ABSTRACT

REMOVAL OF CHLORINATED HYDROCARBONS FROM WATER BY AIR STRIPPING AND SOLVENT SUBLATION

by
Alpana Gami

Removal of trichloroethylene, monochlorobenzene and 1,3 dichlorobenzene from water by air stripping and solvent sublation into an organic phase was investigated. The sublation solvents used were paraffin oil and decyl alcohol. The rate of removal from water by solvent sublation and air stripping was highest for trichloroethylene, followed by chlorobenzene and finally 1,3 dichlorobenzene. For the three compounds, solvent sublation had the greatest advantage over air stripping in the reduction of emission of the compounds to the atmosphere. For the three compounds, the removal was enhanced at higher flowrate in both air stripping and solvent sublation. For the removal of monochlorobenzene and 1,3 dichlorobenzene from water, solvent sublation showed a marked improvement over air stripping at air flowrates of 60 ml/min and 94 ml/min. Solvent sublation did not show any significant improvement in the removal of trichloroethylene from water over air stripping. Solvent sublation was found to be relatively independent of the thickness of the organic solvent floated on top of the aqueous solution. Solvent sublation for the removal of monochlorobenzene, and 1,3 dichlorobenzene from water gave better results with decyl alcohol than with mineral oil. Addition of emulsions to water decreased the rate of removal of monochlorobenzene and 1,3 dichlorobenzene from the aqueous phase.

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by
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This thesis is dedicated to my parents.

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CHAPTER 1

INTRODUCTION

One of the hallmarks of an advanced civilization is its concern for the disposal of its society's waste products and seeing to it that this is done safely and in an environmentally acceptable manner. The presence of organic substances of industrial origin in wastewaters may not always be an unmitigated evil but, it is safe to say, it never is good. Previous sampling and analysis of surface and groundwaters throughout the country have indicated that many have been contaminated by various organic chemicals. The presence of organic substances in drinking water supplies is generally believed to be caused by improper waste disposal practices. The quality of surface, ground and drinking water continues to be a major health concern. Similarly, the air pollution problem is growing progressively worse. The presence of toxic organics in the air has been the subject of increasing concern in both the residences and work places. Long term exposure to toxic contaminants may ultimately create a health problem.

The Clean Air Act of 1970 is widely recognized as a powerful and very important piece of environmental legislation. In 1990 Congress amended the Clean Air Act in significant respects. Under 1990 amendments, 189 substances will be regulated, including both hazardous organics and metals (1). The Federal Water Pollution Control Act was amended by the Clean Water Act of 1977 (2). The latest amendment to this Act was made in 1989. The objective of this act is to restore and maintain the chemical, physical and biological integrity of waters and to develop and implement waste treatment processes for adequate control of sources of pollutants.

Since then the world has become increasingly aware of the water and air cleansing processes.

Of all the toxic compounds detected in air and water, volatile organic compounds (VOCs) are some of the compounds observed most frequently. They are named VOCs because of their distinctive common property of high volatility relative to other organic substances such as phenols, pesticides or PCBs. Several ground water surveys by EPA, like the National Organic Monitoring Survey (NOMS) and the Ground Water Supply Survey (GWSS) have found that chlorinated hydrocarbons are frequently present and in high concentrations (3). Most of them are widely employed in various industrial, commercial, agricultural and household activities and are considered harmful causing potential health risk to continually exposed human beings. The widespread contamination of waters by VOCs and chlorinated hydrocarbons has resulted in many techniques for the removal of such pollutants. Previous studies on treatment techniques indicated that adsorption processes using activated carbon or adsorbent resins, chemical oxidation with ozone or chlorine dioxide and reverse osmosis are capable of removing such pollutants from the contaminated source of potable water supply but, these treatment alternatives are very expensive and operationally complex.

Air Stripping and Solvent Sublation are two processes capable of removing trace hydrophobic organics from aqueous solutions by using air bubbles. Previous studies have shown that the transfer of VOCs to the atmosphere by air stripping may be a convenient and potentially cost effective method to remove these compounds from slightly contaminated wastewater. In the air stripping process a surface-active or volatile solute is transported with air bubbles to the atmosphere (4). In the solvent sublation procedure, (also called flotoextraction) a surface-active or volatile solute is transported from the aqueous phase to an overlying layer of nonvolatile organic liquid on the air-water interfaces or in the interior of bubbles rising through the solvent sublation column (5).

The value of air stripping for improving the water quality has long been known, and this process was among the first to be used for water treatment. The value of this process for stripping trace organic substances was recognized as early as 1935 (4). Stringent air pollution regulations make it difficult to apply air stripping efficiently as it has the following disadvantages:

1. It is not acceptable to release the organic substances to the atmosphere, therefore charcoal filters, biofilters, membranes etc. have to be used in combination with air stripping (6).
2. The compounds removed by air stripping may redissolve into the water.
3. Only volatile and hydrophobic compounds can be effectively removed from water by air stripping.

Solvent sublation improves the efficiency of air stripping, while simultaneously reducing air pollution resulting from stripping. Moreover, the usefulness of sublation lies in its ability to concentrate hydrophobic organics in a small volume of an organic solvent which can then be destroyed using current practices such as incineration (5). Renewed interest in solvent sublation was sparked in the beginning of the 1980s for its advantages in the removal of dissolved hydrophobic organics (7).

Although many publications have mentioned that solvent sublation reduces the emission of volatile organic compounds (VOCs) to the atmosphere, there has been only one systematic study which included analytical determinations of organic pollutants in both the aqueous phase and air phase. Mei (8) recently studied the removal of toluene from water by solvent sublation and analyzed it in both gaseous and aqueous phase. She found a reduction of toluene emission to the atmosphere by solvent sublation of about 30% to 70% under various conditions, when compared to air stripping.

The present study was primarily planned to investigate the removal of a group of chlorinated hydrocarbons from water by means of air stripping and solvent sublation. Our objectives in conducting these experiments were to:

a) Compare the efficiencies of solvent sublation and air stripping techniques in removing chlorinated hydrocarbons with different physical-chemical characteristics from aqueous phase.

b) Estimate the reduction in emission to the atmosphere for some chlorinated hydrocarbons using the solvent sublation process in comparison to air stripping.

c) Ascertain the effects of parameters such as air flow rate, bubble size, and the nature and thickness of organic layer on the removal of chlorinated hydrocarbons from water and their emission to the atmosphere.

d) Perform preliminary experiments demonstrating the possibility of using diluted oil-in- water emulsions for sorption of chlorinated hydrocarbons on oil droplets and their removal by flotation process.

On the basis of the relative frequencies and magnitudes of occurrence of the volatile organic priority pollutants in surface water, ground water, and waste water three compounds were chosen as target compounds in this study. These compounds are trichloroethylene (TCE), monochlorobenzene (MCB) and 1,3 dichlorobenzene (1,3 DCB). These three compounds are on the EPA's list of "priority pollutants" (9). Moreover, these compounds are confirmed human and animal carcinogens. In addition to their carcinogenicities, all three VOCs cause acute and chronic effects on central nervous system, respiratory system, liver, skin and eyes, with common symptoms as headache, dizziness, nausea, vomiting, blurred vision etc. (2). They were also selected to cover a range of volatility and boiling points. Therefore the study of removal of these three compounds could be used as an example for the removal of other volatile organic pollutants with similar physico-chemical characteristics.

CHAPTER 2

LITERATURE REVIEW

2.1 Air Stripping

Volatile organics are generally liquid at room temperature but evaporate easily because they have significant vapor pressures. Furthermore, most organics, especially chlorinated ones are very hydrophobic. High vapor pressure plus the low water solubility of the volatile organics makes air stripping an effective process to remove such contaminants from water (10).

Stripping of volatile organic components from water into air depends upon bringing the two phases into intimate contact under conditions wherein forces for stripping will be most favored. This involves maximizing the interfacial area between the two.

For a given process, the factors of importance in the efficiency of removal of a given volatile organic are the Henry's constant, the relative volumes of air to water in order to achieve definite removal efficiency, and the rate of mass transfer. Henry's constant represents the relationship between the amount of a volatile substance in the gas phase above the liquid and the amount of the substance dissolved in the liquid at a given temperature and at equilibrium (4). The larger the Henry's constant, the greater the equilibrium concentration of the solute in air and more easily it is stripped.

There are many different mechanical processes which can be used for removing volatile organic materials from water (4). In diffused air stripping, the air stream is broken into small bubbles, providing a large surface area as they rise through water. This is a common procedure for introducing oxygen into wastewaters for biological treatment. Mechanical aeration can also be used to produce a similar effect, it results in breaking the liquid into droplets or films which are thrown through the air. Such processes could be used for removal of volatile organic compounds with mass transfer coefficients and Henry's law constants similar to that of oxygen. With less volatile compounds, larger quantities of air than normally used may be required to obtain the desired efficiencies of removal, and for that, different types of stripping towers are used. In a spray tower, air and water flow in a countercurrent fashion. The water is broken into fine droplets by passage through nozzles in order to increase the surface area exposed to the rising air. Some towers are built for horizontal cross flow of air. This type of tower has been used for removing highly soluble gases such as ammonia from wastewaters, and has good potential for some of the less volatile organic components. In summary, air stripping has good potential as an economical water treatment process. It has a long history of usage in the water treatment field for the removal of different types of compounds. It has the potential for direct treatment of surface waters that may contain many different volatile organic chemicals, for disinfected waters containing high concentrations of trihalomethanes, and for contaminated groundwaters that in growing number of cases contain volatile organic chemicals in relatively high concentration. One major concern is that stripping processes result in the transfer of a contaminant from one water to air, and since the overall objective of treatment is to reduce human exposure one must be certain that stripping does not simply substitute one problem for another. Previous studies have suggested that the transfer of VOCs to the atmosphere by air stripping may be a convenient and potentially cost effective method to remove these compounds from slightly contaminated water e.g. drinking water, surface water and ground water. For waters with higher level of VOC contamination, air stripping suffers from the disadvantage of converting volatile dissolved compounds from water pollutants to air pollutants.

In this regard, carbon adsorption, combustion, biodegradation and membrane technology can be used to remediate air stripping effluent (6). Thermal and catalytic combustion can be used in oxidizing VOCs into harmless byproducts. The VOCs from the effluent are routed into a boiler or catalyst chamber, where they are oxidized and the effluent is released. This process is quite economical for high VOC concentrations because the maintenance costs are low and the removal efficiency for thermal oxidation does not degrade over time. However, the process suffers from the disadvantage that if N and S are present in the feed, they get converted to NO_x and SO_2, which cause severe eye, nose, throat irritations and vegetation damage. Biodegradation employs microorganisms to degrade VOCs. The effluent air is routed into a chamber, where the organisms degrade the contaminants to carbon dioxide and water. It can be used to degrade chlorinated hydrocarbons. This technology suffers from the problem of disposing of the used microorganisms. Carbon adsorption is the most widely used process for treating VOC contaminated air streams. The effluent air is routed through a bed of activated carbon, which traps the VOCs. This process allows the recovery and reuse of the solvents. Adsorption is especially important for the treatment of effluents with low VOC concentration. Membrane technology combined with air stripping can also be used for the remediation of contaminated water. The target gas can be removed from an air stream by passing it on one side of the membrane, allowing the target gas to permeate through into a second gas stream. Membranes allow for the direct recovery of organic solvents and the amount of waste for disposal is very less compared to other technologies. This technology suffers from the disadvantage that different types of membranes have to be used for different VOCs. The application of the above different types of air stripping equipments dramatically increases the cost of the air stripping processes. For some cases solvent sublation might be more simple and economical. This reduces the emission of VOCs and SVOCs to the atmosphere, because of the layer of non volatile hydrophobic liquid on the top of the air stripping column. Stringent air pollution regulations have led more people to become interested in the studies of the emission reduction by solvent sublation process. Moreover, the usefulness of sublation lies in its ability to concentrate hydrophobic organics in a small volume of an organic solvent which can then be destroyed using current practices such as incineration (5).

2.2 Solvent Sublation

In the solvent sublation process, hydrophobic compounds are levitated on a bubble surface to the top of an aqueous solution contained in a column, where they encounter a solvent layer (e.g. mineral oil, octanol, decanol, lauryl alcohol) to which the material is transferred as the bubble moves through the solvent layer (5,7,11). The floating organic on top of the column is called the "solvent" and the material levitated by the bubble is called the "sublate". When fine gas bubbles are passed through a column containing hydrophobic compounds in water, because of their inherent tendency to concentrate at the air-water interface, these hydrophobic materials collect on the bubble surface by diffusion through the thin boundary layer surrounding the air bubble. Hydrophobics which are partly volatile will be carried simultaneously in the vapor phase within the bubbles and also in the adsorbed phase on the surface of the bubble. As the bubble transits the aqueous column and moves through the organic solvent layer, the adsorbed phase gets stripped into the organic phase. At the same time if equilibrium between the vapor inside the bubble and the organic liquid phase is established rapidly, the volatile material present in the interior of the bubble may also partition into the organic layer. Therefore, emissions of these compounds to the atmosphere are presumably also mitigated. Solute transport between the aqueous and organic solvent phases in sublation can occur in a variety of ways (12). Karger first described qualitatively the possible transport pathways in solvent sublation (13). There are two predominant transport processes: 1) transport within and on the surface of the bubbles. 2) a diffusive transport between the phases driven by a concentration gradient.

1. *The transport of compounds by air bubbles.*

The organic compounds are either absorbed on the surfaces of the air bubbles or present as vapor inside the bubbles. The mechanism depends on the air flowrate, the bubble radius (r), the mass transfer coefficient of the solute to the bubble in the aqueous phase, the combination of Henry's constant (H_c) and the absorption constant for the solute at the air/water interface of the bubble.

Henry's constant (H_c) is one of the most important parameters that effect the solvent sublation. The higher the H_c the more hydrophobic and volatile the compound is (14). When the compounds are hydrophobic in the aqueous phase, they tend to have high activity coefficients, because this prevents them from competing with the strong hydrogen bonding forces between water molecules. Therefore, these compounds tend to prefer the air/water interface of the rising bubbles rather than the aqueous phase.

2. *Molecular diffusion process depends on the solute concentration gradient between the organic solvent and aqueous phases (12).*

This mechanism can be characterized by a mass transfer coefficient, which depends on the turbulence at the water solvent interface, as well as the solvent/water partition coefficient for the particular solute.

Some of the factors affecting the solvent sublation process are 1) solvent used as a layer 2) bubble radius (r) and gas flowrate and 3) Nature of substance being removed.

1) *Solvent used as a layer*

The organic solvent used as a layer in solvent sublation must be relatively nonvolatile and insoluble in water. The solvent should have low interfacial tension against water. If solvent sublation is to be applied on an industrial scale, the cost and disposition of the organic solvent must also be considered.

For the removal of contaminants from water, solvent sublation is relatively independent of the thickness of the organic layer. This can be explained as follows: since for the most part mass-transfer occurs from gas bubbles crossing the aqueous-solvent interface and not from diffusion of solute across this interface, the amount of material transferred should depend only on the amount of air crossing the interface and not on the organic volume. However, if the organic volume used in solvent sublation is too low, the mineral oil-water interface would be drastically disrupted at higher flow rates and the process would lose its efficiency. In this case, reverse mass transfer of solute from the organic phase to aqueous phase would occur and solvent volume dependence would become significant.

2. *Bubble radius and Gas flowrate*

The rate of removal is related to the gas flowrate. The smaller the bubble radius for a given flowrate the more rapid the removal of the sublate. Higher flowrates enhance the removal of compounds from the aqueous phase, but it also increase the diameter of the bubbles, which leads to increased bubble velocities, shortened bubble/liquid contact time in the column, hence decreased sublation efficiency (14). Moreover, at very high flowrate the overlying organic layer may be disrupted and partially emulsified into the water phase. Therefore, the key to increasing the efficiency of solvent sublation is to keep the bubble size small without reducing the air flowrate. Generally the bubble diameter in solvent sublation is in the range of 0.02-0.07 cm. The bubble size can be decreased by the addition of certain co-solutes. The addition of surfactants even at concentrations as low as 5-20 ppm tend to reduce the surface tension of the aqueous solution quite drastically depending upon their concentration. This decreases the bubble size generated at the sparger. As a result, the population density of small bubble increases and they provide a very large area per unit volume of air, which apparently more than offsets the effects of decreased mass transfer coefficient, and so increase the overall transfer rate (14). Addition of ethanol up to a concentration of 0.03 mol fraction as a co-solute can also change the bubble properties considerably. In the presence of ethanol, the surface tension of water is lowered which prevents the bubbles from growing to larger sizes. As a result the number of very small bubbles is higher in the presence of ethanol. These smaller bubbles provide a very large surface area per unit volume of air which contributes to enhanced mass transfer from liquid phase to bubbles.

3. *Nature of substance being removed*

Like air stripping, solvent sublation is more effective for more volatile and hydrophobic compounds with high Henry's constant. However, for the removal of the contaminants from water, advantages of solvent sublation over air stripping are more significant for hydrophobic compounds of low vapor pressure like pentachlorophenol (PCP) or some chlorinated pesticides. Some chlorinated organics like PCP and trichlorophenols are weak acids and they exists in water in molecular or ionic form depending on pH. The ionic form is hydrophilic and can be removed after formation of hydrophobic complex with cationic surfactant.

The solvent layer in sublation helps to capture any material adsorbed on the air-water interface of the rising air bubbles in addition to the material that is carried within the vapor phase of the bubbles. In air stripping, the adsorbed material is continuously remixed and redistributed within the aqueous section as the bubbles burst at the top of the solution and hence only the material within the vapor phase is removed. This effect is more pronounced for compounds of very low volatility and high hydrophobic character (e.g. chlorinated pesticides, polychlorinated bipheyls, chlorobenzenes and polynuclear aromatic hydrocarbons).

2.3 Previous Investigations

Chlorinated organic compounds such as chlorobenzenes, chlorinated pesticides, polychlorinated biphenyls are known to be major pollutants in wastewater. Many of them are known to be refractory (non-biodegradable). They are of low aqueous solubility and low vapor pressure and are not easily removable by diffused bubble aeration except for compounds of low chlorine content and molecular weight, since stripping by aeration depends primarily on the favorable partitioning of the material into the interior of the air bubbles. On the other hand, most of these compounds are hydrophobic, i.e. in aqueous solutions they tend to have high activity coefficients because of their inability to compete with the strong hydrogen bonding forces between water molecules. These compounds therefore tend to prefer the air/water interface of the rising bubbles rather than the *aqueous phase. This tendency makes* them surface active and makes them amenable to the so-called solvent sublation process (14). Solvent sublation of a number of chlorinated organic compounds was investigated. Their physical properties and some characteristics of the process are represented in Table 1.

Wilson and co-workers (15) first carried out solvent sublation of a highly volatile chlorinated compound, 1,1,1 trichloroethane, into 1-octanol. They found no improvement in the removal using different layer thicknesses. Increasing the flow rate from 60 ml/min to 120 ml/min increased the removal rate. They found 91 percent removal of tirchloroethane in about 60 minutes at an air flowrate of 120 ml/min. The same removal was observed at an air flowrate of 60 ml/min in 120 minutes. They indicated the importance of having fairly small bubbles and long columns, which provide large bubble surface to volume ratios and long bubble contact times, both of which favor increased mass transfer. They also noted that solvent sublation is able to remove nonvolatile materials from water provided these materials are surface-active. Simple aeration is not effective for these, since axial dispersion mixes the enriched upper portion of the column back into the bulk.

Solvent sublation of o-, p- dichlorobenzene and Aroclor 1254 (a mixture of PCB) was studied on a bench scale apparatus by Valsaraj and Wilson (16). The organic solvent used was 2-octanol. Increased removals were observed for all three compounds with an increase in flow rate. They checked their experimental results of o- and p- dichlorobenzene against a theoretical model and found them to be in agreement. The removal of Aroclor 1254 by solvent sublation using 2-octanol as organic phase was very slow, probably because of the back mixing of 2-octanol into water which markedly increased the solubility of the PCB in the aqueous phase. They also carried out solvent sublation of Aroclor 1254 using mineral oil as organic layer. They noted marked improvement in the removal of Aroclor 1254 when mineral oil was used as a solvent.

Table 1 Solvent Sublation of Chlorinated Organic Compounds (Literature Data)

Compound	H_c	V.P. mm Hg	Sol. mg/l	Layer	Comments	Ref.#
1,1,1 trichloroethane	0.21	100.0	4400.0	1-octanol	experimental data on the aeration of TCE and on its solvent sublation were in good agreement with the model	9
o-dichlorobenzene	0.081	1.0	100	2-octanol	a method was developed for estimating boundary layer thickness of the rising bubbles	10
p-dichlorobenzene	0.11	0.4	79			
Aroclor 1254	0.35	1.8×10^{-4}	0.054			
chlorobenzene	0.148	12.0	488.0	mineral oil	rate of removal was enhanced by higher flow rates and was more or less independent of the organic solvent; slight improvement was observed using lauryl alcohol as solvent	14
p-dichlorobenzene	0.069	0.70	80.0	lauryl alcohol		
1,2,4trichlorobenzene	0.070	0.25	37.0			
DDT	0.0016	1×10^{-7}	1.2×10^{-3}			
pentachlophenol	0.0001	0.00011	14.0	mineral oil	solvent sublation gave increased removal than solvent extraction	17
2-chlorophenol	0.001	2.21	28500	diisopropyl ether	recovery of about 70% to 80% of solutes was observed by the analysis of the layer	18
pentachlorophenol	0.0001	0.00011	14.0			

Table 1 (Cont'd)

Compound	H_c	V.P. mm Hg	Sol. mg/l	Layer	Comments	Ref.#
o-dichlorobenzene	0.081	1.0	150.0	mineral oil 1-octanol 2-octanol	sublation with 1-octanol gave the highest removal rate followed by 2-octanol, mineral oil and finally air stripping	19
pentachlorophenol	0.0001	0.00011	14.0	mineral oil	removal was better when decanol was used as a solvent	20
1,2,4, trichlorobenzene	0.070	0.25	37.0	decyl alcohol		
2,3,6 trichloroanisole	0.0118	0.023	31.0			
2,4,6trichlorophenol	0.0002	0.015	800			
heptachlor	0.062	3×10^{-4}	0.056	mineral oil	foam fractionation increased the separation efficiency and it was better than sublation	21
pentachlorophenol	0.0001	0.00011	14.0	mineral oil	a complete model with all transport mechanisms was proposed	12
hexachlorobutadiene	0.43	0.39	2.0	mineral oil	rate of removal was improved by adding HTMAB	22
2,4,6 trichlorophenol	0.0002	0.015	800			
pentachlorophenol	0.0001	0.00011	14.0	mineral oil	the model predictions were marginally satisfactory with experimental results	25
2,4,6 trichlorophenol	0.0002	0.015	800			

Solvent sublation for the removal of mono-, di-, tri- chlorobenzenes and a chlorinated pesticide (DDT) from aqueous solutions was carried out by Valsaraj, Porter, Liljenfeldt and Springer (14). Considerable improvement in efficiency of removal as compared to conventional fine bubble aeration was observed when bubbles of very small size (<0.5 mm dia.) were used. The materials were solvent sublated into mineral oil and lauryl alcohol layer. The removal rate was somewhat enhanced by higher airflow rates and was more or less independent of the volume of the organic solvent floated on top of the column. The study concluded that the organic solvent chosen for solvent sublation should have low volatility and solubility in water as well as low aqueous-solvent interfacial tension, very low aqueous solubility, but should have an affinity for toxic contaminants. It should also be non-toxic and inexpensive. They also concluded that the relative improvement in removal by solvent sublation as compared to simple aeration is higher for more hydrophobic compounds. The largest improvement was found for DDT. The influence of various concentrations of ethanol ranging from 0.0001 to 0.1 mol fraction upon the removal rates of TCB were studied. At low mol fractions (<0.04) enhanced removal rates were observed whereas at mol fractions 0.04 and higher the removal rates were decreased. The enhancement in the removal rates at low mol fractions was due to the change in the bubble properties by the addition of ethanol. Addition of ethanol generates smaller bubbles providing larger surface area per unit volume of air which contributes to enhanced mass transfer from the liquid phase to the bubbles. On the other hand, ethanol concentrations above 0.03 tend to disrupt the water structure considerably and makes the phase behavior of ethanol-water mixture more organic like. This makes TCB more soluble in aqueous solution and hence is more difficult to remove by solvent sublation. Increasing electrolyte ($NaNO_3$) concentrations upto

1M improved the separation efficiency by decreasing the aqueous solubility of the hydrophobic organic. It was found that addition of anionic surfactant sodium lauryl sulfate (1×10^{-4}M) significantly enhanced TCB removal by solvent sublation process.

The removal of pentachlorophenol from aqueous acidic solutions was studied using solvent sublation and solvent extraction by Valsaraj and Springer (17). Both methods gave appreciable removals in highly acidic solutions (pH = 2.0), but solvent sublation had the added advantage of minimal phase contact of the organic solvent with water and increased removals under various conditions. Solvent sublation was also found to be more effective than conventional fine bubble aeration. PCP removal by solvent sublation was enhanced by increasing ionic strength and also by the presence of small amounts of an ionic surfactant in the aqueous phase. 94% removal of PCP was obtained by the addition of 10% w/v NaCl as compared to 77.3% removal without any NaCl present in the aqueous solution. Addition of 1.56×10^{-5} M cationic surfactant hexadecyltrimethylammoniumbromide (HTMAB) increased the removal from 77% to 95%. The technique of solvent sublation was tried on an actual wastewater sample from a wood preserving industry. pH adjustment, removal of suspended solids, addition of sodium chloride and subsequent solvent sublation into mineral oil reduced the PCP concentration in the aqueous waste by 99.7%.

M. Caballero, R. Cela and J. A. Perez-Bustamante (18) carried out the solvent sublation of some phenolic compounds, among them some chlorinated pollutants such as 2-chlorophenol and pentachlorophenol. They applied solvent sublation technique to the development of a procedure for the pre-concentration of the phenolic compounds before GC analysis. This procedure is applied to synthetic sea water samples, previously adjusted to pH 2.0, using stearylamine (3 ppm) and hexadecyltriammonium-bromide (15 ppm) as surfactants and concentrating the pollutants in a small volume of isopropyl ether. They analyzed the organic solvent and calculated the percent recovery of the compounds. The recovery of 2-chlorophenol in one hour was 57.7% when no surfactant was added, 46.4% in the presence of stearylamine and 61.7 % in the presence of HTMAB. The recovery was 100% for pentachlorophenol when no surfactant was added, 71.5% in the presence of stearylamine and 100% in the presence of HTMAB.

Hueng-Soo Shin and R. Coughlin (19) studied the removal of o-dichlorobenzene from water by solvent sublation. The sublation solvents used were mineral oil, 1-octanol and 2-octanol. For the removal of o-dichlorobenzene removal from water, sublation with 1-octanol as solvent gave the highest removal rate, followed by sublation with 2-octanol, sublation with mineral oil and finally, air stripping. The good performance of solvent sublation with alcohols in the removal of solute from water is partly due to their high solubility in water compared to mineral oil and partly to their low interfacial tension against water. Alcohols from the layer are partly dissolved in water and they reduce surface tension and diameter of air bubbles generated by porous frit.

Experimental results on the solvent sublation in continuous countercurrent modes of four chlorinated organic compounds, pentachlorophenol(PCP),1,2,4-trichlorobenzene(TCB), 2,3,6-trichloroanisole (TCA) and 2,4,6-trichlorophenol (TCP) from the aqueous phase to organic solvents are reported by Valsaraj and co-workers (20). TCB, TCA, and TCP were sublated into mineral oil. PCP at pH 2.9 as neutral molecules were sublated into mineral oil and decyl alcohol while ionic PCP at pH 8.9 were sublated as a complex with hexadecyltrimethylammonium bromide into decyl alcohol. The effects of the two organic solvents were compared for neutral PCP sublation from the aqueous phase and it was found that the removal was better when decyl alcohol was used as a solvent. The effects of air flow rates, influent feed rates and the volume of organic solvent were studied. The results showed that continuous countercurrent solvent sublation was a technically feasible method of removing hydrophobic organics. It is found that the removal efficiency was a function of the ratio of air flow rate and the influent feed rate not only led to increased axial dispersion in the column, it also decreased the bubble-water contact time, both of which tend to decrease the removal rate and the steady-state efficiency. Comparisons were made between bubble fractionation and solvent sublation of neutral PCP and TCP into mineral oil and solvent sublation was found to be better. The efficiency of solvent sublation was largest for more hydrophobic TCB, smallest for more soluble TCP.

Hui-Ling Chiu and Shang-Da Huang (21) studied the removal of heptachlor (HTC) and 1-hydroxychlordene (HDCD) from aqueous solutions by air stripping and solvent sublation. The removal of HTC by air stripping was quite effective, with 91% removal in 30 min. The rate of removal of HDCD by air stripping (21% removal in 30 min.) was much slower than that of HTC, presumably due to the much lower volatility of HDCD. Both HTC and HDCD were effectively removed by solvent sublation (96% of HTC and 91% of HDCD) in 30 min. The improved performance of the solvent sublation process as compared to air stripping is presumably due to HDCD and HTC adsorbing on the surface of air bubbles which are trapped into paraffin oil as they transit the solvent phase during the solvent sublation process The presence of 0.3M $NaNO_3$ increased the rate of removal significantly, with 97% removal of HTC in 5 min compared to 79% removal without any salt present in the solution. The rate of separation also increased with increase in ethanol concentration (0.13-0.50 % v/v), this was presumably due to decrease in the bubble size which reduced the surface tension of the solution.

Valsaraj and Thibodeaux (12) investigated the solvent sublation of neutral pentachlorophenol (PCP) molecules ($pH = 3.0$) in mineral oil and ionic PCP molecules as PCP + hexadecyltrimethylammoniumbromide complex ($pH = 8.9$) into decyl alcohol. The presence of NaCl decreased the rate and steady-state removal of the PCP+HTMAB complex due to the shift of the equilibrium toward a larger concentration of sodium pentachlorophenolate, which is hydrophilic. On the other hand, the presence of salts increased the removal of neutral PCP molecules into decyl alcohol. This is due to decreasing solubility or increasing hydrophobicity of PCP molecules as a result of the so-called "salting out" effects. The removal of PCP increased up to 99.9% when 1 M NaH_2PO_4 was used.

Kun-Yauh, Wei-Der Han and Shang-Da Huang (22) studied the removal of hexachlorobutadiene and 2,4,6-trichlorophenol into paraffin oil by solvent sublation. Over 99% of highly volatile hexachlorobutadiene was removed from a solution containing 100 ppb hexachlorobutadiene initially, in 10 min. The rate of removal of hexachlorobutadiene by air stripping is somewhat slower than that by solvent sublation. The rate of separation of hexachlorobutadiene increased as a result of addition of electrolyte (0.01M-1M $NaNO_3$) and ethanol (0.025-5%). About 64% of 2,4,6-trichlorophenol was removed from a 50 ppm solution at pH 1.84 for a 1 hour run by solvent sublation. Cationic surfactant, 10 ppm HTMAB dramatically improved the rate of removal of 2,4,6-trichlorophenol about 95% in one hour. The improvement in the rate of separation was not only due to the decrease in the air bubble size, but also due to the formation of the 2,4,6 trichlorophenolate-complexes which are surface active and can be easily floated.

From this review of the literature devoted to the application of solvent sublation for the removal of chlorinated compounds from water it can be concluded that the rate of removal by solvent sublation depends on the bubble size, uniformity of the bubbles in the column, height of the column, axial dispersion and the flow rate. Axial dispersion is mainly the turbulence in the water induced by non-uniform horizontal distribution of the air bubbles. Higher flow rates enhance the removal rates from the aqueous phase, but it also increases the diameter of the bubbles, which would decrease the interfacial area per unit volume of air and would decrease the bubble residence time and hence would decrease the sublation efficiency. However, at low air flow rates the axial dispersion is not enough to completely mix the aqueous section. Therefore, some compromise have to be made between the air flow rate and the bubble size. The efficiency of solvent sublation is also influenced by the height of the column. The longer the column the better is the removal efficiency. However, this trend reaches a limit when the contact time of the bubbles in the water is long enough to permit a close approach to equilibrium of the distribution of solute between the aqueous and vapor phases.

It can be concluded from the review, that for chlorinated compounds, the larger the hydrophobicity of the compound, the better is the removal efficiency of the compound in comparison to air stripping. Since this separation process depends on the degree of hydrophobicity of a compound, any other co-solute which influences its hydrophobicity would also effect the separation efficiencies by the sublation process. It has been widely recognized that co-solutes like alcohols, inorganic salts and surfactants can influence the hydrophobicities of the molecules.

It should be also noted that the improvement in the removal rates by solvent sublation can be made by the use of very fine bubbles. An innovation in the area of fine bubble generation is the so called " gas-aphron" as is suggested by Sebba (11) which provides bubbles of micron size diameter. They are generated by high concentration of surfactant and are micron-sized air bubbles encapsulated by thin soapy films. Because of their extremely small size and slow rise velocities, they provide large interfacial areas and residence times in the aqueous phase, thus enhancing mass transfer from the aqueous phase to air bubbles.

Chaphalkar et.al (23) studied the removal of pentachlorophenol from aqueous solutions using microgas dispersions. Microgas dispersions, called colloidal gas aphrons, (CGAs) were generated using cationic, anionic and nonionic surfactants, and were used in an adsorptive bubble flotation process in a semibatch mode to remove PCP from aqueous phase. The aqueous solution was maintained at desired pH values by using buffers. In most cases the CGAs were found to have diameters between 30 and 300 μm. CGAs generated with Tergitol, which is a nonionic surfactant, were found to be more efficient for the removal of PCP, and the efficiency remained nearly independent of pH. In the case of an anionic surfactant, sodium dodecyl benzene sulfonate (DDBS), the efficiency of removal improved from 15 to 36% with a change in pH from 10.1 to 3.0. For the cationic surfactant, hexadecyltrimethylammoniumbromide (HTMAB), the removal at pH 10.1 was 81% which decreased to 68.1% at pH 3.0. For all the surfactants an increase in concentration improved the removal efficiency. The results were compared with the removal efficiencies using conventional flotation techniques used by other researchers. They concluded that solvent sublation is effective in the removal of PCP, but even in the presence of a surfactant it required 300% more air volume per volume of liquid when compared with CGA flotation.

One of the major advantages of solvent sublation in comparison to air stripping is the reduction of emission of VOCs and SVOCs to the atmosphere. There have been very few studies about using solvent sublation to reduce the emissions, in the literature.

Mei (8) studied the removal of toluene from aqueous media by solvent sublation and air stripping. The special feature of this investigation was the determination of toluene concentrations in gaseous as well as in aqueous phase. Sublation solvent was mineral oil. It was found that toluene emission to the atmosphere in solvent sublation process is 30-70% less than in air stripping at the same experimental conditions. Emission reduction increased from 40 to 60% when the thickness of mineral oil increased from 5 to 20 mm. It was more pronounced for low values of air flow rate (70% at a flow rate of 32 ml/min, 30% for a flowrate of 94 ml/min) and 10 mm thickness of oil layer. Additions of ethyl alcohol and cationic surfactant HTMAB did not effect emission reduction significantly. However addition of anionic surfactant sodium lauryl sulfate reduced the emission of toluene for solvent sublation and air stripping.

Valsaraj and Thibodeaux (24) also carried out some laboratory investigations for the use of floating oil covers to control volatile chemical emissions from surface impoundments. The experimental VOCs were benzene, acetone and n-propanol. Floating immiscible organic liquids (e.g. mineral oil, lauryl alcohol, octanol) seem to bring about efficient reductions in VOC air emissions both under windy conditions as well as low wind conditions. Significant reductions of up to 85% were observed for certain volatiles under both conditions.

Solvent sublation is also greatly influenced by the nature of the organic solvent. Properties of some solvents are showm in Table 2. Solvent sublation is more or less independent of the volume of the organic solvents. The unhindered motion of the bubbles across the interface is an important criterion for the success of solvent sublation. It then becomes apparent that the aqueous-organic solvent interfacial tension would be a deciding factor. If the bubble encounters a high interfacial tension, then it will tend to coalesce with other bubbles reaching the interface, becoming large and then move across the interface. This would reduce the interfacial area/unit volume of air moving across the interface at any time and would therefore reduce the removal rate from aqueous solution. Apart from low aqueous-organic solvent interfacial tension, the organic solvent should also have very low aqueous solubility.

Table 2 Properties of Solvents Used as a Stagnant Layer in Solvent Sublation Process

Solvent	Boiling Point ^{0}C	Interfacial tension (dyne/cm)	Aqueous Sol. (mg/l) at 25^{0}C
1-Octanol	194.4	8.5	586.0
2-Octanol	180.0	-	1083.0
1-Decanol	232.9	-	37.0
Lauryl Alcohol	255.0	7.8	2.0
Mineral Oil	225.0	33.3	Insoluble

Low solubility of the solvent (e.g. decanol) is favored because slight aqueous solubility of the solvent can change the bubble characteristics in the column and hence enhances the removal rates. In contrast, high solubility of the solvent causes back mixing and decrease in the removal rates as well as loss of solvent.

2.4 Mathematical Models

Models for solvent sublation of volatile compounds and relatively nonvolatile surface-active species have been developed and are available in the literature (7,12,14,15,16,25).

Lionel, Wilson and Pearson (15) developed a model for batch type aeration apparatus containing an aqueous column topped by a layer of organic liquid. They assumed that mass transfer of solute from the liquid to the vapor phase is first order in the difference between the actual vapor concentration and the local equilibrium vapor solute concentration. They varied different parameters of the theoretical model and found the effect of these parameters on solvent sublation as follows: 1) The thickness of the organic layer has no effect on the rate of removal from the water column although the retention of solute in the organic phase improves as the thickness of the organic layer increases. 2) For effective removal of solute per unit volume of air, longer columns are desirable. This trend reaches a limit when the contact time of the bubbles in the water is long enough to permit a close approach to equilibrium of the distribution of solute between the aqueous and vapor phases. 3) The fractional removal rates decreases proportionally to 1/(column radius)^2, when column diameter is changed. 4) If the process is mass transfer limited, the bubble radius should be reduced to achieve higher rate of sublation. 5) Increasing air flow rate increases the rate of removal in the same proportion but it is not true at higher flow rates as bubble size and axial dispersion also increases. The agreement between proposed model and the experimental study of solvent sublation of 1,1,1 trichloroethane in octanol was fairly good. The main discrepancies appeared to be associated with uncertainties in the gas chromatographic analysis and with the decrease in temperature during the initial stages of the runs.

Valsaraj and Wilson (16) developed the mathematical model for predicting the behavior of hydrophobic compounds in solvent sublation apparatus. They described a cell model in which they considered a column of liquid, the base of which is an air-water interface, and is divided into N cells, stacked on top of one another. Each cell was assumed to be of size that it can not hold no more than one molecule. They assumed that only molecules in the cells adjacent to the air-water interface are bound, and their binding energy is negative for stable binding. The expression developed by them simplifies to Langmuir isotherm for dilute solutions and it is given by:

$$T_m = \frac{T_{max}}{(1 + C_{1/2}/C)}$$

where T_{max} = Max. surface conc. of the solute

T_m = Surface conc. of the solute

C = Conc. of solute

$C_{1/2}$ = Constant

They also concluded that the rate of mass transfer from the bulk solution to the air-water interface of a rising bubble is controlled by the thickness of the boundary layer around the rising bubble and the diffusion constant of the solute in water. A method was developed for estimating the boundary layer thickness of the rising bubbles needed for estimating mass transfer rates in solvent sublation. They observed that as the flow rate of air is increased, the value of $C_{1/2}$ required to fit the theoretical model to the experimental data increases, presumably due to the increased back-mixing which occurs at the high flow rate. They found that lighter and less soluble solvent should be used to achieve higher rate of removal. The method was checked against experimental data obtained for o- and p- dichlorobenzene, Aroclor 1254 (a

PCB), lindane and endrin. The experimental data were found to be in good agreement with theoretical results for all the compounds except Aroclor 1254. Results were not good for Aroclor 1254 because of enough back-mixing of 2-octanol into water which markedly increased the solubility of the PCB into the aqueous phase.

Clarke and Wilson (7) described the mathematical model for a continuous solvent sublation column in which a surface-active and/or a volatile solute is being removed from the aqueous phase. They divided the whole column into N theoretical stages with influent coming at stage M, air at stage 1 (at the bottom of the column) and effluent being continuously removed from the first stage. They derived the mathematical model based on the following assumptions: 1) The distribution of the solute between the liquid surface and vapor phases is at equilibrium. 2) The organic layer is sufficiently thin so that it is essentially perfectly stirred and does not require partitioning into theoretical stages. 3) The liquid and vapor phase in the organic layer are able to reach equilibrium. After the development of the mathematical model, they simulated the effect of several parameters of the model on the performance of a sublation column using numerical analysis. They extended their work for cases where mass transfer is a rate limiting factor. Their model accounted for axial dispersion and based on their experimental results, they concluded that axial dispersion is an important parameter which impairs the column performance and should be minimized.

Valsaraj et al (14) developed a model for a single stage batch solvent sublation process. They assume that the air bubble is not in equilibrium with the liquid phase surrounding it and that mass transfer through the boundary layer is rate limiting. For a single stage batch process, the rate of change of concentration of solute with time due to the levitation of the solute by the rising bubbles is given by:

$$\ln(C/C_0) = -3Q_a/4\ r^3(A/BV_L)(1-\exp(-BT))t$$

where C = Conc. of solute at time t

C_0 = Conc. at time $t = 0$

Q_a = Air flow rate, $cm^3\ sec^{-1}$

A = constant = $f(r, K_w)$

r = bubble radius

B = Constant = $f(r, K_w, H)$

V_L = Volume of apparatus

T = rise time of the bubble through the column

H = Henry's constant

K_w = Boundary layer mass transfer coefficient

Experimental removal rate constants (obtained from the slopes of plots of C/C_0 with time) were compared with theoretical values obtained from above expression. They studied the aeration and solvent sublation of monochlorobenzene, 1,2,4 trichlorobenzene and p-dichlorobenzene. They found considerable discrepancy between the aqueous phase model and the experimental results. They attributed the differences to the fact that all model parameters can not be estimated accurately. Choice of a single average bubble radius is also suspect because of the non uniform bubble size in the column. The major drawback of the column is the assumption of a completely mixed section. This assumption is likely invalid at low air flow rates when axial dispersion is not enough to completely mix the aqueous section.

Valsaraj and Lu (25) developed a model for continuous countercurrent solvent sublation for the removal of hydrophobic organics from water. The model for solvent sublation considered the aqueous phase to be made up of N completely mixed aqueous stages with mass transport of solute between the stages. The upward transport of solute by air bubbles was opposed by the counter current flow of influent containing solute. The organic solvent sublation was modeled as a single well mixed slab. They found that the model predictions could at best be described as in satisfactory agreement with experimental data. The important parameters of the model were bubble radius, the solute mass transfer coefficient across the organic solvent-water interface and the aqueous phase solute mass transfer coefficient to the air bubble. The model showed that when the compounds with negligible H_c value are to be removed, adsorption on the bubble surface becomes very important. For such compounds decrease in the air bubble size will greatly increase the removal by sublation. They studied solvent sublation of naphthalene (NAPH), pentachlorophenol (PCP) and 2,4,6 trichlorophenol (TCP). The model prediction was not satisfactory for NAPH. This may be due to the assumption of equilibrium mass transfer of NAPH to the air bubble. The model predictions were marginally satisfactory in the case of TCP and PCP. The trend in the values of efficiencies predicted by the model was in agreement with the experimental values. The model under predicted the removal efficiencies at low flow rates. This may be due to the higher bubble radius used in the theoretical model.

Valsaraj and Thibodeaux (12) developed a model for batch and continuous solvent sublation incorporating all known transport mechanisms for solutes between aqueous and organic solvent phases. They assumed that air bubbles reaching solvent-water interface are in equilibrium with the aqueous phase and the axial dispersion is sufficiently large for effective mixing of both the phases. Their model showed that when molecular diffusion transport becomes important, the organic solvent volume also becomes important. When diffusion transport is unimportant in comparison to transport on the bubbles, the efficiency is also independent of the solvent-water partition constant of the solute. They sublated pentachlorophenol (PCP) into two different solvents to study the mechanism. The predictions from the model with respect to different transport mechanisms were in substantial agreement with experiments on the solvent sublation.

The most important variable parameters for a model are: thickness of organic layer, column radius, column height, bubble radius, flow rate and aqueous mass transfer rate coefficient. Solvent sublation is independent of the organic volume, because mass transfer occurs from gas bubbles crossing the aqueous solvent interface and not from diffusion of solute across the interface, the amount of material transferred should depend only on the amount of air crossing the interface and not on the organic volume. However, if the organic volume is too low, the solvent-water interface would be drastically disrupted at higher flow rates and reverse mass transfer of solute from the organic phase have to be considered. The rate of mass transfer from the aqueous phase to a rising bubble is controlled by the concentration gradient across a thin boundary layer around fine bubbles. In the initial stages of sublation the diffusive gradient is exclusively from the aqueous to organic solvent phase, but as sublation proceeds the solute concentration builds up in the organic solvent, the reverse mass transfer to the aqueous phase by molecular diffusion becomes important. In most cases, unless the physical transport by air bubbles overwhelms the molecular diffusive transport, the decrease in solute concentration in the aqueous phase is distinctly nonlinear. Air bubbles reaching the solvent-water interface do not immediately enter the organic solvent since they have to coalesce to form larger bubbles that can then overcome the solvent-water interfacial tension and rise through the organic phase. As they do so, a thin film of water is dragged into the solvent phase and is then returned as water droplets. Solute is carried by water dragged up;

however, the returning water droplets may be depleted in solute concentration. A complete model should include all these transport mechanisms across the interface. Bubble radius is a very important parameter in model. The increased contact times and surface to volume ratios of small bubbles permit them to come closer to achieving equilibrium solute concentration than is possible for larger bubbles. The models are based on uniform size of the bubbles throughout the column; so in actual experiments this parameter has to be considered. Column radius and height has also the influence on the removal efficiency. The longer the column, the better the removal. The fractional removal rates decrease proportionally to 1/(column radius)^2. Solvent sublation can achieve higher removal efficiencies when higher removal rates and smaller bubbles are used. High air flow rates increase the flux of air through the column while smaller bubbles generate a larger interfacial area per unit volume of air. Therefore, the steady state in solvent sublation is dependent on both gas flow and bubble radii. These two parameters are however related, in that at higher flow rates, the distribution of bubble radius frequently tend to larger ones. Therefore,one may not see the expected degree of improvement at higher flow rates unless the bubble radius is kept constant. Moreover, at higher flow rates axial dispersion increases greatly and should be accounted for in the model. Axial dispersion destroys the concentration gradients in the column. The parameter having the most uncertainty in the model is the coefficient for mass transfer of solute from the aqueous to the vapor phase. The rate of mass transfer from the aqueous phase to a rising bubble is controlled by the concentration gradient across a thin boundary layer around fine bubbles.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 Design of Equipment

A lab-scale solvent sublation apparatus was built for studying the removal of chlorinated hydrocarbons from water. Figure 1 is the schematic diagram of the solvent sublation apparatus. The column used in the experiments was made up of pyrex glass tubing with flared ends clamped together, with a filter funnel having a fine fritted glass disk at the bottom (Fisher Scientific Inc). The column had a height of 70 cm and an inner diameter of 40 mm. Two tubes were inserted in a large rubber stopper sealing the top of the column. One tube was used to the vent the gas and the other one was used to allow the samples to be injected into the gas chromatograph. Another rubber stopper was placed at about 15 cm from the bottom, where a syringe needle could be inserted to the center of the column, to allow liquid samples to be collected. The flow of compressed air from a cylinder was measured by an air rotameter supplied by Scott Speciality Gases. The flowmeter was calibrated against a soap film flow meter, using a stopwatch.

3.2 Design of Experiment

3.2.1 Experimental Procedure

The compounds chosen for study were trichloroethylene (TCE), monochlorobenzene (MCB) and 1,3 dichlorobenzene (1,3 DCB). Table 3 lists the major properties of the compounds. Their aqueous solubility and vapor pressure decreases in order TCE > MCB > 1,3 DCB, while their hydrophobic character increases in the order of TCE <

MCB < 1,3 DCB. The increasing hydrophobic nature as we go from TCE to MCB to 1,3 DCB has been attributed to the increasing size of the relatively non-polar molecules which renders them less and less able to compete with the strong bonding forces between water molecules. Air stripping and solvent sublation runs were carried out at two different flowrates, 60 and 94 ml/min. The sublation solvents used were paraffin oil and decanol. The thickness of paraffin oil was varied from 5 to 20 mm. Some experiments were also carried out using emulsions.

Table 3 Properties of Trichloroethylene, Chlorobenzene and 1,3 Dichlorobenzene

	Trichloroethylene	Chlorobenzene	1,3 Dichlorobenzene
Molecular Weight	131.39	112.6	147.0
Density (g/ml) at 20°C	1.4642	1.1058	1.2475
Vapor Pressure (mm Hg) at 32°C	103.6	17.5	4.0
Aqueous Solubility (mg/l) at 20°C	1000	500	125
Boiling Point (°C)	86.7	131.7	173.0
Melting Point (°C)	-87.1	-45.2	-26.2
Henry's Constant (dimensionless) at 25°C	0.49	0.16	0.11
Exposure Limits (ppm) by OSHA	100	75	50

1. Preparation of solution (without emulsion)

In a flask about 1000 ml of distilled water was taken and about 1 ml of 1,3 dichlorobenzene was added and the solution was vigorously stirred overnight using a magnetic stirrer. The next day the solution was filtered and 600 ml of the saturated solution was taken in a flask. To this was added 60 μl each of chlorobenzene and trichloroethylene by a syringe. The flask was shaken for about few minutes and the solution was immediately transferred into the glass column. The concentration of the

3 compounds in the solution was 100 ppm by volume. For dichlorobenzene, the maximum solubility is 125 ppm by weight which comes out to be 100 ppm by volume at saturated conditions.

2. Preparation of solution (with emulsion)

In a flask about 1000 ml of distilled water was taken and about 1 ml of 1,3 dichlorobenzene was added and the solution was vigorously stirred overnight using a magnetic stirrer. The next day the solution was filtered and 300 ml of the solution was taken in a flask. To this was added 30 μl of chlorobenzene by a 50 μl syringe. In a blender about 500 ml of distilled water was taken and about 1 gm of paraffin oil was added and the mixture was blended for 1 minute. 300 ml of this emulsified solution was immediately added to the solution containing chlorinated hydrocarbons. This solution was then transferred to the glass column.

3. The experiment was carried out as follows:

To commence a sublation run, the column was first rinsed with distilled water, filled with 600 ml distilled water, Valves 1,2 (Figure 1) were opened and the flowrate was adjusted to the desired value. Valves 1,2 were closed, the distilled water was drained off and the column was immediately filled with the experimental solution. On top of this was added the required volume of the organic solvent. The required volume of the organic solvent to produce the desired thickness of layer was calculated by the equation below:

$$\text{Volume of Solvent (ml)} = \pi r^2 L$$

where

r = inner radius of the column, 20 mm

L = thickness of the solvent, mm

The air stripping runs were made without any organic solvent on top of the aqueous solution. Valves 1,2 were then opened. The timer was started and the first aqueous sample was collected. Gaseous sample was analyzed 5 minutes later. The aqueous samples were collected every 15 minutes and the gaseous samples were injected into the GC column every 15 minutes. The flow rates were monitored continuously during runs by a rotameter. The experiment was stopped after about 95 minutes. After the experiment was over, the solution was drained into waste bottle. The glass column was washed with detergent, and rinsed with distilled water. The parameters used in the experiments are given in Table 4.

Table 4 Experimental Parameters

Organic Layer	Paraffin Oil, Decanol
Organic Layer Height	5 - 20 mm
Air Flow Rate	60, 94 ml/min
Bubble Diameter*	0.2 - 0.7 mm
Initial Concentration of solutes	100 ppm
Temperature	Room temp. (20 - 22°C)
Column Run Duration	95 min

* bubble diameters were roughly estimated by video camera technique.

3.3 Methods of Analysis

3.3.1 Aqueous Phase Analysis

1. Collection of sample (without emulsion)

A 2.0 ml of aqueous sample was collected by a syringe and placed into a 3.7 ml vial with a teflon faced septa at intervals of 15 minutes from the beginning of the experiment. These samples were extracted into 0.5 ml ethyl ether and 2.0 μl of the ethyl ether solution was injected by a 10 μl syringe into GC (FID).

2. GC analysis (without emulsion)

The aqueous samples were analyzed using a Varian 3300 Gas Chromatograph, with flame ionization detector (FID). The components were separated on 1/8 inch in diameter and 6 feet long stainless steel column packed with 80/100 mesh acid washed chromosorb P coated with 25% OV-101. Table 5 presents the GC operating conditions. Figure 2 shows the typical peak resolution and the retention times of ethyl ether and the chlorinated hydrocarbons.

Table 5 GC Operating Conditions for Aqueous Phase Analysis (without emulsion)

Detector temperature	250°C
Injector Temperature	200°C
Oven Temperature	80°C (initial) 150°C (final)
Heating rate	15°C/min
Nitrogen (carrier gas)	30 ml/min
Air	300 ml/min
Hydrogen	30 ml/min

A calibration graph was obtained with different concentrations of chlorinated hydrocarbons by adding them directly into ethyl ether. Figures 3,4 and 5 shows the calibration graph for trichloroethylene, chlorobenzene and 1,3 dichlorobenzene respectively.

3. Collection of samples containing emulsified oil

2.0 ml of aqueous samples were collected by a syringe were placed in a 3.7 ml vial with a teflon faced septum at intervals of 15 minutes from the beginning of the experiment and 2.0 μl of the samples were injected directed by a 10 μl syringe into GC equipped with Flame Ionization Detector (FID).

4. GC analysis of samples containing emulsified oil

The aqueous samples were analyzed by a Varian 3700 Gas Chromatograph using flame ionization detector. 2.0 μl of samples were injected directly into the column supplied by Supelco Inc., which was 1/8 inch in diameter and 3 feet long stainless steel column packed with 60/80 mesh carbopack C coated with 1% SP 1000. Here a pre-column packed with glass beads was placed ahead of the column to adsorb the oil from the samples. Table 6 presents the GC operating conditions.

Table 6 GC Operating Conditions for Aqueous Phase Analysis (with emulsion)

Detector Temperature	290^{0}C
Injector Temperature	200^{0}C
Oven Temperature	120^{0}C (initial) 150^{0}C (final)
Helium (carrier gas)	30 ml/min
Air	300 ml/min
Hydrogen	30 ml/min

3.3.2 Gas Phase Analysis

1. Trap and injection system

Figure 6 shows the trap and injection system for gas analysis. The system consisted of two six-port valves, a 60/80 mesh cryogenically cooled trap, a vacuum pump and a ballast tank. The six-port valve 1 was switched to solid-line position (analysis position). 2 ml/min of helium was always passed through the capillary column to maintain the column quality. Dewar flask containing iso-propyl alcohol frozen to a slush with liquid nitrogen (-85.8^{0}C) was placed under the glass microbead trap. The trap was cooled for about 5 minutes. 135 ml ballast volume was evacuated below 1 mm Hg pressure by the vacuum pump. Six-port valve 2 was switched to solid-line position (trap position). The gas sample was allowed to pass through the glass microbead trap into the ballast tank, where the pressure was monitored by Wallace and Tiernan high accuracy pressure gauge (Model 61D-1A-0030). When the pressure in the ballast volume was 1 psig, the valve 2 was switched to dotted-line position (injection position). The Dewar flask was removed from the trap and the trap was heated to about 95°C with a beaker of hot water. The GC oven temperature was raised to 130°C. 2 ml/min helium passing through the trap swept the chlorinated hydrocarbons to the GC column.

The amount of air sample injected is given by:

$$V_s = P\ V_r/P_s$$

where

V_s = Volume of air sample injected at 1 atm (liter)

P = Pressure difference measured by high accuracy gauge (psi)

V_r = Volume of vacuum ballast volume (135 ml)

P_s = Standard pressure (14.7 psi)

In these experiments, the pressure difference was about 1 psig, so the volume of air sample injected was about 0.01 liter.

2. GC operating conditions

The air samples were analyzed using a Varian 3700 Gas Chromatograph with flame ionization detector. A 15 meters long, 0.54 mm in diameter crosslinked methyl fused silica column (Alltech Associates Inc.) with 1.2 micron film thickness of SE-30 was used for analyzing the compounds. Table 7 shows the GC conditions for analysis of air samples. Figure 7 shows the typical peak resolution and retention times of the compounds in the gas phase.

Table 7 GC Operating Conditions for Gas Phase

Detector Temperature	290°C
Oven Temperature	130°C
Helium (carrier gas)	2 ml/min
Air	300 ml/min
Hydrogen	30 ml/min
Nitrogen (make-up gas)	28 ml/min

CHAPTER 4

RESULTS AND DISCUSSION

4.1 The Effect of Air Flowrate

The rate of removal of trichloroethylene, chlorobenzene and 1,3 dichlorobenzene from water by solvent sublation and air stripping was investigated at two different flow rates (60 and 94 ml min $^{-1}$). It was found that the rate of removal from water for all the three chlorinated hydrocarbons increased with increase in flow rate for both air stripping and solvent sublation (thickness of paraffin oil-10 mm).

The effect of air flow rate on the removal of TCE, chlorobenzene and 1,3 dichlorobenzene from water by air stripping is shown in Figures 8, 9 and 10 respectively. The graphs show the fractions of the compounds removed with time. The removal efficiency E is defined as:

$$E = (1 - C_t/C_0)$$

where, C_t = concentration at time t

C_0 = initial concentration

The effect of air flow rate on the removal of TCE, chlorobenzene and 1,3 dichlorobenzene from water by solvent sublation is shown in figures 11, 12 and 13 respectively. It can be seen from the Figures that increase in the flowrate from 60 to 94 ml/min increased the rate of removal for all the three compounds in both air stripping and solvent sublation. The increase in the removal rate is due to higher flowrate, since increase in flowrate produces more bubbles which provide more interfacial area between the bubbles and the solution. However, it was found by Valsaraj and co-workers that if the flowrate is increased beyond a certain point, the removal rate was not proportional to flowrate (14,17). One reason for such an effect is the increase in the mean bubble radius as the flowrate increases which decreases the air-water interfacial area per unit volume of air through the column. Moreover, large bubbles have higher rise velocities and hence shorter residence times in the column. Too high flowrate can give rise to a high degree of axial dispersion which have been found to impair the performance of the sublation process (17). The overall conclusion is that the advantages gained by increasing air flow rates through the column will be minimal unless the bubble sizes are kept as small as possible.

The rate of removal for both solvent sublation and air stripping increased in the order TCE > MCB > 1,3 DCB. This is because TCE is the most volatile.

The effect of air flow rate on the emission of the chlorinated hydrocarbons to the air was examined. The reduction in emission of the chlorinated compounds by solvent sublation in comparison to air stripping was calculated by integrating the areas under the curves of air concentration versus time. Reduction in emission of the chlorinated hydrocarbons by solvent sublation at two different air flow rates, 60 and 94 ml/min for a 10 mm Paraffin Oil layer is given in Table 8 and 9.

Table 8 Emission Reduction by Solvent Sublation at Air Flowrate of 60 ml/min

Compound	% Emission Reduction with solvent layer
TCE	58
Chlorobenzene	69
1,3 Dichlorobenzene	76

Table 9 Emission Reduction by Solvent Sublation at Air Flowrate of 94 ml/min

Compound	% Emission Reduction with solvent layer
TCE	61
Chlorobenzene	70
1,3 Dichlorobenzene	72

4.2 The Effect of Thickness of Organic Layer

It can be seen from Figures 15, 16, 18 and 19 that the rate of removal of the monochlorobenzene and 1,3 dichlorobenzene from water is somewhat higher in solvent sublation than in air stripping. The improvement in separation by solvent sublation is presumably due to the adsorption of the surface-active compounds on the surface of the bubbles. The surface-adsorbed compounds and the compounds in the vapor phase inside the bubble are carried into the organic layer on the top of the column during solvent sublation. Only the vapor inside the air bubble is removed by air stripping (22). During air stripping the adsorbed material simply remixes and is redistributed into the aqueous solution as the bubbles burst at the top of the column. In solvent sublation, however, these materials are trapped by the paraffin oil solvent floating on top of the column and are thus prevented from remixing, thereby improving the removal rates (14,21). For the removal of TCE from water (Figures 14, 17), solvent sublation did not show any significant improvement over air stripping. This is presumably due to the high volatility, high aqueous solubility and low surface activity of TCE in comparison to monochlorobenzene and 1,3 dichlorobenzene. The effect of different thicknesses of organic layer on solvent sublation was investigated. Solvent sublation was carried out with different thickness of organic layer (paraffin oil) varying from 5 mm to 20 mm at different air flow rates. Figures 20-25 show the effect of different thickness of layer. It can be seen from the figures that for monochlorobenzene and 1,3 dichlorobenzene solvent sublation appeared to be more or less independent of the volume of the organic solvent. The reason for this, is that mass-transfer occurs mostly from gas bubbles crossing the aqueous-solvent interface and not from the diffusion of the solute across this interface. Therefore, the amount of materials transferred depends only on the amount of air crossing the interface and not on the organic volume. It should be noted that if the organic layer thickness used in solvent sublation is too low, the mineral oil-water interface would be drastically disrupted at higher flow rates and the process would lose efficiency. In this case, reverse mass transfer of solute from the organic phase to the aqueous phase would occur and solvent volume dependence would become significant (14,19). However, for the more volatile TCE, 20 mm thickness of layer is better because it prevents TCE from mixing back into aqueous phase and increases its reduction in emission to the atmosphere. Table 10 and 11 shows the emission reduction by solvent sublation using different thickness of oil layer.

It can be seen that thickness of layer has some effect on the emission reduction of the compounds to the atmosphere. The effect is more pronounced for the more volatile compound TCE. As mentioned before, hydrophobic compounds which are volatile or partly volatile will be carried by bubbles simultaneously in the vapor phase within the bubbles and also on the surface of the bubbles. When the bubble transits the aqueous section and moves through the organic layer, the compound on the bubble surface is stripped into the organic phase. At the same time, equilibrium between the vapor inside the bubble is being established, and the volatile materials in the interior of the bubble may also partition into the organic layer (14). Thus solvent sublation not only helps to improve the efficiency of air stripping, but may also help to overcome, at least partly, the undesired air pollution problem accompanying a simple air stripping process. Moreover, the presence of the organic solvent reduces the eventual redispersion of the material into the column upon bubble bursting which usually occurs in conventional air stripping process (14,17).

Table 10 Emission Reduction by Solvent Sublation with Different Thickness of Oil Layer at Air Flowrate of 60 ml/min

Compound	Thickness of Layer mm	% Emission Reduction
TCE	5	54
TCE	10	58
TCE	20	68
Chlorobenzene	5	60
Chlorobenzene	10	69
Chlorobenzene	20	75
1,3 Dichlorobenzene	5	71
1,3 Dichlorobenzene	10	76
1,3 dichlorobenzene	20	77

Table 11 Emission Reduction by Solvent Sublation with Different Thickness of Oil Layer at Air Flowrate of 94 ml/min

Compound	Thickness of Layer mm	% Emission Reduction
TCE	5	52
TCE	10	61
TCE	20	70
Chlorobenzene	5	65
Chlorobenzene	10	70
Chlorobenzene	20	73
1,3 Dichlorobenzene	5	70
1,3 Dichlorobenzene	10	72
1,3 Dichlorobenzene	20	75

4.3 The Effect of Nature of Layer

Solvent sublation for the removal of the chlorinated hydrocarbons from water was carried out at two different flow rates using two different organic solvents. The organic solvents used were decanol and paraffin oil and the thickness of the layer was 10 mm in both cases. Figures 26-37 shows the effect of using two different solvents in solvent sublation. The rate of removal of monochlorobenzene and 1,3 dichlorobenzene from water was somewhat higher when decyl alcohol was used as solvent. It was observed that in the decyl alcohol-water system, where the interfacial tension was very small, the bubbles crossed the interface without much coalescence whereas in the oil-water system the bubbles stopped momentarily at the interface, coalesced and then moved sideways and up along the walls of the column along with some smaller bubbles rising through the column. Few bubbles actually passed through the center of the oil layer. Thus for the oil-water system there was reduction in the interfacial area per unit volume of air crossing the interface at any time and there was a reduction in the removal rate from the aqueous solution. When decanol was used as a solvent the bubbles could penetrate the solvent layer. Decyl alcohol, which is partly polar, has a higher aqueous solubility than paraffin oil, thus decyl alcohol has the potential to change both the bubble characteristics and the aqueous solubilities of the compounds (20). Because of reduction of surface tension of water in the presence of even traces of decyl alcohol, the bubble radius decreased and potentially a larger surface area would available for sublation. However, sublation with decyl alcohol as an organic phase did not show any improvement for the removal of TCE from water. This is again presumably due to the high solubility, high volatility and low surface activity of TCE in comparison to monochlorobenzene and 1,3 dichlorobenzene. The type of organic solvent used has a distinct effect on the sublation efficiency. Table 12 shows the emission reduction of the compounds in the presence of both the solvents.

Table 12 Emission Reduction by Solvent Sublation Using different Solvents

Compound	Solvent 10 mm	Flowrate ml/min	%Emission Reduction
TCE	Paraffin oil	60	54
Chlorobenzene	Paraffin oil	60	69
1,3 Dichlorobenzene	Paraffin oil	60	76
TCE	Decanol	60	60
Chlorobenzene	Decanol	60	75
1,3 Dichlorobenzene	Decanol	60	81
TCE	Paraffin oil	94	61
Chlorobenzene	Paraffin oil	94	70
1,3 Dichlorobenzene	Paraffin oil	94	72
TCE	Decanol	94	64
Chlorobenzene	Decanol	94	76
1,3 Dichlorobenzene	Decanol	94	75

4.4 Comparison of Efficiencies of Solvent Sublation and Air Stripping for the Removal of Chlorinated hydrocarbons

Figures 14-19 show that the improvement in the removal rates by sublation over air stripping, is greater for compounds which are more hydrophobic i.e. compounds of low aqueous solubility, low vapor pressure and relatively non-polar. For compounds of high volatility and low surface activity the sublation process may not provide any real improvement in the removal efficiency as compared to air stripping, but it still may reduce the air emission problem because of the presence of the organic layer on top of the aqueous solution. The relative improvement of sublation over air stripping was found to be in agreement with their relative hydrophobicities. The increasing hydrophobic nature from TCE to MCB to 1,3 DCB has been attributed to the increasing size of the relatively non polar molecules which render them less and less able to compete with the strong hydrogen bonding forces between the water molecules. Consequently they are "squeezed" out of the interstitial water structure. As the hydrophobicity increases so does the tendency of the compound to aggregate at the air-water interface of the rising bubbles, contributing to the increasing "surface active" nature of the compound. At the same time their vapor pressure decrease in the order TCE>MCB>1,3 DCB, so that the partitioning into the interior of air bubbles become less and less favorable (14).

4.5 Emulsion

Solvent sublation and air stripping was carried out using emulsions in water for monochlorobenzene and 1,3 dichlorobenzene. The flow rate was 60 ml/min. and the thickness of paraffin oil layer was 10 mm. Figures 38-41 shows the rate of removal from water with emulsions. Addition of 5 ppm of cationic surfactant HTMAB slightly improved the rate of removal of the chlorinated hydrocarbons from aqueous solution. The slight improvement in the rate of removal of the chlorinated hydrocarbons is presumably due to the decrease of air bubble size by the added surfactants, which reduces the surface tension of the solution very effectively (14). The reduced interfacial tension at the water-mineral oil interface as a result of the presence of the surfactants in the aqueous phase helps the bubbles to cross the interface easily without much coalescence (17). Table 13 shows the emission reduction of the compounds in the presence of emulsions.

Table 13 Emission Reduction by Solvent Sublation with Emulsions

Compound	Concentration of HTMAB ppm	%Emission Reduction
Chlorobenzene	0	67
1,3 Dichlorobenzene	0	72
Chlorobenzene	5	63
1,3 Dichlorobenzene	5	70

Comparison of the removal rates from water with and without emulsions (Figures 15, 16,38,39) by air stripping and solvent sublation shows that the of removal is lower in the presence of emulsions and emission redcution is nearly the same with and without emulsions.

CHAPTER 5

CONCLUSIONS

From the bench scale studies of the removal of chlorinated hydrocarbons by air stripping and solvent sublation we conclude that:

1. The rate of removal of chlorinated hydrocarbons from water either by air stripping or solvent sublation was highest for trichloroethylene, followed by chlorobenzene and then 1,3 dichlorobenzene.

2. For all three compounds, the presence of a layer of organic solvent atop the aqueous phase decreased the degree of air emissions, compared to air stripping.

3. For the removal of monochlorobenzene and 1,3 dichlorobenzene from water, solvent sublation showed a significant improvement over air stripping. For the removal of trichloroethylene from water, solvent sublation did not show any real improvement over air stripping, presumably due to its low surface activity, high volatility and high aqueous solubility in comparison to the other two compounds.

4. In both air stripping and solvent sublation, an increase in air flowrate increased the removal of chlorinated hydrocarbons from water.

5. Solvent sublation was found to be more effective in comparison to air stripping, for removing relatively non-polar compounds of high hydrophobic character, low aqueous solubility and low vapor pressure from water. The relative improvement of solvent sublation for the chlorinated hydrocarbons in comparison to air stripping was found to be in agreement with their relative hydrophobicities.

6. The rate of removal of monochlorobenzene and 1,3 dichlorobenzene from water by solvent sublation was better when decyl alcohol was used as a solvent in

comparison to paraffin oil. This is due to the fact that, decyl alcohol which is partly polar has higher aqueous solubility than paraffin oil and it has the potential to change both the bubble characteristics and aqueous solubilities of the compounds. Because of reduction in surface tension of water in the presence of even traces of decyl alcohol, the bubble radius decreased and potentially a large surface area was available for sublation.

In addition the bubbles penetrated the layer more effectively giving better interfacial contact.

7. In solvent sublation, the removal of chlorinated hydrocarbons from water was more or less independent of the volume of the organic solvent present on top of aqueous section. This is presumably due to the fact that mass transfer occurs mostly from gas bubble crossing the aqueous-solvent interface, and not from the diffusion of the solutes across this interface. Therefore, the amount of material transferred depends only on the amount of air crossing the interface and not on the organic volume. The thicker the layer, the larger was the emission reduction of the compounds by solvent sublation.

8. Addition of cationic surfactant HTMAB to water emulsions slightly improved the removal efficiency of the chlorinated hydrocarbons since they reduce the surface tension of the solution and consequently reduce the air bubble size.

9. Addition of emulsions to water decreased the rate of removal of monochlorobenzene and dichlorobenzene from aqueous phase.

APPENDIX

FIGURES

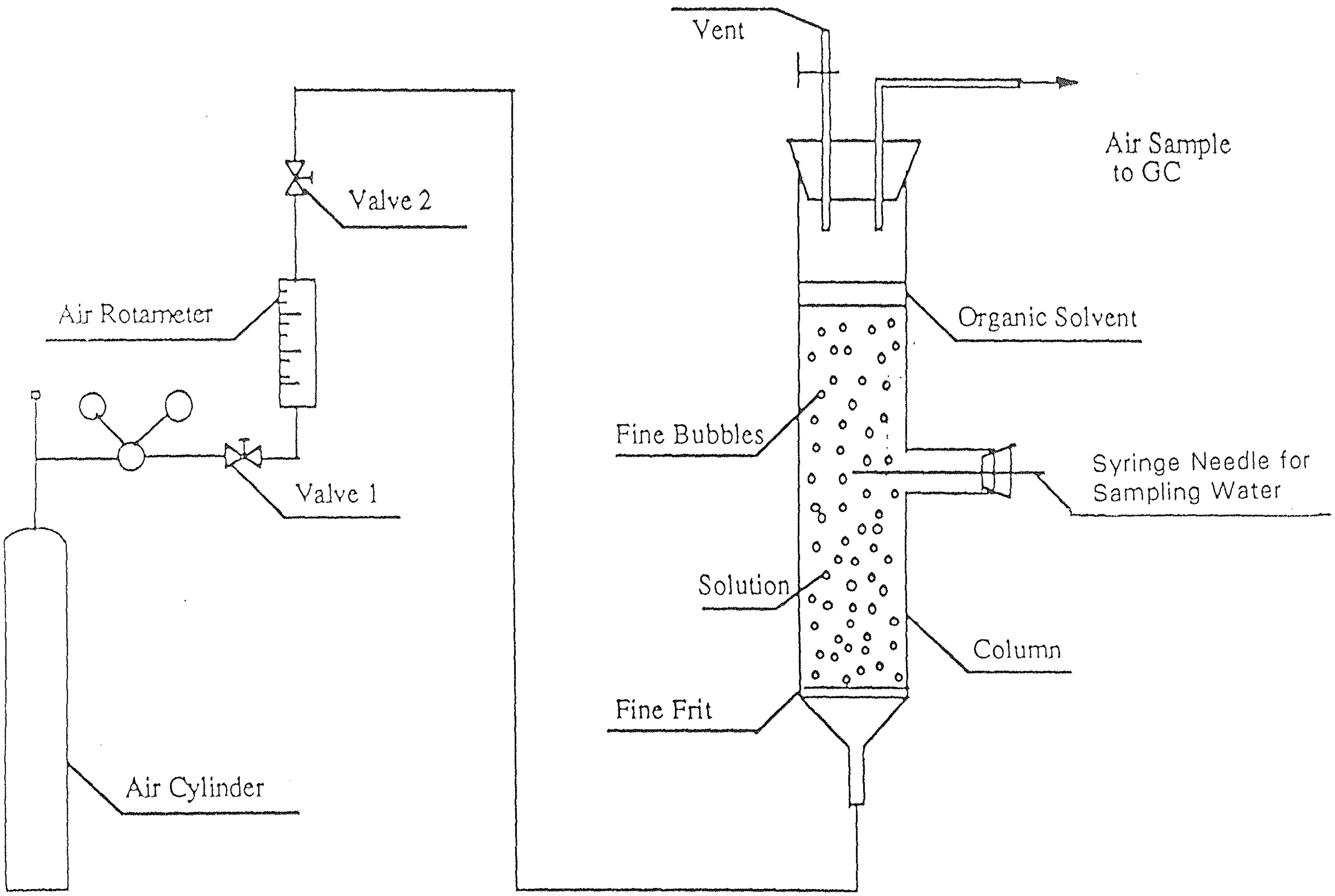

Figure 1 Solvent Sublation Apparatus

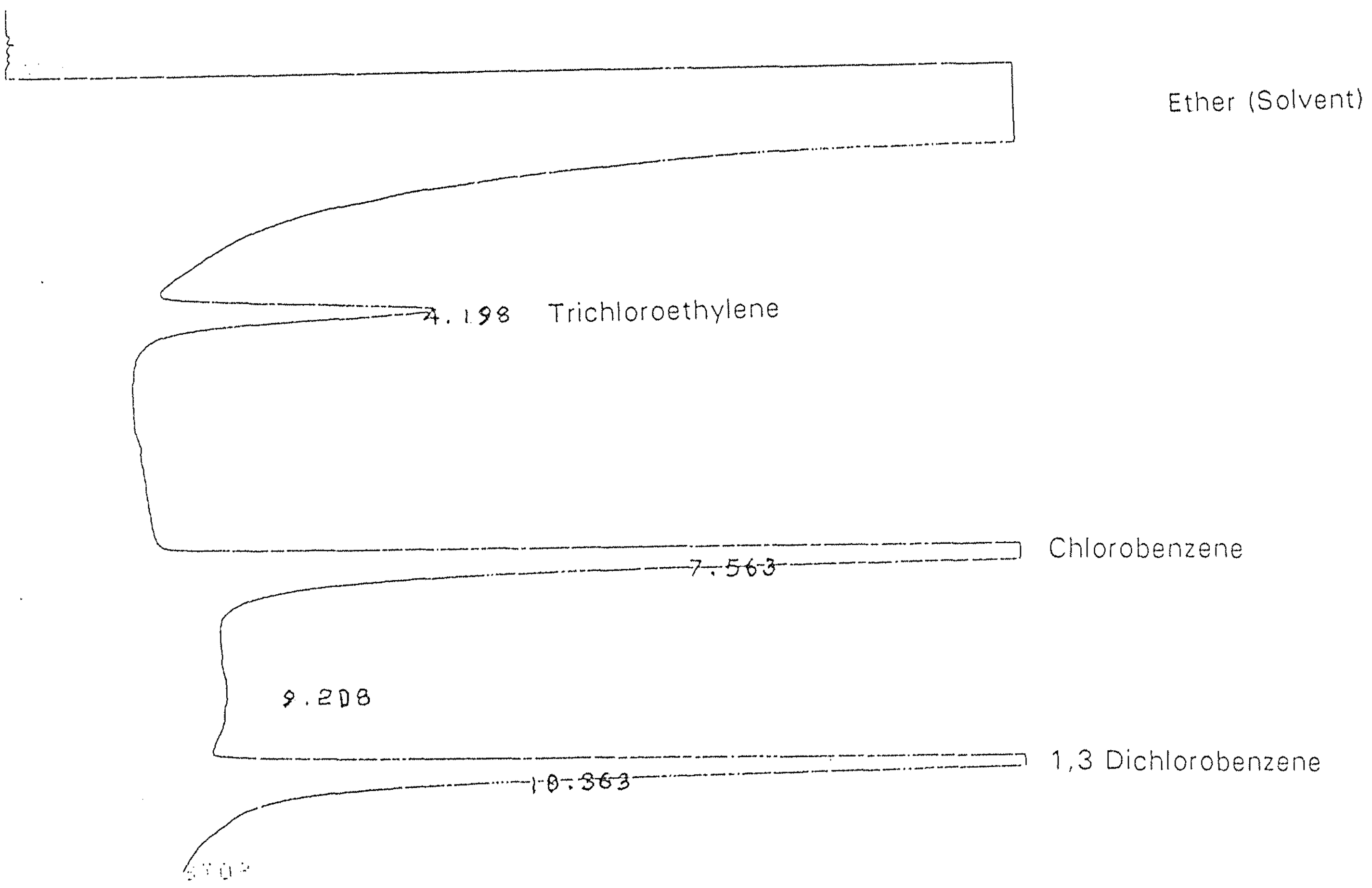

Figure 2 GC Chromatogram of Aqueous Phase analysis

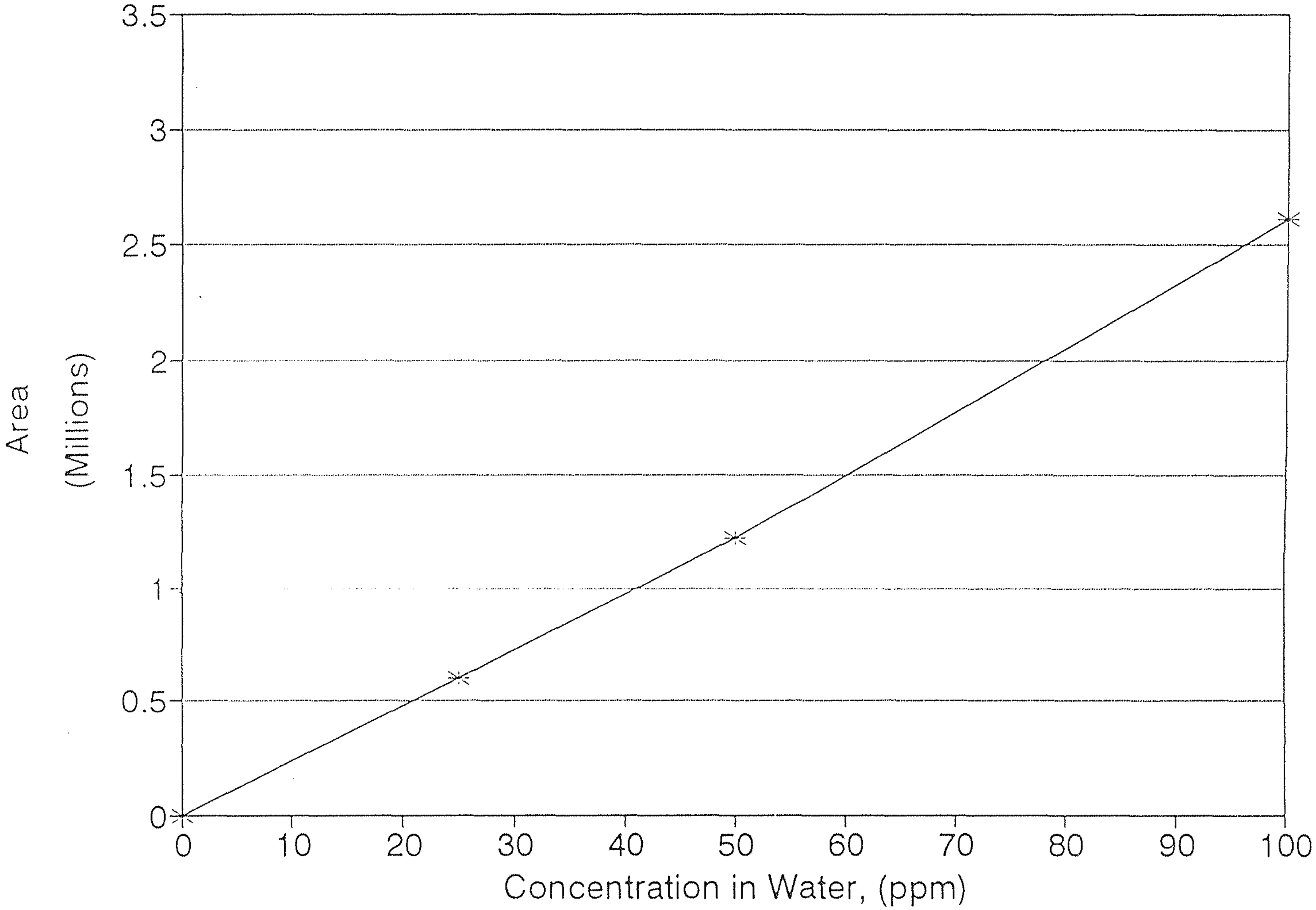

Figure 3 Calibration Graph for Trichloroethylene

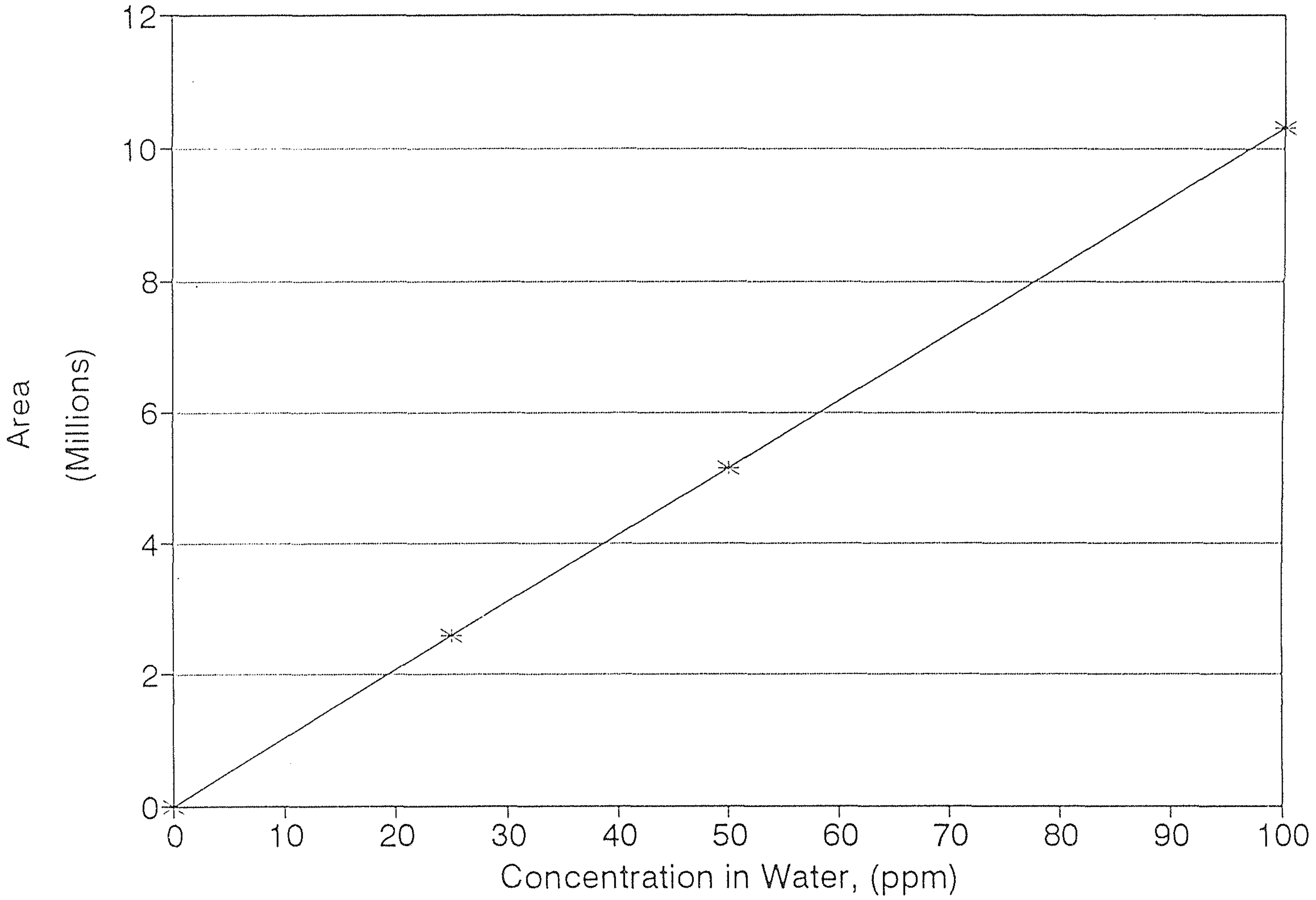

Figure 4 Calibration Graph for Monochlorobenzene

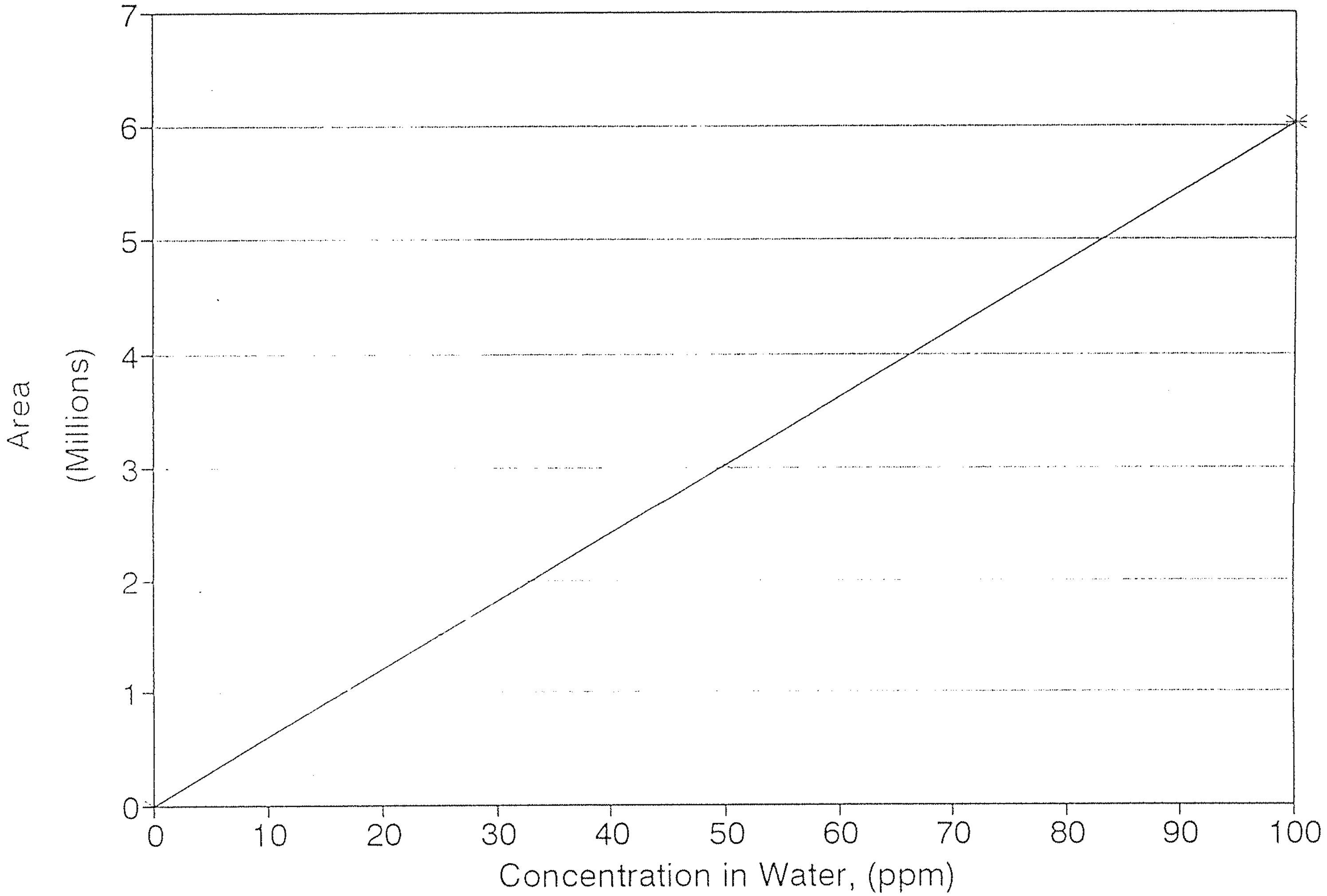

Figure 5 Calibration Graph for Dichlorobenzene

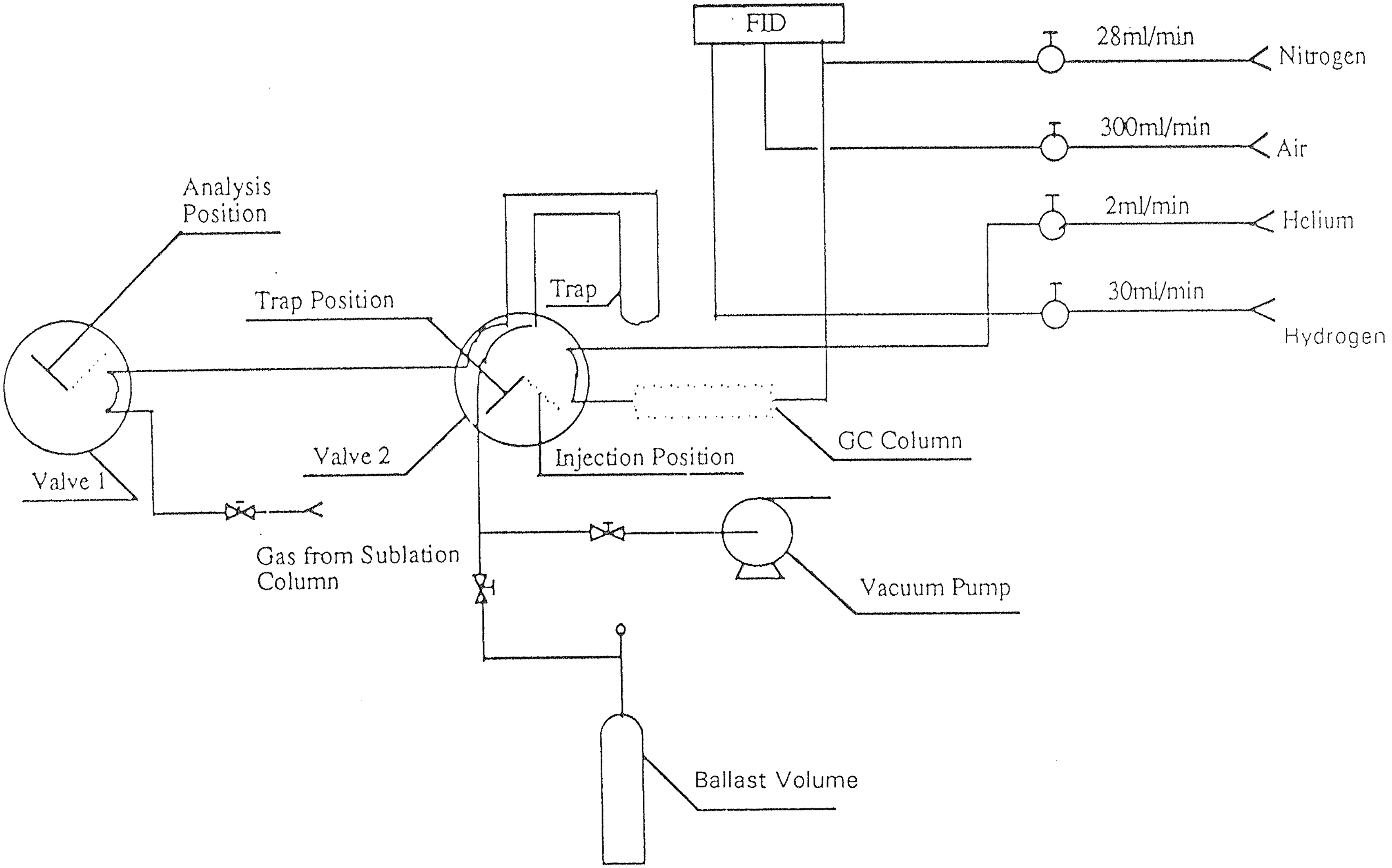

Figure 6 Trap and Injection System for Gas Phase Analysis

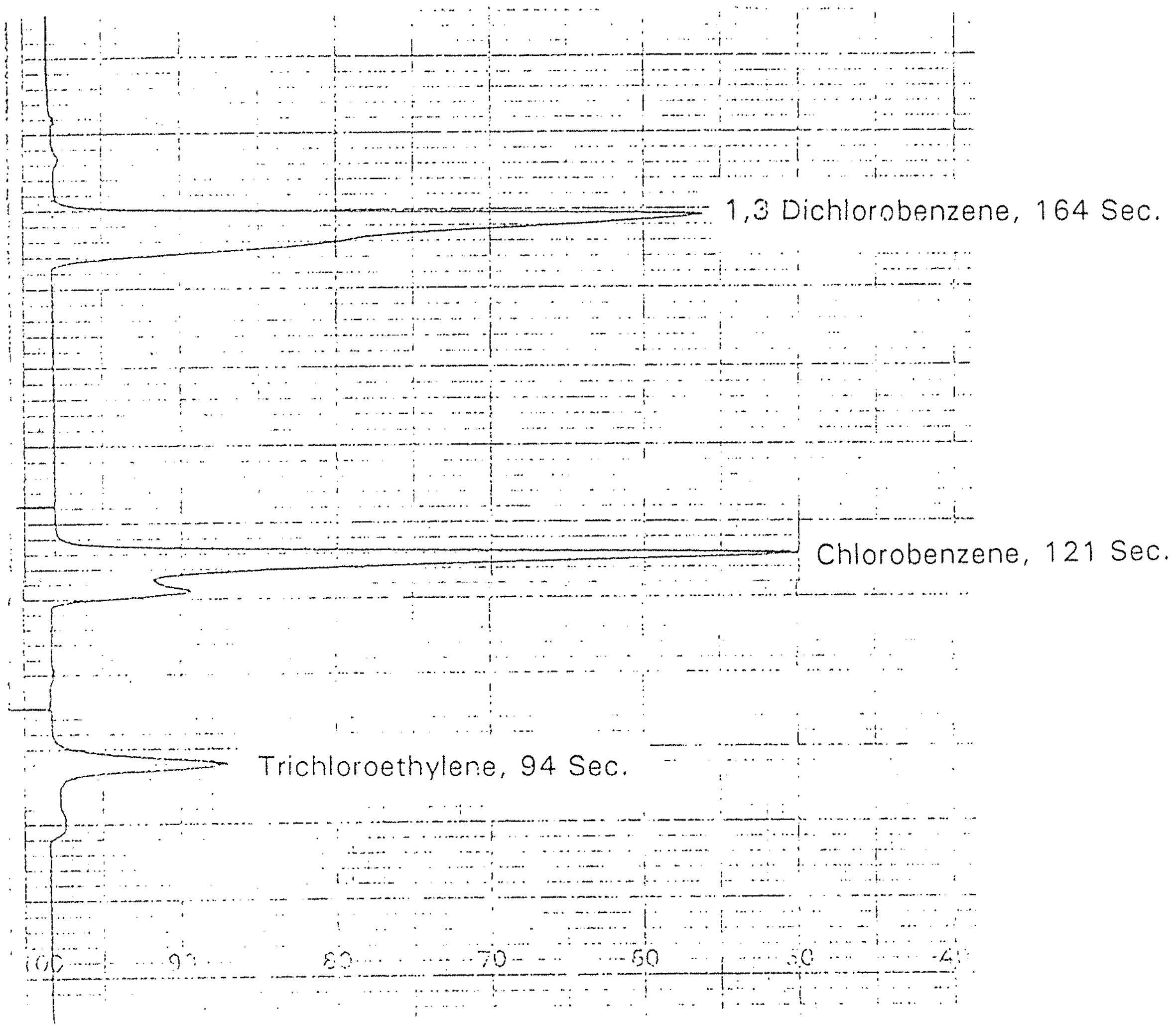

Figure 7 GC Chromatogram for Gas Phase Analysis

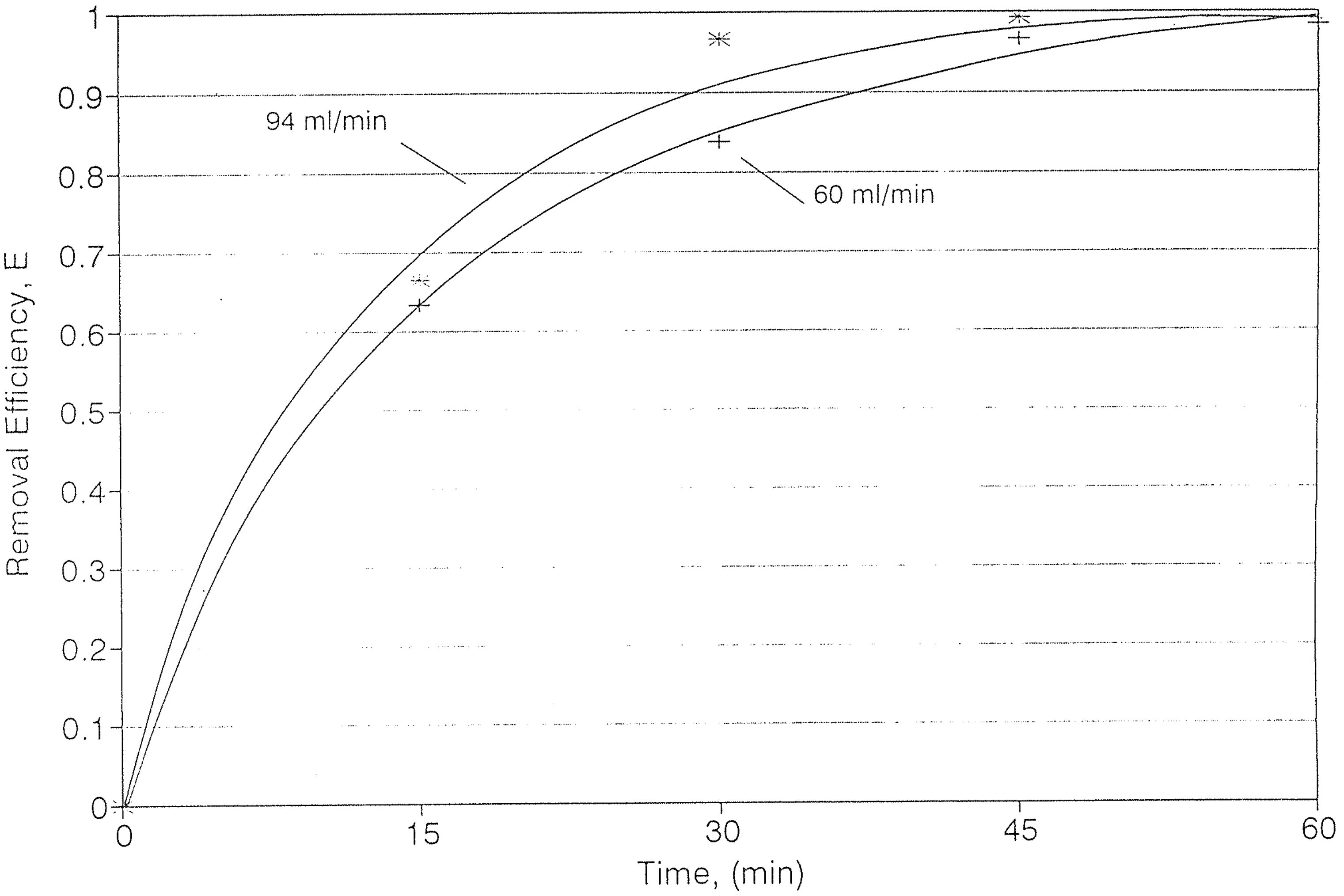

Figure 8 Effect of Air Flowrates on the Removal of Trichloroethylene from Water by Air Stripping

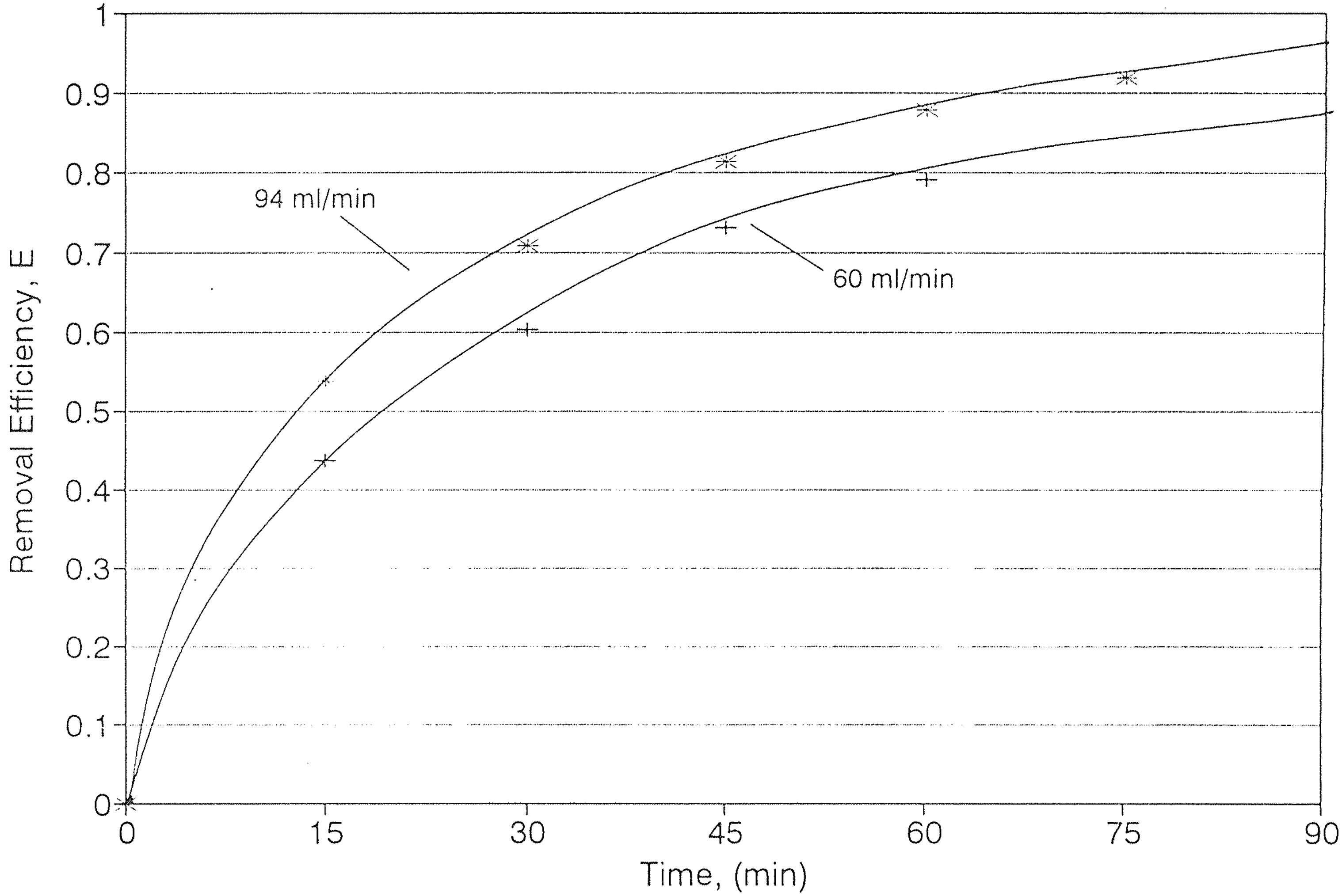

Figure 9 Effect of Air Flowrates on the Removal of Monochlorobenzene from Water by Air Stripping

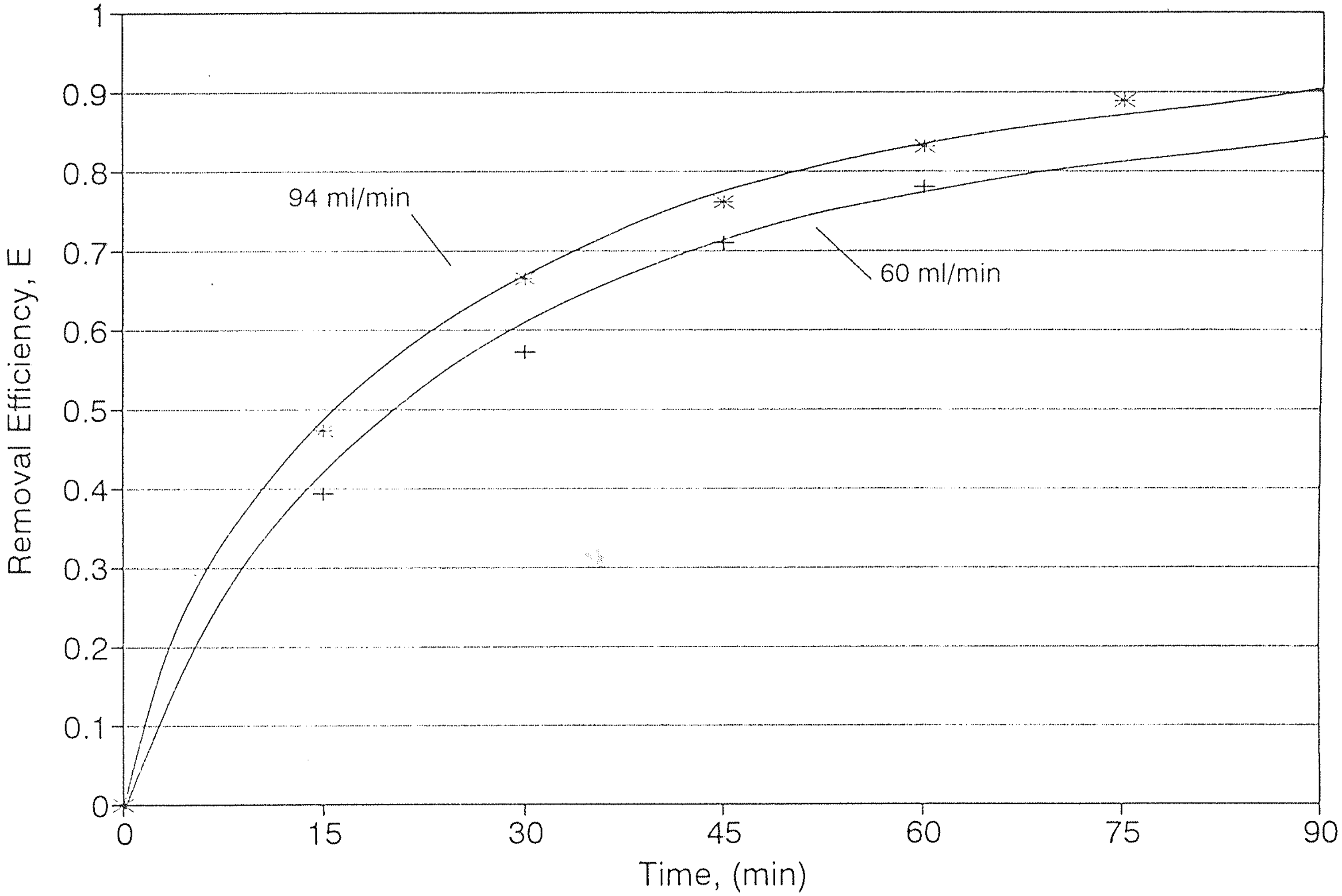

Figure 10 Effect of Air Flowrates on the Removal of Dichlorobenzene from Water by Air Stripping

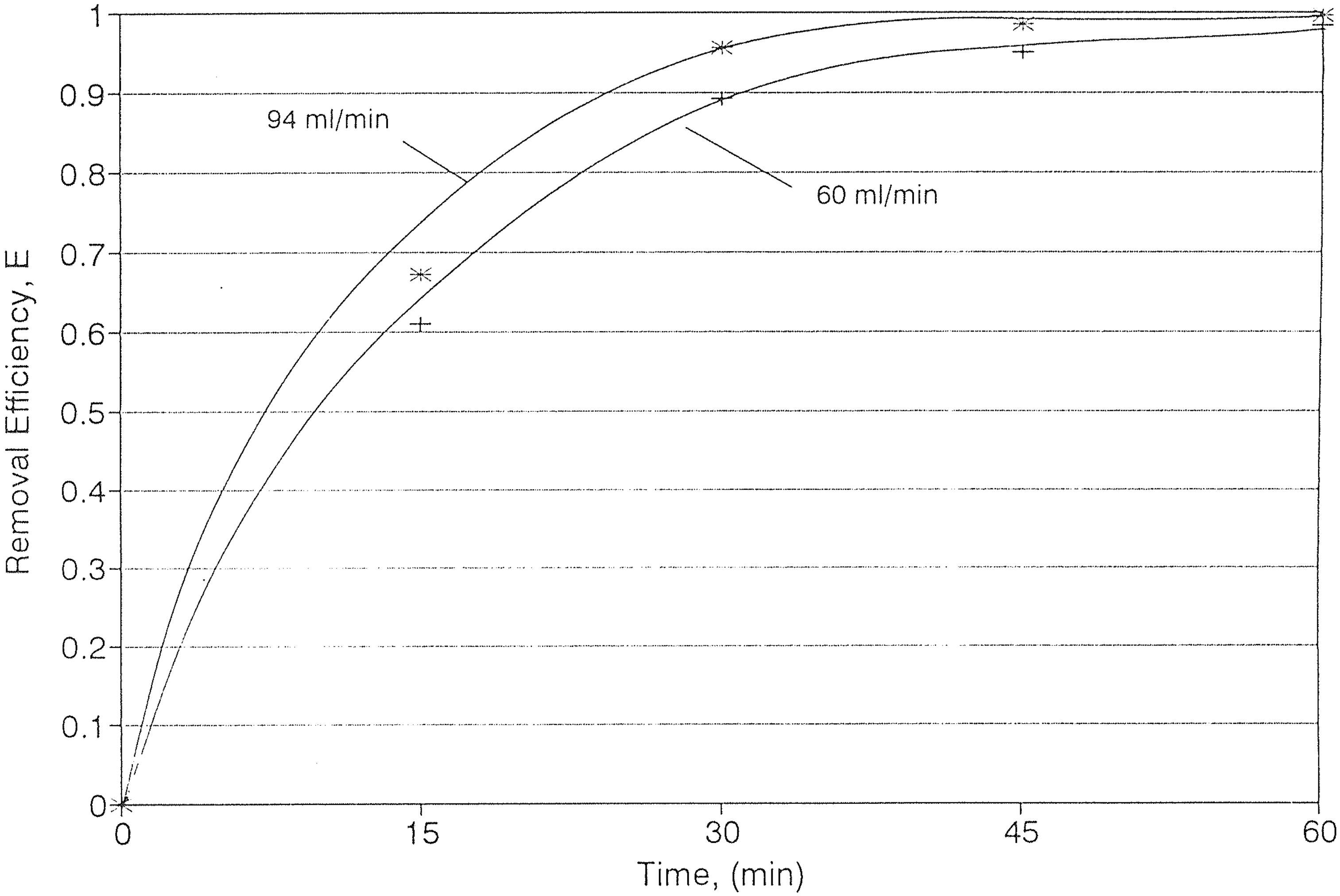

Figure 11 Effect of Air Flowrates on the Removal of Trichloroethylene from Water by Solvent Sublation (10 mm. Paraffin Oil)

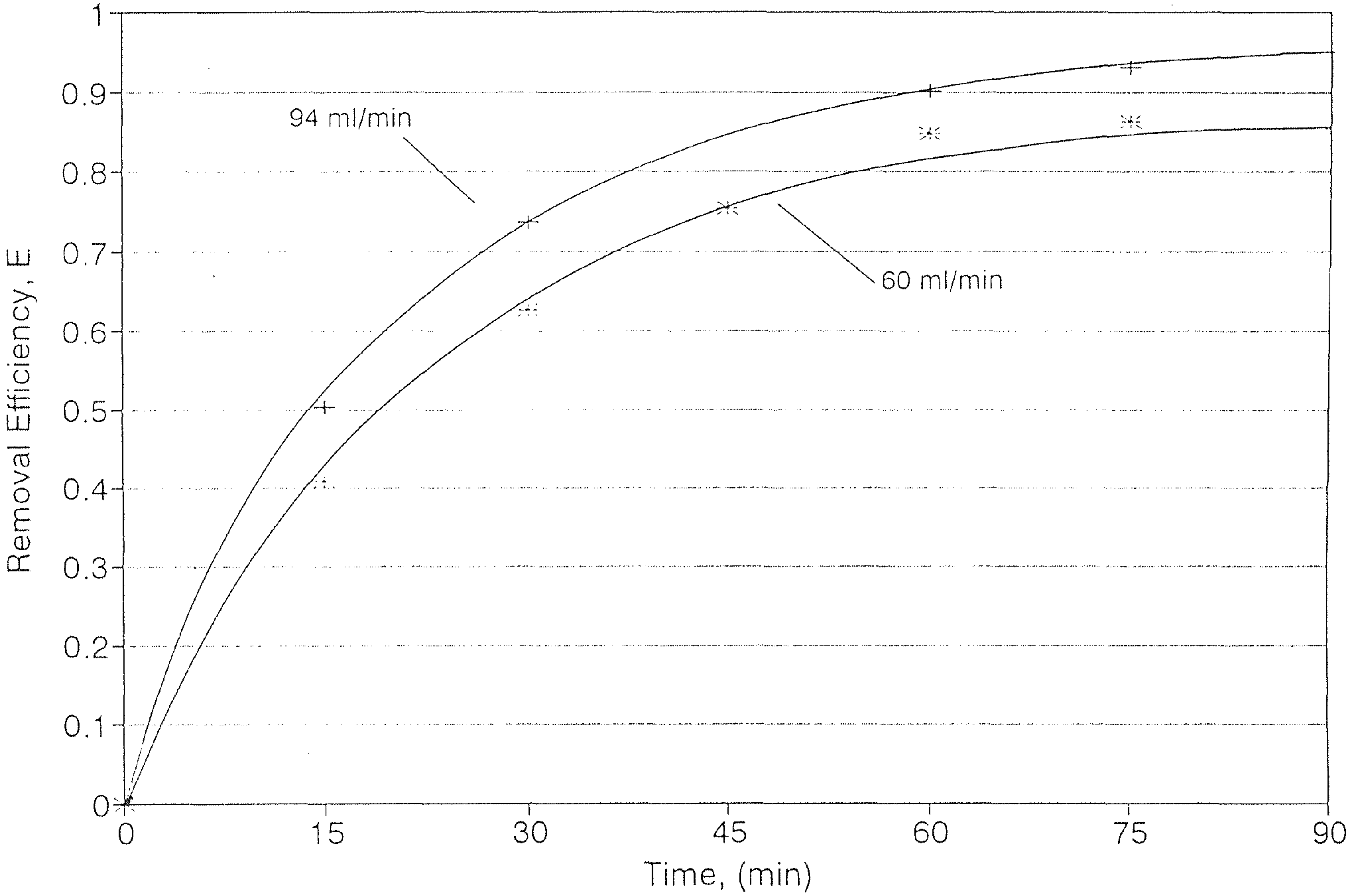

Figure 12 Effect of Air Flowrates on the Removal of Monochlorobenzene from Water by Solvent Sublation (10mm, Paraffin Oil)

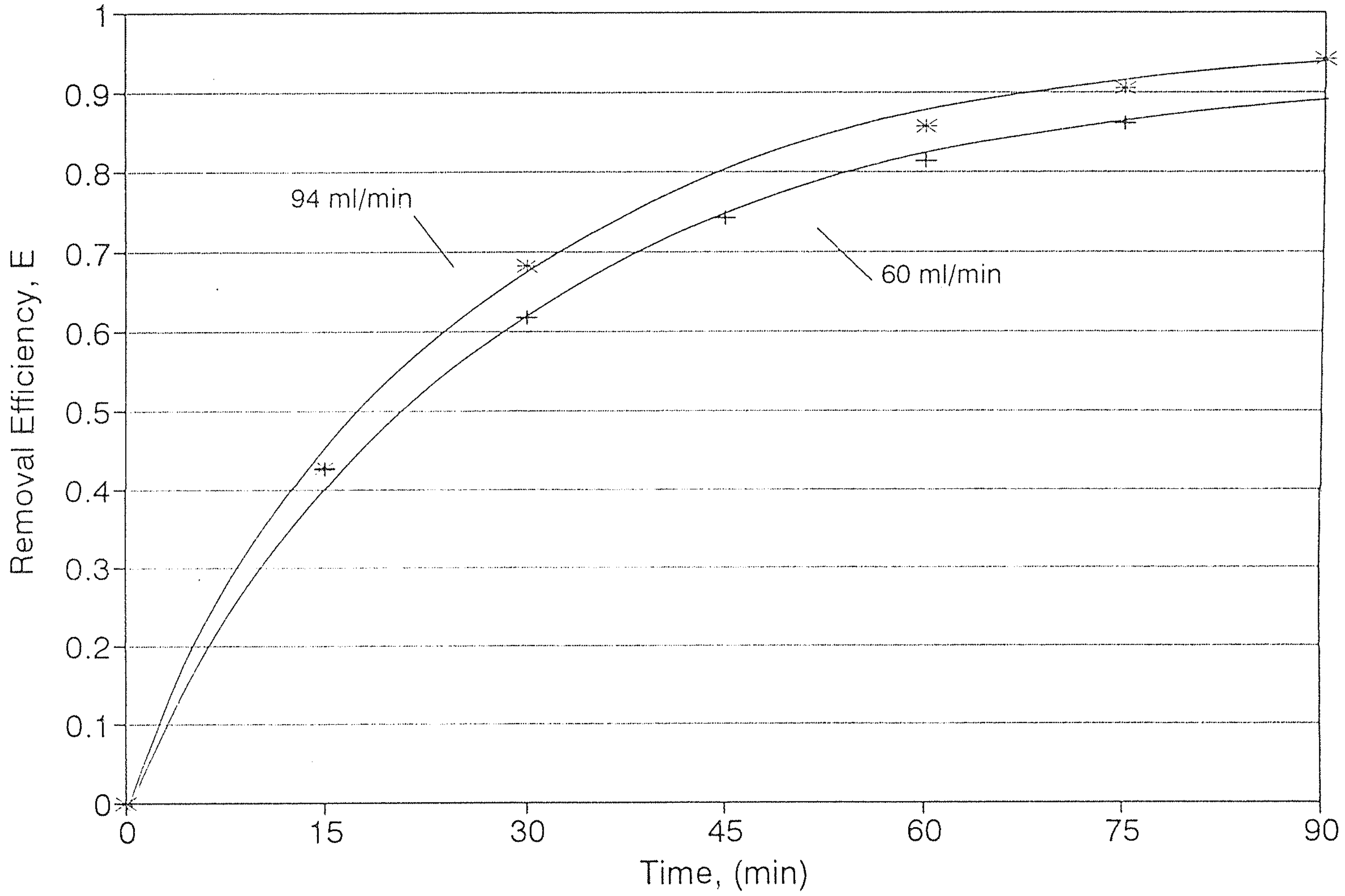

Figure 13 Effect of Air Flowrates on the Removal of Dichlorobenzene from Water by Solvent Sublation (10 mm, Paraffin Oil)

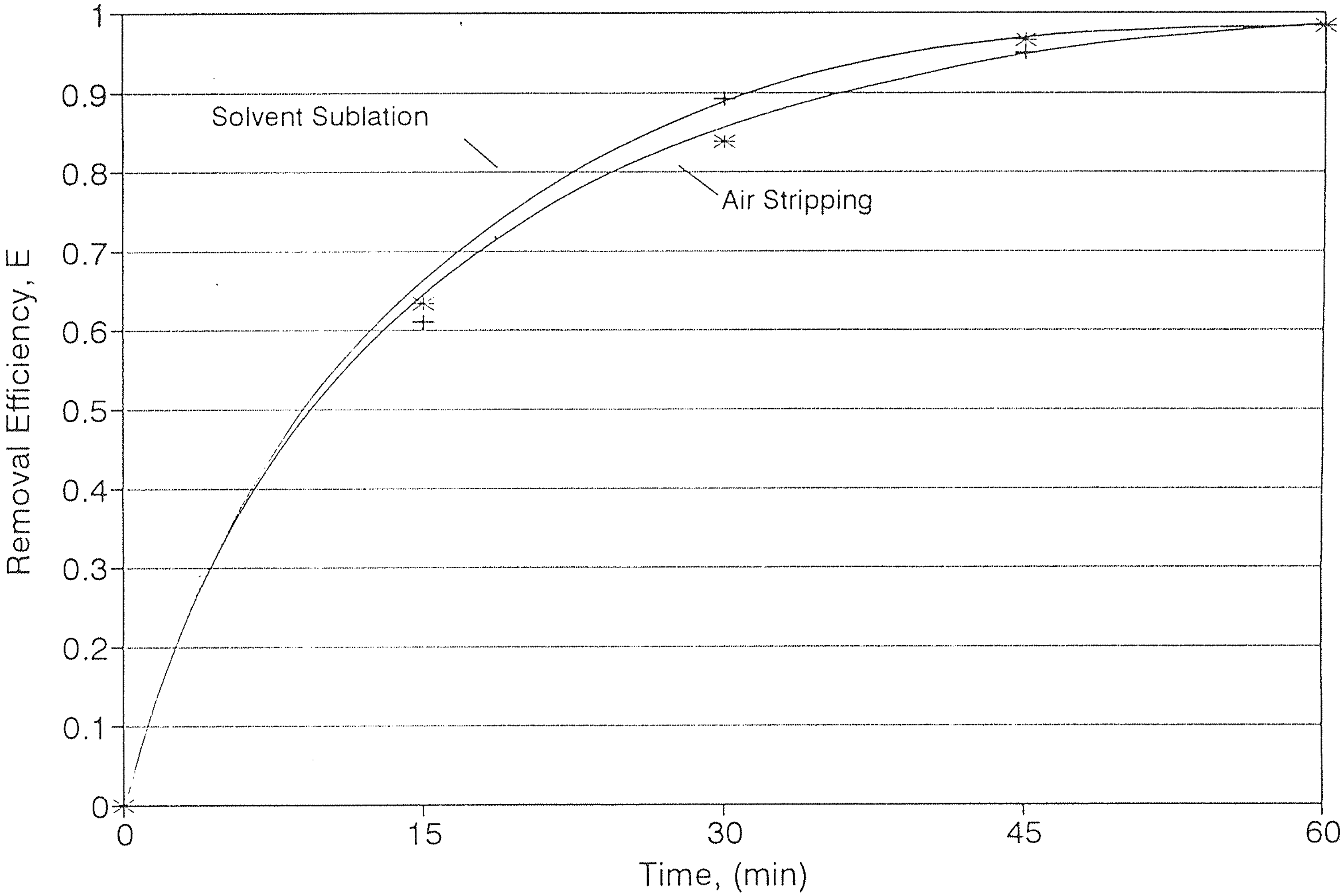

Figure 14 Comparison of Air Stripping and Solvent Sublation (10 mm Paraffin Oil) on the Removal of Trichloroethylene from Water at 60 ml/min

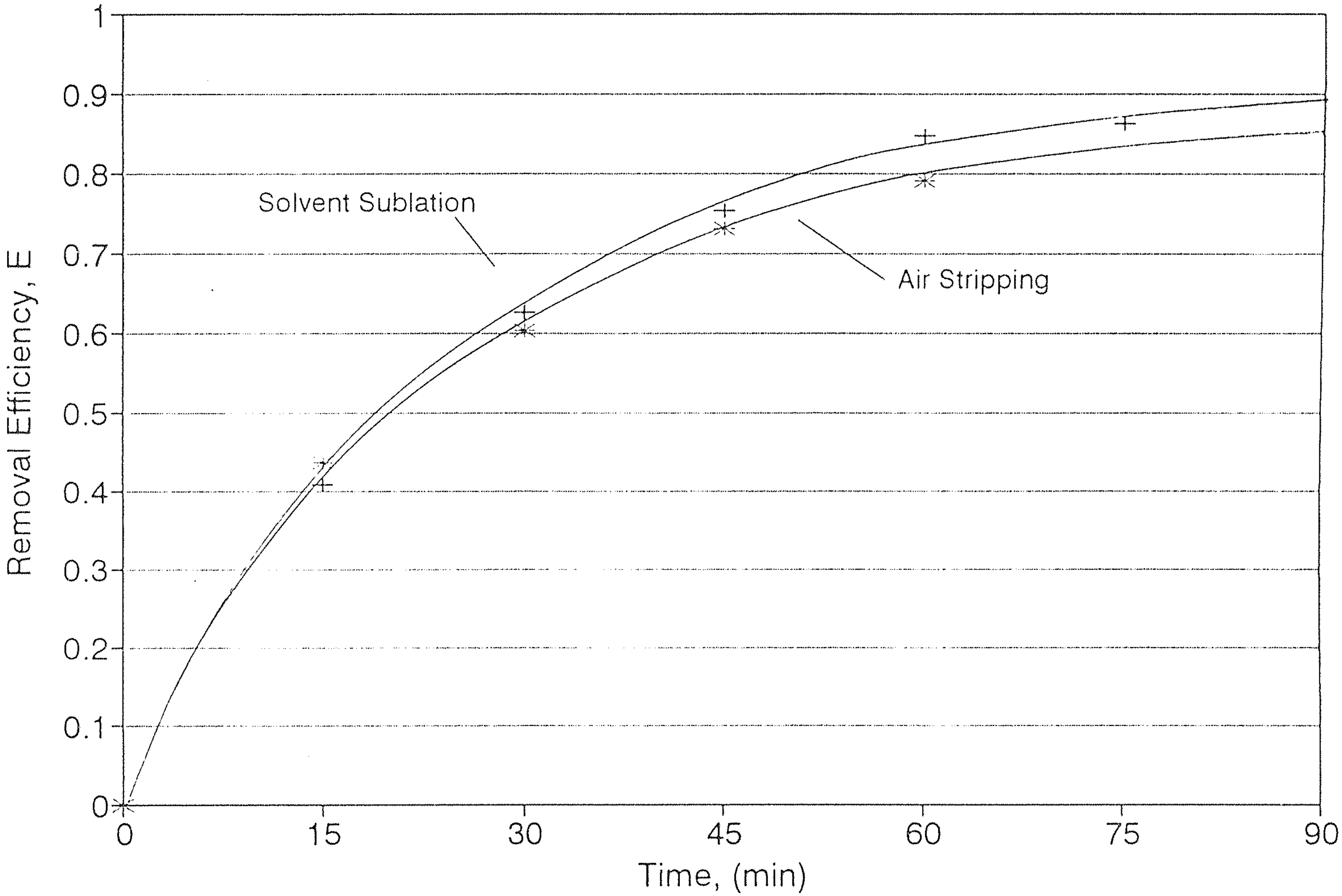

Figure 15 Comparison of Air Stripping and Solvent Sublation (10 mm, Paraffin Oil) on the Removal of Monochlorobenzene from Water at 60 ml/min

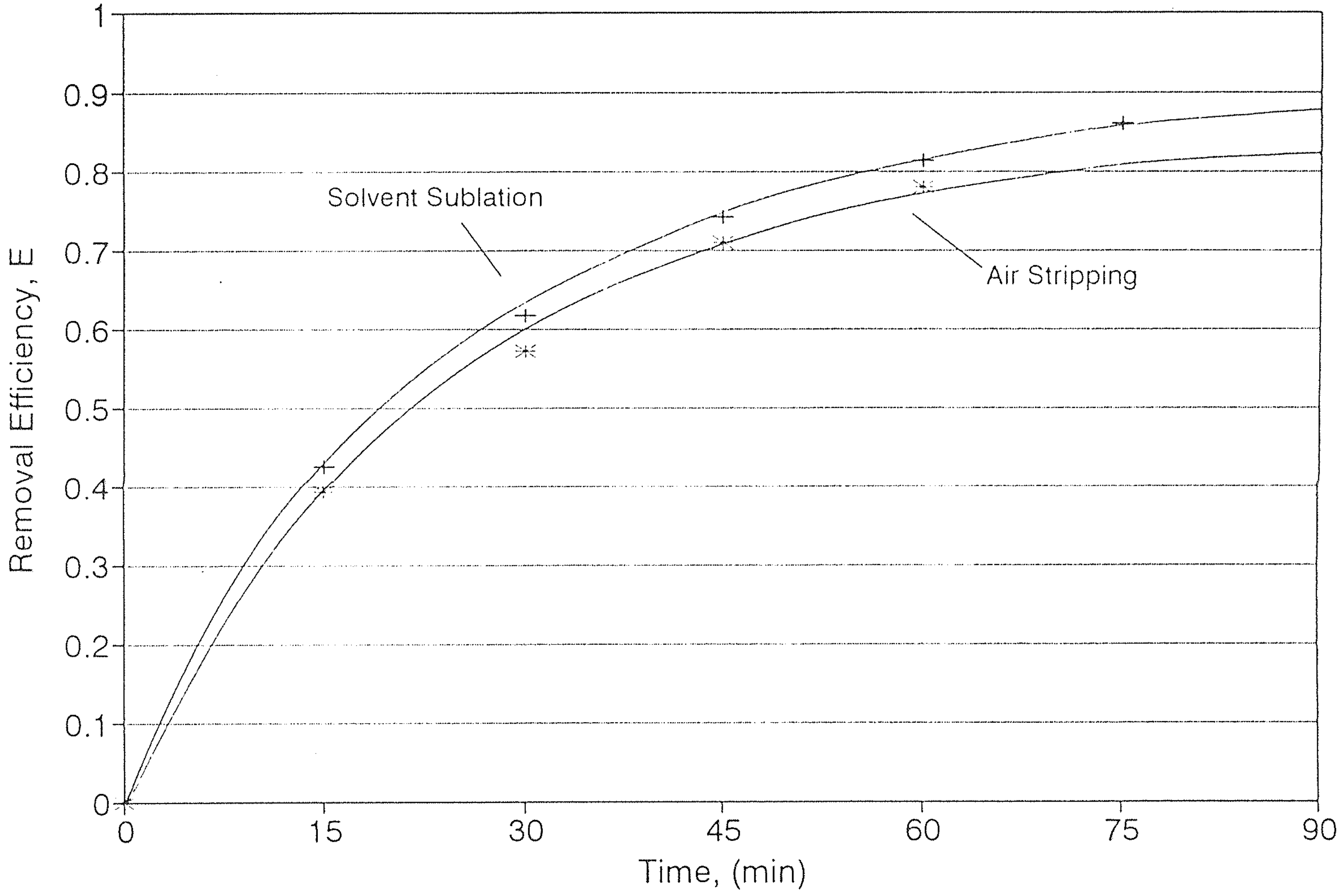

Figure 16 Comparison of Air Stripping and Solvent Sublation (10 mm, Paraffin Oil) on the Removal of Dichlorobenzene from Water at 60 ml/min

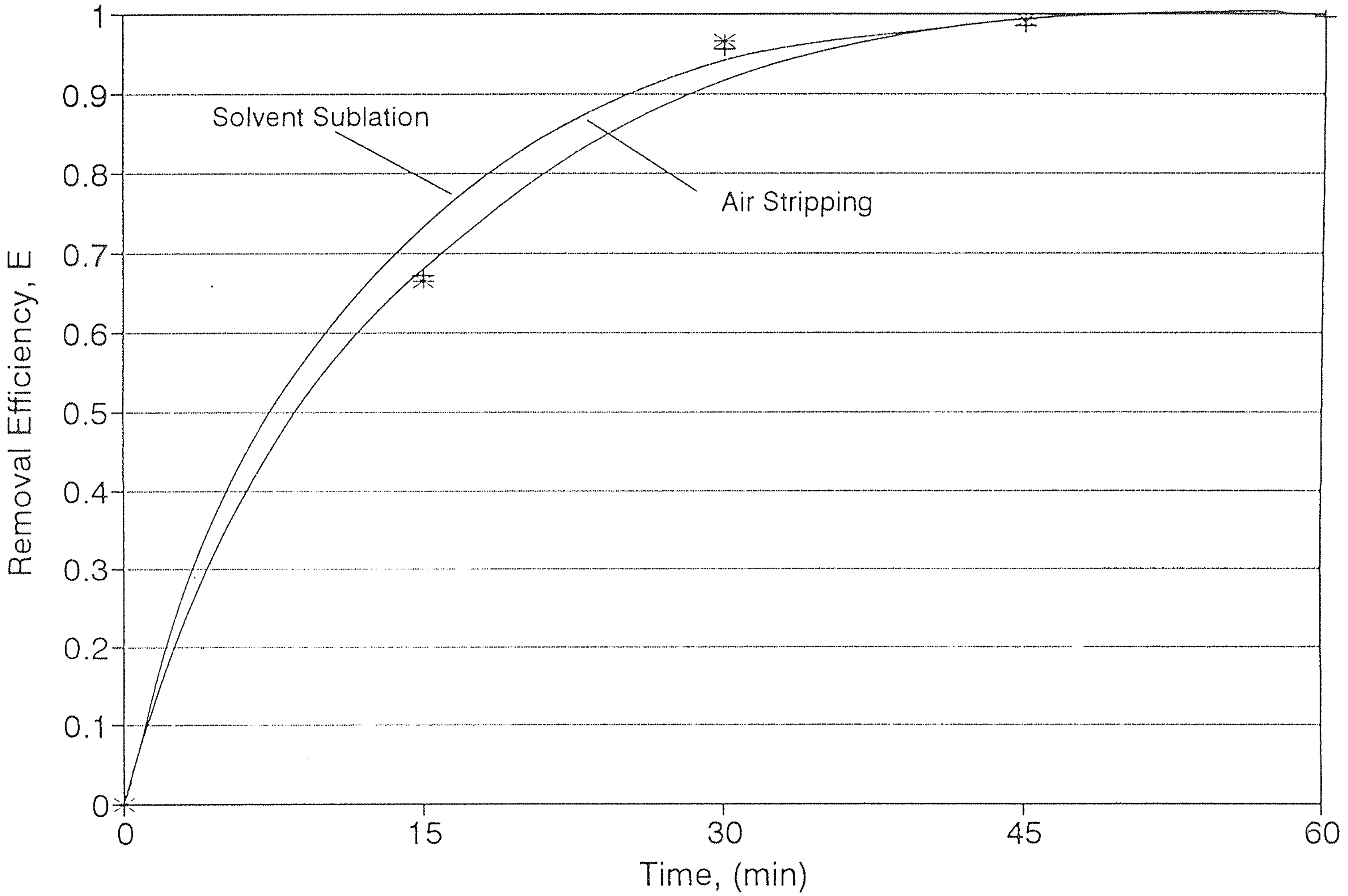

Figure 17 Comparison of Air Stripping and Solvent Sublation (10 mm, Paraffin Oil) on the Removal of Trichloroethylene from Water at 94 ml/min

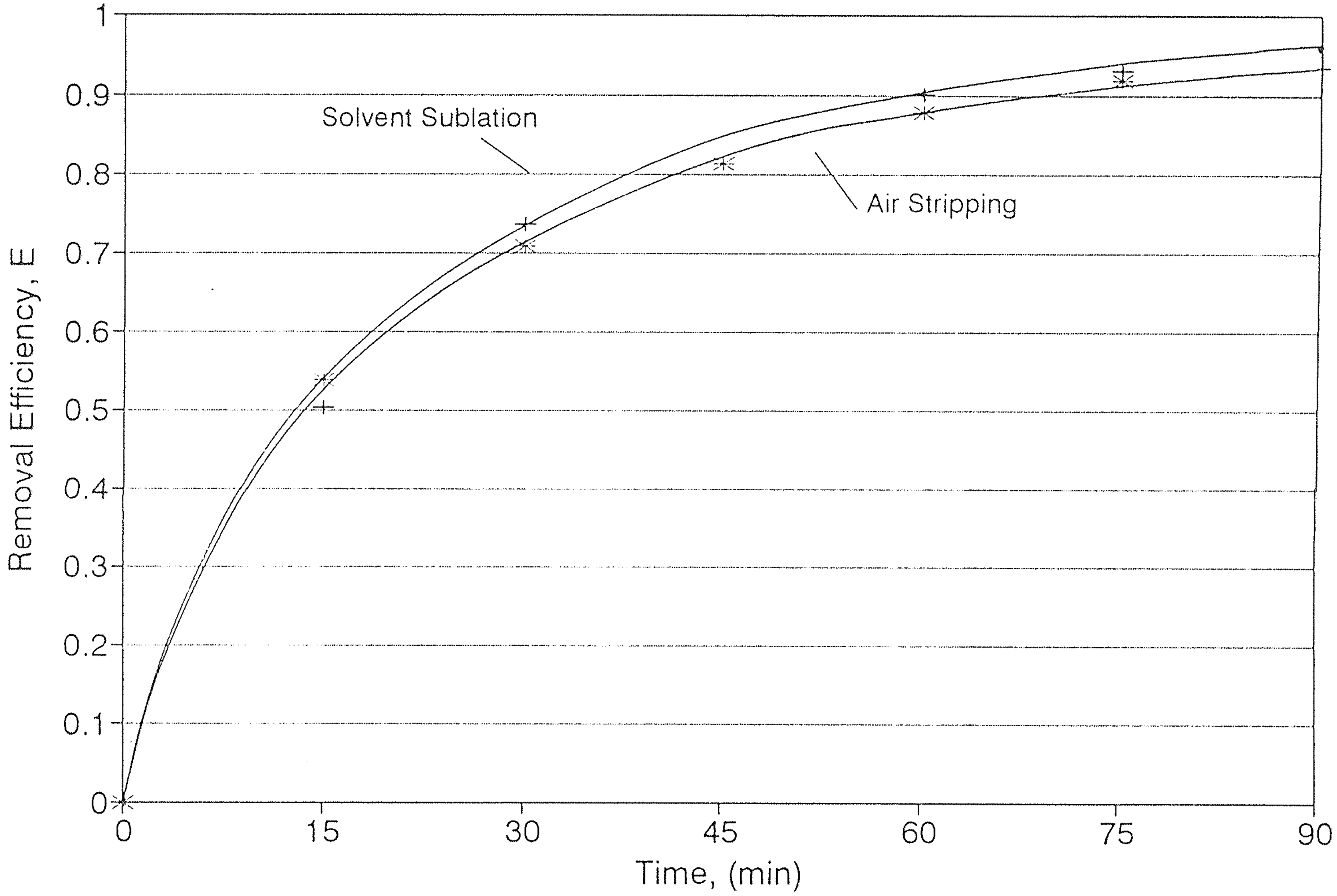

Figure 18 Comparison of Air Stripping and Solvent Sublation (10 mm, Paraffin Oil) on the Removal of Monochlorobenzene from Water at 94 ml/min

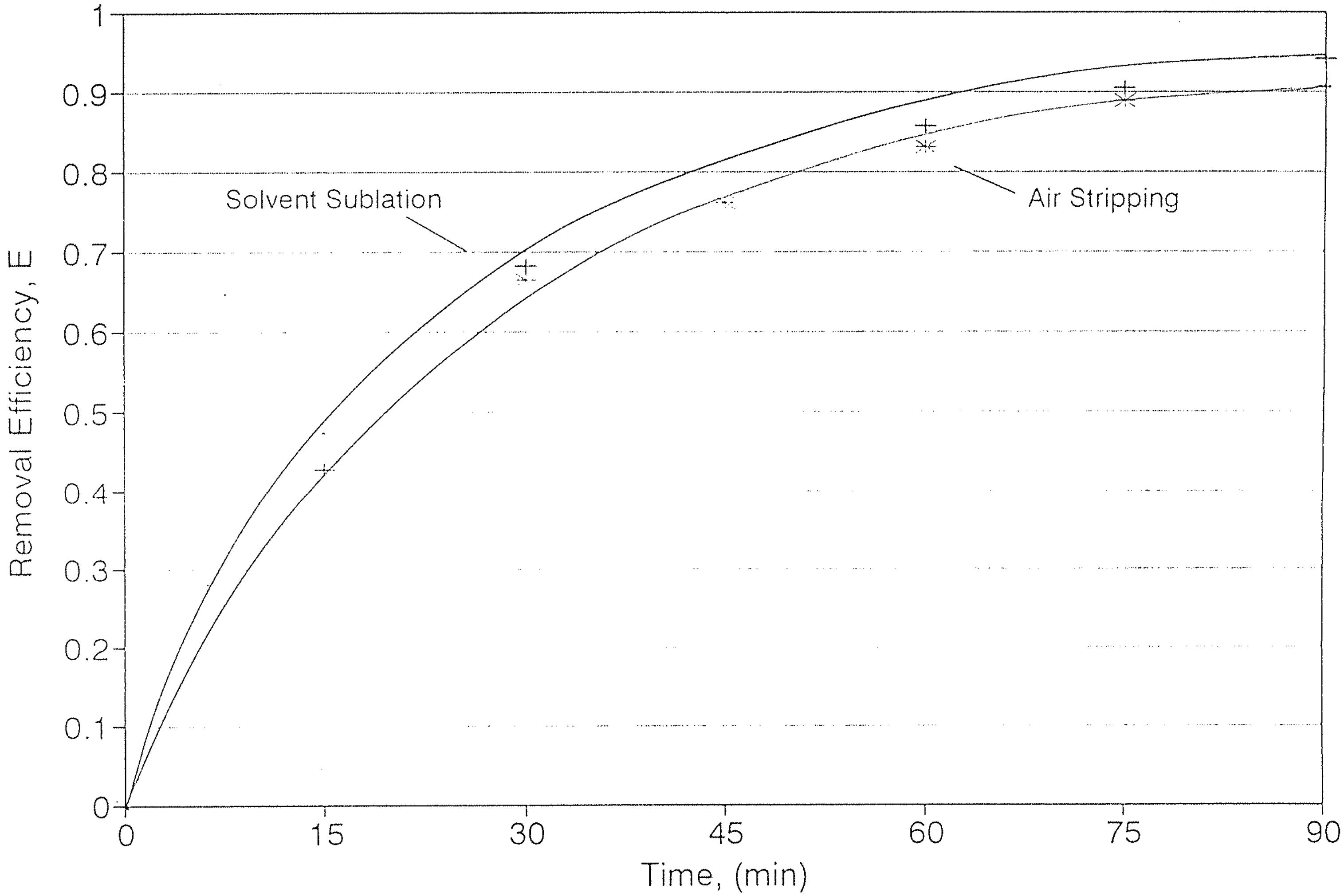

Figure 19 Comparison of Air Stripping and Solvent Sublation (10 mm, Paraffin Oil) on the Removal of Dichlorobenzene from Water at 94 ml/min

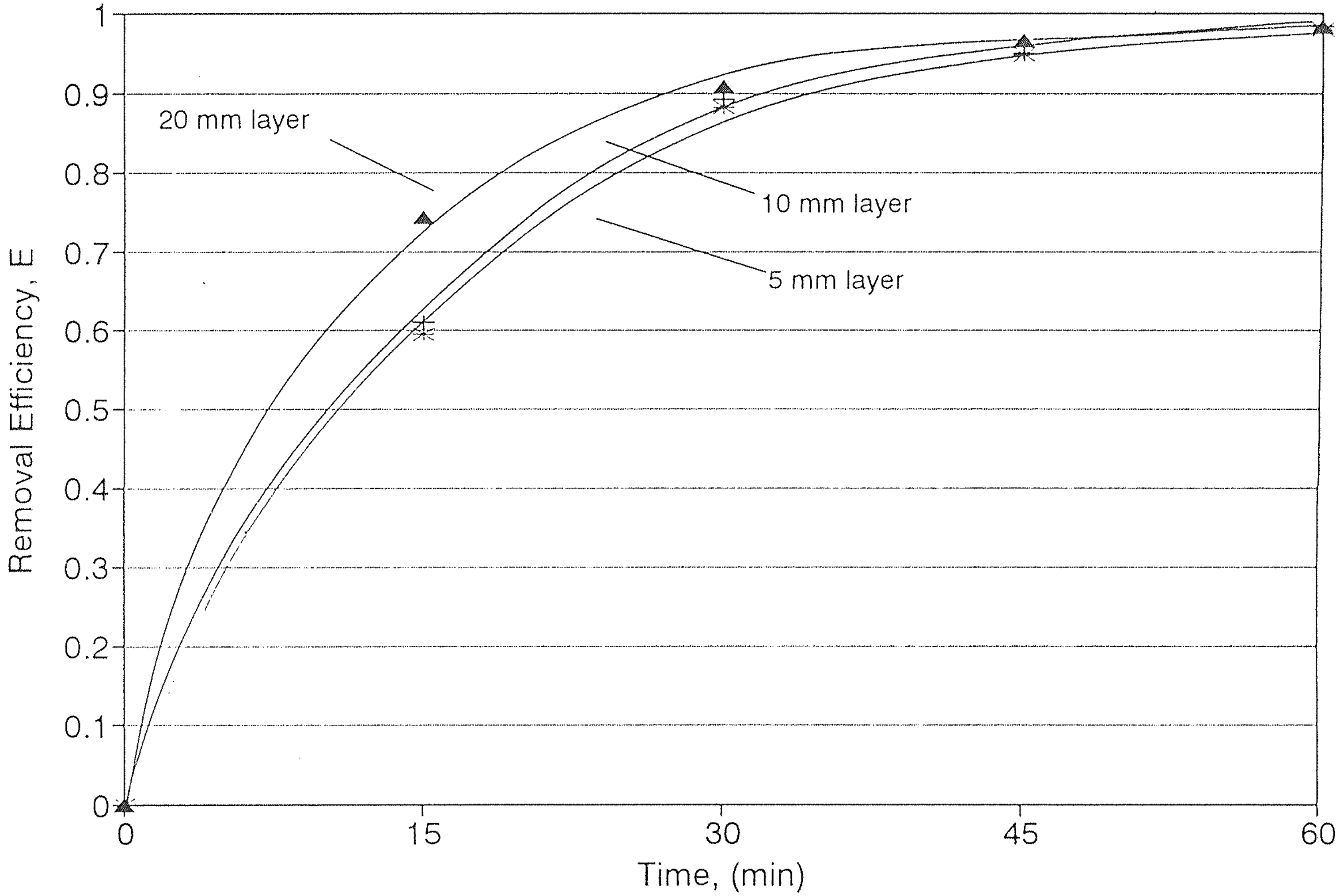

Figure 20 Effect of Different Thickness of Organic Layer on the Removal of Trichloroethylene from Water at 60 ml/min

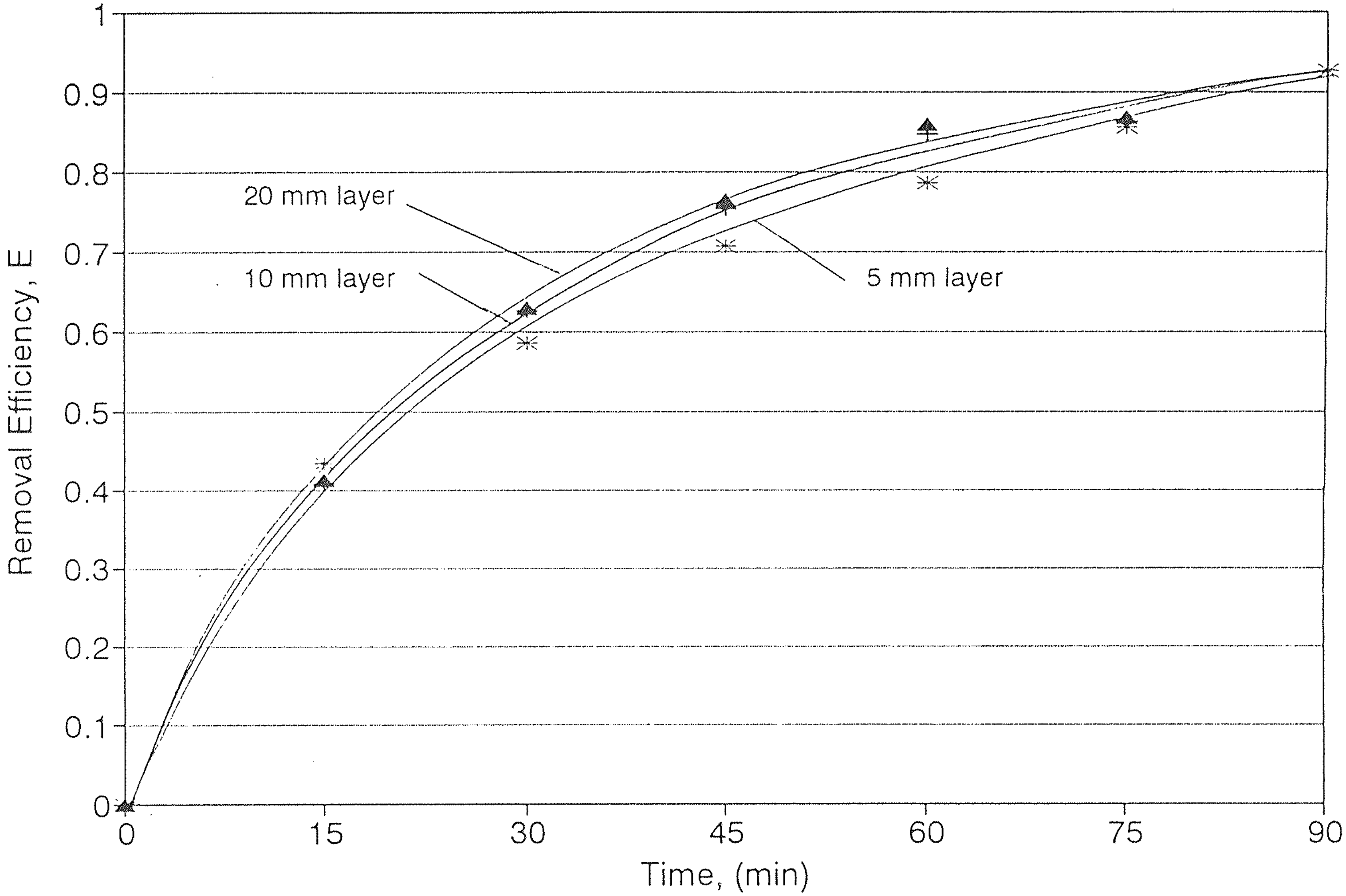

Figure 21 Effect of Different Thickness of Organic Layer on the Removal of Monochlorobenzene from Water at 60 ml/min

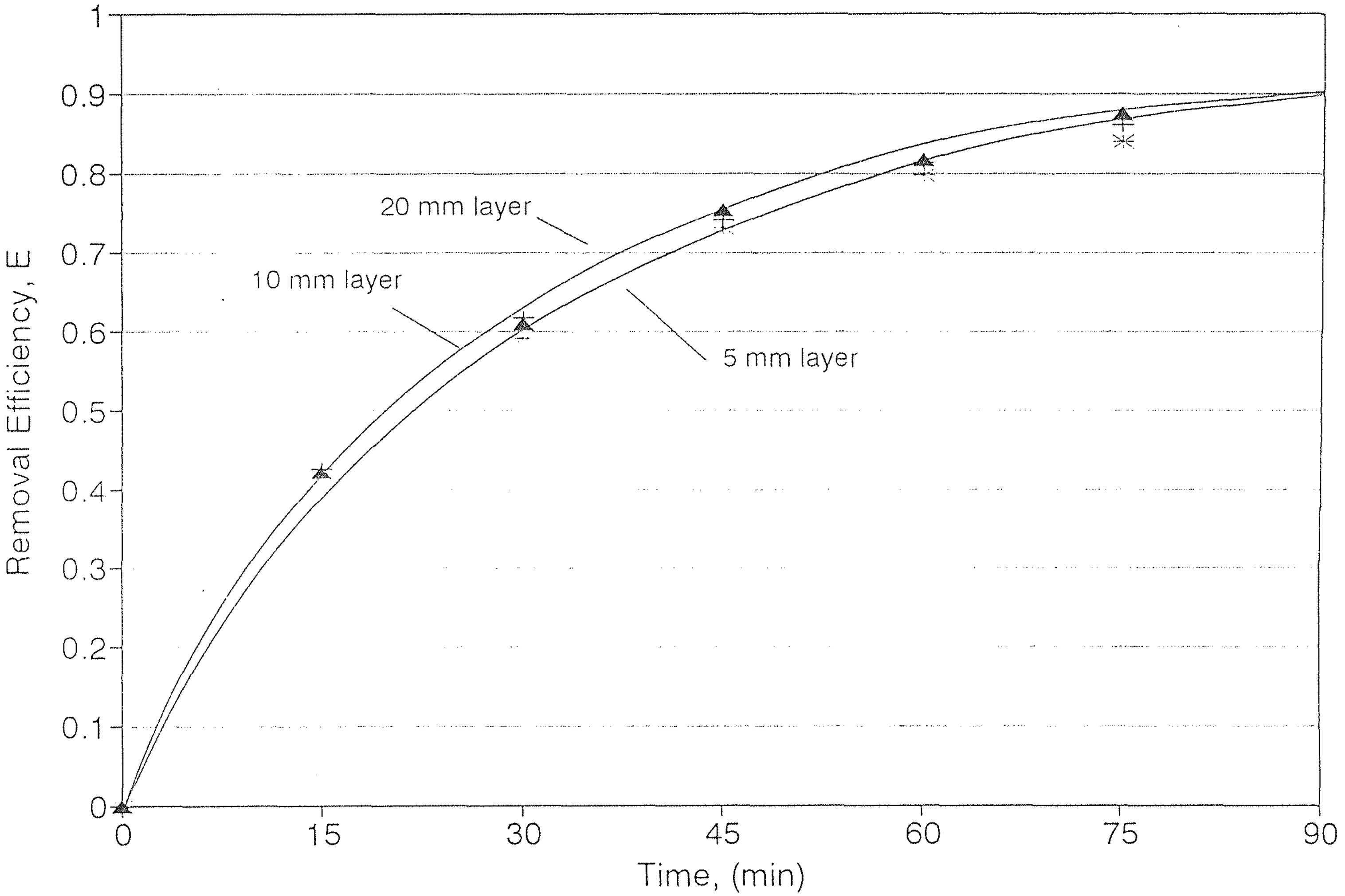

Figure 22 Effect of Different Thickness of Organic Layer on the Removal of Dichlorobenzene from Water at 60 ml/min

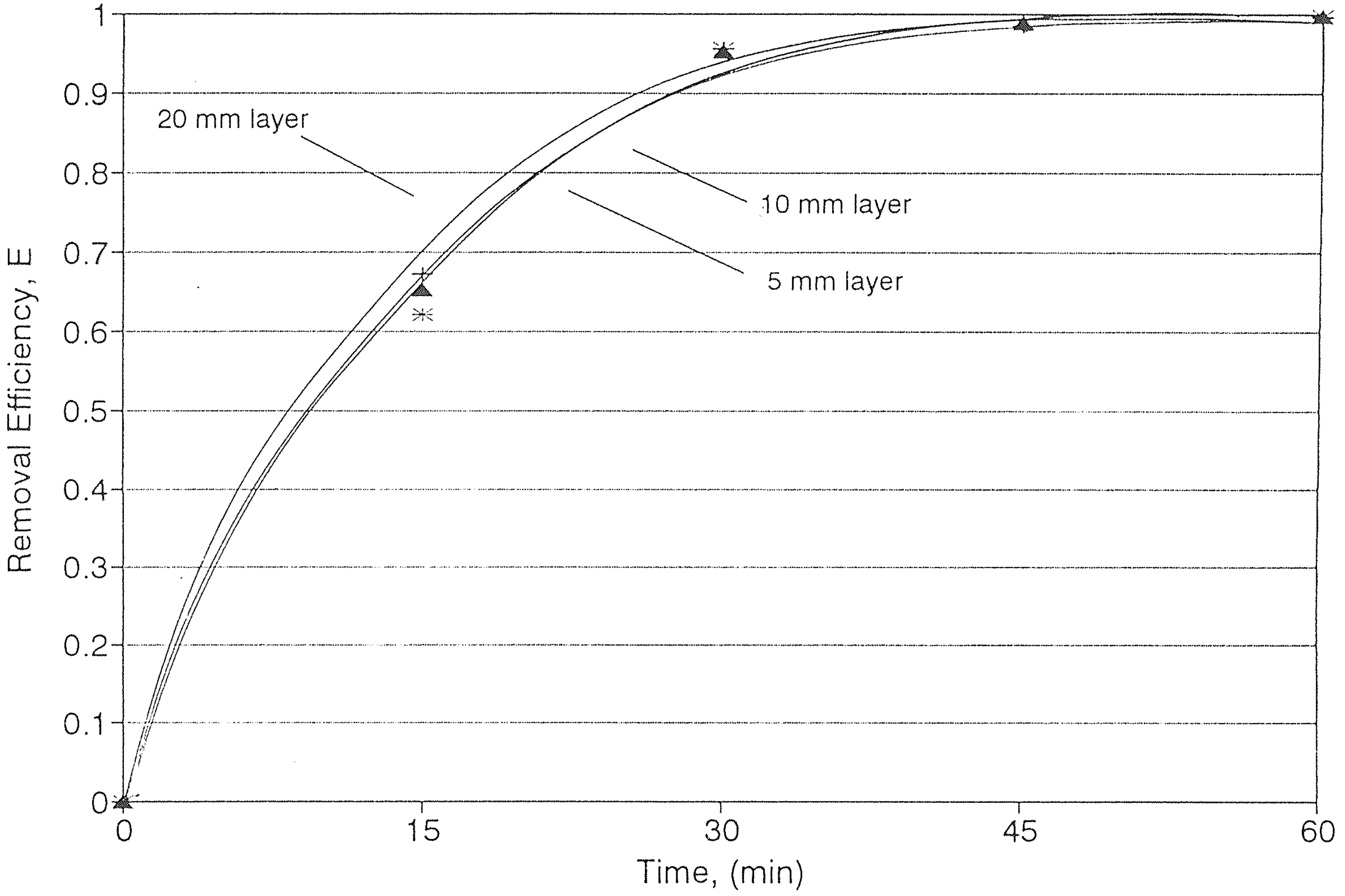

Figure 23 Effect of Different Thickness of Organic Layer on the Removal of Trichloroethylene from Water at 94 ml/min

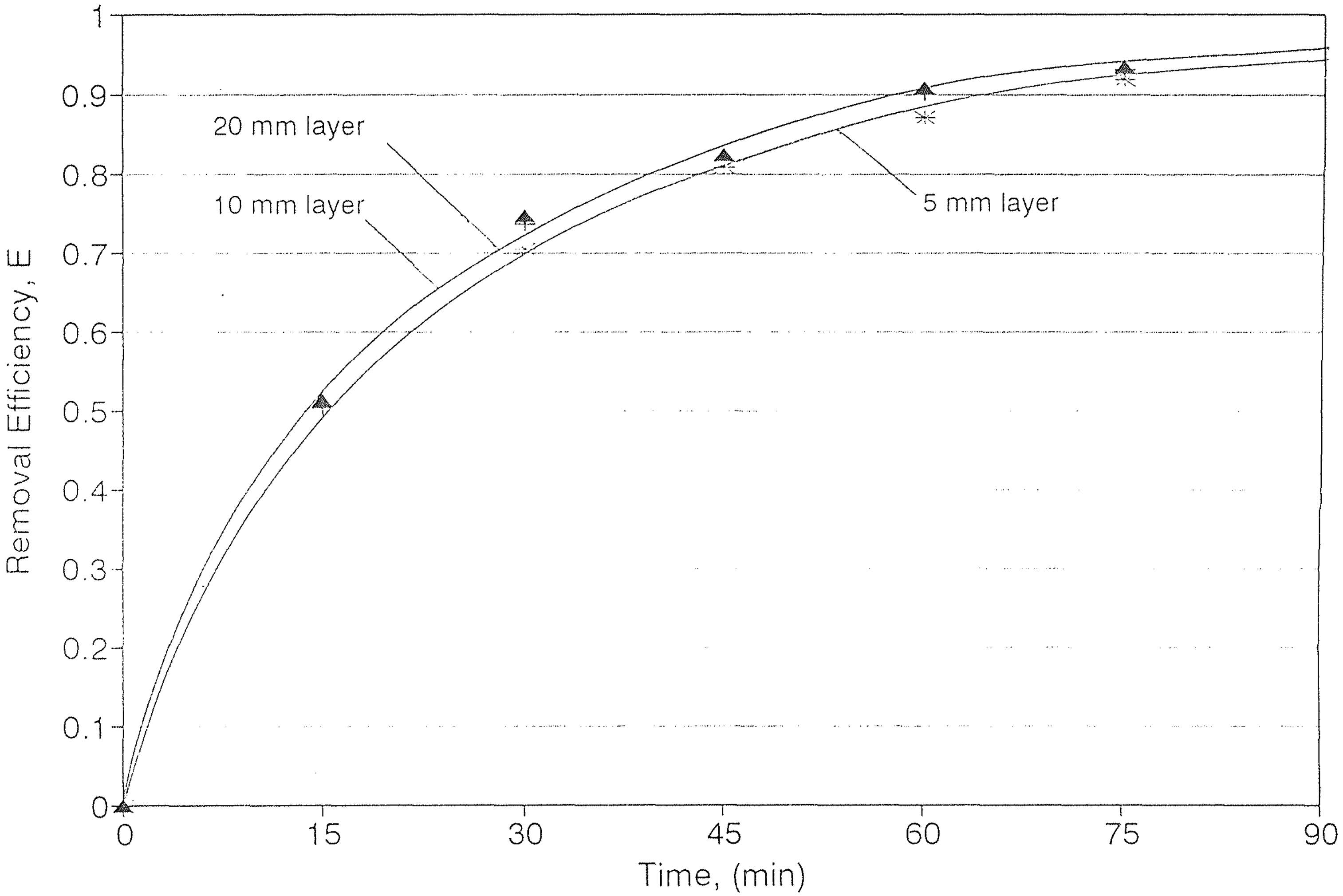

Figure 24 Effect of Different Thickness of Organic Layer on the Removal of Monochlorobenzene from Water at 94 ml/min

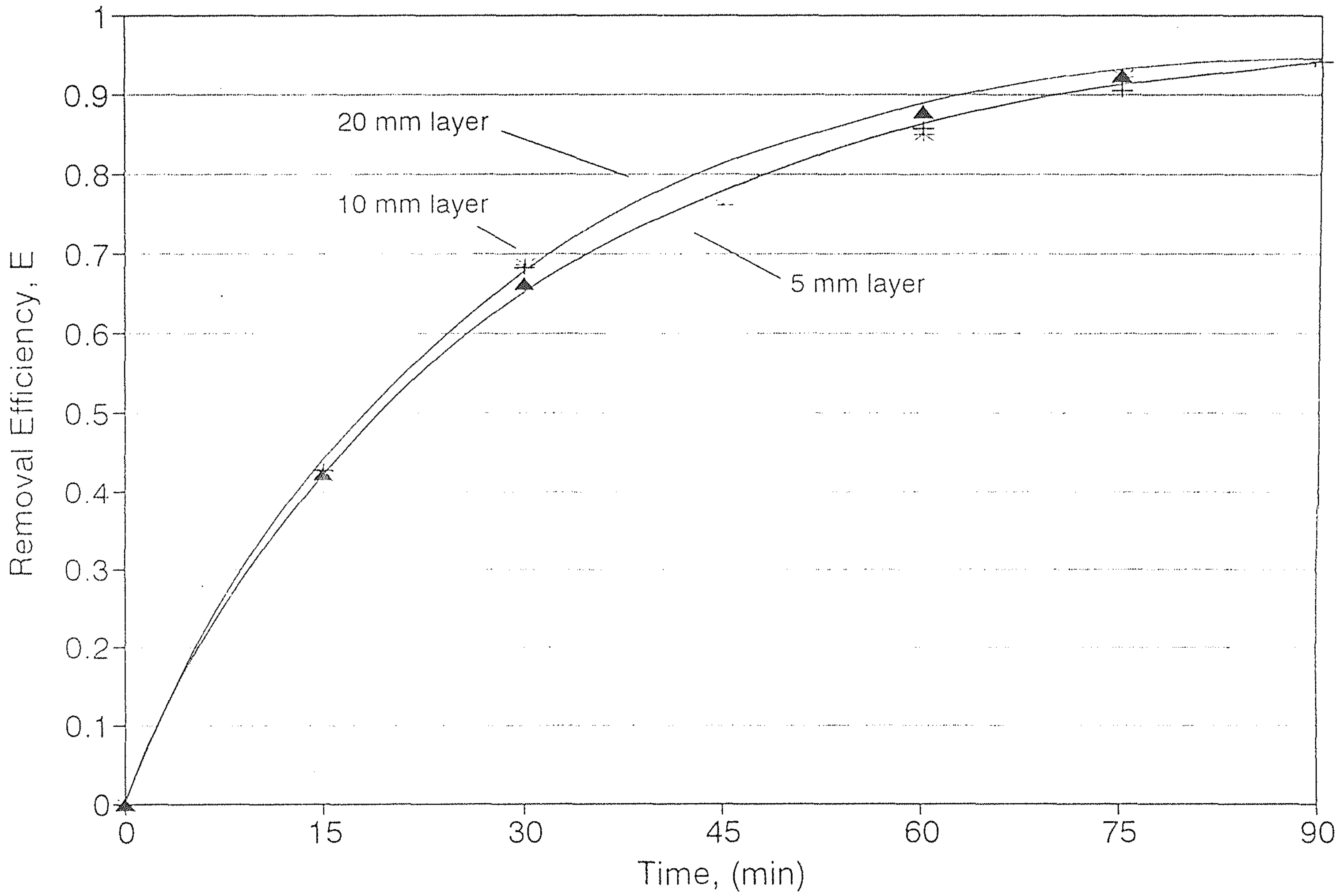

Figure 25 Effect of Different Thickness of Organic Layer on the Removal of Dichlorobenzene from Water at 94 ml/min

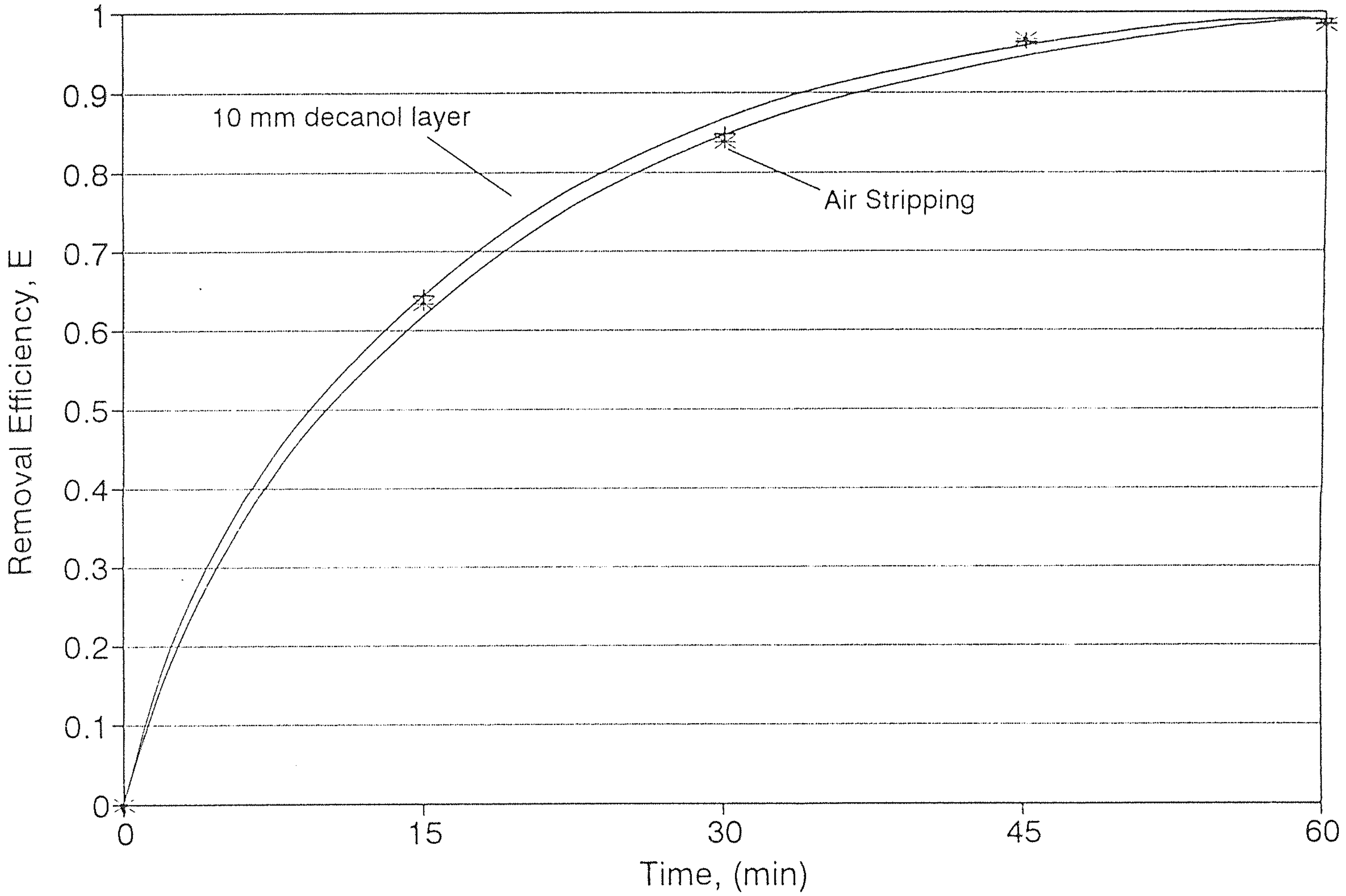

Figure 26 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Trichloroethylene from Water at 60 ml/min

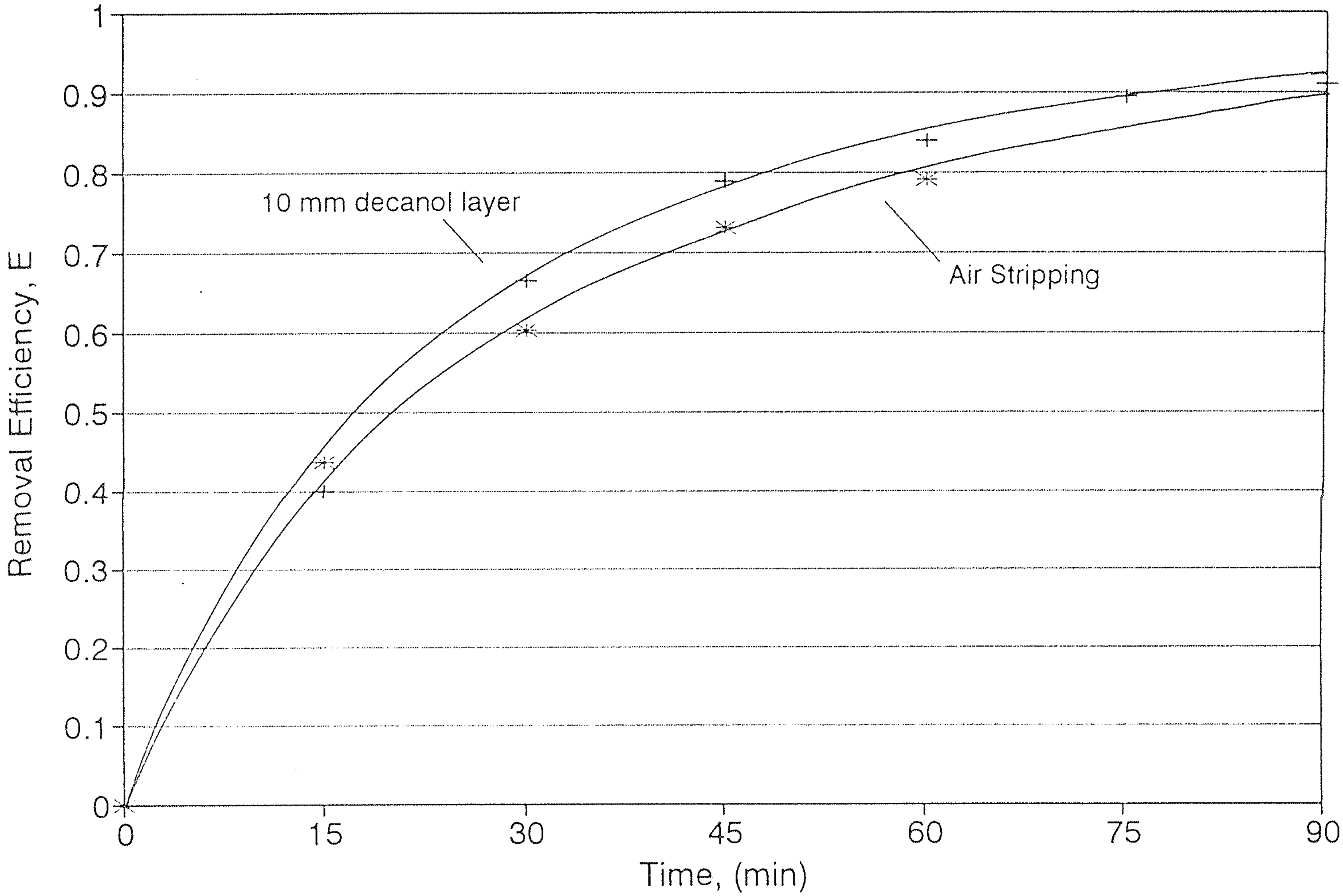

Figure 27 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Monochlorobenzene from Water at 60 ml/min

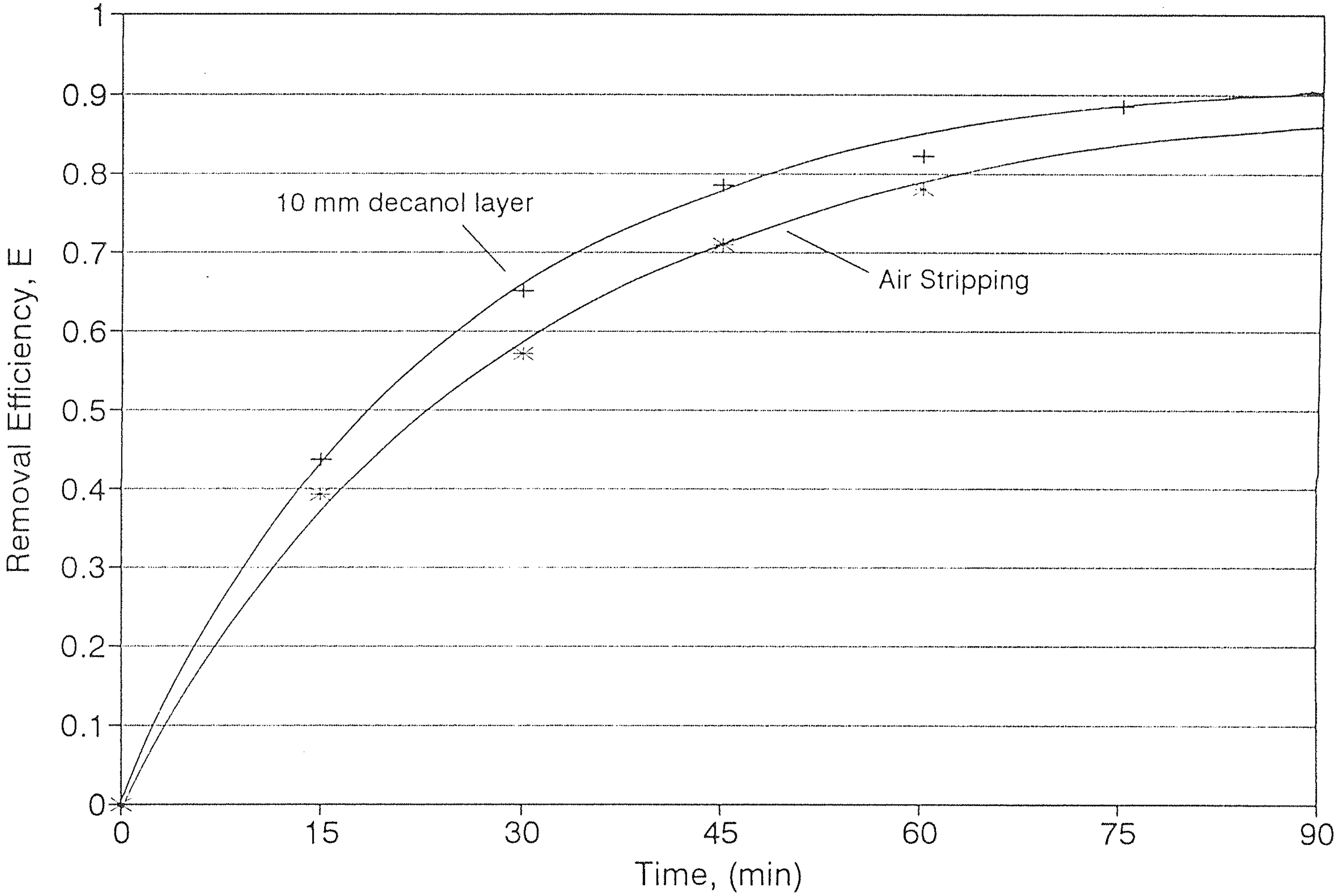

Figure 28 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Dichlorobenzene from Water at 60 ml/min

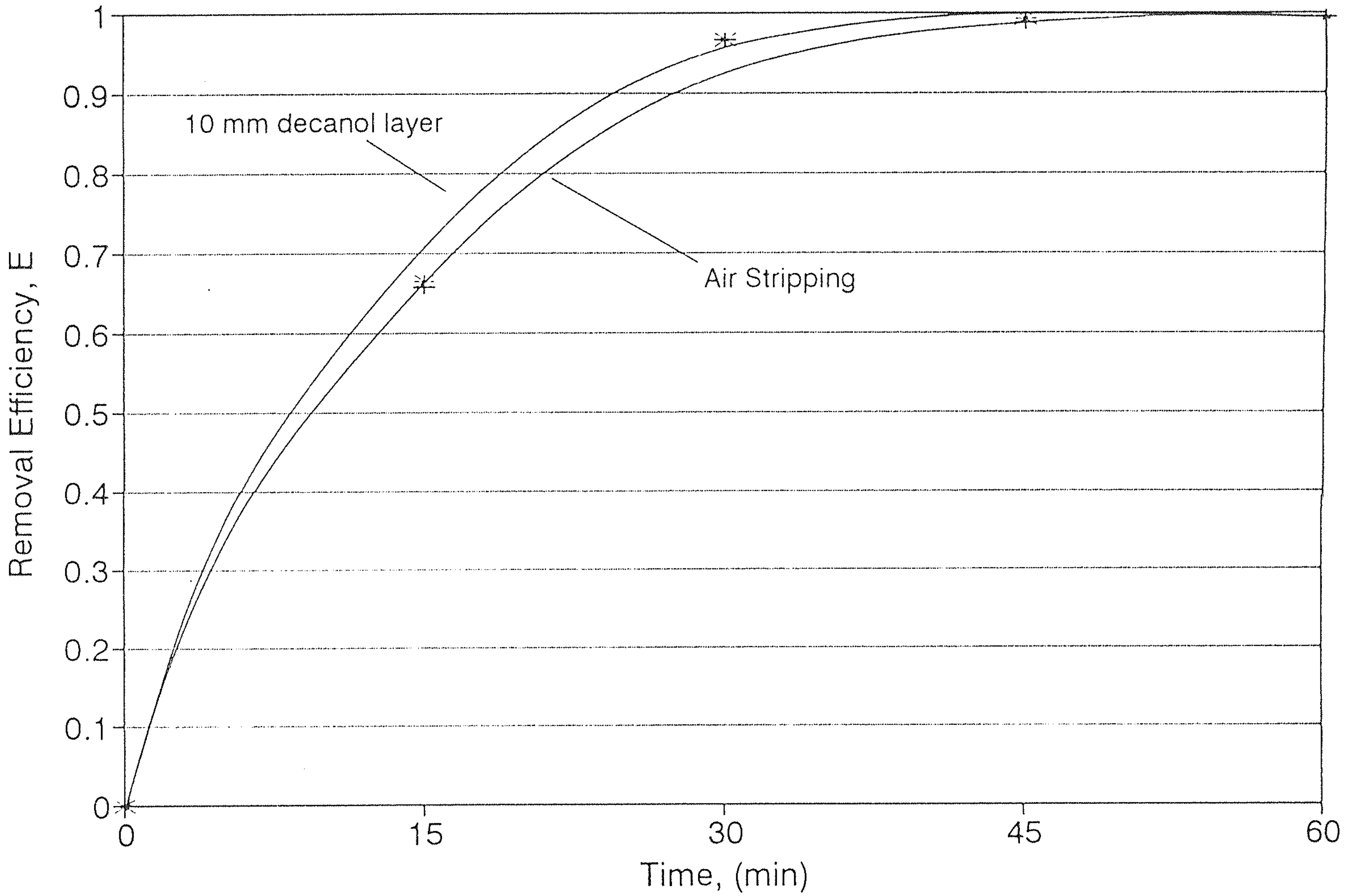

Figure 29 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Trichloroethvlene from Water at 94 ml/min

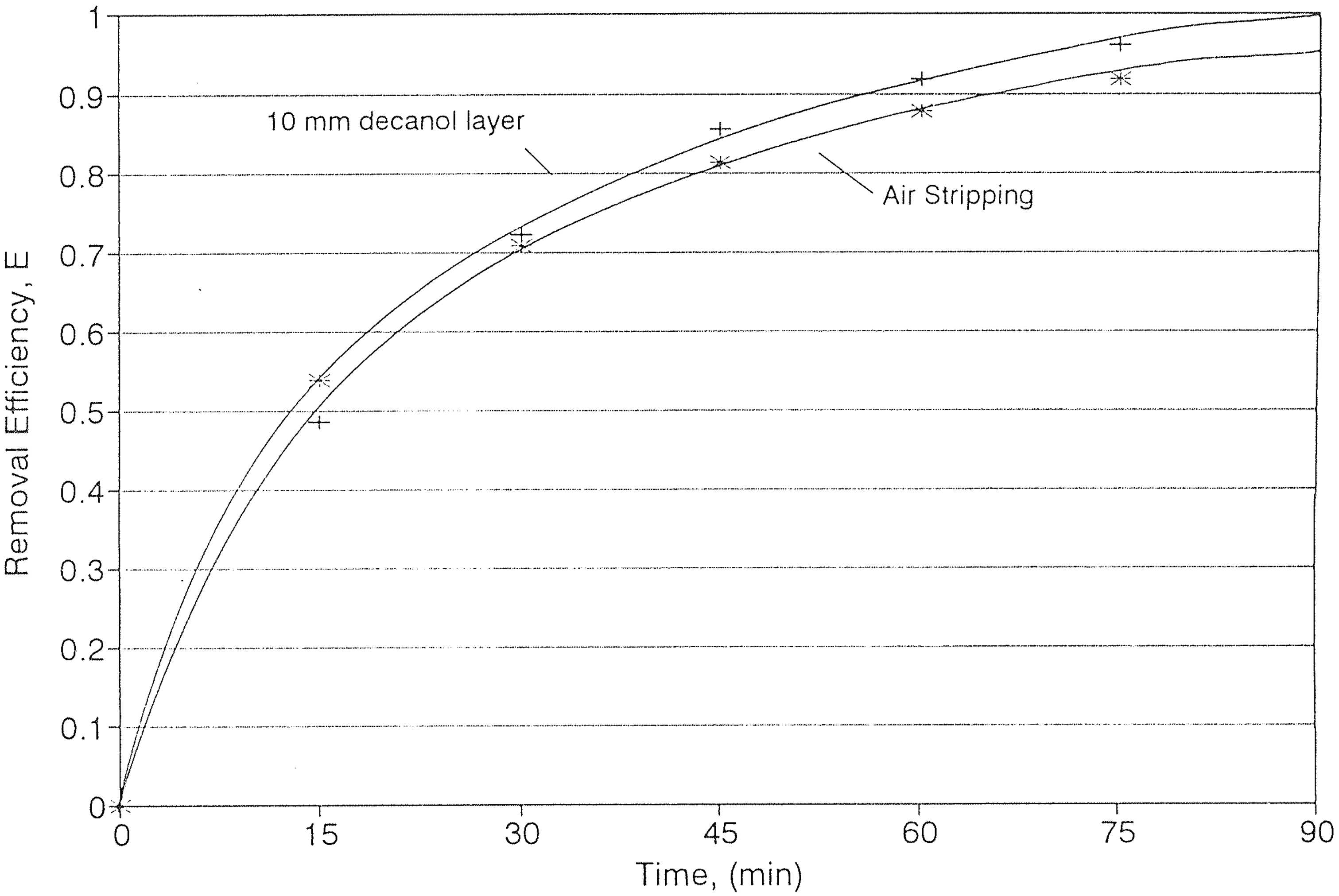

Figure 30 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Monochlorobenzene from Water at 94 ml/min

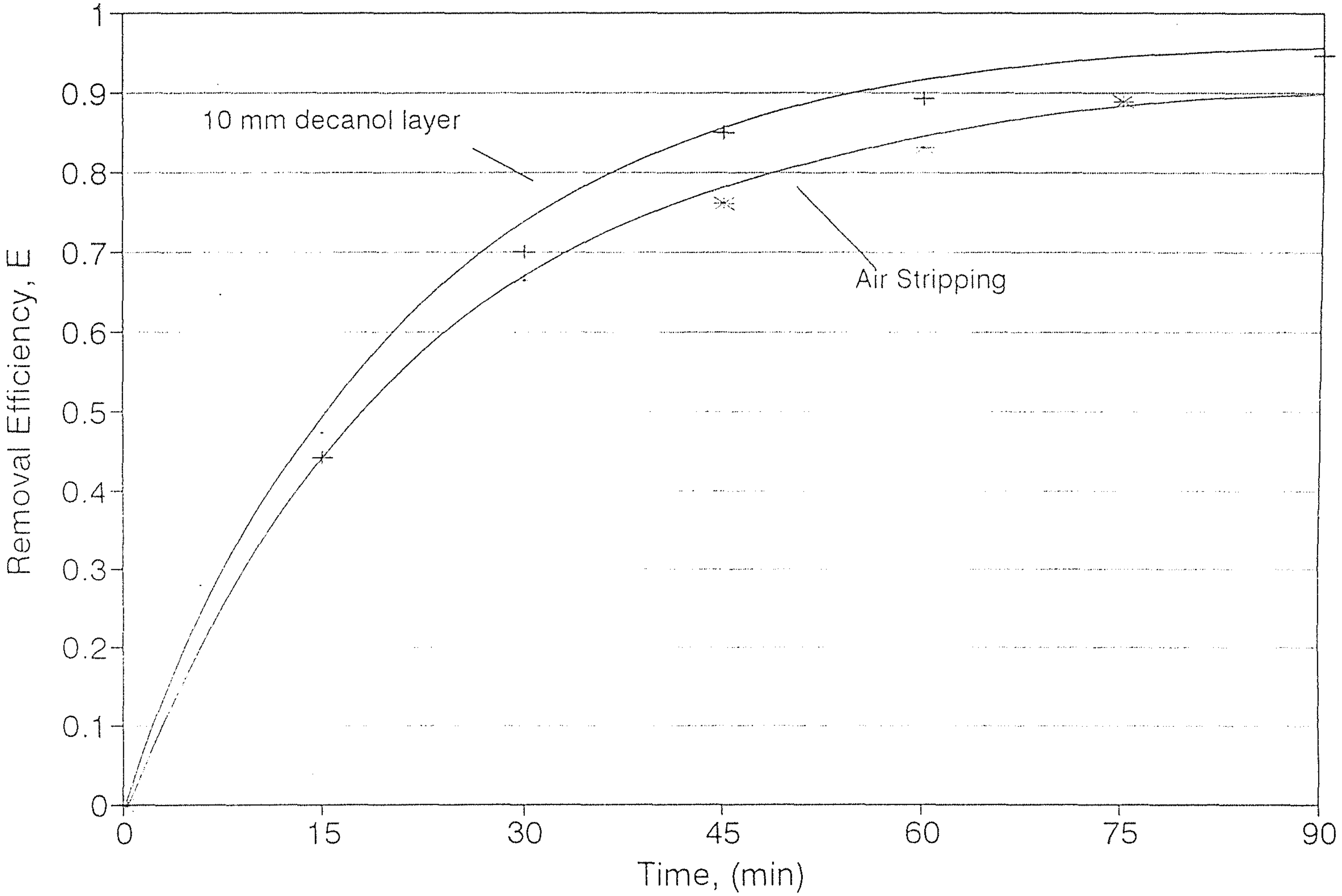

Figure 31 Comparison of Air Stripping and Solvent Sublation (10 mm, Decanol) on the Removal of Dichlorobenzene from Water at 94 ml/min

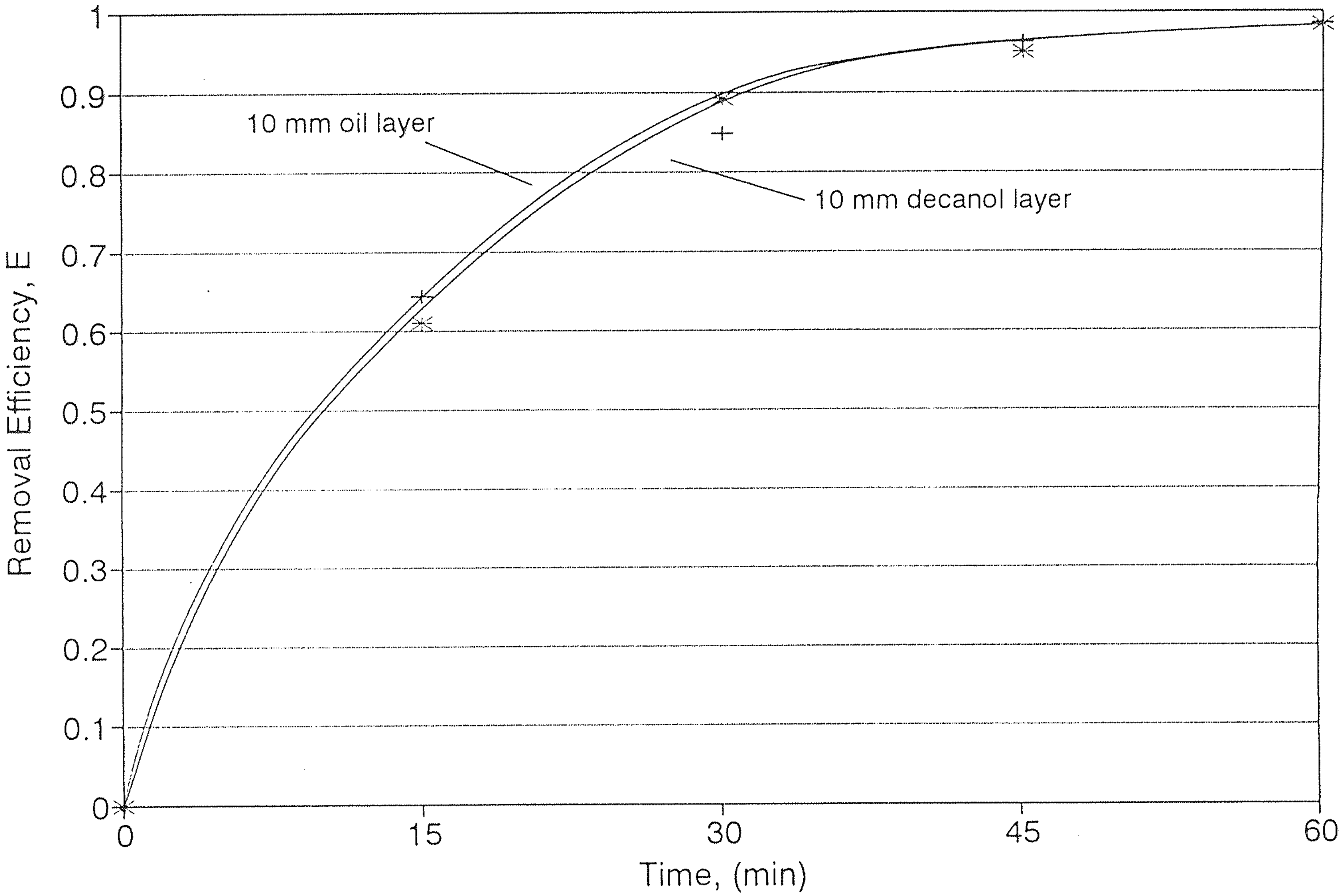

Figure 32 Effect of Different Organic Layers on the Removal of Trichloroethylene from Water at 60 ml/min

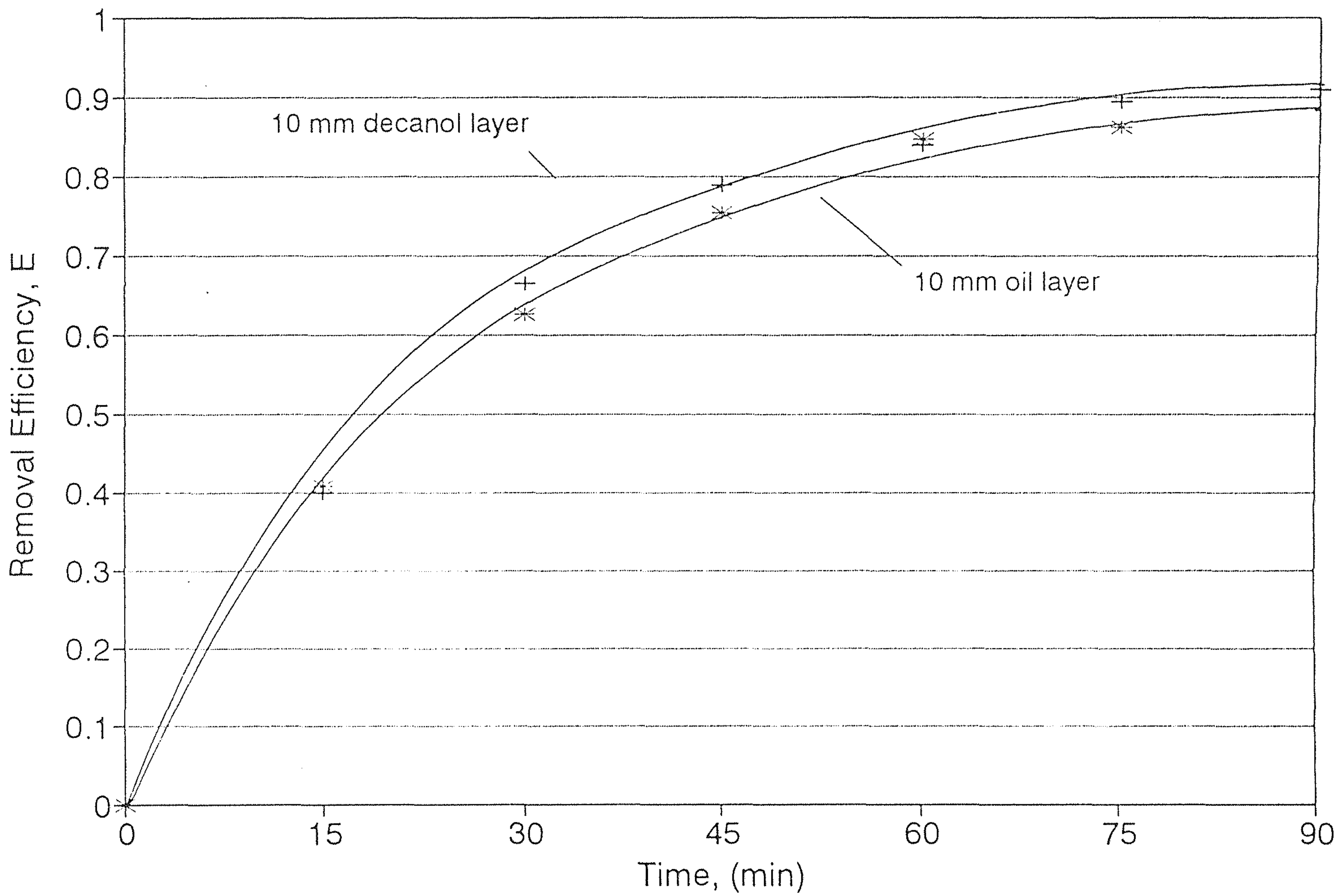

Figure 33 Effect of Different Organic Layers on the Removal of Monochlorobenzene from Water at 60 ml/min

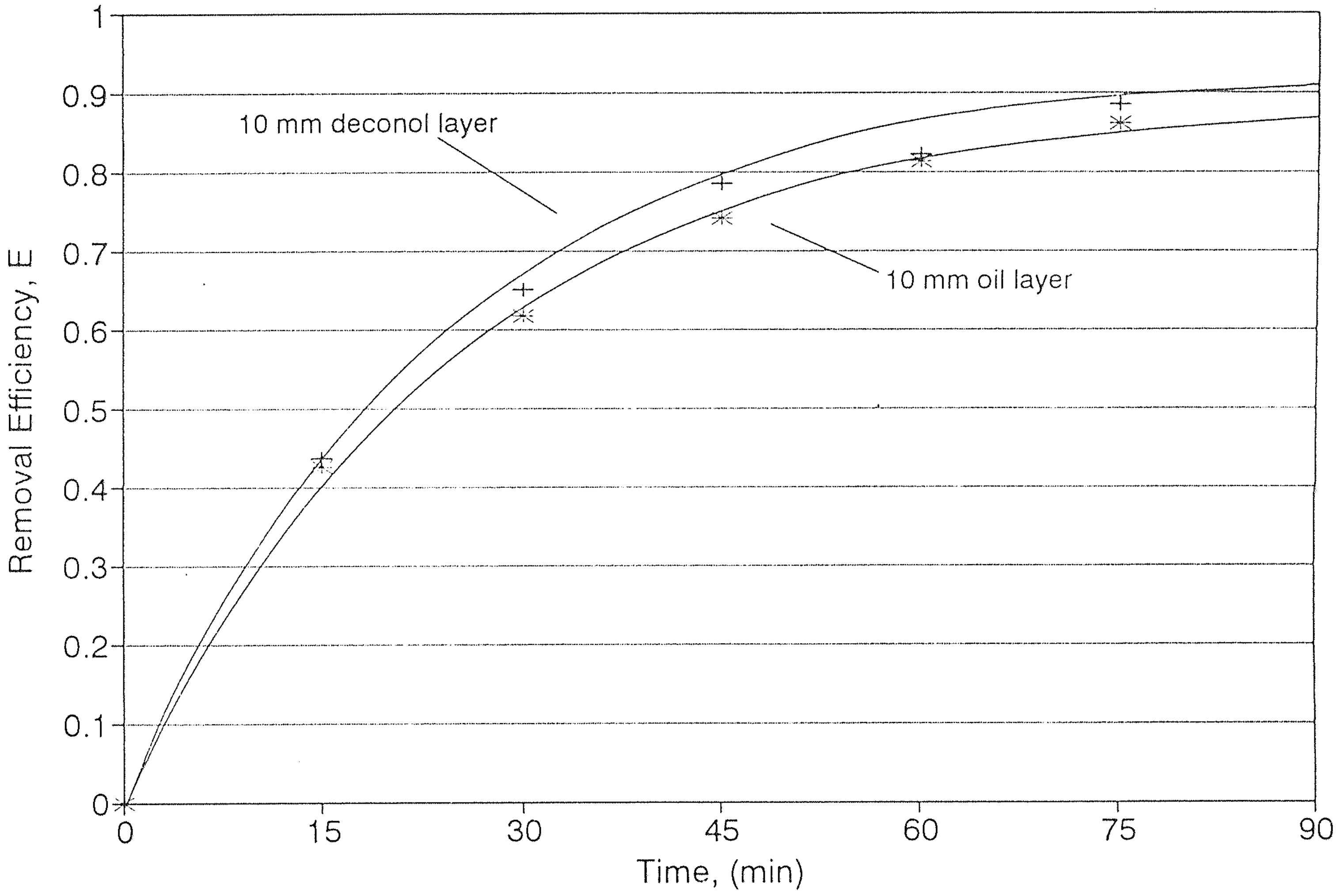

Figure 34 Effect of Different Organic Layers on the Removal of Dichlorobenzene from Water at 60 ml/min

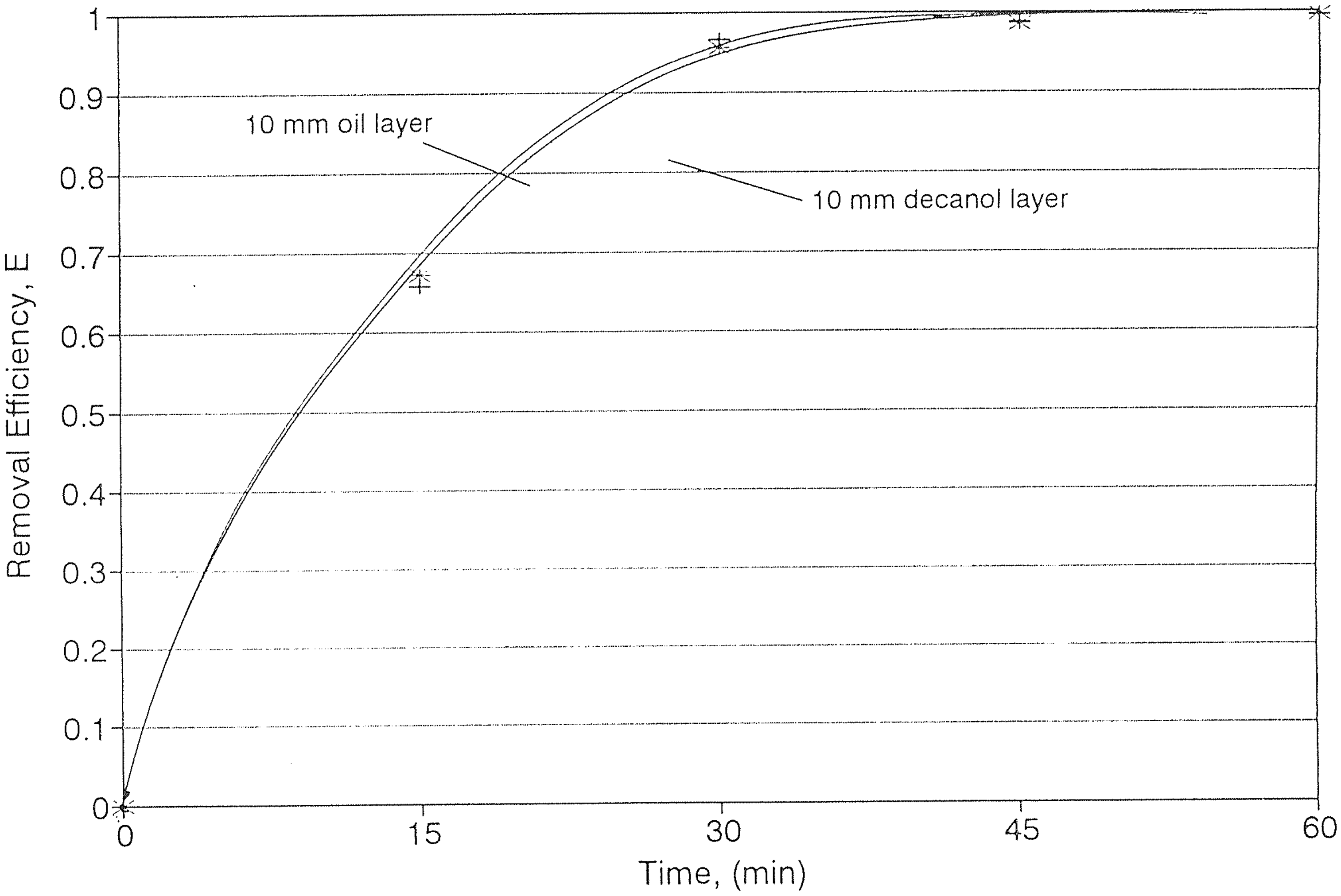

Figure 35 Effect of Different Organic Layers on the Removal of Trichloroethylene from Water at 94 ml/min

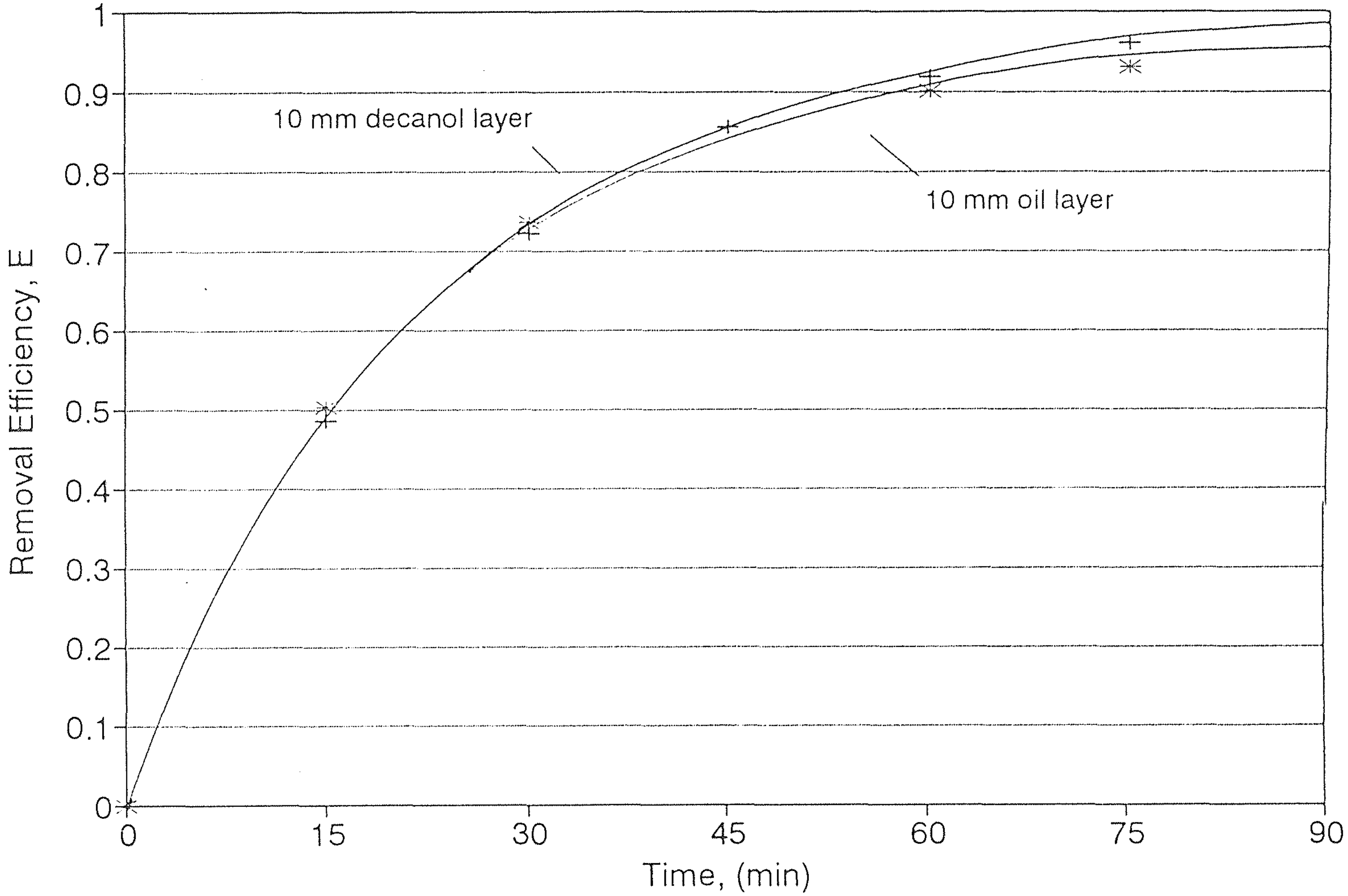

Figure 36 Effect of Different Organic Layers on the Removal of Monochlorobenzene from Water at 94 ml/min

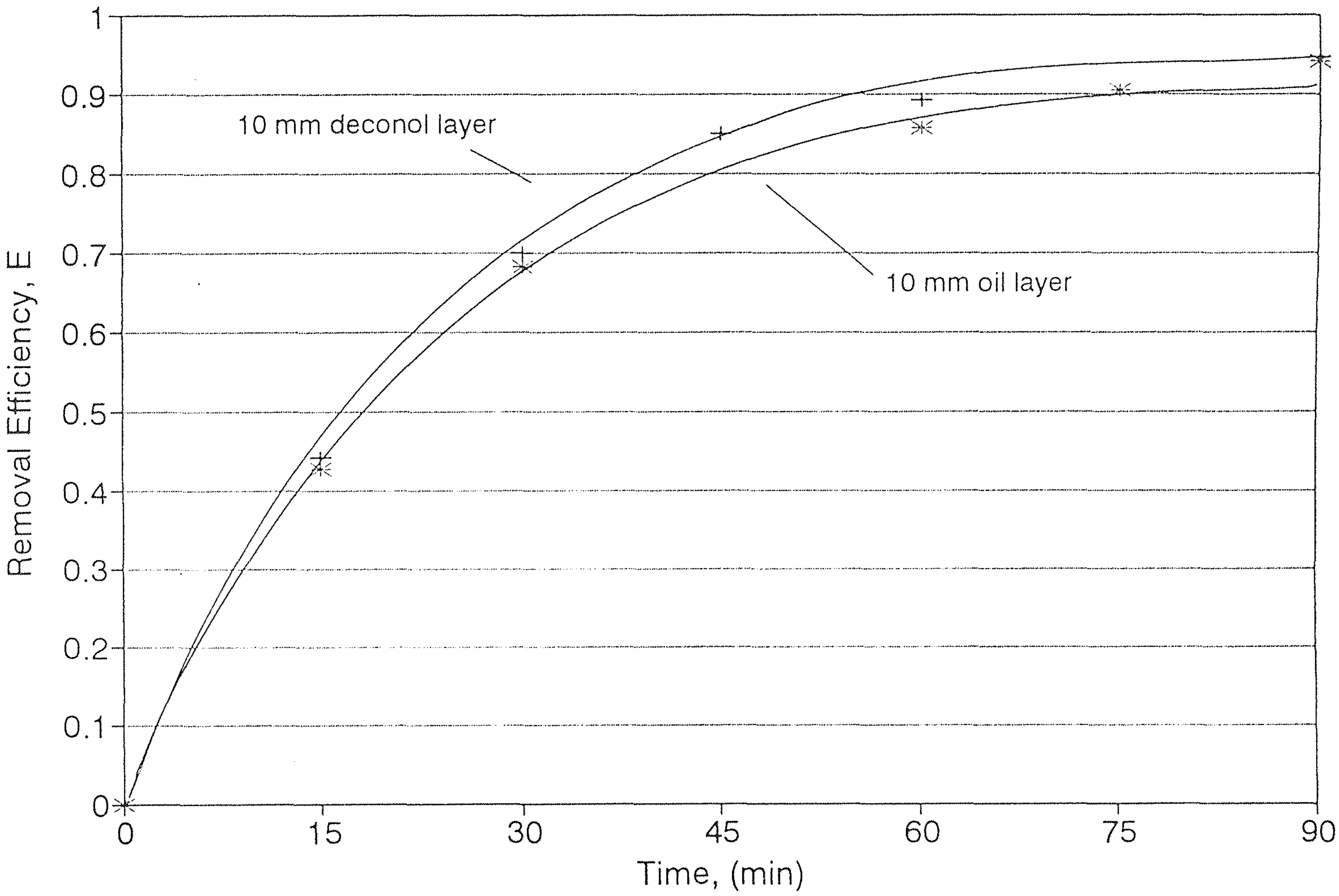

Figure 37 Effect of Different Organic Layers on the Removal of Dichlorobenzene from Water at 94 ml/min

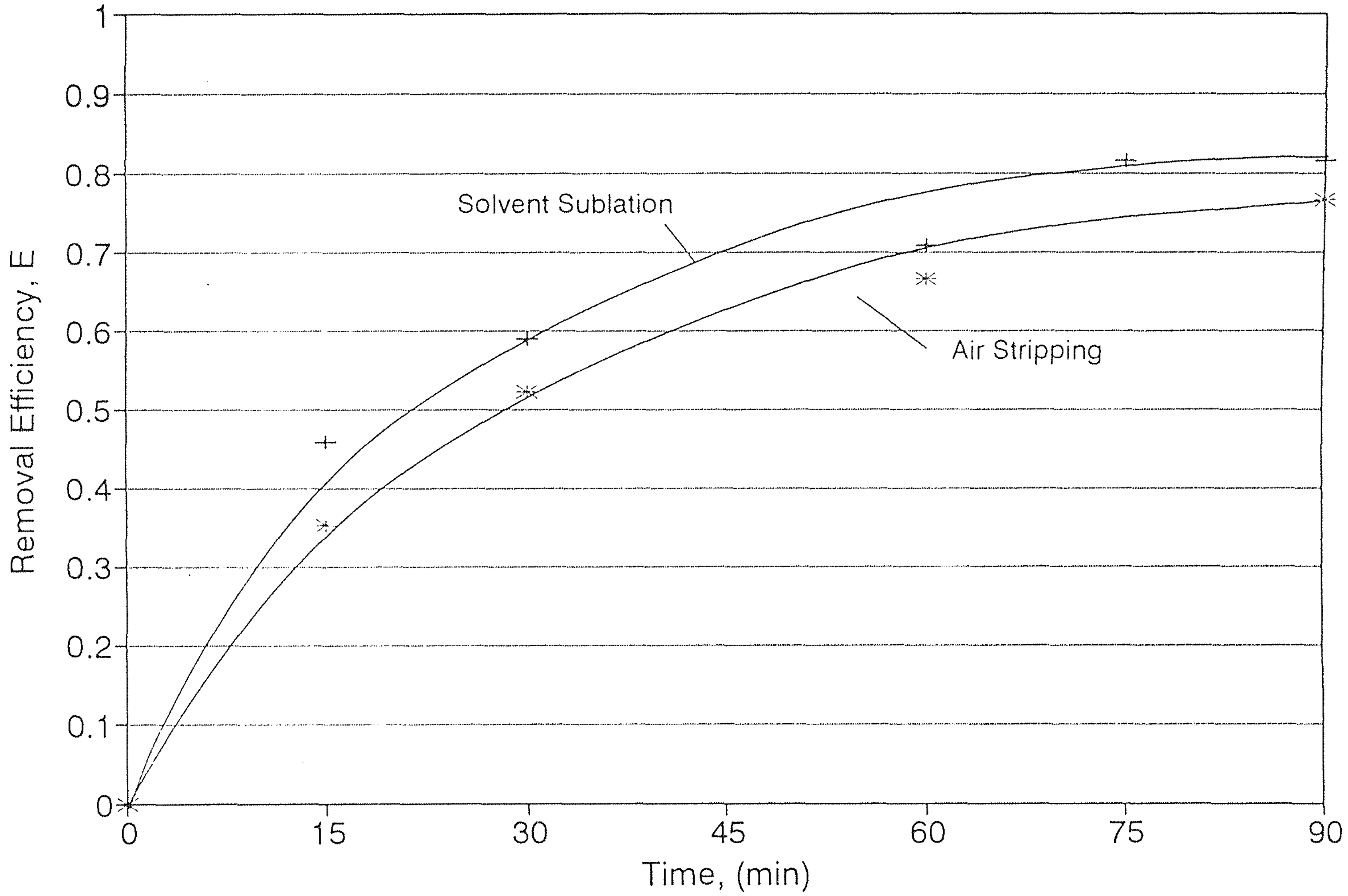

Figure 38 Comparison of Air Stripping and Solvent Sublation for the Removal of Monochlorobenzene from Water Emulsions at 60 ml/min

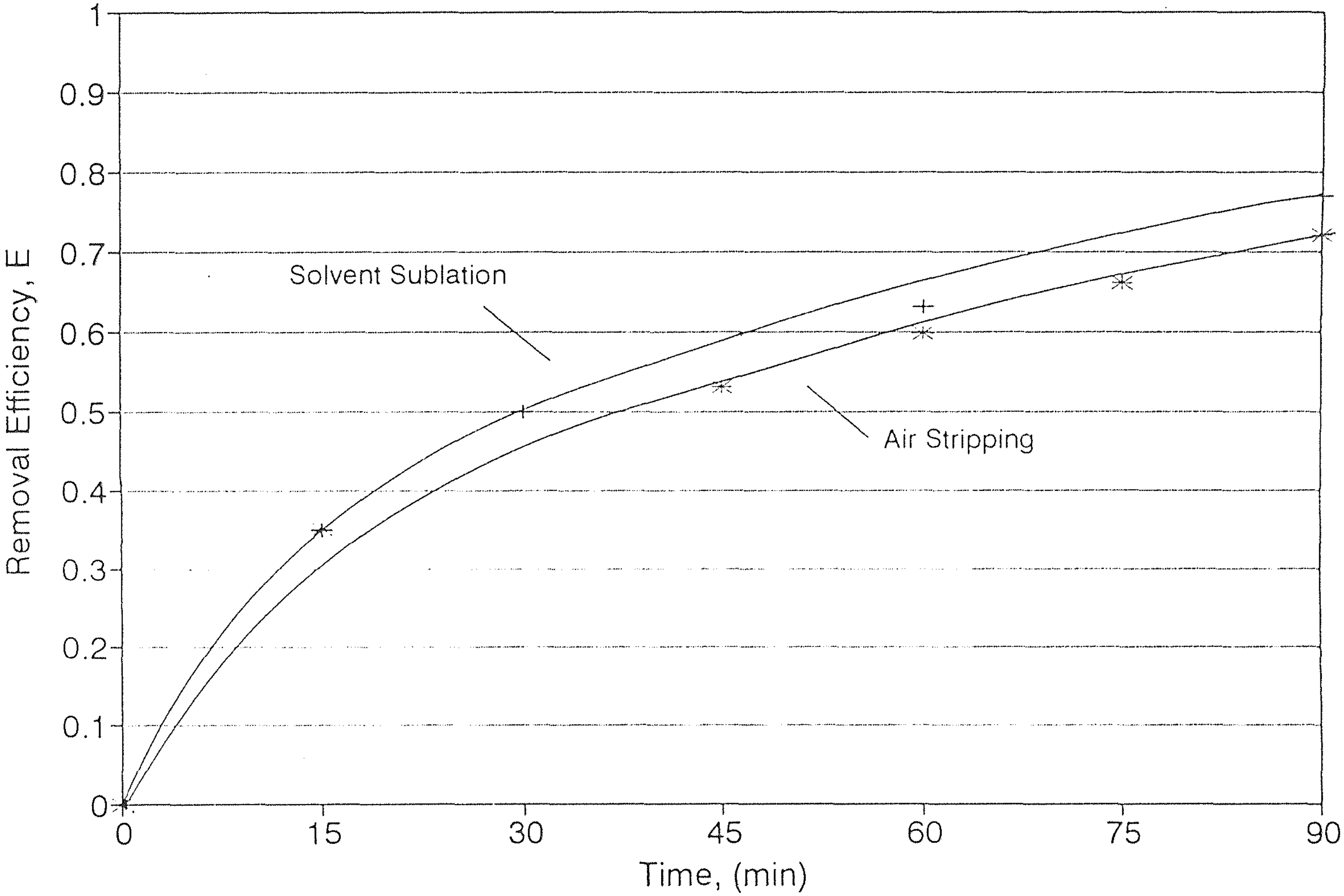

Figure 39 Comparison of Air Stripping And Solvent Sublation for the Removal of Dichlorobenzene from Water Emulsions at 60 ml/min

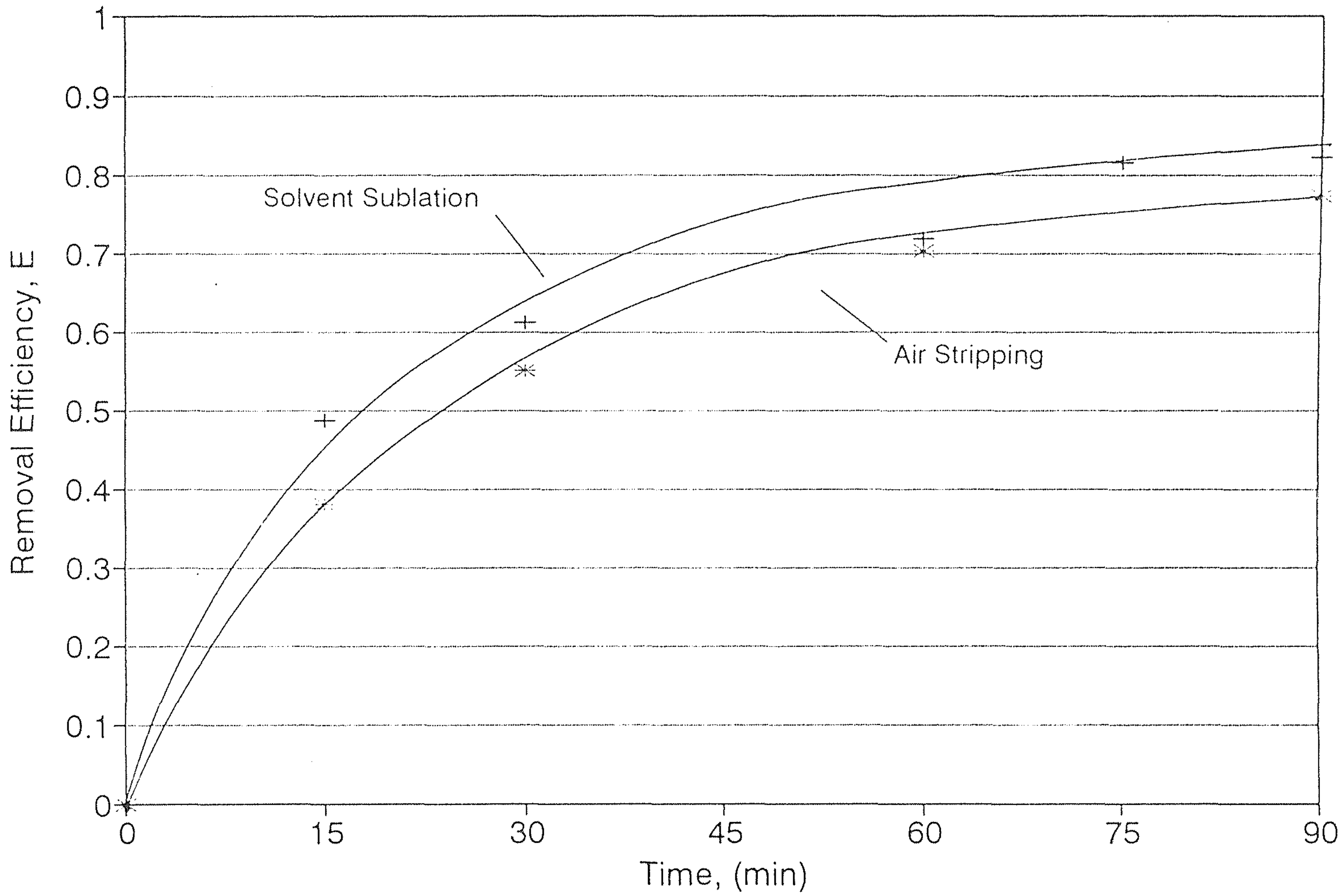

Figure 40 Comparison of Air Stripping and Solvent Sublation for the Removal of Monochlorobenzene from Water Emulsions in the Presence of 5 ppm HTMAB at 60 ml/min

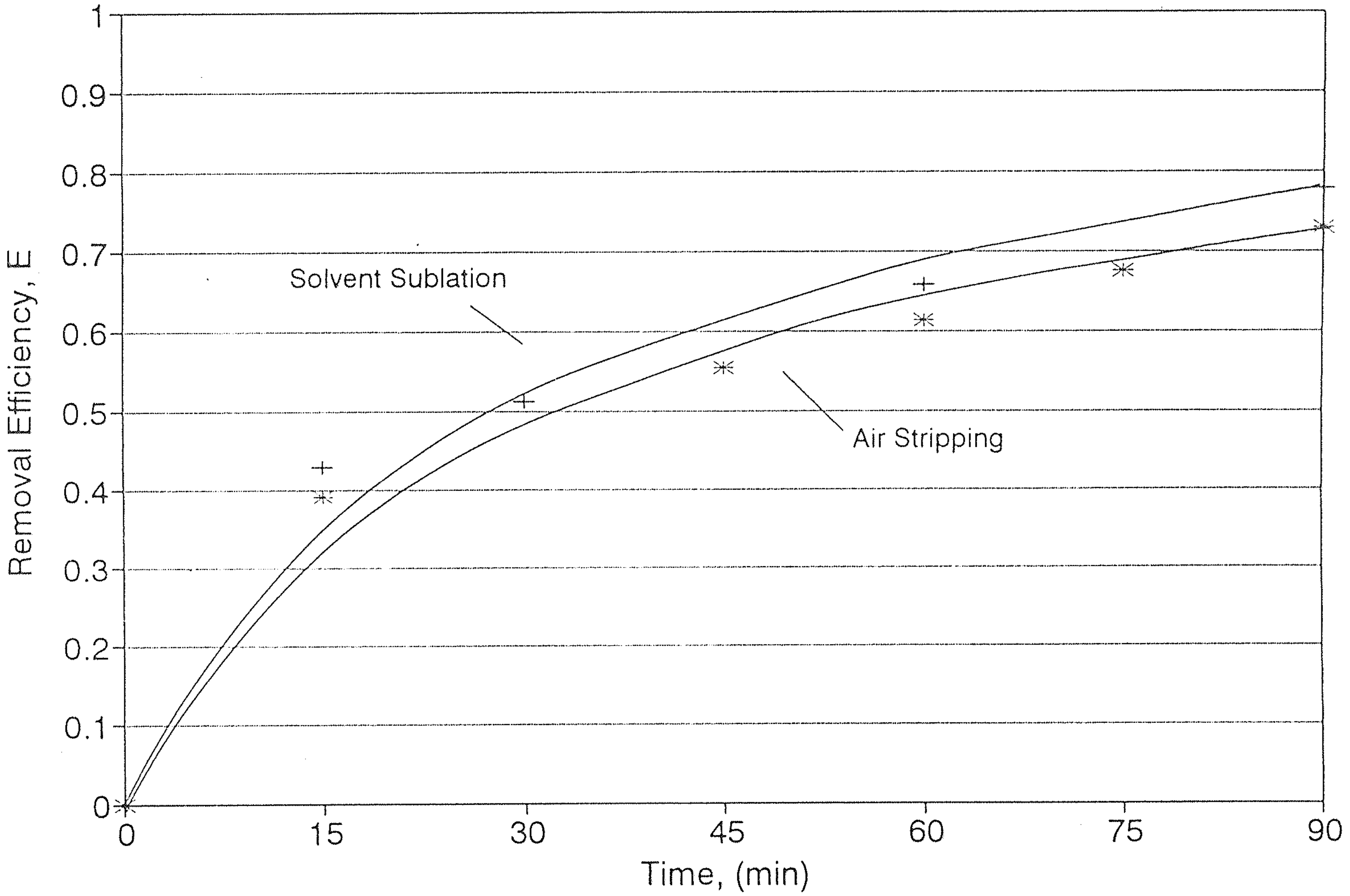

Figure 41 Comparison of Air Stripping and Solvent Sublation for the Removal of Dichlorobenzene from Water Emulsions in the Presence of 5 pp HTMAB at 60 ml/min

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