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SOLVENT-REGENERATED ACTIVATED CARBON

Final Report

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Project Manager
Ed Kear

Prepared by

FLUIDS DESIGN CORPORATION
Bald Mountain Road
RD #6, Box 206
Troy, NY 12180

29 Garfield Street
Marlboro, MA 01752

Principal Investigator
Hugh McLaughlin, Ph.D.

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ABSTRACT

This report summarizes the results of a University/Industry research project, sponsored by the New York State Energy Research and Development Authority and Fluids Design Corporation. The experimental work was performed by the Department of Chemical Engineering at Rensselaer Polytechnic Institute under the supervision of Dr. E. Bruce Nauman. The work was performed under subcontract to Fluids Design Corporation.

The research project studied the solvent regeneration of activated carbon. Activated carbon was used to remove trace organics from aqueous streams, then regenerated by desorbing the adsorbates with organic solvents. The project included a survey of the potential applications in New York State industries, fundamental research on the adsorption/desorption phenomena, and design of a full-scale process. The economics of the full-scale process were evaluated and compared to alternate available technologies.

The result of this work is a versatile process with attractive economics. A wide range of adsorbates and solvents were found to be acceptable for this process. The design methodologies are developed and the techniques for evaluating a new application are delineated.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1-1
2 PROCESS DESIGN MANUAL	2-1
TECHNICAL BASIS OF THE TECHNOLOGY	2-1
HOW TO EVALUATE A POTENTIAL APPLICATION	2-7
ECONOMICS OF A FULL-SCALE PROCESS	2-12
3 UNIVERSITY/INDUSTRY RESEARCH PROJECT	3-1
OVERVIEW	3-1
MARKET SURVEY	3-1
MODIFYING ACTIVATED CARBON BY REDUCTION	3-3
MATRIX OF ADSORBATES AND REGENERATING SOLVENTS	3-4
COLUMN STUDIES	3-10
DESIGN OF THE SOLVENT PROCESS	3-14
UNIVERSITY/INDUSTRY COLLABORATIVE EFFORT	3-14
4 LITERATURE CITED	4-1

ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
2-1 WASTEWATER TREATMENT BY GRANULAR ACTIVATED CARBON	2-2
2-2 SOLVENT REGENERATED ACTIVATED CARBON CYCLE	2-3
2-3 ISOTHERMS OF PHENOL IN WATER AND ACETONE	2-5
2-4 BENCHTOP COLUMN LOADING AND SOLVENT REGENERATION APPARATUS	2-8
2-5 ISOMETRIC LAYOUT DRAWING	2-13
2-6 GENERAL ARRANGEMENT OVERHEAD	2-14
3-1 ISOTHERMS OF PHENOL IN SOLVENTS	3-6
3-2 ISOTHERMS OF 4-NITROPHENOL IN SOLVENTS	3-6
3-3 ISOTHERMS OF NAPHTHALENE IN SOLVENTS	3-7
3-4 ISOTHERMS OF HEXACHLOROBUTADIENE IN SOLVENTS	3-7
3-5 ISOTHERMS OF BUTYLBENZYL PHTHALATE IN SOLVENTS	3-8
3-6 ISOTHERMS OF PHENOL IN ACETONE-WATER MIXTURES	3-8

TABLES

<u>Table</u>	<u>Page</u>
3-1 SOLVENT REGENERATION WITH TETRAHYDROFURAN	3-11
3-2 SOLVENT REGENERATION WITH METHANOL	3-11
3-3 SOLVENT REGENERATION WITH ACETONE	3-12
3-4 REGENERANT VOLUME STUDY WITH ACETONE	3-13

Section 1

INTRODUCTION

The concept of adsorption onto activated carbon being a reversible equilibrium is fundamental to the current understanding of adsorption processes. The concept of organic solvents desorbing the adsorbates is also not new. Hamilton (1963) discusses the considerations for a desorbing solvent in the context of improving an existing process, not inventing one. Indeed, adsorption from water onto activated carbon, followed by desorption by a solvent in a Soxhlet extractor, is an accepted method for low-level detection of aqueous organic contaminants.

What is new, or at least undeveloped as an industrial process, is large-scale solvent regeneration of activated carbon. A few people have discussed the process, and a few commercial processes even exist (Parmele, et.al. (1977,1981), Sutikno and Himmelstein (1983) and references contained therein). Even the underlying phenomena have been elucidated, of which the results of Martin and Ng (1984, 1985) represent the most comprehensive research effort to date.

The capabilities of activated carbon to remove undesired organics from aqueous solutions such as wastewaters, public water supplies and contaminated groundwaters, have long been extolled. Equally as vocal are the condemnation of the economics of the process. This report promotes a process that has the best of both worlds; activated carbon removal efficiencies at economics that undercut the competing technologies.

The result is a versatile process with attractive economics. A wide range of adsorbates and solvents were found to be acceptable for this process. The design methodologies are developed and the techniques for evaluating a new application are delineated.

Section 2

PROCESS DESIGN MANUAL

TECHNICAL BASIS OF THE TECHNOLOGY

In the article "Activated Carbon - the Dilemma Facing Its Use," Miller (1981) notes that activated carbon is the technology of choice for removing trace organics from water to ppb levels, but the cost is often prohibitive. That cost is primarily associated with the cost of thermally regenerating the carbon. The essence of this report is to promote an alternate, cost-effective method of regenerating activated carbon with solvents.

Figure 2-1 shows the typical application of granular activated carbon to wastewater treatment. The carbon is used to remove the organics from the aqueous stream. When the capacity for adsorption of the carbon is exhausted, the carbon is taken off line and regenerated, then reused. For the typical thermal regeneration process, the regeneration involves transporting the carbon to a furnace, thermally regenerating the carbon, then returning the carbon to the adsorber for reuse.

The process is considerably simpler for solvent regenerated carbon. The entire regeneration process is done in the adsorber. Figure 2-2 depicts the in-situ process. As can be seen, the carbon passes in a cycle, first adsorbing from water, then desorbing into a solvent, then returning to adsorption service after removing the solvent. The carbon cycle produces two streams, "A" and "B," that are distilled to recover the solvent, "C," for reuse. The bottoms product resulting from the solvent recovery is a concentrated stream of the contaminants, which is typically either recycled as raw material or incinerated.

FIGURE 2-1

WASTEWATER TREATMENT BY GRANULAR ACTIVATED CARBON

FIGURE 2-2

SOLVENT REGENERATED ACTIVATED CARBON CYCLE

The key to the solvent regenerated carbon process is that many organics preferentially adsorb onto activated carbon from aqueous streams and desorb into solvent streams. This is due to the thermodynamics of adsorption, which depends on the equilibrium of adsorption on the internal surface of the activated carbon versus solvation in the liquid phase. In water, most organics prefer the surface of the carbon, whereas in a solvent, the liquid phase is favored.

The isotherm data can be used to visualize the carbon cycle, and to semi-qualitatively screen solvent choices. Figure 2-3 shows the isotherms of phenol in acetone and water. Considering the adsorption of phenol from an aqueous stream, the phenol is transferred from the aqueous stream to the carbon, gradually loading the carbon. For a 100 ppm phenol stream, the carbon will load to roughly 120 mg of phenol per gram of carbon. This process can be visualized as ascending the aqueous isotherm line.

When the carbon is saturated, the bed is regenerated with solvent. When the solvent replaces the water in the bed, the equilibrium switches to the solvent isotherm line, where the equilibrium is 45,000 ppm of phenol in solution for a carbon loading of 120 mg per gram of carbon. Thus, the phenol is removed as a solution of 45,000 ppm in solvent. This represents a 450-fold concentration increase over the aqueous stream.

As the solvent strips the phenol from the carbon bed, the solvent isotherm is descended. At some point, for example, when the phenol is present at 1000 ppm in the solvent, the regeneration is stopped. The solvent is then removed from the bed by steaming the carbon, and the carbon bed is rewetted with cold water. This transfers the equilibrium back to the aqueous isotherm line, with a residual carbon loading of roughly 13 mg per gram of carbon. Thus, 89% of the carbon capacity has been recovered and the new column effluent is approximately 0.05 ppm or 50 ppb phenol in water.

FIGURE 2-3

ISOTHERMS OF PHENOL IN WATER AND ACETONE

The isotherms provide three measures of the efficiency of the regeneration cycle. They are:

- the magnitude of the increase in concentration of the adsorbate in the solvent stream, as compared with the aqueous stream.
- the amount of capacity recovered after regenerating to a fixed adsorbate level in the solvent.
- the adsorbate concentration in the aqueous solution after the system is returned to service.

The above criteria indicate that the greater the separation between the aqueous isotherm and the solvent isotherm, the more efficient the solvent regeneration will be.

The solvent regeneration process utilizes activated carbon contained in large columns, which are regenerated in situ by chromatographic displacement of the water by the solvent. Thus, the extent of regeneration of the carbon in the bed depends on the location within the bed. Mathematically, this is referred to as a distributed system, which cannot typically be modeled by a non-distributed system of equations.

The information contained in the adsorption/desorption isotherms shows general trends, but must be incorporated into a distributed mathematical model to simulate the behavior of the carbon adsorber. The scale-up and design of the full-size carbon adsorption and solvent regeneration process should be done by an engineering firm with prior experience in designing solvent regenerated carbon systems.

HOW TO EVALUATE A POTENTIAL APPLICATION

The essence of this section is to assemble a simple and inexpensive apparatus for demonstrating feasibility of solvent regenerated activated carbon for a given waste stream. The apparatus has the capability of both loading organics onto the carbon and solvent regenerating the carbon in-situ. The removal of the solvent can be accomplished by an extended water rinse (in excess of ten bed volumes). While this approach would not be feasible for a full-scale process, it certainly is acceptable for the demonstration of the process.

EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES

Benchtop Apparatus

The experimental apparatus is shown in Figure 2-4. The pump is a variable-speed peristaltic pump, called the Rainin Rabbit pump. Any low flow rate laboratory pump will suffice, although pumps with excessive flow pulsations are not recommended. The columns are empty liquid chromatography columns. The columns can be either 316 SS or glass, with minimum internal diameters of one centimeter and minimum lengths of 25 cm. The columns should have frits at both ends, to assure even flow distribution within the column. The four-way valve shown in Figure 2-4 is recommended for the convenience it affords in selecting upflow/downflow modes.

Any type of granular activated carbon can be used in the benchtop columns, with 8x30 or 12x40 mesh being the recommended sizes. The appropriate type of activated carbon is the one with the highest capacity for the adsorbates of interest. In general, small adsorbates require carbons with higher Iodine numbers, whereas larger adsorbates are better adsorbed by carbons with a higher Molasses Index. The companies that supply activated carbon can usually recommend the appropriate carbon for a given application. The carbon may be used without crushing or sieving in the benchtop columns, but may require some conditioning, such as acid-washing, prior to use. The carbon supplier will recommend any appropriate carbon conditioning steps.

FIGURE 2-4

BENCHTOP COLUMN LOADING
AND SOLVENT REGENERATION APPARATUS

Column Loading Procedure

The column loading studies can be done either as a once through flow pattern or in the recycle mode shown in Figure 2-4. If the adsorbate is a few pure components, then it is convenient to prepare a high-strength feed and recycle through the column until the equilibrium loading is reached, as described below. If the wastewater is a complex mixture, it may be necessary to load the column by passing the wastewater through the column until the column reaches saturation. Since the benchtop column holds many grams of carbon, the loading from low-level wastewater sources may require large volumes of wastewater and take several days.

In the studies performed for the NYSERDA research contract, the column loadings were done by filling the feed reservoir with a 1500 ppm phenol solution. The feed was recirculated upflow through the carbon bed until the phenol level in the reservoir stabilized, typically 12 to 20 hours. The flow rate was typically 7 to 15 empty bed volumes per hour. The amount of phenol adsorbed by the carbon was calculated from the amount of phenol removed from the reservoir. The amount of phenol adsorbed on the carbon and the concentration of phenol in solution at equilibrium represent one point on the adsorption isotherm.

For once through column loading, care must be taken that the carbon is fully loaded and the loading on the carbon must be accurately determined. It may be more convenient to measure the column loading by assaying the desorption solvent, instead of integrating the column loading from the aqueous stream.

The experimental results, relating the loading of adsorbate on the carbon to the concentration in solution, are correlated by the the Freundlich isotherm relationship:

$$x/m = k(c^{1/n})$$

where:

x = amount of adsorbate adsorbed

m = weight of activated carbon

c = equilibrium concentration of adsorbate in solution

k, 1/n = constants.

Taking the logarithm of both sides, the following is obtained:

$$\log (x/m) = \log (k) + (1/n) \log (c)$$

This is the equation of a straight line whose slope is 1/n. Therefore if x/m is plotted against concentration on log-log paper, a straight line should be result.

Solvent Regeneration Procedure

The columns, once loaded, are regenerated by passing solvent downflow through the bed in a once through mode. The flow rate during regeneration should be relatively slow, less than two empty bed volumes per hour, and the volume of solvent should be carefully controlled for each regeneration. After the solvent regeneration, the solvent is removed from the carbon by flushing the bed upflow with degassed water. This is similar to the procedure used by Cooney, et. al. (1983). In the commercial process, the solvent would be removed by steaming, but this was not practical for the small columns of the benchtop apparatus.

Assaying the Adsorbate Concentration in Solution

The experimental studies require accurately measuring the results, and this may be a difficult assay depending on the nature of the adsorbates. For complex mixtures, typical of actual wastewaters, the best method may be a non-specific measure such as Total Organic Carbon or Chemical Oxidation

Demand. Direct injection of aqueous samples into gas chromatographs may be possible for some adsorbates, but care is advised if flame ionization detectors are used. For synthetic feeds, the components are known and more specific analytical techniques can be used.

Since the solvent regeneration process is reversible, it may be convenient to measure the capacity of the carbon as evidenced by the amount desorbed. The regenerating solvent can be assayed by gas chromatography to quantify the amount of adsorbate loaded on the carbon and subsequently removed by the solvent.

Scope of the Experimental Studies

The experimental studies serve to demonstrate the feasibility of solvent regenerated activated carbon for removing adsorbates from a given wastewater stream. The primary measure of the process is the reversible capacity of the activated carbon when solvent regenerated. The benchtop apparatus is useful for establishing feasibility and screening solvent choices. Thus, the experimental studies should continue until these objectives are achieved.

The benchtop apparatus is not intended to generate design data for a full-scale process. The columns are too small to accurately reflect the effluent quality achievable from solvent regenerated activated carbon. Such information requires piloting in larger columns under carefully controlled conditions, and additional isotherm data, such as shown in Figure 2-3. As stated earlier, the scale-up and design of the full-size carbon adsorption and solvent regeneration process should be done by an engineering firm with prior experience in designing solvent regenerated carbon systems.

ECONOMICS OF A FULL-SCALE PROCESS

Cost Estimate of a Full-Scale Solvent Process

A full-scale process was designed and costed for the purposes of comparing the economics of the solvent regenerated carbon process with those of other available treatment technologies. The process size is typical of that of a high-strength industrial wastewater stream. The process for the remediation of contaminated groundwater would be different in design but similar in cost.

DESIGN BASIS: Flow rate = 100 gpm
Adsorbate loading = 200 ppm
Loading rate = 10 #/hr
Carbon capacity = 5 wt% @ 200 ppm
Carbon bed life = 50 hrs @ 200 ppm or 2.1 days

The carbon capacity used as the design basis is lower than typically achieved by activated carbon, to provide for a conservative estimate of the process capabilities. The actual working capacity must be determined for solvent regenerated carbon for each application, and can be used to refine the economic analysis. The cost estimate is based on the full-scale plant shown in Isometric Layout Drawing shown in Figure 2-4 and 2-5

Equipment	Size	No.	Mat.	Cost/Installed
Column Feed Tank	15,000 gal	1	CS	\$ 28,900
Solvent Storage	10,000	1	CS	19,600
Column	2'x 15'	1	SS 316	20,500
Still Pot	1,500 gal	1	SS 316	34,000
Accumulator	200	1	CS	2,200
Carbon Adsorbers	6'x 15'	3	SS 316	136,500
Decanter	3,000 gal	1	CS	9,800
Slop Tank	7,500	1	CS	18,800
Pumps	50 & 100 gpm	6	CS	19,800
Heat Exchangers	400 sq ft	2	CS	11,600
	300	2	CS	9,500
Equipment Sub-total				\$ 311,500

FIGURE 2-5
ISOMETRIC LAYOUT DRAWING

ISOMETRIC LAYOUT		FLUIDS DESIGN	
		TROY, NEW YORK	
		WILLIAM D. BRADLEY P.E.	
		TROY, NEW YORK 12180	
		SCALE: DRAWING AND DATE: 2 MAY 80	

FIGURE 2-6
GENERAL ARRANGEMENT OVERHEAD

2-14

GENERAL ARRANGEMENT		FLUIDS DESIGN	
		TROY, NEW YORK	
		WILLIAM D. BRADLEY P.E.	
		RD4, BOX 204	
		TROY, NEW YORK 12180	
		SCALE DRAWN JOB DATE 8 MAY	
		1"=4' CHECKED	

Piping & Valving: Factored Costs

Piping			\$ 192,000
Valving	61	CS	113,400
	15	SS	34,500
Instrumentation			63,000
Computer			18,000
Electrical			58,000
Structures & Foundations			98,000
Rigging			63,000
Engineering			256,800
Contingency			185,900
Subtotal: Capital Investment for Facility Costs			\$ 1,394,000

Process Materials Cost

Activated Carbon	30,000 lbs.	\$ 30,000
Acetone	40,000 lbs.	10,000

Total Project Cost \$ 1,434,000

OPERATING COSTS OF THE SOLVENT PROCESS

The estimated costs of operating a full-scale operating solvent regeneration process are based upon a material and energy balance as follows:

Adsorbers: 6'dia., 15' straight wall 424 cu.ft. + heads

Carbon capacity : 10,000 #'s design
12,000 #'s maximum

6'dia. = 28.3 sq.ft. cross section
Design flowrate: 100 gpm @ < 4 gpm/ sq.ft.

REGENERATION USES : Pumping costs
20000#'s Solvent
5000 #'s L.P. Steam

Yields : 500 #'s Adsorbate
10,000 #'s Water (to distillation)
20,000 #'s Solvent

Excess water to recycle water

DISTILLATION USES : Distill 20,000 #'s Solvent @ 25' BTU/#
Reflux ratio of 2.0 consumes 10,000 #'s steam
Pumping cost

SOLVENT LOSSES TO RECYCLE WATER

Less than 0.5 % /pass = 100 #'s/regeneration
Acetone : \$.25/# or \$ 1.65/gal (1st Q 1988 Quote)
Maximum Acetone loss = \$ 25.00 /regeneration

STEAM COSTS = \$ 5.00/1000 #'s (1st Q 1988 Quote)

Consumption = 15,000 #'s/regen = \$ 75.00/regeneration

PUMPING COSTS = (negligible) estimate @ \$ 10.00/regeneration

SUMMATION OF OPERATING COSTS PER REGENERATION

Acetone Loss	=	\$ 25.00
Steam	=	\$ 75.00
Pumping	=	\$ 10.00

\$ per Regeneration \$ 110.00 = \$ 0.011/# of Carbon

SOLVENT REGENERATION Annual Costs: Basis 330 days/yr = 165 regenerations

Carbon Regenerated = 1,650,000 #'s

Water Treated = 47,520,000 gallons

Contaminants Removed = 82,500 #'s

Energy	=	\$ 18,150
Staffing: 2 operators @ 4000 hrs	=	\$ 60,000
Carbon replacement: 15,000 #'s	=	\$ 15,000
Maintenance	=	\$ 25,000
Reboiler Bottoms Disposal		
82,500 #'s of High Btu Fuel	=	\$ 12,700

Capital Investment: \$ 1,434,000	
20 years at 10 %	= \$ 168,438

SOLVENT REGENERATION Annual Costs = \$ 299,288

COMPARISON TO ALTERNATE TECHNOLOGIES

Off-site Regeneration with Adsorbers On-site

Basis: 1,650,000 #'s of carbon per year

Capital Investment = \$ 186,500

Annual Costs

Carbon regeneration @ \$ 0.55/# = \$ 907,500

Staffing: One Operator = \$ 30,000

Maintenance = \$ 10,000

Capital Investment: \$ 186,500
20 years at 10 % = \$ 21,906

OFF-SITE REGENERATION Annual Costs = \$ 969,406

Once Through Carbon use

Basis: 1,100,000 #'s of carbon per year, due to higher capacity than solvent or thermally regenerated carbon

Capital Investment = \$ 186,500

Annual Costs

Carbon purchases @ \$ 0.88/# = \$ 968,000

Staffing: One Operator = \$ 30,000

Maintenance = \$ 10,000

Carbon Disposal \$ 200/ton = \$ 165,000

Capital Investment: \$ 186,500
20 years at 10 % = \$ 21,906

ONCE THROUGH CARBON Annual Costs = \$ 1,139,906

Biological Treatment

Basis: Capital Investment and operating costs: Estimated from a 150,000 GPD, 500# BOD5/DAY Activated Sludge Plant for Treating Industrial Wastes.

Capital Investment = \$ 1,920,000

Annual Costs

Operating Costs = \$ 255,000

Sludge Disposal: via Secure Landfill
82,500 #'s organics = 165,000 #'s BOD5

at 0.2 # MLSS/# BOD5 = 33,000 #'s Excess Biomass
 at 15% solids = 220,000 #'s contaminated sludge.
 220,000 #'s @ \$ 200/ton = \$ 22,000

Capital Investment: \$ 1,920,000
 20 years at 10% = \$ 225,520

BIOLOGICAL TREATMENT Annual Costs = \$ 502,520

SUMMARY: ALTERNATE TECHNOLOGY COST COMPARISION

TECHNOLOGY	\$ / 1000 GAL	\$ / # CONTAMINANT
Solvent Regeneration	\$ 6.30	\$ 3.63
Off-site Regeneration	20.40	11.75
Once Through Carbon	23.99	13.82
Biological Treatment	10.57	6.09

COMMENTS

An interest rate of 10 % was used for the conversion of the capital investment into an annual operating cost. The overall economics depend on the interest rate chosen and may depend on the individual application. The economic breakdown provided here allows the recalculation of the annual costs depending on the depreciation schedules and capital recovery factors desired.

The comparison of the operating costs assumes that the waste water can be treated by biological digest to acceptable discharge levels. This assumption depends on the nature of the organics in the waste water, and must be evaluated for each waste stream. In general, hazardous wastes cannot be treated to acceptable discharge levels by biological digest alone.

Section 3

UNIVERSITY/INDUSTRY RESEARCH PROJECT

OVERVIEW

New York State Energy Research and Development Authority contracted with Fluids Design Corporation to investigate the potential of solvent regenerated activated carbon for the New York State marketplace. The project was an collaborative effort between Rensselaer Polytechnic Institute and Fluids Design Corporation. The research was funded by the Energy Authority and Fluids Design Corporation.

The research project studied the solvent regeneration of activated carbon. Activated carbon was used to remove trace organics from aqueous streams, then regenerated by desorbing the adsorbates with organic solvents. The project included a survey of the potential applications in New York State industries, fundamental research on the adsorption/desorption phenomena, and design of a full-scale process. The economics of the full-scale process were evaluated and compared to alternate available technologies.

The various tasks and results of the University/Industry research project are summarized in the following sections.

MARKET SURVEY

A search of the literature was conducted to identify potential industries in New York State that could use solvent regenerated activated carbon. To insure uniform identification of the industries, Standard Industrial Identification Codes were used.

Six industries were selected for contact by telephone. These industries had three elements in common that implied the potential for activated carbon use.

Those elements are:

Liquid streams that are process related or liquid waste streams. Some industries will have both conditions.

The liquids streams may contain a component that is low in concentration and is adsorbable on carbon.

The liquids are filterable.

For the Telephone solicitation, the following industries were chosen:

SIC 2491 Wood Preserving
SIC 2631 Paperboard Mills
SIC 2833 Medicinal Chemicals and Botanical Products
SIC 2834 Pharmaceutical Preparations
SIC 2869 Industrial Organic Chemicals Misc.
SIC 4911 Electric Services

Our conclusions, based on the telephone survey and a few written follow up questionnaires, are:

The technology of solvent regeneration was understood by the chemical people contacted. They all responded positively to a potential need in the future if not a current application.

The largest potential market for the technology in New York State is in the control of organics in water, especially in production wastewater and groundwater applications.

A significant potential for the technology may still exist in the process industries that will require a strong research program for its application, in particular, to the biotechnical industries. This industry is still in its infancy and will increase in potential as it matures.

The companies were willing, as a whole, to discuss their basic operations on the phone. More detailed discussion will require further direct contact in order to establish a confidence factor.

Without significant attention from the State or EPA, action toward the use of carbon or other processes will be postponed. In general, the companies contacted were satisfied that they were meeting the demands of the regulations and that any further action by them would depend upon the price of energy or further tightening of the discharge regulations.

The responses to a follow up questionnaire were revealing in their indication of a strong potential for solvent regenerated activated carbon making a significant contribution to wastewater treatment. The underlying potential for groundwater remediation is implied, if not expressly stated.

We concluded that the market for solvent regenerated activated carbon has a strong potential. That potential will be initially realized in those industries recognizing that activated carbon is an efficient system of waste water control. As the industries become confident in this technology, they will search for other possible uses and will come to recognize the utility in processing and purifying their products. This will increase the potential applications of the technology beyond the starting base of wastewater treatment.

MODIFYING ACTIVATED CARBON BY REDUCTION

The modification of the adsorption capability of activated carbon by reduction of the chemical species on the internal carbon surface was investigated. The activated carbon was reduced by sodium borohydride and lithium aluminum hydride. In general, reduction did not result in significant modification of the activated carbon ability to adsorb phenol from water.

No detectable change of the adsorption behavior of the activated carbon was effected by chemical reduction. The unique property of activated carbon to adsorb hydrophobic organics from aqueous solutions appears rooted in the large surface area and pore size distribution of the carbon, and to a lesser extent, the chemical makeup of the surface of the carbon. In light of the tendency of activated carbon to remove dissolved oxygen from aqueous solutions, it is likely that a reduced surface would re-oxidize with time.

In light of the results of this experimental program, the only conclusion supported is that reduction of activated carbon has a negligible effect on the adsorption behavior of the carbon. However, there are significant differences between commercially available activated carbons with respect to surface area and pore size distributions, as discussed by McLaughlin (1980). These factors should be optimized when considering a given activated carbon application.

MATRIX OF ADSORBATES AND REGENERATING SOLVENTS

Adsorption onto activated carbon from aqueous solutions has been extensively studied in the literature, and continues to be so. However, the desorption phenomenon, and the associated isotherms in solvent systems, have received relatively little attention. There are a few good studies that deserve mentioning, all of them occurring in the mid 1980's.

Cooney, et. al. (1983), measured the ability of 19 solvents to desorb phenol from activated carbon. They also did some column studies on the ability of acetone, methanol and dimethylformamide to desorb phenol from carbon. This paper was the first real attempt to study the solvent regeneration process in a systematic manner. The references contained within Cooney, et. al., detail the previous efforts, which in general just discuss a specific application of the technology.

Martin and Ng (1984, 1985) systematically studied the effects of a large number of variables on the desorption phenomenon. They drew the following conclusions, as quoted from their second paper:

There was a marked correlation between decreasing molecular weight of adsorbate and decreasing value of regeneration efficiency; the smaller the adsorbate, the further it could penetrate into the micropores of the carbon, thereby resisting displacement by the regenerant. Furthermore, it was observed that, in general, the smaller the organic regenerant the further it could penetrate into the micropores of the carbon and displace the adsorbate. These complementary observations indicate that where chemical reactions are unlikely between organic regenerant and adsorbate, the success of the regeneration process is governed by the mechanism of physical displacement of the adsorbate molecule by the organic solvent molecule. The importance of the molecular weights and sizes of the adsorbate and the solvent is thus confirmed.

Based on the work of these researchers, the solvent regeneration of activated carbon emerges as a fairly general process, whereby any solvent should effectively desorb adsorbates larger than itself. Thus, a specific interaction between the adsorbate and solvent is not necessary for the desorption phenomenon to occur. In addition, good solvents should desorb a wide class of adsorbates.

These observations point to a desorption process that is a kinetically controlled approach to a thermodynamically favored partitioning of the adsorbate in the solvent phase compared to the surface of the carbon. If that is the case, then the isotherms of the adsorbate in the solvent should be significantly different from the aqueous isotherms.

To test this hypothesis, a matrix of representative adsorbates and possible solvents was studied. This matrix consisted of five adsorbates and four solvents. The five adsorbates were phenol, naphthalene, 4-nitrophenol, butylbenzyl phthalate and hexachlorobutadiene. The four solvent systems, other than water, were acetone, methanol, tetrahydrofuran (THF) and toluene. The aqueous isotherms were either measured or taken from Dobbs and Cohen (1980). The results of these isotherm studies are shown in Figures 3-1 to 3-5. The lines in these figures are least squares linear approximations and occasionally reflect the scatter in the data.

FIGURE 3-1: ISOTHERMS OF PHENOL IN SOLVENTS

FIGURE 3-2: ISOTHERMS OF 4-NITROPHENOL IN SOLVENTS

FIGURE 3-3: ISOTHERMS OF NAPHTHALENE IN SOLVENTS

FIGURE 3-4: ISOTHERMS OF HEXACHLOROBUTADIENE IN SOLVENTS

FIGURE 3-5: ISOTHERMS OF BUTYLBENZYL PHTHALATE IN SOLVENTS

FIGURE 3-6: ISOTHERMS OF PHENOL IN ACETONE-WATER MIXTURES

For all the systems studied, the isotherm of the adsorbate in solvent was significantly shifted to less loading on the carbon. The solvent isotherm capacity was typically 1 to 20% of the loading of the aqueous isotherm. Even the large molecules, such as butylbenzyl phthalate, showed little adsorption onto the carbon from organic solvents.

Figure 3-6 shows the isotherms of phenol in mixtures of acetone and water. The shift of the isotherm, even in the presence of relatively large amounts of water, is remarkable. A study of phenol in mixtures of methanol and water showed similar behavior.

A literature search and the experimental results point to a process that has considerable freedom choosing solvents. There are a few properties that are desirable in the solvent choice. Those properties are:

Miscible in water. Although toluene shows favorable solvent isotherms with the adsorbates considered, the operational problems of removing the water from the pores of the carbon handicap the use of water immiscible solvents.

High solubility for all the adsorbates removed from the aqueous stream. If some components are left behind on the carbon, then the capacity of the carbon will deteriorate, resulting in a form of poisoning.

Capable of being separated from water and the adsorbates by distillation. The solvent is recycled, so a separation process is necessary.

Biodegradable. The solvent regeneration process does result in some solvent loss to aqueous streams, so that additional organic loading should not represent an additional treatment problem.

Economical. The consumption of solvent is an operating cost of the process, and should not significantly deteriorate the process economics.

These qualities point to acetone and methanol for most carbon adsorbables. Tetrahydrofuran is a very good solvent, but is expensive and difficult to handle. Methanol may not be as good a solvent as acetone for larger hydrocarbons, but is less expensive than acetone. Both solvents should be considered for most applications. In addition, if purification capability is available for a particular solvent at a plant site, that solvent should be considered for that application.

COLUMN STUDIES

The essence of the column studies was to assemble a simple and inexpensive apparatus for demonstrating feasibility, in order to develop the methodology for the Process Design Manual. In the course of this task, columns of activated carbon were repeatedly loaded with adsorbate and regenerated by three different solvents; acetone, methanol and tetrahydrofuran. The procedures were discussed in Section 2, the Process Design Manual.

Tables 3-1 to 3-3 show the results of regenerating the carbon in the columns by three different solvents. The data of Tables 3-1, 3-2 and 3-3 show consistent recovery of appreciable adsorption capacity by solvent regeneration of the carbon. The data does not confirm or deny whether the carbon is gradually losing capacity with each cycle. Sutikno and Himmelstein (1983) published some results where carbon was cycled for over 50 cycles, with the capacity stabilizing at about 75 % of the capacity of virgin activated carbon and showing no gradual loss of capacity.

TABLE 3-1
Solvent Regeneration with Tetrahydrofuran

(excess THF used for regeneration)
(flowrate of 15 bed volumes per hour)

Cycle #	Equilibrium Mass Balance	Capacity	Regeneration %
0	111.3 mg/g at 15 ppm	49.4 mg/g at 1 ppm	basis
1	106.4 mg/g at 50 ppm	32.9 mg/g at 1 ppm	66.6 %
2	112.7 mg/g at 50 ppm	37.3 mg/g at 1 ppm	75.5 %
3	97.2 mg/g at 50 ppm	30.1 mg/g at 1 ppm	60.9 %
4	81.2 mg/g at 25 ppm	30.9 mg/g at 1 ppm	62.6 %

TABLE 3-2
Solvent Regeneration with Methanol

(excess Methanol used for regeneration)
(flowrate of 15 bed volumes per hour)

Cycle #	Equilibrium Mass Balance	Capacity	Regeneration %
0	106.2 mg/g at 15 ppm	47.1 mg/g at 1 ppm	basis
1	102.3 mg/g at 30 ppm	36.9 mg/g at 1 ppm	78.3 %
2	105.7 mg/g at 35 ppm	36.4 mg/g at 1 ppm	77.3 %
3	95.9 mg/g at 30 ppm	34.6 mg/g at 1 ppm	73.5 %
4	77.8 mg/g at 20 ppm	31.7 mg/g at 1 ppm	67.3 %

TABLE 3-3
Solvent Regeneration with Acetone

(excess Acetone used for regeneration)
(flowrate of 6 bed volumes per hour)

Cycle #	Equilibrium Mass Balance	Capacity	Regeneration %
0	125.0 mg/g at 25 ppm	47.6 mg/g at 1 ppm	basis
1	110.0 mg/g at 60 ppm	32.2 mg/g at 1 ppm	67.6 %
2	88.1 mg/g at 50 ppm	27.2 mg/g at 1 ppm	57.1 %
3	84.3 mg/g at 25 ppm	32.1 mg/g at 1 ppm	67.4 %
4	88.9 mg/g at 50 ppm	27.5 mg/g at 1 ppm	57.8 %
5	81.1 mg/g at 50 ppm	25.1 mg/g at 1 ppm	52.7 %
6	58.5 mg/g at 25 ppm	22.3 mg/g at 1 ppm	46.8 %
7	81.3 mg/g at 50 ppm	25.1 mg/g at 1 ppm	52.7 %

Effect of Regenerant Volume on Carbon Capacity

A brief study was done to demonstrate the decrease of regeneration efficiency with diminishing solvent volumes. Those results are shown in Table 3-4.

TABLE 3-4
Regenerant Volume Study with Acetone

Cycle #	Equilibrium Mass Balance	Capacity	Regeneration %
0	77.0 mg/g at 3 ppm	55.4 mg/g at 1 ppm	basis
	regeneration with excess acetone at 6 bed volumes per hour		
1	75.5 mg/g at 10 ppm	37.8 mg/g at 1 ppm	68.2 %
	regeneration with 3 bed volumes of acetone in one hour		
2	71.8 mg/g at 10 ppm	37.7 mg/g at 1 ppm	68.1 %
	regeneration with 1.5 bed volumes of acetone in one hour		
3	71.8 mg/g at 15 ppm	31.9 mg/g at 1 ppm	57.6 %
	regeneration with 0.75 bed volumes of acetone in one hour		
4	63.0 mg/g at 25 ppm	24.0 mg/g at 1 ppm	43.3 %
	regeneration with excess acetone at 6 bed volumes per hour		
5	72.3 mg/g at 15 ppm	32.1 mg/g at 1 ppm	57.9 %

Because of the chromatographic regeneration of the carbon column, the effluent quality is essentially independent of regenerant volume, since the carbon at the top of the column sees only clean solvent in every regeneration cycle. It is this carbon, at the top of the column, that dictates the effluent quality when the bed is brought back to water purification service.

DESIGN OF THE SOLVENT PROCESS

The design of a solvent regenerated activated carbon process is essentially the same as the design of a conventional carbon process. That methodology is detailed in several recent literature sources, such as Faust and Aly (1987), Nyer (1985) and Weber and Thaler (1983). As in the case of designing an adsorption process for thermally regenerated carbon process, the determination of the carbon consumption and the mass transfer properties of the adsorbates are critical to the operation of the process. That information is derived from isotherm data and piloting small carbon columns.

The solvent regenerated activated carbon process has one significant difference from the conventional carbon process, that being the regeneration of the carbon in the adsorber. That requires, if possible, that the wastewater be upflow during the adsorption cycle, to allow the downflow, countercurrent regeneration by the solvent. Thus, the design of the adsorber internals is dictated by both the adsorption and regeneration process requirements.

As stated earlier, the benchtop apparatus described in Section 2 is not intended to generate design data for a full-scale process. The scale-up and design of the full-size carbon adsorption and solvent regeneration process should be done by an engineering firm with prior experience in designing solvent regenerated carbon systems. Fluids Design Corporation has developed the capability of numerically simulating the loading and solvent regeneration dynamics of full-scale adsorbers.

UNIVERSITY/INDUSTRY COLLABORATIVE EFFORT

The collaborative effort of this research project involved the resources of the Department of Chemical Engineering at Rensselaer Polytechnic Institute and Fluids Design Corporation. At R.P.I., Dr. E.B. Nauman was the Principal Investigator.

The collaborative effort had some obvious advantages for Fluids Design Corporation, specifically the access to the laboratories and instrumentation at R.P.I. In addition, the expertise of Dr. Nauman would be a valuable resource in the understanding of the underlying physical phenomena of carbon adsorption and solvent desorption.

The conflicting desires of Fluids Design Corporation to develop proprietary technology for future market development and the requirement of public disclosure of research at an university was successfully resolved by carefully demarcating those sections of the research that were to be performed at R.P.I., retaining some sections of the development effort as the exclusive domain of Fluids Design Corporation personnel.

The only difficulty in executing the collaborative effort was the uncertainty associated with all fundamental research. Many proposed research efforts fail in the initial studies, but the learning curve eventually leads to success. A potential improvement in the research program would have been to structure the subcontract to R.P.I. to include a graduate student, who could have used the data in a thesis. That organization would have generated a long term interest for the university and potentially improved the quality of their effort.

Overall, the collaborative effort did serve to unite the resources of the university and industry. The state of the art of the solvent regenerated activated carbon technology was significantly advanced through this combination of expertise and apparatus.

Section 4

LITERATURE CITED

- Cooney, D.O., A. Nagerl and A.L. Hines, "Solvent Regeneration of Activated Carbon", Water Res., Vol. 17, pp. 403-410 (1983).
- Dobbs, R.A. and J.M. Cohen, CARBON ADSORPTION ISOTHERMS FOR TOXIC ORGANICS, EPA-600/8-80-023, April 1980, available through the National Technical Information Service, Springfield, Virginia 22161
- Faust, S.D. and O.M. Aly, ADSORPTION PROCESSES FOR WATER TREATMENT, Butterworths, Boston, pp. 138-165 (1987).
- Hamilton, C.E., "A New Solvent System for Improved Extraction of Activated Charcoal", Water & Sewage Works, pp. 422-423 (1963).
- Martin, R.J. and W.J. Ng, "Chemical Regeneration of Exhausted Activated Carbon - I", Water Res., Vol 18, pp. 59-73 (1984).
- Martin, R.J. and W.J. Ng, "Chemical Regeneration of Exhausted Activated Carbon - II", Water Res., Vol 19, pp. 1527-1535 (1985).
- McLaughlin, H.S., "Wastewater Treatment Evaluation and Redesign", proceedings of the 35nd Purdue Industrial Waste Conference, May, 1980.
- Miller, S. "Activated Carbon - the Dilemma Facing Its Use", Environmental Science and Technology, Vol. 15, p. 502 (1981)
- Nyer, E.V., GROUNDWATER TREATMENT TECHNOLOGY, Van Nostrand Reinhold Company, New York, pp. 61-73 (1985).
- Parmelee, C.S., E.S. Alperin, J.H. Exner and H.S. McLaughlin, "Nondestructive Regeneration of Activated Carbon - A Viable Chemical Engineering Technology", presented at the Annual Meeting of the A.I.Ch.E., New Orleans, November, 1981.
- Parmelee, C.S. and R.F. Fox, "Resource Recovery and Source Control via Activated Carbon Adsorption with Inplace Nondestructive Regeneration", proceedings of the 32nd Purdue Industrial Waste Conference, May, 1977.
- Sutikno, T. and K.J. Himmelstein, "Desorption of Phenol from Activated Carbon by Solvent Regeneration", Ind. Eng. Chem. Fundam., Vol. 22, pp. 420-425 (1983).
- Weber, W.J., and J.O. Thaler, "Modeling for Process Scale-Up of Adsorption and Ion Exchange Systems", in SCALE-UP of Water and Wastewater Treatment Processes, ed. N.W. Schmidke and D.W. Smith, Butterworth Publishers, Boston, pp. 233-257 (1983).

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