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Use of Supported Liquid Membranes for Sulfate Extraction from Acidic Wastewaters

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ABSTRACT

Sulfate pollution is a current target of many national regulatory and enforcement agencies worldwide. The objective of this study was to investigate the possibility of using supported liquid membranes to remove low concentration sulfate ions from acidic wastewater. Alamine 336 was identified as a suitable carrier. It was used together with isodecanol as a phase modifier and kerosene as a solvent to form the liquid membrane. Celgard 2500 was used as a support. It was concluded that sulfate ions could be removed from polluted water by means of a cotransport mechanism in conjunction with ion-immobilization. Sodium carbonate was used to strip the sulfate ions from the organic phase. This technique promises to be a useful tool in combating sulfate pollution.

INTRODUCTION

The main source of fresh-water sulfate contamination is leaching of sedimentary rocks, like gypsum and other gypsiferrous formations. A more important source, from a pollution point of view, is the oxidation of iron pyrite to form iron(III) sulfate, which is a particular problem near mining sites (1).

The contamination of fresh water with sulfate is a pollution problem that has increased in severity over the last few decades. In the past authorities have been very lenient regarding the amount of sulfate that may be dumped into a river by industrial waste streams. This is mainly due to the high cost involved in removing sulfate from water and because sulfate is not a direct threat to hu-

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man health. However, if sulfate is present in excessive amounts, it does have a cathartic effect on humans, which is aggravated by the presence of magnesium in the water. Because of this, it has been recommended that water intended for human consumption should have an upper limit of 250 ppm sulfate (2).

What makes sulfate a greater pollution threat is its corrosive effect on steel and cement, as well as the odors associated with waters that have a high sulfate content. The World Health Organization water standard for sulfate is 400 ppm.

The following methods exist for the removal of sulfates from water (3):

a. Barium precipitation
b. Cold gypsum precipitation
c. Cold lime softening
d. Ion exchange
e. Evaporation
f. Reverse osmosis
g. Biological removal

The problem with the above-mentioned processes is that they are either too expensive or they are ineffective for the removal of low concentration sulfate ions from water.

The possibility of using supported liquid membranes to remove low concentration sulfate ions from wastewater was investigated, and the results are illustrated in this paper.

BACKGROUND

A membrane can most simply be described as a barrier between two phases. Membranes can be used to separate the components of a mixture by using the fact that different components move at different rates through a membrane (4). A supported liquid membrane (SLM) is obtained by immobilizing a liquid, which is immiscible in both the phases, in the pore structure of a microporous support such as a polymeric filter (4).

Separation Mechanisms

Adding a nonvolatile complexing agent (carrier) to the liquid membrane can enhance solute flux through the liquid membrane. This agent will enhance the solute flux by reacting selectively and reversibly with the solute. This is known as facilitated or coupled transport (5). Equation (1) gives an example of such a mechanism:

$$A^- + RB \leftrightarrow RA + B^- \tag{1}$$

Here, the reversible reaction is an ion-exchange reaction. The solute flux is linked to the flux of a second ion. The carrier (RB) is an ion-exchange reagent. This reaction normally occurs at the liquid–liquid interface, since the ions are normally insoluble in the organic phase. Coupled transport is comparable to performing solvent extraction in a thin liquid film. The majority of SLMs involve this mechanism.

Using carriers has the following advantages (4):

1. Higher fluxes are possible
2. Very selective separations are possible
3. Ions can be concentrated since the coupled transport mechanism can "pump" one ion against its concentration gradient due to the concentration gradient of the coupled ion
4. Expensive complexing agents can be used since only a small amount of carrier is required

Coupled transport occurs by one of two mechanisms (5), namely countertransport (Eq. 1) and cotransport (see Fig. 1).

Kreevoy et al. (6) developed a method, using the cotransport mechanism, in which nitrate ions are removed from a water phase together with protons by

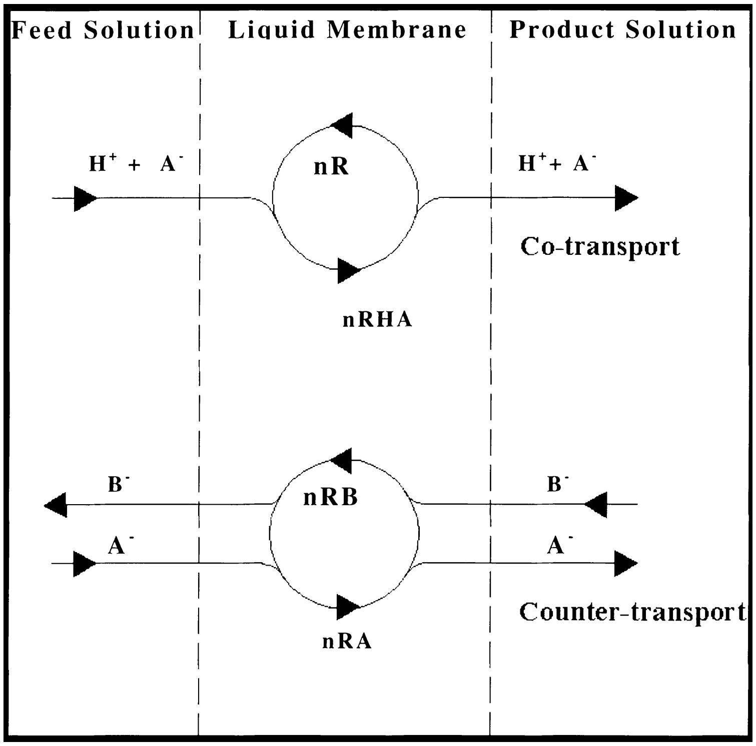

FIG. 1 Countertransport and cotransport mechanisms.

complexation with a very strong lipophilic carrier in a supported liquid membrane. In this process the pH and the nitrate concentrations in the water phases regulate transport. Due to the removal of protons from the feed to the strip phase, equilibrium is soon established, and the driving force for nitrate complexation is diminished. This is the problem with most cotransport processes. This article will demonstrate a method called ion-immobilization designed to overcome this disadvantage and to "pump" sulfate ions against their concentration gradient using a cotransport mechanism.

Neplenbroek et al. (7) developed a method for the removal of nitrate from water by applying the countertransport mechanism. They made use of a continuous anion exchange between nitrate and chloride ions through an SLM. An advantage of such a process, compared to the cotransport of protons, is that the driving force for the "uphill" concentration is provided by the high chloride (co-ion) concentration in the stripping phase which can be easily controlled.

Neplenbroek et al. (7) distinguished the following steps in anion transport through an SLM:

1. Diffusion of the ion from the bulk feed to the membrane surface
2. Complexation at the surface with a carrier molecule
3. Diffusion of the carrier bound ion through the LM phase
4. Decomplexation at the surface with the stripping phase
5. Diffusion of the permeate ion to the bulk of the stripping phase

Almost all research on SLMs is performed on systems in which metal ions are recovered. Very little work has been done on the removal of anions from water, mostly because there is little economic incentive (7). The measured transport rates for anions are lower than those for cations, and the selectivity mostly follows the Hoffmeister series: $ClO_4^- > I^- > SCN^- > NO_3^- > Br^- > Cl^- >> CO_2^-, H_2PO_4^-, SO_4^{2-}$ (4).

Coupled transport will be used for the concentration of sulfate ions. This paper will demonstrate how this mechanism may be exploited to concentrate the sulfate ions against their concentration gradient by means of a cotransport mechanism in conjunction with ion-immobilization. Due to an equilibrium that is established between the feed and strip phases, it is very difficult to concentrate ions against their concentration gradient with the cotransport mechanism. It is proposed to overcome this disadvantage by using ion-immobilization (see Fig. 4 below). The advantage that this mechanism has above the usual cotransport mechanisms is that there is no build up of counterions in the strip phase, therefore no decrease of the pH and no loss of driving force due to that. The formation of H_2O from the strip reaction effectively immobilizes the H^+ ions which enter the strip phase with the sulfate ion. The pH of the strip phase remains constant during the whole extraction process.

IDENTIFICATION OF A SUITABLE CARRIER

High molecular weight amines are possible extractants since they are capable of forming salts with a wide variety of inorganic and organic acids. Various amine salts have already been prepared; for example, amine sulfate and amine bisulfate (8). Amines are bases whose salts can enter into anion-exchange reactions, making them good candidates for use in carrier-mediated transport processes.

Amine-salt solubility depends on the type of amine that is being used and the choice of solvent. The solubility of primary amine salts decreases with decreasing polarity of the solvent, being only very sparingly soluble in aliphatic hydrocarbons. The solubility of secondary and especially tertiary amine salts is higher in nonpolar solvents than the solubility of primary amine salts (7). It would therefore be better to use tertiary amines. Although the tertiary amine salts are more soluble than the primary amine salts, they too have limited solubility in aliphatic hydrocarbons. However, it has been shown that alkylamine salts are more soluble in nonpolar solvents when alcohol is added as a phase modifier (9). Isodecanol is used for that purpose in this report, and kerosene is used as a solvent.

Alamine 336 [tri-(C_8C_{10}) amine] was chosen as an extractant since it is already in wide use in industry (Alamine 336 is a trademark of the Henkel Corporation). The following equations are representative of what takes place during extraction with a tertiary amine (9):

$$[R_3N]_{org} + [HA^-]_{aq} \leftrightarrow [R_3NH^+A^-]_{org} \tag{2}$$

$$[R_3NH^+A^-]_{org} + [B^-]_{aq} \leftrightarrow [R_3NH^+B^-]_{org} + [A^-]_{aq} \tag{3}$$

Equation (2) represents a simple amine-salt formation while Eq. (3) represents true ion exchange. The extent to which B^- will exchange for A^- is a function of the relative affinity of the two anions for the organic cation and the relative stability of the anions in the aqueous medium.

Alamine 336 is commonly used to extract metal anions in liquid–liquid extraction processes. In these processes the amine is stripped by an inorganic salt like Na_2CO_3 or $(NH_4)_2SO_4$. The reaction with Na_2CO_3, as an example, is shown in the following equation (9):

$$[2(R_3NH)^+B^-]_{org} + Na_2CO_{3aq} \leftrightarrow 2R_3N_{org} + [2Na^+\ B^-]_{aq} + H_2O_{aq} + CO_2 \tag{4}$$

where B^- is the metal anionic complex.

EXPERIMENTAL

The apparatus used consisted of an agitated reactor separated into two compartments by a membrane (Fig. 2). The feed solution, consisting of 500 ppm SO_4^{2-}, was placed in one compartment and the strip solution in the other. Each chamber was equipped with an impeller set to run at 185 rpm to ensure well-mixed solutions.

A highly hydrophobic membrane support, Celgard 2500, was used during the experiments (Celanese Plastics Co). This support consisted of a porous polypropylene film with a thickness of about 25 μm, a porosity of 45%, and an effective pore size of 0.04 μm. The membrane surface area in the reactor described above was $\pm 5.03\text{E-}3\ m^2$.

The liquid membrane was prepared by immobilizing a solution consisting of kerosene as the solvent, isodecanol (10% v/v) as the phase modifier, and a given volume % (see Table 1) of Alamine 336 in a polymeric support. Celgard 2500 was used as the support. The liquid was immobilized in the pore structure of the support by letting the support soak in the prepared liquid membrane. After soaking for about an hour the membrane was blotted down with a paper towel to remove excess liquid from the surface of the support.

The reactor can be separated into two parts by removing the wing nuts that hold them together. The SLM is then secured between the two compartments (Fig. 2).

Three hundred milliliters of a 500 ppm SO_4^{2-} solution was poured into one compartment of the reactor and an equal amount of a given concentration Na_2CO_3 solution (see Table 1) was poured into the other compartment.

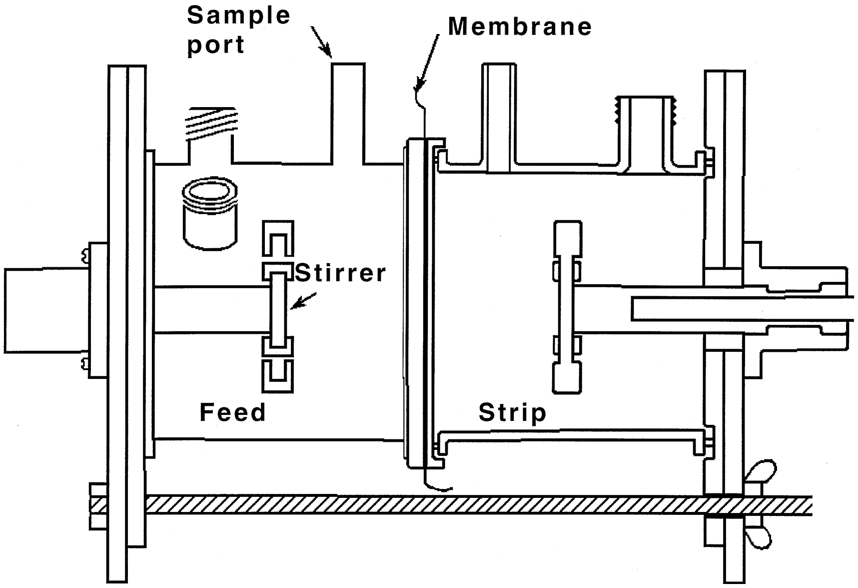

FIG. 2 Experimental setup.

TABLE 1
Experimental Set #2

Experiment	Carrier (volume %)	Sulfate (mass fraction of SO_4 from H_2SO_4)	Na_2CO_3 (mole/liter)
1	10	0.2	0.7
2	10	0.2	1.3
3	10	0.8	0.7
4	10	0.8	1.3
5	30	0.2	0.7
6	30	0.2	1.3
7	30	0.8	0.7
8	30	0.8	1.3
9	32	0.5	1
10	37	0.5	1
11	20	0	1
12	20	1	1
13	20	0.5	0.5
14	20	0.5	1.5
15	20	0.5	1
16	20	0.5	1
17	20	0.5	1
18	50	0.5	1
19	66	0.5	1
20	33	0.5	1

Experimental Set #1: Confirming the Reaction Scheme and Mechanism

For the purpose of the first experimental set the SLM was prepared with a 50% (v/v) Alamine 336 content. The SO_4^{2-} solution was prepared using H_2SO_4 in order to obtain the greatest pH difference across the membrane. A 1 M Na_2CO_3 solution was used as the stripping phase.

The reactor was allowed to run for 5 hours. The pH was measured and a sample was taken for analysis at the end of each hour.

Experimental Set #2: Establishing an Initial List of Parameters Influencing the Extraction Rate

This experiment consisted of a series of 20 2-hour experiments. The purpose of these experiments was to determine the influence of the extractant concentration, pH of the feed, and the Na_2CO_3 concentration in the strip phase on the extraction rate. The statistical design of the experiment was done on STATISTICA, and the different values that these variables have to take during the experiment are given in Table 1.

The pH of the feed solution was controlled by varying the fraction of the sulfates obtained from H_2SO_4 with the balance of the sulfate made up using Na_2SO_4. Table 1 gives the values of the different concentrations employed.

Samples were analyzed photometrically using the Spectroquant 14791 (Merck) reagent kit.

RESULTS AND DISCUSSION

The following results were obtained from the first experiment. (The concentrations given in Table 2 are those of the sulfate remaining in the feed after the specific time.)

Initial feed pH: 2.0
Initial strip phase pH: 10.84

(After 4 hours, less than 18 ppm remains in the feed. This is too small a concentration to be analyzed by the Spectroquant method.)

Figure 3 gives the results of the 5-hour experiment graphically. It can clearly be seen that the sulfate concentration in the feed was driven down gradually until the value was too small to measure. As can be seen from the results, the feed pH increases directly proportional to the amount of sulfate that has been extracted.

Using model Eqs. (2)–(4), the following reaction mechanism can be proposed.

Extraction:

$$H_2SO_4 + 2R_3N \leftrightarrow 2R_3NH^+ + SO_4^{2-} \leftrightarrow (R_3NH)_2SO_4 \tag{5}$$

Stripping:

$$(R_3NH)_2SO_4 + Na_2CO_3 \leftrightarrow 2R_3N + [2Na^+\ SO_4^{2-}] + H_2O + CO_2 \tag{6}$$

Cotransport is identified as the mechanism by which ion transport took place over the membrane (Fig. 4).

TABLE 2
Experimental Set #1: Results

Time (hours)	Feed pH	Strip phase pH	Concentration (ppm)
1	2.28	10.69	319
2	2.73	10.69	128
3	3.10	10.69	46
4	3.44	10.68	<18
5	3.70	10.67	<18

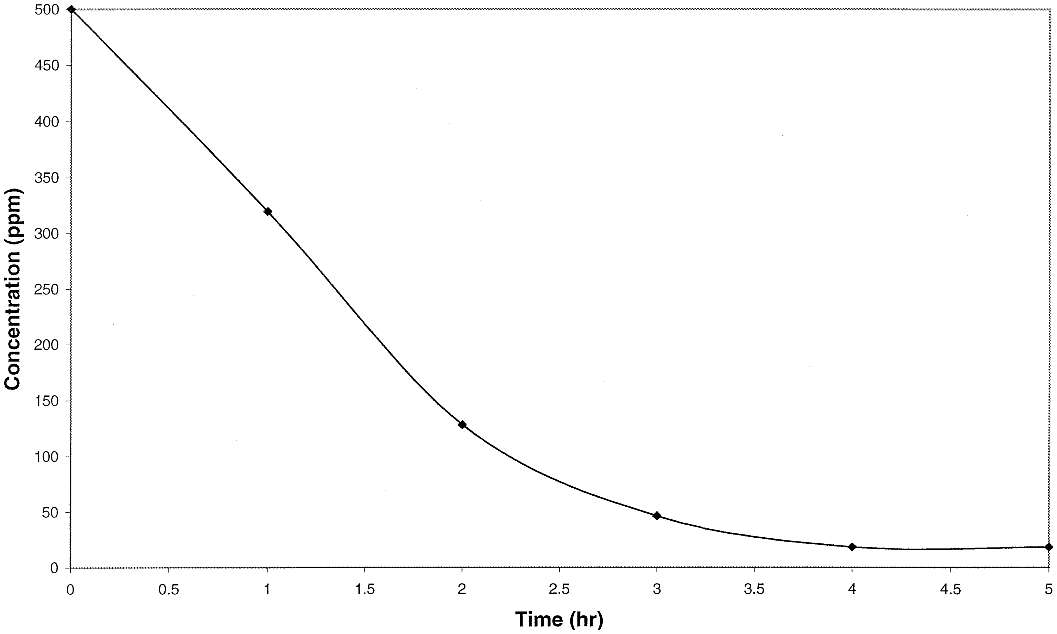

FIG. 3 Sulfate extraction over 5 hours.

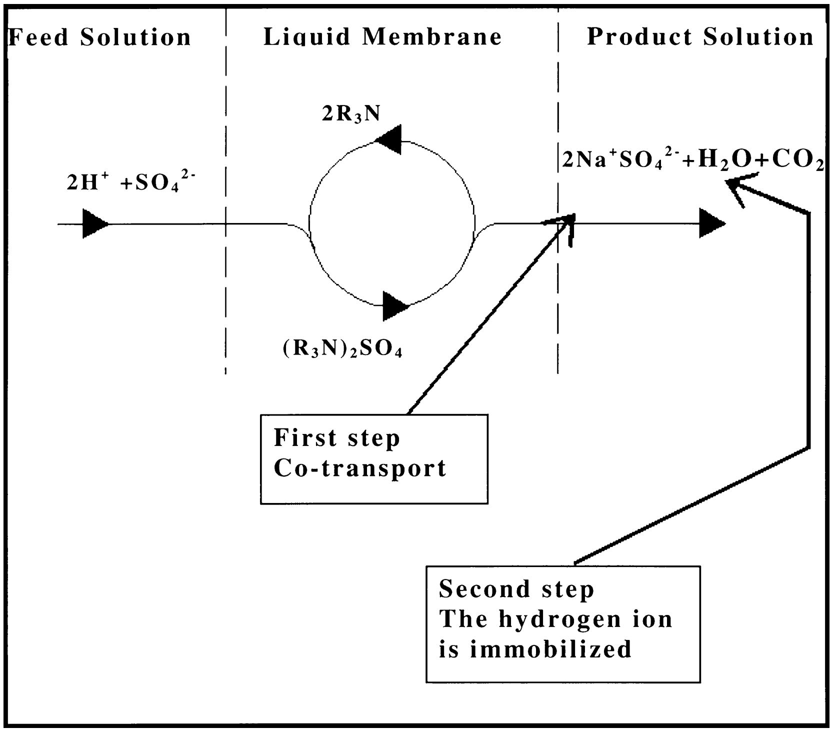

FIG. 4 Ion immobilization.

The results of 20 experiments to determine the influence of the extractant concentration, pH of the feed, and the Na_2CO_3 concentration in the strip phase on the extraction rate are given in Table 3.

STATISTICA was used to fit a second-order polynomial through the measured extraction rates (averaged over the first 2 hours) of the 20 experiments. It was found that only six of the terms are significant. The data were fitted through a curve of the following form (this equation predicts the flux at the initial conditions with an initial feed concentration of 500 ppm SO_4):

$$J = k_1 C_{\text{ex}} + k_2(10^{-\text{pH}}) + k_3 C_{\text{CO}_3} + k_4(10^{-2\text{pH}}) + k_5 C_{\text{CO}_3}^2 + k_6 C_{\text{ex}} C_{\text{CO}_3} \tag{7}$$

The values of the constants were determined as follows:

$$k_1 = -0.1\ (0.045), \qquad k_2 = 2081.7\ (0), \qquad k_3 = 2.5\ (0.113),$$

$$k_4 = -95262.1\ (0), \qquad k_5 = -2.6\ (0.05), \qquad k_6 = 0.1\ (0.064)$$

The variance for this fit is $R = 0.998$, and the significance levels (p-value) for the different terms are given in parentheses. Three of the experiments were repeated to test the reproducibility of the set of experiments. The standard deviation for the three experiments was 0.15 (2.1%).

TABLE 3
Experimental Set #2: Results

Experiment	Percentage carrier in extractant	Feed pH	Na_2CO_3 Concentration (mole/ liter)	Extraction rate (mg/m^2·s) over 2 hours
1	10	2.7	0.7	3.42
2	10	2.7	1.3	2.1
3	10	2.06	0.7	10.24
4	10	2.06	1.3	9.06
5	30	2.7	0.7	3.4
6	30	2.7	1.3	3.01
7	30	2.06	0.7	9.9
8	30	2.06	1.3	10.55
9	32	2.36	1	7.7
10	37	2.36	1	6.2
11	20	4.04	1	0
12	20	2.01	1	11.8
13	20	2.36	0.5	6.63
14	20	2.36	1.5	6.73
15	20	2.36	1	7.04
16	20	2.36	1	7.3
17	20	2.36	1	7.04
18	50	2.36	1	6.3
19	66	2.36	1	6.08
20	33	2.36	1	6.4

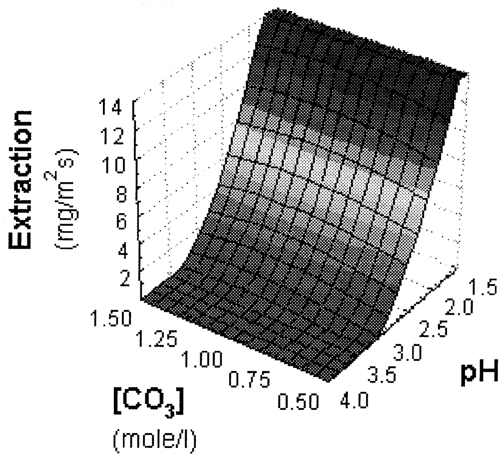

FIG. 5 Influence of CO_3 concentration and pH on the extraction rate.

The dependence of the extraction rate on each variable can be determined from the above equation by keeping all the variables constant and varying the one of interest. Figures 5 and 6 summarize these data.

As expected, the pH has the single largest influence on the extraction rate. The lower the pH, the higher the extraction rate. This is because the proton is used as the co-ion in the transport mechanism. It is also clear that the only cation suitable to serve as the counterion will be the hydrogen ion since there was no transport of sulfates when the entire feed was made up from Na_2SO_4 and not H_2SO_4.

The Na_2CO_3 concentration does not have a large influence on the extraction rate.

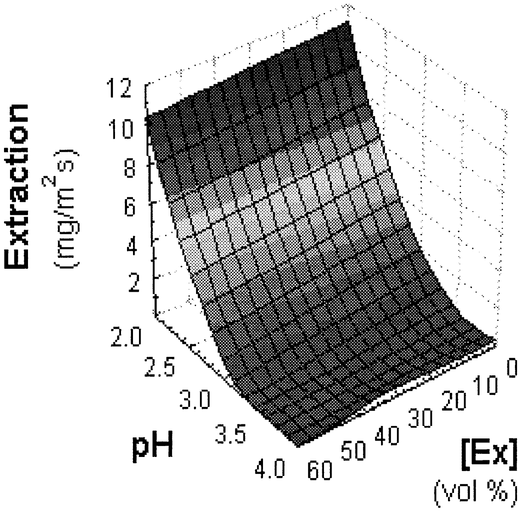

FIG. 6 Influence of pH and carrier concentration on the extraction rate.

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Although the percentage of extractant in the membrane has a larger influence on the extraction rate than the Na_2CO_3 concentration, it too has a relatively small influence compared to the pH. The extractant appears to exhibit an optimum in the vicinity of 20% Alamine 336.

CONCLUSIONS

Alamine 336 was identified as a carrier and successfully used to extract sulfates from water. Na_2CO_3 was found to be a suitable reactant to strip the sulfates from the organic phase. The mechanism by which sulfate is extracted was determined to be a cotransport mechanism in combination with ion-immobilization (see below).

The following reaction scheme and mechanism are proposed.

Extraction:

$$H_2SO_4 + 2R_3N \leftrightarrow 2R_3NH^+ + SO_4^{2-} \leftrightarrow (R_3NH)_2SO_4$$

Stripping:

$$(R_3NH)_2SO_4 + Na_2CO_3 \leftrightarrow 2R_3N + [2Na^+\ SO_4^{2-}] + H_2O + CO_2$$

Mechanism: Cotransport (see Fig. 4)

The extraction rate of sulfates is very sensitive to a change in the pH of the feed solution. The lower the pH, the higher the extraction rate. This is not surprising since the hydrogen proton is transported with the sulfate ion as the coion in the mechanism. This means that the driving force for the “uphill” concentration of the sulfates is pH. The consequence is that the removal of protons from the feed will diminish the driving force for sulfate complexation (see Figs. 5 and 6). The pH drop in the strip phase was prevented by ion-immobilization in the strip phase.

The Na_2CO_3 concentration in the strip solution and the percentage carrier in the membrane appear to have only a small influence on the extraction rate. It is possible to optimize the process for these parameters in order to obtain a greater ion flux through the membrane.

This process makes it possible to remove sulfate ions from water to a point where they are virtually undetectable—without introducing other possible pollutants into the water. This is one of the advantages of the cotransport mechanism above the countertransport mechanism: The sulfate ion is transported together with hydrogen ions from the feed to the strip solution without introducing another ion into the feed phase. The only products formed due to the reactions that take place are CO_2 and H_2O. Both of these products are completely harmless. This makes the process ideal for water treatment.

All of the reactants used in this process are easily obtainable and are inexpensive. Besides this, the process uses very little extractant because it is a membrane process and because it makes use of coupled transport. The sulfate ions are concentrated against the concentration gradient.

Supported liquid membranes successfully remove nearly all sulfate ions from acidic water. This technique promises to be a useful tool in combating the sulfate pollution problem.

NOMENCLATURE

C_{CO_3}	concentration of CO_3 in the strip solution (mol/L)
C_{ex}	extractant (%)
J	rate of sulfate extraction ($mg/m^2 \cdot s$)
$k_\#$	constant
SLM	supported liquid membrane

REFERENCES

1. Department of Water Affairs and Forestry, South Africa. *South African Water Quality Guidelines*. *Volume 3*: *Industrial Use*. 1993.
2. C. N. Sawyer, P. L. McCarty, and G. F. Parkin, *Chemistry for Environmental Engineering*, 4th ed., McGraw-Hill, New-York, NY, 1994.
3. H. C. Van der Merwe, “The Electrochemical Treatment of Water to Remove Dissolved Substances,” M.Eng. Dissertation, Potchefstroom University, 1997.
4. R. A. Bartsch and J. D. Way, *Chemical Separations with Liquid Membranes*, American Chemical Society, Washington, DC, 1996.
5. L. R. Koekemoer, “The Extraction of Nickel with the Use of Supported Liquid Membranes,” M.Eng. Dissertation, Potchefstroom University, 1996.
6. M. M. Kreevoy, A. T. Kotchevar, and C. W. Aften, “Decontamination of Nitrate Polluted Water,” *Sep. Sci. Technol.*, *22*, 361 (1987).
7. A. M. Neplenbroek, D. Bargeman, and C. A. Smolders, “Nitrate Removal Using Supported Liquid Membranes: Transport Mechanism,” *J. Membr. Sci.*, *67*, 107–119 (1992).
8. C. Hanson, *Recent Advances in Liquid–Liquid Extraction*, Pergamon Press, Oxford, 1971.
9. Henkel Corporation, *MID Redbook—The Chemistry of Metals Recovery Using LIX® Reagents*, 1997.

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