

## THE USE OF MACRORETICULAR POLYMERIC ADSORBENTS FOR THE TREATMENT OF WASTE EFFLUENTS

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**Abstract**—One of the most significant advances in ion exchange resin and adsorbent technology has been the development of the macroreticular pore structure. Various synthetic routes have been developed for preparing both ion exchange resins and polymeric adsorbents of high surface area and pore volume. Further, the synthesis has been developed to a degree such that the surface area and pore parameters can be varied over a wide range. Several of these macroreticular polymers based upon the crosslinked styrene and acrylate systems are now available commercially. These polymeric adsorbents are hard, durable, insoluble spheres of high surface area and porosity. They are available in a variety of polarities. The nonpolar adsorbents are particularly effective for adsorbing nonpolar solutes from polar solvents. Conversely, the polar adsorbents are very effective for adsorbing polar solutes from polar solvents.

The polymeric adsorbents are being studied for a host of applications ranging from the recovery of pharmaceuticals to the treatment of waste effluents. Of particular interest is the use of these polymeric adsorbents for the treatment of wastes from the petrochemical, chemical, dye, and paper manufacturing industries. In some of these examples it has been demonstrated that one can recover significant quantities of re-usable chemicals that more than pay for the waste treatment application. The use of the polymeric adsorbents for the treatment of phenolic wastes is an example of such an application. Other related applications include the removal of chlorinated pesticides, TNT residues, and other noxious compounds from waste effluents and water supplies.

### INTRODUCTION

One of the most significant advances in ion exchange resin and adsorbent technology has been the development of the macroreticular pore structure. Various synthetic routes have been developed for preparing both ion exchange resins and polymeric adsorbents of high surface area and pore volume. Further, the synthesis has been developed to the degree that the surface area and pore parameters can be varied over a wide range. Several of these macroreticular polymers based upon the crosslinked styrene and acrylate systems are now available commercially. These polymeric adsorbents are hard, durable, insoluble spheres of high surface area and porosity. They are available in a variety of polarities.

In general, adsorbents are solids that possess high specific surfaces, usually well above 5 m<sup>2</sup> of exposed surface area/g of solid. Adsorbents fall into two major physical classes, porous and non-porous. The porous adsorbents consist of particles that are usually large (greater than 50 mesh) and the high surface area is a result of pores of varying diameters that "permeate" the particle. The diameters of these pores are larger than molecular distances. Non-porous adsorbents are usually finely divided solids (less than 10 μm), and the high surface area of such materials is due to the fine state of subdivision that is achieved by various techniques such as grinding, precipitation, etc. The specific surfaces of several commercial porous and non-porous adsorbents are given in Table 1.

The selection by the author and his associates of the terms "macroreticular" and "microreticular" to characterize the physical pore structure of the new ion exchange resins and polymeric adsorbents requires some explanation in view of the "classical" adsorption terminology. The terms microporous and macroporous, usually used in adsorption terminology, refer to those pores less than 20 Å and greater than 200 Å, respectively. Pores of diameters between 20 Å and 200 Å are referred to as transitional pores and polymeric adsorbents. This classification

Table 1. Specific surfaces of typical porous and non-porous adsorbents

Porous		Non-porous	
Adsorbent	Specific surface (m <sup>2</sup> /g)	Adsorbent	Specific surface (m <sup>2</sup> /g)
Granular carbons	500-2000	Carbon black	100
Silica gel	600	TiO <sub>2</sub> pigment	70-80
Bone char	60-80	ZnO pigment	1-10
Soils	10-100		
Asbestos	17		
Polymeric, macroreticular	100-600		

cation could, of course, also be applied to the macroreticular ion exchange resins; however, the terminology would not distinguish those pores that are part of the organic gel structure of the macroreticular ion exchange resins and polymeric adsorbents.

In essence, the new macroreticular ion exchange resins have both a microreticular as well as a macroreticular pore structure. The former refers to the distances between the chains and crosslinks of the swollen gel structure and the latter to the pores that are not part of the actual chemical structure. The macroreticular portion of structure may actually consist of micro-, macro-, and transitional-pores depending upon the pore size distribution. Confusing as this terminology may appear, the terms defined above are necessary to distinguish the various structures from one another. The use of the terms "microporous" and "macroporous" for distinguishing between the gel-type standard ion exchange resins and the "macroreticular" ion exchange resins is considerably more confusing and, unfortunately, has no direct relationship to the terms "micropores" and "macropores" as normally defined for adsorbents. All too often the term "macroporous" has been used for materials that cannot

be distinguished from ordinary gel-type materials by any of the available physical methods.

The macroreticular, polymeric adsorbents constitute a new and unique class of adsorbents because of the wide range of pore structures that one can develop within the framework of a particular chemical system. For example, for the styrene-divinylbenzene class of polymeric adsorbents having surface areas ranging from 7 to 600 m<sup>2</sup>/g and average pore diameters ranging from 60 to 1,000,000 Å. Pore volumes may be varied from 10 to 90%. Further, the surface characteristics are also quite well-defined. This flexibility is also possible with other polymer systems such as those based upon the acrylates vinylpyridines, and the phenol formaldehyde condensate polymers. The classical adsorbents such as the silicas, aluminas, and the carbons do not offer this flexibility.

#### THE PHYSICAL AND CHEMICAL STRUCTURE OF THE MACRORETICULAR POLYMERIC ADSORBENTS

##### Chemical structure

In contrast to the macroreticular ion exchange resins, the polymeric adsorbents are truly non-ionic and the properties are totally dependent upon their surface characteristics. Figures 1-3 describe the chemical structures of two of the more interesting polymeric adsorbent classes. One is based upon a crosslinked styrene-divinylbenzene polymer and is very hydrophobic. The other is a crosslinked polymethacrylate structure which is a considerably more hydrophylic structure. These macroreticular, polymeric adsorbents are dimensionally and chemically quite stable. They are also quite insoluble.

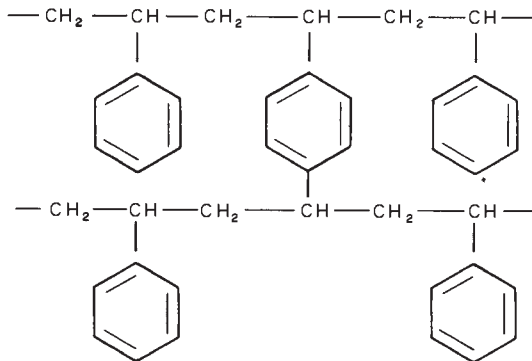


Fig. 1. Structure of Amberlite XAD-2 and Amberlite XAD-4.

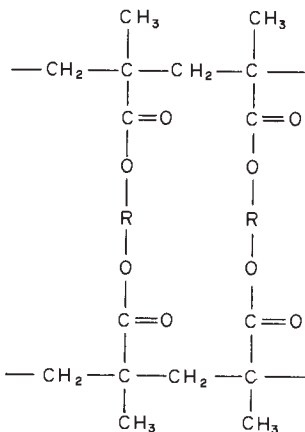


Fig. 2. Structure of Amberlite XAD-7.

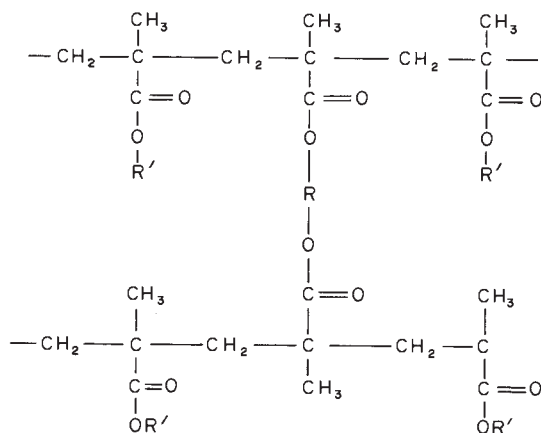
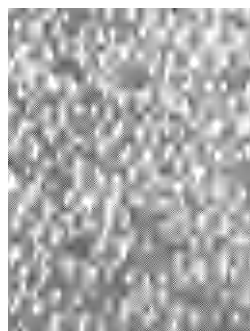


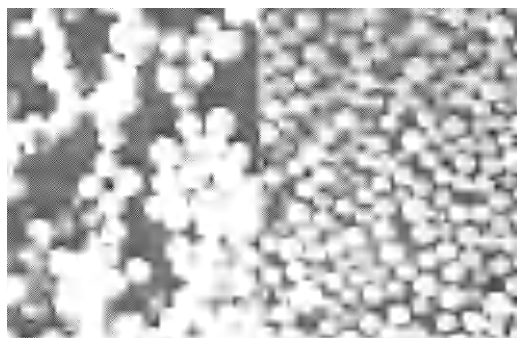
Fig. 3. Structure of Amberlite XAD-8.

##### Physical properties

The physical properties of the above-described macroreticular, polymeric adsorbents are described in Table 2 and Fig. 4. In appearance, the particles are hard, white, and spherically shaped. Figures 4-6 describe their appearance under the ordinary and electron microscopes. Figure 7 describes the pore structures of these adsorbents as measured by mercury penetration.<sup>2</sup>



Gel Copolymer



Amberlite XAD-2 Amberlite XAD-4

Fig. 4. Photomicrographs of macroreticular polymeric adsorbents.

#### ADSORPTION PROPERTIES

Many of the adsorptive properties of these polymeric adsorbents have been previously described. In essence, their adsorptive properties may be predicted from their theoretical solubility parameters and the solubility characteristics of the adsorbate. For example, the less soluble the solute, the more readily is the solute adsorbed.

Table 2. Typical properties of Amberlite polymeric adsorbents

Chemical nature	Helium porosity		Surface area m <sup>2</sup> /g	Average pore diam (Å)	Skeletal density (g/cc)	Nominal mesh sizes	
	Volume (%)	cc/g					
	Nonpolar						
XAD-1	Polystyrene	37	0.69	100	200	1.06	20 to 50
XAD-2	Polystyrene	42	0.69	330	90	1.08	20 to 50
XAD-4	Polystyrene	51	0.99	750	50	1.09	20 to 50
	Intermediate polarity						
XAD-7	Acrylic ester	55	1.08	450	80	1.25	20 to 50
XAD-8	Acrylic ester	52	0.82	140	250	1.26	25 to 50

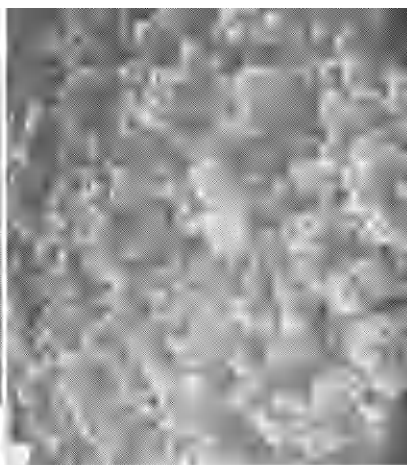


Fig. 5. Scanning electron micrograph of Amberlite IRA-938 at 100× magnification.

Fig. 6. Scanning electron micrograph of Amberlite IRA-938 at 300× magnification.

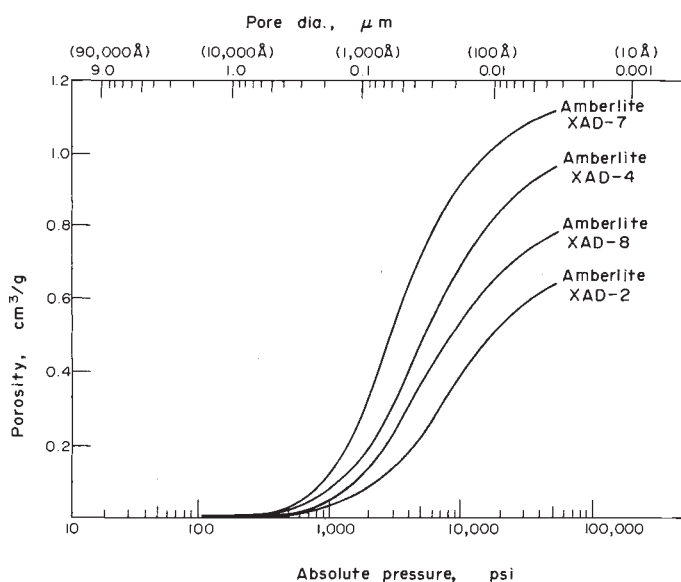


Fig. 7. Pore distributions of some Amberlite adsorbents as determined by mercury intrusion.

Further, the aromatic-based Amberlite XAD-2 resin and the Amberlite XAD-4 resin are more selective for aromatic solutes. Figure 8 and Table 3 describe the effect of the solubility of the solute. The concentration history curve illustrates the adsorption of a series of chlorinated

phenols. As the degree of chlorine substitution of the phenol increases, the adsorptive capacity of the aromatic polymeric adsorbent increases. Elution of the adsorbed solutes is normally achieved with solvents. Elution or desorption of the adsorbed solutes may also be predicted

Table 3. Adsorption of phenol and substituted chlorophenols on Amberlite XAD-4—25°C

Solute	Solubility in water, ppm	Flow rate—0.5 gal/min/ft <sup>3</sup>			
		Solute in influent ppm	Solute in effluent m mol/l	Solute adsorbed, lb/cu. ft Zero leakage	Solute adsorbed, lb/cu. ft 10 ppm leakage
Phenol	82,000	250	2.7	0.78	0.83
<i>m</i> -Chlorophenol	26,000	350	2.7	2.40	2.53
2,4-Dichlorophenol	4,500	430	2.7	5.09	5.49
2,4,6-Trichlorophenol	900	510	2.6	12.02	13.81

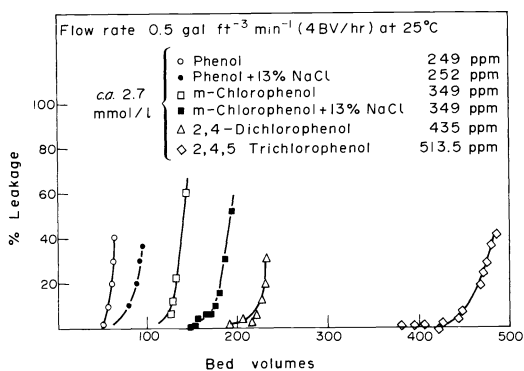


Fig. 8. Column adsorption on Amberlite XAD-4 from aqueous solutions.

by the solubility parameter of the solvent. As the solubility parameter increases, the elution efficiency decreases.

In general, the lower the solubility parameter of a solvent, the better it is as a regenerant. The solubility parameters of several organic solvents are given in Table 4.

Table 4

Solvent	Solubility, cal <sup>0.5</sup> /cm <sup>1.5</sup>
2-butanone	9.3
2-propanone	10.0
1-butanol	11.4
1-propanol	11.9
1-thanol	12.7
Methanol	14.5
Water	23.2

Almost always, methanol is a good regenerant. It washes off the adsorbents easily, and is about the most available and least expensive solvent of those listed. Solubility of the sorbate in the regenerant is also important. Not only must van der Waals' attractive forces binding the sorbate to the adsorbent be overcome, but the solubility must be high enough to permit rapid dissolution after the solvent diffuses to the adsorption site.

Careful selection of the solvent often allows recycling to the process a regenerant stream laden with the adsorbed organic compound. Thus, what would have been a non-productive pollution control step is transformed into a closed loop, materials recovery process. Even when recycling the regenerant stream is not feasible, solvent and sorbate can be separated by common liquid-liquid separation techniques. These adsorptive methods make good sense today when shortages and high prices of raw materials plague the chemical industry.

## APPLICATIONS

These polymeric adsorbents are currently being used for a host of applications in the pharmaceutical industry (recovery and purification of antibiotics and vitamins), as an analytical tool (analysis of drugs and other natural products), and for the treatment of industrial wastes. The remainder of this discussion will be devoted to the treatment of industrial wastes.

### Phenolic wastes

The treatment of wastes containing phenol is a universal problem because of the widespread usage of this chemical. It poses various problems during waste treatment and, if not removed, presents serious problems to municipal water treatment plants. Many industrial wastes contain thousands of parts per million of phenol which not only present pollution problems but also constitute economic losses of a valuable raw material. The ideal waste treatment process would be one that would remove the phenol from the waste and would recover the phenol in a usable form. This has now been accomplished and demonstrated using the polymeric adsorbent, Amberlite XAD-4.

Phenol can be readily adsorbed by Amberlite XAD-4 from solutions containing several thousands of parts per million (ppm) of this moiety and yield effluents containing less than 1 ppm of phenol. Table 3 and Fig. 9 illustrate this

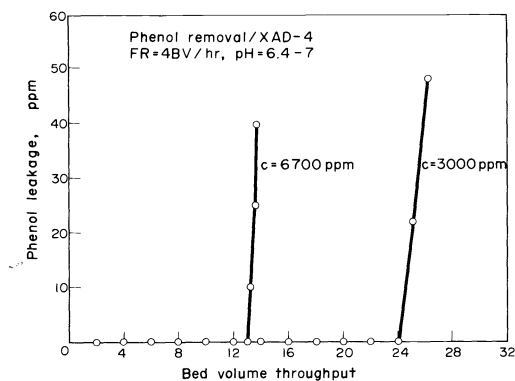


Fig. 9. Removal of phenol from waste effluent using Amberlite XAD-4.

capability of Amberlite XAD-4. The unusual property of Amberlite XAD-4 is the fact that various options are available for eluting and recovering the phenol in a usable form. This property distinguishes it from the classical carbonaceous adsorbents which have been used for phenol removal but which had to be regenerated thermally, destroying the valuable phenol. The various options open for eluting and recovering phenol are summarized as follows:

A. *Regeneration with dilute caustic.* This system will

find the greatest application in those situations where direct recycle of a dilute sodium phenolate stream is desirable, where waste caustic is available, and where raw waste phenol concentrations are below 5000 ppm.

This limitation on phenol concentration in waste streams is a result of less efficient stoichiometric regeneration resulting in an increasingly more dilute sodium phenolate stream, until no concentration effect is observed.

In order to recover the phenol from the sodium salt, a sulfuric acid treatment is recommended. If on-site recovery is not attractive, the sodium phenolate can be sold to firms specializing in recovery of this material.

B. *Regeneration with solvent and recycle of the phenol-solvent mixture.* When recycle of the phenol in a water-wet solvent is acceptable or where waste solvents are available, this system will find the greatest application. The solvents found to be most effective in phenol regeneration from Amberlite XAD-4 are methanol and acetone. Two bed volumes of either solvent are usually effective in removing virtually all of the adsorbed phenol.

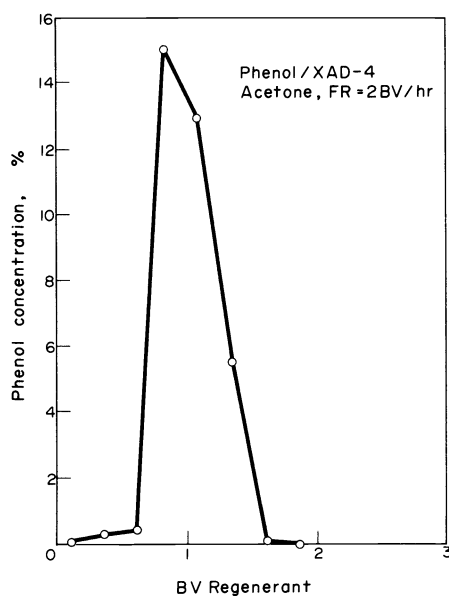


Fig. 10. Acetone regeneration of Amberlite XAD-4 exhausted with phenol.

Since phenol loadings vary with the concentration of phenol in the influent waste stream, the two bed volume regeneration will result in a phenol concentration of from 1 to 10% in the solvent. Note that water entrained in the bed is unavoidably present in the phenol solvent mixture but generally can be held to less than 25%.

C. *Solvent regeneration, recovery of the solvent and recycle of an aqueous phenol stream.* Again two bed volumes of solvent are used to regenerate the resin. The spent methanol or acetone regenerant is fed to a distillation unit where the solvent is recovered for subsequent regenerations. A phenol rich water stream is taken off as a bottoms product. If desired, a second distillation step to recovery solvent washed from the resin bed after the regeneration will increase solvent recovery.

D. *Solvent regeneration, recovery of the solvent and recycle of a concentrated phenol stream.* System C is further modified by adding a distillation column to dehydrate the phenol rich water stream to yield 99% phenol; a small 10% phenol/90% water azeotrope stream is recycled to the influent of the adsorption train. For a continuous distillation operation, the solvent and phenol recovery operation could also be conducted batchwise.

E. If the phenol is to be recovered from the waste effluent of a plant producing phenol formaldehyde resins (Bakelite), it may be eluted with 37% formaldehyde and the eluate recycled.

Some elution data are illustrated in Fig. 10 for a system in which acetone is used as the solvent from which pure phenol is recovered. The entire process is outlined in Fig. 11. The value of phenol recovered in two years is approximately equal to the installed cost of the phenol recovery system.

#### *Trinitrotoluene (TNT) and chlorinated pesticide wastes*

Figures 12-15 describe the performance of Amberlite XAD-4 for the treatment of the waste effluents from a munition plant and a chlorinated pesticide manufacturing plant. In both cases, the data support the excellent performance of the polymeric adsorbent, Amberlite XAD-4. In case of the pesticide waste, the polymeric adsorbent is clearly superior to the conventional carbon adsorbents. In the case of the TNT waste, the use of carbon is clearly not indicated since desorption can only be achieved thermally and such practices are clearly unsafe for a carbon saturated with an explosive such as TNT.

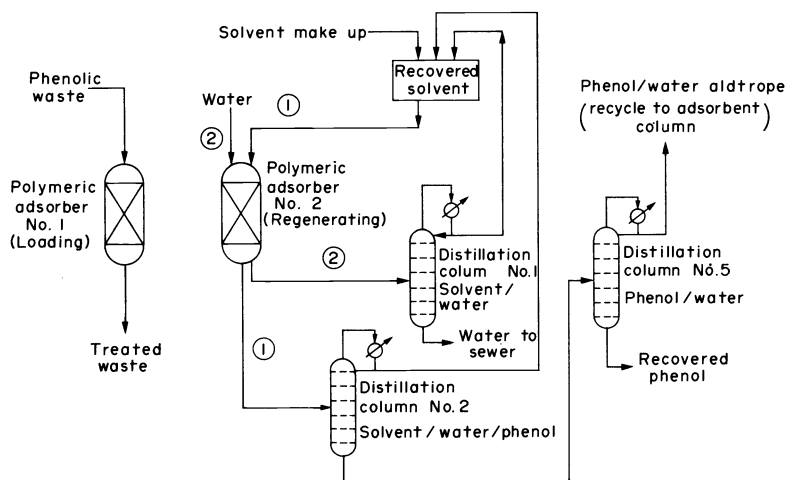


Fig. 11. Phenol removal and recovery system—solvent regeneration of Amberlite® adsorbent.

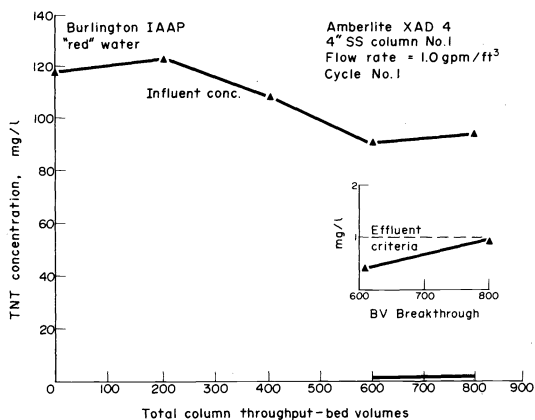


Fig. 12. Adsorption of TNT by Amberlite XAD-4.

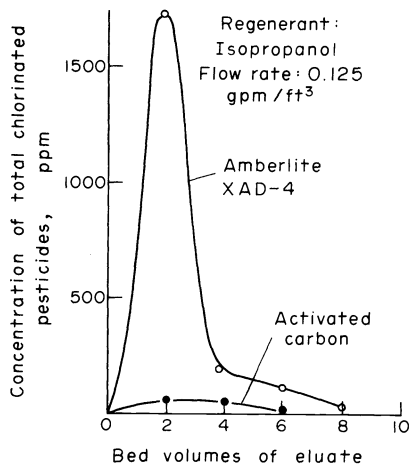


Fig. 15. Elution chlorinated pesticides from Amberlite XAD-4 and granular activated carbon with isopropanol.

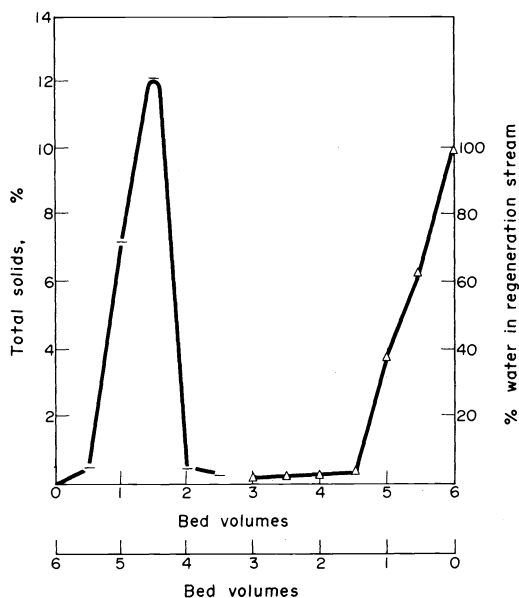


Fig. 13. Acetone regeneration of Amberlite XAD-4, Cycle No. 3.

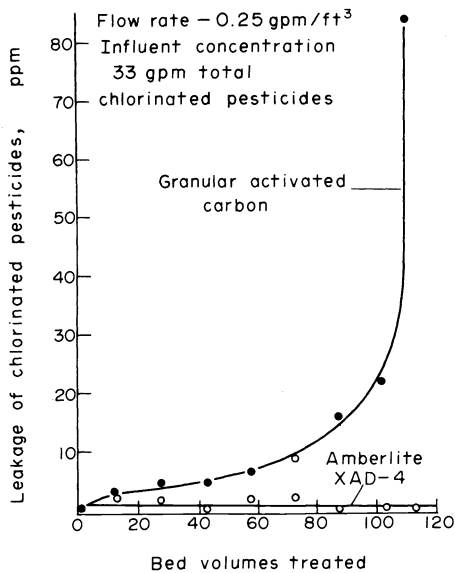


Fig. 14. Treatment of waste effluent from manufacture of chlorinated pesticides.

*Removal of noxious compounds from water*

Regardless of the efficacy of industrial waste control systems, traces (parts per billion, ppb) of many noxious compounds are entering into the drinking water supplies of the water. There has been much concern that has been expressed over this problem and several studies have been initiated on the use of adsorbents to remove these noxious compounds even though there has been no concrete evidence concerning their harmful nature at these trace levels. The macroreticular polymeric adsorbents have shown considerable effectiveness in removing trace levels of such compounds from water supplies.

A recent publication by Professor J. S. Fritz and his associates of the Department of Chemistry of Iowa State University, Ames, Iowa summarizes the results of a comprehensive study on the use of Amberlite XAD-2 and Amberlite XAD-7 for identifying and removing a host of typical organic pollutants from water. Using both Amberlite XAD-2 and Amberlite XAD-7, Prof. Fritz and his associates have developed a method for extracting trace organic contaminants from potable water. They have demonstrated that Amberlite XAD-2 and Amberlite XAD-7 are capable of adsorbing weak organic acids and bases and neutral organic compounds quantitatively from water containing parts per billion to parts per million concentrations of the compounds listed in Table 5.

The acidic components were desorbed with alkali and the basic components with acid. The neutral compounds were eluted with ether.

Table 5. Compounds removed from water with Amberlite XAD-2 and Amberlite XAD-7

Methyl isobutyl ketone	Acenaphthylene
n-Hexanol	1-Methylnaphthalene
Ethyl butyrate	Methylindenes
Benzene	Indene
Naphthalene	Acenaphthene
Benzoic acid	2-2-Benzothiophene
Phenylenediamine	Isopropylbenzene
Phenol	Ethyl benzene
2,4-Dimethylphenol	Naphthalene
p-nitrophenol	2,3-Dihydroindene
2-Methylphenol	Alkyl-2,3-dihydroindene
Aniline	Alkyl benzothiophenes
o-Cresol	Alkyl naphthalenes

Although the work of Prof. Fritz and his associates was analytically oriented, it does point to the potential use of the Amberlite macroreticular, polymeric adsorbents for treating potable water contaminated with various noxious, organic compounds. These studies are being continued by many other investigators in the United States.

#### *The removal of toxins from blood*

Although not generally considered a waste treatment process, the removal of toxins from blood is the most important waste treatment process known to man. When our industrial pollution control and abatement systems do not perform efficiently or are not instituted, man must depend upon his own pollution control system, the kidney, since these toxins may enter into the blood system. The kidney, however, does not have at all times the capacity or ability to treat and cleanse effectively the blood of certain toxins that have been ingested and some device such as an artificial kidney must be employed.

Many drugs commonly implicated in intentional or accidental overdoses are removed by hemodialysis (artificial kidneys). This technique is cumbersome, slow, and requires large volumes of solutions and highly trained personnel. The various studies that have been discussed previously encouraged several investigators to experiment with ion exchange resins and adsorbents for removing these toxic materials by directly treating the blood of a patient and thereby avoiding the need for the hemodialysis procedure. If one considers the low rate of diffusion across membranes, the large surface area of membranes required for hemodialysis to be practical, and compares these factors with the rapid rate of adsorption and high surface area of ion exchange resins, it is obvious that treating blood directly over ion exchange resins and polymeric adsorbents (hemoperfusion) has many advantages over the process of dialysing blood through membranes (hemodialysis). The past 25 yr of research have resulted in techniques for preparing resins and adsorbents that are sterile and free of pyrogen reactions. Further, one may now choose from a host of products to select an optimum product for the hemoperfusion of particular toxins that may occur in the bloodstream of intoxicated patients.

Although much of the above-described effort on hemoperfusion has been devoted to the use of ion exchange resins, the availability of macroreticular polymeric adsorbents has aroused much interest because of their (1) high surface areas, (2) inertness, and (3) ability to adsorb a spectrum of toxic drugs from the bloodstream without altering the ionic composition or pH of the blood. Dr. J. L. Rosenbaum<sup>3,4</sup> of the Albert Einstein Medical Center (Philadelphia, PA) has been quite successful in removing toxins from blood by the hemoperfusion through columns of the macroreticular Amberlite polymeric adsorbents. Dr. Rosenbaum has demonstrated through an exhaustive study on animals and on a number of humans that one can safely and readily remove toxins such as barbiturates and glutethimide from the blood-

stream of comatose patients by the hemoperfusion of the blood over Amberlite XAD-2 and Amberlite XAD-4 polymeric adsorbents. He also compared the procedure with hemodialysis (artificial kidney) and found the hemoperfusion technique using the polymeric adsorbent to be less complicated and faster. Although carbons have also been used in hemoperfusion, their use has been found to be inherently troublesome due to the instability of the carbon particles.

The studies Dr. Rosenbaum performed with Amberlite polymeric adsorbents were conducted with resin that had been carefully treated to remove any potentially harmful impurities, micro-organisms, and pyrogens.

When the hemoperfusion tests<sup>†</sup> were performed on several patients intoxicated with various barbiturates and glutethimide, comparative tests were made using hemodialysis. The patients responded well and the toxins were cleared from the patients much faster using the hemoperfusion techniques with the Amberlite XAD-2 resin adsorbent. Dr. Rosenbaum found further improvements when substituting Amberlite XAD-4 resin for the Amberlite XAD-2 resin.

The overall promise of hemoperfusion with ion exchange resins and polymeric adsorbents for the treatment of drug intoxication can best be summarized with the following quotation by Dr. Rosenbaum:

"The Amberlite XAD-2 resin hemoperfusion systems appears to be clinically superior to hemodialysis in the treatment of drug intoxication . . . It results in higher clearance rates of intoxicants and is mechanically simpler and less expensive. In patients with overwhelming, life-threatening intoxication, hemoperfusion therapy may be of value in reducing coma time and the occurrence of residual complications, particularly pneumonitis. Moreover, the potential range for effective adsorption of toxins by the resin column has not been fully explored and, with the use of combinations of lipophilic, hydrophilic, anion, and cation exchange resins, may be broader than for hemodialysis."

Although the work of Dr. Rosenbaum represents the beginning of a new era in life-saving hemoperfusion techniques, it also culminates a quarter of a century of studies by others in the medical profession. It must be noted, however, that hemoperfusion using resins does not and cannot replace hemodialysis. Whereas it can take over the kidney and liver functions for a temporary period as in the case of drug intoxication, it cannot replace the hemodialysis (artificial kidney machine) procedure for those who have lost their kidney function permanently. In the future, however, hemoperfusion using resins may be a useful adjunct to hemodialysis in such cases. It is the author's opinion that this application represents the ultimate use of polymeric adsorbents for the treatment of wastes.

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<sup>†</sup>Cartridges containing polymeric adsorbents specially prepared for hemodiffusion are being manufactured by Extracorporeal Medical Specialties, Inc. of King of Prussia, Pennsylvania 19046.