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LIQUID-MEMBRANE-PERMEATION AND ITS EXPERIENCES IN PILOT-PLANT AND INDUSTRIAL SCALE

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Abstract

Emulsion-Liquid-Membrane-Permeation (LMP) is an operation for the recovery of several harmful substances from industrial waste water streams. Within this process the substance is separated from the waste water and enriched by a factor up to 1000 in the receiving phase depending on the process conditions. The largest experimental experiences are in the separation of Zn, Cd, Pb, Cu, Ni, NH_3 and phenol from aqueous solutions.

INTRODUCTION

During the last years the separation of heavy metals and organic substances has become more and more important for waste water producers. This was caused by drastic strengthening of environmental protection laws. In the field of the various separation techniques precipitation, extraction, distillation, reverse osmosis and electrodialysis are mostly known. The last two techniques and also LMP belong to the large field of membrane processes. The importance of these processes rose during the last years very quickly, because much progress was made on this topic. The group of Prof. Marr's coworkers in Graz (Austria) performed a large amount of research work to reach an industrial standard in emulsion-liquid-membrane-permeation.

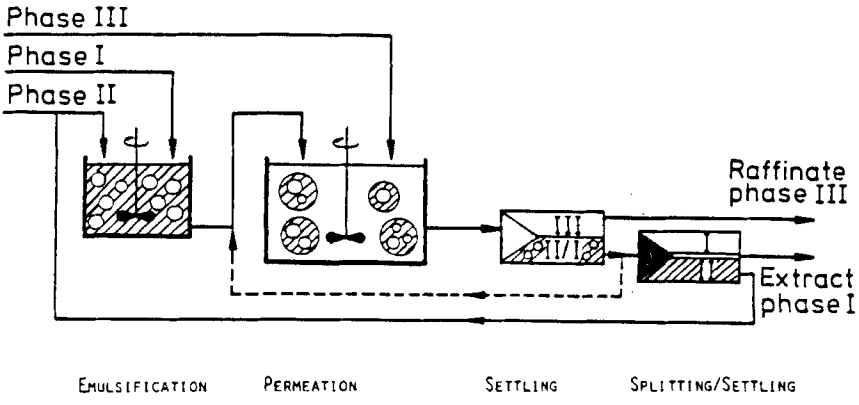


Fig. 1: The continuous LMP-Process

PROCESS AND EXPERIMENTAL DESCRIPTION

In the LMP-process, Fig.1, which is derived from solvent extraction, an emulsion of the membrane phase and the stripping phase is prepared. The emulsion type is water-in-oil (W/O). In the permeation step, this emulsion is dispersed in the waste-water phase. The substance to be recovered permeates through the oil membrane into the aqueous stripping-phase. In the permeation process, the stripping-phase will be enriched by the permeated substance. After settling the emulsion, it is split into its aqueous and organic compounds in a following step. The aqueous product phase may then be sent to a subsequent treatment. The organic phase is recycled to the first emulsification step, resulting in a continuous recovery process.

In our laboratory several separation problems have been investigated in batch and pilot plant-experiments. Two commercial plants using this technology have been built.

In the batch experiments, normally amounts of 0.7 l waste water were treated with emulsion. In this scale the systems were fitted to minimize the osmosis effect, which seem to be the most important problem in our process-development. This effect causes water transport of water molecules from the waste water through the organic membrane phase into the inner receiving phase. This dilutes the product and the volume of the inner phase

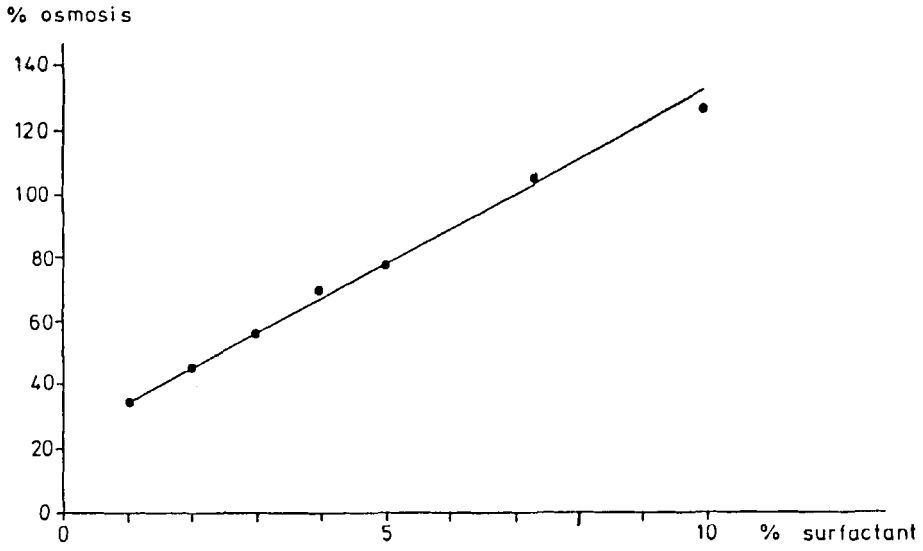


Fig. 2: Percentage stripping solution due to osmosis vs. surfactant concentration

may increase by more than 100%. The osmosis effect depends on surfactant concentration, extractant concentration and on the difference of the ionic strength between the two aqueous phases. The influence of the surfactant-concentration is directly shown in Fig. 2. In the plot of surfactant-concentration vs. percentage of osmosis a linear relationship of these 2 parameters is shown.

Several additional process-requirements must be optimized. These are: amount of needed surfactant to stabilize the emulsion, resistance to mass transfer at the interface, bacteriological and chemical stability, and on the stability of the extractants.

In bench-scale tests, we investigated the separation of zinc, copper, ammonia, phenol, nickel, tungsten, chromium(VI), vanadium, cadmium and lead. All these systems were then went to pilot-plant experiments in order to come to a continuous process. This second step normally is executed in a countercurrent extraction

Tab.1: Separation of various metals in pilot plants

Element	in.conc. [mg/l]	fin.conc. [mg/l]	throughput [l/h]
Zn	4500	4	30
Zn	500	0,8	30
Zn	150	0,5	70
Zn	4	< 0,1	200
Zn	200	5	175
Cu	8000	27	20
Cu	800	3	40
Cu	0,5	< 0,01	175
Cd	14	0,01	60
Cd	2	0,01	175
Pb	8	0,01	60
Pb	0,8	0,01	175
Cr	1500	4	40
Ni	2200	360	20
Ni	2200	20	150
Ni	2200	3	20

column with a diameter of 50 mm and an active height of 3m. During these experiments, the system parameters (throughput, phase ratio, stirring speed and residence time) were optimized.

In table 1 the experimental results are given. The initial and final concentrations of these experiments are shown. Also, the separation limits for the following substances are given:
zinc, copper, nickel, chromium(VI), cadmium and lead.

Some of the data shown in Table. 1 result from tests using an other pilot plant with a column-diameter of 100 mm and an active height of 6m. All these results were obtained with countercurrent extraction columns similiar to the Oldshue-Rushton type. Only the Ni-separation tests were executed in different mixer-settlers.

The experimental limits of the waste water feed were 70 l/h in the 50 mm column and 200 l/h in the 100 mm column. In both cases, a homogenization system developed in Graz was used. This consists of a nozzle system with supporting pumps. The important advantage of this system is the lack of rotating parts, which are subject to corrosion.

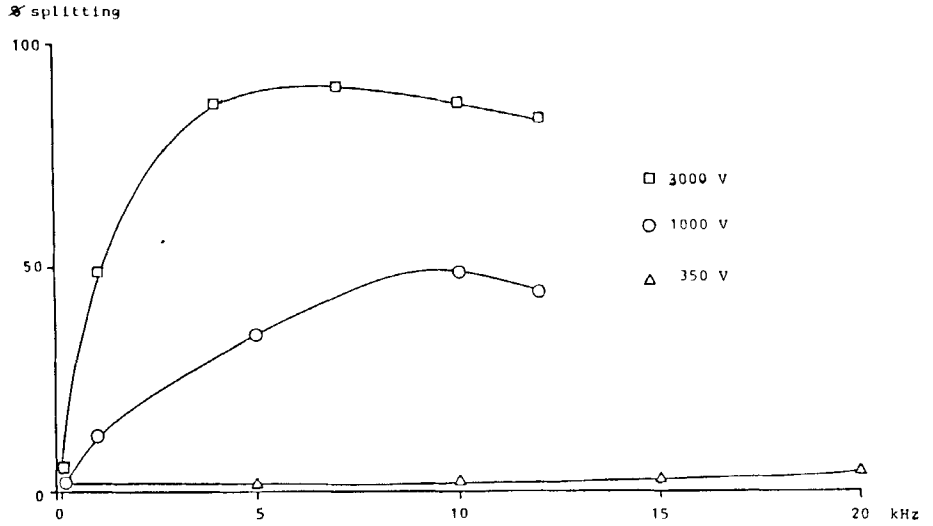
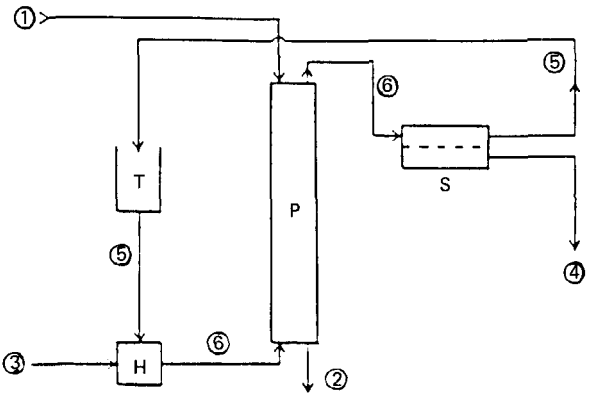


Fig.3 : Dependence of splitting efficiency on frequency

A new emulsion-splitting system has been developed for use in this system. This uses insulated electrodes and ≈ 1000 V at a frequency of 10000 Hz. This caused a high increase in the splitting efficiency and permitted use of lower voltages. This effect is shown in fig.3 .

Zinc separation from the waste water of the artificial fibre industry has been commercialized. The first LMP-Plant was built in Austria in 1986. This plant is able to recover more than 95% of Zn in the waste water. The throughput of the plant is 75 m^3/h waste water. A flow sheet of this process is shown in fig. 4, together with the designed throughputs and concentrations. The permeation column has a diameter 1.6 m and an active height of 10 m. The internals ressemble an Oldshue-Rushton column.

During the first months of operation some problems occured, which were mainly caused by unexpected waste water compositions which were not encountered in the pilot plant experiments. Additionally bacteria appeared which destroyed the surfactant. Therefore a bacteria-resistant surfactant was used.



1 waste water, 75 m^3/h, 500 mg/l Zn
2 waste water, 75 m^3/h, 1-3 mg/l Zn
3 receiving phase, 0.5 m^3/h, 250 g/l H_2SO
4 receiving phase, 0.5 m^3/h, 60 g/l Zn
5 organic phase, 5 m^3/h
6 emulsion, 5.5 m^3/h
P permeation column
H homogenizer
S electrostatic splitter
T tank for organic phase

Fig. 4: Flow-sheet of Zn-recovery plant

One further problem was caused by dereased homogenizer efficiency. This limited the emulsion feed and also the hold-up. Increasing the stirring speed would have caused a higher hold-up, but also a higher break-up of the inner dispersed phase. Thus this was not desired. Increasing the feed of the organic brought the best results. The following operating conditions resulted (after 3 months of operation):

waste water:	70 m^3/h,	init. Zn. conc.	: 350 mg/l
		fin.	: 5 mg/l
membrane phase:	7 m^3/h,		
stripping phase:	0,3 m^3/h,	init. conc.	: H_2SO_4 250g/l
		fin. conc.	: H_2SO_4 100g/l
			Zn 55-60 g/l

Economical analysis of the process was done with these operating conditions. The resuls are listed in table 2.

Tab.2: operating costs in US $/100 kg recovered Zinc

sulfuric acid	:	15,0
neutralisation	:	14,0
electric energy	:	5,6
organic loss	:	7,7
evaporation	:	12,1
total	:	54,4

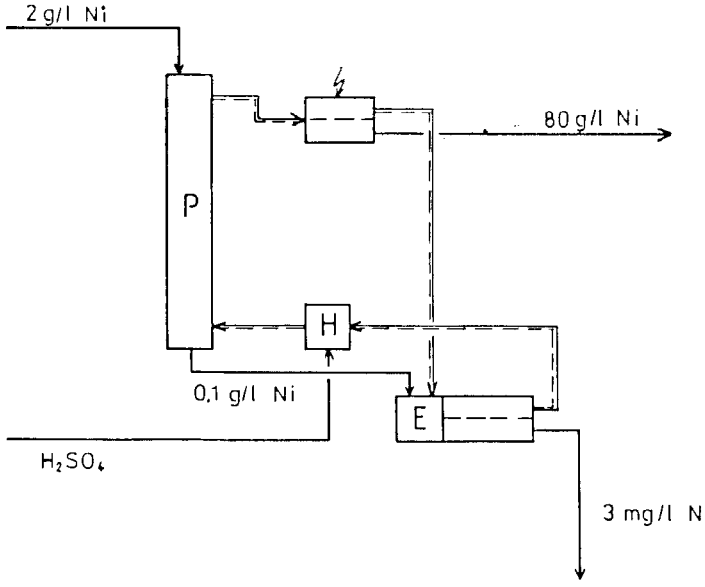


Fig. 5: Flow-sheet of Ni-recovery plant
(E = extraction-stage, ϟ = splitter)

These data are average data over a period of three months.

Neutralization is necessary because of the remaining acid in the product phase. The evaporation is required because a nearly-saturated $ZnSO_4$-solution is necessary for a direct reuse of the solution.

Compared with costs of $ZnSO_4$ of 133 US $/100kg Zn, the economic advantage is evident.

Fig. 5 shows the flow sheet for a Ni-recovery from galvanic waste water. The initial concentration of Ni is ≈2 g/l. As mentioned above in case of Ni a mixer settler plant was used. The experiments showed, that the results with a two-stage mixer settler permeation were not satisfactory. This was mainly caused by osmosis effects and break up, because on one hand osmosis led to low product concentrations (20 g/l) and on the other hand separation limits were in the range of 20 - 30 mg/l Ni.

A combination of extraction and permeation was used, as shown in fig. 5. The final cleaning procedure takes place in the extraction stage, where no osmosis effects occur. With this way a separation up to 3 mg/l is possible together with product-concentrations up to 80 g/l. This process was realized in a plant with a throughput of 150 l/h. This plant was installed in a bicycle factory in Austria. The results led to a process design for a larger plant, which is actually not finished.

SUMMARY

The liquid membrane permeation (LMP) has reached a state of development where industrial application has already taken place. In general the largest experiences are in the field of Zn-recovery especially in the viscous-fiber industry. In these applications, economical calculations showed that the recovery of Zn alone justifies the operating costs. In the case of environmental protection application there are several further possibilities where this is the only technology to remove toxic substances from water without precipitation in a continuous industrial scale.