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Separation of Phenol from Waste Water by the Liquid Membrane Technique

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Abstract

The removal of phenol and other weakly ionized acids and bases from waste water is described when using the liquid membrane emulsion technique. Mathematical relationships are derived for the theoretical distribution and for the rate of permeation of phenol into the emulsion.

GENERAL DESCRIPTION OF LIQUID MEMBRANE SEPARATION PROCESSES

Liquid membranes, in general, are formed by first making an emulsion of two immiscible phases and then dispersing the emulsion in a third phase (continuous phase). The liquid membrane phase refers to the phase in between the encapsulated phase in the emulsion and the continuous phase. Usually the encapsulated phase and the continuous phase are miscible, but they are not miscible with the membrane phase (*1*). The emulsion can be either oil-in-water or water-in-oil. By definition the liquid membrane then will be of the water type in the former case and of the oil type in the latter case. The liquid membrane phase usually contains surfactants, additives, and a base material which is a solvent for all the other ingredients. The surfactants and additives are used to control the stability, permeability, and selectivity of the membrane. For specific applications, liquid membranes can be tailor-made.

When the emulsion is dispersed by agitation in a continuous phase (the third phase), many small globules of emulsion are formed. These globules are stable and do not disintegrate, as would be expected, when the system is agitated. Their size depends strongly on the nature and concentration of the surfactants in the emulsion, the emulsion viscosity, and the mode and intensity of mixing. In most of our laboratory runs, the size was controlled in the range of 1 to 2 mm diameter. Each emulsion globule contains many tiny encapsulated droplets with a typical size of 1 μ in diameter. A large number of globules of emulsion can easily be formed to produce a correspondingly large membrane surface area for rapid mass transfer from either the continuous phase to the encapsulated phase or vice versa. In addition, "facilitated transport" mechanism may be used to enhance the mass transfer. This is usually achieved by incorporating a reagent in the encapsulated phase which can react with the permeating compound from the continuous aqueous phase (*2*, *3*), or by incorporating a compound, such as a complexing agent, in the membrane phase to increase the solubility of the permeating compound in the membrane, and therefore the permeation rate of this compound through the membrane (*4*).

After a desired degree of separation has been achieved, mixing is stopped and the globules of emulsion quickly coalesce and form a layer of emulsion. The emulsion phase can be lighter or heavier than the continuous phase and can be easily separated from the continuous phase. The contacting operation can be either batchwise or continuous, cocurrent or countercurrent.

EXPERIMENTAL

Equipment and Procedure

The water treatment data reported previously (*3*) and in this paper were all obtained from small-scale laboratory experiments. The equipment employed to carry out the separation was quite simple. It involves mainly a mixer with a stirrer.

In a typical laboratory run, the aqueous reagent solution to be encapsulated by liquid membranes is poured at a rate of about 10 cc/min into 200 cc of the hydrocarbon-surfactant solution at a mixing rate of about 1200 rpm. The final weight ratio of the aqueous reagent solution to the membrane-forming solution is usually 1:1. The total time for emulsifying the entire aqueous solution in the membrane-forming solution is about 15 min. The resulting emulsion droplets usually have a diameter of 10^{-3} to 10^{-4} cm. The waste water, containing the contaminant, such as phenol or ammonia, is contacted with the above emulsion in a mixer. Usually good dispersion of the emulsion in the water to be treated is maintained by the use of agitation with a mixing speed of 100 to 200 rpm for a period of about 5 to 20 min. During a run, agitation may be stopped from time to time so that feed sample can be taken for measurement of pH and contaminants concentrations. Waste water to emulsion weight ratio usually varies from 1 to 10, depending on the reagent concentration used which is usually from 0.1 to 20 wt%.

Materials

The reagents sodium hydroxide and sulfuric acid were of c.p. grade. The oil used as the solvent in the membrane phase was dewaxed Solvent 100 Neutral, which is a middle distillate having an average molecular weight of 386.5 and a density of 0.836 g/cc measured at 25°C. The surfactant used was Span-80, which is sorbitan monooleate, manufactured by Atlas Chemical Co.

SEPARATION MECHANISM AND RESULTS

Facilitated Transport

When a water-in-oil emulsion is dispersed in an aqueous phase, the system will consist of individual stable emulsion globules floating in the water phase as shown in Fig. 1. Contaminants dissolved in the continuous aqueous phase will diffuse through the oil membrane into the small drop-

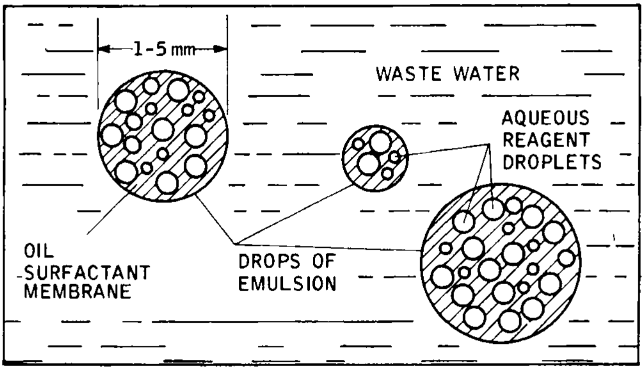

FIG. 1. Water treatment by LM-emulsion.

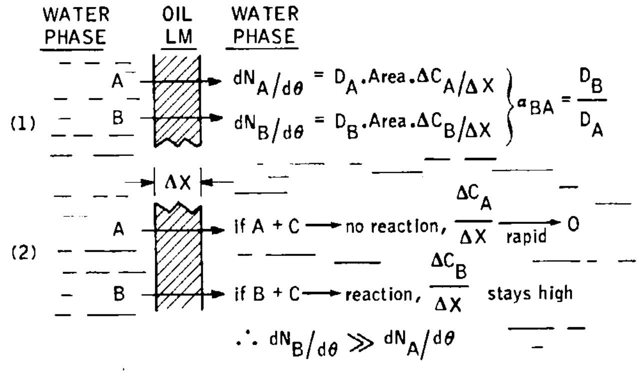

FIG. 2. Two LM separation mechanisms.

lets on the inside of the emulsion as long as there is a driving force for this diffusion, and provided that there is some solubility of the contaminating species in the liquid membrane phase.

A simplified picture of what takes place is shown in Fig. 2. On the left is the waste water stream, or the continuous aqueous phase which contains contaminants A and B. Separating the waste water phase from the aqueous droplet phase on the right, and forming a coherent film, is the liquid membrane oil phase. The upper example (1) shows one mechanism which can accomplish separation of components A and B dissolved in the aqueous phase on the left. This mechanism relies on differential rate of permeation through the membrane. If the permeability of B > permeability of A, B will tend to concentrate in the permeate on the right, while a solution rich in A will stay behind. The reason for the higher permeability of B through the oil may be a higher diffusion coefficient, or a higher solubility of B in the oil phase, or both.

The lower example (2) shows another mechanism, namely how a chemical reaction which consumes B but not A can make this a very selective separation process. As long as reagent C and the product of the reaction between B + C are not permeable through the membrane, this system can be used to accomplish nearly complete as well as highly selective removal of B from the solution on the left.

Essentially what happens is that the concentration (c) driving force

$$\Delta c = c_{\text{left}} - c_{\text{right}} \tag{1}$$

for compound B in the rate equation

$$dN/d0 = (D)(\text{area})(\Delta c/\Delta x) \tag{2}$$

(where $dN'd\theta$ is the quantity of material permeating across a given area of membrane/unit time, Δc is the concentration difference of the permeating species on either side of the membrane, Δx is the membrane thickness through which permeation takes place, and D is the diffusion coefficient of permeating species through the membrane) is maintained high by keeping c_{right} close to zero by the reaction which consumes B.

In short, while separation mechanism (1) is due to differential rates of permeation of the several constituents of a mixture through the liquid membrane, mechanism (2) relies on chemical reaction to affect the driving force of the material to be transferred. In essence, it is providing a sink for the permeating material by reacting it chemically inside the emulsion.

A typical example of such a system is the caustic-in-oil emulsion shown in Fig. 3 which can be used effectively to remove small amounts of phenol from a waste water stream. This example will be discussed in greater detail below. However, what happens, in brief, is that phenol, being somewhat oil soluble, will permeate readily from the outside water phase

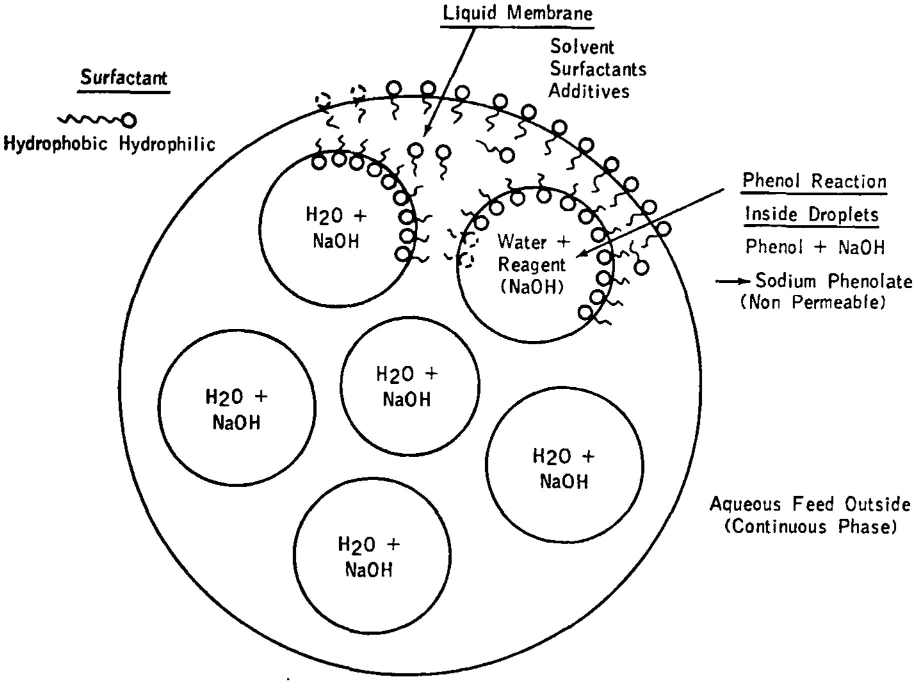

FIG. 3. Schematic diagram of liquid membrane system for phenol removal.

through the oil membrane into the internal aqueous caustic droplets. Here the phenol will be neutralized by the caustic and tied up as sodium phenate which is insoluble in oil and, consequently, cannot diffuse back out again.

Typical examples for the removal of dissolved constituents in waste water by means of the liquid membrane technique are weak acids or bases which are soluble in the liquid membrane. They can therefore diffuse through the membrane in their undissociated form and will be neutralized by the solution of a strong base or acid, respectively, which has been dispersed in the emulsion formulation. Since neither the strong acid or base, nor the resultant ionized salt, are oil soluble, they will remain encapsulated inside the emulsion drops.

Table 1 lists a few examples of waste water constituents which we have removed successfully by means of liquid membrane emulsions.

In all cases the mechanism is the same. The impurity in the waste water, just as with phenol, will permeate across the oil membrane in its undissociated form and will be neutralized by the strong caustic or acid inside the aqueous droplets within the emulsion, preventing its escape back out into the waste water.

Before going into more detail on the mechanism, it will be useful to outline briefly some typical installations which can be considered for the removal of contaminants using the liquid membrane technique.

Figure 4 shows a single-stage installation together with emulsion make-up, recycle, and disposal. If more than one stage is required, as will be discussed later, cocurrent mixers, countercurrent mixer-settler stages, or a mechanically agitated plate tower may be used (Fig. 5). It is unlikely that a simple plate tower used in liquid/liquid extraction will give sufficient agitation to provide the necessary contacting between the two phases.

TABLE 1

Removal of Weak Acids and Bases

Acidic Materials Removed by "Caustic" LM Emulsion
Phenol
H_2S
HCN
Acetic acid
Other organic acids
Basic Contaminants Removed by "Acid" LM Emulsion
NH_3
Amines

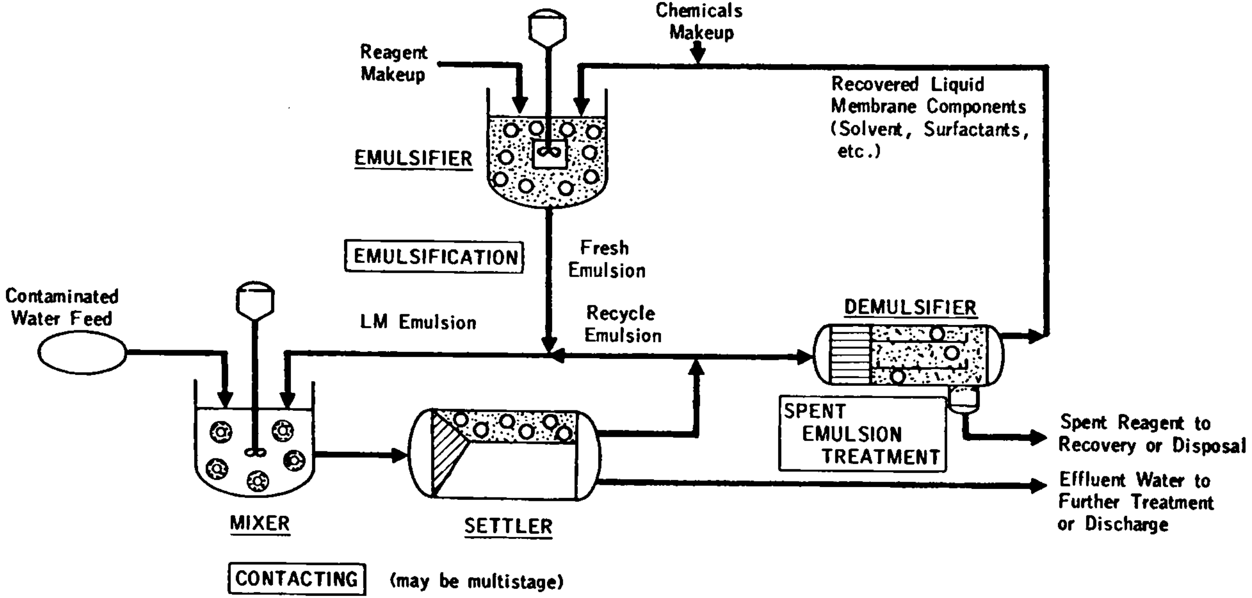

FIG. 4. Schematic diagram of conceptual LM water treating process.

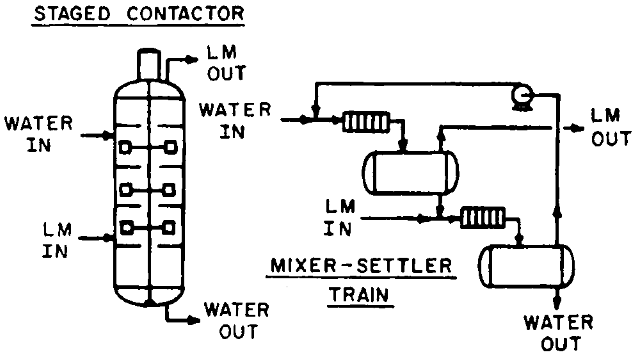

FIG. 5. Multistage countercurrent contactors.

As mentioned previously, the operation may be carried out either batch-wise or in a continuous fashion. Flow of waste water and emulsion phases may be cocurrent or countercurrent.

Equilibrium Distribution Curve

By encapsulating into the emulsion an aqueous solution of either a strong base or acid, it is possible to remove weakly acidic or basic constituents from waste water, provided they are reasonably soluble in the oil phase and also that they have a relatively low dissociation constant.

Phenol is a good example of how to calculate what degree of removal can be achieved in a liquid membrane treater, using the phenol dissociation constant as a guide.

The dissociation constant of phenol in water at 25°C is 1.28×10^{-10}, or

$$\frac{[\mathrm{PhO}^-][\mathrm{H}^+]}{[\mathrm{PhOH}]} = 1.28 \times 10^{-10} \tag{3}$$

Also, at 25°C the ionization product of water is close to 10^{-14}, i.e.,

$$[\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14} \tag{4}$$

With this information it is now possible to construct an equilibrium line for phenol between the waste water at a given pH, say 7, and the emulsified caustic solution, say 10 wt% NaOH. Subscripts *c* and *w* in the following derivation will refer to concentrations in the caustic and waste water phases, respectively.

The derivation of the equilibrium line is based on the fact that at equilibrium the concentration of the undissociated phenol, which is the diffusing species, must be equal on both sides of the membrane.

For the caustic phase (10 wt% NaOH = 2.773 M), electrical neutrality requires that, disregarding the H^+ concentration,

$$[Na^+]_c = [OH^-]_c + [PhO^-]_c = 2.773 \tag{5}$$

or

$$[OH^-]_c = 2.773 - [PhO^-]_c$$

which can be substituted into the water equilibrium (4) to give

$$[H^+]_c = \frac{10^{-14}}{2.773 - [PhO]_c} \tag{6}$$

When this expression is used to replace the $[H^+]$ in the phenol dissociation equilibrium (3), one obtains the following expression for the undissociated phenol in the caustic phase:

$$[PhOH]_c = \frac{[PhO^-]_c \times 10^{-4}}{1.28(2.773 - [PhO^-]_c)} \tag{7}$$

This equation shows that in the caustic phase phenol is essentially completely dissociated, and that for all intents and purposes the total phenol concentration equals the dissociated phenol concentration, or

$$[\text{total PhOH}]_c = [PhO^-]_c + [PhOH]_c \simeq [PhO^-]_c \tag{8}$$

Turning now to the waste water phase, which is assumed to be at pH = 7, i.e., $[H^+]_w = 10^{-7}$, one obtains the following relationship for the phenate ion by again using the phenol dissociation Eq. (3):

$$[PhO^-]_w = \frac{1.28 \times 10^{-10}[PhOH]_w}{[H^+]_w} = 1.28 \times 10^{-3}[PhOH]_w \tag{9}$$

In contrast to the caustic phase, practically all of the phenol in the waste water is therefore present in the undissociated form, or

$$[\text{total PhOH}]_w \simeq [PhOH]_w \tag{10}$$

Now, at equilibrium, since undissociated phenol is the species diffusing through the oil membrane, it must be at the same concentration in the caustic and waste water phases, or

$$[PhOH]_w = [PhOH]_c \tag{11}$$

It is therefore possible to substitute expressions (11), (7) and (8) into Eq. (10) to obtain the equation for the phenol equilibrium distribution curve:

$$[\text{total PhOH}]_w \simeq \frac{[\text{total PhOH}]_c \times 10^{-4}}{1.28(2.773 - [\text{total PhOH}]_c)} \tag{12}$$

Equation (12) is the equilibrium curve which relates the concentration of phenol in the caustic with that in the waste water at pH = 7. The relationship is plotted in Fig. 6, showing that phenol can exist in caustic in equilibrium with waste water even if the concentration of the phenol in the caustic is 10,000-fold that in the waste water.

While this concentrating effectiveness of liquid membrane emulsions is a very desirable and important feature in waste water treatment, the clean-up which can be achieved must next be considered. This can be done easily with the help of the equilibrium curve.

Assume the waste water starts out with 200 ppm phenol. In a single treat, if the caustic is spent to about 50%, no better than an exit phenol concentration of 7.4 ppm can be achieved at equilibrium. Allowing for a reasonable driving force will therefore leave 15 to 25 ppm phenol in the effluent water.

By adding a second and, if required, third contacting stage, the phenol can be cleaned up to a level between 0.25 and 2.5 ppm. Countercurrent flow of emulsion and feed water is necessary to achieve satisfactory chemicals utilization.

The design of a typical countercurrent clean-up system is illustrated in the stage-to-stage diagram of Fig. 7. The operating line of slope (lb waste

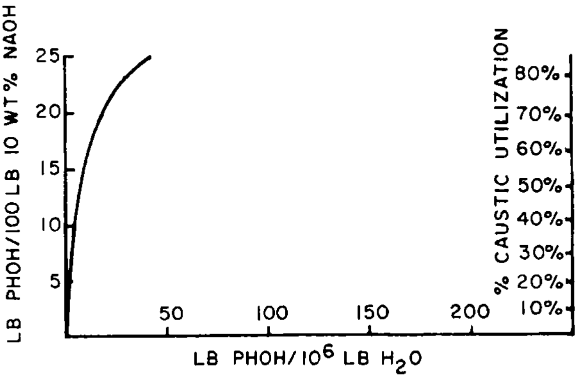

FIG. 6. Phenol equilibrium: caustic vs water.

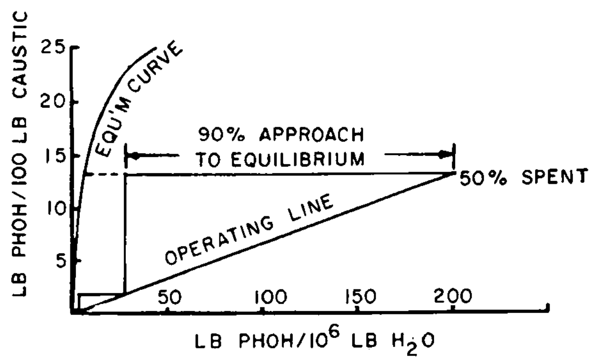

FIG. 7. Stage-to-stage diagram.

water/lb of emulsified caustic solution) is the result of a material balance over the unit. In estimating stage requirements, a 90% approach to equilibrium and below 0.5 ppm phenol in the effluent were assumed. Also, a 50% spent caustic was taken as the desirable maximum utilization.

Similar equilibrium curves and operating lines can be constructed for other systems, i.e., removal of HCN, H_2S, NH_3, etc., from waste water into the appropriate emulsion. In general, the smaller the dissociation constant, the fewer stages will be needed to accomplish a given clean-up.

What is particularly interesting with regard to this removal technique as applied here is that it is so selective in its removal of only that or those materials which (a) can pass through the membrane, and (b) will react with the reagent inside the emulsion and form a nondiffusing product.

In the case of phenol, other weak acids which happen to be present will compete with phenol in permeating through the membrane and reacting with the encapsulated caustic. Thus acetic acid, H_2S, and HCN, all of which have small dissociation constants and good solubility in the organic membrane layer, will permeate along with the phenol and accumulate on the inside. However, strong mineral acids, on account of their high degree of dissociation and low solubility in the oil phase, will not tend to diffuse across the oil membrane. The net result is that Cl^-, SO_4^{2-}, etc. are effectively excluded from the encapsulated caustic. Thus the method can be used to remove phenol even in the presence of large amounts of chloride.

The presence of bases such as NH_3 and amines does not interfere with the removal of phenol. These materials are quite soluble in the oil film, will diffuse across, but since they do not react they will rapidly build up to about the same concentration inside and outside the liquid membrane, and all further permeation will come to a halt.

Rate Equations for Liquid Membrane Permeation

Permeation rates through the liquid membrane have to be determined to allow sizing of contacting stages and agitation requirements.

The rate of permeation of constituent A was defined earlier by the basic rate Eq. (2), repeated here for convenience:

$$dN/d\theta = (D)(\text{area})(\Delta c/\Delta x) \qquad (2)$$

Since the area available for permeation and Δx are difficult to measure for a liquid membrane system, the group $(D)(\text{area})/\Delta x$ can be replaced by $D'(V_E/V_w)$, where D' is an effective permeation rate constant and V_E/V_w is the treat ratio, e.g., volume of emulsion/volume waste water. Essentially, Δx has been lumped into the permeation rate constant, and it has been assumed that when the emulsion breaks up into drops, the area available for permeation is proportional to the amount of emulsion used in the treat per unit of waste water.

Care has to be taken in the handling of the Δc term. Only the concentrations of the un-ionized species must be used in computing this concentration differential, since this is what propels the materials across the membrane, not the difference in total concentration. Thus, in the case of phenol removal from 200 ppm in the waste water into a 10 wt% caustic membrane emulsion, consider the point when the caustic solution is 10% spent, i.e., contains 2.4 lb phenol/100 lb caustic solution. While this represents 23,500 ppm (wt) total phenol content, the concentration of undissociated phenol in the caustic is only 1/30,000 of this value (see Eq. 7), or less than 1 ppm. On the other hand, since the phenol in the pH 7 waste water is essentially completely undissociated (see Eq. 10), all the 200 ppm can be taken as undissociated phenol concentration. Therefore, the driving force for phenol across the membrane is 200 − 1 = 199 ppm or 0.00211 gmole/liter.

The flux of permeating species in the rate equation, $dN/d\theta$, while calculated as undissociated species, is, however, measured as total concentration (ionized plus un-ionized), since there is rapid interconversion between the dissociated and undissociated forms in the aqueous phases, depending on pH.

Permeation rates have been measured for various systems, both in the laboratory and in a pilot plant, and reasonably good correlation between

TABLE 2

LMP Rate Constants for NH_3

Time interval (min)	Oil/aqueous, D' (min^{-1})			
	2/1	1.2/1	0.8/1	0.6/1
0–1	0.60	0.20	0.75	0.99
1–4	0.36	0.48	0.75	0.71
4–9	0.51	0.71	0.71	0.51
9–19	0.65		0.85	0.99
Average	0.53	0.53	0.77	0.80

TABLE 3

Phenol Removal by LMP ($V_E/V_W = 266/500 = 0.532$)

Interval (min)	θ (min)	c_{in}/c_{out} (ppm/ppm)	D' (min^{-1})
0–2	2	1060/61	2.7
2–5	3	61/4.1	1.7
5–18	13	4.1/3	~0
0–5	5	1060/4.1	2.1

continuous pilot unit data and batch runs in a beaker have been achieved. Laboratory data were used to calculate the permeation rate constants for both ammonia and phenol listed in Tables 2 and 3, respectively.

The phenol rates are higher but indicate a marked drop-off as phenol removal approaches completion, while the D''s for ammonia seem to remain reasonably constant over the period of the test. The ammonia rates appear to increase with decreasing oil/aqueous ratio in the emulsion formulation. This is to be expected, since lower oil/aqueous implies thinner membranes, higher diffusion rates.

It should be noted that the oil/aqueous ratio of the emulsion is just one of the variables which affect permeation rate. Others are temperature, mixer design and speed, membrane formulation, vessel design, scale of operation, and many other factors.

The LMP rate constants in Table 2 were calculated from the laboratory data by using the batch permeation equation

$$\ln \frac{c_{in}}{c_{out}} = (D')(V_E/V_w)(\theta) \tag{13}$$

where c_{in} and c_{out} are the initial and final concentrations of the material being removed by LM permeation, respectively, V_E/V_w is the treat ratio, θ is the contacting time for any given interval, and D' is the permeation rate constant.

Equation (13) is easily derived from the generalized permeation Eq. (2).

Once the LMP constant D' has been determined, continuous cocurrent plant-type treating equipment can be designed on the basis of Eq. (14), (15), (16), and (17) listed below. Equation (15) is for a single, well-stirred continually fed reactor for the case where there is no appreciable solute concentration in the emulsion.

For continuous systems, define

$$K = \frac{v_w}{D'}\left(\frac{v_w}{v_e} + 1\right) \tag{14}$$

where v_w is the water rate and v_e is the emulsion rate, both in liters/minute. Then the reactor volume V_R is given by

$$V_{R_1} = K\left(\frac{c_{\text{in}}}{c_{\text{out}}} - 1\right) \quad \text{for a 1-stage system} \tag{15}$$

$$V_{R_2} = 2K\left(\sqrt{\frac{c_{\text{in}}}{c_{\text{out}}}} - 1\right) \quad \text{for a 2-stage system} \tag{16}$$

$$V_{R_n} = nk\left(\sqrt[n]{\frac{c_{\text{in}}}{c_{\text{out}}}} - 1\right) \quad \text{for a } n\text{-stage system} \tag{17}$$

Since the permeation rate is controlled by the effluent concentration, which is low, a multistage cocurrent mixer results in a much smaller required mixer volume. It can easily be shown that for a 2-stage system the minimum vessel volume is obtained when both stages are of equal size, and this is reflected in Eq. (16) for the 2-stage mixer. For the n-stage cocurrent system, application of the 2-equal stage optimum to any two consecutive stages leads to the obvious conclusion that it is best to make all n stages of equal volume. This is the basis for Eq. (17).

Transfer of Ions

The present discussion covers the permeation of phenol, ammonia, H_2S, or other somewhat oil-soluble molecular species which are converted to a predominantly oil-insoluble ionic species by reaction with a base or acid inside the emulsion droplets. It has been possible to remove ionic contaminants from waste water by the addition of solubilizing agents, such as ion exchange compounds and complexing agents, to the oil phase of the membrane emulsion. Then, by maintaining a proper pH differential between the waste water and the emulsified water droplets, respectable permeation rates and concentration build-up of the contaminating metal ions into the emulsion could be achieved.

CONCLUSION

Design and economic studies have been made for a number of systems, and they were found to compare reasonably well with conventional cleanup methods. Particularly when the amount of material to be removed is present in low concentration, the chemicals consumption is correspondingly low and the liquid membrane technique could be a worthwhile alternate for investigation. It can be particularly useful where other methods fail due to the presence of interfering substances, very high or low pH's, or some other special circumstance. In any case, the removal of contaminants from waste waters by liquid membrane permeation is a novel technique which is being actively pursued at the present time.

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