polarities; these investigations are summarized in two excellent reviews by Dressler[14] and Junk.[15]

Amberlite® XAD resins are composed of microspheres held together to form macrospherical beads. This agglomeration results in a macroreticular network. Consequently, XAD resin beads have a microporous gel matrix interspersed with macropores, and can be obtained in different porosities and pore size distributions by altering the composition of the monomers, media of polymerization and adjuvants during production. Their polarities can be varied by appropriate choice of monomers and rigidity can be imparted by extensive cross-linking.[16-18] Moreover, the magnitude of their porosities is least affected by swelling in most solvents and at temperatures below 250 °C. Adsorption studies correlating surface area, porosity and thermodynamic properties of sorbate-interaction suggest that sorption of organic solutes on these resins is due to Van der Waals forces.[19-23] The macroreticular nature and large surface-area relative to their mass permit fast diffusion of the sorbates from the aqueous medium and restricted effusion during desorption.

XAD-2 resin is an agglomerate of minute resin beads synthesized from polystyrene-divinylbenzene copolymer[16] possessing nonionic, hydrophobic properties, and is stable throughout the entire pH range. XAD-7 is a macroreticular resin, the principal constituent of which is polymeric methylacrylate. Since it exhibits non-ionic but highly hydrophilic properties,[17] it is less stable at extreme pH ranges than XAD-2.

Ambersorb®, carbonaceous, polymeric synthetic adsorbents XE-340, XE-347 and XE-348, manufactured by Rohm and Haas Company, have been recently introduced as possible alternatives to activated carbon and are alluded to possess similar or better adsorption characteristics than activated carbon,[25,26] for certain organic solutes. Neely[27,28] and Neely and Isacoff[29] obtained these carbonaceous XE-resins by pyrolysing sulfonated synthetic polymeric styrene-divinyl benzene copolymers in a suitable atmosphere at elevated temperatures ranging from 300° to 800 °C to give highly surface active resins with properties ranging from hydrophobicity to hydrophilicity. The chemical composition, pore structure, pore-size distribution, physical strength and surface properties of these XE-resins are dependent on the parent polymer, temperature and atmosphere during pyrolysis. Depending on the above criteria, the pyrolysed resins are classifed as XE-340, XE-347 and XE-348. These sorbents are unaffected even at extreme pH changes.

XE-340 resin has been shown to possess high adsorptivity for some synthetic organic chemicals in water, and the kinetics of adsorption and facile regeneration properties are similar to those of XAD-2 resin.[30] Due to chemical modification during low temperature pyrolysis and lack of micropores, XE-340 resin exhibits the least activity among the three Ambersorb® resins. It is non-ionic and essentially hydrophobic. However, Ambersorb® XE-347 and XE-348 behave very similar to activated carbon.

All three carbonaceous resins differ in their adsorption behaviour toward different classes of organics. XE-340, however, being the most hydrophobic, tends to adsorb non-polar organics very efficiently. On the other hand, XE-348, being the least hydrophobic, apparently extracts effectively semipolar and π-electron-rich organic components from their aqueous solutions and approaches activated carbon in this behaviour. XE-347 resin stands between XE-340 and XE-348 in its adsorption behaviour toward dissolved organics in water.[31,32]

Most studies pertaining to Ambersorb® XE-resins have dealt with adsorption isotherms, kinetics of adsorption.[26,29–33] Only limited investigations have been reported on their adsorption/desorption characteristics to validate their accumulative efficiency for the recovery of aqueous organic contaminants. Kimoto *et al.*[34] used XE-340 resin for concentrating nitrosamines from tapwater and recovered 58–90% of the spiked level in fortified samples. Blok *et al.*[35] compared the recoveries of 19 organic compounds of different polarities from XE-340 and XE-348 with those from XAD-2, XAD-4 and XAD-8. Because of the artifacts encountered in the resins, these investigators recommended liquid–liquid extraction in preference to adsorption techniques. Harris *et al.*[36] noted the required combination of two dissimilar resins (XAD-2 and XE-347) as a general purpose sorbent for concentrating low levels of organics in water. XE-340 was used as an adsorbent for air sampling of organochlorine pesticides and effected near quantitative recovery for some pesticides.[37] Rixey and King[38] reported the comparative accumulative efficiencies of XE-340 under non-wetting conditions using some polar organics in aqueous medium and observed that XE-340, the most easily wettable of the three XE-resins, showed the same adsorption capacity both in wet and non-wet states.

From the studies of Hunt and Pangaro[39] (XAD-2 and XAD-4), Hunt[40] (XE-340 and XAD-2) and Gibs *et al.*[41] (XAD-2) on organic impurities present in the resins it is evident that none of the resins were devoid of impurities. Hunt and Pangaro[39] have also claimed that XE-resins contained fewer impurities than XAD-resins. Moreover, the analytical procedures employed in most of the accumulative sampling procedures using polymeric resin adsorbents incorporated colorimetric or high resolution capillary gas chromatography or high-performance liquid chromatography techniques with different types of detection systems. Generally, trace levels of organic chemicals were quantitated and corroboratively identified by gas chromatography–mass spectrometry (GC/MS) technique. Furthermore, these techniques are labour-intensive and require (a) elaborate clean-up procedures; (b) an evaporation step to concentrate sample extracts (one of the inherent and major sources of error in the analytical scheme);[42–45] (c) internal or external standards; and (d) corrections due to blanks, response factors, etc.

The primary objective of this investigation was to develop a simple technique to evaluate the enrichment and desorption efficiencies of the carbonaceous XE-340, XE-347 and XE-348 resins for water-borne contaminants and compare their efficiencies with those of the thoroughly evaluated XAD-2 and the less-commonly used XAD-7 which itself requires a detailed evaluation. Prior to determining the performance of each resin, it was necessary to identify the impurities present and clean-up the three XE-resins for proper recovery studies. Further, it was necessary to select appropriate solvent or solvent mixtures and the parameter for maximizing their desorption from the sorbents, and to examine critically the influence, if any, of other classes of compounds (admixed in high concentration) on the effective sorption and desorption of a specific class of compounds. Finally, we were able to propose a simple, alternative analytical technique in order to evaluate accumulative efficiency of sorbents; and to follow the amount of the solute in question in the column effluents to assess precisely the "break-through volume" in fixed-bed adsorption studies.

We report here the results of the recovery of the four radioactive compounds at $<4.0\,\mu g/L$ concentrations, when present along with high concentrations (at least three orders of magnitude higher) of unlabelled organics which are frequently found in surface and treated waters, namely, lindane (γ-BHC, an organochlorine pesticide), fluorene (FL, a polycyclic aromatic hydrocarbon), di-2-ethylhexyl phthalate (DEHP, an ester plasticizer) and 2,4-dichlorophenol (2,4-DCP, a chlorinated phenol) to elucidate the pre-concentration efficiency of the five resins.

EXPERIMENTAL

Materials

The water (pH *ca.* 5.6) used in this study was deionized, glass-distilled and purified as described by Malaiyandi *et al.*[46] and hexane was purified as previously described.[47] Acetone, toluene, benzene, methanol and hexane were purchased from Caledon Laboratories, Georgetown, Ontario, Canada. Carbon disulfide (Fisher Scientific Company) and anhydrous diethyl ether (Mallinckrodt Chemical Company) were obtained from local suppliers. Purified acetone was prepared by refluxing the solvent with potassium permanganate for 12 hr and redistilling in an all-glass apparatus.[48] Toluene, benzene and methanol were redistilled in glass and the distillate was collected in 1-L clean borosilicate containers with glass stoppers. Diethyl ether was freed from peroxide by allowing it to stand over ferrous sulphate heptahydrate (12 hr) and carefully redistilling in glass.[48] Carbon disulfide was also carefully redistilled in glass.

All inorganic reagents were analytical grade. All glassware was cleaned with chromic acid followed by thorough washing with water, rinsing with acetone then hexane and dried at 65 °C. Before use the glassware was rinsed with acetone and dried by purified nitrogen flushing. An ultrasonic cleaner (Branson Model, 220, 100 W) and counting vials were purchased from a local supplier.

Radio-labelled ^{14}C-9 fluorene (FL), ring-UL-^{14}C-lindane (γ-BHC), ring-UL-^{14}C-2,4-dichlorophenol (2,4-DCP) and di-2-ethylhexyl 1-^{14}C-phthalate (DEHP) were >98% pure and were purchased from Pathfinder Laboratories, St Louis, MO, USA. Non-radioactive FL, γ-BHC, 2,4-DCP supplied by Chem Service, West Chester, PA, USA and DEHP from Aldrich Chemicals, Milwaukee, WI, USA were used without purification. The solubilities of FL, γ-BHC, 2,4-DCP and DEHP in water are 1.9 mg/L,[49] 17.0 mg/L,[49] 4500 mg/L[49] and <100 mg/L[50] respectively at 25 ± 1 °C.

Ready-Solv MP was purchased from Beckman Instruments Co., Montreal, Quebec. Macroreticular Amberlite® XAD-2 and XAD-7 resins (Rohm and Haas Company) were purchased from BDH Chemicals Ltd., Toronto, Ontario, Canada. Carbonaceous Ambersorb® XE-340, XE-347 and XE-348 resins were kindly donated by Rohm and Haas Company, West Hill, Ontario, Canada.

Purification of Resins

Amberlite® XAD-2 and XAD-7 with surface-areas of 330 m^2/g and 450 m^2/g resin[9] respectively, were purified by a method outlined by Junk *et al.*[51] and McNeil *et al.*[52] and modified to conform to the purification procedure devised in our laboratory for Ambersorb® carbonaceous resins XE-340, XE-347 and XE-348 with surface-areas of 400 m^2/g, 350 m^2/g and 500 m^2/g, respectively. The modifications are summarized below.

All resins were separately slurried and intermittently stirred for 30 min in 1 M aqueous hydrochloric acid (2 times) to remove any metallic contaminants, allowed to settle and the aqueous layer was decanted to remove any fine particulates. After washing once with water, the resins were sequentially washed with 1 M aqueous sodium carbonate (2 times) and water (4 times) with decantation of the aqueous layer each time. After the final aqueous washing was negative to the silver nitrate-chloride test the resins were rinsed with acetone to remove the water completely. While wet with acetone, the resin beads were transferred to separate cellulose thimbles (*ca.* 100 mL capacity) and exhaustively soxhleted with benzene (or toluene), carbon disulfide, methanol, acetone, diethyl ether and hexane (6–8 cycles/hr) for at least 24 hr for each solvent. [Note: Before change of solvents, between soxhlet extractions, the resin was soxhleted with the same fresh solvent, for 1 hr and the solvent was siphoned off. After careful evaporation the resins from this extract should not exceed 20 μg.] For XE-resins, methanol extraction was continued for a further 48 hr period to get less than 20 μg residue. The solvents finally siphoned from each solvent extraction were nearly colourless.

XE-resins alone were then soxhleted with carbon disulfide (3 days in the case of XE-347 and XE-348) until the final extracts were nearly colourless. Finally, all the resins including XAD-2 and XAD-7 were soxhleted with ether and hexane for a 24 h period for each solvent. The final extracts, after concentration to about 2 ml, were analysed by capillary gas chromatography with flame ionization detector. The resins were then resoxhleted with 250 mL of a solvent mixture containing acetone-ethyl ether-hexane (1:1:1 v/v) concentrated to 1.0 mL and analysed as above to obtain a clean baseline. Immediately after purification the resins were stored in sufficient volumes of methanol.

All the extracts of XE-resins were carefully concentrated using the Kuderna–Danish evaporation technique with a modified Synder column.[42] [Note: XAD-resins were not GC-analysed since identification of their impurities had already been reported].[15,40,41] The concentrates of XE-resin extracts were quantitatively transferred to a weighed 10 mL vial followed by 3 × 1 mL rinsings with the same solvent, and carefully evaporated with a gentle stream of purified nitrogen (30 °) to about 1 mL volume. Final evaporation was carried out at room temperature in a vacuum desiccator until completely dry (30 min). The evacuation and drying was repeated until the weights of vials were constant. The residues from XE-resins were then dissolved in the same solvent and after making appropriate dilutions, the residues were analysed by capillary GC and the components were identified by GC/MS.

Preparation of Standard Solutions of Model Compounds

a) A stock solution of radio-labelled γ-BHC was prepared by weighing the radioactive compound and a calculated amount of the same non-radioactive material, mixing them in a 10-mL volumetric flask and making up to volume with acetone to a concentration of 2 mg/mL to obtain solutions with working levels of radioactivity. An aliquot of the stock solution was pipetted out to obtain 60 μg/mL working standard solution in 10 mL acetone. Similarly, stock and standard solutions of FL, DEHP and 2,4-DCP were prepared to get appropriate dilutions for fortification studies. Duplicate 10 μL of the standard solutions of each of the components were transferred into counting vials and the radioactivity of each component was determined.

b) Individual stock solutions (50 mg/mL) of each of the unlabelled materials in acetone were prepared in separate 5.0-mL volumetric flasks.

Fortification of Water Samples with Radio-labelled Compounds

Exactly 3.6 ppb (500 ± 200 dpm/mL) of fortified water sample containing radioactive γ-BHC was obtained by spiking a known volume of 60 μg/mL working standard labelled γ-BHC solution into 3 L water. To this were added 12 μL of 50 mg/mL stock solutions of each of the other three non-radioactive components FL, DEHP and 2,4-DCP (ca. 60 times more than the weight of radio-labelled γ-BHC was used in order to evaluate the influence of these unlabelled components on the extraction efficiency of the sorbents for the labelled sorbate during the entire recovery scheme.[53] The solution was then shaken and magnetically stirred for 30 min. Similarly, separate 3 L aqueous solutions containing 3.6 ppb labelled FL, DEHP and 2,4-DCP and 12 μL of the other three unlabelled acetone solutions were prepared.

Instrumentation

Routine screening of the impurities present in the Ambersorb® carbonaceous XE-resin extracts was performed on a Varian 6000 gas chromatograph equipped with a flame ionization detector (FID), an on-column injector, a programmable oven and a 401 Varian Vista Data system. A J & W 15 m × 0.25 mm i.d. capillary DB-5 column was used with a helium carrier gas, under the following conditions: carrier gas flow, 2.0 mL/min (velocity 20 cm/sec); chart speed, 2.0 cm/min; injector temperature, 260 °; detector temperature, 300 °; electrometer range, 1.0; attenuation 4×10^{-10} amps full scale; make-up gas flow (He), 30 mL/min; hydrogen flow, 30 mL/min; and air flow, 270 mL/min. The oven temperature was programmed: initial, 50 °/2 min hold; 4 °/min to 170 °/10 min to 200 ° and was held for 8 min; theoretical plates, 8000/m. Internal standard was anthracene-d_{10}.

The components present in the impurities from the resin extract were identified by GC/MS using a Finnigan Mass Spectrometer Model 4500 with Incos Data system. Mass spectrometer conditions: electron energy, 70 eV. GC conditions: capillary column, SPB-5, 30 m × 0.32 mm i.d.; injection port temp., 250 °. Oven temperature programmed as follows: Initial temperature, 50 °/1 min hold; 15 °/min to 100 °; 5 °/min to 270 ° and hold for 10 min. Internal standard: anthracene-d_{10}. Identification of the peaks was carried out using automatic routines based on a library research created from authentic standards of the selected compound. Compounds were located by searching the reconstructed ion chromatogram for each library entry. Tentative assignment (T) was based on 80% probability of fitting four major ion fragments.

Radioactivity counting was performed using a microprocessor-controlled liquid scintillation counter (Beckman Instruments Inc., Scientific Instruments Division, Irvine, CA, USA) equipped with a Texas Instrument Silent 200 electronic data terminal. Each vial was counted for 5 min after equilibration for 30 min in the dark. Using a window setting of 397–655 nm and counting efficiency of 95% carbon-14 standard, duplicate counting was done following the entire carousel had been counted once. Quench correction by the external standard ratio (ESR) method and calibration were performed as described in the Instrument Manual.[54] Recoveries were calculated as the percent of the activity ratio with reference to the activity present in the original aqueous sample. In absolute terms, such recovery indicated the fate of the labelled compounds in the entire analytical scheme.

Recovery Tests Using Adsorbents

Five silanized borosilicate columns (40 cm × 1.2 cm o.d.), provided with a 2 mm polyfluoroethylene (PTFE)-stop cocks at the bottom and a fused 500 mL round-bottomed bulb with a ₸ 24/40 outer joint at the top were used in this study. A plug of pre-cleaned silanized glass wool was placed at the bottom end of the column and a smooth top surface of the plug was prepared by gently tamping with a snug-fitting glass rod. The ₸ 24/40 outer joint was fitted with a ₸ 24/40 inner joint adapter which carried PTFE-tubing packed with Chromosorb 108 followed by the XAD-2 resin packing.

The column was filled to about 2/3 of its height with methanol. Exactly 5 mL of methanol-soaked resin was measured in a 10-mL measuring cylinder. Using a wide-bore pasteur pipette, the resin was transferred directly into the column and the column was gently tapped to get a uniform-surfaced packing. Thus, the five different resins were packed in their respective columns.

The methanol in the columns was drained just enough to leave some solvent at the top surface of the resin. [Note: The resin should never be allowed to get dry.] Methanol draining was followed by careful addition of 10 mL of water (2 bed volumes (BV)) to the inner wall of the column and the water was allowed to stand for about 10 min before it was drained. Another 18 BV of water was allowed to percolate through the absorbent bed in order to remove completely the residual methanol [about 5–10 BV of water are usually recommended].

Prior to the commencement of adsorption tests, two 5 mL aliquots in duplicate of the fortified aqueous sample containing one radioactive component and three other unlabelled compounds were pipetted out into counting vials from the fortified water sample. To these were added 10 mL Ready-Solv MP scintillation fluid and 2–5 mL of isopropanol to get a homogeneous mixture and this was kept aside in the dark until all the fractions from the column were collected for counting.

To each of the columns exactly two 250 mL of the above fortified water sample were transferred into the bulb portion of the adsorption column. After 10 min, the water sample was allowed to percolate through the resin at a flow rate of 4–6 mL/min during a 100 min period (average flow rate was 5 mL/min *ca.* 1 BV/min). Every fifth 5 mL "exhausted effluent" fraction was collected to determine the "break-through" volume and was counted.

After all the fortified aqueous sample had percolated through the resin bed, the inner walls of the bulb and the column were rinsed with 20 mL (4 BV) of water and these rinsings were also collected in 5 mL aliquots after percolation over the resins and counted. The adsorbent was then eluted with a battery of solvents, namely methanol, acetone, diethyl ether and hexane, at a flow rate of 1–2 mL/min and each solvent was allowed to remain in the column for 5 to 10 min before draining. Each time, the trapped air bubbles, if any, in the absorbent bed were removed by gently stirring the packing with a 0.5 mm-thick stainless steel or aluminum wire. After gentle tapping to ensure an evenly packed surface the adsorbent was first eluted with methanol to collect separately 2- and 3-mL fractions (total 5 mL) followed by elution with 4 × 5 mL portions of acetone, ether and 3 × 5 mL of hexane. Each 5 mL fraction of the eluates was collected in separate vials and counted.

The resin from each column was dislodged after drying with purified nitrogen, and transferred into separate vials. A mixture of 5 mL acetone and 2 mL hexane was added to each vial and was sonicated in an ultrasonic bath for about 10 min. Using a pasteur pipette, the solvent mixture from the exhausted resin was carefully transferred into a counting vial. The "spent" resin was then sonicated with 6 mL of benzene containing 4 mL of carbon disulfide and the benzene extract was separately counted. The resins were carefully disposed of following Environmental Safety Regulations.

The acetone–hexane extract after sonication was evaporated at ambient temperature and pressure in the fume hood., When the volume was reduced to 3 mL, toluene (5 mL) was added and the solvent mixture was further evaporated until the concentrate gave a faint odour of acetone. Similarly, the benzene–carbon disulfide extract was also evaporated to completely remove carbon disulfide smell. Aliquots (10 mL) of Ready-Solv MP scintillation liquid were added to all the eluate fractions, selected "exhausted" effluent fractions and sonicated extracts and these were counted as described earlier.

During the measurement of radioactivity of aqueous solutions using the liquid scintillation cocktail Ready-Solv MP it was observed that this cocktail could only tolerate <20% water content in the total counting solution to give a homogeneous medium; a higher water content resulted in emulsion or phase separation or gel formation which could give erroneous results. In order to avoid this situation, a second solvent was sought to avoid phase separation or gel formation. After careful screening, isopropanol was found to be the best. The use of 2.5 mL of isopropanol to 5.0 mL of water sample followed by the addition of 10 mL of Ready-Solv MP was shown to resolve this problem.

When acetone was used as one of the solvents for eluting the sorbate from the resins, low scintillation counting efficiency (*ca.* 40%) was obtained. In order to minimize this effect due to acetone, methanol, hexane and benzene were added separately to the 5.0 mL acetone solution containing a known amount of radioactivity. With radio-labelled DEHP, equal volumes of acetone-benzene proved to give the best efficiency at 72% and hence benzene was used only with concentrated acetone eluates to measure radioactivity.

RESULTS AND DISCUSSION

So far no systematic study on the extraction efficiency and the applicability of the Ambersorb[R] XE-resins for the pre-concentration, isolation and quantification of dissolved organic chemicals in aqueous media have been reported. In the present study XAD-2 (a hydrophobic resin) was chosen as a reference sorbent since the evaluation of concentration efficiency of this resin has been thoroughly investigated.[15] Furthermore, the potentialities of XAD-7 (a hydrophilic sorbent) for the extraction of low levels of environmental contaminants have not been fully evaluated. Hence, this study was instituted to assess the accumulative efficiencies of these resins for water-borne organics and to compare efficiencies with those of XAD-2 resin.

Impurities in Ambersorb® Resins

James *et al.*[55] observed definite interferences from the impurities of synthetic polymers such as XAD-2 during the analysis of trace organic contaminants at levels $<1.0\,\mu g/L$. They concluded that the presence of these artifacts originated from the monomers, catalysts, adjuvants, etc. (used in the synthesis of these resins) would vitiate the inferences and conclusions on the analytical results and biological test data. The major impurities in some of the XAD resins have been isolated and identified.[39-41] Although Hunt and Pangaro[39] have also claimed that XE-340 resin was substantially a "cleaner" resin than the XAD resins, no report has so far been published on the impurities present in all the three XE-resins used in this investigation and hence it was decided to isolate and identify these impurities.

In order to "clean-up" the resins and obtain "impurity-free" resins, a battery of solvents (which are currently being used in such desorption investigations), such as toluene (or benzene), carbon disulfide, methanol, acetone, ether and hexane were serially employed for extraction of the impurities from these resins along with XAD-2 and XAD-7. Since the impurities of some XAD resins had been already reported[15,39,41] and since it is the intent of this paper to evaluate critically the accumulative-desorptive properties of the XE-resins and the possibility of using them for pre-concentration of ultra low-level organic contaminants, and to identify the impurities present, only the XE-resin extracts were analysed by capillary GC and the impurities identified by GC/MS.

The chromatograms (Figures 1 to 4) show the peaks of the impurities present in the concentrates of XE-340, XE-347 and XE-348 extracted by each of the solvents, namely toluene, carbon disulfide, methanol and acetone. [Note: The chromatograms of diethyl ether and hexane extracts are not presented since most peaks in these extracts were small and similar to the ones seen in other extracts.] The bottom-most GC trace in each figure shows the blank chromatogram of the impurities in the final solvent concentrate of one of the XE-resins after that resin has been "exhaustively" extracted by that solvent. Blank GC traces of the other two resins are not presented since they were similar to the blank shown in these figures. Furthermore, blank GC traces from the concentrates also indicate that the resins were clean with respect to the particular solvent.

In the toluene extract (Figure 1), more impurities were found in the XE-340 resin than those present in XE-347 and XE-348. With respect to toluene, the order of cleanliness is XE-348 > XE-347 > XE-340. In contrast, Hunt and Pangaro[39] have reported that XE-340 was substantially cleaner than XAD-2 and XAD-4 resin when methylene chloride was the extraction solvent. It is not surprising that XE-348 adsorbent is the cleanest of the three, since, under the pyrolysis conditions employed during the manufacture of these resins (namely under inert atmosphere and at temperatures of 300°, 500° and 800°C respectively for XE-340, XE-347 and

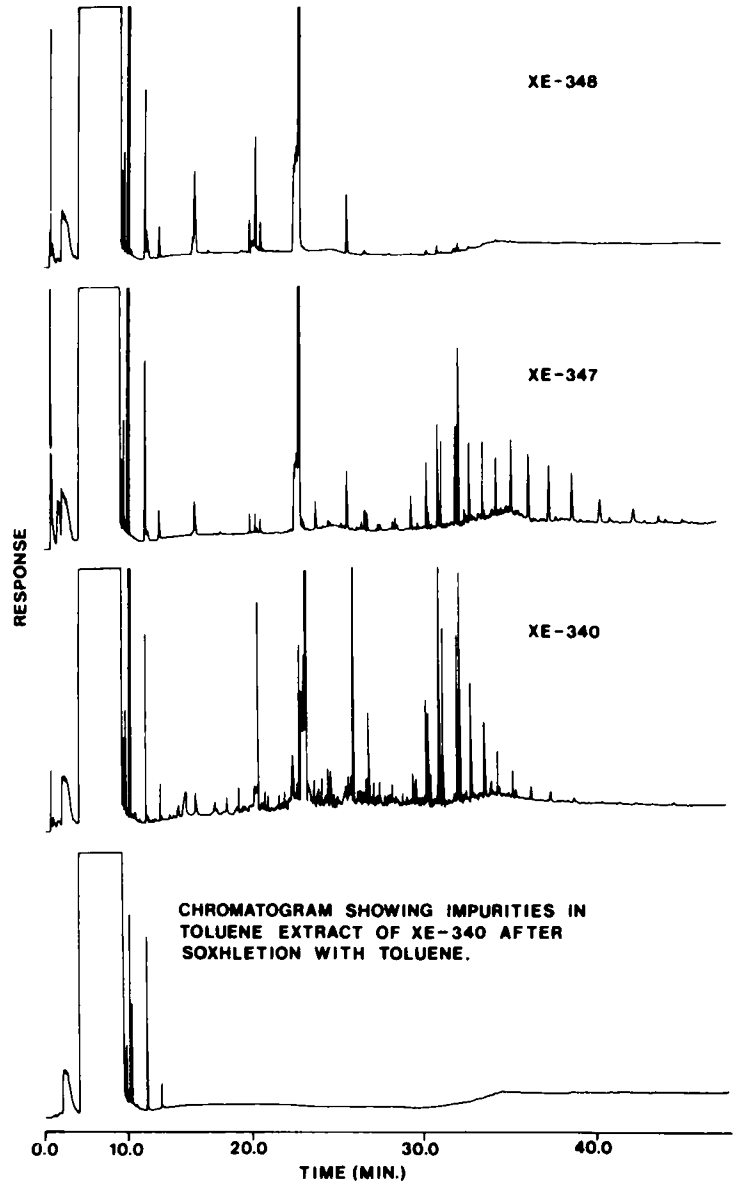

Figure 1 Chromatogram showing impurities in toluene extracts of XE-resins.

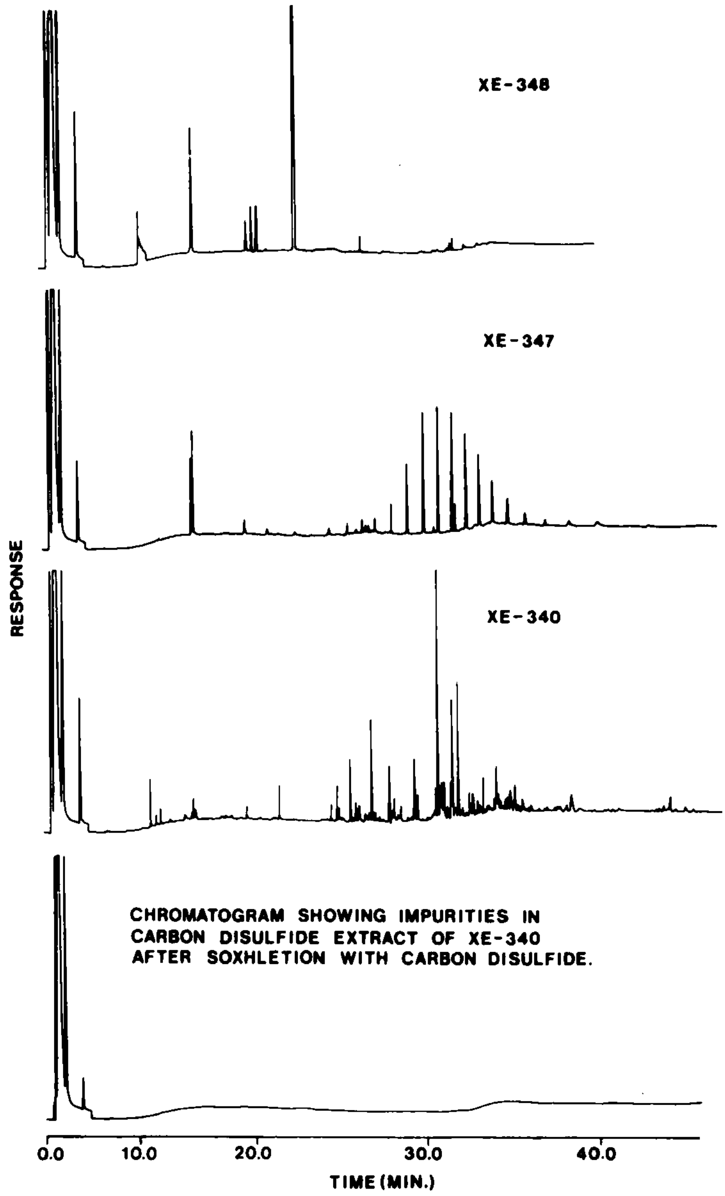

Figure 2 Chromatogram showing impurities in carbon disulfide extracts of XE-resins.

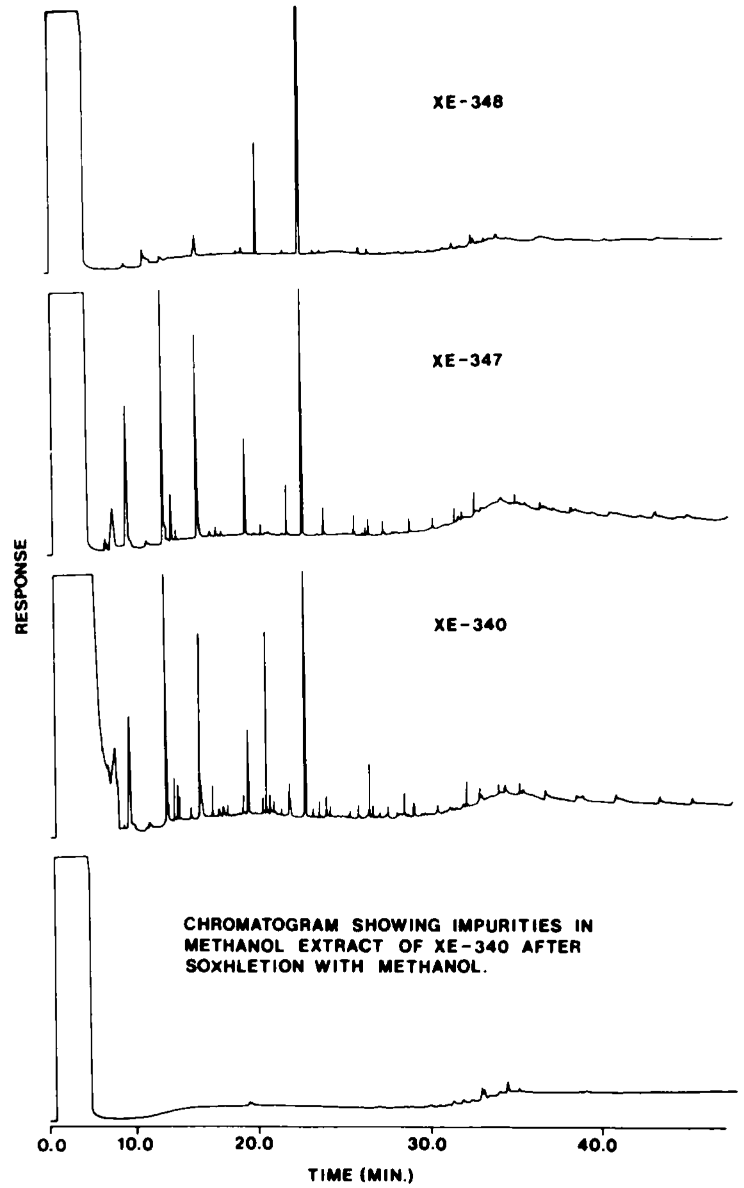

Figure 3 Chromatogram showing impurities in methanol extracts of XE-resins.

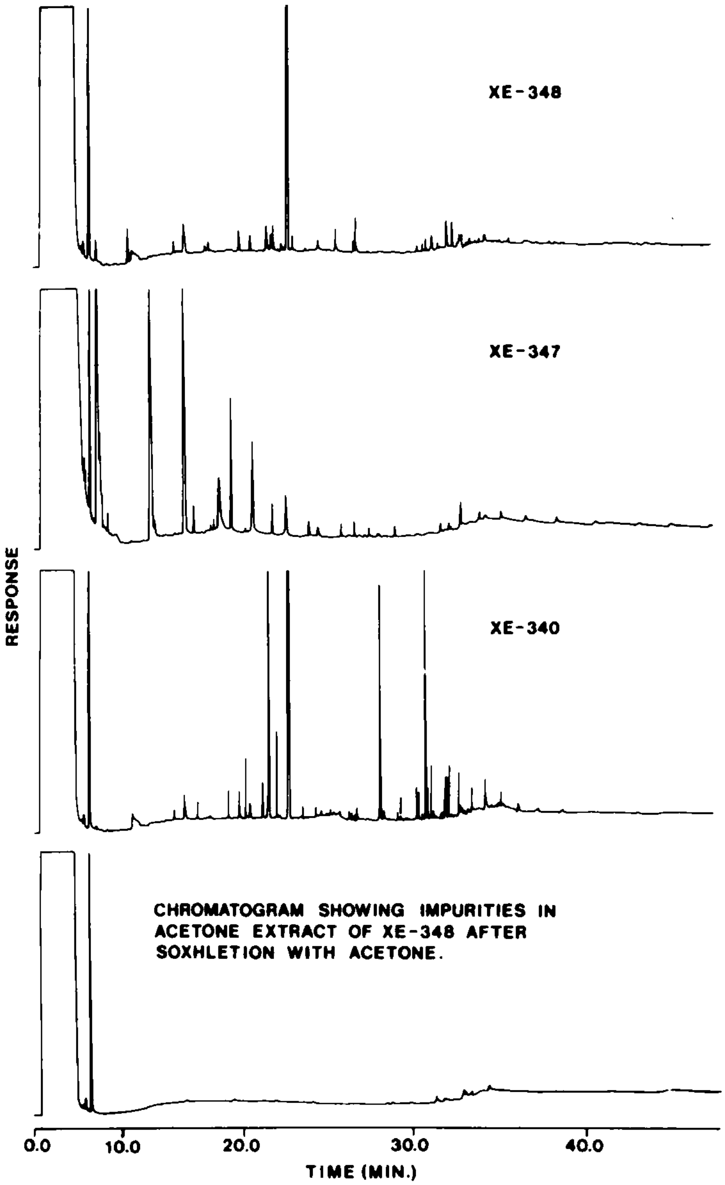

Figure 4 Chromatogram showing impurities in acetone extracts of XE-resins.

XE-348[28,29] from sulfonated, polymeric styrene-divinyl-benzene copolymer), most of the impurities in the polymer XE-348 were probably degraded and volatilized.

When carbon disulfide was used as the extraction solvent (Figure 2) after "exhaustive" soxhletion with toluene, only a smaller number of compounds similar to those found in the toluene extract were observed in the carbon disulfide extract of the XE-348 resin. However, in the case of XE-347 adsorbent, the number and the peak heights of many residues in the carbon disulfide extract were larger than those present in the toluene concentrates. Again, it is noteworthy that the blank GC trace of the XE-resins was very clean indicating that very few impurities could be further extracted by this solvent from these resins. As pointed out earlier, extraction with carbon disulfide was restricted only to the XE-resins.

When methanol was used for extraction of the resins a significantly reduced number of impurities most with smaller peak heights were detected in all the XE-resin extract concentrates as compared to those found in the toluene and carbon disulfide extracts (Figure 3). Similar to the observations made in the extracts of the previous two solvents, fewer number of impurities were identified in XE-348 adsorbent extract followed by XE-347 and XE-340.

Soxhlet extraction with methanol was followed by acetone and the acetone blank GC trace (Figure 4) gave a fairly clean baseline. It is apparent from the chromatograms of the extract concentrates of the XE-resins that some of the impurities which could not be extracted by the above solvents completely were desorbed by acetone. Most impurities are identical with those found in the toluene, carbon disulfide and methanol extracts. It is surprising that, in the XE-348 acetone extract concentrate, a larger number of sizeable peaks are observed at high temperature programming during gas chromatography than those present in the methanol extract.

When the acetone soxhlet-extraction was followed serially by diethyl ether and hexane, the extracts showed identical impurities but the peaks were fewer in number and considerably smaller in size.

Tables 1 to 3 list the impurities extracted from XE-340, XE-347 and XE-348 resins respectively by the six solvents. The XE-340 sorbent yielded 1151, 742, 1362, 191 and 113 μg/g of total residue in the extracts of toluene, carbon disulfide, methanol, diethyl ether, and hexane, respectively. It would seem that, using this sequence of solvents, more impurities were leached out by methanol and toluene although the identified impurities are more numerous in the carbon disulfide extract than in the others. The salient feature observed from this list of identified impurities in XE-340 resin is that several low molecular weight, aromatic hydrocarbons, several polycyclic aromatic hydrocarbons, some sulfur-containing aromatic hydrocarbons, phthalates, and several high-molecular weight aliphatic hydrocarbons were observed. Hunt and Pangaro[39] noted only polycyclic aromatic hydrocarbons which were also identified in the toluene and carbon disulfide extracts of XE-340 resin in this study. Also identified are benzoic acid derivative, elemental sulfur, some aromatic sulfur compounds, di-2-ethylhexyl phthalate, long chain fatty acids and their esters. It is surprising and noteworthy that long chain aliphatic hydrocarbons (C_{21} to C_{36}) were detected in this resin extract and they are also found in the carbon disulfide, diethyl ether and hexane extracts. Most of

Table 1 Impurities in different solvent extracts of XE-340

No.	*Compounds*	*Extraction solvents*				
		Toluene *1151*[a]	*Carbon disulfide* *742*[a]	*Methanol* *1362*[a]	*Ether* *191*[a]	*Hexane* *113*[a]
1	Benzoic anhydride or acid (?)	✓	—	—	—	—
2	Naphthalene	✓	✓	—	—	—
3	Trichlorobenzene isomer	—	✓	—	—	—
4	Benzo(b)cyclobuta(d)thiophene, 1,2-dicarboxylic anhydride-1,2,2a, 7b-tetrahydro (T)	✓	✓	—	—	✓
5	Trichloro benzene isomer	—	✓	—	—	—
6	Benzothiazole	—	✓	—	—	—
7	A nitrogen compound	—	✓	—	—	—
8	2-Methylnaphthalene	✓	✓	—	—	—
9	Methylthiophene isomer	✓	—	—	—	—
10	1-Methylnaphthalene	✓	✓	—	—	—
11	1-1′-Biphenyl	✓	✓	—	—	—
12	Methane, trimethoxy derivative (T)	—	—	—	✓	—
13	Nitrous acid, cyclohexylester (T)	—	✓	—	—	—
14	Diphenylmethane	✓	—	—	—	—
15	$C_{14}H_{12}$PAH	—	✓	—	—	—
16	N-Phenylaniline (T)	✓	—	—	—	—
17	2-Aminobiphenyl (T)	✓	—	—	—	—
18	A hydrocarbon	—	✓	—	—	—
19	A sulfur containing labile compound (?)	—	✓	—	—	—
20	2,6-di-Tertiarybutyl-(4-methylphenol) or (anisole)	✓	✓	—	—	—
21	1.1′-Diphenylethylene (T)	✓	—	—	—	—
22	2,2′-Dimethyl biphenyl	✓	—	—	—	—
23	3,3′-Dimethyl biphenyl	✓	—	—	—	—
24	A long chain hydrocarbon	—	—	—	✓	—
25	2-Methyl benzoyl derivative	✓	—	—	—	—
26	Di-ethylphthalate	—	✓	—	—	—
27	Carbonodithioic acid, S,S-dimethyl ester (T)	—	—	—	✓	—
28	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl (T)	—	✓	—	—	—
29	9-Fluorenone	✓	—	—	—	—
30	Di-benzothiophene	✓	✓	—	—	—
31	Phenanthrene	✓	—	—	—	—
32	Decanoic acid or its ester	—	✓	—	—	—
33	Anthracene	✓	✓	—	—	—
34	Benzene (1.1-dimethyl propyl) or benzene (1,1-dimethylbutyl) (?)	—	✓	—	—	—
35	2-Heptanone, -6 methyl	—	✓	—	—	—
36	1-Phenylnaphthalene	✓	✓	—	—	—
37	4,5-di-Phenyl-1,2,3-thiadiazole	✓	—	—	—	—
38	2-Propenoic acid, octyl ester	—	✓	—	—	—
39	A long chain hydrocarbon	—	✓	—	—	—
40	Undecanoic acid, methyl ester	—	✓	—	—	—
41	2-Phenylnaphthalene	✓	✓	—	—	—
42	1,2-di-Tolylethane	✓	—	—	—	—
43	A long chain hydrocarbon	—	✓	—	—	—
44	Molecular sulfur (S_8)	✓	✓	—	✓	✓

Table 1 (continued)

No.	*Compounds*	*Extraction solvents*				
		Toluene	*Carbon disulfide*	*Methanol*	*Ether*	*Hexane*
		1151[a]	*742*[a]	*1362*[a]	*191*[a]	*113*[a]
45	A labile sulfur compound	—	√	—	—	—
46	Fluoranthene or pyrene	√	√	—	—	—
47	2-Tolylnaphthalene	√	—	—	—	—
48	C_{21} hydrocarbon	—	√	—	—	—
49	A long chain hydrocarbon	—	√	—	—	—
50	Terphenyl isomer	√	—	—	—	—
51	1-Methylpyrene	√	—	—	—	—
52	C_{22} hydrocarbon	—	√	—	—	—
53	Benzofluorene	√	—	—	—	—
54	C_{23} hydrocarbon	—	—	—	√	—
55	A long chain hydrocarbon	—	—	—	√	—
56	Terphenyl isomer	√	—	—	—	—
57	Benzo(b)naphtho-2,1(d)thiophene (T)	√	—	—	—	—
58	Benzo(c)phenanthrene	√	—	—	—	—
59	C_{24} hydrocarbon	—	—	—	√	—
60	Hydroxylamine-o-decyl (or) Octane 1,1'oxybis (T)	—	—	—	—	√
61	An azaarene	—	√	—	—	—
62	A long chain hydrocarbon	—	—	—	√	—
63	Benz(a) anthracene (or) chrysene (or) triphenylene	√	√	—	—	—
64	Benz(a) anthracene or chrysene (or) triphenylene	—	√	—	—	—
65	C_{20} hydrocarbon	—	—	—	√	—
66	Di-2-ethylhexyl phthalate	√	√	—	√	√
67	1,1'-Binaphthyl (T)	√	—	—	—	√
68	C_{25} hydrocarbon	—	√	—	—	√
69	C_{26} hydrocarbon isomer	—	√	—	—	—
70	C_{27} hydrocarbon	—	√	—	—	—
71	A long chain hydrocarbon	—	√	—	√	√
72	Benzo(k)fluoranthene or perylene	√	—	—	—	—
73	C_{28} hydrocarbon isomer	—	√	—	—	—
74	C_{28} hydrocarbon isomer	—	√	—	—	—
75	C_{28} hydrocarbon isomer	—	√	—	—	—
76	C_{29} hydrocarbon isomer	√	√	—	—	—
77	1,1'; 3,1''; 3'',1''' Quarterphenyl (T)	√	—	—	—	—
78	A long chain hydrocarbon	√	—	—	—	—
79	A C_{31} hydrocarbon isomer	—	√	—	—	—
80	A C_{31} hydrocarbon isomer	√	√	—	—	—
81	A C_{32} hydrocarbon isomer	—	√	—	—	—
82	A C_{32} hydrocarbon isomer	—	√	—	—	—
83	A C_{33} hydrocarbon isomer	—	√	—	—	—
84	A C_{34} hydrocarbon isomer	—	√	—	—	—
85	A C_{34} hydrocarbon isomer	—	√	—	—	—
86	A C_{34} hydrocarbon isomer	—	√	—	—	—
87	A C_{36} hydrocarbon isomer	—	√	—	—	—
88	A phthalate	—	√	—	—	—
	And several unidentified compounds					

[a] Weight of residues (μg/g).

Note: Acetone extract analysis is not presented due to loss of sample prior to GC/MS analysis.

Table 2 Impurities in different solvent extracts of XE-347

No.	*Compounds*	*Extraction solvents*					
		Toluene	*Carbon disulfide*	*Methanol*	*Acetone*	*Ether*	*Hexane*
		116^a	*218^a*	*2350^a*	*212^a*	*51^a*	*103^a*
1	Benzo(b)cyclobuta(d)thiophene-1,2-dicarboxylic acid 1,2,2a,7b-tetrahydro or ester (T)	—	√	—	—	—	—
2	Carbonodithioic acid, S,S-dimethyl ester (T)	—	—	—	—	√	—
3	A hydrocarbon	—	√	—	—	—	—
4	Undecane, 4,8-dimethyl	—	√	—	—	—	—
5	1,1′-Biphenyl	—	√	—	—	—	—
6	A long chain hydrocarbon	—	√	—	—	—	—
7	Methane, trimethoxy (T)	—	—	—	—	√	√
8	A long chain hydrocarbon	—	√	—	—	—	—
9	4,5-octadien-3-one-2,2,7,7-tetramethyl (T)	√	—	—	—	—	—
10	Bicyclo-3,1,0-hexan-2-one-1,5-bis (1,1,-t-butyl)-3,3-dimethyl	—	√	—	—	—	—
11	A nitrogen containing compound	—	√	√	—	—	—
12	2,6-di-t-Butyl-(4-methyl phenol) or (anisole)	√	√	√	—	√	√
13	Furan-tetrahydro,2,4-dimethyl derivative (T)	√	—	—	—	—	—
14	Hexane-2,2,3,3-tetramethyl (T)	—	√	—	—	—	—
15	A hydrocarbon	—	—	√	—	—	—
16	3,4,5-trimethyl hexene-1 (T)	√	√	—	—	—	—
17	Butanoic acid, ethenyl ester (T)	—	—	√	—	—	—
18	Hydrazine-1.1′-diphenyl	√	—	—	—	—	—
19	A hydrocarbon	—	—	√	—	—	—
20	Furan tetrahydro-2,5 (or) 2,4-dimethyl	√	√	—	—	—	—

21	4-Heptanone-2-methyl or 4-octanone	—	√	√	—	—	—
22	A hydrocarbon	—	√	√	—	—	—
23	Undecanoic acid, methyl ester	√	—	—	—	—	—
24	Dibenzothiophene (T)	√	—	—	—	—	—
25	Anthracene	√	—	—	—	—	—
26	4,6,8-Trimethyl nonene-1	√	—	—	—	—	—
27	A long chain hydrocarbon	—	√	—	—	—	—
28	2,4,6-trimethyl, nonene-2 (T)	√	—	—	—	—	—
29	1-Phenylnaphthalene	—	√	—	—	—	—
30	Molecular sulfur (S_8)	—	√	√	√	√	√
31	C_{21} hydrocarbon	—	√	—	—	—	√
32	C_{22} hydrocarbon	—	√	—	—	—	√
33	C_{23} hydrocarbon	—	√	—	—	—	√
34	C_{24} hydrocarbon	—	√	—	—	—	√
35	C_{25} hydrocarbon	—	√	—	—	—	√
36	Di-2-ethylhexylphthalate	—	—	—	—	—	√
37	C_{26} hydrocarbon	—	√	—	—	—	√
38	C_{27} hydrocarbon	—	√	—	—	—	√
39	C_{28} hydrocarbon	—	√	—	—	—	√
40	C_{29} hydrocarbon	—	√	—	—	—	√
41	C_{30} hydrocarbon	—	√	—	—	—	√
42	C_{31} hydrocarbon	—	√	—	—	—	√
43	C_{32} hydrocarbon	—	√	—	—	—	√
44	C_{33} hydrocarbon	—	√	—	—	—	√
45	C_{34} hydrocarbon	—	—	—	—	—	√
	and several unidentified compounds						

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*Weight of residues (μg/g).

Table 3 Impurities in different solvent extracts of XE-348

No.	Compounds	Extraction solvents					
		Toluene 140^a	Carbon disulfide 1600^a	Methanol 43^a	Acetone 3996^a	Ether 1665^a	Hexane 1289^a
1	Benzoic acid derivative (T)	—	—	√	—	—	—
2	Ethanol 2,2′-oxy bis (T)	—	—	√	—	—	—
3	Ethane-1,2-bis (methyl thio) (T)	—	—	√	—	—	—
4	Naphthalene	√	—	—	—	√	—
5	Biphenyl	—	√	—	—	—	√
6	2-Propanol-1-ethoxy (T)	—	—	—	—	√	—
7	Methane, trimethoxy (T)	—	√	—	—	—	—
8	Dimethylbiphenyl isomer	—	—	√	—	√	—
9	Benzoic acid	√	—	—	—	—	—
10	Di-2,6-t-butyl-(4 methyl phenol) or (anisole)	—	√	√	√	—	—
11	Carbonodithioic acid,-S,S-dimethyl ester (T)	√	—	√	√	—	—
12	Benzene-1,1′-thio-bis (methylene)bis (T)	√	—	—	—	—	—
13	Benzene-3-pentyl	—	—	—	√	—	—
14	Benzene,1,1′-thio-bis (methylene) (T)	√	—	—	—	—	—
15	Nitric acid, heptyl ester (?)	—	—	—	√	—	—
16	Di-butyl phthalate	—	—	—	√	—	—
17	Molecular sulfur (S_8)	√	√	√	√	√	√
18	An aromatic hydrocarbon	—	—	—	√	—	—
19	Branched long chain hydrocarbon	—	—	—	√	—	—
20	Aliphatic substituted benzene (T)	—	—	—	√	—	—
21	Nonanedioic acid, bis-2-ethylhexyl ester (T)	√	—	—	—	—	—
22	4 nonanol,2,6,8-trimethyl (T)	—	—	—	√	—	—
23	Hydroxylamine-o-decyl (T)	—	—	—	√	—	—
24	Benzene-1-octadecyl	—	—	—	√	—	—
25	Di-2-ethylhexyl phthalate	√	—	—	√	—	—
26	Aromatic hydrocarbon with aliphatic chain	—	—	—	√	—	—
27	Octane-1-chloro (T)	—	—	—	√	—	—
	and several unidentified compounds						

[a] Weight of residues (μg/g).

the polycyclic aromatic hydrocarbons are surmised to have been formed during low temperature pyrolysis (300 °C) of the XE-resin and these are trapped in the pores of the carbonaceous beads.[27-29]

In the XE-347 resin extract, the residue weights were 116 (toluene), 218 (carbon disulfide), 2350 (methanol), 212 (acetone), 51 (diethyl ether) and 103 (hexane) μg/g (Table 2). It is noteworthy that fewer polycyclic aromatic hydrocarbons and sulfur compounds were identified in the XE-347 resin residues. However, the aliphatic hydrocarbons are much more prevalent and prominent in the XE-347 resin residues than in the XE-340 resin. Moreover, as observed in the XE-340 resin, these aliphatics are all found in the carbon disulfide and hexane extracts. It is obvious that, even though the pyrolytic conditions were severe (500 °C), the long chain aliphatic hydrocarbons are still persistent and held firmly in the resin matrix.

The residue weights in various solvent extracts of XE-348 resin were 140 (toluene), 1600 (carbon disulfide), 43 (methanol), 3996 (acetone), 1665 (diethyl ether) and 1289 (hexane) μg/g (Table 3). From the list of compounds it can be seen that only a few aromatic compounds were definitely identified and the maximum weight of the residues was contributed to by elemental sulfur. Numerous compounds (about 40%) were unidentified in these extracts. It would appear that XE-348 resin formed at a very high temperature (800 °C) by the pyrolysis of sulfonated polystyrene-divinyl benzene copolymer has undergone maximum carbonization. This is obvious from its dull greyish-black, graphitic appearance compared to the shiny appearance of XE-340 and XE-347 resin beads.

It should also be expected that, at high temperatures, thermolysis engenders free radicals on the aromatic nucleus in the styrene moiety which can collapse to form poly aromatic structures and benzo- and dibenzo-thiophenes. Moreover, during pyrolysis, the sulfonic acid moiety in the parent resin is apparently reduced to sulfur via the sulfones. When the sulfur atoms are expelled from the carbonized polymer matrix, large pores are formed in the resin. It is also to be anticipated that, as the pyrolytic temperature is increased, the surface activity is enhanced and hence the order of adsorption efficiency as expected should be XE-348 > XE-347 > XE-340. Furthermore, the presence of di-2,6-t-butyl (4-methyl phenol or anisole) and the phthalates are exogenous to the resins as previously reported.[47]

Use of Radio-labelled Compounds

Most of the validation studies on the accumulative efficiency of sorbents have used non-radioactive compounds, gas and liquid chromatographic and/or mass spectrometric techniques as the final determinative step and usually employ careful clean-up steps, use of external or internal standards, etc. We have resorted to ^{14}C-labelled compounds, since radioactivity measurement provides a simple analytical tool for the determination of the components in question. Other compelling factors which influenced us to the use of labelled compounds for this study are: (a) it is easier to study the effect of high-level loading of unlabelled compounds on the recovery of low-level ^{14}C-labelled organic contaminants. [Note: Adsorption of several individual compounds have been studied using these five resins by Malaiyandi and

Shah[53].] (b) It enables us not only to evaluate the entire analytical scheme but also to examine the individual phases in the scheme. Furthermore, in order to determine the amounts of the solutes in the "exhausted" aqueous effluent, high concentrations of the solutes have been employed.[55]

The use of radioactive organics has enabled us to follow the amount of the sorbate in question (if present) in the "exhausted" aqueous effluent and to determine directly the "break-through" by measuring the radioactivity of effluent samples without further concentration and clean-up. Finally this analytical tool provides an alternative method to obtain an indirect evidence for the recovery and irreversibly adsorbed amounts of compounds in question under the elution conditions by taking into account the mass balance.

In this study, we have specifically selected ^{14}C-labelled γ-BHC, FL, DEHP and 2,4-DCP as representative of a class of environmental contaminant. Each ^{14}C-labelled compound spike (*ca.* 3.6 μg/L) was added along with ca. 200 μg/L of the other three "cold" compounds in order to assess the influence of these contaminants on the adsorption/desorption/recovery efficiency of the sorbents. [Note: The levels of "cold" materials have not been determined because we were concerned only with the radio-labelled materials adsorption.]

Choice of Solvents

Most recovery studies by resin sorption have used one or two solvents for desorbing organics from the resin sorbents. The most effective eluents are those which, due to the reversible nature of the interaction between the sorbate and sorbent, achieve maximum quantitative desorption of the solutes from the resin.[14,15,56,57] In order to maximize the desorption efficiency, a gamut of solvents depending on their dielectric constant ε and volatility was considered. In this study we have used a reverse order of polarity for elution: methanol ($\varepsilon_{20} = 32.63$), acetone ($\varepsilon_{20} = 20.7$), diethyl ether ($\varepsilon_{20} = 4.33$) and hexane ($\varepsilon_{20} = 1.89$). Furthermore, these solvents have been used previously in most studies concerned with desorption of organics from XAD-resins.

Recovery Studies: Elution with Solvents

After percolation of the spiked water samples through the fixed-bed adsorbents and completely draining the aqueous layer, the moist resins were eluted with known volumes of methanol, acetone, diethyl ether and hexane. The elution pattern of γ-BHC from the five resins (XAD-2, XAD-7, XE-340, XE-347 and XE-348), using the above four solvents is shown in Figure 5. Under these experimental conditions and with the chosen order of solvent polarity, γ-BHC was quantitatively eluted by methanol and acetone from XAD-2, XAD-7 and partially from XE-340. In the case of XE-347, although acetone seems to be the best eluent, inadequate desorption was observed. However, adequate desorption of this pesticide could not be achieved from XE-348 with any of the solvents used.

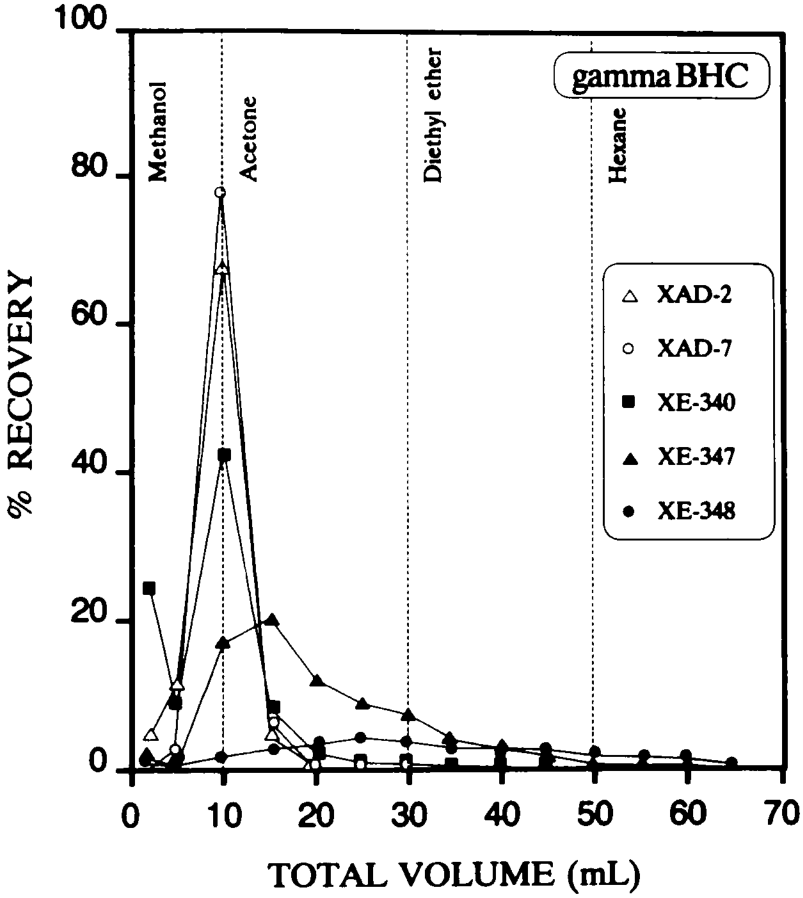

Figure 5 Serial elution profile of gamma-BHC from the five resins by four solvents.

In the case of FL (Figure 6), as with γ-BHC, this aromatic hydrocarbon is almost completely desorbed from XAD-2 and XAD-7 with methanol and acetone. Desorption from XE-340 is comparatively poor and again is achieved primarily with acetone. None of the four solvents is capable of achieving desorption of FL from XE-347 and XE-348.

The elution pattern of DEHP (Figure 7) is more like γ-BHC than FL. Similar to γ-BHC, this phthalate ester is apparently desorbed from XAD-2, XAD-7 and XE-340 sorbents primarily by acetone, but the percent desorption of DEHP is low compared to γ-BHC and FL. Moreover all the four solvents are poor eluents for DEHP from XE-347 and XE-348 resins.

Figure 8 shows the desorption behavior of 2,4-DCP from the five sorbents using the four solvents. It can be seen that this phenol can be quantitatively leached from XAD-2 and XAD-7 by methanol and acetone. Methanol, diethyl ether and hexane show poor eluting power for 2,4-DCP from XE-340. Again, none of the four solvents is capable of desorbing this phenol from XE-347 and XE-348.

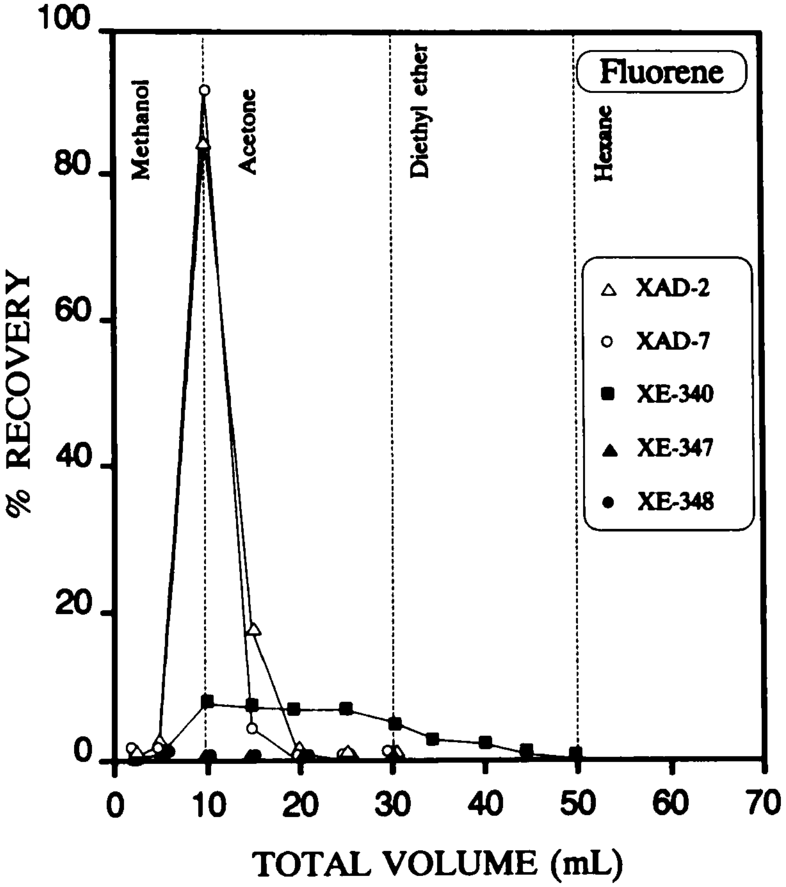

Figure 6 Serial elution profile of fluorene from the five resins by four solvents.

The absorption of the above four radio-labelled model compounds were investigated under dynamic frontal chromatographic conditions by allowing the fortified aqueous samples to percolate through the fixed bed of the five resins in individual columns at a flow rate of 1 BV (av. 5 mL/min). As indicated earlier, each water sample spiked with ^{14}C-labelled compound was doped with known amounts of the other three "cold" materials in order to understand the effects, if any, of high level cohorts on the adsorption/desorption efficiency of the five resins.

Table 4 shows the percent content of the ^{14}C-labelled components and the average of these four components in the "exhausted" aqueous effluents from each resin column. It would appear that γ-BHC, FL and 2,4-DCP were adsorbed and retained by all the resins >97% when *ca.* 3.6 μg/L of these model radioactive compounds were allowed to percolate through *ca.* 4.6 g (5 mL) of the resins. This level would represent the amount in about 10 L of many environmental aqueous samples. However, in the case of DEHP, the average percent DEHP in the effluents from XAD-2, XAD-7 and XE-340, XE-347 and XE-348 were 19.2, 36.5,

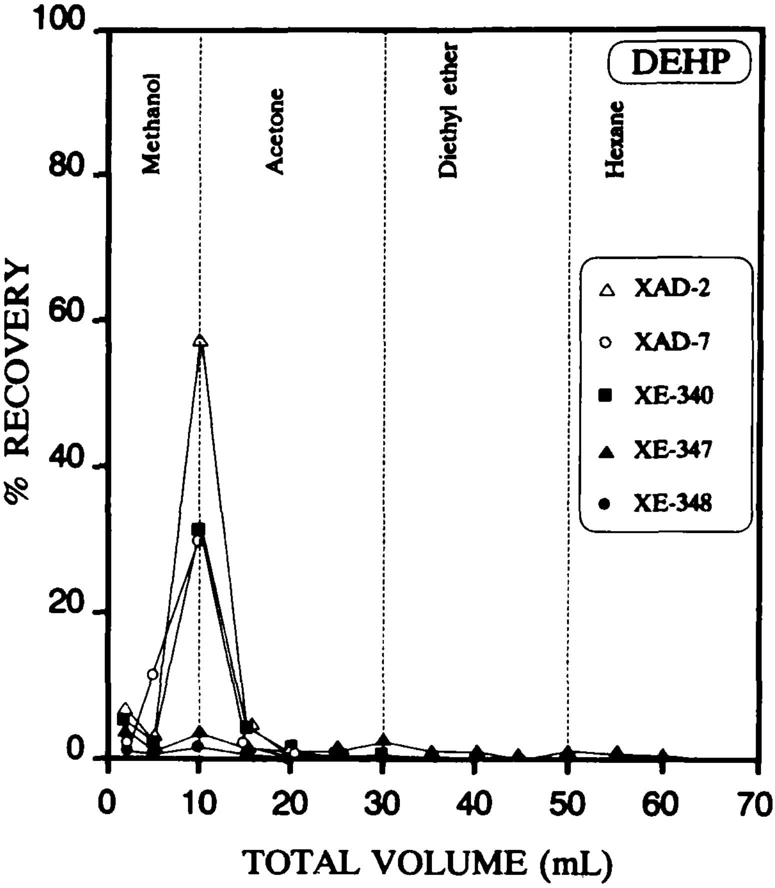

Figure 7 Serial elution profile of DEHP from the five resins by four solvents.

35.7, 24.2 and 27.8% respectively based on the radioactivity content (34.8%) after 24 hr period sample holding time. It is apparent that, for the adsorption and retention of DEHP, XAD-2 is the best among the five resins under investigation and XAD-7 and XE-340 seem to show similar accumulation capacity (≈64%). Furthermore, XE-347 and XE-348 have similar effluent DEHP levels (24.2% and 27.8% respectively). It is probably a fact that DEHP may need a longer contact time. This observation also suggests that, although DEHP is fairly non-polar and has low solubility[50] in water, there is an apparent unfavourable partition coefficient with respect to the resin in spite of the low flow rate (1 BV/min).

[Note: In this study, it was observed that the measured concentration of DEHP was about 72% of the spiked level at 3.6 μg/L in 3.0 L aqueous solution in 1 min; after 30 min, a further drop in concentration was observed. After the 24 hr period, the concentration was apparently steady at 34.8% of the original spiked level. This concentration of DEHP was used in this study. Similar observations were made by Derenbach *et al.*[58] at 100 μg/L level. For additional data see Table 5.]

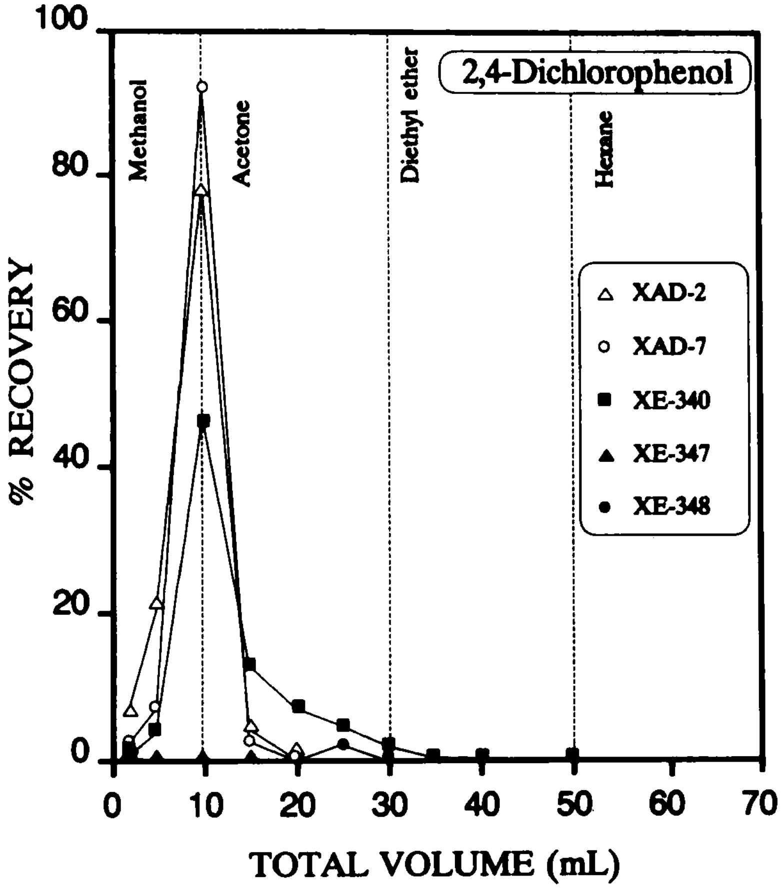

Figure 8 Serial elution profile of 2,4-dichlorophenol from the five resins by four solvents.

Using XAD-2 resin, van Rossum and Webb[59] showed that, at 50 μg/L concentration of DEP-spiked aqueous solution, the effluent contained 43% DEHP, but Chriswell *et al.*[56] noted the absence of this ester in the effluent from the percolation of 100 μg/L DEHP solution. The present study clearly demonstrates that none of these resins are capable of quantitatively retaining DEHP, and a significant "break-through", was observed confirming the findings of Derenbach *et al.*[58] and van Rossum and Webb.[59] It is to be noted that there is an apparent overloading of the resin columns in the studies of Derenbach *et al.*[58], and van Rossum and Webb.[59]

Since the spiked levels of DEHP were decreasing during the storage period, it became necessary to investigate the loss of these four radio-labelled compounds, if any, during sample storage. Musty and Nickless[60] have reported that about 2% of lindane was adsorbed on the inner walls of the glass container. It was also observed[59] that DEHP was sorbed on the walls of the container to the extent of 22%. Similar observations were also made by Derenbach *et al.*[58]

Table 4 Percent concentration of sorbates in effluents from column beds

Sorbents	*Compounds*			
	γ-BHC	*FL*	*DEHP*	*2,4-DCP*
XAD-2	1.6	1.1	20.1	1.6
	0.4	1.5	18.2	0.9
Average	1.0	1.3	19.2	1.3
XAD-7	1.5	3.3	40.9	2.6
	0.4	1.6	32.0	1.9
Average	1.0	2.5	36.5	2.3
XE-340	2.1	1.4	30.6	2.5
	0.4	2.2	40.8	3.3
Average	1.3	1.8	35.7	2.9
XE-37	2.6	2.0	24.4	1.8
	0.3	3.6	23.9	1.1
Average	1.5	2.8	24.2	1.5
XE-348	3.3	1.8	30.6	1.9
	0.7	2.4	25.0	1.3
Average	2.0	2.1	27.8	1.6

Table 5 Absorption of ^{14}C-labelled compounds (at 60 μg/mL) on walls of glass containers

Compound	*Run*	*Counts in original solution (dpm/min)*	*Amount absorbed (dpm/min)*	*Percent absorbed*	*Average percent*
γ-BHC	1	28,880	428.1	1.5	—
	2	716,120	3994.0	0.56	1.0
FL	1	20,840	591.4	2.8	
	2	21,200	582.6	2.7	2.8
DEHP	1	6,430	1259.0	19.5	
	2	8,130	1140.7	14.0	16.8
2,4-DCP	1	38,635	205.0	0.5	
	2	37,460	205.5	0.55	0.53

De Raat and van Ardenne[62] noted that radio-labelled dioctyl phthalate was adsorbed on to XAD-2 and XAD-7 only to the extent of *ca.* 11% and 13% respectively and these investigators were able to recover about 96% of the sorbed ester from the resins. Similarly, low recoveries were reported by van Rossum and Webb[59] from XAD-2 resins. On the contrary, Junk *et al.*[49] and Chriswell *et al.*[56] reported *an overall recovery* of DEHP from XAD-2 resin at 88% and 76% respectively using 100 ppb solutions. Derenbach *et al.*[58] achieved an extraction efficiency of 67.7% for the ^{14}C-labelled phthalate ester from XAD-2 resin from a 25 μg/L spiked aqueous solution. In the present study, nearly 97.8% recovery was obtained from XAD-2 and this recovery is better than the value (67.7%) reported by Derenbach *et al.*[58] and confirmed by Malaiyandi and Shah.[53]

Table 6 Accumulation and percent recovery by desorbing the four compounds from five sorbents

Sorbents	*Compounds*				*Average*
	γ-BHC	*FL*	*DEHP*	*2,4-DCP*	
XAD-2	87.5	112.0	105.7[a]	109.1	96.8
	91.3	103.0	89.8	112.0	
Average	89.4	108.0	97.8	110.0	
XAD-7	86.7	99.1	79.3	108.2	89.6
	94.3	101.0	56.1	101.0	
Average	90.5	100.1	67.7	104.6	
XE-340	87.9	43.7	81.0	74.7	72.3
	91.5	44.3	74.9	80.5	
Average	89.7	44.0	78.0	77.6	
XE-347	74.3	1.1	42.1	5.9	30.8
	80.3	0.5	40.5	0.8	
Average	77.3	0.9	41.3	3.4	
XE-348	20.6	2.2	7.3	0.3	8.3
	24.9	0.3	10.4	0.2	
Average	22.8	1.3	8.9	0.3	

[a] Based on the concentration of sorbed amounts of DEHP on the resins.

In order to verify these observations and to obtain an accurate mass balance of these materials in this study, an investigation on the adsorption of these compounds on the inner walls of the glass containers was undertaken by spiking known amounts of the radiolabelled model compounds and determining their radioactivity after a 24 hr period. Table 5 shows the average percent sorption of these compounds on the walls of the containers. It is apparent that the adsorption of γ-BHC (at low and high levels), FL and 2,4-DCP on the container walls was <3%, whereas adsorption of DEHP was quite significant (16.8%) in less than 1 min. Hence, to minimize adsorption, it was decided to silanize the inner walls of the containers and the adsorption columns with dimethyldichlorosilane in subsequent experiments.[53,61]

Table 6 shows the detailed summary of the desorption of the four ^{14}C-labelled compounds by the solvent train from the five resins. It can be seen that about 90% of γ-BHC is eluted out from XAD-2, XAD-7 and XE-340 (and effluent concentration + container wall adsorption constitutes only 2%). It has been reported that different recoveries were obtained from XAD-2 (>95%,[43,49] 45%[60] and Osterroht[63] obtained only 25% recovery from marine water spiked with γ-BHC). Moore and Karasek[43] obtained 91% γ-BHC using XAD-7 adsorption. Yeboah and Kilgore[37] recovered 95% γ-BHC from XE-340 using hexane extraction. In the case of XE-347 and XE-348, γ-BHC percent recoveries by solvent elution in the present study were 77.3 and 22.8% respectively. The percent recovery of this pesticide from XE-347 using the solvent train is not adequate to warrant its use as an accumulative sorbent for water organics. However, the solvent extraction of γ-BHC from XE-348 is completely ineffective.

Table 7 Percent sorbates eluted by methanol and acetone from the resins[a]

Sorbents	*Compounds*			
	γ-BHC	*FL*	*DEHP*	*2,4-DCP*
XAD-2	99.8	99.0	91.4	99.8
XAD-7	99.8	99.8	99.6	99.9
XE-340	97.8	70.7	97.8	96.0
XE-347	78.1	73.3	54.7	91.2
XE-348	44.3	60.8	68.5	48.6

[a] Based on amounts totally desorbed from the resins by solvent extraction.

Recoveries of FL from XAD-2 and XAD-7 were excellent (108% and 100% respectively) but the recovery from XE-340 resin was only 44%, and was negligible (*ca.* 1.0%) from both XE-347 and XE-348 resins. It is also noteworthy that Junk *et al.*[49] recovered only 84% of FL from XAD-2 by diethyl ether extraction. It would appear that both XAD-2 and XAD-7 have proved to be excellent sorbents for FL and may be used for the pre-concentration of similar aromatic hydrocarbons when present in water; although XE-340, XE-347 and XE-348 resins behave as excellent adsorbents, they do not meet the pre-requisites essential to pre-concentrate some of the aromatic hydrocarbons from aqueous samples because of their poor desorption behaviour.

The extraction performance of the five resins for DEHP and the four solvent desorption capacities indicates that XAD-2 resin is the most superior sorbent to pre-concentrate DEHP (97.8% which is equivalent to ≈78.6% after taking into account the effluent concentration (Table 5) and assuming the spike concentration after 24 hr to be 100%). This performance is followed by XE-340 (78.0%), XAD-7 (67.7%), XE-347 (41.3%) and XE-348 (8.9%). Once again, it is observed that, similar to γ-BHC and FL, DEHP is also strongly sorbed onto XE-348 resin.

When the recovery of 2,4-DCP is considered, the extraction efficiency of XAD-2 and XAD-7 seems to be quantitative (>90%) and that of XE-340 is 77.6%. However, extremely low desorption was observed for XE-347 (3–4%) and XE-348 (0.3%). Chriswell *et al.*[56] reported that only 27% of this phenol was recovered from XAD-2 using a fortified sample containing 0.1 μg/L of the phenol. The recoveries reported for this phenol in present study from XAD-2 and XAD-7 are quantitative at 3.6 μg/L level contrary to the finding of Chriswell *et al.*[56]

When the average recovery of the four model compounds are examined, it is apparent that the extraction efficiency follows the order XAD-2>XAD-7>XE-340≫XE-347⋙XE-348. Blok *et al.*[35] made similar observations when the recovery of 19 model compounds were studied using several adsorbents including XAD-2, XE-340 and XE-348.

From a cursory analysis of Figures 5 to 8, it would appear that both methanol and acetone (the order chosen in this study) were found to extract the maximum amount of the four ^{14}C-labelled compounds from the five sorbents. Table 7 shows that these compounds are eluted primarily by methanol and acetone from XAD-2 and XAD-7 resins. Maximum extraction of all the compounds is noted in the

Table 8 Sorbents using percent recovery of the four compounds from XE-Ambersorb® carbonaceous sonication with solvent mixtures

Sorbents	*Compounds*			
	γ-BHC	*FL*	*DEHP*	*2,4-DCP*
Hexane: Acetone 1:1 (v/v)				
XE-340	9.7	0.6	7.8	0.3
	12.1	0.2	5.1	0.8
Average	10.9	0.4	6.5	0.6
XE-347	3.0	0.7	15.4	0.2
	4.1	1.2	14.5	0.6
Average	3.6	1.0	13.5	0.4
XE-348	0.3	5.4	0.0	3.4
	0.6	5.6	0.2	2.9
Average	0.5	5.5	0.1	3.2
Benzene: Carbondisulfide 3:2 (v/v)				
XE-340	RN	RN	0.0	5.6
			—	5.5
Average			0.0	5.6
XE-347	RN	RN	8.2	8.9
			RN	10.4
Average			8.2	9.7
XE-348	RN	RN	23.6	11.3
			RN	11.8
Average			23.6	11.6

RN: Recovery negligible.

eluates of the two solvents from XE-340 resin with the exception of FL (70.7%). XE-347 sorbent seems to give low recovery of DEHP (54.7%) in the two solvents; and consistently low recoveries are observed for these compounds from XE-348 sorbent.

It has been observed that all the XE-carbonaceous resins, especially XE-347 and XE-348, gave low recoveries for all the four compounds with the solvent train extraction procedures. In order to maximize the recovery, an attempt was made to leach out these compounds by sonication serially with 1:1 (v/v) solvent mixtures of hexane–acetone and benzene–carbon disulfide. The results are shown in Table 8.

It can be seen that with sonication, some radio-labelled γ-BHC was desorbed from XE-340 (10.9%), XE-347 (3.6%) and XE-348 (0.5%) by hexane–acetone mixture. Similarly, this mixture eluted DEHP only to the extent of 6.5% from XE-340, 13.5% from XE-347 and a negligible amount from XE-348 resin., Moreover, only small recoveries were noted for FL and 2,4-DCP.

When the three resins were then sonicated in a benzene–carbon disulfide mixture only negligible recovery was noted for γ-BHC and FL. However, after extraction with hexane–acetone mixture, more than 90% γ-BHC and DEHP were extracted from XE-340. In the case of DEHP, the resins XE-347 and XE-348 gave about 8% and 23% respectively., 2,4-DCP was recovered to the extent of 5.6%, 9.7% and 11.6% from XE-340, XE-347 and XE-348 sorbents respectively.

CONCLUSION

The present study indicated that γ-BHC, FL and 2,4-DCP radio-labelled model environmental contaminants were near quantitatively accumulated by the five adsorbents. These sorbates could be recovered >90% by elution with the solvent train only from XAD-2 and XAD-7. The resin XE-340 is superior to the other two carbonaceous resins as lower recoveries were noted for XE-347 and XE-348 resins. The carbonaceous resins are hard, possess excellent adsorption properties and can be kept clean. These resins should prove equally good or better adsorbents than XAD resins for the concentration of trace organics in water if a suitable elution technique were developed. From the recovery of the labelled compounds and their concentrations in the effluents, it seems that the presence of high-level unlabelled contaminants do not influence the adsorption or recovery of the particular component in question.

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