Emulsion pertraction of heavy metals from waste water

Publication

Reference number	93-078
File number	112329-04150
CB-nummer	078
Date	February 1993

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Abstract

Emulsion pertraction is a new membrane based combined extraction and stripping process for the recovery of heavy metals from waste water. In the emulsion pertraction process the waste water is kept apart from an emulsion phase by means of a hydrophobic microporous membrane. The emulsion used in emulsion pertraction consists of an organic solvent with a dissolved extractant as continuous phase with aqueous droplets of strip liquid dispersed in it. Main advantages of pertraction over normal extraction are: 1) extraction and stripping in one operation, 2) no possibility of emulsion formation in the water phase, 3) volume of extractant is relatively small, 4) compact modular equipment and 5) low energy consumption. Emulsion pertraction can be applied for the recovery from waste water of different heavy metals like Zn, Hg, Cd, Cu, Cr and Ni.

1 Introduction

Even low concentrations of heavy metals that are discharged by effluent streams can be harmful to the environment and public health. Solvent extraction is a proven technology in mineral and nuclear industries to remove metals from solutions. Thus far solvent extraction for waste water treatment has been of limited value to meet discharge limits. Disadvantages of solvent extraction for waste water treatment are:

- possibility of loss of extractant due to emulsion formation in the water phase
- large extractant volume required; applications are limited to inexpensive extractants
- phase separation is often difficult due to formation of stabile emulsions
- process is difficult to adapt to variations in flow rate and concentration level

These shortcomings can be overcome by emulsion pertraction: a new membrane based combined extraction and stripping process for the removal of heavy metals from waste water.

2 Emulsion pertraction

2.1 Principle

Emulsion pertraction is a process evolved from a combination of permeation through membranes and solvent extraction. In the emulsion pertraction process the waste water is kept apart from the emulsion phase by a hydrophobic

microporous membrane.
The emulsion phase consists of an organic solvent with a dissolved extractant as continuous phase with aqueous droplets of strip liquid dispersed in it. The contact surface between water phase and emulsion phase lies in the pores of the membrane. The metal to be removed from the waste water stream is bound by the extractant present in the pores of the membrane. At the other side of the membrane the extractant is regenerated by the strip liquid. The strip liquid is dispersed in the organic phase. There is no need to make the dispersion very stable because the hydrophobic nature of the membrane keeps the waste water and strip liquid always separated. So no aqueous phase can pass the membrane. See also figure 1, the metal indicated as Me is bound to extractant L to form a complex L-Me which is regenerated at the interface of the droplets strip liquid to form for example a concentrated metal sulphate solution. There is no selectivity needed of the membrane itself. The selectivity of the process is provided by the extractant.

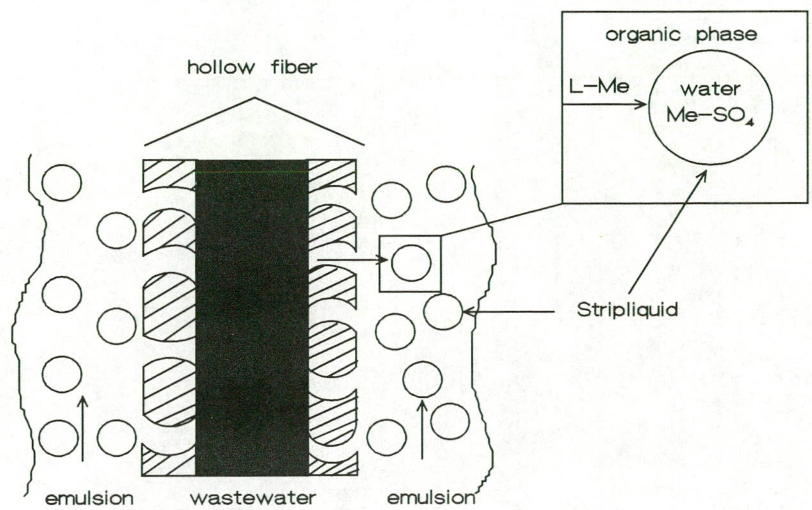

Figure 1 Principle emulsion pertraction

Advantages of emulsion pertraction over normal extraction are:
- extraction and stripping can be done in one operation
- no possibility of emulsion formation in the waste water phase
- volume of extractant is relatively small
- process parameters are very flexible
- phase separation is not necessary
- large specific surface area when using hollow fibre membranes
- short diffusion ways
- compact modular equipment
- low energy consumption

The emulsion used in emulsion pertraction is analog to the emulsion used in the Liquid Membrane Process (LMP) developed by the university of Graz (1). The main advantage of pertraction over the LMP process is that the emulsion may be unstable while LMP requires a stabilized emulsion that is difficult to break.

2.2 Extractants for heavy metals

The selectivity of the extractants is due to pH-adjustable chelating agents which form metal-complexes. These metal complexes are very strong and can be formed with monofunctional ligands like H_20, CN^-, NH_3 or Cl^- in a number equal to the metal coordination number. Metal ions can also interact with polyfunctional ligands, each capable of occupying more than one position in the coordination sphere of the metal. These complexes are called chelates. Neutral chelates are characterised by a low solubility in water and a significant solubility in organic solvents. In general the overall formation constants of chelates are higher than those of similar simple coordination complexes. Most metal complexing agents are also Bronsted bases and will therefore be affected by changes in pH. For example, NH_3, CN^-, ethylenediamine and $EDTA^-$anions will accept protons and hence the fraction of their total concentration, which is available for metal complexation, will vary with the pH. This pH depending mechanism is reversible and allows removal, and recovery at higher concentrations at the same time. Due to the fact that several metals have different pH-dependencies a selective removal of those metals is possible.

In figure 2 an example of pH dependency for copper and zinc of a chelating oxime extractant is shown. The degree of extraction of the metal is given as a function of pH from the waste water. From figure 2 it can be seen that with a pH between 3.5 and 4.5 almost all copper can be extracted while the zinc is retained in the waste water. The zinc can be recovered in a second extraction step with increased pH or with an other type of extractant that is able to extract zinc at a pH between 3.5 and 4.5.

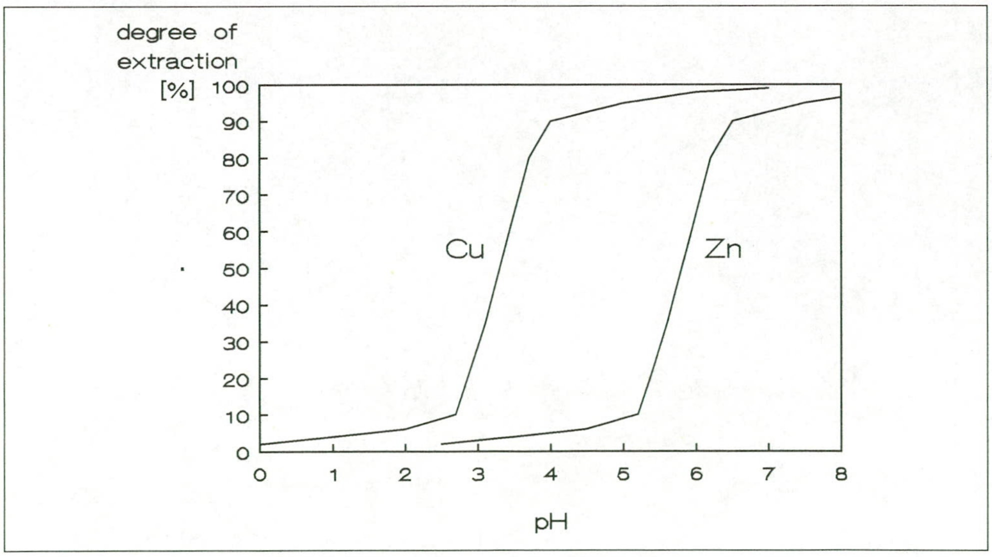

Figure 2 Extraction of copper and zinc as function of pH

2.3 Applications

Pertraction research at TNO started with labscale experiments to remove Zn, Mn, Cu, Cr and Ni from water. Important points in this research program were: membrane and extractant selection, mass transfer, achievable degree of removal of contaminant from water phase and a preliminary economic evaluation.

In this first stage of the pertraction research extraction and stripping were carried out in two different membrane modules. Especially the stripping step turned out to be rate limiting. The pertraction process has been further improved by integrating an emulsion with stripping liquid in the extraction module; this is called emulsion pertraction. The emulsion used is similar to the emulsion used in the liquid membrane process (LMP). However LMP (developed by the university of Graz) uses **stabilized** emulsions of extractants in waste-water whereas emulsion pertraction can be combined with **unstable** emulsion at the permeate side. This has the advantage that no stable emulsion has to be developed and that no special equipment is required for emulsion break-up.

The emulsion-pertraction process has been demonstrated for zinc and on pilot plant scale for the removal of Cr (VI) from waste water (2).

Emulsion pertraction can recover different types of heavy metals like Zn, Mn, Cu, Cr and Ni from waste water when a suitable extractant for the specific waste water is available.

3 Experimental

3.1 Experimental Set up

On labscale recirculation experiments can be used to determine mass transfer characteristics of the process. Both the waste water and emulsion are recycled through a membrane module. The concentration of the metal in the waste water is monitored over time. The decline in concentration is used to model mass transfer of the process. At the end of the experiment the concentration of metals in the emulsion phase is determined to check the mass balance and selectivity of the process.

3.2 Results

In figure 3 the result of a recirculating emulsion pertraction experiment for the removal of zinc from waste water is shown. For the organic phase 20 vol % of DEHPA (di ethyl hexyl phosphoric acid) in odourless kerosene has been used. Sulphuric acid has been used as strip liquid.

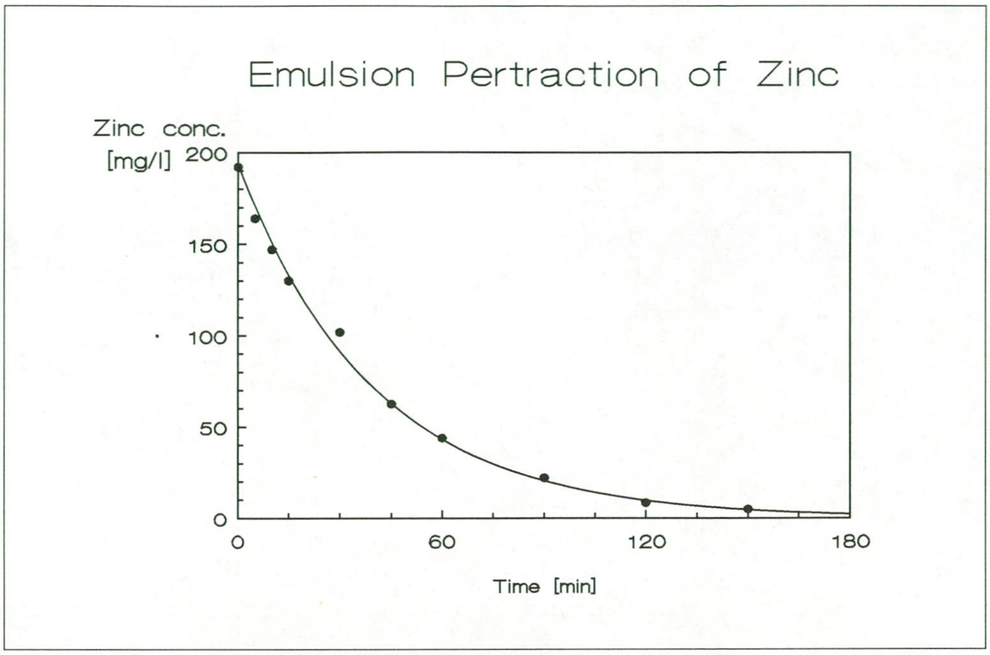

Figure 3 Removal of zinc from waste water with emulsion pertraction

From the decline in zinc concentration over time an overall mass transfer coefficient can be calculated. This mass transfer coefficient can be used to determine the rate limiting step, to perform scale up calculations and to design once through installations.
For zinc the transport from the bulk of the waste water flow to the membrane has been identified as the rate limiting step.

3.3 Discussion

For the pertraction process so far microfiltration hollow fiber membrane modules have been used. The currently available membrane modules have been developed for filtration purposes. At the shellside of those modules channelling and short circuiting can occur whereas pertraction processes need well defined flow regimes at both sides of the membrane to achieve optimal mass transfer.
TNO has developed a new module concept with hollow fiber membranes perpendicular to the waste water flow (3). This module gives improved mass transfer and is easy to scale up.

By using the new module concept with hollow fiber membranes perpendicular to the waste water flow it is expected that mass transfer can be improved with a factor four to five.

4 Economics

Economics of the process depend very much on the nature of the waste water to be treated, the kind of metals that are involved and the degree of removal that must be obtained.
Preliminary cost evaluations indicate that the emulsion pertraction process is competitive with respect to mixer settlers and the liquid membrane permeation process.

5 Conclusions

Emulsion pertraction is a new membrane based process for the removal of heavy metals from waste water. It combines extraction and stripping in one operation, it prevents emulsion formation in the waste water phase, needs a small volume of extractant, is based on low volume flexible modular equipment and has a low energy demand.
This gives emulsion pertraction main advantages over other extraction processes in mixer settlers or collums.

Applications for emulsion pertraction are the recovery of heavy metals like Zn, Hg, Cd, Cu, Cr and Ni from waste water.

Preliminary cost evaluations indicate that the emulsion pertraction process is competitive with respect to mixer settlers and the liquid membrane permeation process.

The process can be further improved with a new cross flow module concept and membrane development.

With the present state of the art it is possible to do emulsion pertraction pilot plant demonstrations.

6 References

[1] Draxler, J., Marr, R.
Emulsion liquid membranes, Part I: Phenomena and industrial applications, Chem.Eng.Process.,20(1986) 319-29

[2] Klaassen, R.
Recovery of heavy metals by pertraction,
TNO report Ref nr. 91-131, April 1991 (in Dutch)

[3] Meulen, B.Ph. ter
Transfer device for the transfer of matter and/or heat from one medium flow to another medium flow.
International patent application PCT/NL91/00001

7 Authentication

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Names of establishments to which part of the research was put out to contract

Date upon which, or period in which, the research took place
February 1993

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