

Solve Wastewater Problems with Liquid/Liquid Extraction

LLE is well-suited to the removal of trace organics from wastewater. This overview offers guidelines on process design and solvent selection.

Roger W. Cusack,
Glitsch Process Systems, Inc.

Chemical process industries (CPI) plants today are faced with more-stringent wastewater discharge regulations than ever before, with the probability of more restrictions on the horizon. Plant designers and operators involved in wastewater treatment often encounter particular difficulties when faced with organic compound contamination.

Liquid/liquid extraction (LLE) is a powerful separation technique that is finding wider application in the CPI to solve difficult environmental problems, particularly in the removal of trace organic compounds from wastewater streams. LLE is usually only applied when more conventional techniques such as steam stripping or distillation are not suitable. This is because LLE usually involves the introduction of a new component (the solvent) to the process, and this has obvious environmental implications.

Liquid/liquid extraction has been applied only sparingly in the past, because engineers are unfamiliar with its possibilities and how to employ this powerful technology. This article will review the advantages and limitations of LLE in general, and outline practical guidelines for wastewater applications. Particular emphasis will be given to the considerations that go into the selection of the solvent for the process.

When to use LLE

The most common method of treating wastewaters to reduce the level of organic contaminants is steam stripping, particularly when the contaminant's boiling point is lower than the boiling point of water. However, there are sometimes cases where stripping is

not feasible. It is in these more difficult cases where LLE is often a viable alternative.

Table 1 lists some typical organic contaminants commonly found in wastewater. Those normally handled by steam stripping are found at the top of the table, and those better handled by LLE are at the bottom of the table.

Boiling point. The first key parameter to consider when deciding between steam stripping and liquid/liquid extraction is boiling point. If the boiling point of the contaminant is significantly below that of water, it is usually handled by stripping.

An example of a compound that can be controlled by steam stripping alone is benzene, which has been identified as a carcinogen and must be reduced to ppm or ppb levels in plant effluent waters. Since benzene boils at 80.1°C, and also forms a low-boiling-point azeotrope that boils at 69.4°C, it can be effectively reduced by steam stripping. The benzene-rich stream produced as an overhead from the stripper can be sent to incineration for final disposal, or recovered and recycled.

However, a boiling point below that of water is not the only consideration in choosing between stripping and extraction. Some organic compounds behave nonideally in aqueous solutions and form minimum boiling azeotropes with water. This allows them to be separated from water even though they boil higher than water.

For example, toluene boils at 110.8°C. But it also forms an azeotrope of 20.2% water and 79.8% toluene that boils at 85°C, allowing steam stripping to be used to remove toluene from wastewater.

Table 1. Some organic contaminants are best removed from wastewater by stripping, others by extraction.

STRIPPING					
Organic Compound	Boiling Point, °C	Solubility, %	Azeotrope		Typical Reduction Levels
			Boiling Point, °C	Water Concentration, %	
Methylene Chloride	40.0	2.0	38.1	1.5	< 50 ppb
Acetone	56.2	∞	—	—	< 50 ppb
Methanol	64.5	∞	—	—	< 50 ppb
Benzene	80.1	0.18	69.4	8.9	< 50 ppb
Toluene	110.8	0.05	85.0	20.2	< 50 ppb

EXTRACTION					
Organic Compound	Boiling Point, °C	Solubility, %	Azeotrope		Typical Reduction Levels
			Boiling Point, °C	Water Concentration, %	
Formaldehyde	-19.0	∞	—	—	< 800 ppm
Formic Acid	100.8	∞	107.1	22.5	< 1,200 ppm
Acetic Acid	118.0	∞	—	—	< 800 ppm
Pyridine	115.5	57	92.6	43.0	< 10 ppm
Aniline	181.4	3.6	99.0	80.8	< 10 ppm
Phenol	181.4	8.2	99.5	90.8	< 10 ppm
Nitrobenzene	210.9	0.04 (approx.)	98.6	88.0	< 10 ppm
2,4-Dinitrotoluene	300.0	0.03	99-100 (est.)	90+ (est.)	< 10 ppm

LLE for high-boiling organics. Now consider the case of phenol. It, too, boils at a higher temperature than water (181.4°C) and forms an azeotrope that boils lower than water (90.8% water, 9.2% phenol, B.P. = 99.5°C). However, in this case, separation by stripping is not feasible because of the narrow difference between the boiling points of the azeotrope and water — just 0.5°C — and because the azeotrope takes so much water overhead with it.

For these reasons, phenol is almost always removed from wastewater by other techniques, usually liquid/liquid extraction, biological treatment, or adsorption onto carbon. Very often LLE is used upstream and in conjunction with these other processes to remove the bulk of the phenol. LLE can typically reduce phenol levels to less than 10 ppm, and in pilot tests has reached levels of less than 20 ppb.

LLE for low-concentration acids. Also shown in the lower section of Table 1 is acetic acid, which has long

been recovered by LLE. It is present in the wastewater discharge of many chemical processes, particularly those which involve an oxidation reaction. The problem is that it is usually present at relatively low concentrations (0.5–3.0%).

Acetic acid boils at 118°C and does not form any azeotrope with water. Therefore, it cannot be stripped out. Since it is not toxic, very often it is treated merely by sending it to a biological treatment plant. However, with ever-tightening requirements for reduction of chemical oxygen demand (COD) in plant outflows, it has recently become economical for companies to remove and recover the acetic acid (plus formic acid, which is often a co-contaminant) before sending the stream to biological treatment.

Liquid/liquid extraction can be economically used to recover acids from even these low-concentration streams.

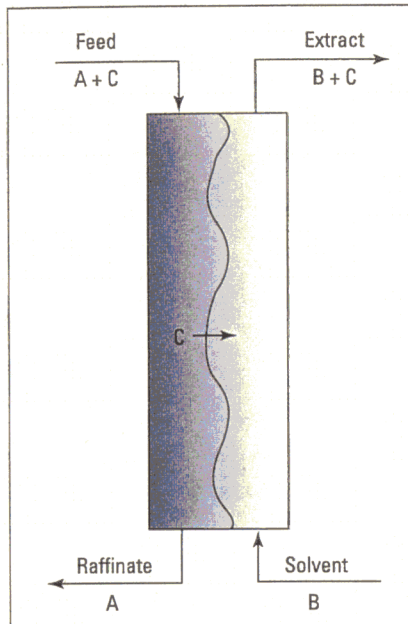
LLE for hydrogen-bonded compounds. A very curious component in the bottom section of the Table 1 is

formaldehyde. Like acetic acid, formaldehyde often appears in the wastewater from chemical operations as a byproduct of oxidation reactions. With its boiling point (-19°C) so much lower than that of water, it would appear to be easily stripped out of water.

However, formaldehyde actually is extremely difficult to remove from water once it has been dissolved. This is due to the hydrogen bonding phenomenon, which bonds the formaldehyde molecules very tightly to the water molecules by means of electrostatic charges.

LLE can be used to extract formaldehyde from wastewater down to levels of less than 1,000 ppm.

LLE for zero-volatility compounds. LLE has been used for many years for the recovery of primary metals, such as copper, nickel, and zinc. Thus, it is not surprising that it is finding applications today for the removal of metals or their organometallic derivatives from the discharges of process plants. These metals or metal



■ Figure 1. Basic extraction process.

compounds are usually the result of contamination from the catalysts used in the process. Since LLE works on the principle of chemical structure rather than volatility difference, it is ideally suited for solving these difficult removal problems.

Strengths of LLE

Some of the particular strengths of liquid/liquid extraction over competing technologies, such as carbon adsorption, wet oxidation, incineration, membranes, and biological treatment, are:

- *Ruggedness.* The liquid/liquid extraction column can handle the wide concentration ranges, chemical aggressiveness, and fouling characteristics typically encountered in CPI wastewater applications. In addition to the particular organic compounds that must be removed, these wastewater streams often contain insoluble oils, tars, and solids, which LLE columns can handle without expensive prefiltering or shutdowns for periodic cleaning.

- *Flexibility.* Liquid/liquid extraction can handle the wide range of flow rates encountered while still maintaining its efficiency. Typically, a well-designed LLE column can have a turn-down ratio of 3:1 to 4:1 (that is, it can

be run effectively at 25–33% of its full design capacity) without a loss in extraction efficiency. This is important because wastewater stream flow rates can vary widely depending on plant operating conditions.

- *Recycle capability.* Unlike other processes that destroy the contaminant, LLE can recover the material for recycle. For example, in the manufacture of polycarbonate resins, water streams are produced that can contain up to 5% phenol. LLE can be used to recover this phenol and recycle it back to the reactors rather than destroying it. Likewise, LLE wastewater processes can be designed to recover acetic or formic acid pure enough for either reuse or resale on the open market.

- *Low energy requirements.* With the proper solvent, LLE is extremely energy efficient compared to other technologies (especially compared to wet oxidation processes using peroxide or ozone). This is because LLE is se-

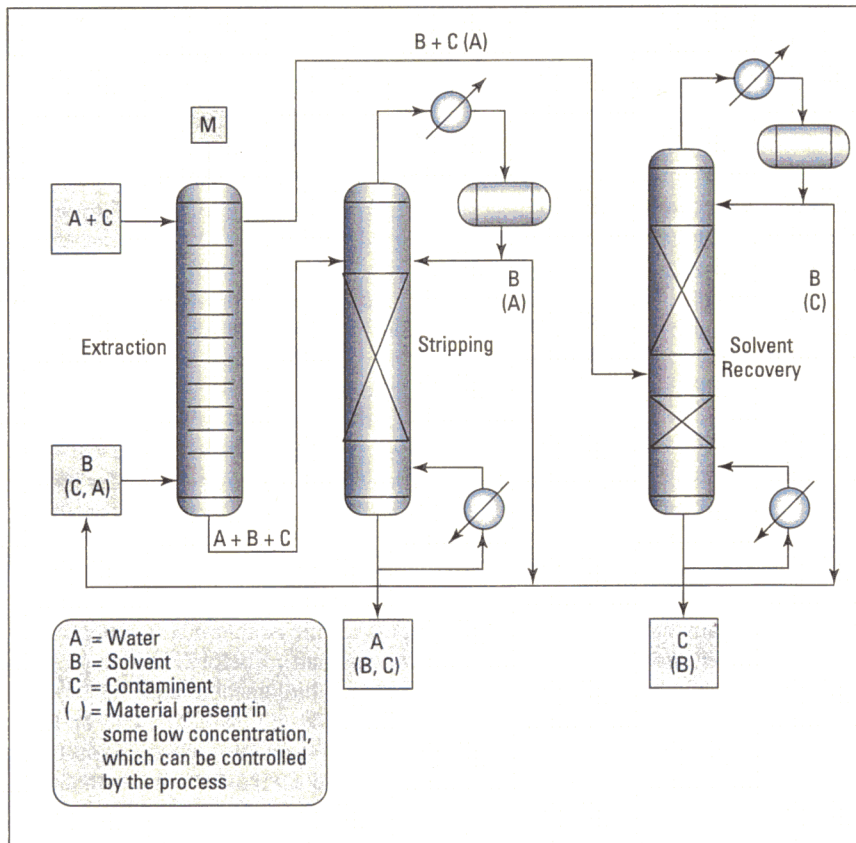
lective and removes only certain components, whereas the oxidation processes destroy essentially all of the waste stream's COD, and this can increase the operating cost significantly.

LLE limitations

Of course, liquid/liquid extraction also has its limitations.

- *May introduce additional solvents.* LLE usually involves the introduction of a new solvent into the process plant. It is important to consider all possible solvents already in use at the plant for possible use in an LLE wastewater project. Be certain the company selling LLE technology has the capability to thoroughly test a wide range of solvents, including ones already present in the plant and processes before automatically specifying a new, and additional, solvent.

- *Selective, so may not reduce total COD.* Because LLE is selective and only removes certain components, it may not



■ Figure 2. Typical extraction process for removing contaminant C from water (A).

reduce the total COD of the stream to the required level. Therefore, LLE is seldom used as a stand-alone treatment. Instead, it is often used in conjunction with other technologies to arrive at a total solution. The advantage of this approach is that the load on the final treatment plant is reduced significantly by the pretreatment of some streams.

Process fundamentals

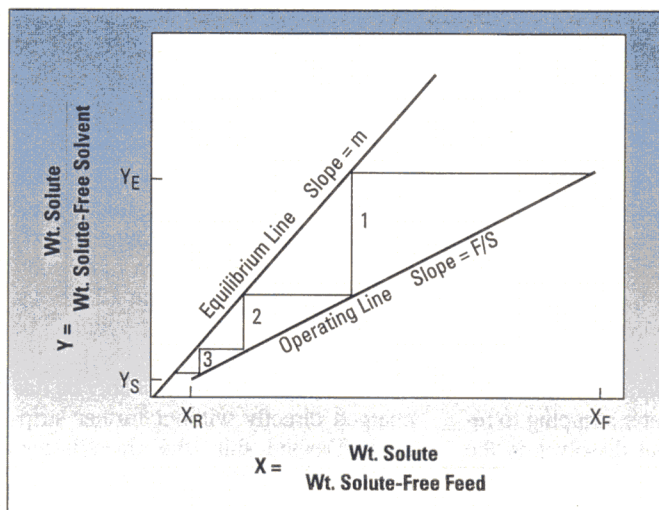
Liquid/liquid extraction (Figure 1) is a mass-transfer process in which a feed material is brought into contact with a specially selected solvent, and this solvent removes (*i.e.*, extracts) some particular chemical compound(s) from the feed stream. The material being extracted is known as the *solute*, the solute-depleted stream leaving the LLE column is called the *raffinate*, and the solute-rich stream leaving the extractor is called the *extract*. The subscripts *F*, *S*, *E*, and *R* are used to refer to the feed, solvent, extract, and raffinate streams, respectively.

A typical extraction system is illustrated in Figure 2. For example, assume that water (A) is contaminated with phenol (C). By bringing this water stream into contact with a suitable solvent (B), it is possible to extract the phenol from the water phase into the solvent phase. The phenol is usually recovered from the solvent phase by distillation.

The important thing is how the streams are brought into contact. One of the liquids must be dispersed into the other in order to produce droplets and, therefore, interfacial area. This is necessary so that mass transfer can take place. The mass transfer can be either from the dispersed phase to the continuous phase, or vice versa.

A very useful chemical engineering tool for looking at this mass-transfer operation is the familiar McCabe-Thiele diagram (Figure 3). A complete discussion of this can be found in (1).

The Kremser equation. Actually, though, it is usually not necessary to make McCabe-Thiele plots to evaluate LLE. As long as the straight-line assumption holds (that is, mutual solubility of the feed and solute is negligible



■ Figure 3. A McCabe-Thiele diagram can be used to understand the extraction operation.

[as is usually true in wastewater treatment applications]), the relationships among the variables can be represented by the Kremser equation:

$$N = \frac{\log \left[\left(\frac{X_F - \frac{Y_S}{m}}{X_N - \frac{Y_S}{m}} \right) \left(1 - \frac{1}{E} \right) + \frac{1}{E} \right]}{\log E}$$

where N is the number of theoretical stages, X_F is the concentration of solute in the feed, Y_S is the concentration of solute in the solvent, m is the distribution coefficient, which is equal to Y/X , X_N is the concentration of solute in the raffinate, and E is the extraction factor, which in turn is equal to $m(S/F)$ where S and F are the solvent and feed rates, respectively. All rates and concentrations must be expressed on a "solute-free" basis.

The equation has been solved graphically, as shown in Figure 4. To use this plot, first determine the degree of solute removal required as defined by the fraction unextracted, X_N/X_F . Once the distribution coefficient for the solvent is known, the solvent/feed ratio is arbitrarily varied to give various extraction factors. For each value of E , find on the abscissa the number of theoretical stages required. In this way, one can conduct preliminary screening of possible solvents, operating conditions, and economics before proceeding to pilot tests and equipment design.

As a general guideline, an LLE process should be run with a minimum extraction factor of 1.3. Below this value, the number of theoretical stages required become excessive and somewhat impractical. Most environmental extraction applications require anywhere from six to ten theoretical stages.

To illustrate the use of the Kremser equation, let us consider again the removal of phenol from wastewater. Several possible solvents for this operation are listed in Table 2.

Suppose that the stream contains 1,000 ppm phenol, which must be reduced to 1 ppm. Therefore, X_N/X_F is approximately 0.001. Referring to Figure 4, we see that at $E = 1.3$, more than 20 ideal stages are needed, at $E = 1.5$, 15 ideal stages are needed, and at $E = 2.0$, 9.2 ideal stages are needed.

To keep the stage requirements within a reasonable range, let us assume operation at an E of about 2.0. Thus, for each 100 lb/h of wastewater passing through the system, the following solvent rate (in lb/h per 100 lb/h of feed) would be required:

Toluene	101.5
Benzene	86.9
Isopropyl ether	6.9
<i>n</i> -Butyl acetate	2.8
Methyl isobutyl ketone	2.5

These results point strongly toward methyl isobutyl ketone (MIBK) as the preferred solvent. And, indeed, MIBK

has been used extensively in phenol LLE applications.

Solvent selection

Because the solvent has such a pronounced impact on the overall process feasibility and economics, solvent selection is probably the most important aspect of any LLE process design.

The impact of solvent selection is evident when examining the overall flow sheet for a typical LLE process. There are three operations involved: (1) extraction, (2) water stripping to remove the solvent that dissolves in the water, and (3) distillation to recover the solvent for recycle. In a typical LLE plant, the extractor itself represents only about 10–15% of the capital investment and 5% of the operating cost. The balance of the investment and operating cost is associated with the water stripper and solvent recovery columns. Hence, from an economic standpoint, the importance of solvent selection is clear.

The "ideal" solvent. An ideal LLE solvent has several characteristics. Let us discuss these characteristics with respect to phenol removal, for which there are several commercially used solvents, as shown in Table 2.

- *High distribution coefficient.* A high distribution coefficient will minimize the solvent circulation rate.

Table 2 shows that the distribution coefficient for MIBK is much higher than that for toluene. As a result, phenol extraction with MIBK can usually be accomplished at a solvent/feed (*S/F*) ratio of 1:15, whereas toluene, due to its poorer distribution coefficient, requires an *S/F* of 2:1. Thus, the net effect on solvent circulation rate is a factor of 30. Since all of this solvent must be distilled for recycle back to the process, it is easy to see that MIBK is a much more energy efficient solvent.

- *Low solubility in water.* This is important because a solvent that is soluble in the water to any extent will have to be removed prior to discharge of the water. Unfortunately, it is a general (but not universal) characteristic of most solvents that the better or more-

efficient the solvent, the higher its mutual solubility with water.

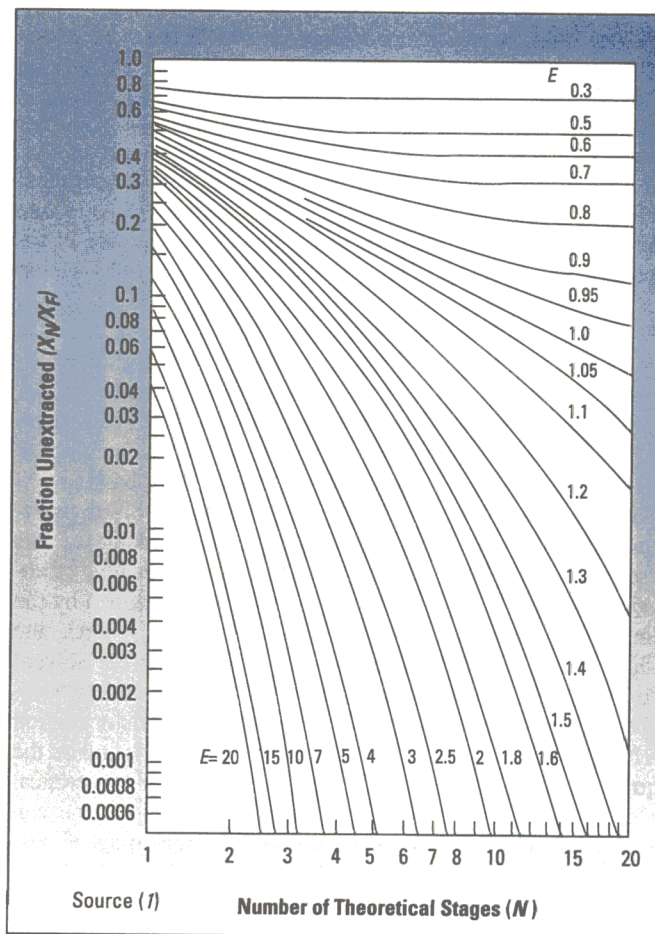
This can be seen in the case of MIBK vs. toluene for phenol extraction discussed above. Although MIBK is much more efficient (by a factor of 30) when looking at the extract side, it is less efficient when looking at the raffinate side. MIBK is much more soluble in water than toluene (2.7% vs. 0.05%) and, therefore, must be stripped from the water, whereas the toluene raffinate could probably be discharged directly without further stripping. Despite this, the overall economics still greatly favor MIBK.

- *Low toxicity.* It is obvious that any solvent selected must have low toxicity, since some of it will necessarily remain in the discharge water, even if only at ppm or ppb levels. Also, the control of solvent vapors must also be considered in the process design.

For example, methylene chloride is a very powerful solvent for organics, but its low boiling point (40°C) indicates the potential for vapor emissions. Also, chlorinated organics are under increasing regulation from environmental authorities and are, therefore, seldom considered.

- *Low solubility of water in the solvent.* This is desirable because any water that dissolves in the solvent must probably be removed, usually by distillation. This aspect is particularly important in the recovery of compounds like acetic acid, which usually has to be recovered in glacial form (less than 0.5% water). The more water carried along with the extract stream, the more energy that must be expended to remove this water and reach the glacial point.

- *Chemical stability and safety.* These characteristics are important because they impact equipment design.



■ **Figure 4.** Graphic solution of the Kremser Equation.

Table 2. Possible solvents for phenol extraction.

Solvent	Boiling Point, °C	Distribution Coefficient	Solubility in Water, wt. %
Toluene	110.8	1.97	0.05
Benzene	80.3	2.30	0.178
Isopropyl Ether	68.5	29.0	0.90
<i>n</i> -Butyl Acetate	126.2	71.0	1.20
Methyl Isobutyl Ketone (MIBK)	116.6	80.0	2.70

For example, diisopropyl ether is a good solvent for phenol extraction. But it also has the tendency to form peroxides, which are explosive hazards, and for this reason would not normally be chosen for this process. Likewise, isopropyl acetate is also a possible solvent, but it has a tendency to undergo a hydrolysis reaction, producing isopropyl alcohol and acetic acid. In this case, not only is there a loss of solvent, but byproducts are produced that must be removed from the system.

- *Ease of recovery for recycle.* There are very few processes where the solvent is used on a once-through basis, and the ease of recovery for recycle should be considered. The most common method of recovery is distillation, and since this works on the principle of boiling point difference, it is important that there be a reasonable difference between the boiling points of the solvent and the solute being recovered.

- *Compatibility with the process.* The recovered material that is recycled to the process will often contain some traces of solvent. Thus, it is important to ensure that the solvent is compatible with the process, and to determine what, if any, levels of this new material are acceptable in the recycle stream.

In today's environment, there is always reluctance to introduce any new raw materials into the plant, since this usually involves obtaining additional permits. So, it is often advisable to try to find a possible solvent from among materials that are already being used in the process or somewhere else in the plant. It may not be the "best" solvent

from a purely LLE standpoint, but it may be the "best" from an environmental standpoint. It is usually better to accept some inefficiency in the extraction operation rather than risk the possibility of creating new process or environmental problems.

Process sequence

Once a possible solvent (or solvents) has been identified, the next step is to evaluate possible variations in process sequence and perform some preliminary process and economic calculations before proceeding to pilot-plant testing. Figures 5-8 illustrate several process sequencing options for a plant having three processes (Processes X, Y, and Z), each of which produces a water effluent with a particular contaminant (contaminants A, B, and C).

Typically these effluents would be combined into a single plant effluent stream for treatment, as shown in Figure 5. The first treatment is usually a stream stripper to remove the volatile components (in this case A and B). But if component C is something that does not strip out (*e.g.*, phenol), it must be handled by other means (such as LLE as shown here). The outlet from the LLE is then sent to final treatment (usually biological) before discharge from the plant.

The main disadvantage of this sequence is that the entire water stream passes through the LLE step. Since the solvent flow is proportional to the feed flow, this increases the solvent circulation rate and, therefore, the investment and operating costs.

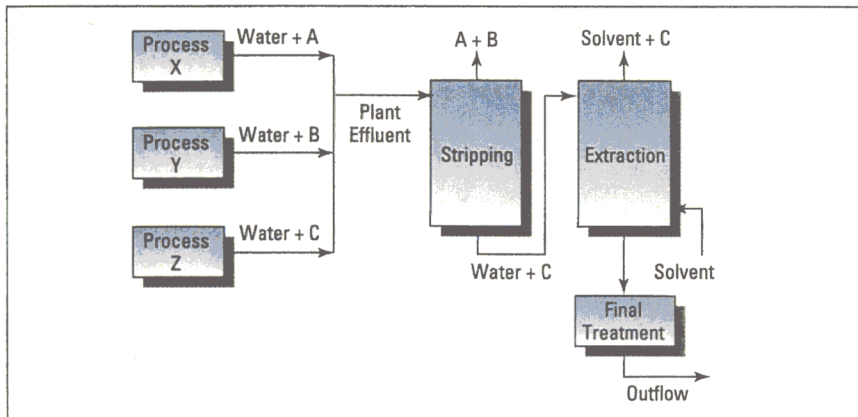
A better arrangement is depicted in Figure 6, where the stream undergoing extraction is segregated from the other effluent streams. This reduces the size of the equipment and the energy requirements for the LLE step. This is often referred to as moving the LLE upstream in the process to treat the contamination at its source.

Both of these schemes (Figures 5 and 6) use a solvent external to the process. But as mentioned earlier, it is beneficial to try to use as a solvent a material that is already present somewhere in the process or plant to minimize problems with compatibility or permitting of new materials. This concept is illustrated in Figure 7, where a solvent used elsewhere in Process Z performs the extraction.

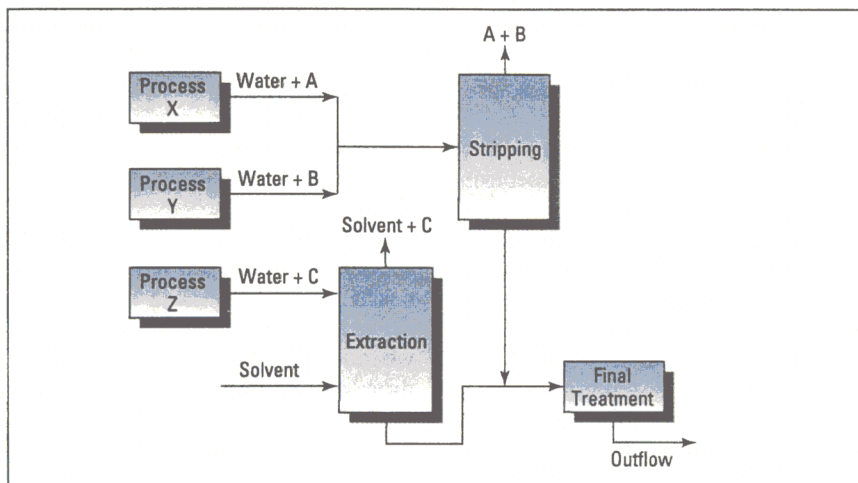
For example, assume again that contaminant C is phenol. As noted previously, the best solvent to extract phenol is probably MIBK. If MIBK is not currently used on-site but toluene is, toluene might be a better choice, even though it is significantly less efficient. In this case, it is the best solution from an overall plant-operation viewpoint.

Current plant design philosophy regarding wastewater treatment emphasizes water recycling. Because of the increasing costs associated with discharging wastewater, the practice of recycling water is becoming more and more common. Water is finally being recognized as one of the most valuable raw materials for the process, and therefore must be conserved to reduce costs.

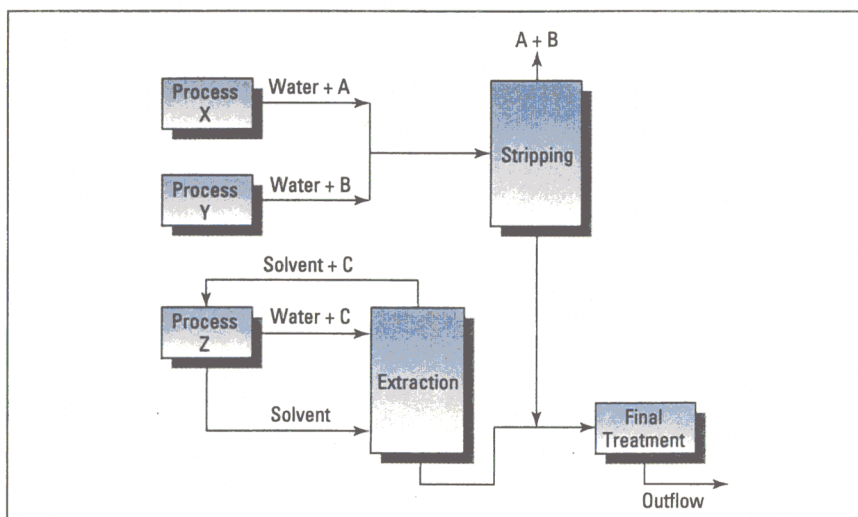
This approach is shown in Figure 8. Here, effluent from each individual



■ Figure 5. In the past, process effluents have been combined into a single stream for treatment.



■ Figure 6. A better approach is to segregate the stream undergoing extraction from the other stream.



■ Figure 7. It is often better to choose a solvent that is already present in the process or plant than to introduce an additional material.

process is treated at its source and each process recycles its water, with a small purge to control quality. This not only saves on the cost of water discharge, but also reduces the size and cost of the final treatment step.

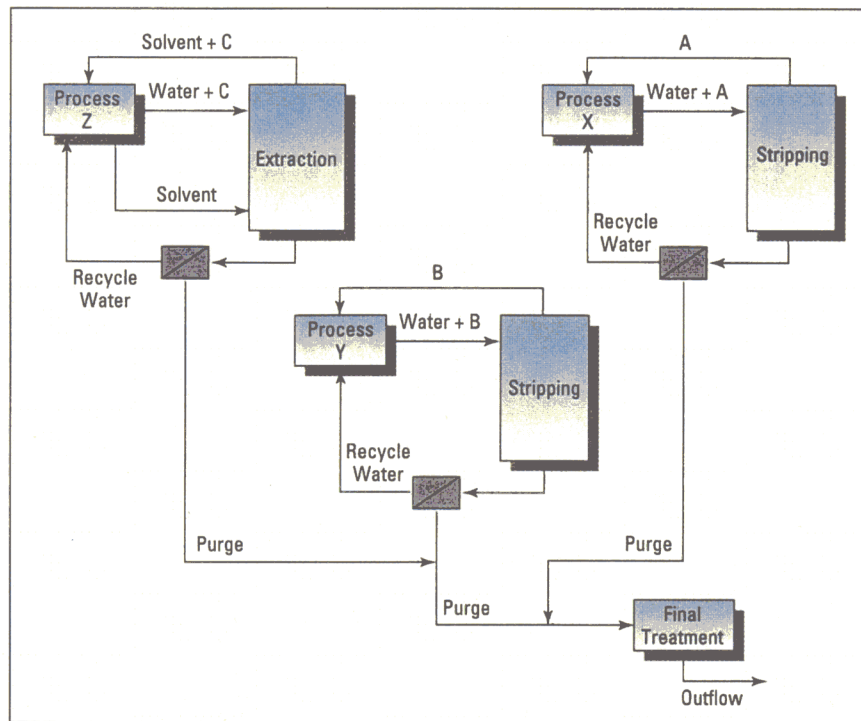
Pilot testing and scale-up

Unlike distillation processes, which can usually be designed from simulations alone, LLE is more complex and almost always requires some type of pilot-plant test to generate the necessary data for process design. This is especially true in environmental applications because the streams being processed can often vary widely in composition and contain trace quantities of other materials that affect the hydraulic capacity or efficiency of the process. Any pilot testing should *only* be done with actual plant materials, as synthetic blends will not reveal these problems. Also, the pilot tests should involve not only the LLE step, but also the stripping and solvent recovery steps, since all three must work together.

Extraction. There are many types of LLE devices available to accomplish the LLE step, including mixer-settlers, packed columns, sieve tray columns, agitated columns, and centrifugal units. A comparison of all of these is beyond the scope of this article, but the reader can find more information on this in (2-3).

The application often dictates that the agitated liquid/liquid extractor be used for pilot testing. If the system requires a large number of theoretical stages, or requires fine droplets for mass transfer (and, thus, intense mixing), then a rotating impeller column is the proper choice. It has a high efficiency per unit of column height compared to other designs.

However, if the system tends to form stable emulsions upon mixing, a reciprocating plate extractor would be better. It mixes fluids by reciprocating plates rather than rotating impellers, producing somewhat larger droplet sizes but at the same time minimizing the possibility of emulsion formation. Other possible columns are the rotating



■ **Figure 8.** The best arrangement is to treat each process effluent at its source and maximize water recycling.

disc contactor and the pulsed extractor, but these are less often applied to environmental applications. If very large flow rates are involved and only a few theoretical stages are required, then a packed extractor may be the best choice. However, the packed extractor will have less flexibility and will be more susceptible to fouling.

After the type of extractor has been selected, the next step is to determine the setup of the experimental equipment and the test plan. For agitated

columns, testing can be conducted in small (1–3-in.-dia.) columns. This has several advantages. First, it minimizes the amount of material required for the tests; tests can usually be completed with only one or two 55-gal drums of wastewater feed. Second, the small size allows equilibrium to be established quickly, which minimizes the time required to collect the data from the tests. A typical experimental program can be completed within one week. For packed columns, testing must usually be conducted in 4–6-in.-dia. columns, obviously requiring much more material and time to collect the data.

Solvent stripping. As mentioned earlier, most solvents have a significant solubility in the water phase, and therefore must be stripped from the water before it leaves the process, both for economic and environmental reasons.

The stripping tests are done using the raffinate from the LLE step. These tests are also conducted in small (2–3-in.-dia.) columns. Like the LLE step, the tests are usually run over a range

of feed rates and steam/feed ratios, and the performance measured at each condition. In addition to measuring the separation, look for any tendency toward foaming and any problems with fouling of the column internals. With these data, the stripper can be designed using conventional design techniques.

The stripping step is sometimes not required if the solvent used has very low solubility in water. In cases such as these, the water leaving the extractor can be discharged directly.

Solvent recovery. As mentioned earlier, one of the most critical aspects of any LLE system design is the solvent recovery step. The importance of this is often overlooked by novices to the LLE field because almost all of their attention is directed toward the LLE step and the selection of the solvent. But if the solvent cannot be effectively recovered for recycle back to the extractor, then the process will not be economically viable.

As with the solvent stripping tests, solvent recovery tests are usually conducted in 2–3-in.-dia. columns that are high enough to meet the product and recycle solvent specifications. Also like the stripping tests, look for foaming and fouling tendencies, in addition to separation characteristics.

From these pilot-plant data, the full-size solvent recovery column can be designed utilizing standard design techniques. CEP

Literature Cited

1. Perry, R. H., and D. W. Greene, eds., "Perry's Chemical Engineers' Handbook," 6th ed., McGraw-Hill, New York, pp. 15-14 to 15-18 (1984).
2. Cusack, R. W., et al., "A Fresh Look at Liquid-Liquid Extraction, Parts 1-3" *Chem. Eng.*, 98(2), pp. 66-76 (Feb. 1991), 98(3), pp. 132-138 (Mar. 1991), and 98(4), pp. 112-120 (Apr. 1991).
3. Godfrey, J. C., and M. J. Slater, eds., "Liquid-Liquid Extraction Equipment," Wiley, New York (1994).

R. W. CUSACK is vice president of Glitsch Process Systems, Inc., Parsippany, NJ (201/299-9350; Fax: 201/402-0335). He has been with the Glitsch organization for 12 years, and has been directly involved with extraction technology for the last decade. From 1990 to 1994, he held a managing director position for Otto York, NV, a European subsidiary of the Glitsch-held Otto York, Inc., where he was responsible for European marketing of all product lines, including solvent extraction. Previously, he was an engineering manager with Chem-Pro Corp. and worked in refinery and petrochemical design for Exxon Research and Engineering. He holds a BSChE and an MSChE from Manhattan College and is a member of AIChE.