



# ENVIRONMENTAL RESEARCH BRIEF

## Evaluation of Innovative Technology for the Treatment of Hazardous Aqueous Waste Streams

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### Introduction

Dilute aqueous wastes have been a treatment problem for many years. Even when the waste materials were readily treatable, the large volumes of water which had to be passed through a treatment system slowed the process, and required inordinately high capital investments. As a result, many such dilute wastes were dumped into streams, or onto the ground where they eventually entered groundwater supplies. These factors, and an anticipation of the ban on landfilling of aqueous wastes prompted EPA to initiate research programs to concentrate, treat, or recover organic or heavy metal pollutants from aqueous streams.

This report summarizes the results of four of the the most recent projects initiated by EPA in the aqueous waste treatment area. We recognize that there is no one solution applicable to the whole gamut of aqueous waste streams, and that several approaches must be tried; consequently, four projects were initiated:

- Concentration of wastes by absorbing the water and excluding the solute using reversible gels;
- Concentration by reverse osmosis, using newly developed composite membranes;
- Adsorption on "pristine lignin"; i.e., lignin derived from steam exploded wood, as opposed to lignin produced by sulfate or sulfite pulping;
- Extraction of pollutants with supercritical carbon dioxide.

### Purpose and Objectives

The purpose of the study was to find economical and effective ways to concentrate aqueous waste streams or to remove pollutants from them, yielding a relatively pure water, and a concentrated waste which could be disposed of in an accepted manner.

The objectives were to determine which types of wastes (inorganic, nonpolar or polar organic) could be treated by one or more of the four processes chosen, obtain throughput rates, compare the processes to existing technologies, and finally, estimate capital and operating costs if enough data were available.

### Technologies Evaluated

Four technologies were evaluated, three aimed at concentrating or extracting the wastes, the fourth was a novel adsorbent.

### Reversible Gel Absorption

The feasibility of using crosslinked polymer gels in a reversible process for extracting pure water from aqueous systems was investigated by Drs. Maier and Cussler of the University of Minnesota (1). Two types of gels were studied, pH sensitive and temperature sensitive, (so called because the reversibility of water absorption could be caused by raising pH in the former, or temperature in the latter).

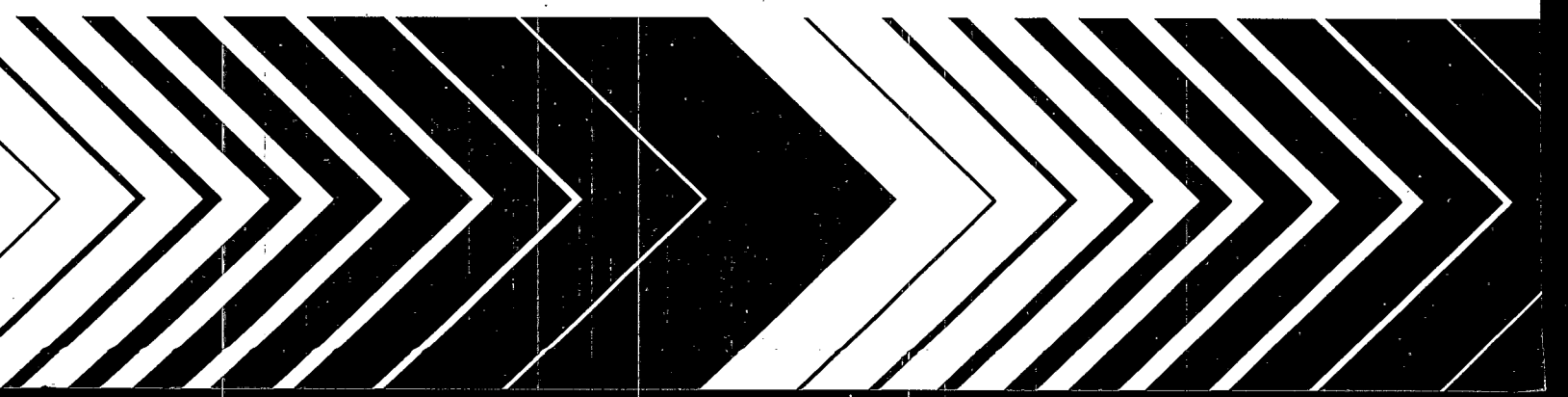
### Objectives

The general objectives of this investigation were to determine if either of those two types of gels, as described below, could be adapted to preferentially absorb water from a solution containing hazardous wastes, and if so, whether this technology could be applied to detoxify "real world" hazardous waste streams.

### Test Results

#### pH Sensitive Gels

The pH sensitive gels were made by copolymerizing acrylamide monomer and N,N'-methylenebisacrylamide



crosslinker in water, after which they were treated with 0.5 M sodium carbonate at 60°C for 24 hours to hydrolyze the amide groups. By varying the ratio of acrylamide and crosslinker, the swelling capacity of the gel may be controlled; the swelling or water absorptive capacity is a function of ionizable group concentration and constriction of elasticity by crosslinks.

When water of pH 6 or above containing a dissolved solute is in contact with a gel of this type, the gel will swell to 10 to 120 times its starting volume, depending on the percent crosslinker, as indicated in Figure 1. The absorption of water concentrates the solution, which may be drained off if a batch process is used; in a packed column, a continuous flow of concentrated solution would be produced. After the gel has reached its maximum capacity, the water is simply eluted by acidifying a rinse stream, as indicated in the lower pH range of Figure 1. Concentration of a number of aqueous solutions or emulsions is illustrated in Table 1. Note that all the solutes in Table 1 are neutral or negatively charged at the pH of separation, and that while larger molecules are excluded, smaller ones are not excluded, and pass into the interior of the gel particles.

Table 2 lists several ionized, negatively charged solutes along with their molecular weight and potential charges. Solute are more efficiently concentrated if they are highly dilute, multiple charged, and have no salt present.

Predictions based on Donnan equilibrium theory confirm these observations fairly closely, as noted in the table.

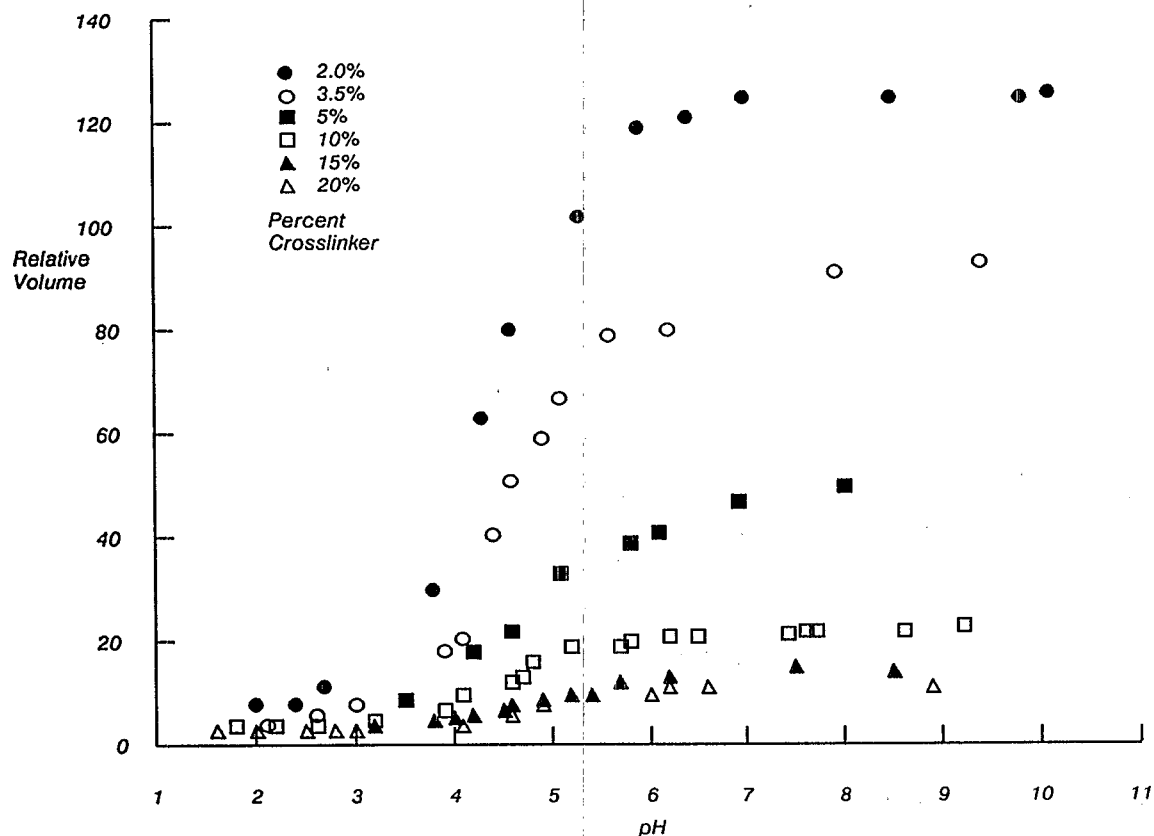
#### Temperature Sensitive Gels

Earlier work had indicated that modified polyacrylamide gels exhibited abrupt changes in volume in response to small changes in temperature. Utilizing this phenomenon would allow concentration of wastes with much lower energy expenditure than conventional evaporation processes.

Two types of these gels were evaluated; one was a terpolymer of diethyl acrylamide and sodium methacrylate, with N,N'-methylenebisacrylamide (MBA) as crosslinker; the second, a copolymer of N-isopropyl acrylamide with MBA crosslinker. The variation of gel volume with temperature shown in Figure 2 indicates that the polyisopropyl acrylamide will lose its imbibed water at a lower temperature, but will hold about 25% as much as the other copolymer.

The temperature sensitive gels are not sensitive to pH. As illustrated in Table 3, the pH sensitive gel decreases to 0.04 of its starting volume as acid is added, while the temperature sensitive gel is relatively unaffected. Low salt concentrations do not cause collapse of the temperature sensitive gels; however, high concentrations will collapse the particles as shown in Table 4.

Figure 1. Gel volume as a function of solution pH. (Source: Reference 1)



**Table 1. Concentration of Aqueous Solutions Using Hydrolyzed Polyacrlamide Gels (Source: Reference 1)**

Solute	Mol. Wt., Daltons	Solute Size, mm	Feed Conc., Wt. %	Raffinate Conc., Wt. %	Percent Efficiency
Polystyrene Latex	--	990 <sup>a</sup>	0.21	0.35	85
Polystyrene Latex	--	34.6 <sup>a</sup>	0.91	1.40	82
Silica	--	5 <sup>a</sup>	1.82	3.03	80
Bovine Serum Albumin	66,000	7.2 <sup>b</sup>	0.08	0.18	93
Hemoglobin	64,500	6.2 <sup>b</sup>	0.73	1.26	91
Polyethylene Glycol	3,000 - 3,700	3.8 <sup>c</sup>	0.56	1.09	6
Sucrose	342	0.84 <sup>b</sup>	1.00	1.09	6
Urea	60	0.53 <sup>b</sup>	3.00	3.00	0

<sup>a</sup> Measured by electron microscopy.

<sup>b</sup> Estimated from the diffusion coefficient in water using the Stokes-Einstein equation.

<sup>c</sup> Reported by the manufacturer from light scattering measurements.

**Table 2. Separation of Charged Solutes with Hydrolyzed Polyacrlamide Gels<sup>a</sup> (Source: Reference 1).**

Monovalent Test Solution	Additional NaCl	$\eta$ (expt)	$\eta$ (Donnan)	Polyvalent Test Solution	Additional NaCl	$\eta$ (expt)	$\eta$ (Donnan)
10 <sup>-4</sup> M NaCl	--	97%	> 99%		--		
10 <sup>-4</sup> M Methyl Orange	--	97%	> 99%	10 <sup>-4</sup> M Congo Red	--	97%	> 99%
10 <sup>-4</sup> M Bromocresol Green	--	94%	> 99%	10 <sup>-4</sup> M Trypan Blue	0.05 M	96%	> 99%
2 x 10 <sup>-4</sup> M Sodium salt of pentachlorophenol <sup>b</sup>	3 x 10 <sup>-3</sup> M	65%	69%	10 <sup>-4</sup> M Trypan Blue	0.1 M	83%	> 99%
				10 <sup>-4</sup> M Trypan Blue	0.1 M	73%	97%
				10 <sup>-4</sup> M Congo Red	0.1 M	71%	79%
10 <sup>-4</sup> M Methyl Orange	0.1 M	55%	49%	10 <sup>-4</sup> M Trypan Blue	0.2 M	69%	92%
0.1 M NaCl	--	55%	50%	10 <sup>-4</sup> M Trypan Blue	0.3 M	52%	89%
10 <sup>-4</sup> M Methyl Orange	0.9 M	14%	18%	10 <sup>-4</sup> M Trypan Blue	0.9 M	34%	36%

<sup>a</sup> Molecular weights and potential charges of the less familiar test solutes are as follows: methyl orange (327,-1); bromocresol green (720,-1); pentachlorophenol anion (265,-1); congo red (697,-2); trypan blue (961,-4).

<sup>b</sup> This experiment used a partially hydrolyzed polyacrylamide polymer synthesized with 5% crosslinks. The added electrolyte here is NaOH. All other experiments used the hydrolyzed P-6 gel.

### Conclusions and Recommendations

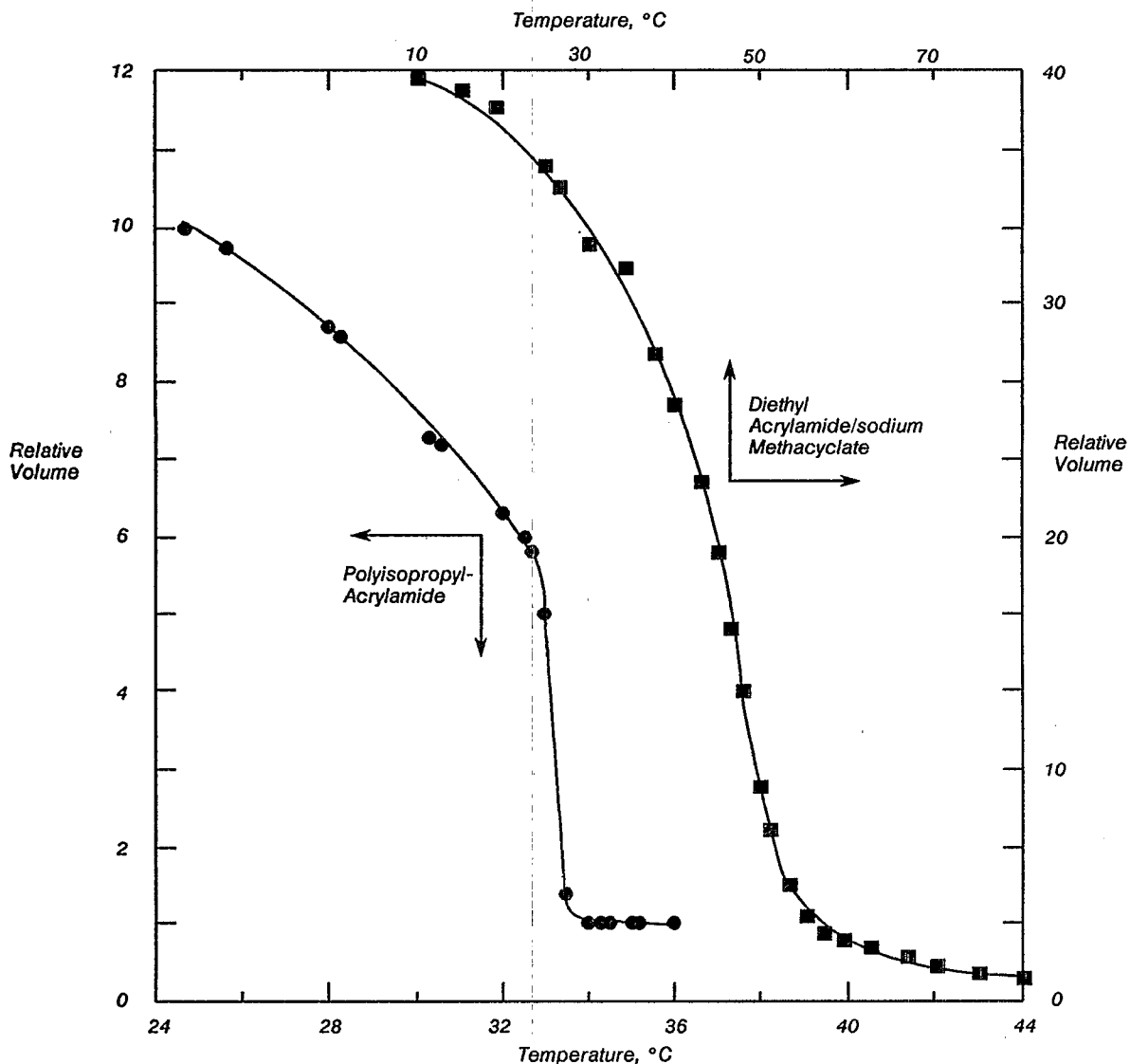
A serious but not insurmountable deficiency of both temperature and pH sensitive gels is their inability to exclude smaller molecules such as urea or methanol while imbibing water from a solution. The selectivity of removal might be enhanced if a semipermeable membrane similar to those used for reverse osmosis were grafted onto the exterior of the particles. This membrane could be composed of the same monomers as the interior, but with a higher ratio of crosslinker in the skin. The tighter molecular structure would allow only smaller molecules or ions to enter into the body of the gel. Another possible approach would be to add formaldehyde to the particles suspended in water, which would bridge amide groups on the particle's surface.

This is an area recommended for development. Such development would greatly broaden the applicability of this technology to concentrate dilute solutions of heavy metal wastes, and to organic separations perhaps; e.g., the separation of ethanol and water, with large savings in energy expenditure.

### Low Pressure Composite Reverse Osmosis Membranes

Concentration of dilute hazardous organic pollutants has been effectively accomplished by Dr. D. Bhattacharyya of the University of Kentucky (2), using FT-30 reverse osmosis (RO) membranes developed by Film Tech Inc. Bhattacharyya's work confirms results reported by Lynch, *et al* in a 1984 EPA report, but carries the study somewhat further. Reverse osmosis processes use pressure to force a fluid through a membrane in the opposite direction of normal osmotic flow (solutions normally tend to become dilute, a state that is the lowest energy state). RO has been used for several years to desalinate water, but was limited in application by the narrow pH and temperature requirements of the cellulose acetate membranes available. The development of new membrane materials has greatly broadened the applications of RO. Composites of two or more polymers combine mechanical strength, the ability to operate over a wider pH and temperature range, higher water flux, and greater rejection for most solutes. Using RO to concentrate dilute organic aqueous wastes greatly

**Figure 2.** Gel Swelling vs. Temperature. Swelling is reported as a volume relative to that at high temperature. The polyisopropylacrylamide shown on the left has a sharp change of swelling at 33°C. The copolymer of diethylacrylamide and sodium methacrylate shown at the right shows a slower change, fastest around 55°C. However, the volume change of the more highly swollen copolymer is larger. (Source: Reference 1)



improves incineration or other treatments. Typical applications of RO in this area would be in concentration of leachate from landfills and contaminated groundwater, or aqueous wastes from chemical processing.

#### Objectives

The objective of this investigation was to determine the applicability of thin film composite membranes to concentrate the following types of organic compounds:

- Slightly soluble organics such as naphthalene, anthracene, phenanthrene, and trichlorobenzene; these

organics were studied both as individual compounds and as mixtures.

- Ionizable organics, including phenol, chlorophenols, and nitrophenols. These were studied as mixtures in order to determine if membrane performance was affected by solute-solvent interactions.

Broader objectives were to find the effect of feed concentration, pH, system pressure, and recovery on solute rejection and water flux. The effects of these factors on membrane stability were also studied.

**Table 3. Polyisopropylacrylamide Swelling vs. Added Acid and Salts (Source: Reference1)**

Added Solution	Relative <sup>b</sup> Volume	Volume of pH <sup>b,c</sup> Sensitive Gel
0 mM HCl/g gel	1.00	1.00
0.04	1.00	1.00
0.11	0.96	0.15
0.14	0.93	0.11
0.19	0.89	0.07
0.23	0.93	0.05
0.32	0.92	0.04
excess 0.05 M NaCl	1.00	1.00
0.10	0.96	0.93
1.00	0.22	0.80
excess 0.05 M CaCl <sub>2</sub>	0.98	

<sup>a</sup> All experiments are at 25°C. The isopropylacrylamide gel was made with 1% crosslinking.

<sup>b</sup> The relative volume is that in solution divided by that in water.

<sup>c</sup> The pH sensitive gel was a partially hydrolyzed polyacrylamide with 5% crosslinking. Similar gels have been reported elsewhere.

### Results and Discussion

The apparatus used in the study is shown in Figure 3. The FT-30 membranes are made up of three layers: a 0.05-0.25  $\mu\text{m}$  layer of aromatic polyamide, 50  $\mu\text{m}$  of porous polysulfone, and a 125  $\mu\text{m}$  polyester backing. Figure 4 illustrates the assembly into a batch test cell, using nitrogen pressure to drive the liquid through the membrane. Separation of selected classes of priority pollutants were studied at 0.52-2.068 MPa (75-300 psig). The batch cell experiments focused on the individual species and mixtures of several slightly soluble PAH compounds (naphthalene, anthracene, phenanthrene) chlorophenols, nitrophenols, phthalates, and chlorobenzene. A wide range of pH values were run on the chlorophenols and nitrophenols to establish the rejection behavior of nonionized and ionized species. Table 5 summarizes the results obtained with PAH compounds. Note that permeate fluxes were nearly all in the same range, and did not vary greatly from the permeate flux of distilled water.

The rejection of chlorophenols is greatly affected by pH, as shown in Figure 4. This effect is thought to be due to the exertion of a repulsive electrostatic force between the membrane and the chlorophenols. Figure 4 also shows the effect of additional chlorine atoms on the molecules, as the rejection increases with increasing chlorine content.

Mass balance calculations were made to determine the adsorption of chlorophenol solutes on the membrane. The calculated concentrations at low pH (5.5) differ significantly from actual concentrations determined by TOC determinations, indicating adsorption on the membrane; if pH is raised to 10.8, adsorption is cut in half. This adsorption was further confirmed by running unstirred vs. stirred samples. Permeate flux dropped over 63% for 2,4,6-TCP as a result of a phenomenon called concentration polarization.

Three chlorobenzene homologs were the last compounds studied. These were monochlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene, all run under unstirred conditions. As might be expected, adsorption on the membrane was even worse than with the nonionized

(low pH) chlorophenols when unstirred, with the dichloro and trichloro compounds adsorbing more severely than the monochlorobenzene. Figure 5 compares unstirred and stirred monochlorobenzene. When stirred, the permeate flux remained high, decreasing only by about 2% during the run, compared to the decrease in the unstirred flux.

### Conclusions

Low pressure composite membranes offer an efficient method of concentrating certain dilute organic wastes. High solute separations are achieved at relatively low pressures of 1-2 MPa (145-290 psi) over the broad pH range of 2-12. The aromatic polyamide membrane tested was Film Tech's FT-30 which showed excellent stability over long operating periods with respect to water flux and permeate quality. Rejection of ionizable compounds such as chlorophenols was 99+% at pH 11, but only 77-89% at pH 4.6; nitrophenols were slightly less affected by low pH. While some compounds, notably chlorobenzenes, adsorbed on the membrane, permeate rejection actually increased at the expense of a drop in permeate flux.

### Extraction with Critical or Near Critical Fluids

While many extractions of organic materials are accomplished with common solvents such as hexane or ethanol, a growing body of knowledge has developed on the use of near critical or supercritical fluids (SCF) as extractants. Perhaps the best known application of SCF is the use of SC carbon dioxide to decaffeinate coffee, replacing the trichloroethylene used previously.

When a liquid is heated in a closed pressure vessel with a vapor space above it, it will boil, but there will be a clearly defined interface between the two phases. If heating is continued, the pressure will rise, and eventually a temperature will be reached where the interface disappears; this is the critical point, above which a single phase having unique properties exists. Table 6 lists the critical properties for a number of compounds, many of which have been evaluated as solvents.

Using SCF as extraction solvents permits tailoring the solvent properties by varying the pressure and/or temperature above the critical point; this simple procedure plus the wide choice of fluids available, gives considerable control over an extraction process. Many variations of solvent characteristics are available. As indicated in Table 6, a nonpolar solvent such as ethylene with low critical pressures and temperatures may be selected for a specific task: an extremely polar solvent such as water may be even more useful. An extreme example of the ability to vary solvency is evidenced in the case of water, which has a dielectric constant of 80 at room temperature. As the temperature is raised toward its critical point, the dielectric constant decreases to about 2, which is very near the value of nonpolar compounds such as hexane. Above the critical point, salts which were soluble at lower temperatures precipitate. Conversely, carbon dioxide (dielectric constant 1.0 at 100°C and 0.1 MPa) rises to about 1.6 at 5.07 MPa. Although this is below the critical pressure of 7.5 MPa, carbon dioxide has been used as an extraction solvent in this pressure region.

The projects summarized here are an extension of work done on the regeneration of activated carbon by extracting

**Table 4. Selectivity of Extractions Using Temperature Sensitive Gels (Source: Reference 1)**

Solute	Mol. Wt.	Polyisopropyl- acrylamide	Copolymer of Diethylacrylamide and Sodium Methacrylate	Copolymer of Diethylacrylamide and Sodium Methacrylate
		1a	4a	2a
Urea		2	3	2
Sodium Pentachlorophenolate	267	18	51	--
Vitamin B12	1,355	32	15	7
Ovalbumin	45,000	97	84	
Polyethylene Oxide	600,000	96	89	92
Gelatin		98	97	96
Blue Dextran	2,000,000	97	99	96
Polystyrene Latex		95 <sup>b</sup>	96 <sup>b</sup>	96 <sup>c</sup>
Polyethylene Glycol	400	10	5	
	3,400	30	19	11
	8,000	56	25	16
	18,500	80	61	48

<sup>a</sup> Percent of crosslinkage used in preparation.

<sup>b</sup> This latex has a diameter of 0.06  $\mu\text{m}$ .

<sup>c</sup> This latex has a diameter of 1.2  $\mu\text{m}$ .

**Figure 3. Batch membrane unit. (Source: Reference 2)**

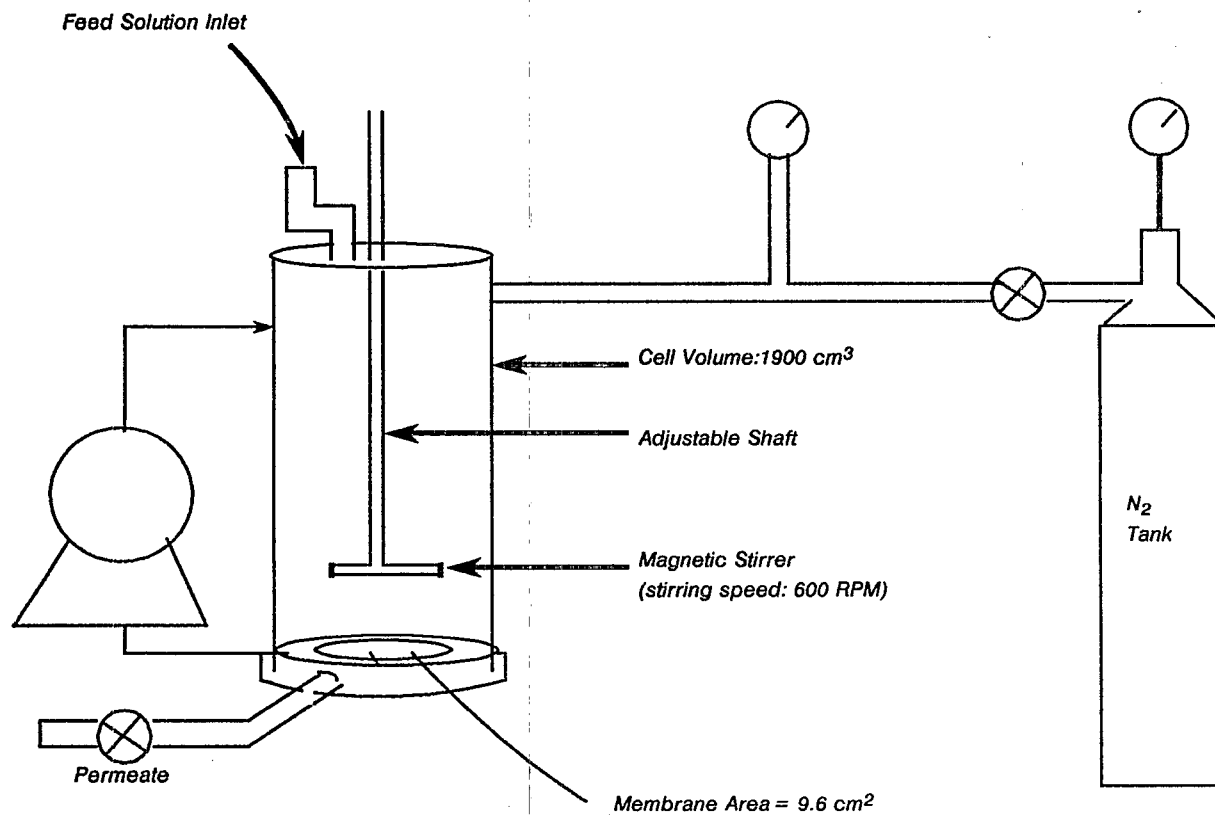


Figure 4. Effect of pH on rejections of chlorophenols at 2.068 mPa. (Source: Reference 2)

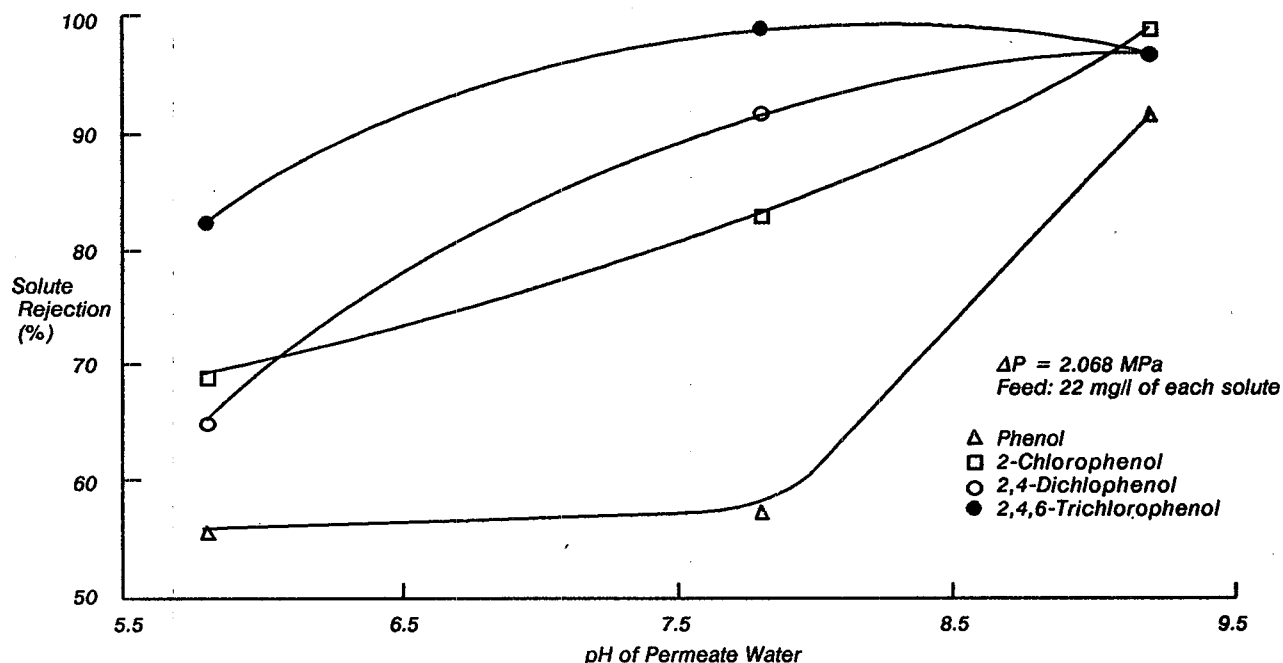


Table 5. Summary of Batch Experimental Results with PAH Compounds.<sup>a</sup> (Source: Reference 2)

Feed	Feed pH	Permeate Flux, cm <sup>3</sup> /cm <sup>2</sup> s	Recovery, percent	Rejection, percent
Naphthalene (21.4)	6.5	9.45 x 10 <sup>-4</sup>	79.3	98.01
Naphthalene (2.22)	5.5	8.63 x 10 <sup>-4</sup>	82.9	97.99
Anthracene (0.12)	6.3	9.08 x 10 <sup>-4</sup>	84.2	>99.10
Phenanthrene (0.574)	6.2	8.92 x 10 <sup>-4</sup>	83.5	>99.96
Mixture of naphthalene (7.08)	5.5	10.25 x 10 <sup>-4</sup>	82.8	88.37
anthracene (0.000999)				94.14
phenanthrene (0.547)				99.24
Distilled water (averaged over 25 days)	7	11.00 x 10 <sup>-4</sup>		

<sup>a</sup>  $\Delta p = 1.72 \text{ MPa}$ , stirred conditions.

with supercritical carbon dioxide reported by Di Filippi *et al.* in 1980 (3). This summary covers basic work done at Louisiana State University (4) and the University of Illinois (5), and applied studies on the extraction of steel mill sludges, pesticide wastes, and toxic water soluble organics done by Critical Fluid Systems, Inc. (6).

### Objectives

The objective of this investigation was to determine whether critical or near critical carbon dioxide could be used to extract and/or recover toxic organic compounds from aqueous waste streams. A further objective, based on these results, was to estimate the capital and operating costs of an extraction system, and furnish a conceptual design.

### Results and Discussion

Carbon dioxide is a convenient solvent; it is cheap, nontoxic, and has a relatively low critical point. On the other hand, when a more polar compound must be extracted, carbon dioxide may not be very effective. Figure 6 shows the results of extraction of a soil which had a starting concentration of 1000  $\mu\text{g}$  DDT/g soil. Extraction was done at 40°C and 10 MPa. Carbon dioxide alone extracts only about half of the DDT, and was only slightly improved by adding toluene, a nonpolar compound, as a cosolvent. When 5 wt% methanol was added, the residual was decreased to about 5% of its starting concentration. While this experiment was run on undried soil, to which the DDT might be quite strongly bound, cosolvents might be a better choice for extracting certain aqueous wastes.

Figure 5. Instantaneous permeate flux as a function of time for stirred and unstirred experimental conditions. (Source: Reference 4)

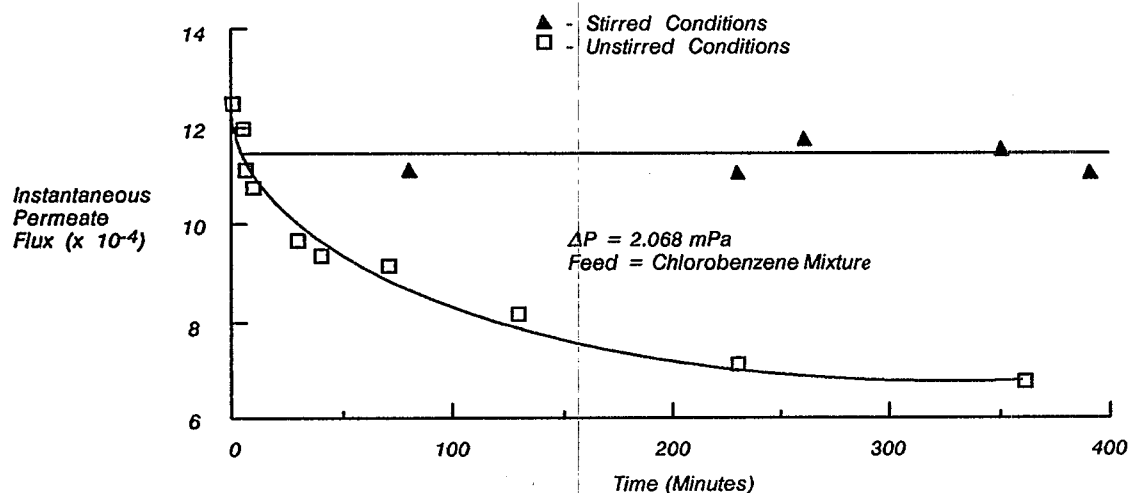


Table 6. Critical Properties for Selected Fluids (Source: Reference 3)

Fluid	Critical Temperature (T <sub>c</sub> ), °C	Critical Pressure (P <sub>c</sub> ), mPa	Critical Density (P <sub>c</sub> ), g/cm <sup>3</sup>
Pentane	296.7	3.4	0.232
Butane	152.0	3.8	0.228
Solvent-12	112.0	4.1	0.558
Propane	96.9	4.3	0.220
Ethane	32.3	4.9	0.203
Ethylene	9.9	5.2	0.227
Carbon Dioxide	31.1	7.5	0.468
Sulfur Dioxide	157.6	8.0	0.525
Ammonia	132.4	11	0.235
Water	374.3	22	0.326

Dry mill scale had previously been deoiled with SC carbon dioxide (4). Since a large portion of mill scale is disposed of in lagoons, an attempt was made to extract sludge from the lagoons, recovering iron and a high heating value oil. The sludge is 30 to 70% solids, and contains oil, water, iron fines and toxic and nontoxic residues. Oil and grease content varies between 6 and 30% by weight of the solids. One plant can produce up to 50,000 tons per year of this sludge, and the pollution potential and economic losses are substantial; an effective extraction method would allow recycling the iron, and reuse of the oil as either fuel or lubricant.

Sludge extraction was attempted with carbon dioxide in a sieve tray extraction column, the only equipment available. The dense sludge was very difficult to handle, plugging lines, valves, and eventually the sieve trays themselves. Solvent to feed ratios and dilution were increased in attempts to keep continuous flow and increase oil recovery, but an oil reduction of 30% was the highest attained. To handle the heavy abrasive sludge, a complete system

redesign was needed. One design considered was a multi-stage mixer-settler operating at or above a 4-1 solvent to sludge ratio. The economics of such a system have not been studied, they may not justify recovery.

Sludge from pesticide manufacturing was tested in a stirred laboratory reactor and later in the sieve tray pilot plant. The sludges contained water, xylenes, carbon tetrachloride, solids, fines, salts, and other insolubles. The purpose of this test was to extract carbon tetrachloride and the mixed xylenes from this waste.

Distribution coefficients determined in the stirred reactor indicated an easy separation, but when tested in the continuous flow reactor with a much lower shear rate, four passes were required to attain an overall reduction of 86% of the carbon tetrachloride. Results with xylene extraction were even more anomalous; the experimenters postulate that soaps and dispersants present in the feed hindered extraction of the xylene from the aqueous phase.

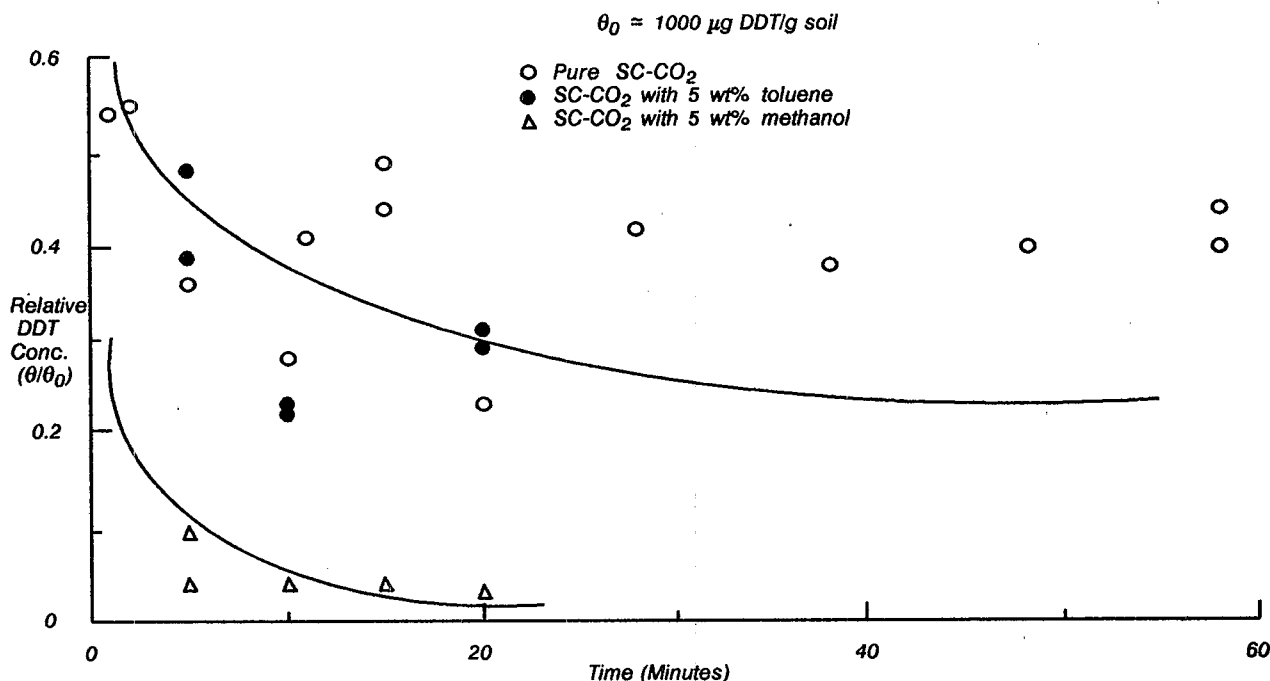
### Extraction of Dissolved Polar Organic Compounds

Carbon dioxide extraction of aqueous solutions of acrylonitrile and acetonitrile were much more successful than any other tests. Much of this success was attributed to the fact that these solutions were clear with a single phase, thus the sieve tray column could function properly; i.e., it could provide better contact between the extractant and the aqueous feed. Using a solvent to feed ratio of 1.5-1 required multiple passes; i.e., the raffinate from the first pass was used as feed for the next. A total of five passes were used to get acetonitrile below the minimum detection limits. Acrylonitrile, as predicted from distribution coefficient data, was much easier to extract; only one pass was required to remove it below the detection limit. The success of these runs resulted in their use as a basis for a conceptual plant design.

A hypothetical wastewater extraction system was designed to process a stream with properties and compositions as shown in Table 7. The economical number of trays for the extraction was determined to be 30, using a tray efficiency



Figure 6. Extraction results. (Source: Reference 4)



of 0.44 and a solvent to feed ratio of 2-1. This system is designed to reduce a waste stream having 1680 ppm acetonitrile to less than 5 ppm, a reduction of 99.7%. A process flow diagram is shown in Figure 7, where the waste stream is contacted countercurrently with an upwardly flowing stream of carbon dioxide at 7.6 MPa (1100 psi). The extract stream has the recovered organics separated at high pressure in a distillation column, thus minimizing the work required to recompress the carbon dioxide, whose heat of vaporization is furnished by the adiabatic heat of compression of the recovered solvent.

Estimated annualized operating costs of a plant processing 20 gpm of an acrylonitrile/acetonitrile feed operating 8000 hours per year are given in Table 8. Processing cost would be about \$0.084/gal. with no credit for recovered product. If the recovered products were purified, they would be worth about \$100,000 total, and would lower the overall processing cost appreciably.

### Conclusions

Supercritical or near critical extraction of organics from aqueous wastes is applicable to certain waste streams, particularly those having very toxic or valuable solutes. Aqueous wastes with suspended solids and sludges must be handled on a case-by-case basis, with very careful consideration of the equipment requirements, and an awareness of construction costs. As the art and science of this process now stands, laboratory determinations of partition coefficients and other parameters must be done before any larger scale extractions are attempted.

### Use of Pristine Lignin to Treat Hazardous Waste

Conventional wood pulping processes are prodigious chemical by-product producers. In addition to the lignin extracted, which is not in its "pristine" form (in the Kraft

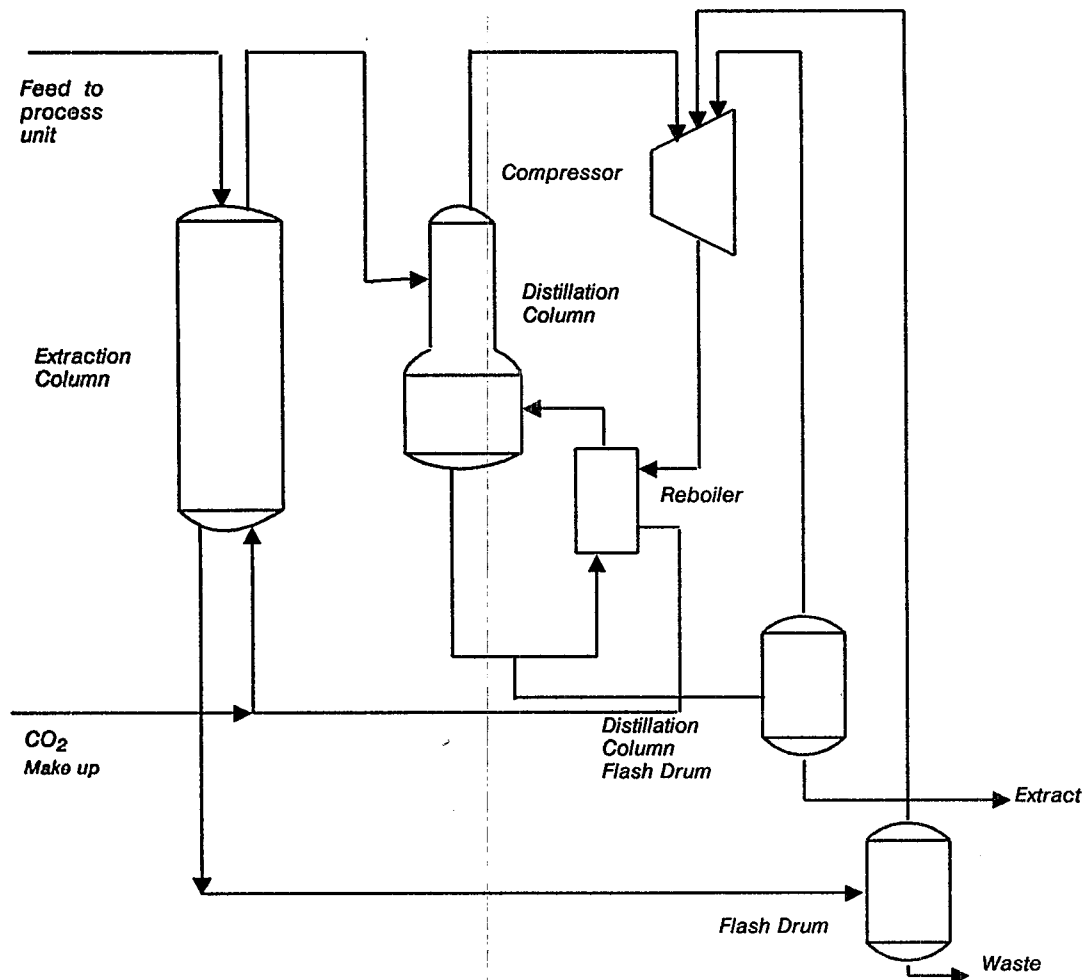
process lignin is converted to thioglignin, and in sulfite processing, much is converted to lignin sulfonates) hemicellulose sugars are produced; these are oxidized to saccharinic acids in the Kraft process. Much of the lignin, saccharinic acids, and hexoses are presently burned as fuel for other parts of the papermaking operation. Some sources have stated that the fermentable hexoses alone could produce two to three times the amount of ethanol presently produced in the U.S. (7).

Newer pulping processes beginning to be adopted use solvents such as ethanol to extract lignin from the wood chips, or explode chips by saturating them with steam in an autoclave, then suddenly releasing the pressure. The lignin thus produced is much nearer to its structure as it existed in nature, and has been dubbed "pristine" lignin. A study of the use of this material to adsorb both organic and inorganic compounds from aqueous media, and to compare its performance to activated carbon, has been performed by Dr. D. J. O'Neil at Georgia Institute of Technology's Georgia Tech Research Institute (8). Since lignin is much cheaper than activated carbon (\$0.03-0.13/kg vs. \$1.00+) it could compete if it were only 1/10 as adsorptive, and instead of regenerating the adsorbent, it could, in many instances be burned, as it has some fuel value. If the same assumption of efficacy is applied to ion exchange resins, an even greater cost advantage would be seen if pristine lignin were used to remove heavy metals. A typical structure of lignin is shown in Figure 8. The rich organic functionality is apparent, with many carboxylic acid, phenolic, quinone groups and others available.

### Objectives

The principal objective of this study was to demonstrate that "pristine" lignin could provide a low cost, yet effective

Figure 7. Flow diagram of proposed extraction process.



and flexible material for the treatment of various aqueous waste streams. To accomplish this, lignin was evaluated as a physicochemical adsorbent of heavy metals and organic compounds. Other objectives included an evaluation of lignin's technical and cost effectiveness in comparison to current treatment technologies such as activated carbon adsorption, as well as a conceptual design of a full-scale treatment plant.

### Results and Discussion

Adsorption studies reported here used lignin derived from tulip poplar, a relatively common, fast growing tree of the Southeastern U.S. Two types of lignin were extracted, the first, a light brown powder, was obtained from steam exploded wood chips using 95% ethanol. Addition of benzene in an attempt to change the character of the extract produced a gummy precipitate upon drying. The fraction of lignin recovered averaged 7.5%, had an average surface area of 30 square meters per gram, and an average molecular weight of 1380. The second type of extract was made with dilute sodium hydroxide, and although an average of 31.9% of the lignin was extracted, the surface

area was only about 0.1-0.3 square meters per gram, but the molecular weight was 2300, with a much broader distribution. The complex structure and presence of many different polar groups presents great difficulties in elucidating the structure of lignin for, as was the case here, the extraction method defines the product.

The adsorptive behavior of ethanol extracted lignin was studied using water spiked with several organic "contaminants" and results are presented in Table 9. Although smooth curves of adsorption were obtained, there does not appear to be any pattern of structure dependency of the adsorption isotherms. Rough estimates of the capacity of the large particle size (30-40 mesh) lignin used indicate that a smaller particle size adsorbent should remove about 5 g/kg of the seven compound mixture in Table 9, and about 0.3 g/kg of 2,4-D. Adsorption of lead and chromium compounds (the investigator does not specify the species) is shown in Figure 9. An adsorption capacity of 1.3 g/kg of these metals is estimated under the conditions of this test. Speed of adsorption is much higher when higher ratios of adsorbent to both organic and inorganic compounds was used, suggesting that an

**Table 7. Properties and Composition of Acetonitrile/Acrylonitrile Waste Streams (Source: Reference 6)**

Feed Rate, gpm	20
Acetonitrile, ppm	1680
Acrylonitrile, ppm	1200
Dissolved Sulfates, weight %	2.5
Water, weight %	97.5
Temperature, °F	80
Specific Gravity	1.0
<u>Characteristics of Recovered Organics</u>	
Organics: Acetonitrile, Acrylonitrile, weight %	98.5
Carbon Dioxide, weight %	0.5
Water, weight %	1.0
Temperature, °F	100
<u>Characteristics of Wastewater Effluent</u>	
Water, weight %	97.4
Carbon Dioxide, weight %	<0.06
Acrylonitrile, ppm	<2
Acetonitrile, ppm	<2
Sulfates, weight %	2.5
Temperature, °F	100

**Table 8. Annualized Operating Costs of 20-GPM Acetonitrile - Acrylonitrile Extraction Plant. (Source: Reference 6)**

	Annual Cost
<u>Utilities</u>	
Electricity (175 kWhr/hr @ \$0.04/kW hr)	\$56,000
Well Water (18 gpm @ \$1.50/1,000 gal)	12,960
Steam (230 lb/hr @ \$10.00/1000 lb)	18,400
<u>Solvent Make-Up</u>	
Carbon Dioxide (15 lb/hr @ \$100.00/2000 lb)	6,000
<u>Labor</u>	
1 Operator @ \$13.00/hr	104,000
Annual Processing Cost	\$802,360*

\* Depreciation, overhead, and miscellaneous operating supplies of \$605,000 included.

increase in surface area would be of great benefit. A comparison of the adsorptive capacity of ethanol vs. alkali extracted lignin indicates that the latter might be as good or better in capacity if the difference in particle size is taken into account. The alkali extracted lignin had much larger particles, partially accounting for its lower surface area per gram. Another factor favoring alkali extracted lignin is the higher yields; more adsorbent may be obtained per pound of wood. Tables 10 and 11 indicate that after an adjustment for surface area is made, alkali lignin would be about as good on organics, and better as a metal adsorbent than ethanol extracted lignin.

A comparison of the adsorption isotherms of alkali extracted lignin and activated carbon, based on Freundlich parameters indicates that approximately 30 times as much lignin as activated carbon is required to achieve a comparable reduction in phenol in a water solution. A comparable figure was obtained for naphthalene. A much more favorable comparison of lignin vs. activated carbon is obtained when Freundlich parameters for metal adsorption

are calculated (Figure 10). The ratio of lignin to carbon is only about 4-1; taking cost into account, lignin might be the preferred adsorbent in this case.

Although data gathered in this report are very preliminary, a conceptual design of a one million gallon per day water treatment plant is shown in Figure 9. Efficient operation of an adsorption plant of this type will depend on developing methods of controlling particle size and surface area of the lignin adsorbents.

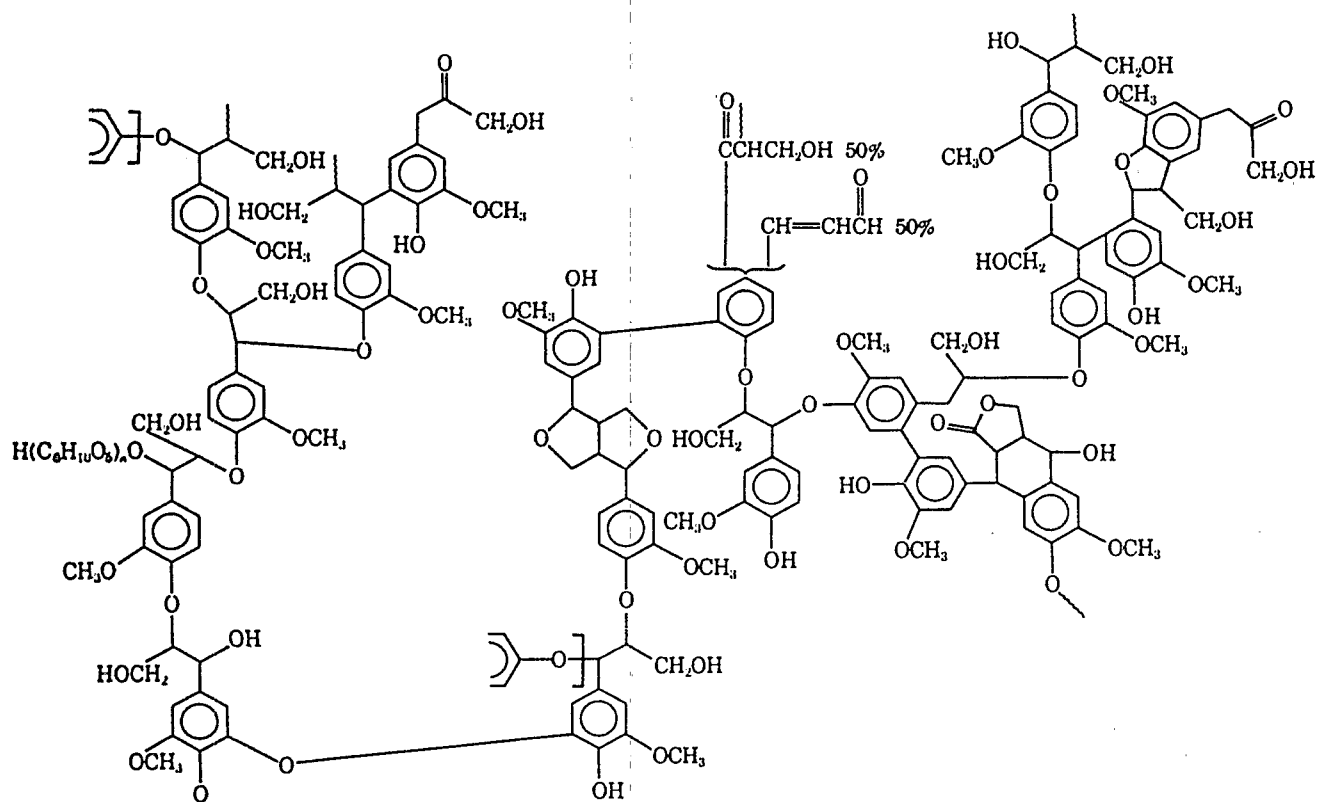
### Conclusions and Recommendations

Pristine lignin, particularly the alkali extracted variety, shows some promise as a low cost adsorbent for aqueous hazardous wastes. This preliminary study indicates that further work must be done to control particle size and expand surface area (expressed in square meters per gram) before a firm conclusion can be drawn. Evaluation of this high surface-controlled particle size material might yield enough data to allow the design of a pilot size test unit to indicate the feasibility and cost of a full-size water purification plant based on this technology.

### References

1. Maier, W. J., and Cussler, E. L. Dewatering of Dilute Aqueous Hazardous Wastes Using Reversible Gel Absorption. EPA Contract 68-03-1957.
2. Bhattacharyya, D. *et al.* Concentration and Purification of Dilute Hazardous Wastes Using Low Pressure Composite Membranes. Cooperative Agreement CR 911976.
3. DeFilippi, R. P. *et al.* Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides, EPA 600/2-80-054.
4. Knopf, C. F. (Louisiana State University) Private communication.
5. Eckert, C. A. (University of Illinois) Private communication.
6. Rice, P. N. *et al.* Supercritical Extraction of Aqueous Hazardous Waste, EPA Contract 68-03-1956.
7. Mayerly, R. C. *et al.* The Forest Refinery. Chemtech. March 1981, page 186.
8. O'Neil, D. J. *et al.* Low Cost, High Efficiency Pristine Lignin for Hazardous Waste Treatment. Cooperative Agreement CR 812223-01-0.

Figure 8. Typical lignin structure. (Copyright 1967 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. From Kirk-Othmer Encyclopedia of Chemical Technology, Anthony Standen, Executive Editor.)



**Table 9. Concentrations of Model Compounds in the Supernatant After Adsorption on the Pristine Lignin (ppm). (Source: Reference 8)**

<u>Time</u>	<u>Aniline</u>	<u>Phenol</u>	<u>Isophorone</u>	<u>Naphthalene</u>	<u>Pentachlorophenol</u>	<u>Bis-(EtHex) phthalate</u>	<u>2,4-D</u>	<u>Trichloro-ethylene</u>
0 hr	5.000	5.000	1.560	1.300	1.540	1.560	1.250	2.500
1 hr	4.09	2.62	1.66	0.97	0.70	0.33	1.08	1.97
	3.20	2.56	1.37	0.74	0.70	0.36	1.27	1.55
2 hr	3.29	2.73	1.29	0.61	0.54	0.29	1.21	1.54
	3.34	2.50	1.41	0.65	0.52	0.23	1.28	1.52
4 hr	3.75	2.56	1.39	0.63	0.49	0.22	1.05	1.93
	4.09	2.66	1.49	0.65	0.49	0.23	1.28	1.52
8 hr	4.14	2.48	1.38	0.57	BDL <sup>a</sup>	0.14	0.74	0.36
	3.97	2.22	1.61	0.64	BDL	0.14	1.03	1.78
1 day	3.52	1.94	1.31	0.56	BDL	0.18	0.67	1.63
	3.25	2.38	1.23	0.51	BDL	BDL	-- <sup>b</sup>	1.73
2 days	1.56	2.26	1.22	0.53	BDL	BDL	0.63	1.97
	2.62	2.16	1.06	0.41	BDL	--	--	1.94
4 days	2.88	1.77	1.16	0.48	BDL	BDL	0.57	1.45
	1.47	2.16	1.02	0.45	BDL	BDL	0.65	--
4 days <sup>c</sup>	0.71	2.05	0.68	0.21	BDL	BDL	0.60	0.54
	1.28	2.06	0.81	0.24	BDL	BDL	0.75	1.26

<sup>a</sup>BDL - Below detection limit.

<sup>b</sup>Samples were lost.

<sup>c</sup>Lignin dose was 0.75 g for organic mixture, 0.5 g for 2,4-D, and metal kinetics study.

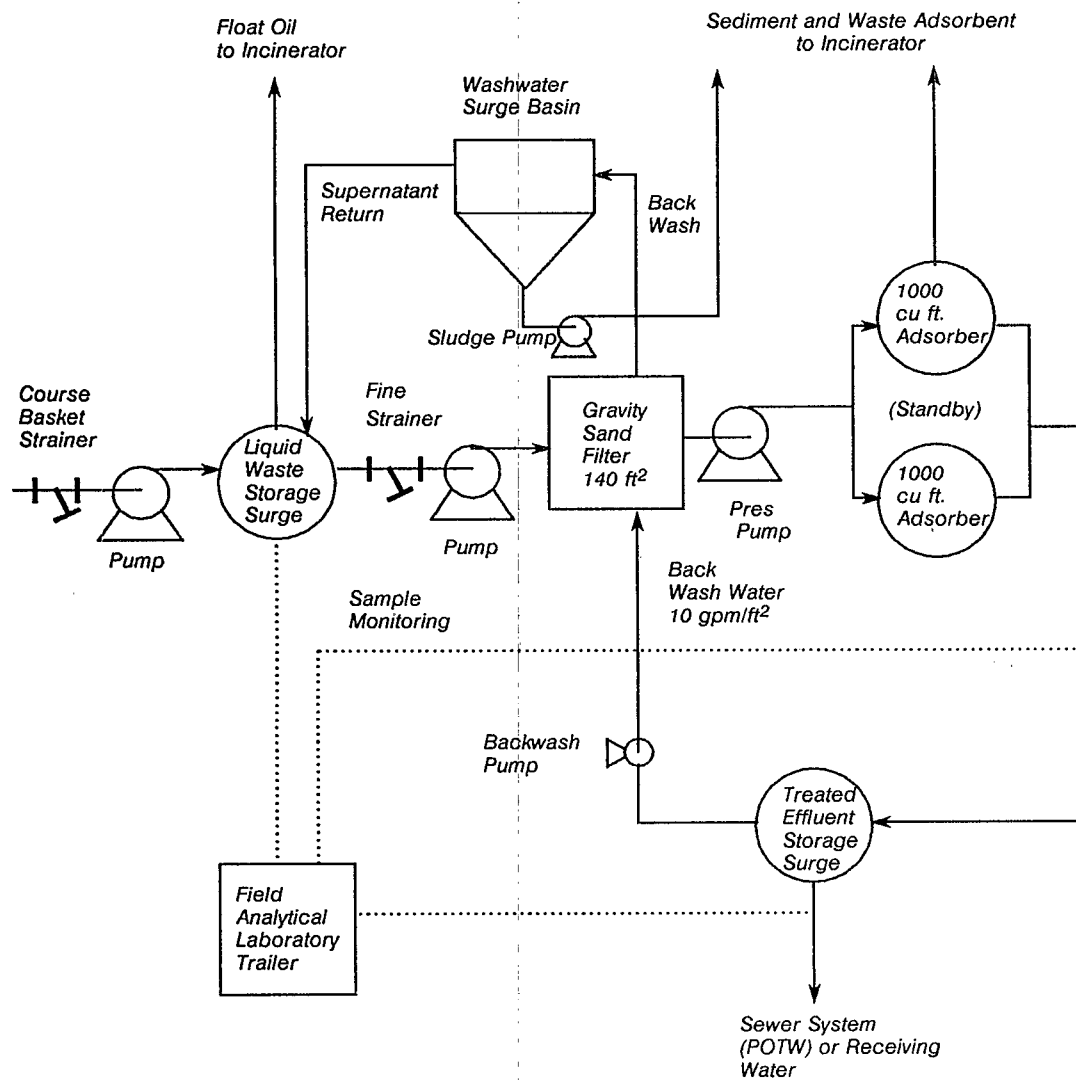
**Table 10. Test Results - Second Size Study (Organics). (Source: Reference 8)**

Concentrations of Model Compounds in the Supernatant After Adsorption on the Pristine Lignin (ppm)  
Equilibrium Time: 4 days

<u>Lignin</u>	<u>Aniline</u>	<u>Phenol</u>	<u>Isophorone</u>	<u>Naphthalene</u>	<u>Pentachlorophenol</u>	<u>Bis-(EtHex) phthalate</u>	<u>Trichloro-ethylene</u>
C <sub>0</sub> Nominal	4.758	5.337	2.043	2.259	2.610	4.031	3.336
C <sub>0</sub> Actual	4.447	4.346	1.985	2.113	1.833	2.790	2.583
	4.130	4.298	2.002	1.856	2.123	3.500	2.604
<u>ETOH Extract</u>							
30x40	3.130	4.346	1.467	0.660	0.360	1.263	2.058
	3.222	4.036	1.500	0.453	--	1.349	1.847
40x60	2.917	4.209	0.969	0.665	--	1.514	1.333
	2.164	4.357	1.003	0.654	--	1.143	1.398
60x100	1.577	3.340	1.434	0.428	--	0.774	1.577
	1.620	3.832	1.340	0.597	--	0.854	1.520
<u>NaOH Extract</u>							
60x100	1.230	3.987	1.695	1.053	0.488	2.392	1.348
	1.420	4.099	1.587	0.857	0.665	2.184	1.477

Note: Sample volumes of 100 ml were used (except for trichloro-ethylene: 120 ml).

Figure 9. Conceptual design of a 1 MGD treatment plant. (Source: Reference 8)

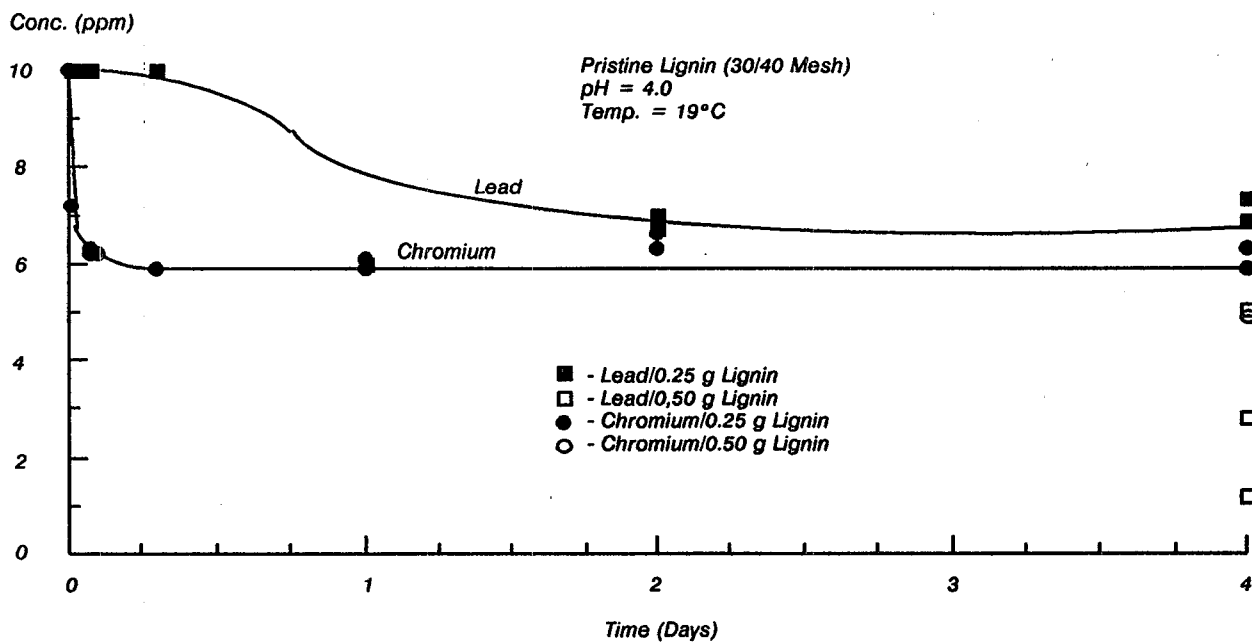


**Table 11. Test Results - Initial and Second Size Studies.**  
(Source: Reference 8)

Adsorption of Lead and Chromium on Lignin, ppm (4 days)

<u>Lignin</u>	<u>Lead</u>	<u>Lead (duplicate)</u>	<u>Chromium</u>
C <sub>0</sub> Nominal	10	10	10
C <sub>0</sub> Actual	8	11.3	9.89
	8	11.02	9.9
<u>Ethanol Extracted</u>			
30x40	7.83	7.5	4.19
	7.3	8.00	5.34
40x60	7.37	6.5	4.55
	7.2	8.50	4.56
60x100	6.4	6.50	4.93
	7.5	6.45	4.65
<u>NaOH Extracted</u>			
60x100	5.5	2.50	0.86
	7	2.00	0.92

**Figure 10. Kinetic study of the adsorption of heavy metals on pristine lignin (Cr and Pb).** (Source: Reference 8)



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