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CHARACTERIZATION OF NON-IONIC DETERGENTS OF THE POLY-ETHOXYLATED TYPE FROM WATER SYSTEMS

I. EVALUATION OF AMBERLITE XAD-4 RESIN AS AN EXTRACTANT FOR POLYETHOXYLATED MATERIAL

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SUMMARY

Amberlite XAD-4 macroreticular resin was studied as a possible extractant for trace non-ionic detergents of the polyethoxylated type present in water systems from domestic and industrial use. Polyethylene glycols were also included in the investigation, as they are important biodegradation products of the detergents.

A number of model compounds, reflecting the expected molecular weight range of the polyethoxylated compounds, were obtained, and distilled water solutions of these used for the evaluation. The XAD-4 resin gave good results for the non-ionic detergents, achieving 80-100% adsorption efficiencies at concentrations as low as 10 ppb with flow-rates of 100 ml min⁻¹. Similar high adsorption efficiencies were obtained for the polyethylene glycols, except for molecular weights below 300, the lowest molecular weight oligomers (the dimer and the trimer) showing little or no adsorption.

INTRODUCTION

Macroreticular resins typified by the Amberlite XAD-2 and 4 (Rohm & Haas, Philadelphia, Pa., U.S.A.) are proving to be very useful for the investigation of trace organic compounds in water systems. These resins are capable of extracting a wide range of non-ionic organic compounds, even when present at the parts per billion (ppb**) level. The relative ease of desorption with organic solvents and the apparent lack of surface catalytic activity offer distinct advantages over other commonly used adsorbants such as activated charcoal.

Burnham *et al.*¹ showed how XAD-2 was used to investigate a taste and odour problem in a ground water sample. At the same time they examined the parameters needed for the efficient extraction and recovery of a number of organic compounds.

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** Throughout this article the American billion (10⁹) is meant.

A more comprehensive study was later published by Junk *et al.*², who developed a common analytical scheme for the quantitative extraction and recovery of twelve classes of organic compounds, dissolved in water at the 10–100 ppb level. The presence of compounds of widespread environmental significance such as chlorinated hydrocarbons has prompted detailed extraction investigations by other workers. Richard and Fritz³ used XAD-2 to adsorb chlorinated pesticides from river water and Harvey⁴ applied the same material to sea water. Musty and Nickless⁵ studied the parameters affecting the quantitative adsorption and recovery of organochlorine pesticides and polychlorinated biphenyls by XAD-4 from standard water solutions. In a recent paper⁶ they compared the performance of the resin on real water systems with polyurethane foam, Carbowax-coated Celite and straight solvent extraction.

Another class of man-made compounds, of interest because of their widespread use, is the synthetic detergents. Evaluation of Amberlite XAD-4 resin as an extractant for trace and ultra-trace amounts, including their possible biodegradation products, would be valuable in two major respects:

- (1) the simplicity of a column flow system compared with a solvent extraction scheme for processing many tens of litres of water, and
- (2) selective desorption of the extracted organics would be a useful isolation step, in view of the large number of other compounds that will be co-extracted.

One type of synthetic detergent that does not seem to have been examined by the Amberlite XAD-4 adsorption technique is the non-ionic polyethoxylated group. Some of these are likely to be of increasing importance, particularly for domestic use, as a replacement for the "harder", less easily biodegradable detergents. The particular non-ionic detergents in question are made by the action of ethylene oxide on an aliphatic alcohol or alkylphenol. The general formula for a completely aliphatic detergent of this type would be $R-(O-CH_2-CH_2-)_nOH$, where R (linear or branched) might contain 15 carbon atoms and n could be between 8 and 20. The original alcohol $R-OH$ might be primary or secondary and the corresponding non-ionic detergent is called a primary or secondary alcohol ethoxylate. Because the linear secondary alcohol ethoxylates undergo rapid biodegradation, they are expected to become important domestic detergents. The analogous detergents containing a benzene ring are usually derived from alkylphenols and possess the general formula $R'C_6H_4-(OCH_2CH_2-)_nOH$, where R' might contain 9 carbon atoms and n is about the same as for the alcohol ethoxylates. These alkylphenol ethoxylates are less biodegradable, and if released through industrial use might persist much longer in water systems. Once the polyethoxylated non-ionic detergents enter the aquatic system they will give rise to biodegradation products. One major product is polyethylene glycol, $H-(O-CH_2-CH_2-)_nOH$, where n could be between 1 and 30. Polyethylene glycol may also be present in water not as a result of biodegradation but through use in industrial processes.

The main purpose for which this work was undertaken was the investigation of secondary alcohol ethoxylate (SAE) as it proceeds through the water system. Associated with this is polyethylene glycol (PEG), a likely biodegradation product. Alkylphenol ethoxylate (APE) was also considered in this study, but only as a possible interferent that should be differentiated in order to allow fuller characterization of SAE residues.

This paper describes an investigation of the parameters affecting the perfor-

mance of Amberlite XAD-4 resin, in the extraction and recovery of three types of polyethoxylated material from water, namely SAE, APE and PEG, which was carried out by using standard solutions of a number of model compounds.

EXPERIMENTAL

Apparatus

For the preliminary work^{5,6}, such as the comparison of XAD-4 with other adsorbents, the extraction apparatus consisted simply of glass liquid chromatography columns, 15 cm long by 2 cm wide.

The detailed evaluation of the resin was carried out in a column designed by Musty and Nickless⁵ for the examination of chlorinated pesticide residues in water, *i.e.*, 20 cm long \times 1 cm I.D., the bottom of which has a fused glass frit (coarse porosity), to hold the resin, and an outlet controlled by a PTFE tap. The top of the column widens to a diameter of 2 cm for a length of 5 cm to act as a small reservoir of approximately 20-ml capacity. For the processing of large volumes of water (over 1 l) the column can be attached to a large glass column, 2 m long and of 2.5 l capacity, by means of a plastic compression screw fitting.

Model compounds

The commercially produced polyethoxylated non-ionic detergents are complex isomeric and polymeric mixtures. For example, a linear SAE designated as C11 to 15-9EO might have several hundred components arising from three factors:

- (a) the variation in alkyl chain length between 11 and 15 carbon atoms;
- (b) the position of attachment of the polyethoxide chain could be at any one of the secondary carbons in the alkyl chain;
- (c) the variation in length of the polyethoxide chain might be between 3 and 12 units (3EO to 12EO), with the major oligomers giving an average chain length of 9EO.

Although this is probably the most complex example it is also the main compound of interest. An APE is simpler because the alkyl chain is not so variable, and the main point of attachment of the polyethoxide group is the *para*-position. A PEG is simpler still because there is only a variable chain of ethoxide units.

The polyethoxide chain is involved in a major way with the more rapid biodegradation mechanisms, and for maximal information on the outcome of this degradation it is important that the XAD-4 resin should extract the full range of polyethoxide chain lengths.

With this in mind, a number of model compounds were obtained in order

TABLE I
CLASSIFICATION OF MODEL COMPOUNDS

For meaning of asterisk, see text.

<i>Chemical type</i>	<i>Model compounds</i>
SAE	3EO, 5EO, 7EO, 9EO* and 12EO
APE	5EO, 7EO, 8EO and 9EO*
PEG	2EO, 3EO, 9EO and 22EO

to assess fully the resin; these are listed in Table I in terms of the average number of ethoxide units (EO) in the polyethoxide chain.

The samples marked with an asterisk are commercially produced detergents and have a broad polyethoxide chain-length distribution, which, as stated previously, might be between 3EO and 12EO or higher. The remaining SAEs and APEs were produced at Unilever Research Ltd. (Port Sunlight, Great Britain) as "cuts" during preparative chromatography of commercial products and, as such, the chain-length distribution will not be as broad. All of the PEGs were obtained through normal chemical suppliers, where they are listed as Digol, Trigol, PEG 400 and PEG 1000.

Stock solutions of the compounds listed in Table I were made up to 1000 ppm (w/v) in both water and acetone. The only trouble experienced was with SAE 3EO, which is fairly insoluble in water. The addition of 10% (v/v) of ethanol to the 1000 ppm standard solution produced a stable milk-white emulsion; the emulsion dissolved on dilution to 1 ppm to produce a clear solution.

Analytical methods

Two analytical methods were chosen for this study, both exploiting the properties of the polyethoxylate group.

(a) Barium chloride-phosphomolybdic acid method

The method was used for the accurate assessment of extraction efficiencies of the resin and is a modification of that described by Heatley and Page⁷ in 1952, reviewed more recently by Rosen and Goldschmidt⁸. The process involves the formation of a non-stoichiometric complex between the polyethoxylated compound, barium chloride and phosphomolybdic acid. The complex precipitates quantitatively from aqueous acidic solution, is isolated by centrifugation, re-dissolved in 2-methoxyethanol and the absorbance measured at 310 nm.

Straight-line calibration plots were obtained for all three chemical types in the range 1–20 ppm, with good agreement between duplicates. Two important points should be noted. Firstly, the slope of the calibration graph (that is, the sensitivity) is not the same for all three chemical types. For SAE and APE it is approximately the same but is much greater, by a factor of between 60 and 70%, for PEG. Secondly, the detection limit is determined by the lowest concentration of polyethoxylated compound that will precipitate as the complex from aqueous solution. The value is close to 1 ppm for nearly all of the model compounds shown in Table I, except for PEG 3EO, which will not precipitate below 500 ppm and PEG 2EO, which will not precipitate at any concentration.

Procedure. To a 50-ml centrifuge tube are added 20.0 ml of the aqueous solution containing the polyethoxylated compound (not more than 1 mg), 1.0 ml of 20% (v/v) hydrochloric acid, 1.0 ml of 20% (w/v) barium chloride solution and 1.0 ml of 10% (w/v) phosphomolybdic acid solution. The tube is well shaken after each addition. When flocculation does not occur in the first minute (the slightest opalescence can be considered as a positive reaction), the solution should be stirred vigorously using a vortex mixer for a further minute. If no change occurs, the solution can be warmed slightly (to not more than 40°) and allowed to stand.

The centrifuge tube is filled close to the top with 0.5 M hydrochloric acid and mixed by inversion. The tube should then be centrifuged for 5 min at 1533.6 g to

compact the precipitate. The supernatant is then decanted off by gently inverting the tube. The tube is again filled with 0.5 M hydrochloric acid, mixed, centrifuged and decanted as before.

The precipitate in the bottom of the tube is dissolved by the addition of a mixture of 5 ml of 2-methoxyethanol and 1 ml of concentrated hydrochloric acid. The dissolution of the precipitate can be greatly speeded up by vigorous vortex mixing, although some warming may also be needed. The solution is transferred into a 25-ml graduated flask, made up to the mark with pure 2-methoxyethanol and the absorbance measured at 310 nm against a blank of the same solvent composition.

Normally a check standard (20 ppm) of the polyethoxylated compound under investigation should be determined at the same time with each batch of analyses.

(b) Thin-layer chromatography—Dragendorff reagent

The thin-layer chromatography (TLC) of polyethoxylated compounds was a valuable complement to the barium chloride–phosphomolybdic acid method. Two different solvent systems need to be used to obtain the maximum information, one system for quantitative determination and the other for qualitative studies of the polyethoxide chain length distribution.

Procedure. The method is based on that used by Patterson *et al.*⁹ in a biodegradation study on similar compounds.

A measured amount of the solution containing the polyethoxylated compound (usually in acetone or chloroform) is spotted on to the starting line of a silica gel TLC plate. The plate is then developed using one of the two solvents (A or B), depending on the information required. After development, the plate is dried at 100°, cooled and sprayed with a modified Dragendorff reagent⁹. The compounds show up as deep pink spots or streaks against a pale yellow background. The sensitivity is reasonably high, and detection limits for nearly all of the model compounds are between 0.5 and 2 μg , being nearer the higher figure when the compound was resolved into a number of spots or was partially resolved into a long streak. One model compound, PEG 3EO, showed only a faint pink colour when present in excess of 100 μg , and another, PEG 2EO, showed no reaction at all. This is to be compared with their performance in the barium chloride–phosphomolybdic acid method.

Solvent A. This solvent is composed of 40 parts of ethyl acetate, 30 parts of water and 30 parts of acetic acid. The SAEs and APEs produce compact spots, all with approximately the same R_F value of 0.8. The PEGs, on the other hand, appear as short streaks of much lower R_F value, the value decreasing with the increasing number of ethoxide units. Quantitative results are obtained by comparison of the colour intensity of the unknown with a range of standards.

Solvent B. This solvent is composed of 70 parts of ethyl acetate, 15 parts of acetic acid and 16 parts of water. The solution is not polar enough to affect movement of the PEGs which remain near the starting line. The situation is different for the SAEs and APEs, which are partially or completely resolved in terms of the polyethoxide chain lengths, the shorter the polyethoxide chain the higher the R_F value. Each APE model compound shows a well defined series of spots, which may spread the whole length of the TLC plate, if the chain length distribution is broad. The SAEs, on the other hand, do not resolve into spots, but each produces a streak which varies in intensity along the length.

RESULTS AND DISCUSSION

The results of the experiments designed to assess the performance of the XAD-4 resin can be conveniently grouped into eight sections:

- (1) comparison of XAD-4 with other adsorbents;
- (2) interfering compounds present in the resin, and their removal;
- (3) comparison of eluting solvents;
- (4) overall percentage recoveries for selected model compounds;
- (5) change in adsorption efficiency of the resin with water flow-rate;
- (6) extraction of very low concentrations from large amounts of water;
- (7) capacity;
- (8) selectivity.

Comparison of XAD-4 with other adsorbents

The results obtained for this comparison were part of a preliminary investigation, and although most of the resin properties were not evaluated at that stage, the potential superiority of the resin became apparent.

The XAD-4 resin was compared with two other adsorbents, activated charcoal, which is still widely used, and polyurethane foam, a promising material for the extraction of chlorinated hydrocarbons from water.

Aliquots of aqueous solution (200 ppm) of SAE 9EO, volume 50 ml, were passed through columns of the three adsorbents at a flow-rate of 5 ml min⁻¹. The columns were washed with a small amount of distilled water and the effluent from each column was analysed for unadsorbed detergent. The washed adsorbents were then eluted with ethanol and the amount of desorbed SAE 9EO was determined by evaporation to dryness, re-dissolving the residue in a known amount of water and taking an aliquot for analysis.

All of the results were obtained using the barium chloride-phosphomolybdic acid method, and the comparison is shown in Table II, all figures being calculated as a percentage of the original amount of SAE 9EO eluted through each column.

TABLE II
ADSORPTION EFFICIENCIES OF TESTED ADSORBENTS

<i>Adsorbent</i>	<i>SAE 9EO unadsorbed (%)</i> *	<i>SAE 9EO desorbed by ethanol (%)</i> *
Polyurethane foam	54	26
Activated carbon (coconut charcoal)	<0.5	<0.5
XAD-4	<0.5	115

* <0.5% corresponds to the limit of detection (1 ppm) for SAE 9EO.

Ideally, of course, none of the detergent should pass through unadsorbed (<0.5%) and the desorption with ethanol should be close to 100%. For both polyurethane foam and activated carbon, it is clear that they will not be useful as extractants for this detergent. Polyurethane foam retained only 46% of the compound and of that 20% appeared irreversibly adsorbed. Activated carbon, although indi-

cating complete adsorption, did not show any desorption with ethanol, even when immersed in the boiling solvent.

On the other hand, the XAD-4 results were very encouraging, but the measured desorption was well over 100% and was an indication of interfering compounds still present in the resin from the manufacture.

Interfering compounds present in the resin and their removal

Results from the preliminary work on XAD-4 resin suggested the presence of interfering compounds. This interference sometimes caused recovery figures to be as high as 130% when determined by the barium chloride-phosphomolybdic acid method. The interference was investigated more fully and a procedure developed for its complete removal.

Approximately 10 g of the resin as received from the manufacturer were extracted with 100 ml of near-boiling acetone, filtered and the filtrate was evaporated to dryness. A portion of the residue was dissolved in water and the barium chloride-phosphomolybdic acid reagents added. A thick, heavy, flocculent precipitate was produced, indistinguishable from that formed by polyethoxylated compounds. TLC examination of another portion of the residue, using solvent A as the developer, showed a long pink streak from the starting line to the solvent front, with the maximum density around R_F 0.3, which compares with SAE 9EO, R_F 0.8, and PEG 9EO, R_F centred at 0.5.

It is clear that the interference could be very serious, particularly when only small amounts of polyethoxylated compounds are extracted by the resin. A private communication from Rohm & Haas stated that "polyanionic" material and gelatin were present during polymerization of the resin. No further information on the polyanionic material was available, but it was considered unnecessary to investigate further, as long as all traces of the interfering compounds were removed before the resin was employed for extraction of water. From the TLC study, the polarity of the interfering compounds varied over a wide range, much wider than any of the model compounds. Any one solvent, therefore, was unlikely to remove all the interference, unless large volumes were employed, which explains why an ethanol pre-wash in the preliminary trials was unsuccessful. A purification method was developed, based on the successive washing with three solvents of increasing polarity, namely acetone-hexane (1:1), acetone and ethanol.

The resin (*ca.* 5 g) was mixed with acetone and slurry packed into the column ultimately to be used for extraction of water. A 50-ml volume of acetone-hexane (1:1) was passed through the column at 5 ml min⁻¹. The eluent was evaporated to dryness, the residue re-dissolved in 0.5 ml of acetone and 10 μ l were spotted on to a silica gel TLC plate. The rest of the plate was masked and the spot sprayed with the Dragendorff reagent. Formation of a pink spot indicates the presence of interfering compounds. Further 50-ml portions of the solvent were passed through until only a very faint pink spot developed. At this point the solvent was changed to acetone and 50-ml portions were passed through the column until again only a faint pink spot was discernible. The procedure was continued with the third solvent, ethanol, but this time 50-ml portions were continued until no trace of pink colour could be seen. As a final check, a further 50 ml of acetone (the chosen eluting solvent for polyethoxylated compounds) was run through, and if no pink colour was detected the resin was washed thoroughly with distilled water (at least 1 l), and the column

was then ready to process a water sample. This procedure may easily be adapted to a batch process.

As a final comment on the purification of the resin, the Soxhlet extraction system used by Junk *et al.*² was found to be unsatisfactory. The adsorption efficiency of the resin measured for all three types of polyethoxylated compounds dropped by an average of 20% after this reflux treatment with acetone.

Comparison of eluting solvents

Although ethanol gave good results in initial investigations, it was not completely satisfactory. A fairly large volume (200 ml) was needed to elute the polyethoxylated compound from 5 g of resin, the last traces being particularly difficult to remove. The relatively low volatility of solvent also meant prolonged evaporation times before a residue was obtained.

After a study of the eluting properties of a number of solvents, acetone was found to give the best results. Acetone is volatile, and complete water miscibility ensures rapid penetration of the water-soaked resin, the medium polarity seeming ideal for desorbing the full range of polyethoxide chain lengths, compared with ethanol which had difficulty in desorbing SAEs and APEs with short polyethoxide chains. Acetone (50 ml) was sufficient to desorb 1-mg amounts of all three types of polyethoxylated compounds from 5 g of resin, as measured by the barium chloride-phosphomolybdic acid method. In further work, 75 ml of acetone were used to ensure desorption of all trace of the compounds.

Overall percentage recoveries for selected model compounds

Adsorption studies on most model compounds at a concentration of 200 ppm gave overall recoveries near 100%; the concentration was far higher than would be expected in water systems, and much lower concentrations were studied for a better assessment of the resin.

Five model compounds were chosen for this investigation: SAE 3EO, SAE 5EO, APE 5EO, PEG 9EO and PEG 3EO. These reflect the full range of certain important physical properties of the polyethoxylated compounds. The short polyethoxide chain SAEs and APEs are the least polar, and not very water soluble, while the short-chain PEGs are highly polar and very water soluble.

Standard solutions of the model compounds were prepared in distilled water, all at 1 ppm concentration except PEG 3EO, which was prepared at 100 ppm. The higher concentration was necessary because of the poor detection limit with the barium chloride-phosphomolybdic acid method. For the test, 1 l of the standard solution was passed through 5 g of the purified resin at 20 ml min⁻¹ (the maximum obtainable by gravity with the small column). The adsorbed compound was then eluted with 75 ml of acetone, the solution evaporated to dryness and the residue analysed by the barium chloride-phosphomolybdic acid method. To prepare the resin column for the next experiment, a further 25 ml of acetone was passed through, followed by 1 l of distilled water, and the column re-packed to remove air bubbles.

All of the measured recoveries, except one, were between 90 and 100% of the original amount passed through the resin. For the PEG 3EO solution, nothing was detected in the acetone residue. With a detection limit of 500 ppm, this means at least 90% was not adsorbed by the resin. These results indicate a fairly rapid

drop in adsorption efficiency of the resin for PEGs between 9EO and 3EO. It is not clear if the drop in efficiency is roughly linear with a shortening in chain length, but it appears that the resin might be limited to the study of PEGs in water for chain lengths greater than 7EO.

Change in adsorption efficiency of the resin with water flow-rate

Results of studies on the adsorption efficiency of 1 ppm solutions of model compounds (except PEG 3EO and 2EO) showed no drop in overall recovery figures when the flow-rate was increased from 5 to 20 ml min⁻¹. To investigate higher flow-rates, a greater "head" of water or a pump was needed. The former method was chosen, as the apparatus already existed in the laboratory, consisting of 2-m long, 2.5-l capacity glass columns, firmly attached to the wall. When the resin column was screwed to the bottom of one of these long columns, the 2-m "head" gave a maximum flow rate of 95–100 ml min⁻¹. Excellent overall recovery figures of 90–100% were obtained for 1 l of 1 ppm standard solutions of SAE 9EO and APE 9EO, processed at 100 ml min⁻¹. The overall recovery figure for PEG 9EO at this maximum flow-rate was lower at 75%. Decreasing the flow-rate to about 50 ml min⁻¹ for PEG 9EO resulted in the recovery figure returning to near 100%. Here we see the reduced performance of the XAD-4 resin for the low-molecular-weight PEGs being extended to the 9EO at high flow-rates, although as discussed in the next section, the previous history of the resin might be a contributing factor. An overall recovery figure of 75% is still acceptable, particularly as it would be very desirable to use high flow-rates to reduce the processing time of large volumes of water. For example, 50 l of water would take 28 h at a flow-rate of 20 ml min⁻¹, but only 7 h at 100 ml min⁻¹.

Extraction of very low concentrations of polyethoxylated compounds from large amounts of water

The ability of XAD-4 resin to adsorb with high efficiency polyethoxylated compounds at very low concentrations is very important, if it is to be used for the examination of all types of water systems, including sea water. When the concentration is very low, then this necessitates the processing of large volumes of water in order to obtain sufficient material for characterization, using methods such as IR, UV and NMR spectroscopy, as well as liquid chromatography.

The performance of the resin in this respect was evaluated by using solutions of a mixture of three model compounds, SAE 9EO, APE 9EO and PEG 9EO. Three

TABLE III
EFFECT OF CONCENTRATION AND VOLUME ON RECOVERY

<i>Volume of solution processed and concentration of the mixture</i>	<i>Overall recovery measured by the barium chloride-phosphomolybdic acid method (%)</i>	<i>TLC examination</i>
1 l, 1 ppm each component	98	—
4 l, 0.1 ppm each component	80	Ratio of PEG 9EO to the non-ionic detergents in right range
10 l, 0.01 ppm each component	82	Ratio of PEG 9EO to non-ionic detergents in right range

different concentrations were investigated, and the results shown in Table III obtained.

After passage of a solution of the mixture through the resin at a flow-rate of 100 ml min^{-1} , the compounds were desorbed with 75 ml of acetone. The acetone solution was evaporated to dryness and the residue re-dissolved in 1.00 ml of acetone. A 10- μl volume was taken for TLC examination, and the remainder (0.99 ml) evaporated to dryness, dissolved in water and analysed by the barium chloride-phosphomolybdic acid method. The TLC examination, using solvent A as the developing solvent, will show if the concentration ratio of PEG 9EO to SAE 9EO and APE 9EO is in the right range, that is 1-2. This is important, because when the total overall recovery of the mixture is not 100%, the decrease in adsorption may be due to one component only.

There is a decrease in adsorption efficiency of about 20% on decreasing the concentration from 1 to 0.1 ppm, but no further decrease at the 0.01 ppm level (Table III). An overall recovery efficiency of 80% is adequate, particularly when using a flow-rate of 100 ml min^{-1} . It must be remembered that the column contained only 5 g of resin with a mesh range of 15-50 B.S.S. A further investigation of column design, with a finer mesh resin and high-throughput pump, could increase the flow-rate even further, while still maintaining a high adsorption efficiency.

In this set of experiments, the resin did not seem to show a lower adsorption efficiency at 100 ml min^{-1} for PEG 9EO, when compared with SAE 9EO and APE 9EO (as reported in the previous section), which can be seen particularly for the 1 ppm mixture (overall recovery 98%). Also for the other two concentrations of 0.01 and 0.1 ppm, the difference in adsorption efficiencies was not significant enough to show up in the TLC examination.

One possible explanation is that a deterioration in the adsorptive properties of the resin may occur after repeated contact with organic solvents. For the study on very low concentrations, fresh purified resin was used for each experiment, whereas for some of the previous studies the resin may have been re-used as many as five or six times. At flow-rates of 20 ml min^{-1} this re-use of the resin appeared to make little difference to the overall recoveries, but if the adsorption efficiency is slightly affected, it may well show up at much higher flow-rates with the most polar highly water-soluble compounds such as the PEGs. This is further supported by the extreme case, where a fairly large drop in resin adsorption efficiency occurred for all three types of polyethoxylated compounds, when the resin was purified by a 24-h Soxhlet extraction with acetone. It is advisable, therefore, to use the resin once only if maximal efficiency is to be maintained. Even so, the adsorptive properties of the resin will not be good enough for the extraction of the very low-molecular-weight PEGs, and a rapid decrease in the performance must be expected between PEG 7EO and 3EO.

Capacity

The extraction columns contain approximately 5 g of XAD-4 resin, and when loaded up to a maximum of 200 mg of SAE 9EO no breakthrough was detected. This value is high, and should be sufficient for river and sea water. On the other hand, when processing large volumes of sewage, particularly influent, the overall amount of soluble organic compounds adsorbed could easily exceed the maximal capacity of such a small column.

Selectivity

It is not expected that XAD-4 will preferentially adsorb polyethoxylated compounds from water systems, except that at the high flow-rates used the adsorption efficiency of the resin for many other compounds might be much lower. For example, the optimal flow-rate for chlorinated hydrocarbon pesticides, using the same apparatus, is 8 ml min^{-1} (ref. 5).

CONCLUSION

Amberlite XAD-4 resin proved to be an excellent adsorbent for the extraction of polyethoxylated compounds from water, with the exception of polyethylene glycols with molecular weight below 300. The performance of the resin is even more impressive when it is considered that flow-rates as high as 100 ml min^{-1} could be used with only 5 g of the resin. The presence of fairly large amounts of interfering compounds is not serious, provided that the rigorous purification procedure is followed. To maintain optimal extraction efficiency of the resin, prolonged contact with organic solvents should be avoided, and the resin used for one water extraction only.

REFERENCES

- 1 A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec and R. Willis, *Anal. Chem.*, **44** (1972) 139.
- 2 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. D. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, **99** (1974) 745.
- 3 J. J. Richard and J. S. Fritz, *Talanta*, **21** (1974) 91.
- 4 G. R. Harvey, *U.S. Nat. Tech. Inform. Serv. PB Report*, 1972, No. 213954/5, 37 pp.; *Gov. Rep. Announce. (U.S.)*, **73**, No. 4 (1973) 49.
- 5 P. R. Musty and G. Nickless, *J. Chromatogr.*, **89** (1974) 185.
- 6 P. R. Musty and G. Nickless, *J. Chromatogr.*, **120** (1976) 369.
- 7 N. G. Heatley and E. J. Page, *Water Sanit. Eng.*, **3** (1952) 46.
- 8 M. J. Rosen and H. A. Goldsmith, *Systematic Analysis of Surface Active Agents*, Wiley, New York, 2nd ed., 1972, p. 348.
- 9 S. J. Patterson, E. C. Hunt and K. B. E. Tucker, *J. Proc. Sew. Purif.*, (1966) 190.