HYBRID TECHNOLOGY FOR COMPLETE DESTRUCTION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

For complete destruction of chlorinated volatile organic compounds an in-line treatment train is proposed. Membrane technology in the form of 'Pervaporation', is chosen as the initial VOC stripper followed by Photocatalytic degradation or Corona destruction. From the experimental studies performed with pervaporation and literature review of photocatalytic degradation/ Corona destruction it is found that the hybrid technology have significant potentialities as an emerging substitute of the conventional processes. In this article some of the important results, with pervaporation as a stripper technology, is provided. A removal efficiency of 90 - 98% can be easily obtained. It is expected that improvement and modification may produce even better results. Thus it may be concluded that pervaporation may very well be used for this purpose. While both photocatalytic degradation and corona destruction are reported to produce a 99% degradation. Thus an overall treatment efficiency of close to 99% can be achieved by this hybrid technology. This amount of efficiency will in most cases enable to meet the regulatory discharge standard.

KEYWORDS

Pervaporation, Trichloroethylene, 1,1,1 Trichloroethane, Photocatalytic Degradation, Corona Destruction

1 INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) threaten the entire biosphere and the human race by its extremely harmful power as a pollutant. Many of these compounds exhibit the properties of being mutagenic, carcinogenic, teratogenic etc. Though the extent of toxicity and hazards of many of such compounds are yet to be established, however it goes beyond doubt that these compounds pose serious environmental pollution. These CVOCs are already put in the group of priority pollutant or their usage have been legally stopped by many countries. These compounds are used in various industrial processes. Among the most commonly used compounds, Trichloroethylene (TCE) and 1,1,1 Trichloroethane (TCEthane) are used abundantly in such processes like dry cleaning, degreasing, deoiling, solvents for waxes, fats and so on.

After use, these compounds are usually led to the wastewater drain along with other impurities. It is at this point that these compounds become pollutants and pose serious hazards. Due to there inherent tendency of volatilizing (as soon as they come into contact with the atmosphere) they are liable to serious air pollution. Also if seepage or spillage takes place they can very well contaminate the ground water, due to their poor affinity for soil.

An immediate solution to such a problem is therefore required to reduce the possibility of this uncontrolled volatilization or seepage which is the main objective of this research study.

2 TREATMENT PHILOSOPHY

While an end-of-pipe treatment may allow sufficient time for uncontrolled volatilization or seepage by leaking, an in-line treatment may reduce the problem in many ways. An in-line treatment is expected to have higher efficiency (due to less interference from additional impurities to be encountered at the end of the pipe wastewater), reduced size of equipment, lower power requirements etc. The benefit can be even extended to recovery of valuable solvents if necessary or found feasible technically and economically.

An in-line treatment train can be composed of a CVOC stripper followed by the final treatment technology. The primary function of the CVOC stripper will be to remove the VOC from the wastewater, concentrate it and pass it over to the ultimate destruction technique or recovery equipment. The CVOC free wastewater can be led to the drain while the CVOC can be captured in a vacuum or an inert gas or simply as air stream. The following figure schematically represents the proposed treatment train.

3 TECHNOLOGIES

While conventionally air stripping can be used for the stripper mechanism, recent researches (Lipski and Cote, 1990) show that membrane technology can have tremendous potentialities for the same. Out of the common membrane technologies, pervaporation seems to be the most promising in such type of application. Pervaporation has long been established as a common technique in separating dissolved compounds from a solution, breaking azeotropic mixture, dehydration of alcohol etc. Only by the foresight of Cole and Genetelli 1970, that researchers have turned their attention towards usage of pervaporation for stripping VOC. The partial success of air stripping together with its high cost requirements has further strengthened the competance of pervaporation.

In pervaporation, the VOC is first vaporized and then transported across the membrane barrier. Furthermore only few compounds (depending on the property of the membrane used) are allowed to pass through the membrane while other molecules are retained back. Thus a selective stripping can be achieved, the selectivity being highly dependent on the membrane penetrant relationship/ affinity.

Pervaporation can be operated in two fashions. The most commonly used is the one where vacuum is used to withdraw the permeating molecules and more recently the other mode in which any inert gas or air is used as a scavenger fluid has been under active study. Considerable debate lies as to which method is better and both the modes have its own advantages and disadvantages. However generally if recovery of VOC is the objective vacuum aided pervaporation may be more suitable while gas sweep pervaporation may be the choice for destruction of large scale CVOC laden wastewater stream. In the present study air sweep pervaporation or air perstripping (Acda and Mora, 1992) is used with an objective of introduction of pervaporation in the industrial scale level.

4. POST TREATMENT TECHNOLOGIES

Once a good separation is achieved and a concentrated VOC stream is generated many technologies are available to treat the waste stream. Incineration is by far the most common technique followed by catalytic combustion and activated carbon absorption. Chemical oxidation and biodegradation can also be used with partial success.

However more recently two emerging technologies seems to be promising in this aspect. These are
(1) Photocatalytic Degradation and
(2) Corona Destruction

In photocatalytic degradation photons can be used to oxidize the VOCs into less harmful products. Photons can be obtained from sunlight, artificial light or from an U-V source. Catalyst like Zinc Oxide, Cadmium Sulfide or Titanium Dioxide can improve the rate of reaction and efficiency, 99% conversion of TCE could be achieved within a short time (Dibble and Raupp, 1992). It was also found that presence of moisture in the feed gas was essential. This particular point strongly supports the usage of pervaporation as a pre-treatment. In which case some of the moisture which will diffuse along with CVOCs will aid photocatalytic degradation.

Researches on corona destruction of VOCs which have been carried out by US, EPA since 1988, have shown significant potentialities too. In corona destruction, electrons are bombarded on the target compound which is thereby destructed. There are two types of reactors, packed bed and wire-in-tube reactor. Studies (Nunez et al,

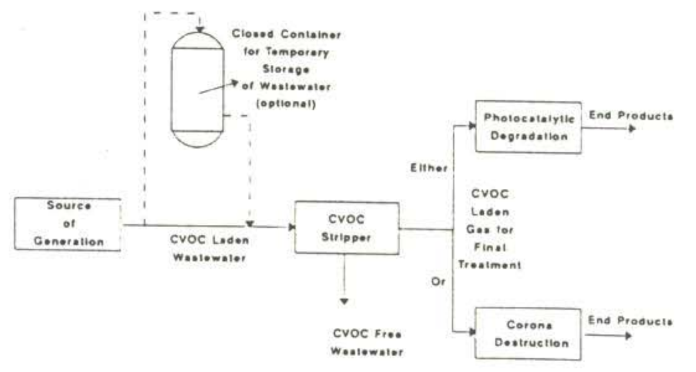

Figure 1 Schematic diagram for proposed hybrid technology

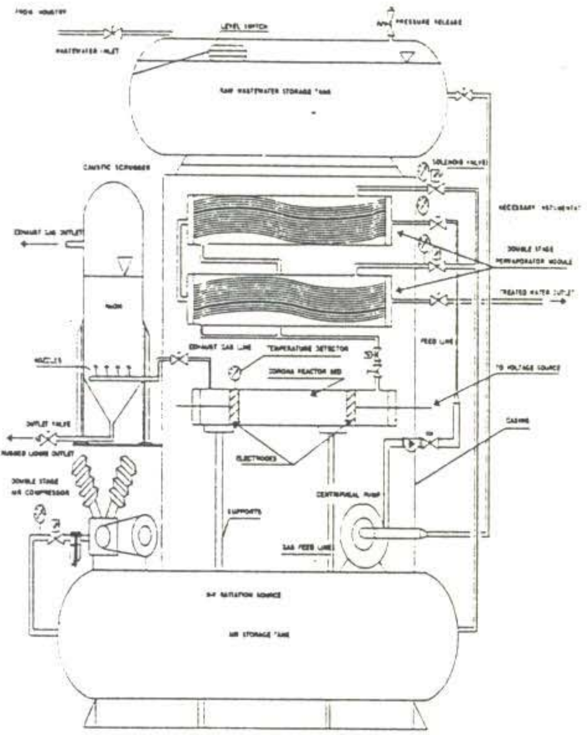

Figure 2 Conceptual scheme for a combination of perstripping corona destruction

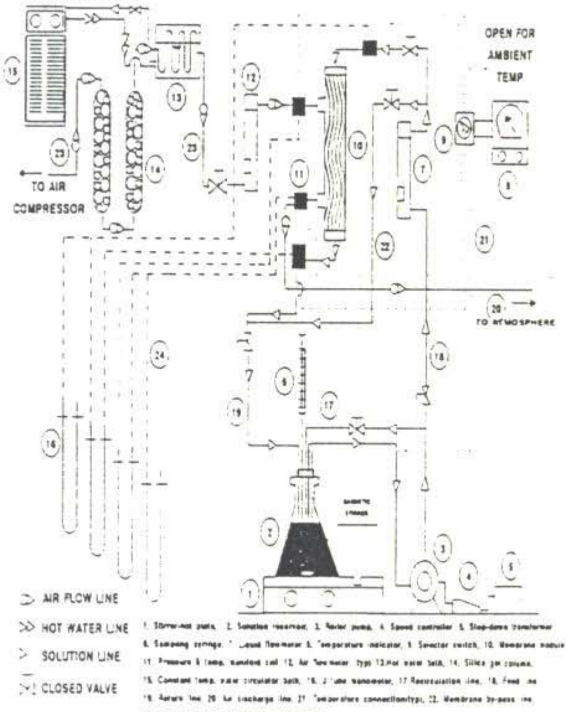

Figure 3 Schematic arrangement for experimental apparatus

1993) show that industrial scale corona reactor can reduce single component VOC in air from 10 ppmv to 10 ppbv efficiently and cost effectively. This technology has several advantages over conventional ones, namely

(a) Operates at ambient temperature and pressure.

(b) Eliminates disposal, regeneration and post treatment problems.

(c) Eliminates sensitivity to poisoning at sulfur or halogen containing compounds.

(d) Easy maintenance and low O & M cost.

A hybrid system can therefore be proposed using pervaporation as an initial stripper followed by photocatalytic degradation or corona destruction of CVOCs. A diagram of the proposed hybrid system is shown in figure 2.

In the first part of the research, pervaporation is tested as an stripper mechanism. Some of the important results are presented in this article to show that pervaporation can be used in this aspect, effectively.

6 EXPERIMENTS

The layout of the equipment is shown in fig 3. Two flow modes were used in the experiments, (i) cocurrent flow mode and (ii) cross flow mode. Fig 3 shows the equipment with the cocurrent flow mode, later on, the cocurrent flow mode was replaced by the cross flow mode and necessary adjustments made. Sampling was done directly from the feed reservoir at definite time terval to measure the CVOC lost from the feed solution. The loss was converted to CVOC flux.

Dense silicon composite membranes supported over a relatively thick polyethersulfone layer in the form f 15 capillary fibers were used. The membrane were bought from SEMPAS Membrantechnik GmbH, ermany. Head space analysis was performed using Shimadzu CR14A Gas Chromatographic machine.

Reagent grade compounds were dissolved in 2% (v/v) methonal solution to prepare the feed solution of fferent concentrations. TCE was used when experiments were done with single compound while a mixture f TCE and TCEthane was used as a binary feed to study the influence of one compound on another. The xperimental organization is given in table 1 and additional details of the experiments are given elsewhere asu 1994).

RESULTS

It was found that flux varies with average concentration almost exponentially irrespective of the mpound(s) used. This is shown in fig 4. This suggests that solution- diffusion Model (Mulder and Smolders, 91) can be used for practical purposes, which can be given as

$$J_i = \frac{D_{oi}\,[\exp(\gamma_i C_{if} - 1)]}{\gamma_i \,.\, d} \qquad (1)$$

However a more simple relationship given below can also be used.

$$Ji = \frac{D_{oi}\, C_{if}}{d} \qquad (2)$$

Provided that C_i is taken as the log-mean average (instead of the arithmetical average) in line with the log-an drive commonly used in diffusion processes. The relationship is shown in figure 5. Values of Doi, i has to determined from laboratory scale studies.

Secondly it was found that presence of more than one compound influences the flux of each other. It was erally found that due to presence of one compound the flux of the other was reduced. This may be due to mutually sharing of the active sites inside the membrane polymer which reduces, flux of either compounds mpared to when present alone. Moreover due to the presence of TCEthane, TCE removal efficiency also uced from an average of 95.4% to 92.2%. The reduction is due to the lowering of the flux by the mutual pling effect. Figure 6 shows the removal efficiency with initial concentration for single compound and binary mpound permeation.

The membrane exhibited preference towards TCE molecule compared to that of TCEthane molecules. s can be attributed to spatial arrangement of TCE molecule and also its dipole moment. Spatially TCE ecules are more sleak and therefore easily diffuse through the membrane. Also TCE molecules are less polar are therefore better sorbed. This preference is reflected by the selectivity values calculated from the owing equation;

$$\text{Selectivity} = \frac{J_i/C_{if}}{J_j/C_{jf}} \qquad (3)$$

Where i stands for TCE and j for TCEthane. The selectivity values are given in table 2. The diffusion fficient (Doi) of TCE was found to be above 10% higher than the TCEthane.

the above results suggest that presence of additional impurities will affect the efficiency and behavior of vaporation which has to be considered while designing treatment systems in practice. It also indirectly cates that an in-line treatment may be a better choice because chances of interference from additional mpounds will be low compared to the end-of-pipe treatment.

Removal efficiency in a crossflow mode was found to be higher than the cocurrent flow mode for both le and binary feed solution. Almost in all cases removal efficiency greater than 90% was obtained and removal efficiency more than 98% was obtained in some cases. The mean value lies between 93 - 96%, which indicates that pervaporation is an highly efficient system. It is further expected that with more knowledge on this subject, modifications and improvements can be done by which efficiency as high as 98-99% can be easily and economically obtained.

Table 1 Summary of experimental conditions

Mode of Flow	Compounds used	Concentration Ranges (ppm)	Air Flow Rates (Lpm)	Other Conditions
Co current flow	TCE	1000 - 800 800 - 600 600 - 400 Below 400	10, 12, 14, 16, 18, 20	Feed flow = 0.5 Lpm Feed temp.= 38 - 42°C Air temp. = 28 - 34°C
	TCE and 1,1,1 Trichloro ethane	1,1,1 Trichloroethane 800 - 600 600 - 400 400 - 300 Below 300	10, 12, 14, 16, 18, 20	Feed flow = 0.5 Lpm Feed temp.= 38 - 42°C Air temp. = 28 - 34°C TCE conc. 600 - 400 ppm.
	Distilled water	-	10, 12, 14, 16, 18, 20	Feed flow = 0.5 Lpm Feed temp.= 38 - 42°C Air temp. = 28 - 34°C
Cross flow	TCE	1000 - 800 800 - 600 600 - 400 Below 400	10, 12, 14, 16, 18, 20	Feed flow = 0.5 Lpm Feed temp.= 38 - 42°C Air temp. = 28 - 34°C
	TCE and 1,1,1 Trichloro ethane	1,1,1 Trichloroethane 800 - 600 600 - 400 400 - 300 Below 300	10, 12, 14, 16, 18, 20	Feed flow = 0.5 Lpm Feed temp.= 38 - 42°C Air temp. = 28 - 34°C TCE conc. 600 - 400 ppm.

Table 2 Values of selectivity

Experiment Run	Selectivity	Experiment Run	Selectivity
32	1.117	44	1.197
33	1.117	45	1.155
34	1.124	46	1.118
35	1.136	47	1.132
36	1.127	48	1.096
37	1.123	49	1.140
38	1.133	50	1.199
39	1.124	51	1.166
40	1.133	52	1.200
41	1.164	53	1.159
42	1.172	54	1.144
43	1.096	55	1.128

Flux production was found to be higher in the crossflow mode than in the cocurrent flow mode which is shown in fig 7, the higher flux was due to the better sweeping condition achievable in the cross flow mode. Higher flux production indicates better stripping also.

Time required for 50% and 90% removal of TCE and TCEthane concentration from the feed solution gives an indication of the detention time needed. Results indicated that the detention time required was less in the cross flow mode than in the cocurrent flow mode for the same percentage removal. This is clearly very important and a specific advantage of the cross flow mode with regards to pervaporation engineering. Moreover it was found that the difference was appreciable in cases of low concentration of the compounds in the feed solution. Usually the concentrations encountered in the practical situation is very low and therefore under these circumstances cross flow mode may be an ideal choice.

From the above it is found that pervaporation can be used as a stripper mechanism. Furthermore crossflow mode may be a better choice where concentrations of CVOCs are low though disadvantages with the crossflow mode viz higher cost, greater space requirement, uneven distribution of air etc. are to be considered before final selection.

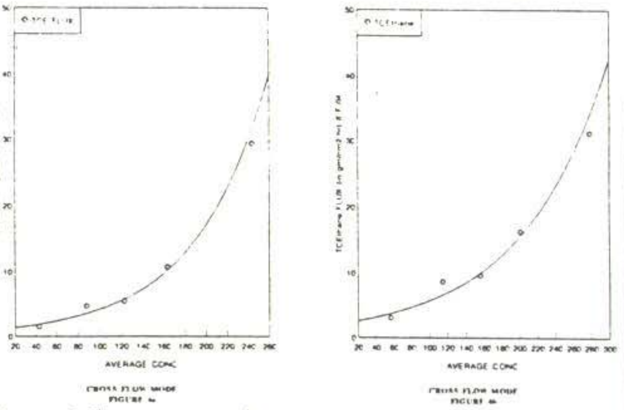

Figure 4 Flux variation with average concentration

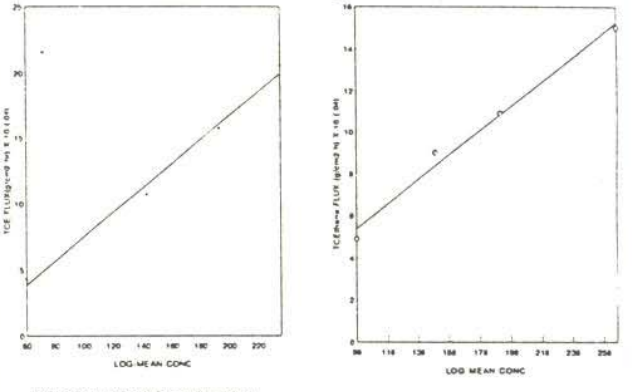

Figure 5 Variation of flux with log mean concentration

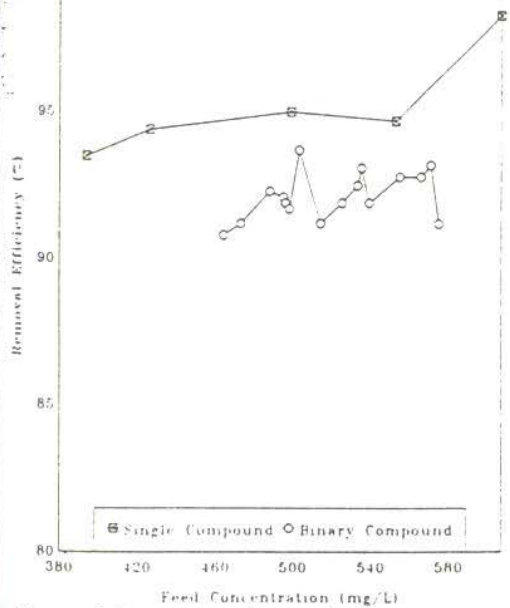

Figure 6 Comparison of removal efficiency

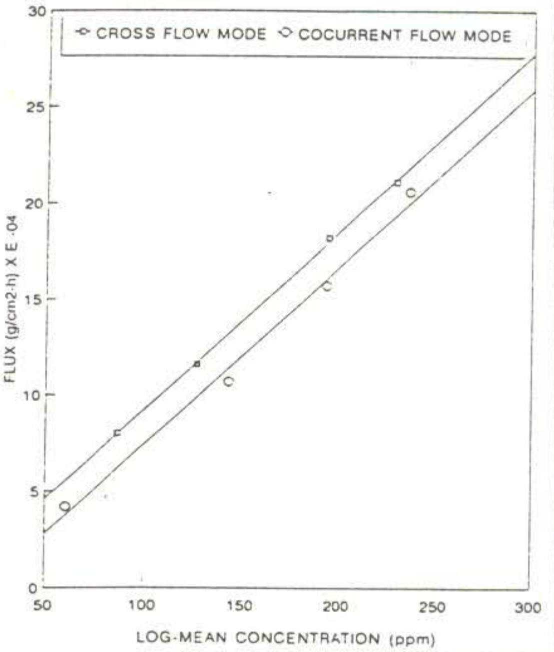

Figure 7 Comparison of flux production

CONCLUSION

For a complete treatment of CVOCs an in-line treatment train can be proposed. Pervaporation can be used as a stripper mechanism followed by complete destruction by either photocatalytic degradation or corona destruction. Such a hybrid technology can be a future possibility. Experiments with pervaporation as a stripper mechanism indicate that 90% removal efficiency even in the worst condition (binary feed) can be easily obtained with pervaporation. The mean value of stripping efficiency lies between 93-96% while efficiency as high as 98.8% could be obtained. This indicates that chances of success with pervaporation as a stripper mechanism are high. The presence of additional compound(s) reduce(s) the efficiency and performance compared to a single compound permeation, due to the mutual coupling effects. This may justify usage of an in-line treatment technology which will have less impurities compared to the end-of-pipe treatment.

Out of the two flow modes tested, the performance of the cross flow mode is found to be better than the cocurrent flow mode with regards to the overall removal efficiency, flux production and detention time. The difference is appreciable specially in the case of low feed concentration of CVOCs (which is more often the situation with actual wastewater). However disadvantages of the crossflow mode of operation should be taken into account for final selection.

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