Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gopal, Vikram , April, Gary C. and Schrodt, Verle N.(1998) 'Selective Removal of Copper from Muitication Dilute Aqueous Solutions Using the Membrane-Electrode Process', Separation Science and Technology, 33: 5, 723 — 738

To link to this Article: DOI: 10.1080/01496399808544785

URL: http://dx.doi.org/10.1080/01496399808544785

SEPARATION SCIENCE AND TECHNOLOGY, 33(5), pp. 723–738, 1998

Selective Removal of Copper from Multication Dilute Aqueous Solutions Using the Membrane-Electrode Process

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ABSTRACT

The presence of metallic contaminants (in the form of cations) in wastewater streams has long been a source of concern to process industries. Conventional methods of removal of metallic components from wastewater result in products which have little or no further use and are subsequently landfilled (6). This research involves developing a method, i.e., the membrane-electrode (M-E) process, to selectively recover heavy metals from dilute aqueous waste streams (cation concentrations less than 1000 ppm) in forms that can be recycled. Preliminary results for copper–nickel systems are presented to demonstrate the selectivity of this new treatment method.

INTRODUCTION

Environmental pollution is one of the major problems facing mankind today. The rapid growth and advancement of science and technology and a corresponding lack of understanding of associated environmental impacts and of methods to assess these impacts have resulted in a mismatch between process development and regulatory control of discharges (5). This research proposes to address one such problem; the problem of metal contaminants in wastewater streams.

The methods currently being used for heavy metal removal from wastewaters include pH adjustment, chemical oxidation, chemical reduction, ion

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exchange, electrodialysis, and electrochemical reduction. Of these methods, the most common are pH adjustment and chemical oxidation which result in the precipitation of cations in the forms of hydroxides, sulfides, carbonates, and oxides (1). Chemical reduction also results in precipitation of insoluble metallic forms. Bioreduction of metal sulfates to insoluble metal sulfides in treatment of wastewater generated during mining has been successfully demonstrated (1, 2). Ordinarily, all these precipitates do not find any further use and are land-filled, once again leading to concerns with leaching of heavy metals into groundwater.

One solution to this problem lies in recovering these metallic compounds in forms which can be recycled. Ion-exchange processes have been used for recovering cations from dilute aqueous solutions. However, in general, these processes are nonselective and thus have limitations in recovering products which can be recycled. Electrodialysis is used as a reconcentration process for electroplating baths (3); however the method lacks selectivity. Electrochemical reduction, typically a method of choice for selective cation recovery, has severe limitations in dilute aqueous solutions due to the possibility of dissociation of water at low cation concentrations (4). Moreover, this process becomes uneconomical for cation recovery from dilute aqueous solutions.

Individually, each of the conventional treatment processes has shortcomings. Nonetheless, properties of ion-exchange techniques (cation recovery from dilute aqueous solutions) combined with electrochemical reduction processes (selective cation recovery) would likely address the problem of selective cation recovery from dilute aqueous solutions. The process under development, i.e., the membrane-electrode (M-E) process, is a hybrid between ion exchange and electrochemical reduction techniques.

Preliminary studies with mixed streams containing Cu^{2+} ions and Ni^{2+} ions have shown a threefold increase in selectivity* in the M-E process as compared to conventional ion exchange. Also, it has been found that factors governing Cu^{2+} selectivity in the M-E process are the applied voltage and cation concentrations. In order that the process be selective, the applied potential must lie within a *critical applied potential range*. For instance, in a 400 ppm Cu^{2+}–400 ppm Ni^{2+} system, it is found that selectivity varies from 2.25 at 0.05 V to 1.05 at 0.1 V, indicating a very strong potential-selectivity correlation. This potential range is found to be system specific, and for the Cu^{2+}/Ni^{2+} system is found to be within 0.0 and 0.1 V. The magnitude of selectivity can be increased by increasing the Cu^{2+} concentration and the $Cu^{2+}:Ni^{2+}$ ratio in solution. It is observed that for a solution containing 100 ppm Ni, with an

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* Selectivity is defined as the ratio of the rate of Cu^{2+} ion recovery to the rate of Ni^{2+} ion recovery from solution per cm^2 of a membrane.

applied potential of 0.05 V, varying the $Cu^{2+}:Ni^{2+}$ ratio from 1:1 to 8:1 increases the selectivity (at 30 minute contact time) from 1.75 to 3.

EXPERIMENTAL

Chemicals Used

Chemicals Used for PSM-10 Membrane Preparation*

ACS reagent-grade styrene, divinyl benzene, benzoyl peroxide, and toluene from Aldrich chemicals were used for the preparation of 10% crosslinked polystyrene. Sulfonation was carried out using 98.1 wt% sulfuric acid from J.T. Baker Chemical Co. ACS reagent-grade sodium hydroxide (NaOH) from Fisher Scientific was used for converting the acid form membranes into Na^+ form membranes.

Chemicals Used for Simulating Waste Effluent Streams

ACS reagent-grade copper(II) sulfate pentahydrate and nickel(II) sulfate hexahydrate from Aldrich Chemicals were dissolved in deionized (DI) water to prepare mixed cation solutions of required concentrations.

Membrane Preparation and Characterization

PSM-10 Sodium Polystyrene Sulfonate Membrane Preparation

Sodium polystyrene sulfonate cation-exchange resins with 10% crosslinking density were prepared by the procedure described by Salmon and Hale (7). Swelling of this polymer to the extent of total dissolution was carried out using toluene. Subsequently, the polymer solutions were evaporated in a rotary evaporator (Rotavapor-R, Buchi Laboratories) until a predetermined viscosity of 50 cSt[†] was achieved in order to effect proper coating of the polymer onto conducting rubber bases (8). The membranes were then dried at 70°C in a conventional oven for 12 hours followed by 12-hour washes in 0.5 N NaOH and deionized water solutions, respectively.

Membrane Characterization

Ion-exchange capacity, specific resistance, swelling behavior, permselectivity,[‡] and long-term stability of membranes were determined by the proce-

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[*] Sodium polystyrene sulfonate, PSM-10, ion-exchange membranes prepared in-house were used in this study.

[†] Viscosity was measured using a Cannon-Fenske Routine Viscometer.

[‡] Permselectivity is the ratio of transport of electric charges by specific counterions to the total transport of electric charges through the membrane.

dures described by Strathmann (3). Cell potentials of a cation-exchange membrane-saturated calomel electrode (cation-exchange II calomel electrode) were also determined.

Cation-Exchange Membrane—Calomel Electrode, Cell Potential Determination

Potential difference between a cation-exchange membrane and saturated a calomel electrode was measured in deionized water using a voltammetric analyzer (IBM Instruments Inc., EC-225). This was further verified by measurements using a high precision digital multimeter (Protek, Model B-845). These measurements indicated that the PSM-10 membranes had an anodic potential of 0.53 V with respect to a calomel electrode.

Analytical Procedures—Cation Analysis

Cation concentrations in aqueous solutions were determined using a Perkin-Elmer (Model 2380) Atomic Absorption Spectrophotometer. A wavelength of 324.8 nm and a slit width of 0.7 nm were employed for copper analysis while a wavelength of 231.1 nm and a slit width of 0.2 nm were employed for nickel analysis.

MEMBRANE-ELECTRODE (M-E) PROCESS

The M-E process (8) is a *hybrid* process between ion-exchange and electrochemical reduction technologies. This process consists of a number of electrochemical cells placed in parallel. A single electrochemical cell, as shown in Fig. 1, consists of a cation-exchange membrane* cathode and a graphite plate anode.† A variable voltage dc supply (0–5 V range) is used to apply a potential difference between the electrodes. The potential difference applied across the electrodes is dependent upon the cation species present in the aqueous streams; the applied potentials are such that cations can be recovered sequentially in the order of increasing reduction potentials. The depleted membranes with the heavy metal cations are moved into a cation recovery system (usually an acid wash), followed by a membrane regeneration system (usually a caustic wash). The regenerated membranes are reused in the M-E cell. The electrodes in each cell are placed 3 mm apart in order to minimize solution resistance. An agitation‡ speed of 600 rpm is fixed such that concentration polarization

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[*] Membrane dimensions 35 mm × 70 mm, base thickness 0.5 mm, polymer coating thickness 0.076 mm.

[†] Graphite plate dimensions 35 mm × 70 mm, plate thickness 2.50 mm.

[‡] Agitation is achieved using a laboratory stirrer with a two-blade impeller.

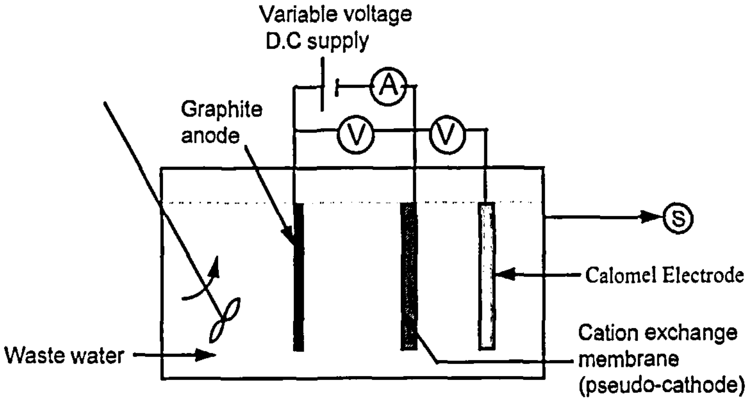

FIG. 1 Schematic representation of the M-E cell.

is minimized and the rate-controlling step is the ion-exchange taking place on the membrane surface.

All references to *applied potential difference* in this paper are the potential difference (pd) measured between the membrane and the calomel electrode. The *applied potential difference* depends upon the cathodic potential applied onto the membrane by the dc power supply. When the cathodic potential applied is 0 V, the measured pd between the membrane and the calomel electrode, i.e., the applied pd, is maximum. As the cathodic pd on the membrane is increased, the applied pd decreases.

$$E_{\text{applied pd}} = E_{\text{membrane}} + E_{\text{calomel}} \qquad (1)$$

where $E_{\text{applied pd}}$ = measured pd between the calomel electrode and the membrane

E_{membrane} = half-cell electrode potential of the membrane

E_{calomel} = half-cell electrode potential of the saturated calomel electrode [0.241 V with respect to a standard hydrogen electrode (SHE)]

Thus, as $E_{\text{applied pd}}$ decreases, the anodic tendency of Na^+ ions on the membrane surface decreases.

Electrical connections are made 10 mm apart along the length and 10 mm apart along the width of the membrane. This strategy ensures that the entire membrane behaves as an equipotential surface. In the M-E process there is a slight enhancement in the migration of cations in the bulk solution, while at the membrane surface a controlled ion-exchange takes place (9). Though the cation-exchange membrane is a cathode in the M-E process, both oxidation and reduction reactions take place on the membrane surface while oxidation takes place on the graphite anode. The oxidation and reduction reactions taking place at the two electrodes are as follows.

Oxidation Reactions:

$$2OH^- \Rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^- \qquad \text{(graphite anode)} \qquad (2)$$

$$2RSO_3Na \Rightarrow 2RSO_3^- + 2Na^+ \qquad \text{(cation-exchange membrane)} \qquad (3)$$

where R denotes the polystyrene (polymer) "backbone" of the membrane

Reduction Reactions:

$$Cu^{2+} + 2RSO_3^- \Rightarrow 2RSO_3Cu \qquad \text{(cation-exchange membrane)} \qquad (4)$$

$$Ni^{2+} + 2RSO_3^- \Rightarrow 2RSO_3Ni \qquad \text{(cation-exchange membrane)} \qquad (4.1)$$

The total currents involved in the M-E process are in the range of 50 to 100 μA, and thus the effects of anodic oxidation (Eq. 1) are neglected in this study.

The energy supplied at the cathode (membrane) surface allows a preferential cation exchange of the more noble cation onto the membrane surface. This fact can be explained using Gibbs free energy and energy conservation principles.

Free energy possessed by a sodium atom on the membrane surface is represented as

$$\Delta G_{Na/Na^+} = (-)nFE_{Na/Na^+} \qquad (5)$$

where n = number of gram equivalents of Na on the membrane surface (determined from the ion-exchange capacity of the membrane)
F = Faraday = 96,500 (C/g-equivalent)
E_{Na/Na^+} = half-cell potential of Na form cation-exchange membrane (V)

Application of the law of conservation of energy to a steady-state process can be represented as:

(Energy supplied to the system)
= (energy utilized for reduction of cations) + (energy utilized to overcome resistance in cation separation from solvent anions) (6)

where

(Energy into the system) = $\Delta G_{Na/Na^+}$

(Energy required to exchange Cu^{2+} ions from waste stream) = $\Delta G_{Cu^{2+}/Cu}$

where

$$\Delta G_{Cu^{2+}/Cu} = (-)n_1FE_{Cu^{2+}/Cu} \tag{7}$$

and

(Energy required to exchange Ni^{2+} ions from waste stream) = $\Delta G_{Ni^{2+}/Ni}$

where

$$\Delta G_{Ni^{2+}/Ni} = (-)n_2FE_{Ni^{2+}/Ni} \tag{8}$$

n_1 and n_2 represent the number of gram equivalents of Cu and Ni, respectively, in the waste stream, and $E_{Cu^{2+}/Cu}$ and $E_{Ni^{2+}/Ni}$ represent the reduction potentials of Cu and Ni ions, respectively, in the waste streams.

Energy utilized for reduction of cations (resulting in Cu^{2+} and Ni^{2+} cation exchange) is

$$(-)n_1FE_{Cu^{2+}/Cu} + (-)n_2FE_{Ni^{2+}/Ni} \tag{9}$$

The widely accepted Debye–Huckel theory for dilute cation solutions represents ions in solution as diffuse, symmetrical, spherical clouds of negative charge (solvent anions) surrounding a central cation (10, 11). The energy required to be supplied in order to separate the cation from the surrounding anions is described by the following expression:

(Energy utilized to overcome resistance in cation separation

$$\text{from surrounding anions)} = \left[-\frac{(z_1z_2)}{(4\Pi\epsilon_0\epsilon_r)}\frac{1}{r}\right] \tag{10}$$

where z_1, z_2 = cation and anion carrying charges z_1 and z_2, respectively
ϵ_0 = vacuum permitivity,
ϵ_r = dielectric constant (relative permitivity) of the solvent
r = distance between the central cation and surrounding solvent anion(s)

Substituting Eqs. (1), (5), and (6) into Eq. (2) results in

$$(-)nFE_{Na/Na^+} = (-)n_1FE_{Cu^{2+}/Cu} + (-)n_2FE_{Ni^{2+}/Ni} + \left[-\frac{(z_1z_2)}{(4\Pi\epsilon_0\epsilon_r)}\frac{1}{r}\right] \tag{11}$$

Equation (7) represents the energy balance in a conventional ion-exchange process. In the M-E process the application of a cathodic potential on the membrane can be represented as follows:

$$(-)nFE_{\mathrm{Na/Na^+}} + nFE_{\mathrm{cathodic}} = (-)n_1FE_{\mathrm{Cu^{2+}/Cu}} + (-)n_2FE_{\mathrm{Ni^{2+}/Ni}} + \left[-\frac{(z_1z_2)}{(4\Pi\epsilon_0\epsilon_r)}\frac{1}{r}\right] \quad (12)$$

Increasing cathodic potential decreases the free energy available with Na atoms on the surface of the membrane. This decrease in free energy results in lower energy available for ion exchange, which likely results in more selective ion-exchange of the cation having a lower reduction potential. Also, it is speculated that this decrease in energy into the system will likely result in a lower rate of cation exchange.

RESULTS AND DISCUSSION

Ion Exchange Using Conventional Cation-Exchange Membrane Process

In order to determine the selectivity of cation exchange using a conventional ion-exchange process, 6.25 cm^2 samples of PSM-10 membranes were contacted with 30 mL of Cu/Ni mixed solutions. The solutions were kept in agitation using a magnetic stirrer. Cation analyses were performed prior to and after membrane-solution contact, at 5-minute intervals for a period of 60 minutes to determine the recovery of Cu^{2+} and Ni^{2+} ions from solution.

Figure 2 is a plot of Cu^{2+} and Ni^{2+} recovery with respect to time for a 100 ppm Cu^{2+}, 100 ppm Ni^{2+} solution mixture. It is observed that rates of Cu^{2+}

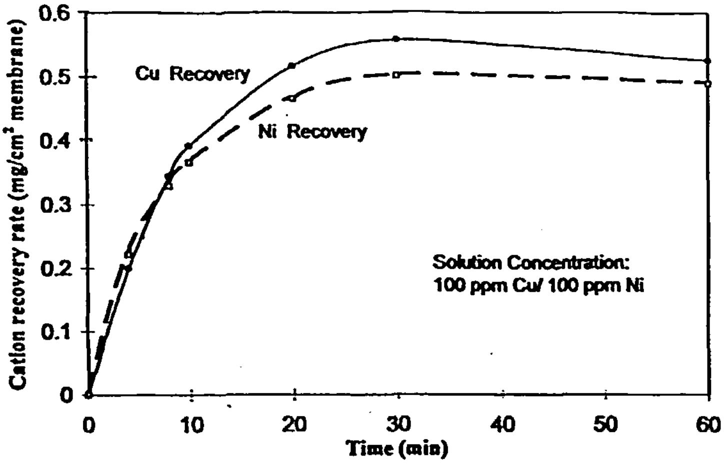

FIG. 2 Ion exchange in a conventional ion-exchange process.

and Ni^{2+} recovery are 0.040 mg/(min·cm^2 membrane) during the first 10 minutes of membrane-solution contact and drop down to 0.005 mg/(min·cm^2 membrane) for the next 20 minutes. Thereafter, virtually no ion exchange takes place. Selectivity (represented by Eq. 13)* of Cu^{2+} ions is approximately equal to 1, indicating nonselective ion exchange, a characteristic of conventional ion-exchange processes.

$$\text{Selectivity} \equiv \left(\frac{\begin{array}{c}\text{rate of } Cu^{2+} \text{ ion recovery from waste}\\ \text{stream per square centimeter of membrane}\end{array}}{\begin{array}{c}\text{rate of } Ni^{2+} \text{ ion recovery from waste}\\ \text{stream per square centimeter of membrane}\end{array}} \right) \qquad (13)$$

Ion Exchange in the M-E Process

When Cu^{2+} and Ni^{2+} recovery rates for a 100 ppm Cu^{2+}, 100 ppm Ni^{2+} solution mixture are observed in the M-E process with an applied potential difference of 0.05,[†] the copper recovery rate remains constant at 0.01 mg/(min·cm^2 membrane) until the membrane reaches equilibrium with the solution. The ion-exchange rate is 25% of the maximum attainable in a conventional ion-exchange process. Figure 3 shows a comparative analysis of the copper recovery rates between a conventional ion-exchange process and the M-E process. It is found that PSM-10 membranes have an inherent anodic potential with respect to calomel electrodes (refer to the Membrane Preparation and Characterization section). Application of a cathodic potential on the membrane results in inhibition of Na^+ ions on the membrane surface to go into solution. This results in a much slower cation exchange. However, this cathodic potential shows a three fold improvement in selectivity for Cu^{2+} exchange over a conventional ion-exchange process under the conditions described earlier.

For an applied potential difference of 0.20 V in a 100 ppm Cu^{2+}, 100 ppm Ni^{2+} solution mixture, the Cu^{2+} exchange rate averages 0.017 mg/(min·cm^2 membrane) while the Ni^{2+} exchange rate averages 0.0125 mg/(min·cm^2 membrane). Figure 4 shows Cu^{2+} and Ni^{2+} recovery rates in the M-E process at 0.20 V. At short contact times (less than 20 minutes), selectivity for Cu^{2+} ions averages 2. However, this selectivity decreases with increasing time and

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[*] Selectivity is defined as the ratio of the rate of Cu^{2+} recovery to the rate of Ni^{2+} recovery from solution.

[†] All voltages are the potential difference between cation-exchange membrane and saturated calomel electrode. In order to determine the potential with respect to standard hydrogen electrode (SHE), subtract 0.241 V from the voltages reported in this paper (refer to membrane-electrode process description).

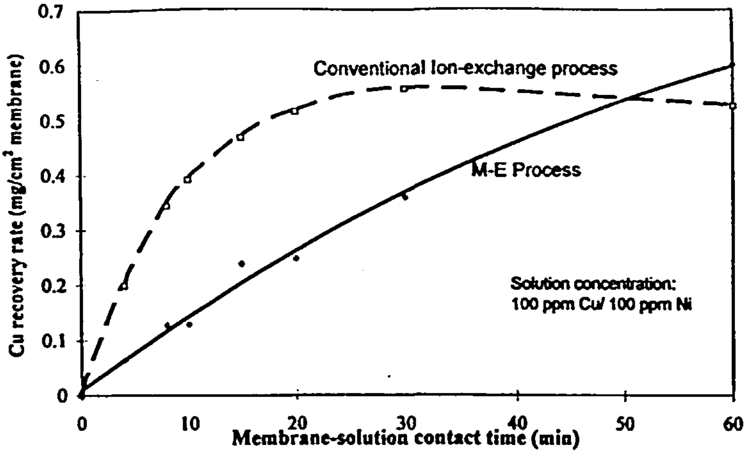

FIG. 3 Comparative Cu recovery rates in conventional ion-exchange and M-E process.

approaches 1 at 40 minutes. High initial selectivity can be explained as due to controlled ion-exchange taking place at the membrane surface, and since Cu^{2+} ions have a lower reduction potential they tend to preferentially exchange with Na^+ ions on the membrane surface. Nonetheless, since the solution contains equal amounts of Cu^{2+} and Ni^{2+} ions and with the passing of time the Cu^{2+} ion concentration decreases in the boundary layer, Ni^{2+} ion-

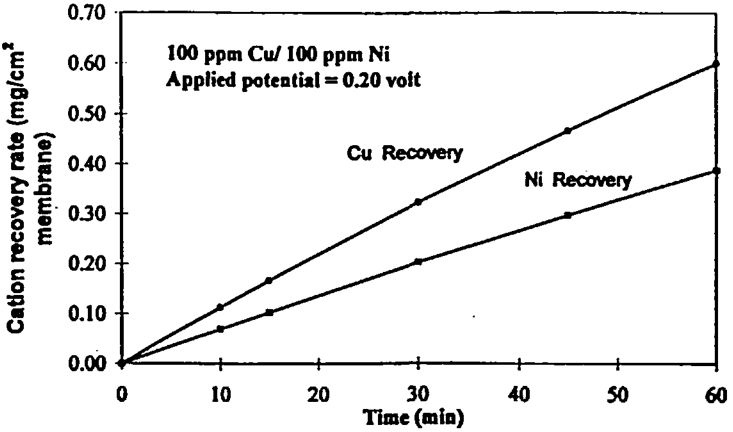

FIG. 4 Cation recovery rate for 100 ppm Cu/100 ppm Ni solution mixture.

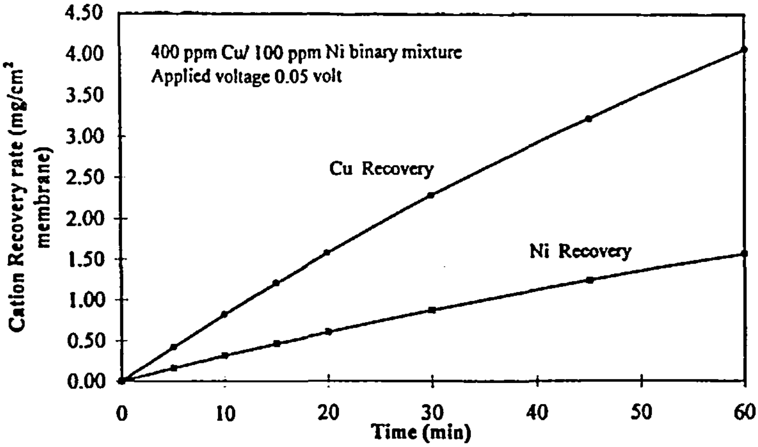

FIG. 5 Cation recovery rate for 400 ppm Cu/100 ppm Ni solution mixture.

exchange takes place. This results in the decrease in selectivity seen at longer membrane-solution contact times.

On increasing the concentration of Cu^{2+} ions in solution to 400 ppm while maintaining Ni^{2+} ion concentration at 100 ppm in the solution mixture, the Cu^{2+} recovery rate is found to average 0.0625 mg/(min·cm^2 membrane) while the Ni^{2+} recovery rate averages 0.02 mg/(min·cm^{2}membrane). Figure 5 shows Cu^{2+} and Ni^{2+} recovery rates in the M-E process for a 400 ppm Cu^{2+}, 100 ppm Ni^{2+} solution mixture subjected to an applied potential of 0.05 V. Selectivity for Cu^{2+} ions increases from 2 at 5 minute contact time to 3.2 at the end of 60 minutes. High selectivity can be attributed to two factors: low applied potential and high Cu^{2+} ion concentration in solution. Low applied potential decreases the energy supplied at the membrane surface, resulting in preferential Cu^{2+} ion-exchange while a higher Cu^{2+} concentration prevents Cu^{2+} depletion in the membrane boundary layer. In fact, with increasing time the concentration gradient of Cu^{2+} ions in the boundary layer probably is much higher than that of Ni^{2+} ions. During the initial contact time Ni^{2+} ions reach an ion-exchange equilibrium with the PSM-10 membranes. This results in an increased selectivity in the M-E process with increasing contact time.

Figure 6 shows the cation recovery rate in the M-E process from a solution mixture containing 400 ppm Cu^{2+}, 400 ppm Ni^{2+} with an applied potential of 0.20 V. It is seen that both Cu^{2+} and Ni^{2+} recovery rates average 0.038 mg/(min·cm^2 membrane) with a selectivity of 1, again indicating nonselective ion-exchange. The loss in selectivity can be attributed to two factors: higher Ni^{2+} concentration and a higher applied potential. The former results in com-

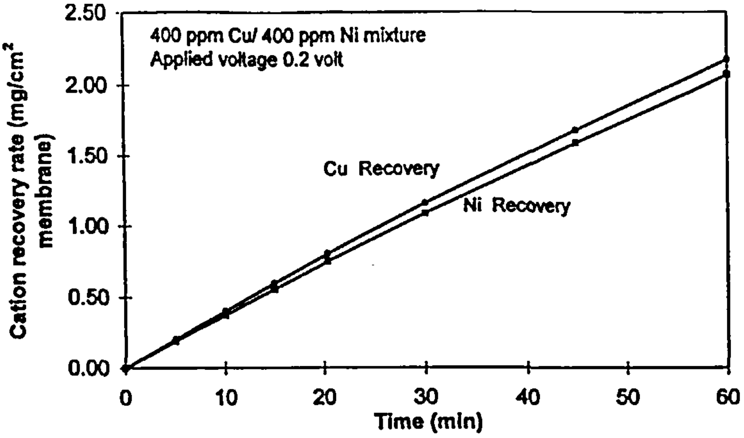

FIG. 6 Cation recovery rate for 400 ppm Cu/400 ppm Ni solution.

petitive ion exchange with Cu^{2+} while the latter results in non-selective ion exchange.

In order to determine the effect of applied potential on selective ion-exchange, potentials applied were varied between 0.05 and 0.5 V for 400 ppm $Cu^{2}+$, 400 ppm $Ni^{2}+$ solution mixtures. Figure 7 shows the effect of varying

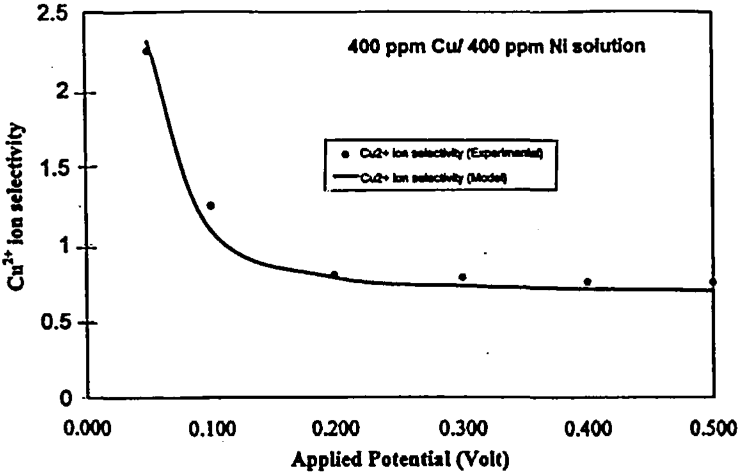

FIG. 7 Effect of applied potential on Cu^{2+} ion selectivity.

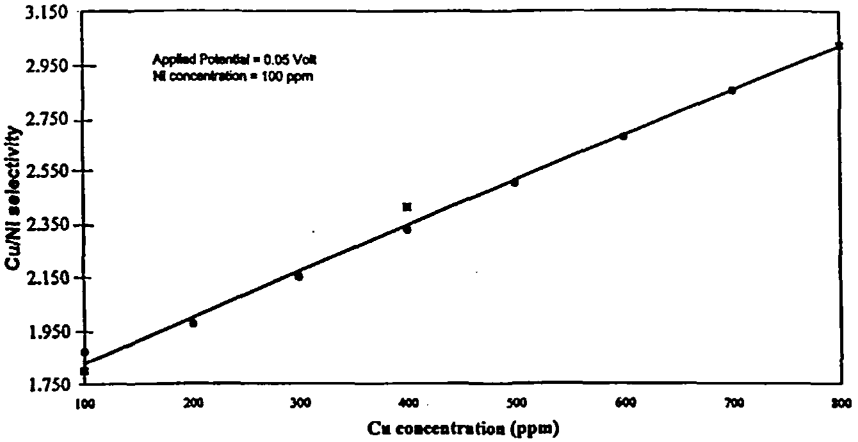

FIG. 8 Effect of Cu concentration on Cu^{2+} ion selectivity.

applied potentials on selectivity. It is observed that at lower potential ranges, the selectivity decreases from 2.25 at 0.05 V to 1.25 at 0.1 V. However, when the applied potential is increased beyond 0.1 V, the selectivity approaches 1. This establishes the *critical applied potential range* in which selective copper recovery is possible in the M-E process. The figure also shows close agreement between the values generated by the parametric model and actual experimental values. The extent of selective removal is dependent on Cu^{2+} ion concentration and the Cu^{2+} ion to Ni^{2+} ion ratio in solution. This effect of varying the $Cu^{2+}:Ni^{2+}$ ratio in solution on Cu^{2+} selectivity in the M-E process with an applied potential of 0.05 V is seen in Fig. 8. It is observed that varying the ratio from 1 : 1 to 8 : 1 increases the selectivity (at 30 minutes contact time) from 1.75 to 3. Again, close agreement is observed between the parametric model and actual experimental values.

Parametric Model of the M-E Process

A two-level, three-factorial design of experiments was performed in order to determine the effect of various process parameters on the selectivity of the M-E process. Table 1 lists the experimental variables along with their upper and lower level values. In order to validate the model, additional data points were collected within and outside the experimental space. During all the experiments, agitation speed was maintained at 600 rpm and the distance between the electrodes at 3 mm.

TABLE 1
Experimental Space in a Two-Level, Three-Factorial Design

Experimental variables	Lower level	Higher level
Cu^{2+} concentration (ppm)	100	400
Ni^{2+} concentration (ppm)	100	400
Applied voltage[a] (volt)	0.05	0.5

[a] Potential difference between the membrane and saturated Calomel Electrode

The model was developed by analyzing the effect of each of the parameters taken one at a time prior to combining the various parameters using an optimization routine. It is found that selectivity (S) of the M-E process is positively influenced by the inverse square of the applied voltage and the Cu^{2+} ion concentration, and is adversely affected by the Ni^{2+} ion concentration.

$$\text{Selectivity}_{\text{Cu/Ni}}\ (S) = k_a[\text{Cu}^{2+}] - k_b[\text{Ni}^{2+}] + k_c[\text{applied voltage}]^{-2} \quad (14)$$

where $k_a = 1.75\text{E}-03$, $k_b = 4.84\text{E}-05$, and $k_c = 4.08\text{E}-03$ are the model constants
$[Cu^{2+}]$ = Cu^{2+} ion concentration (ppm)
Ni^{2+} = Ni^{2+} ion concentration (ppm)
[applied voltage] = measured pd between the membrane and calomel electrode in volts

CONCLUSIONS

1. It is found that PSM-10 membranes have an inherent anodic potential (0.53 V with respect to saturated calomel electrode) due to the high electropositivity of the Na^+ ions on the membrane surface. This anodic potential indicates an inherent tendency of Na^+ ions on the membrane surface to undergo ion exchange with other cations in solution. Ion-exchange rates are controlled by the applied cathodic potentials and cation concentrations in solution.
2. High ion-exchange rates result in nonselective cation-exchange taking place, a short-coming of conventional ion-exchange processes.
3. In the M-E process a cathodic potential is impressed on the PSM-10 membranes, resulting in a lower ion-exchange rate due to the inhibition of Na^+ ions to go into solution. The rate of ion exchange varies inversely as the magnitude of the applied cathodic potential.

4. In a dilute Cu^{2+}, Ni^{2+} system, when the impressed cathodic potential does not lie within a *critical applied potential range*, high initial selectivity is lost with increasing membrane–solution contact time. For instance, for a 100 ppm Cu^{2+}, 100 ppm Ni^{2+} solution mixture, when the contact time is less than 20 minutes, selectivity for Cu^{2+} ions averages 2. However, this selectivity decreases to 1 when the contact time is 40 minutes.

5. The cathodic potential in the M-E process also determines the selectivity of cation exchange. In a 400 ppm Cu^{2+}, 400 ppm Ni^{2+} system, it is found that selectivity varies from 2.25 at 0.05 V to 1 at 0.1 V, indicating a very strong potential–selectivity correlation.

6. The magnitude of selectivity can be increased by increasing the $Cu^{2+}:Ni^{2+}$ ratio in solution. However, in order that the process be selective, it is essential to operate it within the critical applied potential range, viz., the potential range in which the M-E process becomes selective.

7. For the Cu^{2+}, Ni^{2+} system, it is found that the *critical applied potential range* between 0 and 0.1 V makes the M-E process cation selective. Any further increase in the applied cathodic potential causes the membrane to behave as a metallic electrode. It is suspected that the cations have a high overvoltage deposition potential on PSM-10 membranes. Thus, an increase in the applied cathodic potential will result in polarization of water prior to any cation deposition. In order for the M-E process to operate effectively, it must be within the critical applied potential range.

FUTURE WORK

Future work will involve improving selectivity of the M-E process by application of a continuously varying potential with time in order to compensate for the changing cation concentration in solution. Also, an attempt will be made to correlate selectivity to both the charge density of the cations and the cation–cation interaction. This will be followed by testing the M-E process on actual waste streams containing multiple cations.

In order to make the M-E process continuous, a strategy (moving membrane–electrode or the MM-E) is being developed in order to keep the membranes in continuous motion. The movement of the belt-like membrane will provide an optimum contact time between the membrane and the solution such that selective cation-exchange is achieved. Further, the depleted membranes will be regenerated continuously.

In order to increase the concentration of cations in solution, it might be essential to employ a series of M-E cells, each cell acting as an enriching section until a point is reached where the cations can either be recovered electrolytically or in solution forms with the desired purity. This scheme will be tested on the bench-scale in the near future.

ACKNOWLEDGMENTS

The authors thank the Gulf Coast Hazardous Substance Research Center (GCHSRC), Beaumont, TX for funding this project. Also, the authors thank Dr. S. S. Kulkarni of the National Chemical Laboratory, Pune, India for help during initial development of membranes, and Mr. S. Gopala Krishnan, CEO, Pune Instrumentation, Pune, India for his technical insight during the course of this project.

REFERENCES

1. W. J. Eilbeck and G. Mattock, *Chemical Processes in Waste Water Treatment*, Ellis Horwood Ltd., Chichester, UK, 1987.
2. H. G. Bayer, A. L. de Vegt, and C. J. Buisman, *Biological Sulfate Removal and Metal Recovery from Mine Waters*, Presented at SME Annual Meeting, Denver, CO, February 24–27, 1997.
3. W. S. W. Ho and K. K. Sirkar (Eds.), *Membrane Handbook*, Reinhold, New York, NY, 1992.
4. S. H. Maron and C. F. Pruton, *Principles of Physical Chemistry*, 4th ed., Oxford University Press and IBH Publishing Co., Bombay, 1972, Chapter 12.
5. Environmental Protection Agency, *1992 Toxics Release Inventory*, Public Data Release, April 1994.
6. J. W. Patterson, *Industrial Wastewater Treatment Technology*, Butterworths, 2nd ed., Boston, MA, 1985.
7. Salmon and Hale, *Ion Exchange, Laboratory Manual*, Academic Press, New York, NY, 1959.
8. McMaster-Carr Supply Company, *Catalog 99*, Atlanta, GA, 1993.
9. V. Gopal and G. C. April, *Removal of Metal Contaminants from Industrial Effluents: A New Perspective*, Presented at Fifth World Congress of Chemical Engineering, San Diego, CA, July 14–18, 1996.
10. V. Gopal and G. C. April, *Selective Removal of Metallic Ions Using the Membrane-Electrode Process*, Presented at the 1996 Annual AIChE Meeting, Chiago, IL, November 10–15, 1996.
11. R. G. Crompton and G. H. W. Sanders, *Electrode Potentials*, Oxford Science Publications, New York, NY, 1996, Chapter 2.

Received by editor January 3, 1997
Revision received July 1997