Application of solvent sublation for the removal of trace elements in wastewater

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Some examples of application of the solvent sublation are presented. Our results on separation and pre-concentration of a trace of some metals (Co (II), Ni (II), and Cu (II)) with the use of the solvent sublation approach are given.

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1 Introduction

The solvent sublation technique, one of adsorption bubble separation techniques, is initially proposed by SEBBA (1962). This process can be considered as a solvent extraction with the additional removal mechanism (air or purge gas stripping). The technique has advantage over ion flotation or solvent extraction; it has attracted many attentions in the wastewater treatment and the recovery of many metals.

The removal of trace elements from waste water is one of significant task of environmental engineering. Although the adsorptive bubble separation techniques have been studied extensively, the literature on the subarea of solvent sublation is rather sparse. Recently some industrial applications of solvent sublation for waste water treatment were proposed by BRYSON & VALSARAJ (2001).

The determination of trace elements in water requires highly sensitive as well as accurate analytical methods. If a water sample is complicated like sea or wastewater, it becomes very difficult to analyze the sample due to very low concentration of impurities. With the use of solvent sublation technique the preliminary concentration of impurities (e.g. trace elements) for further analytical determination can be realized (KIM *et al.* 2001).

2 Experimental Study

Separation in solvent sublation is due to the ability of some species to orient themselves in the air-water interface, and the adsorption on the bubble surface is due to the presence of certain functional groups. In solvent sublation equilibrium state cannot be established in the bulk of the system but only at the aqueous-organic interface. As a result, as the solvent sublation process is not limited by the equilibrium constant, the recovery of trace elements can eventually reach 100%.

In a particular experiment in solvent sulation process, surface-active material will be present in a bulk aqueous phase, on top of which is placed an immiscible liquid. Gas bubbles are generated in the aqueous media and are buoyed upward into the organic phase. The bubbles selectively adsorb surface active material while in the water (as in any adsorptive bubble process) and transport this material to the nonaqueous phase. The material is either deposited in the top phase after the bubbles burst at the air-liquid interface or dissolved during the passage of the bubble through the immiscible phase. In fact, the name – “Solvent Sublation” arises from that an ionic species, called the *colligend*, is removed by addition of a surface-active collector of opposite charge to that on the colligend. The complex formed by coulombic attraction is called the “Sublate”, and the process of lifting the sublate by gas bubbles – “Sublation”. According to F. Sebba, it is not necessary that the sublate dissolve fully in the organic layer, only that the salt be wetted by the solvent. Thus, both the formation of true solutions and suspensions of the sublate in the organic phase should be possible.

In this paper we present our results on separation and pre-concentration of a trace of some metals (Co (II), Ni (II), and Cu (II)) with the use of one of the perspective separation method – solvent sublation. Water example solution was placed to the flotation cell 2.5 cm in diameter and 80.0 cm in height. According to the solvent sublation technique the surfactant (sodium dodecylsulfate) was added to the bulk aqueous phase containing trace amounts of cations Co, Ni, Cu. The initial concentration of trace elements (cobalt, nickel and copper sulfate) was $< 10^{-3}$ mol/L. The floated adsorbed solute was collected and dissolved in 10 mL of heptanoic acid on the surface of dilute aqueous solution. The nitrogen gas was bubbled at the flow rate of 10 mL/min during 60 min. The floated metal - dodecylsulfate ion complexes were collected in upper heptanoic acid layer. The residual concentrations of metal- and dodecylsulfate - ions were determined by colorimeter and potentiometer methods.

The basic advantage of solvent sublation over predispersed solvent extraction is that intimate contact between the organic solvent and the aqueous phase is prevented. This feature overcomes the problem of residual solvent in the aqueous phase.

There have been a number of examples where the hydrophobic nature of neutral-nonpolar compounds has been utilized to remove them in solvent sublation. Some examples appear in Table 1 (a: neutral compounds) in which the solute removed. A surfactant is only necessary when the compound to be removed is ionizable, ionic dyes, metal complexes, or phenols, as illustrated in Table 1 (b: ionic comounds). In the cases of weakly ionizable species, such as phenols, the use of surfactant can be avoided by adjusting the pH (VALSARAJ & THIBODEAUX 2001).

In solvent sublation, volatile and nonvolatile compounds are recovered in the solvent phase, just like they are recovered in the solvent phase used in the extraction process. Besides in sublation only one stage of solvent-water contact is required and mixers and settlers are not needed, which makes sublation less expensive.

The recoveries of 80—90 percents of elements from original solution showed that the solvent sublation method can be used both for the removal of trace elements from waste water and for the quantitative determination of impurities in dilute water solutions.

3 Conclusions

S.S. is a nonforming adsorptive bubble process which is capable of removing trace levels of nonvolatile and volatile organic compounds from waste-water. The advantage of S.S. over foam separation or air stripping is that higher removal efficiencies are possible. Like liquid-liquid extraction, S.S. utilizes water - immiscible solvent for contaminant recovery; however, in sublation, mixers and phase separators are not needed. The effluent water from a sublation column does not require further treatment to remove residual solvent.

4 Acknowlegments

This research was supported by the Russian President Program “Leading Scientific Schools of Russian Federation” (№ SS - 4241.2006.3).

Table 1: Survey of solvent sublation literature.

Compound	Surfactant (or Complex Agent)	Solvent	Column Dimensions, cm	Investigators
a) Neutral Compounds				
Lindane, Endrin	None	Mineral oil	3.5 x 85	Valsaraj & Wilson 1983
1,1,1-trichloroethane, Dichlorobenzenes nitrophenols, PCBs,	None	1-octanol Mineral oil	5.2 x 116	Lionel *et al.* 1981
Naphthalene, phenanthrene	None	Mineral oil	3.5 x 85	Huang *et al.* 1983
Alkyl phthalates	None	Mineral oil	3.6 x 90	Tamamushi & Wilsor 1984, 1985
Indene, aldrin	None	Mineral oil,	3.1 x 90	Foltz *et al.* 1986
Pentachlorophenol (PCP)	HTMAB	Mineral oil Decyl alcohol 1-octanol	5.0 x 100	Valsaraj & Springer 1986
Diphenyl	None	Mineral oil	3.2 x 100	Wang & Huang 1988
o-Dichlorobenzene, toluene	None	Mineral oil 1-octanol 2-octanol	8 x 50	Shin & Coughlin 1990
Hexachlorobutadiene, 2,4,6-trichloro-phenol (TCP)	None	Mineral oil (white oil, Texaco Houston)	3.5 x 60	Shin *et al.* 1990
PCP, TCP, naphthalene	None	Mineral oil	5.0 x 100	Valsaraj *et al.* 1992
b) Ionic Compounds				
Methylene blue and orange	HTMAB	2-octanol	3.5 x 87	Womack *et al.*1982
Magneta (cationic dye)	Sodium lauryl sulfate	Mineral oil	3.5 x 60	Sheu & Huang 1987
Eleven phenolic compounds	HTMAB, Stearyl-amine	Di-isopropyl ether, isopropyl alcohol	Not specified	Caballero *et al.* 1988
Phenols	ethyl-hexadecyl-ammonium bromide	MIBK	6 x 76	Nolan & McTernar 1988
Gold	HTMAB	2-octanol, MIBK, n-butyl acetate, tri-butyl phosphate	3.7 x 40	Wang *et al.* 1993
Hexacyanoferrate (II)	Dodecylpyridinium chloride	2-octanol	9 x (2 lt.)	Spargo & Pinfold 1970
Thulium and americium	Citric acid	-	-	Stachurski & Szeglowski 1974
Neutral and Ionic, PCP, TCP, 1,2,4 - trichlorobenzene, 2,3,6 - trichloroanisole	HTMAB	Mineral oil, decyl alcohol	2.3 x 100	Valsaraj & Thibodaux 1991b; Lu *et al.* 1991
Methyl orange, Rhodamine B	HTMAB	2-octanol	4.5 x 46	Karger *et al.* 1967a
Copper	Sodium dodecyl sulfate	geptanoic acid	2.5 x 40	Lobacheva *et al* 1998
Copper, nickel	Sodium dodecyl sulfate	geptanoic acid	2.5 x 80	Lobacheva & Levichev 2002; Kim *et al.* 2001 ; Lu & Zhu 2001
Cobalt	Sodium dodecyl sulfate	geptanoic acid	2.5 x 70	Lobacheva 2002; Lu & Zhu 2002

5 References

BRYSON, B. G. & VALSARAJ, K. T. (2001): Solvent sublation for waste minimization in a process water stream — a pilot-scale study. – Journal of Hazardous Materials, **B82**: 65—75.

KIM, Y.-S., SHINA, J.-H., CHOIA, Y.-S., LEE, W. & LEE, Y.-I. (2001): Solvent sublation using 8-hydroxyquinoline as a ligand for determination of trace elements in water samples. – Microchemical Journal, **68**: 99—107.

VALSARAJ, K. T. & THIBODEAUX, L. J. (1991): Studies in Batch and continuous Solvent Sublation. II. Continuous Countercurrent Solvent Sublation of Neutral and ionic Species from Aqueous solutions. – Journal of Sep. Science Technology, **26**(3): 367—380.

VALSARAJ, K. T. & WILSON, D. J. (1983): Removal of Refractory Organics by Aeration. IV. – Colloids Surf., **8:** 203.

LIONEL, T., *et al.* (1981): Removal of Refractory Organics from Water by Aeration. I. – Journal of Sep. Science Technology, **16**(8): 907—935.

HUANG, S.D., *et al.* (1983): Removal of Refractory Organics from Water by Aeration. I. – Journal of Sep. Science Technology, **18**(10): 941—968.

TAMAMUSHI, K. & WILSON, D.J. (1984-1985): Removal of Refractory Organics from Water by Aeration. VI. – Journal of Sep. Science Technology, **19**(8): 1013—1023.

VALSARAJ, K. T. & SPRINGER, C. (1986): Solvent Sublation for the Removal of Hydrophobic Chlorinated Compounds from Aqueous Solutions. – Water Research, **20**(9**):** 1161 – 1175.

SHIN, H. S. & COUGHLIN, R V.(1990): Removal of Organics Compounds from Water by Solvent Sublation. I. – Journal of Colloids International Science, **138**(1): 105 – 112.

VALSARAJ, K. T., *et al.* (1992): Continuous Nonfoaming Adsorptive Bubble Separation Processes for the Removal of Hydrophobic Organics Compounds from the Aqueous Phase. – ACS Symp. Ser., **509**: 116 128.

WANG, Y., *et al.* (1993): Gold Recovery with Solvent Sublation from Chloride Solutions. – International Journal of Mineral Processes, **40**: 57 – 58.

SPARGO, P. E. & PINFOLD, T. A. (1970): Studies in the Mechanism of Sublate Removal by Solvent Sublation. – Separation Science, **5**(5): 619 – 635.

STACHURSKI, J. & SZEGLOWSKI, Z. (1974): Verification of Stochastic Model for a Frothless Solvent Ion Flotation Using Thulium and Americium, – Separation Science, 9(4): 313 – 324.

KARGER, B. L. & CARGER, A. B. (1967): Use of Rate Phenomena in Solvent Sublation Separation of Methyl Orange and Rhodamine B. – Analytical Chemistry, **38**(4): 652-654.

LOBACHEVA, O. L. *et al.* (1998): Solvent Sublation of Cu+2 from Aqueous Solutions by Sodium Dodecylsulfate. – X Conference of Surfactants. – Abstracts, Belgorod, Russia: 38.

LOBACHEVA, O. L. & LEVICHEV, S. A. (2002): Adsorption Processes in the mutual system: Na+,Co+2,Ni+2‖DS-, SO4-2. – XIV Conference on Chemical Thermodynamics, RCCT, Russia, St.-Petersburg: 452.

LU, Y.J. *et al.* (2002): A mathematical model and mechanism of sublation of some surfactants. – Talanta, 57(5): 891-898.

WOMACK, J.L., *et al,* (1982): Removal of Refractory Organics from Water by Aeration. II.– Journal of Sep. Science Technology, 17(7): 897 – 924.

SHEU, G. L. & HUANG, S. D. (1987): Solvent Sublation and Adsorbing Colloid Flotation of Magneta. – Journal of Sep. Science Technology, 22(11): 2253 – 2252.

CABALLERO, M., *et al.* (1988): Solvent Sublation of Some Priority Pollutants (Phenols). – Analitical Letters, 21(1): 63 – 76.