Liquid-Liquid Extraction: A Pretreatment Process For Wastewater

This process was found to be more cost-effective than others for the main reduction of toxic pollutants before biotreatment.

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Liquid-liquid extraction was found to be the preferred pretreatment process for the main reduction of toxic pollutants from some industrial wastewater streams followed by biotreatment for futher reduction of impurities. At first glance, liquid-liquid extraction did not look as attractive as a carbon-bed or a resin-bed adsorption process. In simple laboratory experiments, virgin granular activated carbon or resin beads could be added to a toxic wastewater sample and most of the toxic components could be removed in one step.

By contrast, an immiscible solvent could be added to a toxic wastewater sample in the laboratory in one step, but then there were three problems that remained. First, the toxic components were only partially removed in one contact. Second, the contaminants that were removed from the water ended up contaminating the solvent. And third, the water was left saturated with the solvent that was used. These observations and logic have probably stopped many chemists and engineers from pressing on further into the use of liquid-liquid extraction as a pretreatment process for wastewaters.

Design criteria

The keys that unlock the technology and lead to an economically attractive liquid-liquid extraction process lie within the thermodynamics and design used in the process. Generally, there are at least three operations associated with a liquid-liquid extraction process: 1) the liquid-liquid countercurrent contact; 2) the solvent recovery; and 3) the raffinate cleanup. The example in Figure 1 uses a low-boiling solvent that is recovered by distillation and the raffinate that is cleaned up by steam stripping.

The flowrate of solvent required to extract a given impurity from water is set by the liquid-liquid equilibrium distribution coefficient of the impurity, the degree of impurity reduction required, and the number of theoretical stages designed into the countercurrent contact equipment. Typically, an impurity level may need to be reduced by a factor of 10 to 1,000 in the water stream. And, liquid-liquid contactors can reasonably be designed to give performance equivalent to two or up to ten theoretical countercurrent stages. The main criteria left then is to select a solvent that can give high distribution coefficients for the impurities and a low operating cost for the rest of the process.

At thermodynamic equilibrium, the fugacity (i.e., escaping tendency) of an impurity in the water layer is the same as the fugacity in a solvent layer as follows:

$$\gamma_{iw} x_{iw} = \gamma_{is} x_{is} \tag{1}$$

where
γ = activity coefficient in liquid phase
x = mole fraction in liquid phase
i = impurity
w = water phase
s = solvent phase

Consequently the distribution coefficient, K, is equal to the inverse ratio of the activity coefficients as:

$$K = \frac{x_{is}}{x_{iw}} = \frac{\gamma_{iw}}{\gamma_{is}} \tag{2}$$

The activity coefficient of the impurity in water, γ_{iw}, will already be fixed and can only be altered by changing the temperature or salt content in the water. Thus, the activity coefficient of the impurity in the solvent phase, γ_{is}, is the prime consideration in selecting a solvent to give a high distribution coefficient.

Raoult's Law

The activity coefficient of a solute in a solvent is controlled primarily by the hydrogen bonding and electron donor-acceptor interactions between the two. If there is no interaction between the solute and the solvent, the activity coefficient of the solute will be 1.0 and the escaping tendency of the solute from the solvent will obey Raoult's Law. But, if the solute can hydrogen bond with or form a complex with the solvent, the activity coefficient can be reduced to a value less than 1.0 and the escaping tendency will be less than that predicted by Raoult's Law. Consequently, negative deviations from Raoult's Law; i.e., negative log γ_{is}, will give high distribution coefficients, K. One example that illustrates this point occurs when acetone is to be extracted from water. The carbonyl group in the acetone is a hydrogen acceptor and can form a complex with a solvent containing an active hydrogen, e.g., chloroform. The activity coefficient of acetone is reduced to a value less than 1.0 in a chloroform solution.

The deviation from Raoult's Law can be quantified by the deviation of the logarithm of the activity coefficients above or below zero. Positive deviations give higher escaping tendencies than predicted by Raoult's Law and form minimum boiling point azeotropes; negative deviations give lower escaping tendencies and form maximum boiling point azeotropes; and no deviation gives a nonazeotropic system.

Several large collections of data have now been thoroughly screened and tabulated to categorize the hydrogen donor-acceptor interactions between groups in molecules and classified as either positive, zero, or negative, Table 1. Some of the interactions were easily established by the presence of either maximum or minimum boiling point azeotropes (1). Some interactions were established from activity coefficients that could be calculated from vapor-liquid equilibrium data (2, 3, and 4); from liquid-liquid equilibrium data (5 and 6); or from solubility data (7). The number of classes used originally by Robbins (8) was just nine, but the number of classes have been increased here to twelve because of the amines behaving different from the other classes of hydrogen acceptors.

The fundamental approach of evaluating the hydrogen donor-acceptor characteristics of the solute and solvent can narrow the solvent selection down to a few solvents quite rapidly. If the hydrogen bonding characteristics of a solute are not known, a series of solvents can be used as class representatives to develop an interaction profile by experimentally measuring distribution coefficients. The best classes of solvents then can be evaluated further to find the best solvent. Some of the solute-solvent interactions can be evaluated by computer calculations using the UNIFAC Method (9 and 10).

The impact from solvent selection can be quite dramatic for reducing the size of the extraction and solvent recovery equipment required to purify wastewater by liquid-liquid
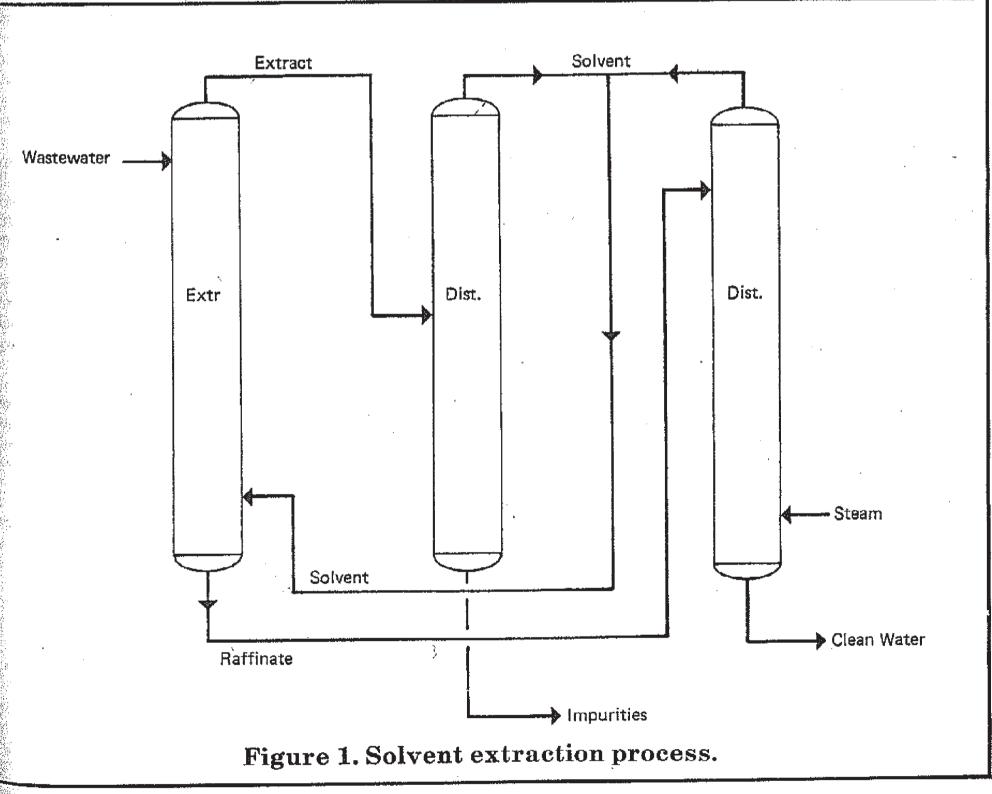

Figure 1. Solvent extraction process.

Table 1. Organic group interactions based on 900 binary systems.

Solute Class	H-Donor Groups	1	2	3	4	5	6	7	8	9	10	11	12
1	Phenol	0	0	−	0	−	−	−	−	−	−	+	+
2	Acid, Thiol	0	0	−	0	−	−	0	0	0	0	+	+
3	Alcohol, Water	−	−	0	+	+	0	−	−	+	+	+	+
4	Active-H on Multihalo Paraffin	0	0	+	0	−	−	−	−	−	−	0	+
	H-Acceptor Groups												
5	Ketone, Amide With no H on N Sulfone, Phosphine Oxide	−	−	+	−	0	+	+	+	+	+	+	+
6	Tert Amine	−	−	0	−	+	0	+	+	0	+	0	0
7	Sec Amine	−	0	−	−	+	0	+	+	0	+	0	0
8	Pri Amine, Ammonia, Amide with 2H on N	−	0	−	−	+	+	0	0	0	0	0	+
9	Ether, Oxide, Sulfoxide	−	0	+	−	+	0	0	+	0	+	0	+
10	Ester, Aldehyde, Carbonate, Phosphate, Nitrate, Nitrite, Nitrile, Intra Molecular Bonding, e.g., O-nitro Phenol	−	0	+	−	+	+	0	+	+	0	+	+
11	Aromatic, Olefin, Halogen Aromatic, Multihalo Paraffin without Active-H, Monohalo Paraffin	+	+	+	0	+	0	0	+	0	+	0	0
	Non H-Bonding Groups												
12	Paraffin, Carbon Disulfide	+	+	+	+	+	0	+	+	+	+	0	0

Table 2. Equilibrium distribution coefficients.

Component	K′*
A	286
B	46
C	5.2

*K′ = wt % pollutant in solvent at equilibrium divided by wt % pollutant in water.

extraction. One good example is the dephenolization of coke oven wastewater which required a solvent flow equal to the wastewater flow in old processes. But, the newer Jones-Laughlin process (11) requires a solvent flow of only 0.05 times the wastewater flowrate. Chem-Pro (12) has shown a high return on investment from the phenol recovered.

Extraction process

When solvents are used that give high distribution coefficients, the total operating cost for liquid-liquid extraction, solvent distillation and raffinate steam stripping has been found to be less than the total operating costs for granular-activated carbon or resin bed adsorption process. This has been observed even though the initial capital investment is higher for the liquid-liquid extraction process. Because the extraction process uses only liquids and vapors, on-stream time is usually very high.

These processes require only a minimum of monitoring because they are continuous processes and the solvents can usually absorb large concentrations of impurities from wastewater that can be present during upsets. Previously, liquid-liquid extraction was only used where the economic return was favorable from the value of materials recovered. Today, there is an economic incentive when liquid-liquid extraction simply costs less to operate than other processes for detoxifying wastewater streams sufficient for final treatment by bio-oxidation.

In one actual case, the wastewater from a process came from a decanter where the water and product were in contact. The water was saturated with product and contained three other impurities which were quite soluble in water. The problem was that the product and two of the impurities were relatively biorefractory and needed to be reduced to low levels to be nontoxic to fish. The third impurity was easily degraded by bio-oxidation. Several alternatives were evaluated for detoxifying this wastewater including granular-activated carbon bed adsorption and

Table 3. Pilot plant extraction column data for wastewater detoxification.

	kg/h	Agitation Intensity*	ppm, Component in water					
			Feed			Raffinate		
Feed	Solvent	m/s	A	B	C	A	B	C
1.8	0.64	0.133	520	5.2	17.8	<0.3	<0.3	<0.3
2.5	0.95	0	520	10.8	23.0	<0.3	<0.3	1.6
12.2	4.45	0	122	8.4	17.9	<0.3	<0.3	<0.3
10.8	4.36	0.038	122	8.8	16.0	<0.3	<0.3	<0.3

*Agitation intensity = stroke length times strokes per second. Solvent phase dispersed.

resin bed adsorption; the technologies were developed for design of these commercial processes.

Early attempts to select the best solvent for an extraction process had failed because of the lack of good analytical methods for individual components in water. After a good component analysis was developed, an optimum solvent was quite rapidly selected by using the hydrogen donor-acceptor interaction chart, Table 1, as a guide. One of the impurities, component C, was exceptionally difficult to extract from water. But, one solvent was found that could give a distribution coefficient of 5.2 for that pollutant between the solvent layer and the water layer, Table 2. The other toxic pollutants, A and B, were easier to extract. Thus, component C became the key impurity for the design of the extraction column. When pollutant C was extracted below a target level of 2 ppm in the raffinate, the other pollutants were down to lower levels.

At first, crossflow equilibrium experiments were carried out in the laboratory to study the effect of pollutant concentration on the distribution coefficient and to demonstrate the feasibility of achieving low pollutant levels in the raffinate water. Then, drum samples of the wastewater were obtained from the plant and extracted in a 25-mm diameter pilot plant Karr column. The Karr column was equipped with a 3-m platestack with 50-mm spacing between each of the plates. The plates were purchased from Chem-Pro Equipment Co. (13).

Agitation was provided by reciprocating the platestack vertically with a variable speed drive on an eccentric that was adjusted to give a stroke length of 19 mm. The desired target effluent of less than 2 ppm of components A, B, and C was readily achieved, Table 3. When the flowrates were turned down low, the high extraction efficiency could still be achieved by increasing the agitation intensity in the column. This simply involved increasing the speed of reciprocation of the platestack. This extraction equipment had been chosen because of the reliability of scale up and the low research cost required to generate design data (14). The design and scale-up procedures have been reported by Karr and Lo (15).

In conclusion

During the development of the liquid-liquid extraction process for wastewater detoxification, a couple of additional interesting points were observed. In one run, the extract stream leaving the extractor contained a pollutant C concentration that was 12 times higher than the concentration in the feed water, Table 4, even though the distribution coefficient was only 5.2, Table 2. At first, this appeared to be thermodynamically impossible. But, after close evaluation, the condition was found to develop because the solvent had a high solubility in water.

In a theoretical equilibrium countercurrent stage, the extract leaves in equilibrium with the raffinate from the feed stage, not in equilibrium with the feed. This unusual condition can only happen in countercurrent contact and would not be observed in laboratory cross-flow experiments. The net result was that a highly soluble solvent could be used to extract impurities from wastewater with no deleterious affects on the economics when a countercurrent contact scheme was used. More of the solvent was simply stripped from the raffinate instead of being distilled from the impurities. The raffinate, leaving the steam stripper, was sent to a biotreatment process for further reduction of impurities before the effluent discharged into a river.

This case revealed that the optimum economic approach to achieve a desired effluent quality was neither obvious nor anticipated by preliminary studies. In a free enterprise system where creativity and innovation are allowed, the environmental quality can be maintained at a high level without destroying the quality of life or the standard of

Table 4. Column extract concentrations higher than equilibrium values with feed.

kg Solvent per kg Feed	kg Extract per kg Feed	ppm Component, C		
		Feed	Raffinate	Extract
0.350	0.077	17.8	<0.3	230
0.375	0.088	23.0	1.6	243
0.405	0.148	16.0	<0.3	108

living. The governmental regulatory agencies would appear to best serve society with a concern for the quality of the environment, e.g. final effluents to rivers and lakes, but not by dictating the methods used to achieve the quality. Improved control methods can then be freely developed. The optimium approach is not the same for every wastewater stream.

Liquid-liquid extraction was found to be cost-effective when compared to other processes for the main reduction of toxic pollutants from some industrial wastewater streams before biotreatment. The first key is to select a solvent that can give high distribution coefficients for the pollutants and then to use the solvent even though it has a high solubility in water. The solute-solvent interaction table can expedite the task of selecting a high-performance solvent. The next key is to use a high number of countercurrent stages in the extractor to minimize solvent flow. The use of a Karr column can reduce the research cost and reduce the risk in scaleup of extraction equipment. The success of this process in the case reported can presumably lead to a higher utilization of liquid-liquid extraction processes in the future. #

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