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SOLVENT SUBLATION: THEORY AND APPLICATION

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ABSTRACT

The solvent sublation technique, one of adsorption bubble separation techniques, is initially proposed by Sebba[1] as an option for ion flotation, in which the material adsorbed on the surface of ascending bubbles and then collected by a solvent in the column upper zone. The technique has advantage over ion flotation or solvent extraction, so it has attracted many attentions in the wastewater treatment and the recovery of many metals. But as to now, the review on the solvent sublation is very sparse. The present paper reviews the theory and application in the solvent sublation.

Key Words: Solvent sublation; Theory; Application

1. INTRODUCTION

Lemlich[2] proposed the term "Adsubble Techniques", based on a contraction of "adsorption bubbles". There are a number of separation methods based on differences of surface tension, in which dispersed materials are adsorbed on an ascending gas stream, and thus separated from the liquid mass where they are initially. This separation is due to the ability of some species to orient themselves in the air-water interface, and adsorption on the bubble surface is due to the presence of certain functional groups. The substances to be separated by means of these techniques must either already possess these groups or be given them by addition of some surfactant agent. As shown in Fig. 1, Karge et al.[3] classified these techniques in two large groups based on foam formation, non-foaming techniques (including the solvent sublation and the bubble fractionation) and foam separation (including the foam fractionation and flotation).

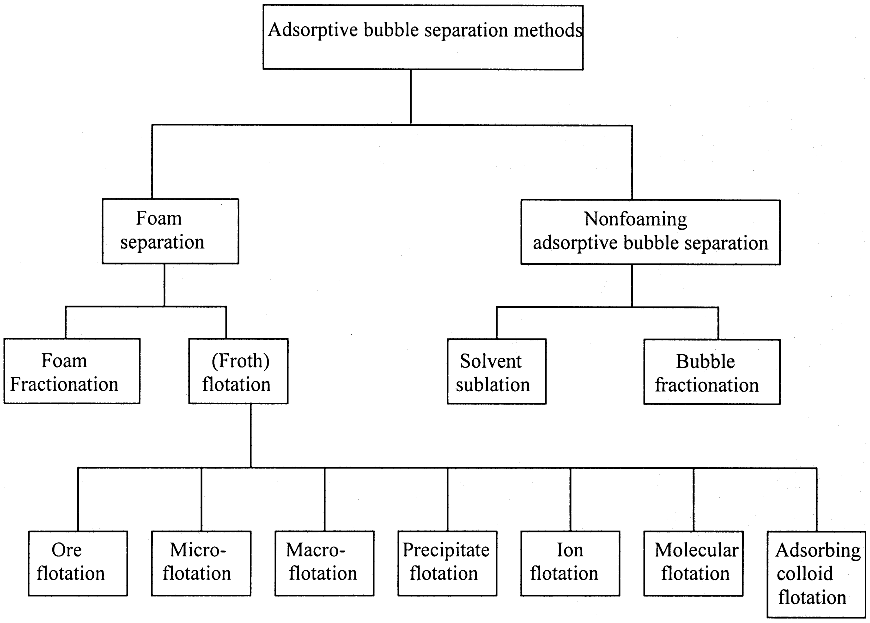


Figure 1. The classified system of adsubble techniques.

The solvent sublation technique, a non-foaming technique, is originated by Sebba[1] as an option for ion flotation, if excessively copious foam formation occurred. Although the adsorptive bubble separation techniques have been studied extensively, the literature on the subarea of solvent sublation is rather sparse. Lemlich's book on adsorptive bubble separation includes an excellent review on solvent sublation by Karger[2]. Wilson et al. included material on this subject in a more general review[5] and two books[6,7]. The solvent sublation technique has shown promise for the removal of certain types of organic compounds from aqueous systems. But these reviews are not completely described the theory and application of solvent sublation technique. So in this paper, it will be reviewed thoroughly.

There are a number of features that make this technique attractive[2]:

a. The possibility of easy handling of large volumes of aqueous samples, whereby the concentration factors can easily exceed ratios of 100:1, thus making the techniques of great potential interest for the analysis of natural, residual and marine waters for trace elements.
b. The active material is carried by the gas bubbles and goes into the upper immisciable liquid layer without bringing about mixing of the aqueous and organic phases, so that the separation process can offer high selectivity, potentially greater than that of other flotation tech-

niques. On the other hand, as a minimum fraction of the aqueous phase comes into contact with the organic phase, the solvent extraction thermodynamic parameters controlling the extent of extraction can be defined from the establishment of an equilibrium state. In solvent sublation this equilibrium state cannot be established in the bulk of the system but only at the aqueous–organic interface, which can remain virtually immobilized when the gas flow–rate is kept sufficiently low. As a result, as the solvent sublation process is not limited by the equilibrium constant, the recovery of trace elements can eventually reach 100%.

c. In addition, the phase stirring process associated with liquid-liquid extraction frequently leads to the formation of undesirable emulsions, especially when surface–active species have to be extracted, whereas in solvent sublation processes emulsion formation is negligible owing to the absence of phase mixing processes.
d. On the basis of similar arguments, the extent of recovery in extraction processes is dependent on the organic to aqueous phase volume ratio whereas solvent sublation is independent of this ratio.

As concluded by Karger[3], solvent extraction processes pose a number of practical problems when dealing with large volumes of samples, and great potential advantages might therefore result from solvent subltion processes for trace element pre-concentration purposes as it is much less dependent on such limitations.

2. BUBBLE GENERATION METHODS

A solvent sublation technique requires the generation of small gas bubbles, surfactant and organic solvent. The size of bubbles is of major importance[8], with preference in very small bubbles, often less than 100μm. It should be noted that this agree with the maximum bubble size for complete laminar flow, which is calculated and found to be 130μm[9]. A photographic technique has been used[10] to measure the size of the bubble in solvent sublation. A special camera is constructed, based on earlier trials in solvent extraction, with a suitable lens having a long probe (0.33m in length), whose end is immersed in the sublation cell at a certain angle, to photograph the dispersion with proper illumination. The size of the bubbles is then measured by projecting the film, with a total magnification of approximately 200 times.

Generally there are three methods used for the generation of bubbles.

2.1 Dispersed-Air

This method generates bubbles by introducing air directly into the sublation cell. In large agitated cells, air is usually introduced through the bottom of the agitator shaft and small bubbles are obtained mainly by the shearing effect of impellers.

In smaller cells, a “sparger” is often used. The material used for the sparger may be rigid (e.g. porous ceramic, stainless steel or polyethlene, glass) or soft (filter cloth, rubber etc.), Whereas its shape may vary (plate or cylinder). The dispersed-air method is often used in the solvent sublation technique.

2.2 Dissolved-Air

The dissolved-air (or pressure) is based on the varying solubility of air in water, according to the pressure in the sublation cell. Initially, water is saturated with air at a relatively high pressure. When this water is introduced in the sublation cell, the change to normal (atmospheric) pressure releases the air bubbles. Alternatively, vacuum may be used to decrease the pressure, after first saturating the water at atmospheric pressure. The amount of air dissolved in water for a given pressure may be easily calculated using Henry’s law.

The technique found an early application in fine coal cleaning in U. K. Now it is the established method of bubble generation in effluent treatment, particularly in refineries and for oil-contaminated surface waters and waste water[11].

2.3 Electrolysis

Electrolysis of the aqueous part of the pulp generates the gas bubbles (mainly hydrogen and oxygen) in the dispersion. The technique is developed particularly in the USSR. It has found many applications in industrial effluent treatment[12].

This method offers certain advantages over the other methods of bubbles generation, i. e. the conventional dispersed-air and dissolved-air. The electrode grids can be arranged so as to provide good coverage of the whole surface area of the cell avoiding any by-pass. The gas generation, sublation time and other operating conditions can be checked quickly and are easily controlled. The equipment is reliable and safe in operation.

3. APPARATUS FOR SOLVENT SUBLATION[13]

There are no apparatus on the market for these techniques, and because of the simplicity of the necessary devices, these are tailored according to the task in hand. However, all solvent sublation set-ups include the followed basic parts, which are shown in Fig. 2.

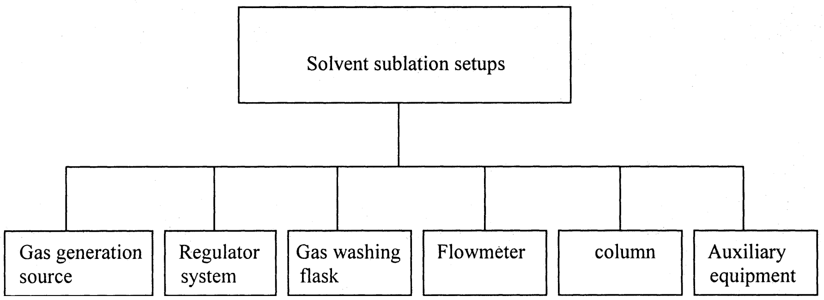


Figure 2. The basic parts of experimental setups for solvent sublation technique.

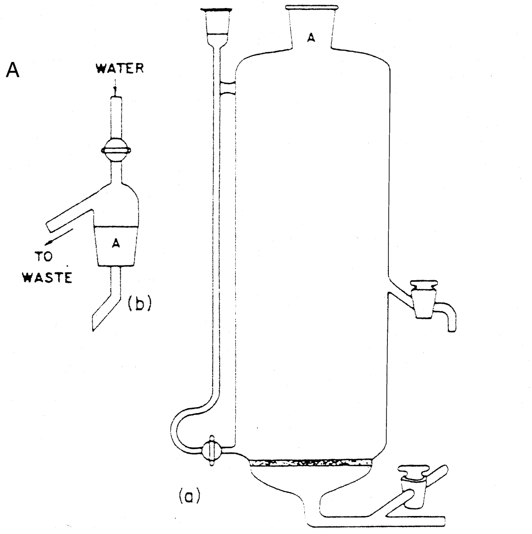
a. Gas generation source. This can be a small air compressor or gas cylinder. Air is the gas most commonly used, nitrogen, helium or argon is also used.
b. Regulator system for controlling pressure and gas flow (needle valves, etc.)
c. Gas washing flask. Its purpose is to presaturate the gas with water or other suitable solvent, to avoid any change in the volume of the system. In some cases it is used to eliminate carbon dioxide from the system to avoid undesirable reactions in the column.
d. Flowmeter. This is for measuring the gas flow-rate through the column; normally a soap-bubble flowmeter is used.
e. Column. Glass is generally used, but plastic columns are also used. The size and form are based on the system needs, but there is always a sintered-glass plate at the bottom with adequate porosity (usually G3 or G4). The gas passing through this porous plate produces the small ascending bubbles, which generate the foam.

Auxiliary equipment, varying from case to case, may include peristaltic pumps (generally used for continuous operation), magnetic stirrers, lateral taps (to allow monitoring the kinetics of the process, or as an outlet for effluent in continuous flow operation), and a thermometer.

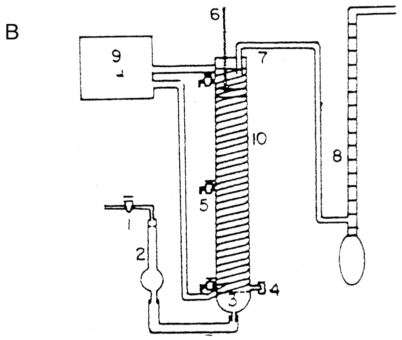
The typical solvent sublation apparatus are illustrated in Fig. 3.

4. MAIN PROCESS PARAMETERS

Several factors influence the process: some affect the solution and others are operational factors. Some of the first group are of basic importance for the solvent sublation technique (surfactant concentration, pH, ion strength, ethanol, organic solvent). The operational parameters include gas flow-rate, temperature.



(a) The sublation cell. (b) Attachment used for discharging radioactive solutions.



The apparatus: (1) air needle valve, (2) glass wool column, (3) fritted glass disk, (4) outlet port, (5) sampling tap, (6) thermometer, (7) vent, (8) soap film flowmeter, (9) controlled temperature bath, (10) wrapped Tygon tubing.

Figure 3. Some examples of solvent sublation apparatus. Reproduced from (A) reference 14, p.621; (B) reference 15, p.927; (C) reference 16, p.39; (D) reference 17, p.215.

(*continued*)

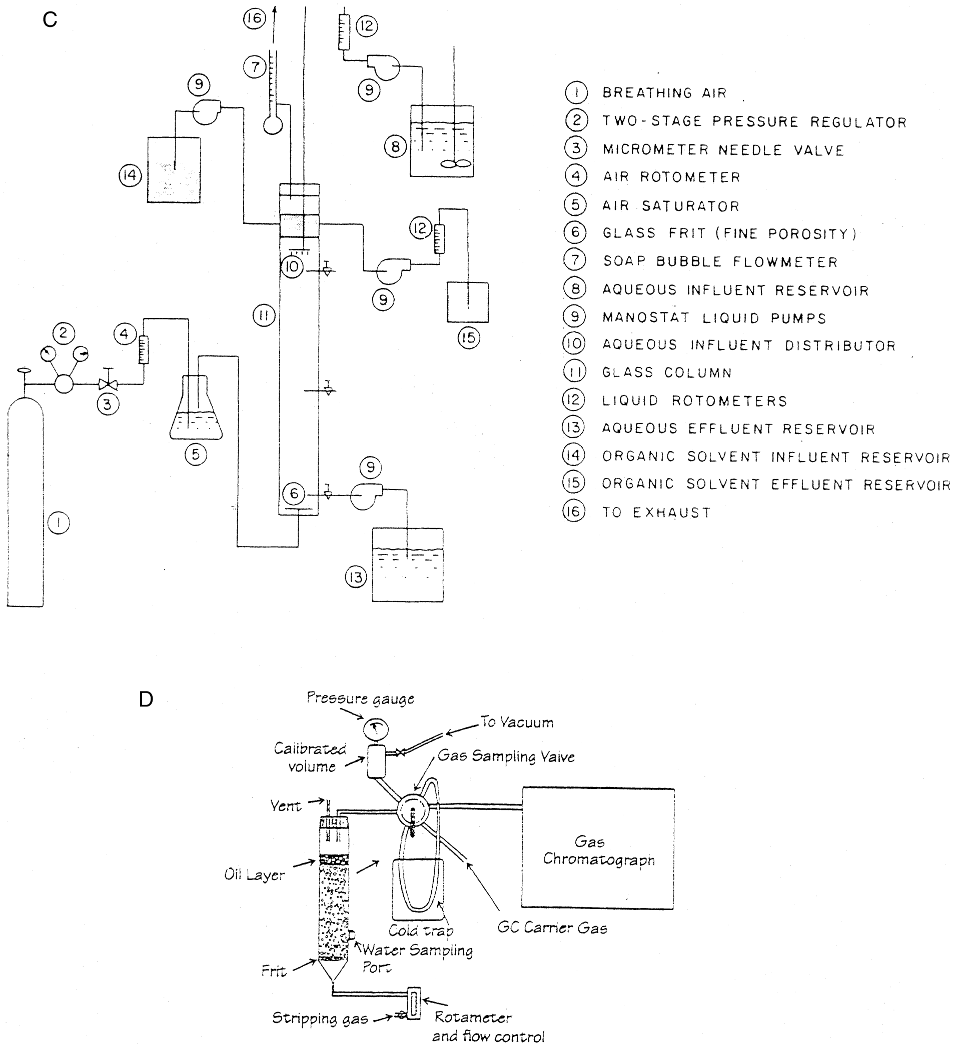


Figure 3. Continued.

4.1 Surfactant Concentration

The presence of surfactants at the air-water interface have been known to reduce the diffusion constant of solutes through the “skin” around the air bubble [18,19]. However, surfactants tend to reduce the surface tension of the aqueous solution quite drastically depending upon their concentration. This decreases the size of the bubbles generated at the sparger. As mentioned earlier, as the population density of small bubbles increase, they provide a very large interfacial area per unit volume of air, which apparently more than offsets the effects of decreased mass transfer rate[20]. Moreover the reduced interfacial tension at the water-organic solvent interface as a result of the presence of surfactants in the aqueous phase helps the bubbles to cross the interface easily without coalescence. All of these factors would tend to increase the efficient of the solvent sublation process.

However, if too high a concentration of surfactant is present, the excess of surfactant will compete for sites in the bubble surface, and even as the critical micelle concentration is approached, there is the probability that the self-aggregates of the surfactant molecules can trap hydrophobic molecules within their hydrophobic core. Moreover, at a high concentration of surfactant, the formation of large foam at the top of the column is a major problem.

The effects of ionic surfactants are important from another consideration, that of the contemplated use of “micro-gas dispersions” or “colloidal gas aphrons” which are micrometer sized bubbles produced by entraining air in soap films [21]. These small bubbles (10–50μm dia) provide several fold increase in interfacial area per unit volume of air than the fritted disk method used here and they rise through the solution at very low velocities and are therefore expected to increase the efficiency of a sublation process tremendously.

4.2 pH of Solution

The pH of solution is a very important parameter, since it will determine the surface and some of the ionic species involved in the process. Variations of pH can produce colligend charge variations by hydrolysis or by formation of other complexes. The material could be separated selectively by controlling the pH of solution[22].

4.3 Ionic Strength

The influence of the ionic strength of the medium varies from system to system in the solvent sublation process. Usually an increase in the ionic strength will decrease the effectiveness of separation, probably because of competition between the colligend and other ions for the collector. For example, in the solvent sublation of Cu-Dithizonates, when the salt concentration approaching to 3.5% a white turbidity is observed initially[23], which can be ascribed to the possible precipitation of the surfactant added in considerable concentrations although the turbidity phenomenon is shown to disappear finally, the formation of froth over the organic phase. The ion strength results in a change in the interfacial tension, thereby facilitating mixing of the phase. However, the presence of inorganic salts increases the removal rate by sublation of TCB from aqueous solutions[24]. This due to the so-called “salting out” effect whereby the presence of salts tend to decrease the aqueous solubility of a hydrophobic organic compound like TCB. This effect is due to the “tying up” of the water molecules in the hydration shells of the ions and thereby reducing the number of “free” water molecules available for solubilizing the hydrophobic in solution. Therefore the removal of the hydrophobic on the air-water interface of the rising bubbles also increase. These effects can also be explained quantitatively using the McDevit-Long theory of “salt-effects” as is shown by Aqua-Yeun et al. [25].

4.4 Temperature

The effect of temperature varies according to the particular system. Increase or decrease in the separation efficient as the temperature increases can be explained as due to material adsorption being a temperature-dependent physical or chemisorption process. In generally, the adsorption on bubbles is an exothermic process and a decrease in temperature therefore leads to greater concentration of surfact–active material on the bubbles and to higher efficient. It may be explained the viscosity of the aqueous phase increase with the increase of the temperature, and hence effect the speed of the bubbles. These changes may in turn affect the rate with which bubbles pass across the organic solvent–water interface and also their residence time in the aqueous solution[26].

4.5 Presence of Ethanol

Addition of small quantities of ethanol (or any other substance for the same purpose) to the solution has several functions, such as avoiding micelle formation and decreasing bubble size, which will improve the separation. At low mol fraction enhanced removal rates whereas at mol fraction 0.04 or higher the removal rates start to decrease, the effect becoming quite predominate at 0.10mol fraction[27]. The enhancement in removal rates at low mol fractions may be due to the two factors. Firstly, the addition of ethanol change the bubble properties considerably, the number of very small bubbles increase. This is well known effect arising from the lowering surface tension of water which prevents the bubbles from growing to larger size at their point of formation on the fritte disk [28]. These smaller bubbles provide a very large surface area per unit volume of air (since the ratio of area to volume increases with decreasing bubble radius) which contributes to enhanced mass transfer from the liquid phase to the bubbles. Smaller bubbles also have slower rise velocities [29] and hence contribute to longer residence time within the aqueous section for mass transfer to occur. Secondly, according to Ben-Naim[30], mol fractions of up to 0.03 of ethanol would, in fact, increase the hydrogen bonding of water thus making the aqueous phase "less comfortable" for organic molecules. This means that the material of aqueous would prefer the air-water interface of the rising bubbles to the aqueous phase. Ben-Naimi [31]pointed out that the ethanol mol fractions of above 0.03 tend to disrupt the water structure considerably and makes the aqueous phase "more comfortable" for materials by solvent sublation.

4.6 Gas Flow Rate

Gas flow rate is one of the most important parameters in solvent sublation technique. The separation rate increase with the increase of the gas flow rate. The increase in separation rate is almost proportional to the increase in gas flow rate for lower rate (80mls^{-1}) whereas it is not quite so for higher rate[24]. This is probably due to the increased mean bubble radius, which would decrease the interfacial area per unit volume of air (which is given by 3/r), and would also decrease the bubble residence time since larger bubbles have higher rise velocities. Also, axial dispersion would certainly increase with increasing gas flow rate. Nevertheless, the results do suggest that increased flux of air through the column would improve the performance of the solvent sublation process provided the bubble sizes are kept small. Increasing gas flow rates may be the only way to increase the performance of a severely overloaded counter current column[7].

4.7 Organic Solvent

The unhindered motion of the bubbles across the interface (aqueous-organic solvent) is an important criterion for the success of solvent sublation. It then becomes apparent that the aqueous-organic solvent interfacial 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. Valsaraj et al.[24] study the different organic solvent effect on the solvent sublation of TCB. It is observed that for lauryl alcohol -water system where the interfacial tension is very small the bubbles cross the interface without much coalescence whereas for mineral oil-water system the bubbles stop momentarily at the interface, coalesce and then move sideways and up along the walls of the column along with some smaller bubbles rising through the center of the column. During the lauryl alcohol experiment, the solvent layer is not observed to get cloudy, nor is water entrainment, channeling or bubble hold-up observed. So in the solvent sublation process, we should choose low-aqueous-organic solvent interfacial tension. In addition to that, the organic solvent should have a high solubility for the material of interest. The solvent should be non-toxic, and non-volatile so as not to cause additional environmental contamination. One thing to be attended is that the long–chain alcohols as solvent is their expense as compared to petroleum-based heavy oils such as mineral oil.

5. THEORY AND MODEL

Sebba was the first person who explained the mechanism of the solvent sublation[1, 32]. The sublate moved across the water-organic solvent interface in one direction only, namely into the organic phase with the rising bubbles. But the mechanism is very simple, the factor is not considered that sublate moved downwards across the liquid-liquid interface should be rapidly carried into the bulk of aqueous because of the marked turbulence.

Consideration of it, Karger, Pinfold et al.[33–38] made a complex mechanism. The sublate moved in both directions across the liquid-liquid interface. Greater upward movements of sublate occurred because the flow of bubbles is in this direction. The bubbles arriving the organic-aqueous interface are small and have too little kinetic energy to overcome the interfacial tension; coalescence must occur before the bubbles transfer across the interface. Since the surface of the bubbles possess a zeta-potential rapid. The volume below the interface, therefore, contains many stationary bubbles, and the liquid trapped between them is effectively protected from the turbulence of the solution below. Some of the liquid entrained in this interfacial region will be dragged into the organic phase by the larger bubbles moving upward. Collector and colligend contained in this water and adsorbed on the bubbles readily dissolve in the organic phase. When the bubbles finally burst into the atmosphere the water surrounding each of them form globules, which then returns across the liquid-liquid interface. Because of small size of these droplets, a larger area of organic-aqueous interface is exposed, and it is likely that a liquid-liquid equilibrium is established between the two phases. Since the total volume of water in the organic phase is very small, the amount of sublate carried back into the aqueous solution is minimal. Herein lies an essential difference between solvent extraction and solvent sublation. In the former process the organic phase con-

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tents are in equilibrium with the bulk of the aqueous solution, while in solvent sublation, equilibrium exists with only the small amount of water that is entrained. Because of the protection afforded by the stationary bubbles at the interface, the small amount of water that moves down from the organic layer is not carried into the bulk of the aqueous solution. Rather it is transported back to the organic phase in the form of layers around other bubbles and carries with it a small amount of sublate. A steady state is ultimately attained in which the amount of sublate traveling into the organic layer was equal to that carried back across the interface by the returning droplets.

The above studies gave a better qualitative approximation to the separation mechanism that controls solvent sublation. In fact, they allow rational justification of most of the experimental phenomena associated with this technique. Nevertheless they were not translated into a mathematical model suitable for a theoretical and predictive treatment of these phenomena. Wilson's groups have remedied this since 1981[39–44]. In this series of papers, the equations that constituted with the theoretical model were deduced in full detail and have been submitted to continuous refinement by the authors. As follows, only main results are listed[13].

In practice, Wilson's model did not accept Karger's hypothesis, because it was considered that the experimental results contradict it.

The Wilson's group has developed different models, which initially based on the adsorption of volatile compounds on a stream of bubbles. In these models the rate-limiting step is the mass transfer of solute from the solution to the air-water interface. The next approximation is the consideration of non-volatile compounds, taking into account the Langmuir isotherm of adsorption in the air-water interface, as well as the mass transfer throughout the bubble limiting layer. Finally models are developed for single or multiple stage columns controlled by an equilibrium or a mass transfer process.

The first work of the series deal the solvent sublation of volatile organics 1,1,1-trichloroethane and developed a rather straightforward mathematical model. Later, the solvent sublation of two ion pairs (Methylene Blue-sodium tetradecylsulfate and Methyl orange-hexadecyltrimethylammonium bromide) is studied. Three possible mechanisms are examined in detail, mass transfer rate effects in the vicinity of the bubble-water interface are examined theoretically, and the empirical time constant for mass transfer related to the lowest eigenvalue of a suitably selected diffusion problem. Then a fast algorithm is developed for modeling the operation of batch and continuous flow solvent sublation columns. Mass transfer kinetics and axial dispersion are taken into account, and a Langmuir isotherm is used.

In the first case, a molecular (nonionic) surface-active, volatile solute is removed from the aqueous phase by solvent sublation. For the axial mixing is sufficiently rapid and be treated as a single, well-stirred pool. It is assumed that the rate of mass transfer to the bubble is proportional to the difference between the actual mass of solute associated with the bubble (in surface and vapor phase) if the bubble is at equilibrium with the surrounding liquid. The rate of change of solute mass associated with a single bubble of (constant) radius as it rises through the water layer can be expressed:

$$\frac{dm_b}{dt} = 4\pi r^3 k\left[\frac{4}{3}\pi r^3 K_w c_w + \frac{4\pi r^2 \Gamma_m}{(1 + c_{1/2}/c_w)} - m_b\right]\Bigg/\left(\frac{4}{3}\pi r^3\right) \tag{1}$$

where

t = time elapsed after bubble information
m_b = moles of solute associated with a bubble
r = bubble radius
k = mass transfer rate coefficient (cm/sec)
K_w = Henry's law constant for the solute in water, ($=c_{vap}/c_{water}$ at equilibrium)
c_w = solute concentration in the aqueous phase
Γ_m = Langmuir's isotherm parameter(saturation concentration of the solute in the air-water interface)
$c_{1/2}$ = Langmuir isotherm parameter (concentration in the aqueous phase at which the surface concentration is $1/2\ \Gamma_m$

The solute mass separated from the aqueous phase by a bubble, if we accept that c_w does not change during the time necessary to allow a bubble to pass through the liquid mass, is obtained by integrating equation (1)

$$m_{b(out)} = \frac{4\pi r^3}{3}\left[K_w c_w + \frac{3\Gamma_m}{r(1 + c_{1/2}/c_w)}\right] \times \left[1 - \exp\left(-\frac{3kh_w}{ru_w}\right)\right] \tag{2}$$

where

h_w = aqueous column height
u_w = bubble ascension velocity (which is a function of the density and viscosity of the aqueous phase)

Taking into account the volume of air introduced into the column as bubbles, the following equation is obtained:

$$V_w \frac{dc_w}{dt} = -N_b \frac{4\pi r^3}{3}\left[1 - \exp\left(-\frac{3kh_w}{ru_w}\right)\right] \times \left[K_w c_w + \frac{3\Gamma_m}{r(1 + c_{1/2}/c_w)}\right] \tag{3}$$

where

V_w = aqueous phase volume
N_b = number of bubbles introduced into the aqueous phase per second
t = time elapsed from the beginning of the process (sec)

If the solute is a non-volatile species, equation (3) is simplified to

$$\frac{dc}{dt} = -A\,(1 + c_{1/2}/c_w) \tag{4}$$

where A incorporates a group of constant factors. By integration the following equation is obtained:

$$c_w\,(t) - c_w\,(0) + c_{1/2}\,[\ln c_w\,(t)/c_w\,(0)] = -At \tag{5}$$

when $\mathrm{Inc}_w(t)/c_w(0)$ is plotted vs. t, Womack et al[39]. Obtained plots that are in disagreement with the experimental results for the Methylene Blue-tetradecylsulphate pair, and it is necessary to consider the value of the mass transfer coefficient (k). To do this the diffusion of solute through the boundary layer around the air bubbles had to be taken into account.

Starting from this conclusion and from the calculations of the solute chemical potential, they obtained the expression

$$K = r\,\lambda_1/3 \tag{6}$$

Where λ_1 is a time constant associated with the diffusion process and r is the bubble radius. This is thus a limiting factor of the separation rate, that causes the formation of curves similar to those obtained experimentally.

It is assumed that formation of ion-pairs between the solute (ionizable) and the surfactant gives rise to the sublate that has to be separated, assuming that the surface concentrations of the surface-active species are given by linear isotherms.

Assuming the establishment of the following equilibrium in solution:

$$AC + BD \Leftrightarrow AD + BC$$

$$K_e = \frac{[AD][BC]}{[AC][BD]} \tag{7}$$

where

A = surfactant anionic agent
B = solute anion
C = solute cation
D = surfactant cationic agent
AC = sublate (ion-pair)
AD = non-dissociated surfactant

The species AC and AD are surfactants and will compete for the gas bubbles. The anion B cannot be separated by means of solvent sublation, so

$$[BC] + [BD] = [B] = \text{constant} \tag{8}$$

Furthermore, there is only one possible way for the solute cation to be separated from the solution, so

$$\frac{d}{dt}\,([AC] + [BC]) = -K_{AC}[AC] \tag{9}$$

where K_{AC} is the mass transfer rate parameter for AC.

In contrast, the surfactant can be separated in two ways:

$$\frac{d}{dt}([AC] + [AD]) = -K_{AC}[AC] - K_{AD}[AD] \tag{10}$$

The K parameters depend on the bubble radii, the gas flow-rate, the volume and height of the aqueous phase, and the rising velocity of the bubbles.

Therefore we have four equations for the four unknown. This system is conveniently solved,[39] yielding the expression:

$$K_e = \frac{([AD]_0 - [AC])([BC]_0 - [AC])}{[AC]([BD]_0 + [AC])} \tag{11}$$

where the subscript zero indicates the initial nominal concentration.

Equation (11) is arrived at from equation (10) by choosing the root of this equation that conforms to all the following conditions:

$$[AC] \geqslant 0; \qquad [AD] = ([AD]_0 - [AC]) \geqslant 0;$$
$$[BC] = ([BC]_0 - [AC]) \geqslant 0; \quad \text{and} \quad [BD] = ([BD]_0 + [AC]).$$

From these initial values the differential equations (8) and (9) can be solved, yielding expressions to calculate the curves of the separation kinetics during the process.

On studying the effect of the equilibrium constant shown in equation (7) on dissociation of the ion-pair, it is observed that when this increases, the sublate separation velocity decreases, In this case, the theoretical curves are similar to the experimental ones.

At the same time it is observed that decreasing the surfactant concentration would be expected to give a lower yield and separation velocity, in accordance with the experimental results. Finally, the effect is examined of adding salts, which would obviously displace the formation equilibrium of the ion-pair and, therefore, cause a serious loss of efficiency when the technique is applied to brines or seawaters.

This theoretical treatment accounts very well for the experimental behavior of the technique, with the exception that in practice the rates of removal early in a run are much higher than those predicated by the model. Womack et al. accounted for these differences by considering the occurrence of secondary ionic equilibria.[39]

Because one of the most useful characteristics of the technique is the possibility of working with large volumes of sample, there is an obvious interest in obtaining theoretical treatment of systems working in the continuous flow mode. This technique should be useful in chemical analysis (avoiding the use of large experimental devices; increasing the sensitivity of determinations by means of greater preconcentration factors etc.) as well as in chemical engineering (treatment of large quantities of water). Wilson and Valsaraj have suggested a quick and efficient algorithm for the treatment of this situation, taking into account that the axial dispersion is not great enough, in a continuous feed regimen of the column, to guarantee homogeneity.[40]

This model allows design and adjustment of the device in the continuous operation mode, which is of obvious interest industrially, and this mode of operation could also be used in same analytical work.

In a later work, these authors develop another theoretical model that allows the calculation of the adsorption isotherm, at the air-water interface, of the compounds of interest when they are intrinsically hydrophobic. In this way it is possible to predict the applicability of this method for the removal of as yet unstudied compounds.

Valsaraj et al. have done a series studies titled for "studies in batch and continuous solvent sublation".[16,45,46] Solvent transport between the aqueous and organic solvent phase in solvent sublation can occure in a variety of ways. These are depicted in Fig. 4 along with a comparison with the conventional solvent extraction process. A complete model incorporating all known transport mechanisms for solutes between aqueous and organic solvent phase in solvent sublation is proposed. In the most cases, unless the physical transport by air bubbles overwhelms the molecular diffusive transport, the decrease in solute concentration in the aque-

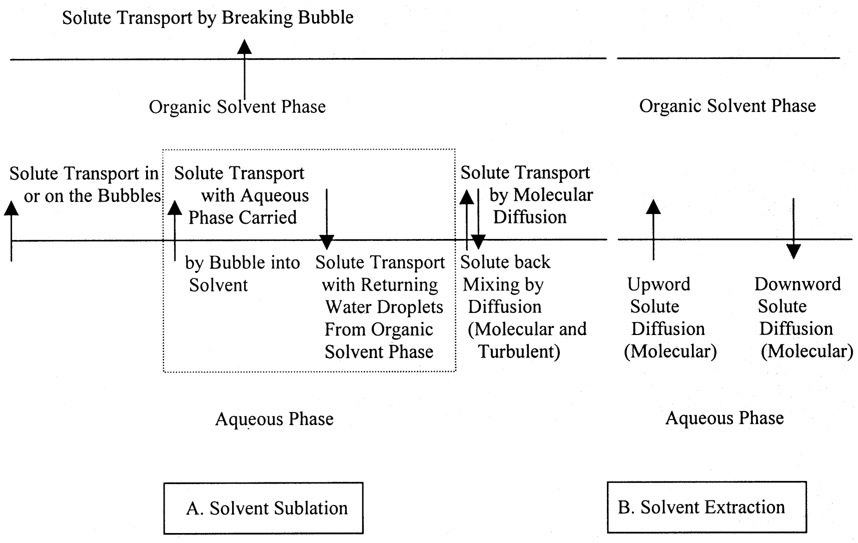

Figure 4. The solute transport mechanism in solvent sublation process, compared with that of solvent extraction process.

ous phase is distinctly nonlinear. Air bubbles reaching the solvent-water interface do not immediately enter the organic solvent phase 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 the water dragged up, however, the returning water droplets may be depleted in solute concentration. The process of water drag-up and return as droplets reaches an eventual steady state as shown by the dash lines in Fig. 4. A complete model should include all of these solute transport mechanisms across the interface. Existing models fail to do so and the current work is the first in this regard.

It is assumed that air bubbles reaching the solvent-water interface are in equilibrium with the aqueous phase. We also assume that axial dispersion in both phases is sufficiently large to make both phases completely mixed. Relaxing this assumption will require that the differential equations be solved numerically.[7, 40]

A solute mass balance in the organic solvent layer gives

$$\begin{aligned} V_o \frac{dC_o}{dt} = Q_a\left[H_c + \frac{3}{a} K_a + \frac{3}{a} d_i\right] C_w + \Pi\, \Gamma_c^2\, k_l \\ \times [C_w - C_o/K_{ow}] - Qa\left[\frac{3}{a} d_i + H_c\right] \frac{C_o}{K_{ow}} \end{aligned} \tag{12}$$

The term $Q_a[H_c + (3/a)K_a]C_w$ gives the transport of solute within and on the surface phase of the bubbles. H_c is the dimensionless Henry's constant for the solute between vapor and aqueous phases. K_a is the linear adsorption constant for the solute between the air-water interface of the air bubbles and the aqueous phase (in centimeters) (see Ref.24 for details). A is the radius of an air bubble in the solvent phase; The term $Q_a(3/a)d_iC_w$ gives the amount of solute carried up with the water layer of thickness d_i around the bubble. The term $\Pi r_c^2\, k_l\, [C_w - C_o / K_{ow}]$ is the molecular diffusive transport with an aqueous phase controlled mass transfer coefficient k_l (cm/s) across the cross-sectional area Πr_c^2, where r_c is the radius of the column. K_{ow} is the solute partition constant between the organic solvent and aqueous phases. The sign and magnitude of the diffusive transport depend on the values of k_l, C_o, C_w, and K_{ow}, The term–$Q_a(3/a)d_i\, C_o/K_{ow}$ gives the amount of solute returning with the water droplets from the solvent phase to the aqueous phase. While the last term,- $Q_aH_cC_o/K_{ow}$, is the amount of solute lost to the atmosphere as the material carried within the vapor phase of bubbles at the top of the organic solvent section.

For the semibatch process, an overall solute mass balance across both organic solvent and aqueous phase gives

$$V_w\, C_{wi} = V_w\, C_w + V_oC_o \tag{13}$$

Where C_{wi} is the initial solute concentration in the aqueous phase (mol/cm^3), and V_w and V_o are, respectively, the aqueous and organic solvent volumes.

From Eq. (13):

$$V_o \frac{dC_o}{dt} = -V_w \frac{dC_w}{dt} \tag{14}$$

Along with the initial condition that $C_w = C_{wi}$ at $t = 0$, we get from Eqs. (12)–(14) the following:

$$E = 1 - \frac{C_w}{C_{wi}} = \left(1 - \frac{\beta}{\alpha}\right)(1 - e^{-at}) \tag{15}$$

where

$$\beta = \frac{1}{K_o w V_o}\left[\Pi r_c^2 k_l + Q_a\left(H_c + \frac{3}{a} d_i\right)\right] \tag{16}$$

and

$$\begin{aligned} \alpha = \frac{Q_a}{V_w}\left(H_o + \frac{3}{a} K_a + \frac{3}{a} d_i\right) + \frac{\Pi {r_c}^2 k_l}{V_w} \\ \times \left(1 + \frac{1\ V_w}{K_{ow}\ V_o}\right) + \frac{Q_a}{K_{ow}\ V_o}\left(H_o + \frac{3}{a} d_i\right) \end{aligned} \tag{17}$$

Notice that if $k_l = 0$, we regain the equations originally derived by other investigators who excluded reverse mass transfer from the solvent phase[7, 24]. In order to illustrate the effects of various parameters in the model, such as k_l, V_w, V_o, K_{ow}, d_i, Q_a, K_a, and α, we choose PCP as the solute and our experimental column dimensions and conditions.

The Valsaraj group have built a complete mathmatical model for the continuous countercurrent operation of a solvent sublation column. Experiment results is used to check the model. Use of two-suffix Margules equation and UNIFAC to predict the solubility of pentachlorophenol in alcohol-water mixtures and it effects on solvent sublation.

Zhu et al. study the separation mechanism of solvent sublation, with two types of sublates as the objects. The experiment shows that the bubble absorption of the solvent sublation is the key to the separation efficiency. The processes are obedient to first order kinetics and a new characteristic parameter, apparent activation energy of attachment of the sublate to bubble is proposed to describe the separation efficiency of the solvent sublation[47].

Palagyi et al. do a series of works titled for "transport extraction for trace element separation and preconcentration" [48–50]. According the Langmuir type isotherm:

$$m = K_s C \tag{18}$$

where K_s is the transport extraction concentration, m is the amount of the solute adsorbed in the form of a surface-active substance, which is collected (transport extracted) into the water immiscible liquid. The concentration of a solute in the bulk aqueous phase (c) can also be expressed as a ratio of the difference between the total amount of a solute (m_o) and its transport-extracted amount to the volume of the aqueous phase (V_{aq}):

$$c = (m_o - m)/V_{aq} \tag{19}$$

Combining Eqs. 18 and 19, the transport-extracted fraction (m/m_o), i.e., the separation efficiency of transport extraction ($E_s = m/m_o$) can easily be calculated as:

$$E_s = K_s/(K_s + V_{aq}) \tag{20}$$

Eq. 20 represents a possible theoretical separation efficiency for transport extraction under static (batch) conditions with stagnant organic phase, neglecting possible variations in the values of K_s or V_{aq} and supposing an unlimited transport extraction capacity of the water immiscible liquid (V_{org}) on the top of the column.

By comparison of this equation with the well-known equation[4] for the separation efficiency of conventional solvent extraction under static (batch) conditions (E_e):

$$E_e = K_d/K_d + (V_{aq}/V_{org}) \tag{21}$$

Where K_d is the equilibrium distribution radio of a solute between the volumes of the aqueous (V_{aq}) and organic (V_{org}) phased, it is possible to evaluate the theoretical separation and /or preconcentration potentials of the two techniques.

6. APPLICATIONS

Solvent sublation, in comparison with other flotation techniques, has an advantage in that it is easily handle during the treatment process. Solvent sublation has practical and theoretical advantages over solvent extraction. The equilibrium in solvent sublation is only established in the aqueous-organic interface. The quantity of sublate collected by the organic layer is independent of its volume because no equilibrium is established in the overall system, and the passage of a sublate into the organic phase through the interface is a process forced by the gas stream, not a spontaneous distribution process related to the relative solubility of the sublate in the two phases. Further advantages over solvent extraction arise from the absence of formation of emulsions, because the interface remains practically immobile, and the possibility of handling large volumes of samples. In solvent sublation process, it is important to control of the gas flow-rate and bubble size to obtain a good separation result.

However, the solvent sublation technique is not used widely by far. In this paper, the application is reviewed from the two aspects, which are shown in Fig. 5.

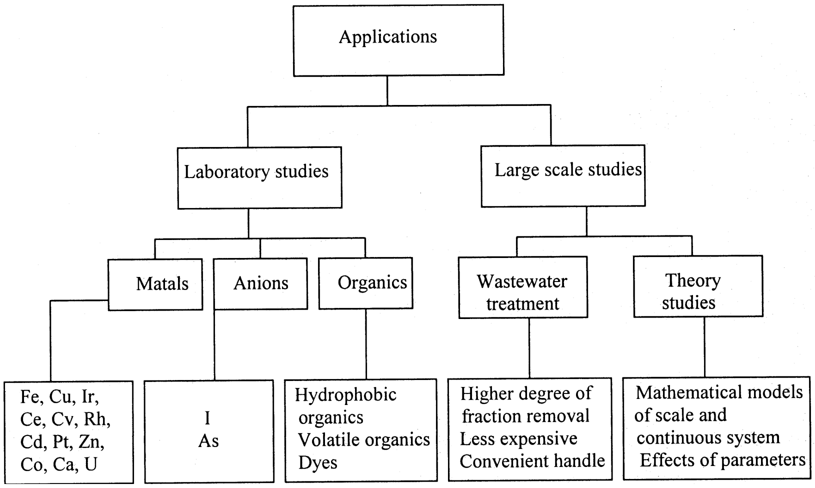

Figure 5. The application of solvent sublation technique.

6.1 Laboratory Studies

6.1.1 Metals and Anions

The solvent sublation technique is used for the separation and determination of trace metals. Kotsuji et al. separate Fe using 3-(2-Pyridyl)-5,6-diphenyl-1,4-triazine complex and surfactant sodium lauryl sulphate. The Fe of sea is determinated by spectrometer, concentration factor 100, with the efficiency of 97%[51].

Sodium lauryl sulphate is used for a collector in connection with dithizone solutions in isolutyl methyl ketone. Trace amounts of Cu is quantitative separation, and several experimental parameters are studied.[52].The Ir (IV) is selectively collected in n-butyl acetate from the aqueous solution of mixtures of $RhCl_6^{3-}$ and 0.05% Ce(IV) with hexadecyl tripropylammonium bromide [53]. Cr, Cv, U are separated with the different complex agent, sodium lauryl sulphate for surfactant. The different solvents effects on the solvent sublation are studied [54]. Trace amount of Co is determinated by radio chemical method. Several added salts effects on the process are reported. Comparison with ion flotation, the solvent sublation results are better[55]. Trace Cd in water is collected by Cadion 1B. The influence of acidify surfactant, absorbent and others on the solvent sublation have been investigated[56]. Sepectrophotometric determination of trace Pd after solvent sublation is reported, the recovery reached 100% [57].

Determination of trace Pt by solvent sublation spectrophotometry is reported based on the ion-associated formed by $[Pt\ (SnCl_3)_5]^{3-}$ and cetylpyridine bromide), The detection limit is 0.17Hg/200ml, With the recovery of 100%. The method can be used to detect pt-containing waste materials[58]. Solvent sublation is used to concentrate trace Cu using diethyldithioocarbanate as a collector[59]. The mechanism of solvent sublation of Fe(III) with tri-n-octylamine is studied [60]. A sensitive and precise method for the determination of microgram amounts of zinc(II) has been developed. The ion associate of the anionic zinc(II)-thiocyanate complex with malachite green is sublated to to-luene[61]. Wada et al. determine the trace amount of Ca, Cu, Ni, Pb in water by coprecipitation solvent sublation[62]. Qian et al. report the method of enrichment and determination of trace Ca by solvent sublation[63]. The experimental conditions of determination of Cu in solvent sublation are predicted by theory[64].

The determination of trace iodide by preconcentration using solvent sublation and subsequent spectrophotommetric measurements is described using cetyltrimethy lammonium bromide(CTMAB) as a collector. The method is applied to the iodide content in seawater and results are compared with the iodide-starch method[65]. Trace As contained in oil is determined by solvent sublation-spectrophotometer[66]. Ueno et al. study the spectrophotometric determination of traces of anionic surfactants by solvent sublation[67].

6.1.2 Organics

The solvent sublation of hexadecyltrimethylammanium chloride is studied[68]. The separation of phenol from dilute alkaline aqueous solution by solvent sublation is reported. Comparison with solvent extraction and foam fractionation, the mechanism is proposed that solvent sublation may couple with the mechanism of foam fractionation and of solvent extraction [69].

Naphthalene and phenanthrene are readily removed from aqueous systems by solvent sublation into mineral oil. The process is slightly enhanced by added salts, and slightly retarded by acetone and ethanol. The naphthalene results are used to test a mathematical model for solvent sublation column operation, and satisfactory agreement is obtained[70]. The solvent sublation of diethyl, di-n-butyl, and bis (2-ethylhexyl) phthalates in a batch-type laboratory scale apparatus is reported. Removals of all three are accelerated by added NaCl and markedly decreased by ethanol. The rate of removal of diethyl phthalate is much slower than the rates of removal of di-n0butyl and bis(2-ethylhexyl) phthalates[44].

The solvent sublation of indene and aldrin from aqueous systems into mineral oil is studied. With indene, the effects of Ni(II) and Zn(II) are investigated, the usual salting-out effect is observed, with no indication of complex formation between the olefin and the nickelous ion. The effects of a number of alcohols on the solvent sublation of aldrin are determined; very small concentrations of alcohol increase the rate of aldrin removal, while larger concentrations. Decrease it by roughly an order of magnitude at mole fractions of alcohol of the order of 0.10. Methanol is less effective than ethanol or n-propanol in decreasing the removal rate at mole fractions above 0.02 [71]. Hexachlorobutadiene and 2,4,6-trichlorophenol are removed from aqueous solutions into paraffin oil by solvent sublation. Over 99% of hexachlorobutadiene is removed from a solution containing 100 ppb hexachlorobutadiene initially in 10 min. The rate of removal of 2,4,6-trichlorophenol can be improved by adding the cationic surfactant, hexadecyltrimethylammonium bromide (HTA)[72].

Valsaraj et al. study the removal of volatile hydrophobic from aqueous solution by solvent sublation[73]. They compare the effects of ethanol on the solvent sublation and bubble aeration of a typical hydrophobic organic, p-dichlorobenzene from aqueous solution. The experiments are thus further proof for the "loose sorption" of hydrophobics at the air-water interfaces which becomes noticeable only in sublation and not in aeration. Thus sublation is a definite improvement over conventional diffused aeration[74]. The removal of pentachlorophenol from acidic aqueous solutions is studied using solvent sublation and solvent extraction. Both methods give appreciable removals in highly phase contact of the organic solvent with water and increase removals under certain circumstances. Solvent sublation is also found to be more effective than considerably smaller at pH's near the pK_a of Pentachlorophenol. The removal by solvent sublation is enhanced by increasing ionic strength and also by the presence of small amounts of an ionic surfactant in the aqueous phase. The technique of solvent sublation tried on wastewater from a wood preserving industry reduces the pentachlorophenol concentration in the aqueous waste by 99.7%[75]. Solvent sublation is used to remove a taste and odour causing hydrophobic organic 2, 3, 6-trichloroanisole from aqueous solution. Considerable improvement over conventional fine bubble air stripping operations is observed. The effects of organic to aqueous phase volume ratio, the air flow rates, interferences from electrolytes upon the separation rate, and the effects of nonhydrophobic organics (e.g. ethanol, propanol) are studied [76].

Huang et al. have done a series of work for the removal of organics by solvent sublation. Magneta is removed from aqueous solution into paraffin oil by solvent sublation of a magenta-lauryl sulfate complex. Over 96% of magenta is removed in 25 min.. A stoichiometric amount of surfactant is found to be most effective for magenta removal (1 mol of surfactant to 1 mol of dye). First–order kinetics is not followed [77]. Diphenyl is readily removed from aqueous systems by solvent sublation into mineral oil. The progress is slightly enhanced by increasing aeration rate, added salts, and surfactants, and slightly retarded by organic solvent[78]. C. I. Directed Red 1, an anionic dye, is removed by solvent sublation of Direct Red-hexadecyltrimethylammonium complex into paraffin oil. Over 90% of Direct Red is removed in 15 min. A stoichiometric amount of surfactant (one mole of surfactant to one mole of dye) is found to be most effective for Direct Red removal. The rate of separation and ultimate removal of Direct Red increased with increasing air flow rate, and increased with increasing concentration of $NaNO_3$, Na_2SO_4, and alcohol[79]. Heptachlor and its hydrolytic product, 1-hydroxychlordene are removed from aqueous solutions by air stripping, solvent sublation, and foam fractionation. The effects of air flow rate, added salt, ethanol, and surfactants are studied[80]. Two organophosphorus pesticides, ddvp (phosphoric acid 2,2-dichlorovinyl dimethyl ester) and phorate (phosphorodithionic acid o, o-diethyl s-[(ethylthio)methyl]ester) are removed from the aqueous solution by three adsorptive separation techniques. The effects of pH, air flow rate, added salt, ethanol, ionic strength and surfactants are studied on the removal efficiency. Over 97% of phorate is removed by solvent sublation, but the separation of ddvp is not effective[81]. C.I. Direct Blue 1, an anionic dye, is removed from synthetic wastewater by solvent sublation. A stoichiometric amount of surfactant is found to be most effective for the removal. The separation efficiency increase with increasing rate of air flow and decreased with increasing concentration of $NaNO_3$[82]. Nitrobenzene, isophorone, 2, 6-dinitrotoluene and 2, 4-dinitrotoluene are removed from aqueous solution by solvent sublation. The separation efficiencies of three solvents (4-methyl-2-pentanone, 1-octanol and paraffin oil) as the overlaying layer are compared. The rate of separation of these organic pollutants by solvent sublation depends strongly on the size of air bubbles, which is affected by the overlaying solvent, and concentrations of sodium dodecyl sulfate, inorganic and polar organic solute[83].

A new procedure for the preconcentration and analysis of the eleven phenolic compounds covered by the E. P. A. 604 method is developed. The new procedure is applied to stearylamine and hexadecyltrimethylammonium bromide as surfactants and concentrating the pollutants in a small volume of di-isopropylether. Experimental conditions have been optimized by means of a simplex algorithm. Under the final conditions established recoveries for the investigated compounds range within 80–95%, except for phenol, only 60% of which is recoved[84]. Toluene and o-dichlorobenzene are removed by solvent sublation and the solvents used are mineral, 1-octanol, and 2-octanol. The experiments show that under some circumstances the removal of organic hydrocarbons from water by stripping with air bubble can be enhanced significantly using solvent sublation. The effects of solute volatility and solvent properties on the removal of hydrocarbons are investigated quantitatively[85]. An analytical procedure is presented for the routine determination of trace amounts of ethoxylated nonionic surfactants in samples of raw and treated wastewater of sewage treatment plants. The alcohol ethoxylates are isolated by solvent sublation and Soxhlet extraction. Interferences are removed by open-column alumiana chromatography. Following sample cleanup, the nonionic surfactants are derivatized with phenyl isocyanate and analyzed with RP-HPLC with UV detection. This method can be used to detect the ethoxylated nonionic surfactants in environmental samples[86].

Solvent sublation is found to be highly efficient in the removal of hydrophobic and low vapor pressure such as monochlorobenzene from an aqueous solution. The removal efficiency is 81%, the values from the removal mechanism model accord well with experimental results[87]. Shibata reports that the removal of toxic organic compounds from the aqueous solution by solvent sublation[88].

6.2 Large Scale Studies

Solvent sublation may be thought of as a combination of conventional liquid- liquid extraction and bubble fractionation. In the extraction process, multiple stages are required, however, in solvent sublation, mixers and settlers are not needed, which makes sublation less expensive. The biggest an advantage over both conventional extraction and bubble fractionation is that a higher degree of fractional removal is possible under certain circumstances.

Most of the solvent sublation work has been conducted on small-scale laboratory columns operating in a batch mode relative to the liquid phase. Through this type of information is important for studying the transport mechanisms in sublation, it is not useful for ascertaining scaleup or industrial feasibility. Valsaraj group[45–47, 89] investigate semicontinuous operation and examined the column diameter. These studies demonstrate the feasibility of operating continuously and show that solvent sublation consistently outperformed bubble fractionation in terms of fractional removal. Furthermore, sublation performance is found to be less dependent on the column diameter.

Valsaraj group describe a mathematical model for the transfer of hydrophobic compounds from aqueous to an immiscible organic phase by solvent sublation. The limitations of the model are explored by simulating experimental results both for a batch scale and a continuous process. The qualitative predictions of the model with respect to the influence of the organic layer are tested by performing experiments using chloroform and 2, 3, 6-trichloroanisole as hydrophobic compounds in the aqueous phase[90]. The removal of two hydrophobic compounds (penta- and trichlorophenols) from the aqueous phase is studied, a steady-state mathematical model for the process. Solvent sublation is conducted in a continuous countercurrent mode, and the theory and experimental details on the effects of process variables on removal efficiency is reported [91].

The group investigate aspects of solvent sublation at the pilot-scale[92–94]. These aspects include (i) the develop of a steady–state mathematical model more suited for engineering applications and scaleup; (ii) the effect of novel bubble spargers on the bubble size and other hydrodynamic properties; (iii) the effects of air, solvent, and water flow rates on the performance of a three-phase continuous sublation column.

In part 1 of this series, the mechanisms of transport in solvent sublation are discussed and mathematical models are developed to predict the steady–state pollutant concentrations in all three phases of a continuous sublation column. The effects of the operating variables, thermodynamic variables and design variables on sublation performance are studied[92]. In part 2, the hydrodynamics numbers such as bubble size and gas holdup, for two types of gas spargers used in a pilot-scale sublation column are presented[93]. In part 3, steady-state fractional removal data collected from a continuous, pilot sublation column and a bubble fractionation column are presented[94].

7. RECENT TRENDS IN SOLVENT SUBLATION

The solvent sublation is a potential technique in industrial and environmental aspects. The trends are described and shown in Fig. 6.

7.1 The Recovery or Removal of Metals

Takeuchi et al. report that the removal of heavy metal ions from the dilute aqueous solution by a continuous solvent sublation technique[95]. Solvent sublation technique has been investigated for separating gold for dilute chloride solutions using Hexadecyltrimethylammonium bromide both as collector and surfactant. The 10% 2-octanol in kerosene with 0.05M Aliquot 336 is chosen as the organic phase. The gold can be separated quantitatively from a solution with only 10 ppm

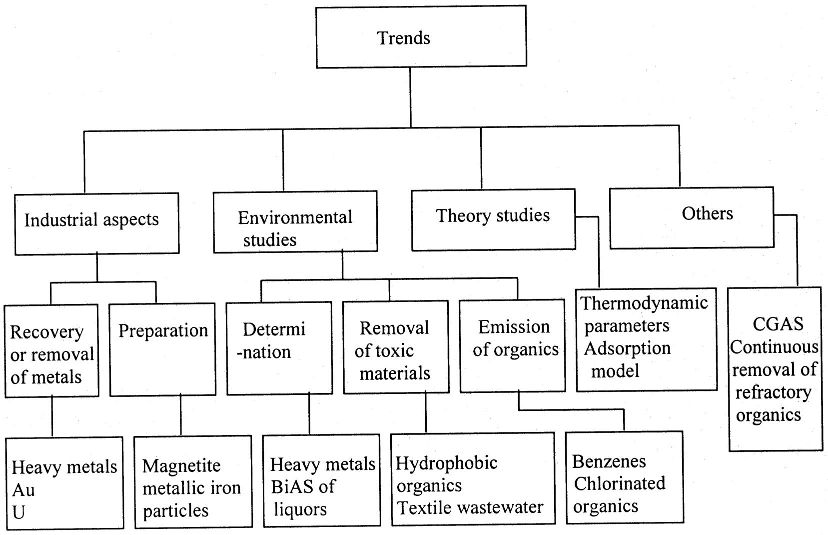

Figure 6. The trends of solvent sublation technique.

Au, with enrichment of 20[96]. The Uranyl ions from aqueous solutions at 298K with di (2-ethylhexyl) phospharate in heptane or containing trioctylphosphite oxide in kerosene is removed from dilute aqueous solution by solvent sublation. The effects of operating factors on the percent removal of U are examined in countercurrent operation[97].

7.2 The Removal of Toxic Materials

Nolan et al. apply the solvent sublation to the simultaneous removal of emulsified coal-tar and dissolved organics[98]. The removal of hydrophobic compounds from the aqueous phase by continuous countercurrent solvent sublation is reported[99]. Three hydrophobic organic compounds naphthalene, pentachlorophenol and 2, 4, 6-trichlorophenol are removed by continuous countercurrent solvent sublation[100]. The organic compounds mono-chlorobezene, trichlorobenzene and naphthalene are removed from the aqueous solution by solvent sublation with high efficiency. A model for the removal mechanism is constructed and the removal percentage calculated from the model is compared with experimental results. The experimental parameters are also discussed[101]. Experiments in a packed bed reactor are conducted to investigate the efficiency of sublation in reducing the color, turbidity and COD of the textile wastewater obtained from a dyeing and finishing plant[102].

7.3 Determination of Material in Environmental Samples

A solvent sublation is studied for the determination of trace of Cd, Co, Cu, Ni in water samples. Ammonium pyrrolidine dithiocarbamate is used a complexing agent, sodium lauryl sulfate as a surfactant and bubbling with nitrogen gas, methyl iso-butyl ketone as organic solvent. The analytes preconcentrated are determined by a graphite furnace atomic absorption spectrophotometry (GF-AAS). Extractability of each element is 88%for Cd, 86%for Co, 95% for Cu, 76% for Ni, respectively. The method could be applicable for the determination of trace elements on various water samples of a large volume[103]. The preconcentration and determination of trace elements (Cu, Ca, Co, Ni) in water samples are studied by solvent sublation utilizing dithizonate complexation, sodium lauryl sulfate as a surfactant and bubbling with nitrogen gas, methyl iso-butyl ketone as organic solvent, detected by GF- AAS. The method is applied to the analysis of real water samples and good results of more than 85% recoveries are obtained in spiked samples[104].

In Europe, the bismush active substances (BiAS) procedure of procedure of Wickhold has been officially adopted as the means for determining alkoxylated nonionic surfactants in biodegradation test liquors. Using the solvent sublation and ion-exchange as environmental sample pretreatment, a more satisfactory result can be obtained in monitoring of nonionic surfactants-particularly in sewage[105].

7.4 The Emission of Organics to the Atmosphere

The mass of volatile organic compounds emitted to the atmosphere during the solvent sublation is determined experimentally, using toluene as a test compound. It is shown that the emission of toluene to the atmosphere can be significantly reduced by using solvent sublation instead of air stripping under the same experimental conditions. The parameters affecting emission are discussed[17]. The mass of trichloroethylene, chlorobezene, and 1, 3-dichlorobezene removed from the aqueous solution and emitted to the atmosphere during solvent sublation is determined experimentally. The reduction of emission over air stripping is more effective for the more hydrophobic and less volatile compounds. Removal of the chlorinated volatile organic compounds from water by solvent sublation at an elevated temperature of 45^0C is significantly faster than at room temperature. However, the emission to the atmosphere are also increased[106].

7.5 Mechanism Studies of Environmental Organics

The partitioning of organic chemicals to the air-water interface can be significant and must be quantified in several situations of environmental interest including partitioning of chemicals into small air bubbles in water into small water drops in air (for example, fogs), and between the phases present in relatively dry soils. Experimental data are reported for interface-air partitioning of a variety of chemicals and are consolidated with previous data to show that interface partitioning is primarily controlled by chemical's hydrophobicity. Correlations are derived for interface-air and interface-water coefficients from data for 44 polar and nonpolar chemicals[108]. Thermodynamic parameters such as free energy, ethalpy and entropy of transfer from the bulk aqueous phase to the air-water interface at 25°C for 41 hydrophobic compounds of environmental interest are calculated from literature data on adsorption. A simple adsorption model based on interfacial energy changes predicts the values satisfactorily, however, the prediction is sensitive to the orientation of the molecule at the air-water interface[108].

7.6 Preparation

Yokoi et al. report a method to prepare magnetite and metallic iron particles by solvent sublation and adsorbing colloid flotation technique. Upon the precipitation of iron hydroxide (Fe $(OH)_3$) and magnetite in the presence of poly (vinyl alcohol) (PVA), PVA is bound to the precipitates in very high yields[109].

7.7 Others

Carter et al. use online ultraviolet visible spectrophotometry to monitor the solvent sublation process[110].

Microgas dispersions called colloidal gas aphrons (CGAS) are generated using cationic, anionic, and nonionic surfactants, and are used in a semibatch mode to remove pentachlorophenol from the aqueous phase. The CGAS may be an improvement on the solvent sublation[111]. CGAS in connection with coflotation processes is used to determination of heavy-metals (Cu, Co, Cd, Ni) in water with recovery over 90%, which takes advantage over the solvent sublation[112].

Valsaraj et al. describe the promise of the solvent sublation, which aim at the removal of the refractory organics by continuous countercurrent solvent sublation, and the design of bubble-column reactors, wastewater treatment and so on[113].

8. CONCLUDING REMARKS

Solvent sublation is a nonfoaming adsorptive bubble process, which is capable of removing trace levels of nonvolatile and volatile organic compounds from wastewaters. The advantage of solvent sublation over bubble fractionation or air stripping is that higher removal efficiencies are possible. The sublation process doesn't need mixes and phase separators, which is needed in the solvent extraction. Furthermore, the effluent water from a sublation column doesn't require further treatment to remove residual solvent. The handles are simple and expenses are cheap, so the solvent sublation has the potential in the environmental treatment.

On the other hand, the recovery of valuable trace metals is a very important aspect in the future. Maybe the materials can be recovered from the sea by solvent sublation techniques.

Although many works have been done about the solvent sublation, but many aim at the laboratory studies, the investigations on the large-scale studies are sparse. Though the solvent sublation technique has many advantages over many traditional techniques, the road is very long to utilize the technique to the wastewater treatment and the usable materials recovery in the near future.

In the applications, one problem should be solved that the recycling of surfactants in the recovery of ionic material by solvent sublation. The mechanism of solvent sublation need further develop to direct the applications.

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