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ABSTRACT

Treatment of water contaminated with volatile organic compounds (VOCs) is a major problem for the United States chemical industry. Currently, VOCs are removed from moderately contaminated wastewater streams by processes such as steam stripping and from dilute wastewaters by air stripping combined with a carbon adsorption off-gas treatment system. This paper describes the development and performance of a hybrid process that combines air stripping with membrane organic-vapor separation to recover VOCs from the stripper off-gas. A number of prototype systems have been constructed and evaluated. The optimum system appears to be a tray stripper fitted with a high-pressure compression-condensation membrane separation unit. Such a system can remove 95 to 99% of the VOCs present in contaminated water; the removed VOCs are recovered as a liquid condensate. The economics of the technology are competitive with alternative processes, particularly for streams containing more than 500 ppm VOC and having flow rates less than 10 to 30 gal/min.

INTRODUCTION

Contamination of industrial wastewater or groundwater with volatile organic compounds (VOCs) is a common problem throughout the industrial world. By far the least expensive method of removing these volatile organics is air stripping, which can reduce the level of VOCs in the water to the parts per billion range at a cost of \$0.20 to \$0.50 per 1000 gallons of water (1). Air stripping exchanges water pollution for air pollution,

however, and environmental regulations now limit the amount of vapor that can be discharged from a stripper to 1 to 10 lb/day. Most air strippers must, therefore, be fitted with an air-treatment system to remove organic vapors from the vented air streams. Currently carbon adsorption is widely used, but the operating and capital costs of a carbon adsorption system are generally considerably more than the costs of the air stripper itself. As a result, the cost of the complete treatment unit is often too high to make the technology practical. This is particularly true for industrial wastewater, which contains a high concentration of VOCs and, consequently, requires a large carbon adsorption unit. In such cases, steam stripping systems may be used.

This paper describes the development of a hybrid process in which air stripping is combined with membrane organic-vapor recovery. The overall concept is illustrated schematically in Fig. 1. Wastewater enters the top of an air stripper and flows down to the sump. The strip gas enters the bottom of the tower and flows countercurrent to the liquid phase. The VOC-rich gas leaving the stripper is fed to the membrane system, where the membrane modules separate the strip-gas stream into a VOC-rich permeate and a VOC-depleted residue, which is fed back to the stripper. The VOC-rich permeate is cooled, and the VOC is condensed out and recovered as a liquid.

In the membrane separation step, VOC-laden air contacts one side of a membrane that is permeable to organic vapors but relatively impermeable to air. A pressure difference across the membrane causes the organic vapor to preferentially permeate the membrane; the permeate vapor is

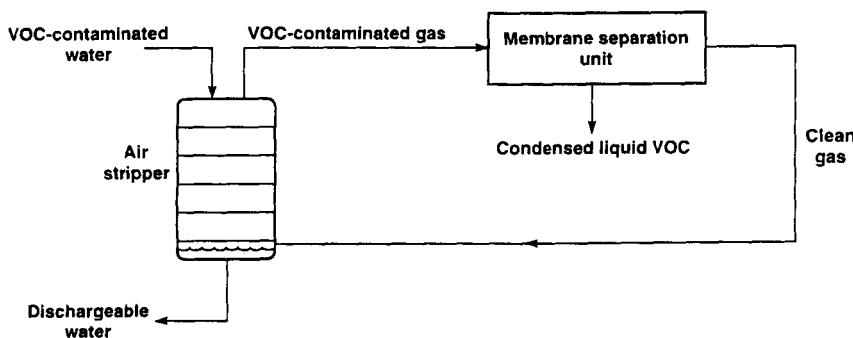


FIG. 1 The hybrid air stripping/membrane organic-vapor separation process. The unit treats VOC-contaminated water, producing dischargeable water and condensed liquid VOC for recycle or disposal.

then condensed to recover the organic fraction. The purified airstream is removed on the feed side as the residue gas. Membrane Technology and Research, Inc. (MTR) has been developing membrane vapor separation systems for a number of years; more than 30 industrial plants have been installed. The background to this membrane separation technology and the design of the particular membrane units used in this work are described in the Appendix.

The cost of a membrane vapor separation system is relatively independent of the concentration of the organic vapor in the air stream to be treated, but increases in proportion to air flow rate. To minimize the total cost of the air stripper/membrane hybrid, the air stripper must operate with the minimum amount of air. When the air stripper discharges the VOC-contaminated air directly to the atmosphere, the volume of air used to treat a volume of water—the air-to-water ratio—is often very high, on

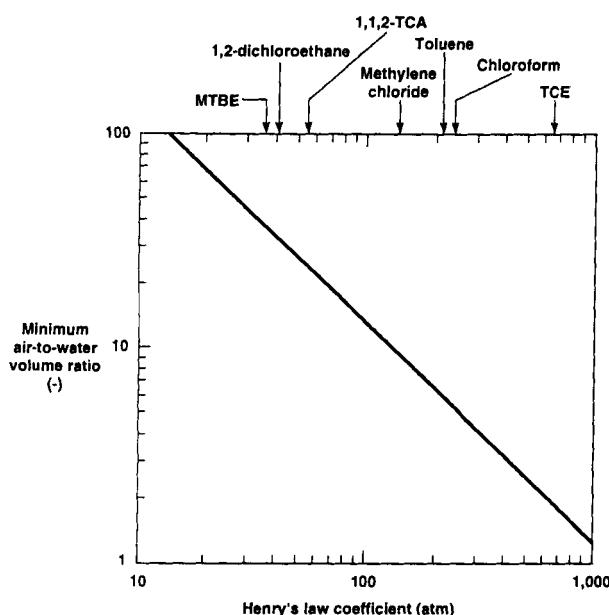


FIG. 2 Minimum air-to-water volume ratio as a function of the Henry's law coefficient of the VOC to be removed for an infinitely large, and hence efficient, air stripper. Most air stripper systems that discharge directly to the atmosphere use a less than perfect air stripper, and the air-to-water ratios employed are 10 to 100 times larger than the theoretical minimum. Our work shows that an air-to-water ratio three to four times the theoretical minimum will achieve 95% VOC removal with current commercial air strippers.

the order of 100 to 200 or more. The theoretical minimum amount of air required is much less.

The minimum air-to-water ratio required to strip the VOC from the water is proportional to its Henry's law coefficient, a measure of the volatility of the VOC. The Henry's law coefficient of the organic compound, H_i , is defined by the equation:

$$P_i = H_i X_i \quad (1)$$

where P_i (atm) is the equilibrium partial pressure of the organic in the nitrogen or air phase and X_i is the mole fraction of the organic in the water phase. A high Henry's law coefficient is desirable: the higher the coefficient, the higher the organic concentration in the gas stream and the lower the gas flow rate required to remove the organic from the water stream. A minimum air-to-water volume ratio can be calculated by assuming that the stripper has an infinite exchange area. This minimum ratio is solely a function of the Henry's law coefficient; the relationship is shown in Fig. 2 (2).

Based on Fig. 2, theoretical air-to-water ratios between 2 and 40 are required to achieve complete removal of VOC from the water with a perfect air stripper. Even very crude cost calculations show that, at these air-to-water ratios, an air stripper/membrane hybrid system would be very competitive with alternative treatment technologies for VOC-contaminated water.

EXPERIMENTAL PROCEDURES

A flow schematic of the test system used to develop this process is shown in Fig. 3. A continuous wastewater stream was simulated by continuously feeding liquid VOC to a water mixing station. The resulting VOC-contaminated water was then fed to the stripper. The process generally reached steady state after 1 to 2 hours of operation. In each experiment the process was operated for at least 4 hours at steady-state conditions. The performance of the process was characterized by sampling the liquid and gas streams and analyzing the VOC content of the samples by gas chromatography. Nitrogen rather than air was used as the stripping gas to eliminate safety issues regarding gas flammability.

During the development program two types of air stripper were used: a 60 to 100 gpm packed-tower stripper and a 2 to 20 gpm tray stripper. Three membrane separation systems were used: a 30-scfm compression-condensation system, and two multistage, low-pressure, 30 to 70 scfm systems (see Appendix). The results obtained with each type of air stripper are detailed below.

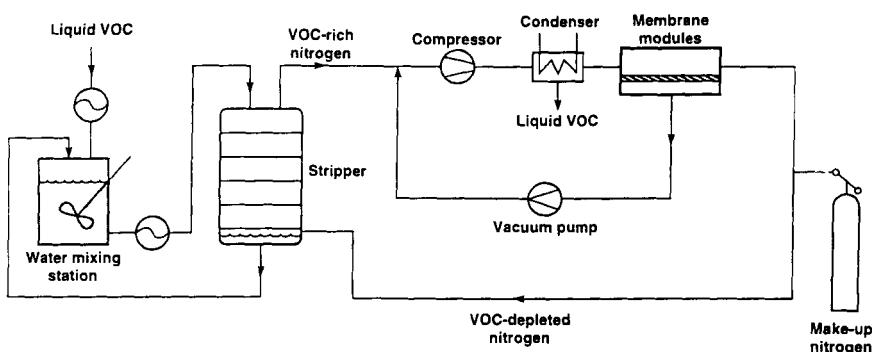


FIG. 3 Hybrid air stripping/membrane separation test system with mixing station to simulate a continuous wastewater stream.

RESULTS AND DISCUSSION

Packed Column Air Stripper

The packed-column air stripper used in our initial work was 1 m in diameter and 4 m tall; the effective column height was 3 m. The membrane separation system was a three-stage system able to treat 50 to 70 scfm of VOC-laden air. Because the membrane system removed 90 to 95% of the VOC from the effluent air stream, the overall performance of the system was determined by the performance of the air stripper. Some typical data obtained with dilute TCE solutions are shown in Fig. 4.

These results show the balance between the efficiencies of the stripper and the membrane unit. If the air-to-water ratio in the stripper is very large compared to the theoretical minimum, then the stripper performance will be good provided the membrane unit removes the VOC from the stripper discharge air. The efficiency of the membrane VOC-removal step then becomes very important. On the other hand, if the air-to-water ratio is close to, or below, the theoretical minimum value for complete removal, then the performance of the system is controlled by the stripper even if the membrane system achieves high removals. In the results shown in Fig. 4, an air-to-water ratio of 8 to 10 is required to achieve greater than 95% TCE removal. This is a significantly higher air-to-water ratio than the theoretical minimum ratio suggested by the calculations in Fig. 2. Figure 2 indicates that an air-to-water ratio of 2 to 3 would be sufficient for TCE; therefore, at an air-to-water ratio of 3 to 6, the efficiency of the

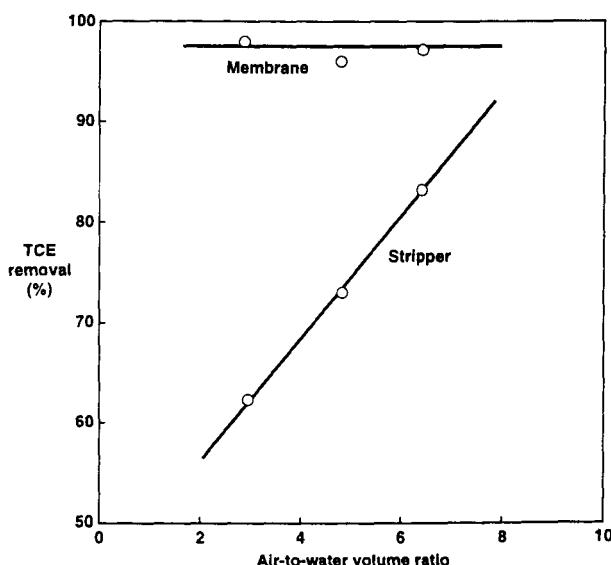


FIG. 4 TCE removed by the air stripper (feed water to discharge water) and the membrane system (feed air to residue air) as a function of air-to-water volume ratio. Air flow rate: 46 to 48 scfm; water flow rate: 55 to 120 gpm; TCE feedwater concentration: 4 to 8 ppmw.

system is stripper-controlled. At an air-to-water ratio of 10 or more, it would be membrane-controlled.

Additional experiments were performed at a fixed air-to-water ratio of about 5 for the model VOCs carbon tetrachloride (CCl_4), trichloroethylene (TCE), chloroform ($CHCl_3$), and dichloroethane (DCE). The Henry's law coefficient of these compounds covers a wide range, from 65 to 1600 atm/mole fraction. The results, shown in Fig. 5, also illustrate how the efficiency of each subsystem influences the overall removal. First, the overall VOC removal decreases with decreasing Henry's law coefficient because the driving force for VOC removal by the air stripper decreases. This is observed for all conventional air-stripping operations. Second, the overall VOC removal decreases with decreasing VOC concentration because the ability of the membrane system to recover VOC from the recirculating air stream is reduced as the VOC concentration in that stream decreases. The dependence on the VOC concentration is not strong; if the VOC concentration is reduced by a factor of 10, the VOC removal is reduced by a factor of only 1.5. At higher VOC concentrations, this dependence disappears.

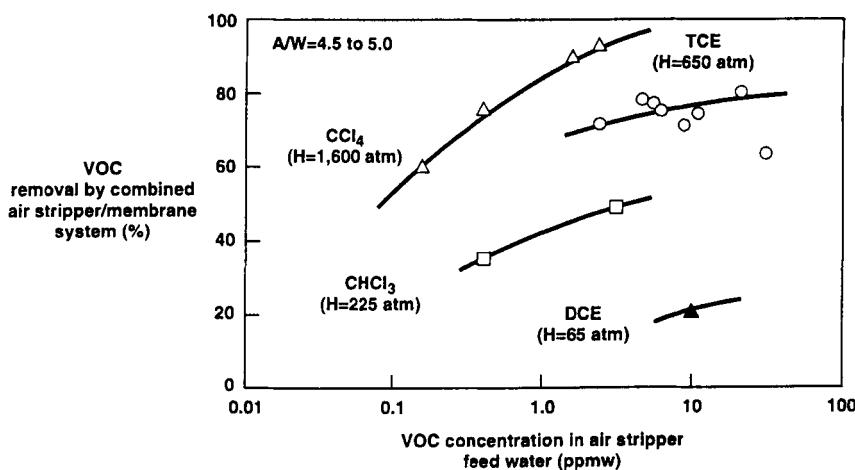


FIG. 5 Removal achieved by the combined air stripper/membrane vapor separation system as a function of the VOC concentration in the air stripper feedwater. Air-to-water ratio: 4.5–5.0; feedwater flow rate: 100 gpm; air flow rate: 65 to 70 scfm.

A key result, shown by the data in Fig. 5, is that actual VOC removals at an air-to-water ratio of 5 are significantly less than expected. When these results are compared to the theoretical minimum air-to-water ratios shown in Fig. 2, it appears that the air-to-water ratio in the actual stripper has to be three to four times higher than the theoretical minimum value to achieve better than 95% removal. We tried to produce higher air-to-water ratios in the packed tower air stripper by reducing the water flow from 100 to 20–30 gpm. The air flow was maintained at 70 scfm, the maximum value that could be handled by the membrane unit. Unfortunately, when the water flow is reduced below the design value of about 60 gpm, channeling begins to occur, and the efficiency of the air stripper then falls drastically.

Tray Air Stripper

The low-profile tray air stripper (ORS Environmental Equipment, Greenville, NH) is designed to operate at higher air-to-water ratios. A drawing of the stripper, illustrating the operation of the trays, is given in Fig. 6. In this stripper the VOC-contaminated water is fed to the top of a stack of six distribution trays. The liquid flows down from one tray to another through pipes connecting the liquid phases in the trays; the

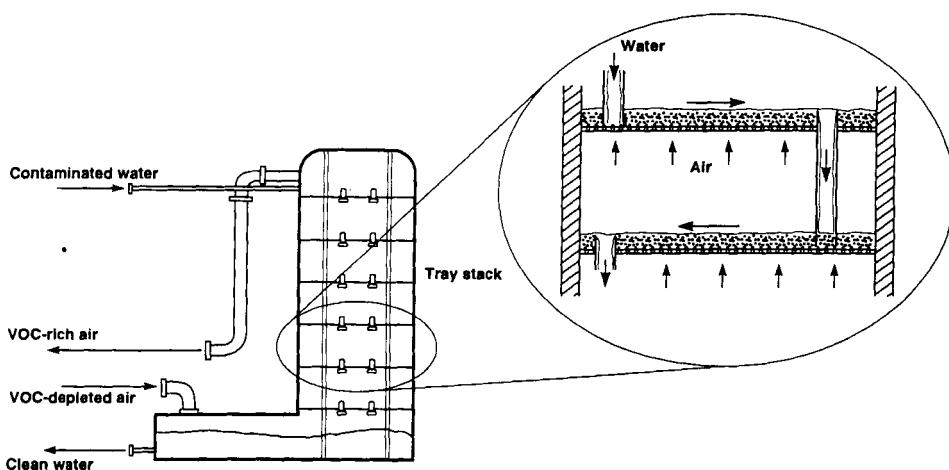


FIG. 6 Schematic drawing of the low-profile tray stripper.

connecting pipes are arranged so that the water flows from one side to the other within one tray. Air is withdrawn from the top of the tower, causing an air flow countercurrent to the liquid flow. The air bubbles through small holes in the trays, removing the VOC from the water. The stripper can handle a liquid flow rate of 2 to 20 gpm at a gas flow rate of 30 scfm, which translates to an air-to-liquid ratio of 10 to 100. Depending on the application, the efficiency of the stripper can be altered by adjusting the water flow rate and the air-to-water ratio or by adding more trays to the stack, a task requiring only hand tools.

Two membrane vapor separation systems were used with the tray air stripper. The first was a low-pressure, two-stage unit which generally removed about 90% of the VOCs in the low-concentration air stream leaving the air stripper. Later, a high-pressure compression-condensation membrane system was installed. This unit was more efficient than the low-pressure unit and provided better than 95%, and often better than 99%, VOC removal from the air stream. Both membrane systems could treat about 30 scfm of air. These systems are described in the Appendix.

Because the air-to-water ratio of the stripper was now in the 10 to 40 range, VOC removal by the air stripper was often greater than 95%. At these high air-to-water ratios and high VOC removals, the efficiency of the membrane system can affect the overall separation achieved by the hybrid system. The effect of the membrane system efficiency on the total VOC removal by the unit is illustrated by the results in Figs. 7 and 8.

Figure 7 shows removal of TCE from a 10-gpm, 100-ppmw water stream using the tray stripper fitted with the two-stage, low-pressure membrane unit. The air-to-water ratio in the stripper was about 20. This is about 10 times the theoretical minimum air-to-water ratio shown in Fig. 2, so the air stripper operates quite efficiently. Under these conditions the air stream sent to the membrane unit contained about 3500 ppm TCE. Because the low-pressure membrane vapor separation system only removed 85 to 90% of the TCE from this stream, the air returned to the air stripper still contained about 400 ppmw TCE. This is high enough to affect the performance of the air stripper even though the air-to-water ratio is 10 times the theoretical minimum value. Under these conditions the air stripper removed about 97.5% TCE from the feedwater. A more efficient membrane unit would allow much better TCE removal.

Figure 8 shows results obtained with the tray stripper fitted with the high-pressure membrane system using toluene-containing solutions. Toluene has a much smaller Henry's law coefficient than TCE, so the air stripper was operated at an air-to-water ratio of 39, approximately 4 times the minimum theoretical air-to-water ratio. The high-pressure membrane system is considerably more efficient than the low-pressure, two-stage system, and removed 99.6% of the toluene from the feed air to the membrane unit. As a result, the combined system achieved 95.6% removal of toluene from the feedwater. Thus, the removal efficiency in this case is determined by the air stripper.

The effect of the air-to-water ratio on the removal of a specific VOC (methylene chloride) is shown in Fig. 9. Based on the Henry's law coefficient of methylene chloride, the minimum air-to-water ratio required for

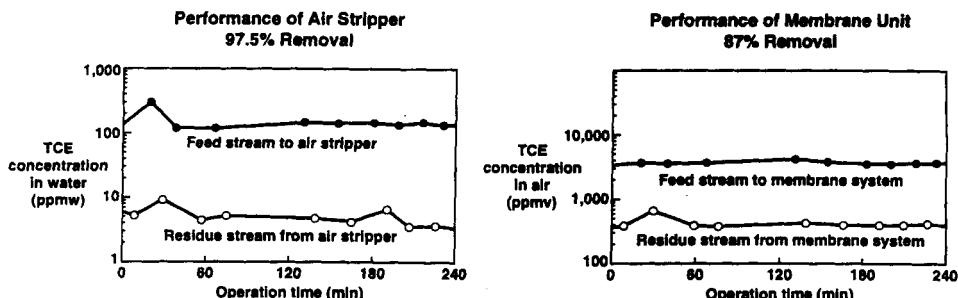


FIG. 7 Performance of the low-profile tray stripper fitted with a two-stage, low-pressure membrane vapor separation system. Water flow: 10 gpm; air flow: 28 scfm. In this experiment the air stripper has a higher VOC removal efficiency than the membrane unit. The membrane unit's performance then begins to affect the overall efficiency of the process.

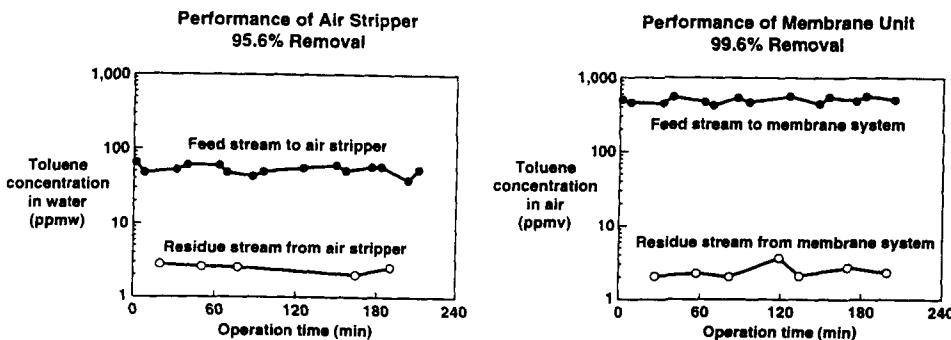


FIG. 8 Performance of the low-profile tray stripper fitted with a high-pressure membrane vapor separation system. Water flow: 5 gpm; air flow: 26 scfm. In this experiment the high-pressure membrane system has a very high removal efficiency for toluene from air, so the overall performance of the combined system is controlled by the efficiency of the air stripper.

an infinitely large stripper is 10. At a ratio of 10, the six-tray unit actually only strips about 75% methylene chloride from the feed, but at an air-to-water ratio of 30, 3 times the theoretical value of the system, 95% removal is achieved.

It is desirable to increase the efficiency of the stripper so that lower air-to-water ratios can be used; this reduces the size of the air stream sent

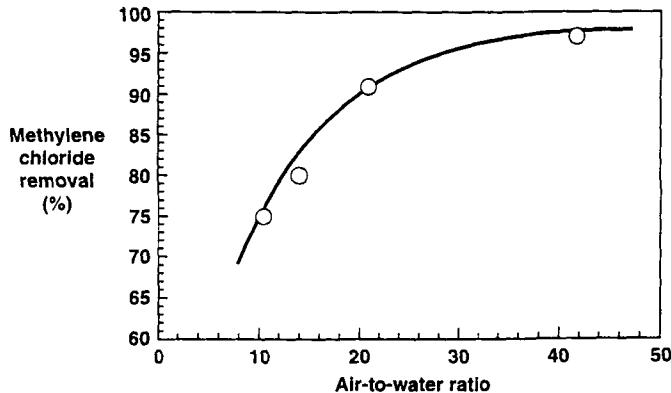


FIG. 9 Removal of methylene chloride by tray air stripper as a function of the volumetric air-to-water ratio. Air flow rate: 27 scfm; water flow rate: 5 to 20 gpm. The minimum air-to-water ratio required for an infinitely large and efficient air stripper to achieve complete removal is 10.

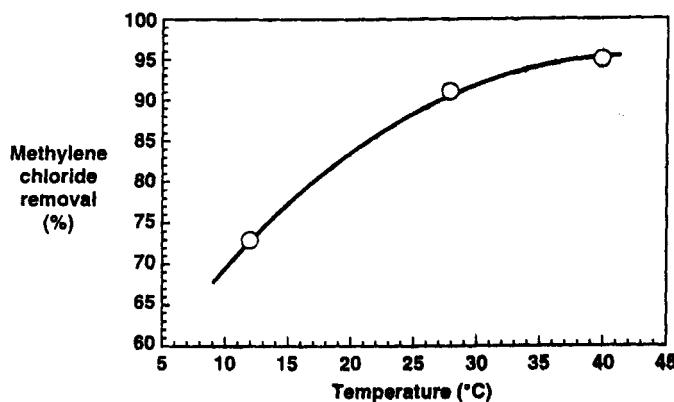


FIG. 10 Removal of methylene chloride by air stripper from a contaminated water stream as a function of the water temperature at an air-to-water ratio of 20. Air flow rate: 27 scfm; water flow rate: 10 gpm.

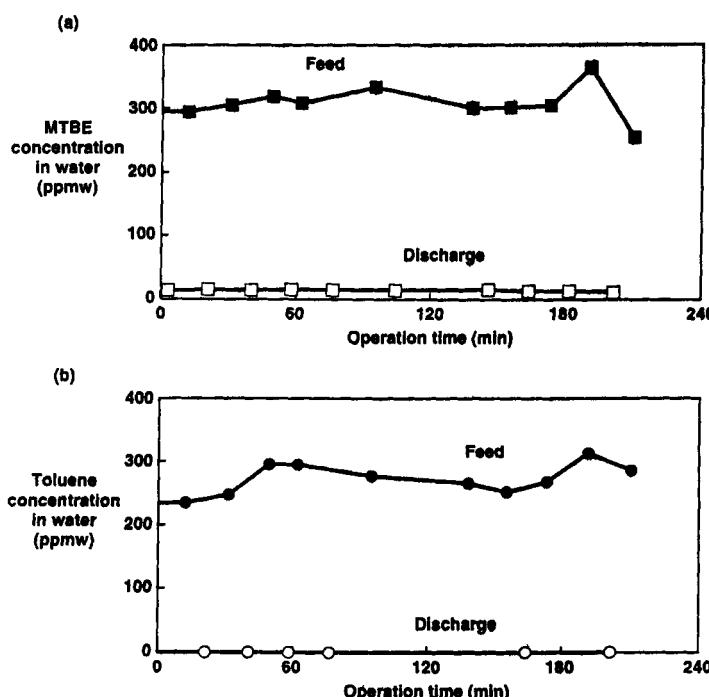


FIG. 11 Concentration of (a) MTBE and (b) toluene as a function of operation time for a mixed model wastewater stream entering and leaving the stripper. The unit removes about 96% of the MTBE and more than 99% of the toluene.

to the membrane unit, hence the membrane area and cost. The efficiency of the stripper can be improved by adding more trays; addition of an extra two or three trays to the air stripper used in these experiments would be a worthwhile and low-cost improvement. Another simple method of improving stripper efficiency is to increase the temperature of the feed-water. The surprisingly large effect of water temperature on the air stripper efficiency is shown in Fig. 10. At an air-to-water ratio of 20, increasing the water temperature from 10 to 40°C increases the removal of methylene chloride by the system from 73 to 95%.

Most of our work was performed with one-component VOC solutions, but we also performed a few experiments with mixed VOC solutions. No anomalous effects were noticed. Figure 11 shows the results obtained with an MTBE (methyl tertiary butyl ether)-toluene mixture representative of a mixed wastewater found at a refinery or gasoline terminal. Based on its Henry's law coefficient, MTBE requires a minimum air-to-water ratio of 40, whereas toluene needs a minimum of about 6. In the experiment the air-to-water ratio was 50. The membrane unit achieved better than 99% VOC removal, so the combined air stripper/membrane system removed 96% of the MTBE and more than 99% of the toluene.

BENEFITS AND COSTS OF HYBRID AIR STRIPPER/ MEMBRANE VAPOR SEPARATION PROCESS

The air stripper/membrane vapor separation process offers a number of advantages over alternative technologies:

- The process is completely closed-loop and produces no secondary wastes other than the separated concentrated organic fraction.
- Because the stripping gas is recycled, nitrogen can be used instead of air. The use of nitrogen considerably reduces the scaling and fouling problems that plague air stripping plants. Contaminated groundwater in particular often contains a high concentration of ferrous iron, which oxidizes in the stripper and causes severe fouling. Consequently, pre-treatment of these waters by precipitation, coagulation, and filtration of the iron is often required.
- As detailed below, the economics of the process are competitive with those of alternative processes, particularly for small streams containing relatively high VOC concentrations, that is, VOC concentrations greater than 500 ppmw and flows less than 10 to 30 gpm.

An economic analysis of the process was performed with a base-case calculation for a 10,000-gal/day feed. The unit is designed to remove 99% of hydrophobic VOCs, such as benzene, toluene, and trichloroethylene,

and 95% removal of VOCs with relatively low Henry's law coefficients, such as methylene chloride. Based on the experimental data, an air-to-water ratio of about 40 is required, which translates to a strip gas flow rate of 37.5 scfm. Capital and operating costs of the system are given in Table 1.

The capital and operating costs shown in Table 1 are competitive with those of alternative technologies. The two most cost-competitive technologies are hybrid air stripping/vapor-phase carbon adsorption and steam stripping. We eliminated liquid-phase carbon adsorption as a competitive technology based on the results of a study by Adams and Clark (3). Their cost analysis compares direct liquid-phase activated carbon treatment with packed-tower air stripping combined with vapor-phase activated carbon as emission control. For virtually all the VOC contaminants examined, air stripping followed by vapor-phase carbon treatment is more cost effective than liquid-phase carbon treatment.

A major cost in the air stripping/vapor-phase carbon adsorption process is the cost of replacing or regenerating the carbon. For the streams being considered, off-site replacement would be prohibitively expensive, so on-site regeneration must be used. The cost of vapor-phase carbon treatment depends on the amount of VOC to be adsorbed onto the carbon; Vatavuk (4) gives methods to estimate capital and operating costs for carbon adsorption systems. The costs of steam stripping were estimated using procedures and data taken from EPA guidelines (1). Steam stripping plants

TABLE 1
Estimated Capital and Operating Cost for a 10,000-gpd Air Stripper/
Membrane Wastewater Treatment Plant Designed for 99+%
Recovery of TCE, Benzene, and Toluene, and 95% Recovery of
Methylene Chloride

Capital cost:	
Total FOB cost	\$132,000
Project installation at customer site	<u>20,000</u>
Total installed cost	152,000
Annual operating cost (360 days, 24 h/day)	
Module replacement (assuming a 3-year lifetime)	3,200
Power (20 kW at \$0.05/kW·h)	8,600
Nitrogen use at 20 ft ³ /h (\$10/1000 ft ³)	1,800
Depreciation at 10% capital	15,200
Maintenance at 5% of capital	7,600
Labor at 10% of capital	<u>15,200</u>
Total annual operating cost	51,600
Cost/1000 gal of water treated: ~\$14.10	

have considerable economies of scale, and a 10,000-gpd plant is at the bottom end of the normal stream-stripping range. Steam stripping costs are, therefore, relatively high.

The annual operating costs of the three technologies—calculated on an equivalent basis (same location, labor, energy cost, etc.)—are compared in Fig. 12 as a function of VOC concentration for methylene chloride in a 10,000-gpd wastewater system. As shown in Fig. 12, the costs of a membrane system designed for a 10,000-gpd wastewater stream remain constant as the VOC concentration increases, because any increase in concentration actually increases the overall recovery. In contrast, the capacity of the carbon adsorption system increases with the amount of VOC to be captured from the stripper off-gas, so operating costs increase with VOC concentration. For concentrations of 500 ppmw up, the stripper/membrane process is more economical than the stripper/carbon adsorption process. Steam stripping is often used at high VOC concentrations, and the EPA guidelines (1) indicate that stream stripping is not sensitive to the VOC concentration. At the flow rate considered, however, the cost of stream stripping is almost twice that of the combined stripper/membrane process.

Figure 13 compares the treatment costs for a stream containing 500 ppm methylene chloride as a function of flow rate. At the flow rates and VOC concentration considered, the treatment costs of stream stripping and air

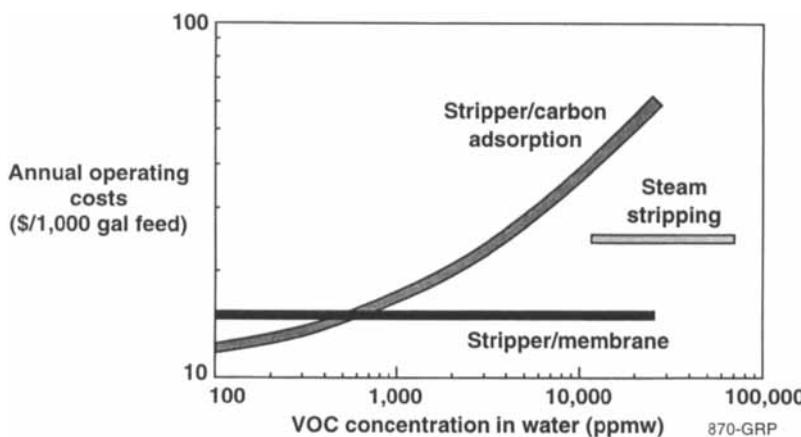


FIG. 12 Treatment costs of competing technologies as a function of VOC concentration for a 10,000-gpd stream containing methylene chloride. Stripper/membrane costs determined by MTR; stripper/carbon adsorption costs (4) and stream stripping costs (1) obtained from the literature.

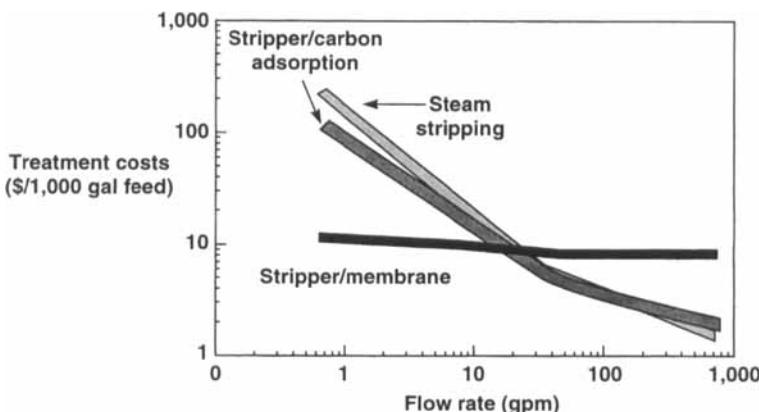


FIG. 13 Treatment costs of competing technologies as a function of flow rate for wastewater streams containing 1 wt% methylene chloride. Stripper/membrane costs determined by MTR; stripper/carbon adsorption costs (4) and steam stripping costs (1) obtained from the literature.

stripping/carbon adsorption are approximately equal and a strong function of flow rate. Air stripping/membrane strip-gas treatment is almost independent of flow rate in the range studied. At flow rates below 30 gpm, the stripper/membrane process becomes more economical.

SUMMARY

A new method of treating VOC-containing wastewaters—a hybrid air stripping/membrane organic-vapor separation process—has been developed. At the 10 to 30 gpm scale, the process achieved better than 95% removal for methylene chloride and better than 99% removal for VOCs with higher Henry's law coefficients. The process appears to offer a number of advantages over competitive technologies such as air stripping plus carbon adsorption or steam stripping.

APPENDIX: BACKGROUND TO MEMBRANE VAPOR SEPARATION TECHNOLOGY

The heart of the process described in this paper is the membrane separation step (5). The membranes developed by MTR for the separation of organic compounds from air are composite structures as illustrated in Fig. 14. The tough, open, microporous layer provides strength, and the

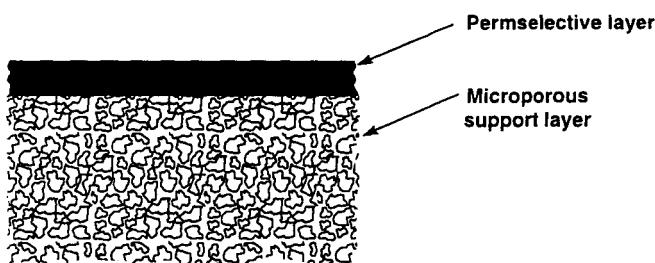


FIG. 14 Schematic drawing of an MTR composite membrane. Membranes in rolls 100–200 yards long and 40 inches wide are produced at MTR.

ultrathin permselective coating is responsible for the separation properties.

Certain membrane materials, particularly hydrophobic rubbery polymers, have an intrinsically high selectivity for organic vapors over air, allowing useful separations to be performed. A measure of the efficiency of a membrane to separate a particular vapor from an air stream is the selectivity (α), defined as the ratio of the vapor permeability through the membrane (P_{vap}) to the air permeability through the membrane (P_{air}):

$$\alpha = P_{\text{vap}}/P_{\text{air}} \quad (\text{A1})$$

Our experience has shown that a membrane selectivity of greater than 10, and preferably greater than 20, is required for an economically viable membrane process. The selectivity of the standard MTR membrane for a number of common industrial organic vapors is listed in Table 2.

The composite membranes are incorporated into spiral-wound modules of the type illustrated schematically in Fig. 15. The spacers on either side of the membrane leaves create flow channels for the feed and permeate gas streams. Feed gas enters the module and flows between the membrane leaves. The component of the feed that is preferentially permeated by the membrane spirals inward to a central permeate collection pipe. The remainder of the feed flows across the membrane surface and exits as the residue. To meet the capacity and separation requirements of a particular application, modules are connected in serial or parallel flow arrangements.

System Design

Three membrane separation systems were built and operated with air stripping systems during the development of this process: a multistage

TABLE 2
MTR Membrane Selectivity to Common Organic
Vapors at Ambient Temperature

Vapor	Membrane selectivity
Octane	90-100
1,1,2-Trichloroethane	60
Isopentane	30-60
Methylene chloride	50
CFC-11 (CCl ₃ F)	45
1,1,1-Trichloroethane	30-40
Isobutane	20-40
Tetrahydrofuran	20-30
CFC-113 (C ₂ Cl ₃ F ₃)	25
Acetone	15-25
CFC-114 (C ₂ Cl ₂ F ₄)	10

system, a two-stage partial recycle system, and a high-pressure compression-condensation system.

Multistage System

The system used with the packed tower air stripper was a three-stage low-pressure unit as shown in Fig. 16 (6). We recognized that the VOC

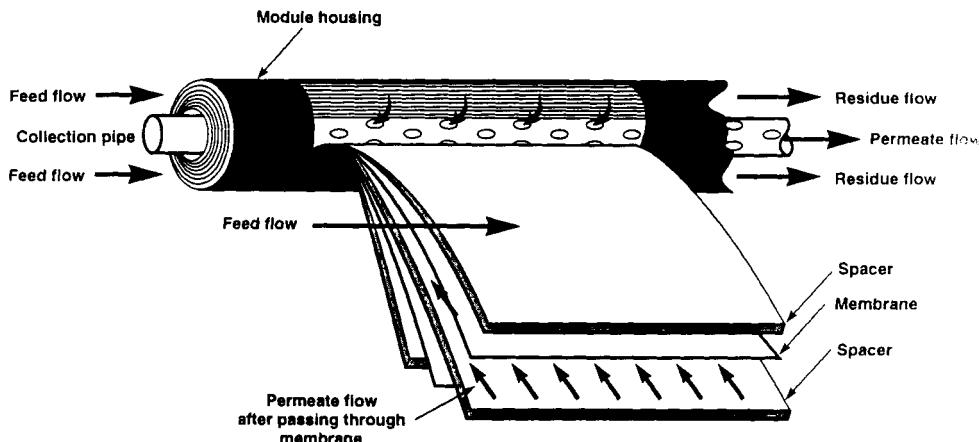
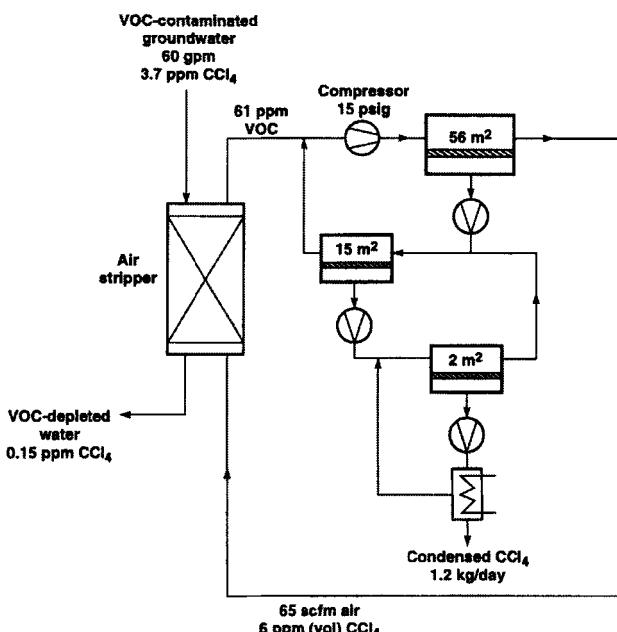


FIG. 15 Schematic diagram of a spiral-wound membrane module. The membrane area ranges from 4 m² for laboratory modules to 15 m² in industrial-scale modules.



Stream	Gas Stream CCl_4 Concentration (ppm)		
	Stage 1: 56 m^2	Stage 2: 15 m^2	Stage 3: 2 m^2
Feed	65	419	3,400
Residue	6	54	1,410
Permeate	271	2,190	46,700

FIG. 16 Performance of an air stripper/membrane vapor separation system in removing carbon tetrachloride from a 60-gpm water stream containing 3.7 ppm carbon tetrachloride. The combined air stripper-membrane vapor separation system removes over 96% of the VOC.

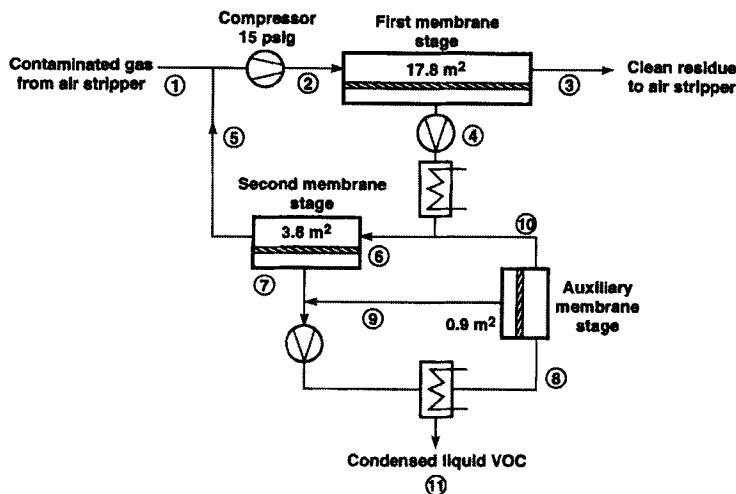
concentration in the off-gas from this air stripper would be low, requiring 100 to 1000 times concentration to allow convenient condensation temperatures. Therefore, a three-stage membrane design was used to achieve the separation required. Each membrane stage concentrated the VOC from 4 to 14 times, producing an overall concentration of more than 700-

fold while removing 90% of the VOC from the air stripper off-gas. The performance of the system with model groundwater containing carbon tetrachloride is also shown in Fig. 16.

In this multistage system, each succeeding stage becomes smaller as the volume of gas to be treated is reduced. Nonetheless, the overall system is rather large and, more importantly, contains four pieces of rotating equipment. The cost and loss in reliability associated with this degree of complexity is an issue.

Two-Stage Partial-Recycle System

The first membrane system combined with the tray air stripper was a two-stage partial-recycle system shown in Fig. 17. The first two stages each concentrated the VOC 5 to 10 times, as with the three-stage system shown in Fig. 16. A dilute feed gas is thereby concentrated to approxi-



Stream	1	2	3	4	5	6	7	8	9	10	11
Flow (scfm)	28.0	32.6	27.9	4.7	4.6	5.2	0.57	0.63	0.15	0.48	0.86*
TCE Concentration (%)	0.35	0.403	0.045	2.52	0.721	2.33	15.5	6.49	25.6	0.49	100

*kg/hr

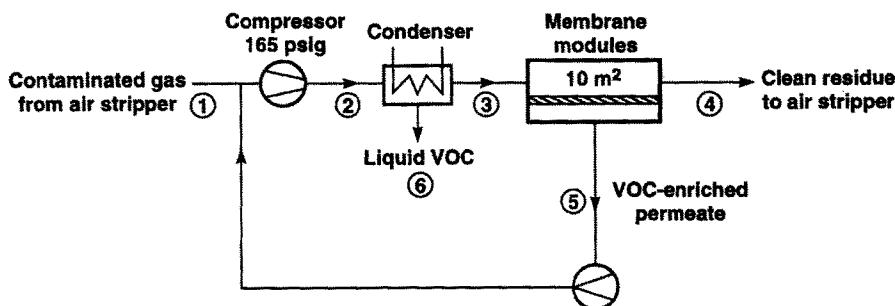
FIG. 17 A flow schematic of the two-stage, partial-recycle system used with the tray air stripper. Typical flows and concentrations in this system when used with TCE are shown.

mately 25 to 100 times in the second-stage permeate. Depending on the temperature of the VOC condenser placed after the second-stage vacuum pump, a portion of the VOC might be condensed and removed at this point. However, the off-gas from the condenser will still have a high VOC concentration. Rather than remix the concentrated gas with the relatively dilute permeate from the second stage, essentially negating most of the separation obtained, the stream is treated by a small auxiliary membrane stage. The partial recycle achieved by this auxiliary membrane, called a half-stage (7), allows the VOC concentration to build up rapidly in the second-stage loop, allowing easy removal as a liquid by the condenser.

On a cost and performance basis, the two-stage partial-recycle design is a considerable improvement over the three-stage system. This unit contains one less piece of rotating equipment and uses less membrane area to achieve an equivalent separation. Nonetheless, it is still a relatively large and complex system.

High-Pressure, Compression-Condensation Membrane System

The second membrane system combined with the tray stripper was a high-pressure, compression-condensation design (8, 9). Such a system is



Stream	1	2	3	4	5	6
Flow (scfm)	26.0	40.1	40.1	26.0	14.1	0.07 ^a
TCE Concentration (%)	0.040	0.134	0.108	0.002	0.305	100

^akg/hr

FIG. 18 A flow schematic of the high-pressure, compression-condensation membrane system used with the low-profile tray air stripper. Typical flows and concentrations in this system when used with TCE-contaminated gas are shown. In this example the system removes 98% of the TCE from a 400-ppm feed gas.

simpler and cheaper. The overall design of this system is shown in Fig. 18. The air stream from the stripper is compressed and sent to a condenser. The fraction of VOC that condenses at this point is collected as a liquid in a storage tank. The noncondensed portion of the mixture passes through to the membrane modules which separate the gas into two streams: a clean air stream that is recirculated back to the air stripper and a small, concentrated VOC-containing stream that is recirculated to the front of the compressor. Because of this recirculation, the VOC concentration builds up rapidly in the recirculated gas stream. This system uses significantly more energy to compress the gas than a multistage, low-pressure unit of the same capacity, but the overall design is much simpler, and the capital and operating costs are much lower.

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REFERENCES

1. *Control of Volatile Organic Compound Emissions from Industrial Wastewater*, EPA-453/D-93-056, September 1992.
2. C. Yaws, H.-C. Yang, and X. Pan, "Henry's Law Constants for Organic Compounds in Water," *Chem. Eng.* (November 1991).
3. J. A. Adams and R. M. Clark, "Evaluating the Costs of Packed-Tower Aeration and GAC for Controlling Selected Organics," *J. Am. Water Works Assoc.*, 83(1), 49 (1991).
4. W. M. Vatavuk, *Estimating Costs of Air Pollution Control*, Lewis Publishers, Chelsea, MI, 1990.
5. R. W. Baker and J. G. Wijmans, "Membrane Separation of Organic Vapors from Gas Streams," in *Polymer Gas Separation Membranes* (D. R. Paul and Y. P. Yampol'skii, Eds.), CRC Press, Boca Raton, FL, 1994.
6. J. G. Wijmans, R. W. Baker, H. D. Kamaruddin, J. Kaschemekat, R. P. Olsen, M. E. Rose, and S. V. Segelke, *Combined Air Stripper/Membrane Vapor Separation System*, DOE Report #CH-9209 (November 1992).
7. J. G. Wijmans, J. Kaschemekat, and R. W. Baker, "Membrane Process and Apparatus for Removing a Component from a Fluid Stream," US Patent 5,147,550 (September 1992).
8. J. G. Wijmans, "Process for Removing Condensable Components from Gas Streams," US Patent 5,089,033 (February 1992).
9. R. W. Baker, J. Kaschemekat, J. G. Wijmans, and R. W. Baker, "Process for Removing an Organic Compound from Water," US Patent 5,273,527 (December 1993).

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