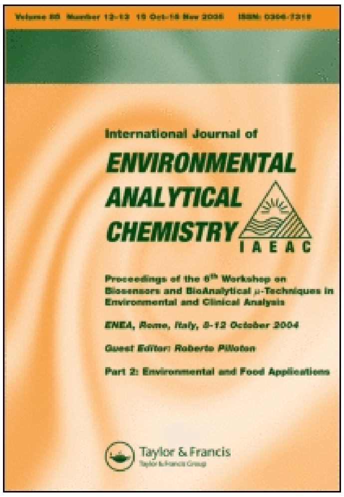

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COMPARATIVE ENRICHMENT CAPABILITIES OF SOME CARBONACEOUS AND MACRORETICULAR RESINS USING SELECTED RADIOACTIVE MODEL COMPOUNDS IN FORTIFIED AQUEOUS SAMPLES

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The concentration efficiency of synthetic macroreticular resins, XAD-2 and XAD-7 and carbonaceous resins, XE-340, XE-347 and XE-348 was evaluated and compared using trace levels of eight radioactive model environmental contaminants present in aqueous medium. Influences of chemical functionalities of the solvents, physical characteristics of the sorbents, and pH of the aqueous medium on sorption of the model compounds were investigated under frontal dynamic chromatographic conditions. The elution behavior of these sorbates and desorption properties of the polymer adsorbents with respect to solvents of different polarities were studied.

In the case of the organochlorine pesticide, lindane, the sorption abilities of XAD-2, XAD-7, and XE-348 were nearly quantitative (>97%) at the influent pHs of 3.0 and 5.6; but, XE-340 showed nearly 95% average sorption of lindane at both pHs, whereas, with XE-347, ca. 97% and 92% respective adsorptions were observed at the influent pHs of 3.0 and 5.6. The sorbed lindane was eluted >90% from XAD-2 and XE-340 at both pHs of the influent, and from XAD-7 (pH 3.0), XE-347 and XE-348 (pH 5.6). Lower recoveries were observed for XAD-7 (pH 5.6) and XE-347 and XE-348 (pH 3.0).

When the influent pHs were 3.0 and 5.65, all the chosen resins had quantitatively sorbed the hexachlorobiphenyl; but at pH 5.65, the statistical aberration was more pronounced than at pH 3.0. The sorbed chlorinated biphenyl was eluted >90% from all the resins using a battery of solvents and the standard deviation was high when the influent pH was 5.65.

As previously observed, di-2-ethylhexyl phthalate was not effectively accumulated on all resins and between ca. 18–57% of this plasticizer was found in the effluents from the resin columns indicating inefficient mass transfer from aqueous medium. Marked pH effects were observed on the adsorption behavior of this phthalate ester on the resin sorbents. Desorption of the sorbed phthalate ester for the resins was found to be quantitative from the accountable recoveries.

In the case of polycyclic aromatic hydrocarbon, fluorene was quantitatively sorbed onto the five resins. Both XAD-2, and XAD-7 showed quantitative recoveries, and the pH of the aqueous medium did not influence adsorption/desorption efficiency. However, in the case of XE-resins, XE-340 gave quantitative recovery for fluorene whereas poor recovery of this polycyclic aromatic hydrocarbon was observed for the resins XE-347 and XE-348. When sorption of benzo(a)pyrene is considered, accumulation of this polycyclic aromatic hydrocarbon onto all the resins seems to be somewhat dependent on the influent pH. Adsorption at pH 3.0 was quantitative for all resins, whereas, at the influent pH of 5.65 XAD-7, XE-340 and XE-348 showed inferior sorption efficiency to XAD-2 and XE-347. The sorbed aromatic was quantitatively released from XAD-2 and XAD-7, whereas, only an average of 60% was eluted from XE-340. Very low recoveries, however, were obtained from XE-347 and XE-348.

In the case of polar organics, namely, 2,4-dichlorophenol, 2,4-dichlorophenoxy acetic acid, and

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2,4-dichloroaniline, the enrichment efficiency follows the order, XAD-2≈XAD-7>XE-340≫XE-347>XE-348. As expected, the pH of the aqueous media of these polar compounds has in some cases definitely influenced the adsorption/desorption capacity of these resins and especially in the case of 2,4-dichlorophenoxy acetic acid, extremely low adsorption was noted for XAD-7 and XE-340 at the influent pH of 5.54.

INTRODUCTION

The ubiquity of innumerable organics in surface, underground and finished waters contributes substantially to water pollution problems. Some of these contaminants are very persistent and some are sparingly soluble in water, hence occurring in extremely low concentrations. Depending on the degree of water processing, they surreptitiously find their way into finished waters. Even at these low levels, the recognition and partial identification of these organics have caused concern in reference to their potential toxic properties to aquatic fauna and flora, and may constitute a health hazard to terrestrial beings, including humans.

The sources of these potentially toxic anthropogenic substances have been attributed to the effluents from industries, agricultural run-offs and to chlorine disinfection at water treatment facilities.[1–8] Cheh *et al.*[9] have clearly demonstrated the formation of non-volatile mutagens during chlorine disinfection of treated waters and very little is known about the potential adverse effects on human health due to these non-purgeable organic residues derived from chlorine disinfection. Furthermore, several researchers have suggested that non-volatile acidic and neutral residues might contribute significantly to the mutagenic potential of "finished" waters.[10–13]

Numerous reports have stressed the health implications of the potential toxicants and the importance and generation of an adequate data base to decipher the toxicity of these noxious substances.[14–18] The genotoxic potential detected in drinking water is only an indicator of potential human health risk. Although the characteristics of mutagens in drinking water have been described in terms of polarity, volatility, etc., the exact chemical identity of many of these compounds is still unknown.[15,19] Furthermore, many of the toxic contaminants so far identified in potable water are usually present below parts per million (ppm) range and the mutagenic potential is accounted for only by a small fraction ($<10\%$) of the total mutagenic activity.[20] To substantiate the health risk estimates related to consumption of such finished water for regulatory purposes, it is very essential to preconcentrate these pollutants for the isolation, quantitation and identification of particular component(s) from the complex mixture for the assessment of their potential hazard by biological testing.

Several reviews and research reports have detailed the efficacy of the currently available procedures for accumulating ultra trace levels of complex organic mixtures by stripping large volumes of water.[21–24] Among these procedures the adsorption technique using synthetic solid sorbents has been most widely used. In the class of synthetic polymeric sorbents, XAD-macroreticular resin beads have been used for a large number of applications for the solid phase extraction of organics from a variety of aqueous matrices including biological and pharmaceutical fluids; and these are comprehensively and concisely reviewed by Dressler[25] and Junk.[26] Among the XAD-resins, XAD-2 is the most exhaustively studied for a variety of applications.

XAD-resins are macroporous, rigid, polymeric adsorbents with unusual chemical stability and high sorption capacity for polar and nonpolar organics from aqueous samples. These resins have the following advantages: They are (a) relatively inexpensive; (b) commercially available in varying pore sizes with different polarities and surface areas; (c) less affected by pH variations; (d) capable of easy desorption of sorbates and facile regeneration (sometimes even during elution of the sorbates) and (e) stable at high temperatures ($<250\,°C$) and ambient pressures.

The carbonaceous Ambersorb® XE-resins are recent incumbents of the synthetic resin series and are introduced to replace activated carbon, because of their comparable adsorption properties.[2–7] The general characteristics of XAD-2, XAD-7, XE-340, XE-347 and XE-348 have been adequately summarized.[28]

So far, investigations related to XE-carbonaceous resins were primarily devoted to obtain data on adsorption isotherms and kinetics of adsorption in order to unravel the mechanisms of adsorption.[29–35] Very little information is available on the actual applicability of the three carbonaceous resins namely XE-340, XE-347 and XE-348 to validate their enrichment efficiency by abstracting organics from their water solutions.

Using XE-340 resin as the adsorbent, Kimoto *et al.*[36] obtained 58–90% recovery of nitrosamines from spiked tap water samples. In the recovery studies of 19 standard organic compounds, Blok and coworkers[37] compared the efficiencies of XAD-2, XAD-4, XAD-8, XE-340, XE-348 and Tenax GC and noted that XAD-4 proved to be a better adsorbent than the others in terms of mean recovery of the above organics. Similarly, XAD-2 and XE-347 were compared by Harris *et al.*[38] and they suggested that the combination of these two resins could serve better as the sorbent of choice for trapping water-borne organics.

In our preliminary communication[28] we have reported the adsorption/desorption of some ^{14}C-labelled organic compounds using XAD-2, XAD-7, XE-340, XE-347 and XE-348 to determine the influence of excessive amounts of other contaminants on the recovery of the individual radio-labelled organic compound. That study also focussed on retention behaviour of these resins. The objective of this investigation was to evaluate and compare the enrichment efficiency of the four resins, namely XAD-7, XE-340, XE-347 and XE-348 with that of the well-studied XAD-2 resin using ultra trace levels of eight radioactive, model organic compounds. The model compounds were chosen to represent organochlorine pesticides (lindane); polychlorinated biphenyls (2,4,5,2′,4′,5′-hexachlorobiphenyl; PCB-153;[39] polyaromatic hydrocarbons (fluorene, and benzo(a)pyrene, B(a)P); plasticizers (di-2-ethylhexyl phthalate, DEHP); phenol (2,4-dichlorophenol); aromatic acids (2,4-dichlorophenoxy acetic acid, DCPAA); and aromatic amines (2,4-dichloroaniline). Furthermore, the effect of the pH variation of the aqueous samples on the adsorption behavior of these compounds for the five resins was studied. Experimental data illustrate the merits and limitations of these different resins for stripping applications of low-level water organics. Moreover, this study sheds some light on the equally superior ability of XE-resins for trapping organics, although they are inferior in performance as preconcentrators. Finally, from the mass balance data, this study shows the potentials of the XE resins to concentrate low levels of water borne organics and suggests the necessity for further research on desorption of organics from these resins.

EXPERIMENTAL SECTION

Materials Water used in the investigation was deionized glass-distilled and further purified according to the method described by Malaiyandi *et al.*[40] All inorganic reagents were analytical reagent grade and were obtained from local suppliers. The pure nitrogen used in this study, was prepurified by passing through Chromosorb 108 and XE-348. Acetone, hexane, methanol and toluene were purchased from Caledon Laboratories, Georgetown, Ontario, Canada. Carbon disulfide (Fisher Scientific Company) and anhydrous diethyl ether (Mallinckrodt Chemical Company) were supplied by local suppliers. Purified acetone was prepared by refluxing the solvent with potassium permanganate for 12 h, and distilling in an all-glass apparatus.[41] Hexane was purified as described previously.[42] Methanol and toluene were redistilled in glass and the distillates were collected in clean, borosilicate containers provided with glass stoppers. Diethyl ether was purified by destroying the peroxide with ferrous sulfate heptahydrate and carefully distilling the solvent in an all-glass apparatus. Carbon disulfide was also carefully distilled in glass and the distillate was collected in the original containers which were pre-cleaned and flushed with purified dry nitrogen and, as far as possible, kept free of peroxide.

All glassware was cleaned with chromic acid, thoroughly washed with water, followed by rinsing with acetone and hexane and finally dried at 65 °C. Prior to using, the glassware was rinsed with acetone and flushed with purified, dry nitrogen. Ultrasonic cleaner (Branson model 220, 100W) and counting vials were purchased from local suppliers.

Candidate radioactive compounds chosen for this study were: ring UL-^{14}C-lindane; ring UL-^{14}C-2,4,5,2′,4′,5′ PCB-153; DEHP-1-^{14}C; fluorene-9-^{14}C; Benzo(a)pyrene-7-^{14}C, (B(a)P); ring-UL-^{14}C-2,4-dichlorophenol; ring-UL-^{14}C-DCPAA, and ring-UL,^{14}C-2,4-dichloroaniline were purchased from Pathfinder Laboratories, St. Louis, MO, USA. The unlabelled candidate compounds were purchased from Chem Service, West Chester, PA, USA except 2,4-dichloroaniline and DEHP which were supplied by Aldrich Chemical, Milwaukee, WI, USA. Ready-Solv MR was obtained from Beckman Instruments Co., Montreal, Quebec, Canada. Macroreticular, Amberlite® XAD-2 and XAD-7 resins (Rohm and Haas Company) were supplied by BDH Chemicals Ltd., Toronto, Ontario, Canada. Ambersorb®, carbonaceous XE-340, XE-347 and XE-348 resins were generously donated by Rohm and Haas Company, West Hill, Ontario, Canada.

Instrumentation Radioactivity measurements were performed using a microprocessor-controlled liquid scintillation counter, Model LS 7500 (Beckman

Instruments Inc., Scientific Instruments Division, Irvine, CA, USA) coupled with a Texas Instrument Silent 200 electronic data terminal.

Counting After equilibration in the dark for 30 min the sample vials were counted for 5 min using a window setting of 397–655 nm and counting efficiency of 95% carbon-14 standard. Duplicate measurements were carried out by repeating the counting of the vials after the entire carrousel was counted once. Quench correction by the external standard ratio (ESR) method and calibration was performed as described in the Instrument Suppliers Manual.[43] Recoveries were calculated as the ratio of percent radioactivity in relation to the original count of the aqueous sample prior to the adsorption tests.

Purification of the Resins

The purification of the resins XAD-2, XAD-7, XE-340, XE-347 and XE-348 was carried out according to the method described by Zhou *et al.*[28] Minimization of adsorption of the model organic compounds on borosilicate containers and borosilicate resin bed columns was achieved by silanization of the active sites of the borosilicate surfaces with dimethyl dichlorosilane as outlined by Malaiyandi *et al.*[44]

Each of the five silanized borosilicate columns used for packing the purified resins (40.0 cm x 1.2 cm o.d.) was provided with a 2 mm polyfluroethylene (PTFE) stopcock at one end and a fused 500-mL round-bottomed bulb with a 24/40 outer joint at the other end of the column. A plug of pre-washed silanized glass wool was placed above the stopcock and the top surface of the plug was levelled by gently tamping using a glass rod with a snug fitting flat end. The outer joint of the top bulb was fitted with a 24/40 inner joint adapter which was then attached with a 10 cm PTFE tubing (8 mm, o.d.). The PTFE tubing was loosely-packed with silanized glass wool followed in series by chromosorb 108 packing, a wad of silanized glass wool, XAD-2 packing and a plug of silanized glass wool to prevent extraneous contamination during aqueous sample percolation through the resin bed.

The packing of the column with the five purified resins was carried out according to the method outlined by Zhou *et al.*,[28] except that the packing was washed serially with 50 mL portion of 20%, 50%, 80% water-methanol mixture and 100 mL of water before charging with test samples.

Preparation of Standard Solutions of Radio-labelled Compounds

A stock solution of the individual candidate ^{14}C-labelled lindane was prepared by transferring a known weight of the radioactive material and a calculated amount of the same "cold" substance into a 10 mL volumetric flask (a stock solution containing 2 mg/mL) and making to volume in acetone. A known aliquot of this stock solution was pipetted into a 10 mL volumetric flask to give 60 μg/mL working standard in acetone. Similarly, the radioactive working standard solutions of PCB-153, DEHP, fluorene, B(a)P, dichlorophenol, DCPAA and dichloroaniline were prepared. Prior to making large scale aqueous samples of these candidate compounds for recovery studies, aliquots (10 μL) of these working standards in duplicate were transferred to the counting vials to determine radioactivity.

Preparation of Aqueous Samples Fortified with Radioactive Compounds for Recovery Studies

A fortified water sample (3.0 L) containing 3.6 μg/L (450 ± 200 dpm/mL) of radioactive organic compound was obtained by spiking a known volume (450–600 μL) of the working standard (60 μg/mL) ^{14}C-labelled solution. The aqueous solutions (pH 5.6–5.7) were adjusted to the desired pH using 0.1 M aqueous phosphoric acid or sodium hydroxide. The solution was magnetically stirred for about 1/2 h and allowed to stand overnight. Before sampling, the solution was restirred for about 10 min.

Adsorption/Desorption Studies

Prior to the recovery studies on the resins, exactly 2 × 5.0 mL aliquots of the fortified aqueous sample were pipetted out from the fortified solution to determine initial radioactive counts/mL of the fortified sample. The sorbent beds were prepared by individually packing the five columns with 5.0 mL of the purified XAD-2, XAD-7, XE-340, XE-347 and XE-348 resins as previously described by Zhou *et al.*[28] Exactly measured volumes (250 mL) of the fortified aqueous sample containing the ^{14}C-labelled sorbates were transferred to the bulb of the resin bed column. After standing for 10 min the aqueous sample was allowed to flow through the resin bed at a flow rate of one bed volume (BV) per min. When 45 mL of the aqueous sample had percolated through the sorbent bed, exactly 5.0 mL volume of the "exhausted" effluent was collected in a calibrated, silanized measuring cylinder and quantitatively transferred into a counting vial. Thus 5.0 mL aliquots of the effluent which were collected in a 500-mL container after every 45 mL of the effluent fraction were also kept aside for radioactivity counting. Similarly, a second 250 mL portion of aqueous sample was allowed to percolate through the adsorbent bed and the 5.0 mL effluent fractions were collected to determine the "break-through" volume.

After percolation of the aqueous solution (ca. 500 mL) through the resin bed, 2 × 5.0 mL portions of the "exhausted" composite effluent were sampled for radioactivity counting. Also, the inner walls of the entire column and the resin beds were washed with 50 mL of water and the final 5.0 mL water-wash was collected for radioactivity counting. All the 5 mL aliquot samples so far collected for counting were kept aside in the dark until all the different solvent eluates of the adsorbents were ready for counting.

Prior to the commencement of elution of the sorbates from the resins, water traces in the columns were flushed into the respective effluent receivers by passing a gentle stream of nitrogen for about 20 sec. The inner walls of the top bulb and column were then rinsed with 2 mL of methanol. The resin packing was then gently stirred using a stainless steel wire (1 mm thick). The wire and the entire column were again rinsed with a further quantity (3 mL) of methanol. [Note: In the case of the highly polar compounds, namely dichlorophenol, DCPAA and dichloroaniline, methanol elution was preceded by 5 mL 0.1 M sodium hydroxide made up in a (4 + 1) methanol-water mixture. Basification was employed to provide an alkaline coating on the unused surface with respect to the sorbates so that the eluted polar compounds are not resorbed on the unused resin.] After equilibration for about five minutes, the eluate was drained into the respective, marked vials at a flow rate of 0.5 mL/min (0.1 BV/min). When the draining of the eluate had stopped, the remaining eluate in the sorbent bed was flushed using a gentle stream of nitrogen and the tip of the stopcock was rinsed into the respective marked vials using the same eluent.

Elution with methanol was followed by isooctane (7 mL) and diethyl ether (7 mL). The elution was carried out as described above for methanol and the eluates were collected in the respective, marked vials. Between each solvent elution, the resins were flushed with nitrogen for 20 sec.

To the vials containing diethyl ether eluates, were added 5 mL of toluene and the solvents were evaporated to about 5 mL at ambient temperature in the fume hood, and precautions were taken not to contaminate with exogenous materials. Following diethyl ether elution, the XAD-2, XAD-7 resins were eluted with 2 x 10 mL portions of carbon disulfide and the eluate was received in respective marked 24/40 100-mL round-bottomed (R.B.) flasks. To each of the R.B. flasks were added 5 mL of toluene and the solvents were evaporated using a Būchi rotary evaporator at 30 °C and 100 mm Hg pressure to a volume of ca. 4 mL. After further addition of 5 mL of toluene, the contents of the flask was evaporated in the fume hood at ambient temperature until no odor of carbon disulfide could be detected (final volume, 3–4 mL). [Note: Toluene was exchanged for diethyl ether as a retainer solvent. In the case of carbon disulfide, toluene not only acted as a retainer solvent but also eliminated quenching due to carbon disulfide.]

After diethyl ether elution of the carbonaceous resins, i.e. XE-340, XE-347 and XE-348, nitrogen was passed through to dislodge resin packings. When dry, the resin was free-flowing and each resin was transferred to individual marked counting vials. After moistening the resins with 3–5 drops of water, a measured volume (10 mL) of carbon disulfide was added to each vial and sonicated at ambient temperature for 5 min. After the particulate (if any) settled down, the supernatant clear carbon disulfide layer was transferred to marked 100 mL 24/40 R.B. flasks using narrow bore pasture pipettes, and care was taken to avoid any black particulates getting into the R.B. flasks. Sonication was repeated with each resin using 3 x 10 mL portions of carbon disulfide and the supernatant solvent layers were pipetted into their respective R.B. flasks.

After adding 5 mL of toluene to each flask the carbon disulfide eluates were concentrated (30 ° and 100 mm Hg) using a Büchi rotary evaporator to reduce the volume to about 3–5 mL. Further two 5 mL portions of toluene were added to each flask and the solution was again evaporated as before to a volume of ca. 5 mL. The concentrates were transferred to respective marked counting vials using 3 x 1 mL portions of toluene, and the contents of the R.B. flasks were quantitatively rinsed into their respective counting vials. The solvent was then evaporated to a 3–4 mL volume at ambient temperature in the fume hood until no odor of carbon disulfide was detected.

To all the aqueous samples in the vials were added 3 mL of isopropanol followed by 7 mL of Ready-Solv MP®. The eluate concentrates in the vials after exchange with toluene also received 7 mL of Ready-Solv MP®. After transferring all the samples to the carrousel of the Beckman liquid scintillation counter and holding them for 1/2 h in the dark, the samples were counted twice for radioactivity content. All experiments were repeated in duplicate or triplicate for statistical treatment.

RESULTS AND DISCUSSION

Liquid-liquid extraction, freeze-drying and other similar concentration methods fail to provide totally representative concentrates of organics from different environmental samples.[45] The applicability and usefulness of polymeric synthetic adsorbents with reference to the analysis of "total" organics in surface and finished drinking waters, after sorption, desorption and characterization of contaminants, though not critically evaluated, have been sufficiently explored.[25,26] Tremendous amounts of effort and resources have been expended in the application for concentrating organic contaminants in aqueous matrices; however, very few reports have dealt with the evaluation of the accumulation efficiency and mass balance of different classes of organic compounds. Moreover, in spite of the tremendous advancement in the analytical techniques, the implemented methods of enrichment have not been fully assessed.

Many factors generally affect the aqueous phase adsorption. Consideration of certain properties of the sorbent such as polarity, pore size, pore size distribution, surface area, surface energy, etc. is critical to the selection of an adsorbent. Similarly, as far as the sorbates are concerned, the properties such as size, molar volume, polarity, polarizability, concentration, solubility, etc. can be significant. Furthermore, solution conditions, such as temperature and pH can also have pronounced effects on the adsorption process.[31]

Macroporous resins have a distinct superiority over other types of solid sorbents in that, the trapping of organic compounds from the aqueous matrix and their elution with concomitant regeneration are facilitated by the non-restricting pores. In addition, the claim on extraction efficiency of these polymer beads for concentration applications is based on high recoveries of the sorbates, and this is contingent upon the facile reversibility of the interaction between the sorbents and solutes.

Very few studies have been devoted to evaluate the accumulation efficiency of carbonaceous Ambersorb® XE-340, XE-347 and XE-348 and the macroreticular Amberlite® resin XAD-7. Since some of these resins differ in chemical nature and physical properties, the interaction between these sorbents and different classes of organic solutes would involve hydrophobic-hydrophobic, hydrophobic-hydrophilic and hydrophilic-hydrophilic interactions.

Central to the theme of this investigation is not only the evaluation of the restricted capacity of a sorbent for certain types of sorbates by determining the particular solute in the effluent from the sorbent bed, but also the gaining of some evidence for irreversible adsorption of the solutes (i.e. ineffective desorption with respect to the solvent(s) employed) from the mass balance data. This information is crucial, since the effectiveness between high loading capacity of the resins due to adsorption and facile desorption may result in the production of regenerated resins which is vital to the repeated use of these adsorbents, especially with reference to industrial applications. These data are essential to develop appropriate methods and processes for eliminating or minimizing sorbate levels on adsorbents. Moreover, in order to circumvent the labor-intensive, time-consuming currently available methods of analysis, such as chromatographic and mass spectrometric techniques, the simple radioactive tracer technique using ^{14}C-labelled selected organic compounds as an analytical tool[28] was employed in this study.

EFFECT OF pH VARIATIONS

Oehme and Martinole[46] noted that unlike ion-exchange resins, XAD-polymeric adsorbent beads derived from styrene-divinylbenzene copolymers and the cross-linked acrylic copolymers are quite insensitive to pH variations. However, XE-carbonaceous resins derived from the pyrolysis of sulfonated styrene-divinylbenzene polymeric beads, might behave slightly differently depending on the residual sulfonic acid moieties. In spite of their hydrophobic or hydrophilic properties, these resins are essentially non-ionic in character. Hence, by suppression of ionization of polar compounds, these adsorbents would have better adsorptivity for un-ionized, molecular organic species.

Ringhand *et al.*[45] have observed that lowering of pH (2.0) is critical to the complete stripping of the acidic mutagens from aqueous samples by XAD-2 and XAD-8 resins. Furthermore, they have shown that higher levels of mutagens were observed in lyophilized concentrates as compared to those in XAD-resin concentrates and they surmized that some polar mutagens could not be eluted from the XAD polymer beads. Kronberg and co-investigators[47] have also made similar observations.

Moreover, Wigilius and coworkers[10] have reported better recoveries of mutagens at acidic pH than at neutral pH from chlorinated drinking water using an XAD-2 stripping procedure. They have therefore concluded that acidification should be incorporated as an essential step prior to XAD-2 stripping of organics. Furthermore, they have noted about half of the mutagenic response to be present in the second column eluates and this has indicated that, even in the "protonated" form, the acidic mutagens are not completely adsorbed in the first column. Similar observations were also made by Pietrzyk *et al.*[48]

On the contrary, Grabow and coworkers[49] noted that acidification of water samples reduced the recovery of mutagens by XAD-2 accumulation method. Furthermore, Moore and Karasek[50] have reported that acidification of the water samples containing multiple components, followed by XAD-2 stripping gave high recoveries except for n-hexyl benzene. However, in the case of XAD-7, lower recoveries were observed at neutral pH and no improvement in recoveries was achieved by acidification. They have also noted that in the case of some phenols, lower recoveries were obtained from XAD-4 accumulation after acidification of the aqueous sample. Because of these contradictory reports on acidification of aqueous samples on recovery, it was decided to investigate the influence of pH variation on the recovery of the selected compounds using these adsorbents. Numerous investigators have recommended to bring the pH of the aqueous samples to 2.0 or less prior to any pre-concentration step to strip quantitatively low-levels of organics from aqueous matrices. However, it is well-known that the integrity of some of the organics, such as organic esters, α, β-unsaturated ketones, active olefinic compounds, etc., if present in aqueous samples, would be affected at this low pH of 2.0. Hence, it was decided to use two acidic pHs i.e., 3.0 and ≈5.6. [Note: In this study, it is observed that acidification of aqueous samples to pH 3.0 was adequate to sorb quantitatively most classes of organics except DEHP. From the elution pattern, even DEHP is shown to be unaffected at this pH of 3.0. Furthermore, pHs 3.0 and ≈5.6 would refer to the pHs of the sorbate influents.]

SELECTION OF CHEMICALS

A judicious choice was made regarding the selection of the organic compounds to represent a diverse array of chemicals: from non-polar chlorinated organics to semi-polar and polar organics including a plasticizer, polycyclic aromatic hydrocarbons, a chlorinated phenol, an aromatic-aliphatic acid and a chlorinated aniline. These compounds have been selected on the basis of their frequency of occurrence in the ecosystem.

The aqueous sample was allowed to percolate at a pre-determined flow rate (ave. 5 mL/min, ca. 1 BV/min). The effluent was collected in several 5-mL fractions at regular intervals (for every 50 mL effluent) for the determination of "breakthrough" volume. The loading was also pre-determined such that 10 dpm/mL could be accurately determined in any single fraction containing the selected organic compound. In contrast to the previous study,[28] the solvent eluate (5 to 7 mL) was collected directly into the respective counting vials except for the carbon disulfide fraction (40 mL) which after exchange with toluene was reduced to low volume by evaporation.

In this study, we have used the polar solvent, methanol, as the initial eluting medium to displace traces of moisture adhered to the sorbent surface so that the subsequently-used less polar solvents could have access to the surface and penetrate the pores of the sorbents to effectively desorb the solutes. Griest and coworkers[51] observed the need for a more polar, initial solvent for better penetration of the solvents used in the recovery studies of B(a)P. Furthermore, very few reports deal with improvement of recoveries even when the recoveries were low. Most often, single solvent or a combination of two solvents, such as, methanol, hexane, acetone, diethyl ether, etc., was used. In this study, attempts were made to maximize recoveries of sorbates by using sequentially a battery of solvents, namely, methanol, isooctane, diethyl ether, and carbon disulfide to assess their elution characteristics. Moreover, carbon disulfide was previously used as an eluent with activated carbon. Since some of these resins resemble activated carbon, we have chosen to incorporate carbon disulfide as the final solvent in the elution scheme in an attempt to improve desorption of the sorbates.

Lindane

The percent recoveries of lindane from XAD-2, XAD-7, XE-340, XE-347 and XE-348 are given in Table 1 and the recoveries are compared when the influent sample pHs were 3.0 and 5.6. Also are given (Table 1) the percent recoveries of the sorbate (based on initial load) by elution with methanol, isooctane, diethyl ether and carbon disulfide when used sequentially. [Note: Throughout the discussion section percent recovery means accountable percent recovery (which includes effluent concentration) based on initial concentration of sorbates in the influent.]

The lindane concentrations in the "exhausted" effluents from XAD-2, XAD-7 and XE-348 at the influent pHs of 3.0 and 5.6 were similar (low), indicating that sorption of lindane was unaffected at these acidic pHs. The data also show that an average of about 5% lindane (considering the standard deviation) was found in the effluent of XE-340 at both pHs whereas in the case of XE-347 only marginal difference in rejection, namely 3% and 8%, respectively at the pH of 3.0 and 5.6 was observed. It can be concluded that both XE-340 and XE-347 definitely show less adsorption for lindane than the other three resins.

Using methanol as the initial solvent the order of elution is XE-340> XAD-2>XAD-7>XE-347>XE-348. When isooctane was used as the next eluent the recovery % follows the order: XAD-2>XAD-7>XE-340>XE-347>XE-348 at pH 3.0. [Note: The isooctane elution was not carried out when the influent pH was 5.6. Hence, the recoveries of lindane with diethyl ether eluent are very high.] However, this oversight in the design of the experiment does not vitiate the observed elution pattern of lindane from the resins, since identical conditions were employed for all the five resins at that pH. Diethyl ether followed isooctane to elute lindane from the resins. With this eluent, lindane is desorbed better from XAD-7 followed by XAD-2>XE-340>XE-347>XE-348, at the influent pH was 3.0. On the other hand, at the influent pH of 5.6, the elution order for lindane is XAD-2>XAD-7>XE-340>XE-347>XE-348.

With carbon disulfide, nearly all the remaining adsorbed lindane on XAD-2 and XAD-7 was leached out; when the influent sample pH was 3.0, carbon disulfide seems to have eluted most of the lindane from XAD-2; however, nearly 19% lindane could not still be released from XAD-7 when the aqueous sample had a pH of 5.6. Furthermore, carbon disulfide apparently removed most of the lindane from XE-340, XE-347 and XE-348 indicating carbon disulfide is the solvent of choice for desorbing lindane from XE-resins.

The carbon disulfide extraction data show some marked effects of pH on the elution of lindane from these resins with the exception of XAD-2, which appears to show no pH effect. In the case of XAD-7, higher percent of the pesticide was eluted at the influent pH of 5.6 than at pH 3.0. Also, all carbonaceous resins gave

Table 1 Percent accountable recovery of Lindane from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*
VEHICLE											
Effluent	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	1.29	2.19	0.42	0.56	7.05	10.19	3.09	8.07	0.70	2.38
	STD	0.29	1.09	0.27	0.06	2.17	5.43	0.41	1.93	0.13	1.34
MeOH	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	19.30	12.16	10.48	4.28	23.65	12.61	5.37	5.70	1.23	1.01
	STD	4.70	6.20	1.93	5.19	5.26	4.01	3.73	4.66	0.09	1.00
Isooctane	N	3	NU	3	NU	3	NU	3	NU	3	NU
	MEAN ±	33.32	—	22.36	—	18.25	—	11.65	—	3.37	—
	STD	4.33	—	4.03	—	4.70	—	1.95	—	0.36	—
Diethyl ether	N	3	1[a]	3	2	3	2	3	2	3	2
	MEAN ±	37.60	80.87	47.60	52.62	33.09	48.82	26.48	26.01	10.47	8.41
	STD	6.03	—	2.67	11.65	5.53	5.18	3.20	3.41	0.51	2.62
Carbon disulfide	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	5.89	4.56	12.89	23.94	12.05	24.62	39.95	55.37	72.92	79.51
	STD	1.16	3.40	2.82	0.09	2.16	5.23	11.28	3.05	0.50	0.19
Total	N	3	1	3	2	3	2	3	2	3	2
	MEAN ±	97.40	97.03	93.75	81.39	94.09	96.25	86.54	95.15	88.69	91.32
	STD	2.16	—	3.19	6.60	2.14	0.96	7.06	0.13	0.19	0.08

[a] One eluate split.

NU—Not used.

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student t' test.

higher yield of lindane when the influent pH was 5.6. It is noteworthy that, at both pHs, the recovery of lindane was nearly quantitative with XAD-2 and XE-340. More than 90% recovery of the pesticide was obtained from XE-347 and XE-348 at the influent pH of 5.6, whereas at this pH, only ca. 81% lindane was accounted for from XAD-7. Furthermore, when the influent was pH 3.0, lower recoveries (<90%) were noted for XE-347 and XE-348.

McNeil *et al.*[52] obtained 77% recovery for lindane from an XAD-2 concentration technique when the pH of the influent was adjusted to 8.4–8.6. Furthermore, Moore and Karasek[50] compared the recovery of this pesticide from XAD-2 and XAD-7 when the influent pH was at 7.0 and 2.0 and noted only marginal differences due to the pH effect. In this study, similar observations were noted for XAD-2 and XE-340. On the other hand, some marked influence of pH is apparent in the case of XAD-7. In addition, the accountable recoveries from XE-347 and XE-348 are affected by variation of the influent pH. Moreover, increased efficiency is noted when the influent pH was 3.0 for XAD-7 whereas better recoveries are obtained from XE-347 and XE-348 when the influent pH was adjusted to 5.6.

PCB-153

Table 2, shows the percent recoveries of PCB-153 from the five adsorbents. It would appear that (a) in the "exhausted" effluent more PCB-153 was found at the influent pH of 5.65 than that found at pH 3.0 thus showing some marginal influence of pH on adsorption of PCB-153 on the resins; (b) the effluent from XAD-2 resin contained low levels of PCB-153 at both pHs indicating sorption was complete; (c) all the resins have sorbed an average of more than 95% of PCB-153. However, as far as the mean sorption behavior is concerned at pH 5.65, the order is XAD-2 > XE-347 > XE-340 ≈ XE-348 ≈ XAD-7.

When methanol was used as the eluting medium for PCB-153 from these resins, the % desorbed is between ca. 8 and 15 except for XE-348 (ca. 5%) at pH 5.65. When the % solute desorption from different resins is compared, it can be seen that isooctane has eluted the PCB-153 slightly better when influent pH was 3.0 than at pH 5.65 except that XE-347 and XE-348 showed similar eluate concentration of PCB-153 at both pHs. Moreover, at the influent pH of 3.0 this chlorinated biphenyl has been eluted to the extent of 77.4% from XAD-7 followed by 29.7%, 14.2%, 6.1% and 3.5% from XAD-2, XE-340, XE-347 and XE-348 respectively. With diethyl ether as eluent, nearly 47.9% of PCB-153 has been leached from XAD-2 to indicate this solvent is better than isooctane for desorbing PCB-153 from XAD-2. In the case of XAD-7, although only 12 to 13% of PCB-153 (almost all the residual PCB-153 in the resin) was extracted from the resin by diethyl ether, due to the particular design of the experiment, it is difficult to predict whether diethyl ether or isooctane is a better eluent for extracting PCB-153 from XAD-7.

Carbon disulfide has apparently eluted the residual PCB-153 from XAD-2 and XAD-7. It can be seen that, for XE-resins, extraction of PCB-153 is best achieved by carbon disulfide elution which quantitatively leached the chlorinated compound. In terms of total recovery, when the loading of the aqueous sample was at

Table 2 Percent accountable recovery of PCB-153 from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.65*	*3.00*	*5.65*	*3.00*	*5.65*	*3.00*	*5.65*	*3.00*	*5.65*
VEHICLE											
Effluent	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	1.28	2.01	1.52	7.91	1.72	5.84	1.34	5.02	0.94	7.04
	STD	1.20	1.37	0.18	5.43	0.66	3.17	0.74	3.45	0.34	4.83
MeOH	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	14.64	13.89	8.42	10.25	12.73	10.29	9.36	12.02	9.04	5.36
	STD	6.37	5.50	1.16	3.42	0.15	3.81	0.59	4.30	2.12	1.44
Isooctane	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	29.66	27.99	77.41	65.01	14.16	12.81	6.09	5.72	3.50	2.83
	STD	1.33	4.28	0.49	9.73	1.17	2.30	0.17	0.72	0.39	1.26
Diethyl ether	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	47.89	40.94	12.93	13.11	39.96	37.83	17.75	14.82	7.38	5.51
	STD	8.87	3.71	1.70	3.81	2.47	5.93	0.37	2.44	0.74	0.78
Carbon disulfide	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	6.14	5.86	1.53	1.39	25.68	25.59	63.33	62.25	77.48	72.27
	STD	1.32	1.36	0.45	0.25	0.13	4.57	2.04	10.18	3.93	4.79
Total	N	2	3	2	3	2	3	2	3	2	3
	MEAN ±	99.61	90.68	101.81	97.67	94.23	92.36	97.87	99.82	98.34	93.01
	STD	3.76	2.64	1.66	13.68	2.69	4.19	0.91	8.66	0.35	2.02

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student t' test.

pH 3.0, desorption was better from all resins than at pH 5.65 leading to quantitative recoveries.

Chriswell and coworkers[53] reported a 78–96% recovery of Arochlor 1254 from XAD-2 at 1 μg/L spike level. Furthermore, it is reported that a recovery of 77.6 to 86.4% from XAD-2 was achieved from aqueous samples fortified with PCBs 1242, 1254, and 1260 at 250 μg/L.[54] LeBel and Williams[55] obtained 88 to 110% recovery from XAD-2 resin by spiking different Arochlors at 1.0 and 10.0 ng/L in potable water. De Raat and van Ardenne[56] using ^{14}C-labelled Arochlor 1254 at 2 μg/L concentration in urine samples studied the enrichment efficiency of XAD-2 and XAD-7 and recovered 56% and 53%, respectively with a single solvent extraction. In the present study, using the solvent regimen the total recovery of PCB-153 was quantitative irrespective of the resin type confirming the recoveries reported by LeBel and Williams.[55]

DEHP

Data presented in Table 3 show the % recovery of DEHP from the five sorbents. It is important to carefully examine the data of DEHP concentration in the "exhausted" column effluent since significant levels of this plasticizer are unadsorbed. The effluent from XAD-2 resin bed shows nearly 47% and 31% of DEHP, when the influent pHs were 3.0 and 5.6 respectively. On the contrary, the effluents from the other four resins contained higher levels of DEHP when the influent pH was 5.6 than at pH 3.0. Furthermore, at pH 3.0, the order of retention of DEHP by the resins is XE-340$\approx$XE-348>XE-347>XAD-7>XAD-2; however, when the original aqueous sample pH was 5.6, the order of retention is XAD-2>XE-348$\approx$XE-347$\approx$XAD-7>XE-340 and the last two resins have rejected more than 50% of DEHP from the influent at this pH. This study clearly confirms the findings of van Rossum and Webb,[57] Derenbach *et al.*,[58] and Zhou and coworkers[28] and significant "break-through" was noted to indicate that these resins are incapable of quantitatively accumulating DEHP under this loading condition.

Blok *et al.*[37] reported low recoveries of methyl myristate (C_{14}-acid) and nonadecane while significantly high recoveries were noted for diethylphthalate from XAD-2, XE-340 and XE-348. Moreover, Moore and Karasek[50] obtained low recoveries for n-hexylbenzene and methyl myristate in contrast to the high recoveries noted for dibutyl phthalate from XAD-2 and XAD-7, irrespective of pH variations. It is apparent that, as the length of the aliphatic chain moiety increases, the sorption and mass transfer decreases. In addition, it would seem that the Π-electron density of the benzene nucleus and the p electron pairs of the oxygen (or in other cases having chlorine, nitrogen, etc.) atom could be responsible for most of the sorption properties of these resins. In the case of DEHP, these clouds are shielded by the aliphatic chain moiety, especially when the number of carbon atoms in the aliphatic chain exceeds six thus favoring steric exclusion from the pores.

It is known that most sorption behavior is explainable on the basis of sorption non-equilibrium in which the local equilibrium assumption[59] contributes greatly to

Table 3 Percent accountable recovery of DEHP from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*
VEHICLE											
Effluent	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	46.79	30.89	30.19	51.50	18.15	56.75	26.95	47.10	19.25	46.41
	STD	17.99	8.12	7.99	7.79	4.74	1.36	5.03	1.39	1.30	4.62
MeOH	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	33.93	23.25	44.93	13.36	57.68	14.53	41.45	11.85	45.78	4.79
	STD	16.33	7.02	4.80	0.49	6.47	3.70	4.69	1.48	5.32	1.59
Isooctane	N	3	NU	3	NU	3	NU	3	NU	3	NU
	MEAN ±	11.45	—	25.99	—	7.20	—	3.65	—	2.29	—
	STD	2.03	—	8.30	—	0.13	—	2.43	—	0.98	—
Diethyl ether	N	3	1[a]	3	2	3	2	3	2	3	2
	MEAN ±	9.41	44.21	2.82	33.09	14.35	31.05	5.96	7.64	3.77	2.05
	STD	2.29	—	0.85	8.44	1.71	1.19	1.83	2.16	0.79	1.65
Carbon disulfide	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	1.33	7.77	0.51	6.41	4.11	7.88	21.22	43.00	26.42	45.02
	STD	0.26	0.81	0.27	0.10	0.34	1.57	1.52	5.54	2.24	11.67
Total	N	3	1	3	2	3	2	3	2	3	2
	MEAN ±	102.91	105.91	104.44	104.35	101.49	110.20	99.24	109.58	97.47	98.25
	STD	3.02	—	1.41	1.00	0.37	2.72	3.05	4.82	2.75	10.30

[a] One eluate split.

NU—Not used.

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student *t'* test.

the conventional solute transport equation. For the local equilibrium concept to be valid, the rate of sorption must be faster compared to other processes affecting solute concentration such as, hydrodynamic dispersions, advection, etc., so that there exists an equilibrium of solute concentration between the sorbent and the solvent occupying the pores. However, in the case of sorption of DEHP on the resins, the high levels of phthalate found in the column effluents are nearly uniform from the initial to the final stages of percolation, although 50–70% of the plasticizer were sorbed onto the resins at pH 5.6. If the local equilibrium assumption were valid, the solute "break-through" curve obtained from packed column experiments should be symmetrical. However, in this study, the concentration of DEHP in column effluent was found to be uniform and parallel to the volume (time) axis (not shown) and the sorption non-equilibrium seems to be inoperative resulting in a steady low level of mass transfer.

Similar to the elution procedure used to extract lindane and PCB-153, methanol was used as the first solvent to leach out DEHP from the five sorbents. As observed with lindane, methanol apparently extracts more DEHP from all the resins when the adsorption was carried out at pH 3.0 compared to those when the pH of the influent was 5.6. The influence of pH on desorption of DEHP from all the resins is significant, but was less conspicuous with XAD-2. Almost 1.5 to 4 times more DEHP were extracted from XAD-2, XAD-7, XE-340 and XE-347 resins by methanol when the influent pH was 3.0. In the case of XE-348, more than nine times the concentration of DEHP were found in the eluate from the column with the influent pH at 3.0 than in the eluate with influent pH 5.6. It would also appear that methanol is one of the best eluents for DEHP from these resins.

Isooctane was used only on the resin packing percolated with aqueous sample at pH 3.0. It is noteworthy that the residual DEHP is very easily desorbed from XAD-7 by isooctane. However, XE-resins tenaciously hold the DEHP and elution with isooctane is shown to be ineffective with the influent pH at 3.0.

With diethyl ether as eluting solvent and when the influent pH was 3.0, the desorption of the remaining DEHP is almost complete from XAD-2 and XAD-7 whereas, ca. 14.4%, 6.0% and 3.8% of DEHP of the residual DEHP based on initial load have been eluted from XE-340, XE-347 and XE-348 respectively. When the initial aqueous sample pH was 5.6, diethyl ether has proved to be a better eluent than methanol for eluting DEHP from XAD-2, XAD-7 and XE-340 resins. From XE-347 and XE-348 only 7.6 and 2.1% respectively of the initial load are found in the eluate.

Carbon disulfide used as the final eluent, has leached residual DEHP retained by all the resins at both pHs. It is important to note that, when influent pH was 5.6, carbon disulfide seems to be the solvent of choice to elute the residual DEHP from XE-347 and XE-348 and probably also from all the other resins, as observed in the case of lindane and PCB-153. [In the case of XAD-2, XAD-7 and XE-340 however anyone of the solvents used in this study could have eluted >90% of the sorbed DEHP.] Furthermore, as far as the accountable recovery is concerned, quantitative elution of the adsorbed DEHP is achieved by this elution regimen.

Using ^{14}C-dioctylphthalate, De Raat and van Ardenne[56] obtained 11% and 13% recoveries from XAD-2 and XAD-7 at 250 μg/L spike level. In their accumulation efficiency studies, van Rossum and Webb[57] noted 19% recovery of DEHP from XAD-2 from 50 μg/L spiked sample and 33% from a 100 μg/L fortified sample. They have also observed a lower recovery (22%) of the plasticizer from XAD-7. Moore and Karasek[50] reported a quantitative recovery of dibutylphthalate from XAD-2 and XAD-7 at pHs 7.0 and 2.0 without any indication of losses in the effluent and concluded that XAD-7 extraction consistently gave lower recovery of DEHP. However, Derenbach *et al.*[58] using acetone-water eluent, recovered 67.7% ^{14}C-labelled DEHP from XAD-2. Moreover, Zhou *et al.*[28] have recently reported that, using their solvent elution system, they have quantitatively recovered the adsorbed DEHP from XAD-2, XAD-7 and XE-340 resins, but lower recoveries were noted for XE-347 and XE-348. It is apparent that quantitative recovery of DEHP was achieved using the solvent system outlined in this study.

Fluorene

Data in Table 4 show the recovery of fluorene from the five resins after adsorption/desorption at two pHs namely 3.0 and 5.6, similar to the previous sorbates. In the "exhausted" effluent from all resins the levels of fluorene are found to be less than 3%. However, there seems to be some marginal influence of pH in that, when the influent pH was 3.0, slightly higher levels of fluorene were noted in the effluents irrespective of the resin type. This observation indicates that all these resins seem to possess an excellent capacity for trapping fluorene from aqueous media.

When methanol was used as the initial solvent for desorbing fluorene from the resins, a slight increase in extraction efficiency of this polycyclic aromatic hydrocarbon (PAH) is noted for all resins (except XAD-7) when the initial aqueous sample pH was 3.0. It was also observed that, with respect to the elution of this PAH with methanol, the order of desorption efficiency seems to be XAD-7 > XAD-2 > XE-340 $\gg$ XE-347 $\approx$ XE-348. However, isooctane apparently, leaches fluorene in nearly equal amounts from both XAD-2 and XAD-7 and negligible levels of this PAH are desorbed from XE-340, XE-347 and XE-348.

With diethyl ether extraction a large percent of fluorene is leached out from XAD-2 and XAD-7 (67% and 73% respectively) indicating the superiority of diethyl ether. The same solvent has extracted about 17% and 9.0% from XE-340 when the pHs of the influent were 3.0 and 5.6, respectively thus indicating a marked effect of pH variation. Furthermore, only insignificant recoveries were obtained from XE-347 and XE-348 resins by diethyl ether extraction.

When carbon disulfide was used as the eluent the residual fluorene from XAD-2, XAD-7 and XE-340 resins have been completely desorbed. However, from XE-347 and XE-348, ca. 34% and 24%, respectively of fluorene at pH 5.6 have been stripped. It is apparent from the mass balance data, quantitative recoveries were achieved by trapping fluorene using XAD-2, XAD-7 and XE-340, whereas XE-347 and XE-348, although excellent accumulators, failed miserably in their ability for concentrating this PAH for analytical purposes because of their intolerably incomplete desorption efficiency. It is concluded that the solvent system used in this study is inadequate and a different extraction procedure has to be developed

Table 4 Percent accountable recovery of Fluorene from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*
VEHICLE											
Effluent	N	3	3	3	3	3	3	3	3	3	3
	MEAN ±	2.01	1.30	1.73	1.18	2.70	1.40	2.18	1.56	1.81	1.58
	STD	0.33	0.54	0.41	0.27	0.91	0.33	0.69	0.25	0.36	0.10
MeOH	N	3	3	3	3	3	3	3	3	3	3
	MEAN ±	5.79	3.67	13.81	15.02	3.59	1.17	0.60	0.26	0.38	0.19
	STD	1.56	0.70	7.68	4.02	0.97	0.67	0.11	0.09	0.01	0.02
Isooctane	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	17.00	20.00	18.46	15.00	2.29	1.39	0.14	0.05	0.13	0.05
	STD	1.55	0.63	3.01	1.34	0.53	0.63	0.02	0.01	0.05	0.00
Diethyl ether	N	3	3	3	3	3	3	3	3	3	3
	MEAN ±	66.98	67.76	72.29	70.44	16.76	8.88	0.42	0.35	0.46	0.15
	STD	2.61	5.56	2.90	3.00	5.53	2.62	0.14	0.27	0.13	0.09
Carbon disulfide	N	3	3	3	3	3	3	3	3	3	3
	MEAN ±	16.15	17.63	2.16	11.78	71.14	85.38	35.61	33.83	26.50	24.02
	STD	3.62	9.22	1.45	8.23	4.68	2.56	6.11	0.65	5.38	2.89
Total	N	3	3	3	3	3	3	3	3	3	3
	MEAN ±	107.93	103.70	108.45	108.42	96.48	97.76	38.96	36.03	29.28	25.97
	STD	5.85	0.87	4.09	5.32	6.39	1.21	5.82	1.16	5.64	2.99

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student t' test.

to retrieve fluorene from XE-347 and XE-348. It is noteworthy that, from mass balance data, the order of performance in total recovery terms, is XAD-7 ≈ XAD-2 > XE-340 ≫ XE-347 > XE-348.

It can be seen that fluorene with its 12 Π-electrons seems to be strongly adsorbed to all the resins showing greater affinity of the Π-electrons to the surface and pores of the XE-resins. If this is true, it can be predicted that benzo(a)pyrene with its 20 Π-electron system should be much more tenaciously bound to the XE-resins than fluorene.

B(a)P

Table 5 shows the data for the recovery of B(a)P from the five adsorbents using sequentially the same battery of solvents. From the levels of B(a)P in the "exhausted" effluent, it is apparent that, in the case of XAD-7 and XE-340, a recognizable influence of pH variation is observed, whereas marginal pH effect is noticed with XAD-2, XE-347 and XE-348. Furthermore, only about 94% and 92% of B(a)P are retained by XAD-7 and XE-340, respectively, when the influent pH was 5.58. However, when the initial aqueous sample pH was 3.0, adsorption B(a)P on all the resins was quantitative.

Methanol, as the desorbing vehicle, extracted about double the quantity of B(a)P from all resins when the influent pH was 5.58 compared to the concentration of B(a)P for the influent pH at 3.0. In the case of XE-348 about 7 times more B(a)P was found in the eluate when the influent pH was 5.58 than with initial aqueous sample pH of 3.0 before percolation. When isooctane was used to elute B(a)P from the resins, about 7% of the sorbate was found in the XAD-2 eluate; whereas the same eluent desorbed a slightly higher percent of this PAH from XAD-7 at the influent pH of 3.0 than when the eluent was at pH 5.58. Isooctane elution gave very low recoveries of B(a)P for XE-resins.

Diethyl ether leaching of B(a)P from XAD-2 and XAD-7 gave higher average leachate concentration of this PAH (49% and 42% respectively) at the influent pH of 3.0 and 5.58. Only about 6% of B(a)P was desorbed from XE-340 and very poor elution was noted in the case of XE-347 and XE-348. When carbon disulfide was used to extract this PAH from the resins, all the residual B(a)P was eluted from XAD-2 and XAD-7. With XE-340, carbon disulfide extraction of B(a)P was superior (38%) when the pH of the aqueous sample before adsorption was 3.0 than at PH 5.58 (26%). Again, very poor recoveries were obtained for XE-347 and XE-348. Considering mass balance data, it would indicate that the order of superior performance of the resins for concentration and analytical purposes is XAD-7 ≈ XAD-2 > XE-340 ≫ XE-347 > XE-348.

De Raat and van Ardenne[56] reported a recovery of 29% and 77% of ^{14}C-B(a)P from XAD-2 and XAD-7 respectively when the pH of the influent was 2.0 using 18 μg/L spiked water samples. Landrum and Giesy[60] obtained 57% recovery of ^{14}C-B(a)P using XAD-4 (a resin similar to XAD-2). In our studies, we obtained quantitative recoveries for B(a)P from XAD-2 and XAD-7. Furthermore, while comparing several methods of accumulation of PAHs from aqueous media, Caton *et al.*[61] noted a recovery of 75% of ^{14}C-B(a)P using XAD-2 resin with different

Table 5 Percent accountable recovery of B(a)P from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.58*	*3.00*	*5.58*	*3.00*	*5.58*	*3.00*	*5.58*	*3.00*	*5.58*
VEHICLE											
Effluent	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	0.99	2.37	1.38	6.34	0.87	7.88	0.86	3.62	1.03	4.21
	STD	0.74	0.57	1.59	0.00	0.90	0.30	0.45	1.10	1.64	0.86
MeOH	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	8.79	19.56	7.01	14.27	12.11	27.73	8.44	23.77	1.51	10.87
	STD	4.67	0.02	1.55	2.50	4.05	2.67	4.33	3.32	0.93	2.53
Isooctane	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	7.40	7.21	34.67	26.79	1.04	1.47	0.52	1.24	0.91	2.72
	STD	1.37	1.15	8.27	1.82	0.25	0.37	0.06	0.31	0.69	0.52
Diethyl ether	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	55.50	43.61	45.61	40.25	7.05	5.56	0.73	1.22	1.06	3.31
	STD	9.97	3.94	2.76	2.33	0.46	0.04	0.04	0.49	0.47	0.83
Carbon disulfide	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	25.42	23.69	10.34	9.36	38.05	26.45	1.70	1.60	0.85	1.53
	STD	3.23	3.99	3.66	0.06	1.20	3.95	0.46	0.96	0.14	1.16
Total	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	98.10	96.45	99.03	97.01	59.71	69.10	12.24	31.46	5.36	22.64
	STD	4.13	6.24	3.02	3.07	5.18	6.00	5.07	2.66	2.48	0.88

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student *t*' test.

solvent elutions. With 15 mL of methanol they obtained 22% (compared to our findings of 19.6% with 5 mL of methanol) and 53% with 30 mL of methylene chloride (compared to our combined recovery of 74% with isooctane, diethyl ether and carbon disulfide). Moreover, they detected 11% residual activity in the XAD-2 resin. In this study, using XAD-2 and XAD-7 we report quantitative recovery of B(a)P. However, the recovery of B(a)P from XE-340, XE-347 and XE-348 at pH of 5.58 were about 69%, 32% and 23%, respectively. We did not measure the residual radioactivity since carbonaceous resins almost completely quenched fluorescence during measurements. Griest and coworkers[51] also compared liquid-liquid extraction with XAD-2 resin adsorption technique using ^{14}C-B(a)P and recovered 82% of the sorbate from the resin as compared to our recovery of 98%.

In our discussion on the desorption of fluorene from the XE-resins, it has been suggested that an increase in Π-electron cloud density may decrease the desorption of B(a)P compared to fluorene from the XE-resins even with the solvent regimen used in this study. In fact, it can be seen that fluorene was quantitatively desorbed from XE-340 whereas only 60–69% of B(a)P was retrieved from the same resin. Furthermore, using the same solvent system at the same loading pH of 3.0, desorption of fluorene from XE-347 and XE-348, respectively, were 39% and 29% of the PAH whereas B(a)P was eluted under identical conditions to the extent of 12% and 5% respectively from XE-347 and XE-348. It would appear that the increase in Π-electron density in the aromatic nucleus does decrease the desorption ability of the XE-resins in terms of PAH. Moreover, it should be recognized that the pore diameter, pore shape and size may play an important role on the desorption capabilities of the XE-resins with respect to PAHs.

2,4-Dichlorophenol

In Table 6 are shown the percent recovery data for 2,4-dichlorophenol from the five resins with influents at both pHs (3.0 and 5.6). All the resins quantitatively retained the phenol irrespective of the influent pH at 3.0 or 5.6 indicating that variation of pH between 3.0 and 5.6 would have very little influence on sorption of the phenol.

An aqueous solution of methanol-sodium hydroxide ($\approx$pH 8.4) was used prior to pure methanol in the solvent sequence outlined above. When basified methanol eluent was used, 2,4-dichlorophenol was desorbed slightly better from XAD-2 when the pH of the aqueous percolate was 5.6 (29%) than when the influent pH was 3.0 (24%). However, with XAD-7 desorption with the same eluent, almost double the concentration of 2,4-dichlorophenol (15%) was found in the eluate when the percolating fluid pH was 3.0 than at pH 5.6 (8%). However, very little influence of pH variation was noted for XE-340, and XE-348. With XE-347, about six times more phenol was eluted by methanol-alkali solution when the pH of the influent was 5.6 than when the pH of the aqueous solution for resin adsorption was 3.0.

When methanol followed basified methanol solution, during the elution process at pH 3.0, the 2,4-dichlorophenol was leached to the extent of 47% and 41% from XAD-2 and XAD-7 resins and only marginal effect of pH was observed on

Table 6 Percent accountable recovery of 2, 4-Dichlorophenol from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*	*3.00*	*5.60*
VEHICLE											
Effluent	N	4	4	4	4	4	4	4	4	4	4
	MEAN ±	1.91	1.10	0.63	0.93	2.06	1.83	0.85	0.63	0.68	0.98
	STD	0.69	0.80	0.21	0.28	0.72	0.68	0.19	0.28	0.20	0.91
MeOH-NaOH	N	2	2	2	2	2	2	2	2	2	2
	MEAN ±	23.98	29.05	15.06	7.51	10.77	9.46	0.83	5.14	0.23	0.37
	STD	2.20	11.90	3.25	7.98	2.02	0.40	0.18	6.28	0.03	0.01
MeOH	N	4	4	4	4	2	4	2	4	2	4
	MEAN ±	47.49	44.73	40.72	44.55	13.26	11.12	1.08	2.54	0.46	0.61
	STD	5.70	17.13	23.93	26.76	1.02	2.37	0.24	3.45	0.10	0.38
Isooctane	N	2	2	2	2	2	2	2	2	2	2
	MEAN ±	31.41	27.85	15.70	10.67	1.69	1.75	0.08	0.11	0.10	0.08
	STD	5.98	4.67	11.40	7.50	0.21	1.03	0.01	0.02	0.06	0.02
Diethyl ether	N	4	4	4	4	4	4	4	4	4	4
	MEAN ±	17.69	16.03	36.37	37.19	32.16	30.59	2.17	1.83	1.41	2.52
	STD	2.44	9.67	23.18	21.69	2.83	0.43	0.66	0.33	0.49	1.67
Carbon disulfide	N	4	4	4	4	4	4	4	4	4	4
	MEAN ±	3.21	3.37	2.08	3.11	19.93	27.08	12.06	12.94	8.73	14.05
	STD	1.46	2.81	0.65	2.20	5.00	3.40	1.16	2.98	1.65	4.12
Total	N	4	4	4	4	4	4	4	4	4	4
	MEAN ±	97.99	93.69	95.07	94.86	73.65	76.22	16.61	20.56	11.44	18.37
	STD	1.48	4.77	0.91	3.09	8.93	3.95	2.18	8.61	2.10	5.68

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student *t'* test.

desorption from these two resins. It is apparent that from XE-340, methanol apparently extracted similar levels of the phenol (13% and 11% respectively) when the influent pHs were 3.0 and 5.6. Once again, the methanol eluent gave less than 2.0% recovery from XE-347 and XE-348 and the change in pH did not affect the leaching ability of methanol.

When isooctane was used as the eluent, an average of about 30% and 14% of 2,4-dichlorophenol were recovered from XAD-2 and XAD-7 respectively, with marginal effect of pH used during adsorption. About 1–2% of 2,4-dichlorophenol was recovered from XE-340 and very poor recoveries were noted for XE-347 and XE-348. However, nearly 17%, 36% and 31% average recoveries of the residual phenol were extracted from XAD-2, XAD-7 and XE-340, respectively by diethyl ether when the influent pH was 3.0 or 5.6. In the case of XE-347 and XE-348, diethyl ether could leach only about 1–2% of the phenol.

When carbon disulfide was used for extraction of 2,4-dichlorophenol, almost all residual sorbate was leached out from XAD-2, and XAD-7 while nearly 25% of the phenol was extracted from XE-340, and comparatively better recoveries were noted for XE-347 and XE-348. In the case of XE-340 and XE-348, carbon disulfide extraction was apparently influenced by the influent pH i.e. when the percolate pH was 5.6, a better desorption was noted. Finally, the performance in terms of desorption follows the order XAD-2 $\approx$ XAD-7 $>$ XE-340 $\gg$ XE-347 $>$ XE-348.

De Raat and van Ardenne[56] observed that XAD-2 and XAD-7 sorbed p-chlorophenol to the extent of 85% and 89% respectively from normal urine samples and they did not report the recovery of the phenol from these resins. Better recoveries were observed from XAD-2 than XAD-7.[50] Van Vliet *et al.*[32] also showed that XE-347 has lower adsorption capacity for phenol compared to XE-340 and XE-348 in fixed bed experiments. In their studies on the adsorption of phenol and chlorophenol, Stepan and Smith[62] observed that XAD-7 was superior to XAD-2 for concentration of polar organics. In their comparative study, Zhou *et al.*[28] demonstrated that quantitative recovery of 2,4-dichlorophenol was achieved from XAD-2, and XAD-7 absorption technique while XE-340 gave only ca. 78% recovery. However, XE-347 and XE-348 behave as poor accumulators for phenol recovery studies. In this study, we have confirmed the findings of Zhou *et al.*[28] by obtaining almost quantitative recoveries of this phenol from XAD-2 and XAD-7 and nearly 76% of the phenol was leached out from XE-340.

DCPAA

The percent accountable recovery data of DCPAA (Table 7) reveal that there is significant influence of the initial pH of the aqueous sample used in this study. Only 1 to 3% of DCPAA was rejected from XAD-2, XE-347 and XE-348 with a negligible influence due to pH variation. However, alteration of pH has a remarkable effect on the loading capacity of XAD-7 and XE-340. When the pH of the influent was ca. 5.5, nearly 72% of DCPAA was not adsorbed whereas at pH 3.0 of the influent, quantitative adsorption has occurred on XAD-7 resin.

Table 7 Percent accountable recovery of DCPAA from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.54*	*3.00*	*5.54*	*3.00*	*5.54*	*3.00*	*5.54*	*3.00*	*5.54*
VEHICLE											
Effluent	N	5	3	5	3	5	3	5	3	5	3
	MEAN ±	2.35	3.40	0.92	71.73	6.55	55.48	2.69	2.31	1.60	0.94
	STD	1.23	1.57	0.33	3.35	3.08	6.01	1.04	1.14	1.32	0.36
MeOH-NaOH	N	3	1[a]	3	1[a]	2	1[a]	2	1[a]	2	1[a]
	MEAN ±	73.56	67.24	76.85	19.38	1.44	13.51	10.52	1.61	0.04	0.12
	STD	8.10	—	20.61	—	0.30	—	5.70	—	0.03	—
MeOH	N	5	3	5	3	5	3	4	3	4	3
	MEAN ±	1.36	20.72	2.21	2.88	24.46	4.94	38.57	0.36	0.18	0.07
	STD	1.76	3.11	1.65	0.73	5.84	1.46	7.24	0.32	0.06	0.05
Isooctane	N	2	2	2	2	2	2	2	2	2	2
	MEAN ±	NU	4.72	6.09	4.14	0.45	10.13	0.03	0.52	0.04	0.13
	STD	—	0.43	2.07	0.74	0.02	0.02	0.01	1.13	0.02	0.06
Diethyl ether	N	5	3	5	3	5	3	4	3	4	3
	MEAN ±	2.80	2.13	3.62	0.56	15.61	6.03	4.84	1.10	0.67	0.38
	STD	1.47	1.03	2.80	0.24	2.40	3.02	5.18	0.30	0.38	0.16
Carbon disulfide	N	5	3	5	3	5	3	4	2	4	3
	MEAN ±	0.53	0.21	1.16	0.09	4.16	11.09	2.26	15.38	4.68	11.62
	STD	0.74	0.06	1.45	0.06	1.98	8.29	2.36	8.73	1.88	4.97
Total	N	5	3	5	3	4	3	4	3	4	3
	MEAN ±	81.04	98.42	90.85	98.78	52.64	101.35	44.07	21.52	7.17	13.13
	STD	4.17	2.85	3.24	5.70	8.95	2.63	5.34	6.50	1.85	5.41

[a] Only one run was extracted with MeOH-NaOH STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student *t*' test.

NU Not used.

Similarly, with the influent pH at 5.5, ca. 55% of DCPAA has been rejected by XE-340; whereas, at the influent pH of 3.0, about 7% of the sorbate was found in the effluent, indicating that, in the case of this aromatic acid and probably with any compound with strong acidic functionality, lowering of pH to 3.0 and below will favor increase in adsorption, on XAD-7 and XE-340. It is important to note that, in the case of 2,4-dichlorophenol, a weak acid, the influence of pH was not significant with these resins.

When elution was carried out with basified methanol it was noted that the pH variation had only marked influence on the elution of DCPAA from certain resins. In the case of XAD-2, nearly 74% versus 67% of the sorbate was eluted when the respective pH of the influents were 3.0 and 5.5 indicating that a higher percentage of DCPAA could be eluted (influent pH, 3.0) from XAD-2. Similarly, a major portion of DCPAA (nearly 19%, taking into account the unadsorbed DCPAA) was also desorbed from XAD-7 at the influent pH of 5.5. However, when the influent pH was 3.0, nearly 77% of the DCPAA was recovered by elution with basified methanol. [Note: Unfortunately, the standard deviations with elution using basified methanol are unusually high with the result, that the data has been interpreted with caution.] From XE-340, more DCPAA was eluted at the influent pH of 5.5 than at pH 3.0; however the reverse elution was observed with XE-347 and nearly 11% was leached out at the influent pH of 3.0 compared to almost 2.0% at pH 5.5. Very little of the acid was leached out from XE-348.

Using pure methanol as eluent, more DCPAA was desorbed from XAD-2 (21%) when the initial pH of the aqueous solution was 5.5 whereas ca. 2% of the sorbate was leached out at the influent pH of 3.0 indicating a significant influence of pH on the elution of DCPAA from the resin. During the elution of the same adsorbed acid from XAD-7, low levels of the sorbate was leached out from the resin at both pHs of the influent. In the case of XE-340, ca. 24% and 5% of the sorbate were retrieved with methanol at the respective influent pHs of 3.0 and 5.5 suggesting a reverse elution pattern compared to XAD-2. Similar to XAD-7, desorption of DCPAA from XE-347 with methanol gave nearly 39% of the sorbate at the influent pH of 3.0 versus 0.36% at the influent pH of 5.5. In the cases of XE-340 and XE-347, pH variation has remarkably affected the recapturing of DCPAA with methanol. Very poor elution was observed with XE-348 for the same sorbate. Furthermore, isooctane gave poor recoveries of the acid sorbate from all the resins (less than 10%). However, only in the case of XE-340, a marked pH effect was observed when nearly 20 times more DCPAA were eluted with isooctane at the influent pH of 5.5 than at pH 3.0.

Diethyl ether, in the sequential elution did not appreciably desorb the residual DCPAA from all the resins except in the case of XE-340. When the influent pH was 3.0, ca. 16% of the sorbed acid was leached out of the resin. When carbon disulfide was used as the final eluent to desorb DCPAA, better leachings were observed in the case of XE-resins at the influent pH of 5.5. [Note: The residual acid in XAD-2 (pH 5.5) and XAD-7 are very low and hence elution with carbon disulfide was also very low.] However, nearly 10% of DEPAA could not be released from XAD-2 at the influent pH of 3.0. Higher percent of DCPAA was found in the carbon disulfide eluates when the influent pH was 5.5 than at 3.0

indicating lowering of pH of the influent adversely affected the desorption the sorbate with carbon disulfide from XE-resins in spite of initial elution with basified methanol. In terms of total recoveries consistently better leaching of DCPAA was noted at the influent pH of 5.5 than at pH 3.0 except from XE-347. Best accountable recoveries were obtained from XAD-7, XAD-2 and XE-340 at the influent pH of 5.5.

Niederschultz and Ballschmiter[63] reported quantitative recovery of DCPAA at pH 2.0 using XAD-2 and XAD-7 resins. In mutagenicity studies, Ringhand *et al.*[45] observed that acidification of aqueous samples was critical to completely strip acidic mutagens from aqueous sample using XAD-2 and XAD-8. [Note: XAD-8 is very similar to XAD-7 except for surface area.] They also suggested that polar mutagens are irreversibly adsorbed on XAD-2 resin. Furthermore, Kronberg and coworkers[47] also noted that mutagenic activity of sample extract at the influent pH of 2.0 using XAD-4/8 was substantially greater than the extract with the influent pH of 8.0. Similar observations were made by Wigilius *et al.*[10] who reported that about 42% of the mutagenic activity was found in the resin extract of the second column. They reasoned that, even in the molecular or the protonated form, the acidic mutagens were not retained completely in the first column. Furthermore, Moore and Karasek[50] obtained better recoveries after acidification of water samples. However, with XAD-7 resin lower recoveries were obtained at neutral pH, and no improvement was noticed under identical conditions after acidification of the water sample before adsorption. In contrast, Grabow and coworkers[49] found that acidification of water samples reduced the recovery of mutagens after adsorption on XAD columns.

The present study demonstrates that: (a) higher adsorption of DCPAA was noted in the case of XAD-7 at lower pH of the influent similar to the findings of previous workers;[10,45,47,63] (b) in the case of XAD-2, lowering of pH did not affect the adsorption of DCPAA in contrast to some of the previous observations;[10,45,47,63] (c) lowering of pH definitely increases the retention of DCPAA by XAD-7 contrary to the findings of Moore and Karasek;[50] and (d) increase of pH to 3.0 of the influent decreased the desorption of DCPAA from XAD-2, and XE-348 but increased the desorption from XE-347.

2,4-Dichloroaniline

In Table 8 are given the percent recovery data for 2,4-dichloroaniline from the five resins at the two influent pHs of 3.0 and 5.7. The "exhausted" effluents from all the resins contain ca. 2% of the amine irrespective of the pH of the influent indicating sorption of the amine was unaffected by variation of pH of the aqueous sample. In separate experiments we have determined the adsorption of this amine at the influent pH of 9.0, and the amine was sorbed quantitatively to the five resins at this pH.

Elution with basified methanol released about 14%, 11% and 4.5% of the sorbate in the eluates from XAD-2, XAD-7 and XE-340 respectively at both pHs of the influent showing pH variation did not affect the desorption of this amine by the solvent. Very poor recoveries were observed for XE-347 and XE-348 resins.

Table 8 Percent accountable recovery of 2,4-Dichloroaniline from accumulation using the five adsorbents

		RESIN TYPE									
		XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
pH		*3.00*	*5.71*	*3.00*	*5.71*	*3.00*	*5.71*	*3.00*	*5.71*	*3.00*	*5.71*
VEHICLE											
Effluent	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	1.97	0.88	1.06	1.54	1.30	2.11	1.42	2.32	1.08	1.38
	STD	0.30	0.46	0.16	0.42	0.25	1.06	0.75	1.68	0.28	0.73
MeOH-NaOH	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	13.85	13.57	10.15	11.83	4.80	4.27	1.14	0.64	0.28	0.19
	STD	0.87	0.92	3.02	0.31	1.04	0.48	0.04	0.47	0.02	0.08
MeOH	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	38.56	43.14	50.17	53.16	8.54	7.55	1.09	0.52	0.42	0.28
	STD	4.78	2.76	7.29	1.32	0.63	1.43	1.08	0.35	0.14	0.08
Diethyl ether	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	35.18	34.84	28.10	25.52	30.95	29.18	2.50	2.17	1.42	1.56
	STD	2.39	5.08	6.79	1.00	2.60	1.30	0.23	0.95	0.06	0.50
Carbon disulfide	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	3.18	5.16	3.79	4.51	25.78	39.86	35.45	35.61	23.81	38.84
	STD	2.76	1.61	2.73	1.02	1.64	3.42	2.66	0.80	0.84	2.61
Total	N	3	2	3	2	3	2	3	2	3	2
	MEAN ±	92.74	97.59	93.27	96.56	71.38	82.97	41.60	41.26	27.02	42.25
	STD	2.09	0.66	2.23	1.23	4.77	1.75	2.87	4.26	1.01	4.00

STD—For more than three data points, standard deviation was calculated and for two readings, the STD shown is obtained from Student t' test.

Better retrieval of the amine was noted with pure methanol elution and the order of elution performance for methanol eluent was XAD-7>XAD-2>XE-340>XE-347>XE-348. Equally high recoveries of the residual amine from the resins XAD-2, XAD-7 and XE-340 were obtained using diethyl ether as the eluent. Less than 3% of 2,4-dichloroaniline were found in the diethyl ether eluates of XE-347 and XE-348.

When carbon disulfide extraction was carried out on the residual amine retained on the five resins, nearly quantitative recovery of the residual sorbate was obtained from XAD-2 and XAD-7. An average of 25.8% of the residue was leached from XE-340 at pH 3.0. It is noteworthy that lowering of pH of the influent gave lower amount of the amine (26%) than with the influent pH of 5.7 (40%) from XE-340. Furthermore ca. 36% of the amine was released from XE-347 at both pHs of the aqueous influent. Similar to XE-340, the release of the amine into carbon disulfide eluate from XE-348 was markedly affected by the influent pH (24% and 39%) at pHs 3.0 and 5.7 respectively. It would appear that for the desorption of the amine from XE-resins, carbon disulfide proved to be the best solvent. Moreover, the elution performance of the resins follows the order, XAD-2≈XAD>7>XE-340>XE-347>XE-348.

De Raat and van Ardenne[56] reported the adsorption of ^{14}C-3,4-dichloroaniline was 74% and 67% on XAD-2 and XAD-7 when the amine was spiked in urine at pH 5.8. In the present study, 2,4-dichloroaniline was quantitatively adsorbed on all the resins. No recovery data were presented.

The data presented in Table 9 compare the mean accountable recoveries of the selected eight compounds spiked at 3.6 μg/L, percolated through the two macroreticular resins and the three carbonaceous resins, and sequentially desorbed by a battery of solvents. Both XAD-2 and XAD-7 resins have given almost quantitative recoveries for the combined classes of compounds. It is interesting to note that, although we have observed some significant effects of pH variation on the sorption of some of the compounds on these two resins, these effects are not discernible on the "accountable" recoveries of these compounds. For the compounds studied by Blok *et al.*,[37] the combined recoveries were about 59% and 69% for XAD-2 and XAD-8, respectively. We ascribe their lower recoveries to the use of a sufficiently large volume of a single solvent, namely, diethyl ether.

When the recoveries from XE-resins are compared, XE-340 has shown somewhat lower recoveries than those from the two Amberlite resins confirming the observations of Blok *et al.*[37] However, their mean recoveries for the fifteen compounds from XE-340 and XE-348 were only 28% and 18%, respectively. In this study, we have obtained mean accountable recoveries of ca. 85%, 55% and 47%, respectively, from XE-340, XE-347 and XE-348. These increased recoveries are achieved by a battery of solvents sequentially used for elution. Furthermore, Blok and coworkers[37] did not account for loss of materials in the effluents.

XE-340 resin has proven to be superior to XE-347 and XE-348 sorbents. As far as the mean recovery is concerned, XE-340 is the only resin showing some significant influence due to pH variation (ca. 80% at pH 3.0 and 91% at pH = 5.6. Both XE-347 and XE-348 apparently show mean recoveries of 45–57%, which are much higher than those obtained by Blok *et al.*[37] Moreover, the results of this

Table 9 Comparisons of adsorbents based on percent recovery of selected compounds from their aqueous solutions

	RESIN TYPE									
	XAD-2		*XAD-7*		*XE-340*		*XE-347*		*XE-348*	
No. COMPOUND *pH*	*3.00*	*≈5.6*	*3.00*	*≈5.6*	*3.00*	*≈5.6*	*3.00*	*≈5.6*	*3.00*	*≈5.6*
1. Lindane	97.40	97.03	93.75	81.39	94.09	96.25	86.54	95.15	86.69	91.32
2. PCB-153	99.61	90.68	101.81	97.67	94.23	92.26	97.87	99.82	98.34	93.01
3. DEHP	102.91	105.91	104.44	104.35	101.49	110.20	99.24	109.82	97.47	98.25
4. Fluorene	107.93	103.70	108.45	108.42	96.48	97.76	38.96	36.03	29.28	25.97
5. B(a)P	98.10	96.45	99.03	97.01	59.71	69.10	12.24	31.46	5.36	22.64
6. 2,4-Dicholorphenol	97.99	93.69	95.05	94.86	73.65	76.22	16.61	20.56	11.44	18.37
7. DCPAA	81.04	98.42	90.85	98.78	52.64	101.35	44.07	21.52	7.17	13.13
8. 2,4-Dicholoaniline	92.74	97.57	93.27	96.56	71.38	82.97	41.60	41.26	27.02	42.05
% Mean recovery	97.22	97.93	98.33	97.38	80.46	90.76	54.64	56.89	45.60	50.02

Table 10 Typical properties of polymeric adsorbents in this study[a]

Adsorbent Properties	*RESIN TYPE*				
	XE-340	*XE-347*	*XE-348*	*XAD-2*	*XAD-7*
Chemical nature	Carbonaceous ambersorb, slightly resembling activated carbon	Carbonaceous ambersorb, resembling activated carbon	Carbonaceous ambsersorb, resembling activated carbon	Co-polymer of styrene-divinylbenzene	Cross-linked aliphatic polyacrylic ester polymer
Polarity	Non-polar (hydrophobic)	Intermediate polarity	Polar (hydrophilic)	Non-polar (hydrophobic)	Intermediate polarity
Cumulative pore volume (cc/g)	0.34	0.41	0.58	0.89	0.55
Surface area (m^2/g)	400	350	500	330	450
Average pore diameter (Å)	100[b]	100[b]	100[b]	90	90
Micro pore size (Å)	6–40	5	5	Not available	Not available
Mesh–Size	20–50	20–50	20–50	20–60	20–60

[a] Data from manufacturer.

[b] Rough estimate from Incremental Pore Volume Analysis (J. C. Harris *et al.*, IERL-RTP-1100, Technical Report Data, Report # EPA-600/2/80-193.

study suggest that increased recoveries are obtainable from the XE-resins by careful choice of the solvent regimen.

Earlier, it was mentioned that the properties of the selected chemicals have definite influence on their adsorption/desorption relative to the physical and chemical properties of the solid sorbents. In order to understand fully the implications of the recovery results, the mass transfer, as well as the partition properties of the solutes from the mobile phase to the sorbent surface, it is important to take into consideration the physico-chemical properties of the resins.

Table 10 shows some of the typical properties of these five resins. The carbonaceous resin chemicals differ from the macroreticular resins in that the former are sulfonated styrene-divinylbenzene copolymer resins (XAD-2, XAD-4 types)[27] which are pyrolysed under different temperatures in an inert atmosphere. With variation in temperature during pyrolysis, the properties of the XE-resins vary depending on the loss of acidic functionalities, formation of micropores, shrinkage of micropores, surface area etc., to form bidispersed pore size distributions (macro pores with <100 Å dia; and micropores with ≈ 5 Å.) Thus, the properties of XE-340, XE-347 and XE-348 are different, XE-340, XE-348 respectively resembling macroreticular resins and activated carbon. Further, it would appear that most of the sulfonic acid moiety has been dispelled from XE-348 to impart a graphitic appearance to the resin and to provide a very large surface area/activity.

Considering the polarities of these resins, XE-340, like XAD-2 is non-polar while XE-348 is polar, whereas, XE-347 like XAD-7, possesses intermediate polarity. Increase in cumulative pore volumes (cc/g) follows the order: XE-340 < XE-347 < XAD-7 ≈ XE-348 < XAD-2. On the basis of cumulative pore volume, the accumulative efficiency of XAD-2 should be the highest followed by XE-348 ≈ XAD-7 > XE-347 > XE-340. Di Mambro *et al.*[33] suggested the effectiveness of adsorption is related to the relative volume of the pores in the 100 Å diameter range. Thus, all these XE-resins are capable of trapping effectively low molecular weight aromatic compounds. Analysis of the data presented in this study indicates that the capacity for accumulation follows the order: XAD-2 > XE-348 > XAD-7 > XE-347 > XE-340 for hydrophobic solutes.

If the adsorption efficiency of the resins is based on the surface area (activity) and micropore size, XAD-2 and XE-347 have similar surface areas but they differ in their abundance micropore volume (the diameter of the micropore being 5 Å). Although XE-347 has lowest surface area among the XE-resins the absorption efficiency is more than that of XE-340. Van Vliet and Weber[32] in their comparative adsorption studies on the three XE-resins and XAD-4 concluded that the shape and roughness of the surface of the resin should be taken into account to explain the external mass transfer. Hence we expect that the mass transfer in the macropores may proceed rapidly, while into the micropores, diffusion may be severely retarded due to steric hindrance imparted by the relative size of the solute molecules. Although macro and micro-pore diffusion may occur simultaneously but, due to steric hindrance and steric attraction/repulsion properties of the organic molecule, mass transport into the micropores may be retarded and adsorption may take place rather slowly to reach equilibrium. This is evidenced by the high rejection of DEHP, (presumably, all aliphatic long chain hydrocarbons and esters).

The facile desorption of many organic chemicals with concomitant regeneration of the resins XAD-2 and XAD-7 can be explained in terms of lowest surface area and abundance of macropore volume. In the case of XE-347, in spite of its lower surface area than the other XE-resins and because of the high percent of volume due to micropores, the organic chemicals are trapped in the pore fluid in these "pockets". Therefore, the mass transport of chemicals between the pore fluid in the "pockets" and the mobile eluting solvent is precluded. The same situation exists in the case of XE-348 which has higher surface area and is more polar than XE-347, with identical micropore diameter. Hence, desorption of organics from XE-348 should be more difficult than from XE-347. The data presented here confirms these concepts.

CONCLUSION

It would appear that both XAD-2 and XE-340 exhibit hydrophobic properties with reference to non-polar organics such as lindane, and PCB-153. Having intermediate polarity, both XAD-7, and XE-347 exhibit both hydrophobic-hydrophobic and hydrophobic-hydrophilic interactions. It is noteworthy, that XE-347 possesses predominantly hydrophilic properties.

From the adsorption/desorption behavior, it seems that DEHP adsorption on XAD-2 is less prone to pH variation below 7.0; whereas, lowering of pH has significant influence on the adsorption of the ester on XAD-7, XE-340, XE-347 and XE-348. From the desorption behavior of DEHP, and from the characteristics of the resins, it appears that all resins exhibit hydrophobic-hydrophobic and hydrophobic-hydrophilic hydrophilic-hydrophilic interactions. The high rejection of DEHP from the influent is ascribed to steric hindrance, due to the long chain portion of the molecule.

When polycyclic aromatic hydrocarbons (PAH) are considered, all the resins are found to be very good adsorbents. From the data on desorption of fluorene and B(a)P, and the extraction efficiencies of different solvents on the resins laden with PAH, it can be seen that diethyl ether and probably carbon disulfide elute PAHs readily from XAD-2 and XAD-7. However, from the carbonaceous resins, a better leaching was observed with carbon disulfide. The Π-Π interaction between the carbonaceous resins and the PAHs are so strong that both XE-347 and XE-348 tenaciously retained more than 60% of the PAH. Extraction with sequential elution of PAH using different solvent is intolerably incomplete and results in very poor recoveries. Hence, methods should be developed to leach the aromatics from XE-347 and XE-348 resins.

In the case of polar and ionic contaminants, adsorption takes place *via* hydrophobic-hydrophilic interaction with XAD-2, XAD-7 and XE-340; whereas, a non-definitive interaction is operative for XE-347 and XE-348. Carbonaceous resins, during the desorption process of 2,4-dichlorophenol, DCPAA, and 2,4-dichloroaniline, show hydrophilic-hydrophilic interactions; whereas XAD-2 and

XAD-7 exhibit a non-definitive interaction. The hydrophilic-hydrophilic interaction between polar molecules and XE-347 and XE-348 is so strong that these compounds could not be desorbed from the XE-Ambersorb® resins, although XE-340 stands between XAD-2 and XAD-7 on one side and XE-347 and XE-348 on the other.

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