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Project Summary

Laboratory Studies of Priority Pollutant Treatability

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This report describes a screening investigation of several methods currently available for removal of priority pollutants from industrial plant wastewaters. A sample from an actual industrial stream was used for laboratory bench scale treatment tests on five priority pollutants present at significant concentrations. Results are of interest in evaluating best available technology for removal of priority pollutants and will be helpful to those planning further research including demonstration units for treating similar wastes.

The study focused on carbon adsorption, resin adsorption and steam stripping technologies and developed order-of-magnitude cost relationships for each technology. The results of the study indicate high removal efficiency for the priority pollutants nitrobenzene, p-dichlorobenzene, chlorobenzene, phenol and dinitrotoluene by both carbon adsorption and resin adsorption. Steam stripping was not effective under the test conditions for removal of phenol or dinitrotoluene. The steam stripping data also indicated that removal of the non-conventional pollutant aniline was ineffective.

Operating costs for treating streams similar to the stream tested are estimated to be in the order of $2 to $3 per 1000 liters (265 gallons) for flows of about 1130 liters per minute (300 gallons per minute). Cost effectiveness may favor use of carbon adsorption over resin adsorption and combination systems appear to offer no economic advantage at pollutant levels present in the sample.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A wastewater grab sample was taken from a typical medium sized petrochemical manufacturing complex which met study criteria for (a) the presence of at least five priority pollutants, (b) a multiproduct manufacturing operation, (c) a demonstrated toxicity of the waste and (d) lack of a specific treatment background. Concentrations of the tested priority pollutants were obtained from gas chromatograph/mass spectrometry (GC/MS) and gas chromatography (GC) analyses.

An earlier literature search (1) had indicated carbon adsorption, resin adsorption and steam stripping as potential treatment methods. These technologies were evaluated for effectiveness using laboratory bench scale tests on the wastewater sample. Studies, based on results of the bench scale tests, demonstrate potentially achievable degrees of removal and allow estimation of order of magnitude removal costs utilizing the three treatment methods.

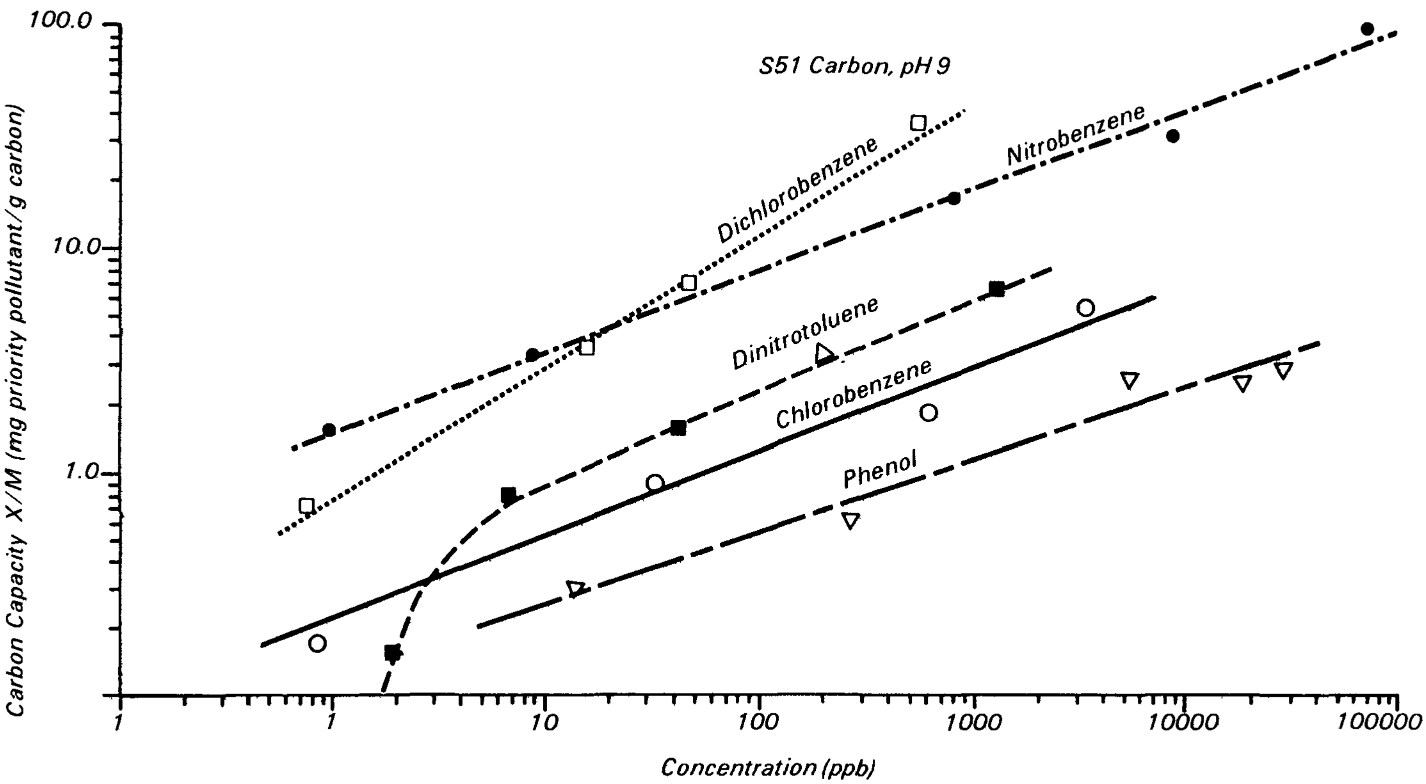

Figure 1. *Activated carbon isotherm studies – priority pollutant reduction from an industrial waste stream.*

Applicable Technologies

Application of carbon adsorption as a treatment technique requires the collection and evaluation of laboratory and pilot plant data from which realistic engineering design decisions can be made.

The suitability of a particular carbon is first indicated by batch equilibrium (isotherm) evaluations of adsorptive capacity as a function of residual pollutant concentration, as shown for the sample in Figure 1. However, dynamic test data are required to provide a basis for equipment design. Such dynamic data can be scaled up to develop equipment requirements for plant size operations and costs for the adsorption and regeneration systems.

For the purpose of this study, equilibrium isotherms were developed for two carbons at three pH conditions. Dynamic tests, in a three column pilot plant were performed on one of the two carbons, at pH 9 and through five successive carbon regenerations.

Resin adsorption, like carbon adsorption, requires fundamental laboratory data and suitability is first indicated by isotherm studies (Figure 2). Potential

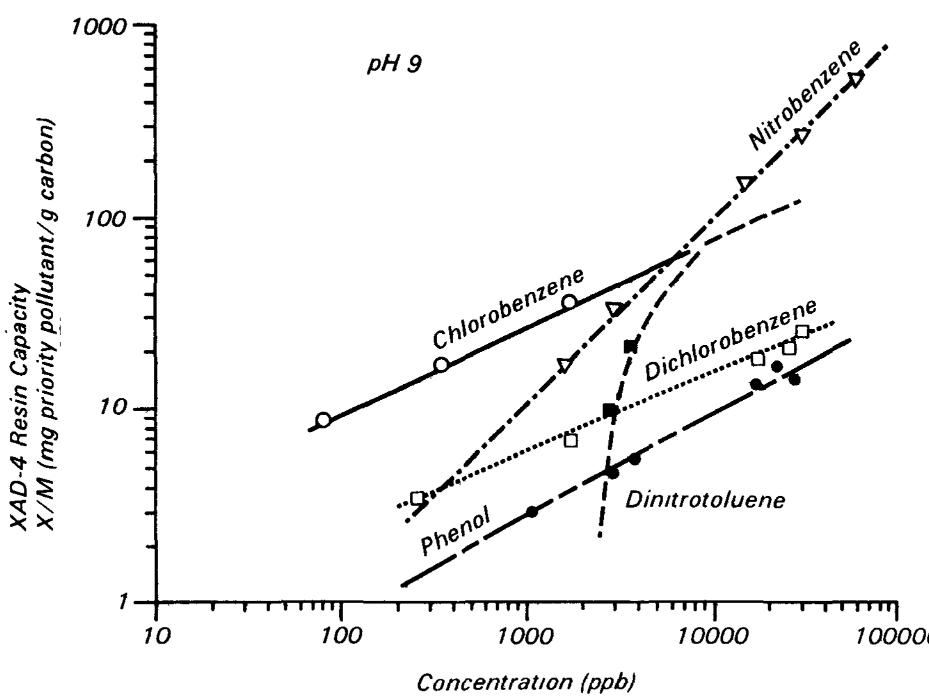

Figure 2. *XAD-4 resin isotherm studies – priority pollutant reduction from an industrial waste stream.*

advantages of resin adsorption include (a) adsorptive selectivity through resin choice, (b) possible recovery of pollutant materials, (c) low energy consumption and (d) durability of the resin matrix. Adsorption of polymeric resins is normally carried out in fixed beds which require periodic regeneration to maintain adsorptive capacity. Cited commercial applications (2) point to useful resin life exceeding several hundred cycles over a period of years.

Steam stripping relies on the combination of volatility and relatively low solubility of each organic pollutant. Design of stripping systems often can be accomplished without laboratory evaluation since rigorous calculations based on thermodynamic data may satisfactorily simulate performance. The economics of steam stripping are particularly sensitive to amount and cost of steam or other energy sources used for heating the water to be treated and for providing stripping vapor flow.

Experimental Procedures

Initial qualitative and quantitative data on the wastewater sample received were obtained employing EPA's priority pollutant GC/MS procedures wherein an internal standard of d_{10} - anthracene is used to provide a basis for both relative retention time measurements and semi-quantitative mass spectrometric analysis. Based on the GC/MS quantitative analysis, five priority pollutants (chlorobenzene, p-dichlorobenzene, nitrobenzene, dinitrotoluene and phenol) were selected for study in the test program. For routine quantitative analysis, during the tests the simpler gas chromatography with flame ionization detection was employed. Total organic carbon (TOC) analysis was also employed to continuously monitor organic removal during the dynamic test program.

The activated carbon equilibrium studies were performed in a batch mode by exposing a fixed volume of the test waste stream to five carbon dosages for each of the two carbons selected for evaluation. A volume of 100 ml was mixed with 0.1, 0.5, 1.0, 5.0 and 10.5 grams of activated carbon and the batches sealed and then agitated for 18 hours. After allowing the carbon to settle, samples were withdrawn from the aqueous phase, filtered and analyzed for TOC content and for concentration of individual priority pollutants.

The equilibrium studies were followed by dynamic studies in which a series of three continuous-flow adsorption runs were performed. Carbon regeneration studies (up to five carbon regenerations during each series) were performed at various regeneration temperatures.

In order to analyze resin effectiveness, a registered trademark item, Amberlite XAD-4 manufactured by Rohm & Haas, was selected for evaluation. The pore size of the resin selected allows for smaller molecules such as single ring aromatics to migrate easily to active surface points. Substantially larger molecules are excluded. Prior to dynamic testing, an equilibrium isotherm study was performed in a batch mode similar to the one used for carbon adsorption. The dynamic studies with resin regeneration by methanol were performed in a series of six runs. Time-history-related samples were collected and analyzed.

The feasibility of steam stripping the organic priority pollutants was investigated by running batch and continuously operated bench-scale stripping columns.

Experimental Results

Analysis of the untreated industrial waste stream was reported during the course of the five month test program. These tests indicated a minimal change of composition with time. The sample was stored at 4°C and at a pH of approximately 9. The compounds of interest were all present at concentrations greater than 1 ppb.

The data indicate that carbon removal capacity is pH sensitive and that dinitrotoluene exhibits poor adsorption at low concentrations (see Figure 1). Regeneration was conducted at several temperatures up to 800°F and carbon regenerated at 800°F demonstrated that greater adsorption capacity can be maintained through higher regeneration temperatures. The amount of carbon required to treat a given volume of waste to specific concentration levels was determined for each pollutant from breakthrough data based on a fixed amount of carbon in the test columns. A typical breakthrough curve for TOC is shown in Figure 3.

Resin isotherm data indicate dinitrotoluene is not adsorbed well as concentration decreases (see Figure 2). Results of the dynamic resin study indicate that phenol and dichlorobenzene breakthrough occurs early in a continuous column effluent. A typical resin breakthrough curve for TOC is shown in Figure 4.

The results of steam stripping tests indicated varying degrees of removal for

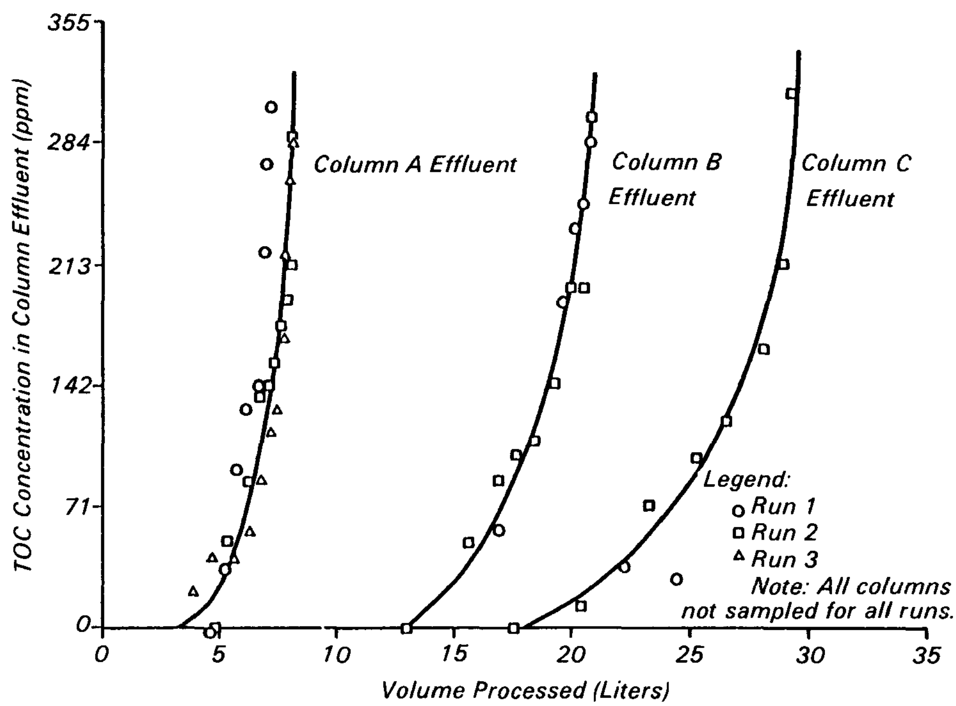

Figure 3. *Adsorption performance of virgin S-51 carbon.*

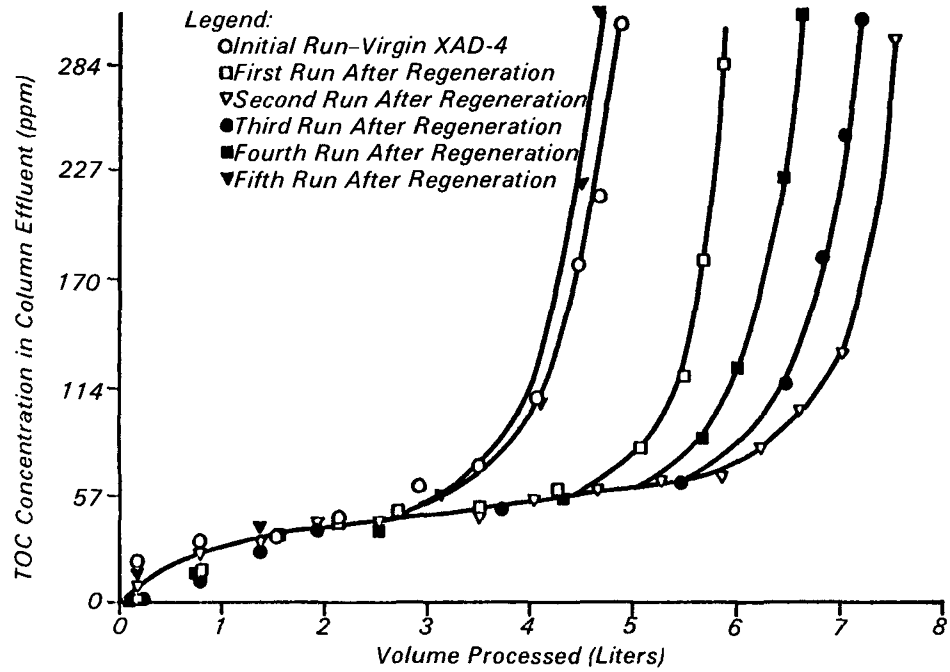

Figure 4. *Adsorption column performance of XAD-4 resin with methanol regeneration.*

the pollutants tested as shown in Table 1. It should be emphasized that the results of the laboratory steam stripping tests are considered approximate, but they do indicate that theoretical and test values compare reasonably well.

Process Design

In order to provide for economic comparisons, design studies for each of the treatment technologies were made with the following common bases: a)treatment of a waste stream of comparable composition to the waste stream tested, b) a 1,130 liter (265 gallons) per minute waste stream flow rate and c) a treatment objective of 1 ppm in the final effluent for the most difficult-to-remove priority pollutant.

Economics

An economic study was made for the three treatment technology designs. Equipment sizing and energy and material balances from testing and fundamental calculations provided information for these evaluations. Cost factors for carbon adsorption, resin adsorption and steam stripping at common influent concentrations, flow rates and other bases are presented in Table 2. Combined treatment systems were also evaluated but are of doubtful value since they offer no economic advantage over single treatment operations.

Conclusions and Recommendations

Both carbon and resin adsorption systems as evaluated appear capable of effectively removing the five selected priority pollutants to levels of 0.1 ppm or lower. Of the two adsorption systems, carbon adsorption appears slightly more cost effective.

Total annual cost for either adsorption system is expected to be in the order of $2 to $3 per 1,000 liters (265 gallons) for flows of about 1,130 liters (300 gallons) per minute and for removal down to 1 ppm. Below the treatment level of 1 ppm, costs are relatively insensitive to the degree of removal. Unit costs for either system would decrease with increased wastewater throughput and may drop to less than $2 per 1000 liters for facilities with very high flow rates.

Steam stripping was not effective at the pH level tested (pH of 9) for the removal of the priority pollutants phenol and dinitrotoluene or for the non-conventional pollutant aniline. Combining steam stripping, as a pretreat-

Table 1. *Comparative Stripping Material Balances (Experimental and Calculated[a])*

		Batch			*Continuous*			*Calculated*		
		Bottoms[b]	*Distillate[b]*		*Bottoms[b]*	*Distillate[e]*		*Bottoms[b]*	*Distillate*	
Component	*Feed[b]*		*(b)*	*(c)*		*(b)*	*(c)*		*(b)*	*(c)*
Chlorobenzene	*8.8*	*4.1*	*8,950*	*4.7*	*2*	*22,800*	*6.7*	*Trace*	*26,800*	*8.8*
p-Dichlorobenzene	*36*	*13*	*44,400*	*23*	*21*	*50,500*	*15*	*Trace*	*111,000*	*36*
Nitrobenzene	*166*	*5.0*	*307,000*	*161*	*15*	*507,000*	*151*	*31*	*416,000*	*135*
Aniline	*1,329*	*1,050*	*531,000*	*279*	*1,271*	*195,000*	*58*	*1,260*	*209,000*	*68*
Phenol	*31*	*29*	*3,430*	*1.8*	*31*	*673*	*0.2*	*31*	*457*	*0.15*
Dinitrotoluene	*7.9*	*6.9*	*1,900*	*1.0*	*6*	*6,530*	*1.9*	*0.4*	*22,900*	*7.5*
Other Organics[(d)]	*421*	*367*	*103,000*	*54*	*356*	*218,000*	*65*	*349*	*218,000*	*71*

[a] *Basis: Calculation Made to Predict Laboratory Results.*
[b] *Parts Per Million.*
[c] *Parts Per Million Parts Feed.*
[d] *Estimated, from TOC Measurements.*
[e] *Adjusted to close material balance relative to feed and bottoms. G.C. at high concentrations judged least reliable.*

Table 2. Treatment Costs

	Carbon Adsorption	Resin Adsorption	Steam Stripping
Investment	$1,775,000	$1,700,000	$1,000,000
Treatment Costs/Year			
Materials	537,500	475,000	111,000
Processing	877,000	1,226,000	963,000
Total Treatment	1,414,500	1,701,000	1,074,000
Cost Per 1000 liter	2.38	2.86	1.80

ment, with either carbon or resin adsorption is not cost effective for the pollutant levels studied.

Treatment costs developed by this study should be compared to production volumes of manufactured products contributing to the pollutants to test the effect of such treatment systems on product costs.

References:

1. U.S. Environmental Protection Agency, *Priority Pollutant Treatability Review* (Contract 68-03-2579), July 1978.
2. Fox, C.R., "Plant Uses Prove Recovery with Resins," *Hydrocarbon Process,* November, 1978.

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***Kenneth A. Dostal** and **David R. Watkins** are the EPA Project Officers (see below).*

The complete report, entitled "Laboratory Studies of Priority Pollutant Treatability," (Order No. PB 81-231 235; Cost: $12.50, subject to change) will be available only from:

National Technical Information Service
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