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# SELECTIVE REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY DIAFILTRATION OF MACROMOLECULAR COMPLEXES

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## ABSTRACT

A process for the selective removal of heavy metal ions with macromolecular chelating agents or emulsified liquid ion exchange materials in combination with ultrafiltration is described. The theoretical limitations of the procedure are discussed, and several practical applications are presented.

## INTRODUCTION

In recent years ultrafiltration and reverse osmosis have become standard procedures for the separation of molecular solutions. In ultrafiltration, the different chemical components are separated exclusively according to their molecular dimensions. In reverse osmosis, in addition to size, chemical nature is also of importance. But neither ultrafiltration nor reverse osmosis are particularly specific processes.

In many cases it is desirable to remove certain chemical species selectively from a multi-component mixture. This is true, for example, when highly toxic or valuable constituents, such as certain heavy metal ions, are to be removed from an industrial waste water containing these ions in comparatively low concentrations in a mixture with other salts. Reverse osmosis is not suited to this type of separation problem, since all other waste water

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constituents would also be more or less completely retained by the membrane, and the osmotic pressure in the concentrated solution would soon become unacceptably high.

Ultrafiltration, however, can be effectively and economically applied when combined with a water soluble macromolecular complex or an emulsified liquid ion exchanger which selectively binds certain metal ions or groups of ions. The principle of this process, which was first suggested by A. S. Michaels (1), is shown schematically in Fig. 1. The solution containing the metal ion to be removed, in a mixture with other salts, is fed into a reactor vessel containing a 5 to 10 wt % solution of a macromolecular chelating agent which selectively binds the metal ion. The solution that is drawn from the reactor vessel is then filtered through an ultrafiltration unit which retains the macro-

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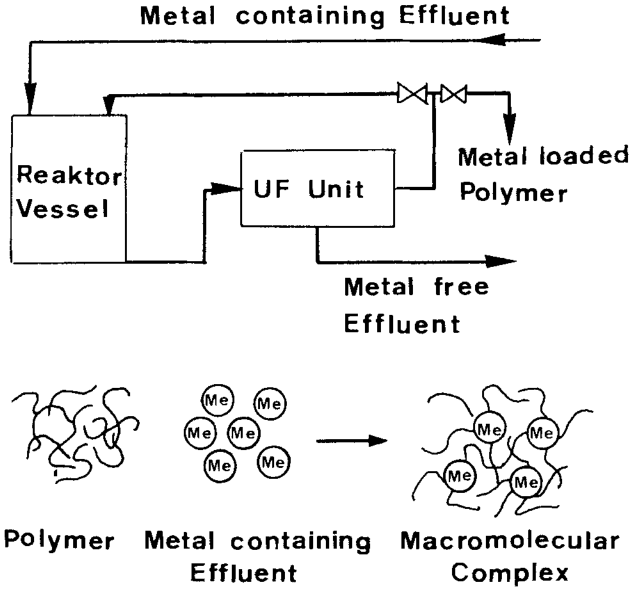

FIGURE 1. Schematic diagram of a diafiltration process for the selective removal of heavy metal ions with macromolecular complexes.

molecular complex completely, but does not reject any salts or other low molecular weight components, so that a metal-ion-free filtrate is obtained. The rejected macromolecular complex is either fed back into the reactor or collected for further treatment when completely loaded.

## THEORETICAL CONSIDERATIONS

For the process to be effective, certain requirements have to be fulfilled by the complex as well as by the membrane. The complex should have a high selectivity, a high binding capacity, a narrow molecular weight distribution, and a high water solubility. The membrane should have a high flux and a sharp molecular weight cut-off. These are the key parameters which determine the technical feasibility and the economic efficiency of the entire process.

### Complex Capacity, Polymer Solubility, and the Enrichment Factor

The technical feasibility of the process is determined mainly by the selectivity of the macromolecular chelating agent. Its economic efficiency is strongly governed by the maximum enrichment factor of the metal ion which can be achieved. The enrichment factor, which is expressed as the ratio of the metal ion concentration in the feed solution to that in the reactor, can easily be calculated from the mass balance of a diafiltration process. The schematic diagram in Fig. 2 demonstrates the process.

If all metal ions in the reactor are bound by the complex, the enrichment factor $\alpha$ is given by

$$\alpha = \frac{C_r}{C_o} = \frac{1 - \exp\,[-(V_o/V_r)(1 - R)]}{1 - R}, \qquad (1)$$

in which $C_r$ and $C_o$ are the concentrations of the metal ion in the reactor vessel and in the feed solution, $V_o$ and $V_r$ are the volumes of the feed solution and the reactor vessel respectively,

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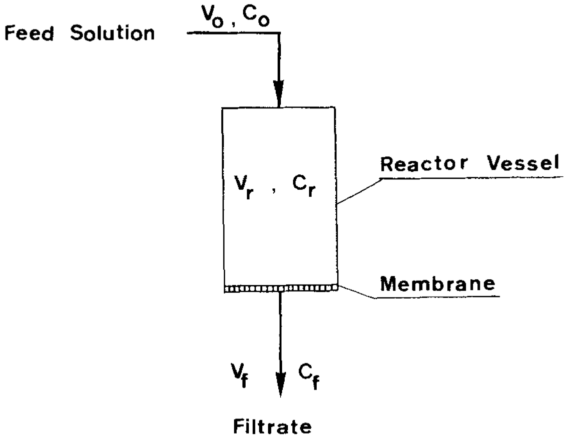

FIGURE 2. Schematic diagram of mass transport in a diafiltration process.

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and R is the rejection of the membrane for the macromolecular complex. The dependence of this parameter on polymer concentration is given by the expression

$$R = (1 - \frac{C_r^p}{C_f^p}), \tag{2}$$

where $C_r^p$ is the polymer concentration in the reactor vessel and $C_f^p$ that in the filtrate.

If no metal ions are bound by the complex, or if the membrane does not reject the complex, the enrichment factor is given by

$$\lim_{R \to 0} \alpha = 1 - \exp(-V_o/V_r); \tag{3}$$

this means that α would always be less than unity, and that the concentration in the reactor can never exceed that in the feed solution.

If all metal ions in the reactor are bound to the complex and the membrane rejects the complex completely, Eq. (1) reduces to yield

$$\lim_{R \to 1} \alpha = \frac{V_o}{V_r} . \tag{4}$$

In this case, the enrichment factor is given by the ratio of the volume of the feed solution to that of the reactor vessel. In Fig. 3 log $\alpha$ is plotted as a function of the ratio of feed solution to reactor vessel volume for various rejection rates. However, even if the macromolecular complex is completely retained by the membrane, the enrichment factor cannot be infinitely high. It is limited by the binding capacity and the concentration of the complex. The maximum enrichment is achieved when the complex is completely loaded. The enrichment factor is then given by

$$\alpha_{max} = \frac{C_r^p\ k}{C_o}, \qquad (5)$$

where k is the polymer binding capacity, expressed as gram of metal per gram of polymer.

Experimentally, the capacity of a complex is determined by measuring the metal ion concentration in the filtrate in a diafiltration experiment and plotting the ratio of the filtrate concentration to the feed solution concentration versus the ratio of the volume of the feed solution to that of the reactor vessel. This is shown schematically in Fig. 4 for a system in

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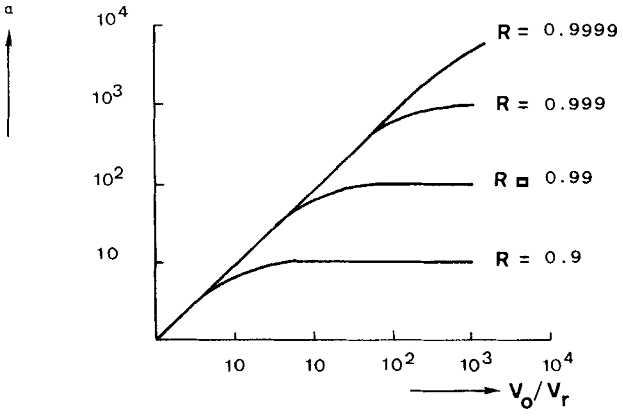

FIGURE 3. Calculated enrichment factors as a function of rejection.

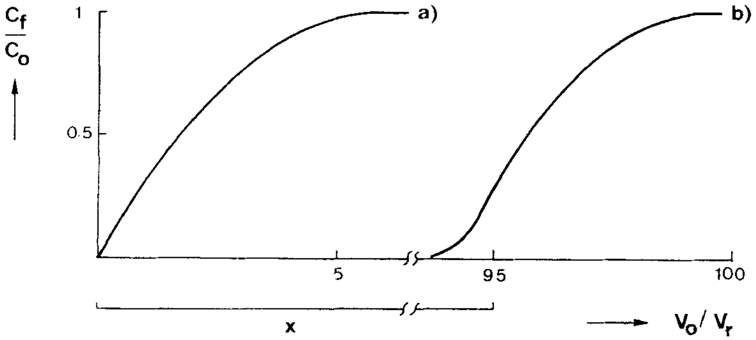

FIGURE 4. Schematic diagram showing the concentration change in the filtrate for a system (a) without a macromolecular complex and (b) with a macromolecular complex.

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which no metal ions are bound by the complex. The ion concentration in the filtrate is identical with that in the reactor, and the ratio of $C_f$ over $C_o$ will asymptotically approach unity according to Eq. (3). For a system in which the metal ion is bound completely to the complex, the concentration in the filtrate is zero until the complex is completely loaded. Only then does it increase, in accordance with Eq. (3) (see Fig. 4b).

The capacity of the polymer can, therefore, be experimentally determined from the ratio of feed solution to the reactor vessel volume, the polymer concentration in the reactor, and the metal ion concentration in the feed solution;

$$k = \frac{V_o C_o}{V_r C_r^p} , \qquad (6)$$

where k is the load factor. The complex capacity depends on the number of functional groups in the macromolecular complex and the atomic weight of the metal. In practice, load factors between 0.1 to 1 g metal/g polymer are obtained. By Eq. (5), the enrichment which can be achieved depends sensitively on the metal ion concentration in the feed solution. For very dilute solutions, enrichment factors of more than $10^3$ or $10^4$ can be obtained, as demonstrated in Fig. 5, where the maximum

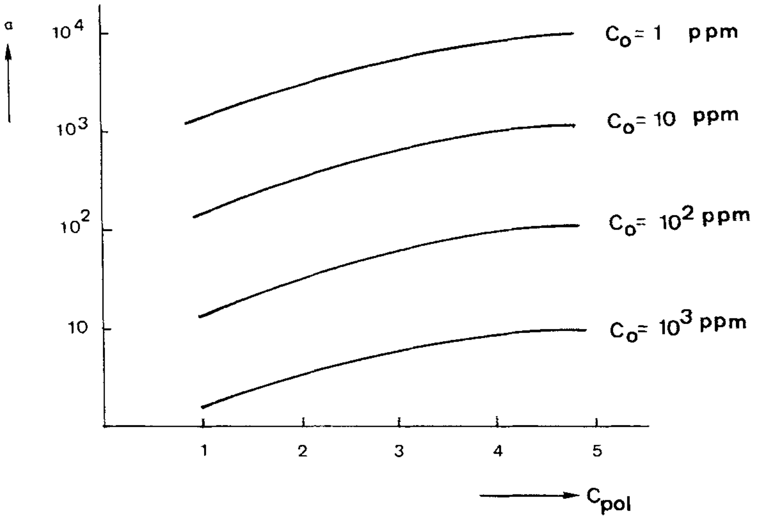

FIGURE 5. Maximum enrichment factors as a function of the polymer and the feed solution concentration at a load factor of 0.2.

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enrichment factor is shown as a function of the polymer concentration for various feed solution concentrations at a load factor of two.

## Fractional Loss of Metal Due to Incomplete Rejection of the Complex

If the metal ion complex is not completely retained by the membrane, part of the metal is lost with the filtrate. This fractional loss δ can be expressed by the ratio of the filtrate concentration to the feed concentration, since the filtrate volume is identical with the feed solution volume. Thus

$$\delta = \frac{V_f C_f}{V_o C_o} = \frac{C_f}{C_o} \, . \qquad (7)$$

The filtrate concentration in a system with incomplete rejection of the complex is given by

$$C_f = (1 - R)C_r \, . \qquad (8)$$

The combination of Eqs. (1), (7) and (8) gives the fractional loss of the metal as a function of the complex rejection and the enrichment factor or the ratio of feed solution volume to that of the reactor vessel volume;

$$\delta = \frac{C_f}{C_o} = (1 - R)\alpha = 1 - \exp\left[-(V_o/V_r)(1 - R)\right]. \qquad (9)$$

In Fig. 6, the fractional loss of metal, as calculated by Eq. (9), is plotted as a function of the ratio of the feed solution to reactor vessel volume for three different rejection rates. This figure indicates quite clearly that for a system with incomplete rejection, not only is the enrichment factor rather limited, but also the fractional product loss may be extremely high.

In most practical applications of this process, where the concentrations of toxic or valuable metal ions in the feed solutions are rather low, high enrichment factors and little product loss is desirable. Therefore, the rejection of the complex must be close to 100%. On the other hand, all low molecular weight particles should pass through the membrane completely; thus, membranes used in this process should have a sharp molecular weight cut-off and should be free of defects.

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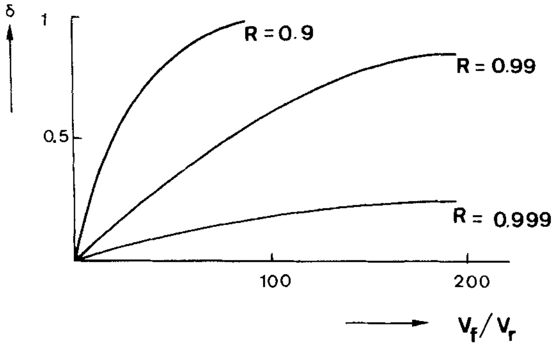

FIGURE 6. Fractional loss of product as a function of $V_f/V_r$ and membrane rejection.

### Concentration Polarization and Polymer Precipitation

The concentration of the macromolecular complex in the reactor vessel should, for economical reasons, be as high as possible. This leads to excessive concentration polarization and gel-formation at the membrane surface (2), which affects the filtration rate considerably. In the ultrafiltration of macromolecular solutions, the flow rate of the feed solution parallel to the membrane surface has a large effect on the filtration efficiency (3). Thus, only filtration systems in which the feed solution flow distribution is well controlled are suited for this process.

## EXPERIMENTAL PROCEDURES AND RESULTS

### The Macromolecular Complex

From the theoretical consideration discussed above, it is clear which properties a macromolecular complexing or chelating agent should have to be suitable for the diafiltration process. First of all, it should have the desired selectivity for certain metal ions or groups of metal ions. The molecular weight and the molecular weight distribution must be adjusted to the ultrafiltration membrane so that virtually 100% rejection of the complex is obtained. The ion binding capacity and the solubility of the macromolecular agent should be as high as possible.

The structures of several macromolecular complexing agents used in this study are identified in Fig. 7. A whole series of complexing or chelating agents is currently available. These reagents have a high selectivity for certain metal ions or groups of metal ions (4). Most of these agents are, however, low molecular weight compounds and so cannot be used directly for the process under consideration. In order to be useful, they must first be converted into macromolecules. This can easily be done by binding them to a water soluble polymer. These polymers must have the desired solubility and have certain reactive groups to which the complexing agents can be bound.

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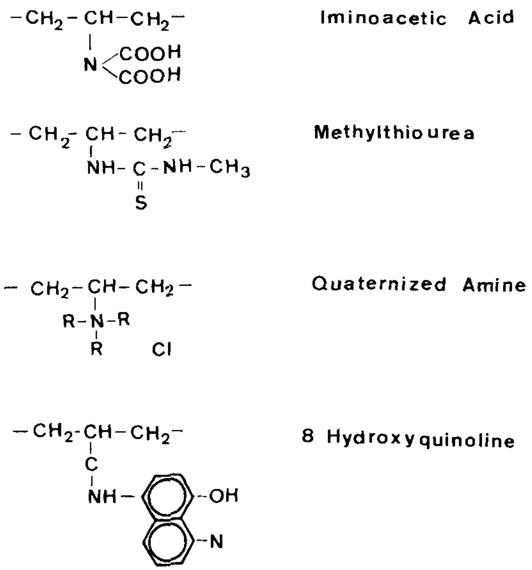

FIGURE 7. Macromolecular complexing agents used in this study.

Polymers used successfully in this study are polyethylenimine, polyvinylalcohol, polyvinylpyrolidone and polyacrylic acid.

The Emulsified Liquid Ion Exchanger

Instead of a water soluble macromolecular chelating agent, an emulsified liquid ion exchange material can also be used. In hydrometallurgical processing of low grade ores, liquid ion exchange materials are applied to extract certain heavy metal ions from a mixture with other components. These liquid ion exchange materials are hydrophobic in character and virtually insoluble in water. Their metal binding capacity is pH-dependent. A material widely used in the copper industry is LIX 64 N*. At high pH-values, copper ions are bound, whereas at low pH-values the copper is released and replaced by $H^+$-ions. The structure of the material and the distribution coefficient of copper ions between an aqueous phase and LIX 64 N is shown in Fig. 8.

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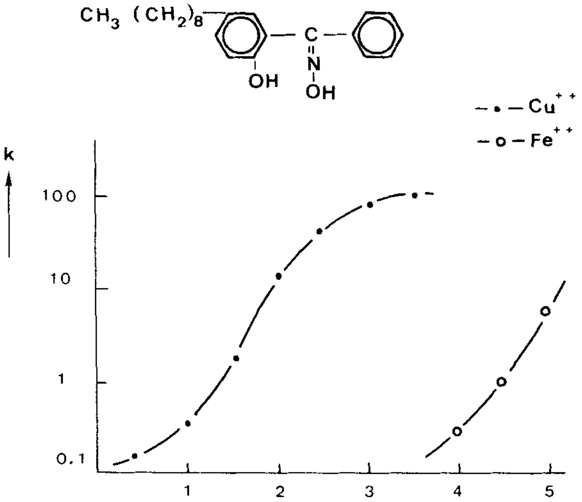

FIGURE 8. Structure of LIX 64 N and the distribution coefficient of $Cu^{++}$ and $Fe^{++}$ ions between LIX 64 N and an aqueous solution as a function of pH.

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The data displayed in Fig. 8 indicate that the distribution coefficients of $Cu^{++}$ and $Fe^{++}$ ions change by three orders of magnitude with changing pH. The data also demonstrate that at low pH values $Cu^{++}$ ions are preferred to $Fe^{++}$ ions. Thus, at low pH values the chelating agent is highly selective for $Cu^{++}$ ions.

There are many different cation or anion selective liquid ion exchange materials available today. An example of a cation exchange material, the reaction of $Cu^{++}$ ions with LIX 64 N, and of an anion exchange material, the reaction of Alamin 336* with an uranium salt, are shown in Fig. 9.

The use of liquid ion exchange materials in hydrometallurgical processes is affected by two problems. First, the transport of the metal ions from the aqueous to the organic phase is slow. This requires relatively long residence time and intensive mixing. The second problem involves separation of the organic

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Reaction of LIX 64 N $^R$ with $Cu^{++}$

$$2(CNOHR_2OH)_{org.} + Cu^{++}_{aq.} \longrightarrow (CNOHR_2O)_2Cu_{org.} + 2H^{+}_{aq.}$$

Reaction of Alamin 336 $^R$ with $UO_2(SO_4)_3^{4-}$

$$R_3N_{org.} + H_2SO_{4aq.} \longrightarrow (R_3NH)_2SO_{4org.}$$

$$2(R_3NH)_2SO_{4org} + Na_4UO_2SO_4)_{3aq} \longrightarrow (R_3NH)_4UO_2(SO_4)_{3org} + 2Na_2SO_{4aq.}$$

$$(R_3NH)_4UO_2(SO_4)_{3org} + 4NaOH_{aq.} \longrightarrow 4R_3N_{org} + Na_4UO_2(SO_4)_{3aq} + 4H_2O$$

FIGURE 9. Reaction schemes for various liquid ion exchange materials.

and the aqueous phases. Much faster ion transfer rates can be obtained when the hydrophobic ion exchange material is used in the form of an emulsion. The emulsion is then separated from the aqueous phase by ultrafiltration, as shown in Fig. 1.

## Determination of Chelating Agent Selectivity and Capacity

The selectivity and the capacity of a polymer complexing agent were determined in a diafiltration experiment as described by the setup displayed in Fig. 2. A metal ion-containing feed solution was passed through a reactor which contains polymer complexing agent and then into an ultrafiltration unit. The concentrations of the various ions in the filtrate were analyzed and plotted as a function of filtrate volume. The selectivity and the capacity of the polymer for different ions were studied. These data, which are presented in Fig. 10, demonstrate the selectivity of polyethylenimine for different metal ions. The polymer concentration was 1.5 wt % and the feed solution concentration

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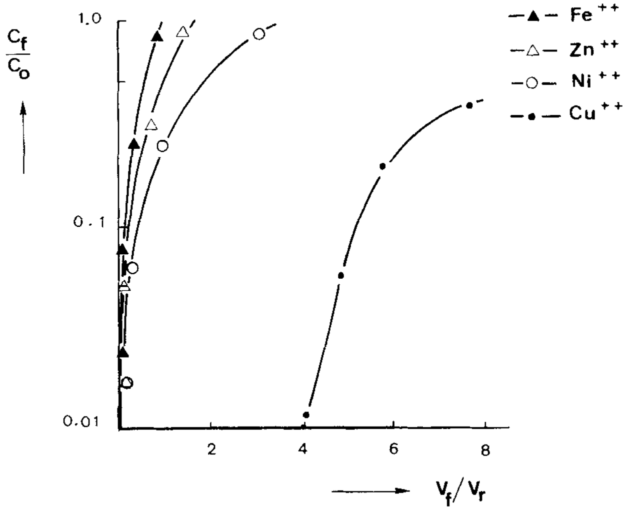

FIGURE 10. Selectivity of polyethylenimine for various metal ions determined at pH 4.2.

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was 250 ppm for each ion at pH 4.2. The data indicate that no $Fe^{++}$, $Ni^{++}$, or $Zn^{++}$ ions, yet a substantial quantity of $Cu^{++}$ ions, are bound by the polymer. The binding capacity was calculated to be 0.07 g metal/g polymer.

The selectivity of polyiminoacetic acid at pH 3.5 is shown in Fig. 11. The concentration of the different metal ions in the feed solution was 500 ppm each. The reactor volume was 100 ml and the polymer concentration was 5 wt %. Here again the complex with $Cu^{++}$ ions is much stronger than with $Zn^{++}$ or $Ni^{++}$ ions.

## Characterization of Different Chelating Agents in Terms of their Selectivity and Load Factor

The majority of the tests were performed with four different macromolecular complexes which had a molecular weight in excess of 30,000. A 5 wt % aqueous solution was prepared, and the selectivity was determined in a diafiltration test with a feed

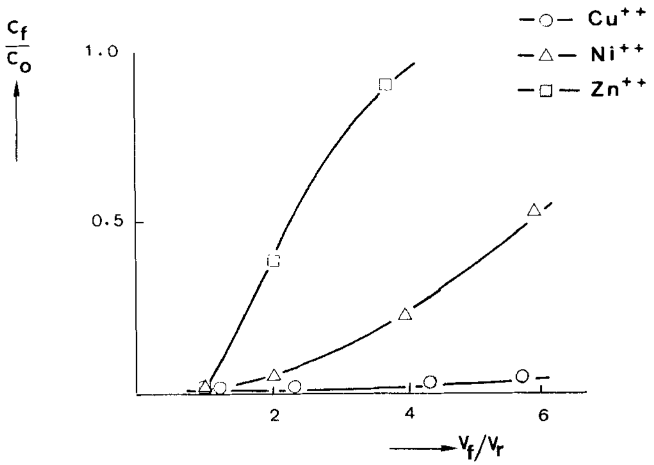

FIGURE 11. Selectivity of polyiminoacetic acid for various metal ions determined at pH 3.5.

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solution which contained 100 ppm concentration of the metal ion being examined. The results are summarized in Table 1. These results indicate that polyethylenimine shows a good selectivity for $Cu^{++}$ and $Cd^{++}$ ions. Polyiminoacetic acid also shows a high selectivity for $Cu^{++}$ and is somewhat less selective for $Zn^{++}$ and $Ni^{++}$ ions. The quaternized polyethylenimine has a good selectivity for Pd, Pt, Hg, and Au ions, and an exceptionally high capacity. Lastly, polythiourea is especially suited for Hg ions. The concentration in the filtrate was between 1 and 100 ppb. The relatively high concentrations in the filtrate are not necessarily a reflection of the stability of the complex, but are rather more likely caused by the molecular weight distribution of the polymer.

## The Use of Various Liquid Ion Exchange Emulsions for the Selective Removal of Heavy Metal Ions

In this study, four different ion exchange materials were used: Kelex 100*, Kelex 200*, Alamin 336 and LIX 64 N. Various

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TABLE 1

Selectivity and capacity of various complexing agents for different metal ions

| Complexing agent | Metal | pH range | Capacity (g metal/g polymer) |
|---|---|---|---|
| Polyethylenimine | Cu | 6 | 0.1 |
| | Cd | | 0.3 |
| Polyiminoacetic acid | Zn | 1.5 | 0.02 |
| | Ni | | 0.05 |
| | Cu | | 0.1 |
| | Ag | | 0.2 |
| Quaternized polyethylenimine | Pd | 1.5 | 0.4 |
| | Pt | | 0.5 |
| | Hg | | 0.6 |
| | Au | | 0.2 |
| Polythiourea | Hg | 1 | 0.75 |

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industrial effluents were simulated as feed solutions. An emulsion of 10% organic material was prepared by commercial surfactants. An ultrafiltration membrane with a nominal cut-off of molecular weight 10,000 was used for the filtration process. The test results are summarized in Table 2.

## SELECTIVE REMOVAL OF HEAVY METAL IONS FROM INDUSTRIAL EFFLUENTS

In a second series of laboratory tests, diafiltration with macromolecular complexes was applied to various industrial effluents to remove certain highly toxic or valuable heavy metal ions. The results which are summarized in Table 3 indicate that the diafiltration process can successfully be employed to remove various heavy metal ions from industrial effluents. More extensive pilot plant tests were carried out with a mercury-containing effluent from a chloralkaline electrolysis. The experimental arrangement

TABLE 2

Selective removal of metal ions by liquid ion exchange emulsion and ultrafiltration

| Metal ions | Ion exchange material | $C_o$ (ppm) | $C_f$ (ppm) | Load factor (mg ion/g) | pH |
|---|---|---|---|---|---|
| $Cd^{2+}$ | Kelex 100 | 37 | 0.005 | 63 | 7 |
| $Cd^{2+}$ | Kelex 200 | 100 | 0.16 | 95 | 3 |
| $Cu^{2+}$ | LIX 64 N | 80 | 0.09 | 28 | 5 |
| $UO_2(SO_4)_3$ | Alamin 336 | 20 | 0.1 | - | 1 |
| $CrO_4^{2-}$ | Alamin 336 | 100 | 1.0 | - | 1 |
| AuCN | Alamin 336 | 2 | 0.1 | - | 1 |

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corresponds to the schematic in Fig. 1. The waste water, which contained 2 to 5 ppm of mercury, among other salts, was fed into a stirred reactor vessel. The reactor contained a 5% solution of polyethylenimine.

The reactor solution was ultrafiltrated with a recovery rate of 5 to 10% in a capillary membrane unit (5). The bleed-off is fed back into the reactor or collected for further treatment when loaded by more than 20 wt %. The enrichment factor in this process was 2,000 to 5,000. The ultrafiltration unit was equipped with capillary membranes with an inner diameter of 50 mils and a molecular weight cut-off of 30,000. It was operated at 15 psi and yielded a flux of about 30 gsid.

A cost analysis, which was based on the pilot plant tests, indicated that the price of the polymer determined to a large extent the costs of the process, and only for very dilute solutions do the costs for the diafiltration procedure become significant. For valuable metals, such as silver, gold, etc. the costs of the separation process are generally recovered by the cost of the metal reclaimed.

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TABLE 3

Recovery of heavy metal ions from various simulated industrial effluents

| Metal | Solution | Industrial process | Feed conc. (ppm) | Filtrate conc. (ppm) | Complex |
|---|---|---|---|---|---|
| Cd | NTA-complex | Photoindustry | 100 | 0.5 | PEI |
| Cd | CN-complex | Electroplating | 30 | 0.1 | PIA |
| Au | CN-complex | Electroplating | 20 | 0.1 | QPEI |
| Zn | $Zn^{++}$ | Process water | 50 | 0.1 | PIA |
| Ag | $Ag^{+}$ | Electroplating | 4-400 | 0.2 | PIA |
| Ag | $S_2O_3$-complex | Photoindustry | 40 | 0.2 | PIA |
| Cu | Cu EDTA | Metal | 4 | 0.2 | PEI |
| Hg | $Hg^{+}$ | Chloralkaline Electrolysis | 2 | 0.001 | PTU |

| | |
|---|---|
| PEI | Polyethylenimine |
| PIA | Polyiminoacetic acid |
| PTU | Polythiourea |
| QPEI | Quaternized polyethylenimine |
| NTA | Nitrilotriacetic acid |

It is generally more practical to use emulsified liquid ion exchange materials rather than macromolecular chelating agents, since the basic material is less costly, the retention of the membrane for the emulsion is virtually 100%, and the metal ion can easily be released from the organic material by a change in pH.

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