



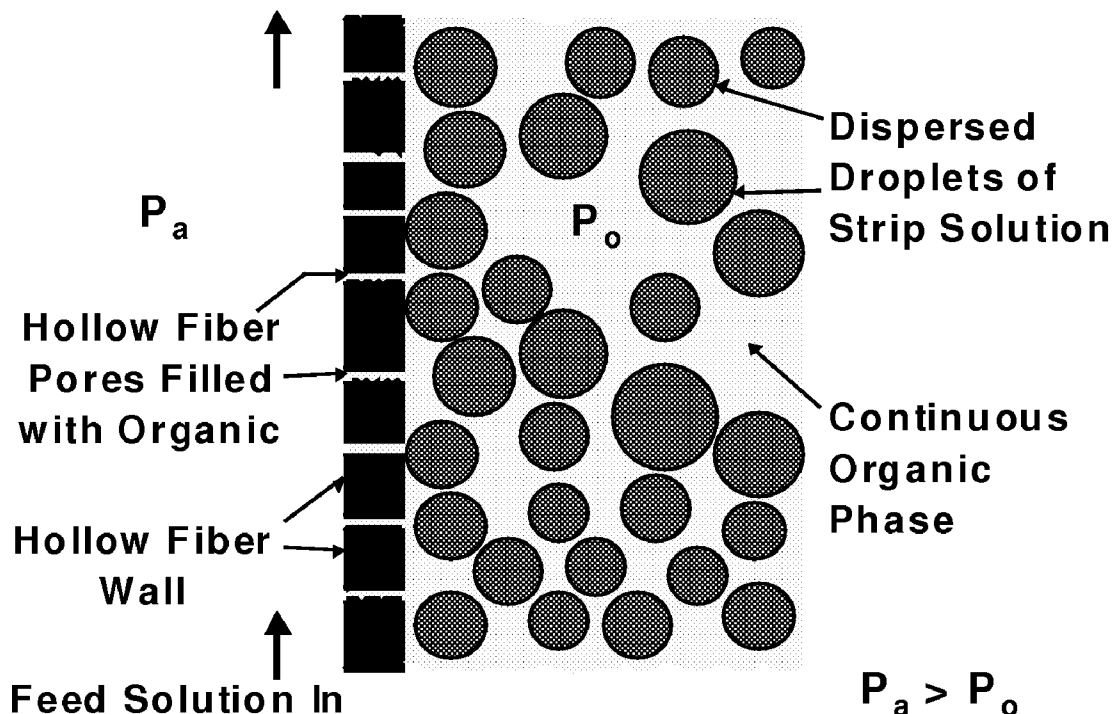
US 20100224030A1

(19) **United States**(12) **Patent Application Publication****Liu et al.**(10) **Pub. No.: US 2010/0224030 A1**(43) **Pub. Date: Sep. 9, 2010**(54) **INDIUM RECOVERY BY SUPPORTED
LIQUID MEMBRANE WITH STRIP
DISPERSION**(21) Appl. No.: **12/397,818**(22) Filed: **Mar. 4, 2009**(75) Inventors: **Ying-Ling Liu**, Taoyuan (TW);
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(TW)**Publication Classification**(51) **Int. Cl.**
C22B 58/00 (2006.01)(52) **U.S. Cl.** **75/711**

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County (TW)(57) **ABSTRACT**

The present invention provides a process for the removal and recovery of indium from waste waters and process streams. The process of the present invention utilizes a combination of a supported liquid membrane (SLM) and a strip dispersion to improve extraction of indium while increasing membrane stability and decreasing processing costs. This novel process selectively removes indium from the feed stream, provides the increased flexibility of aqueous strip/organic volume ratio, and produces a concentrated strip solution of indium.

Feed Solution Out

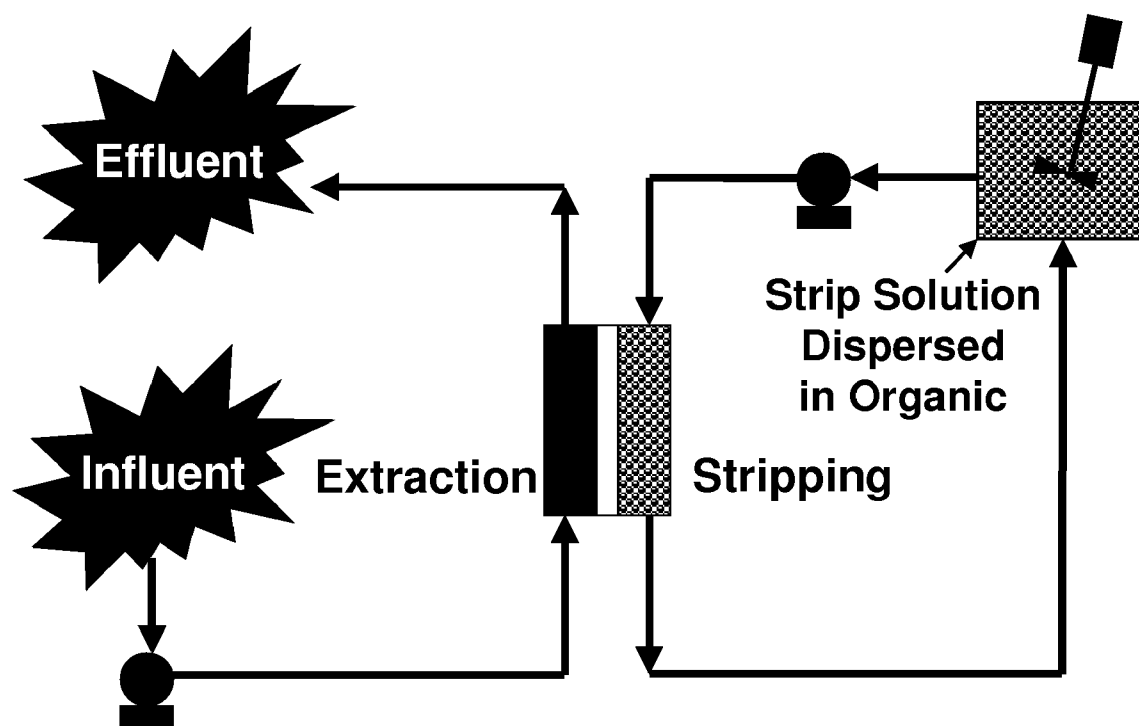
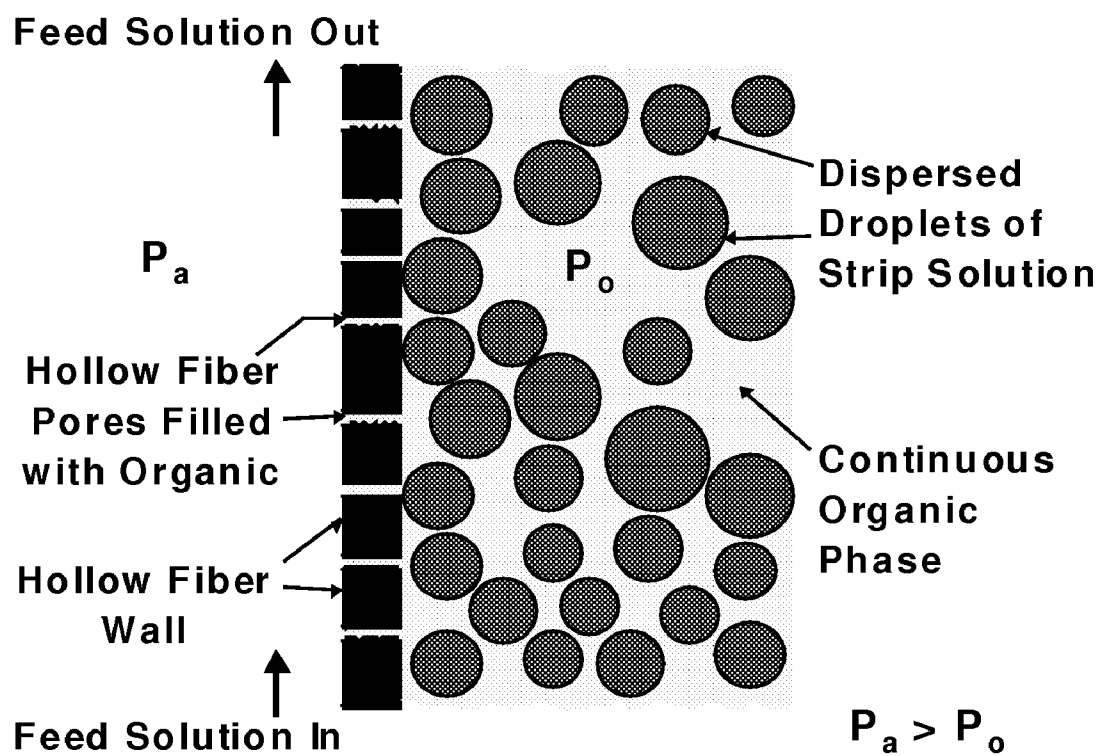
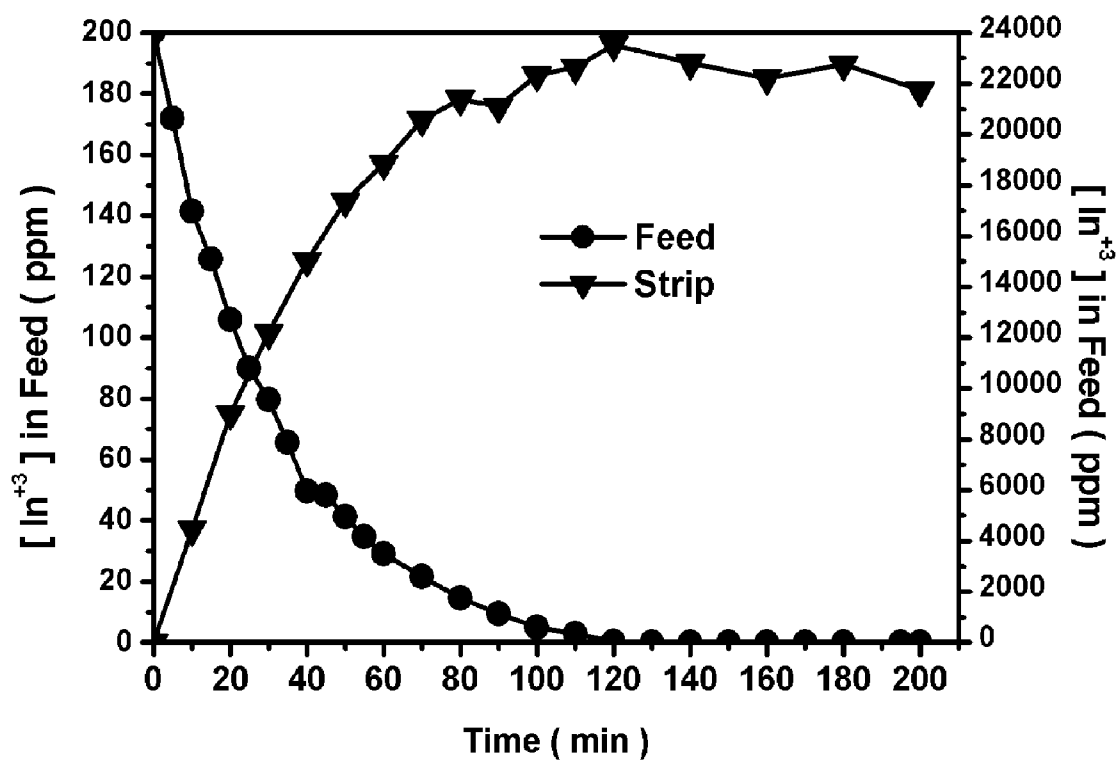
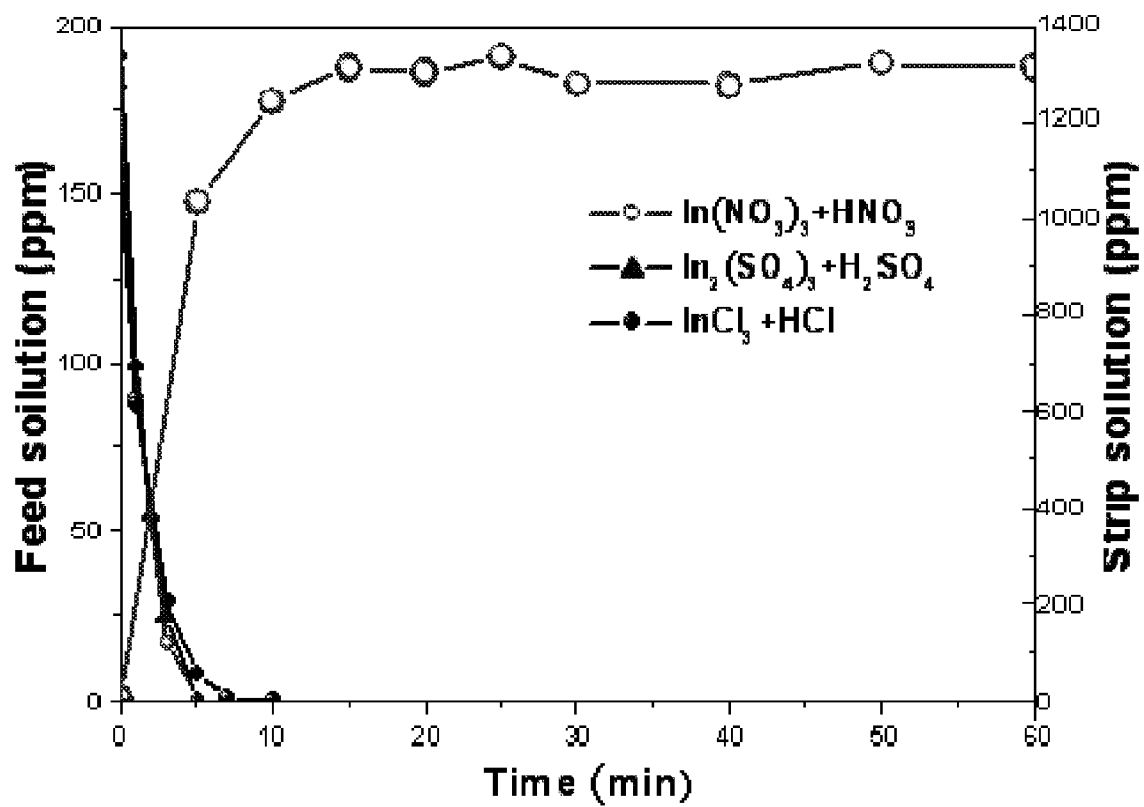
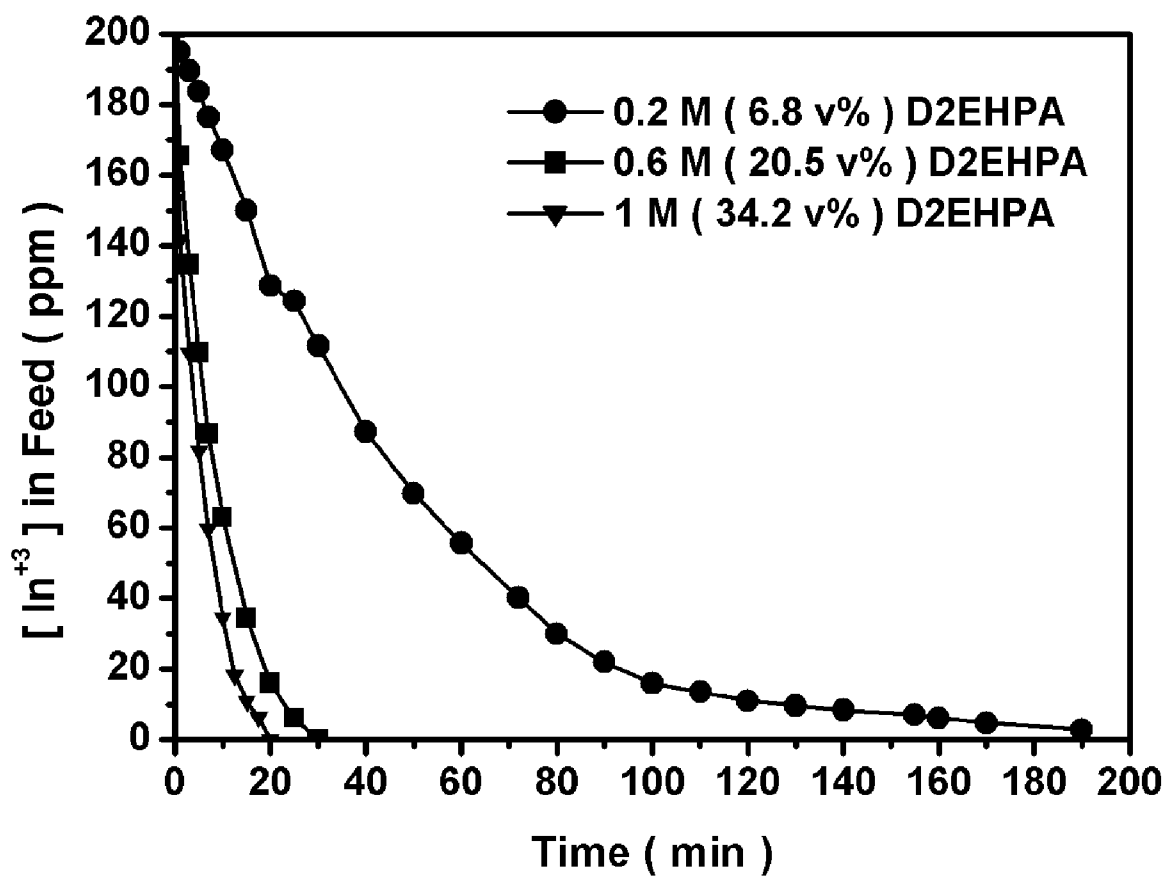


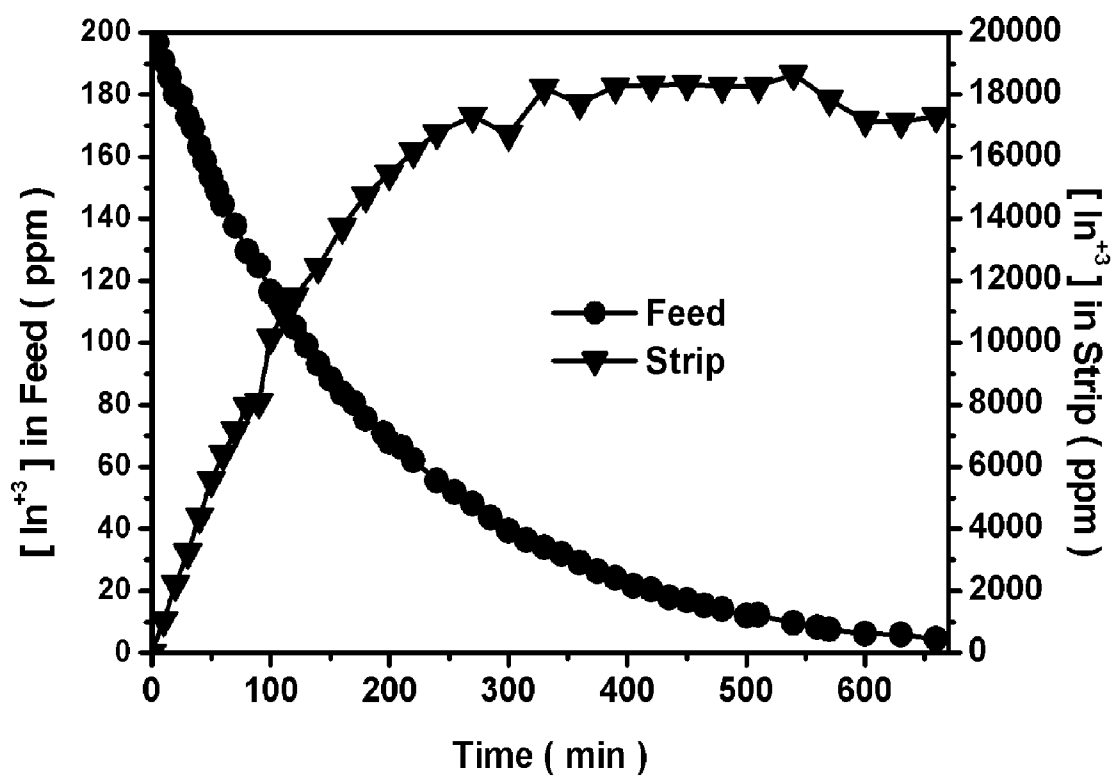
Figure 1

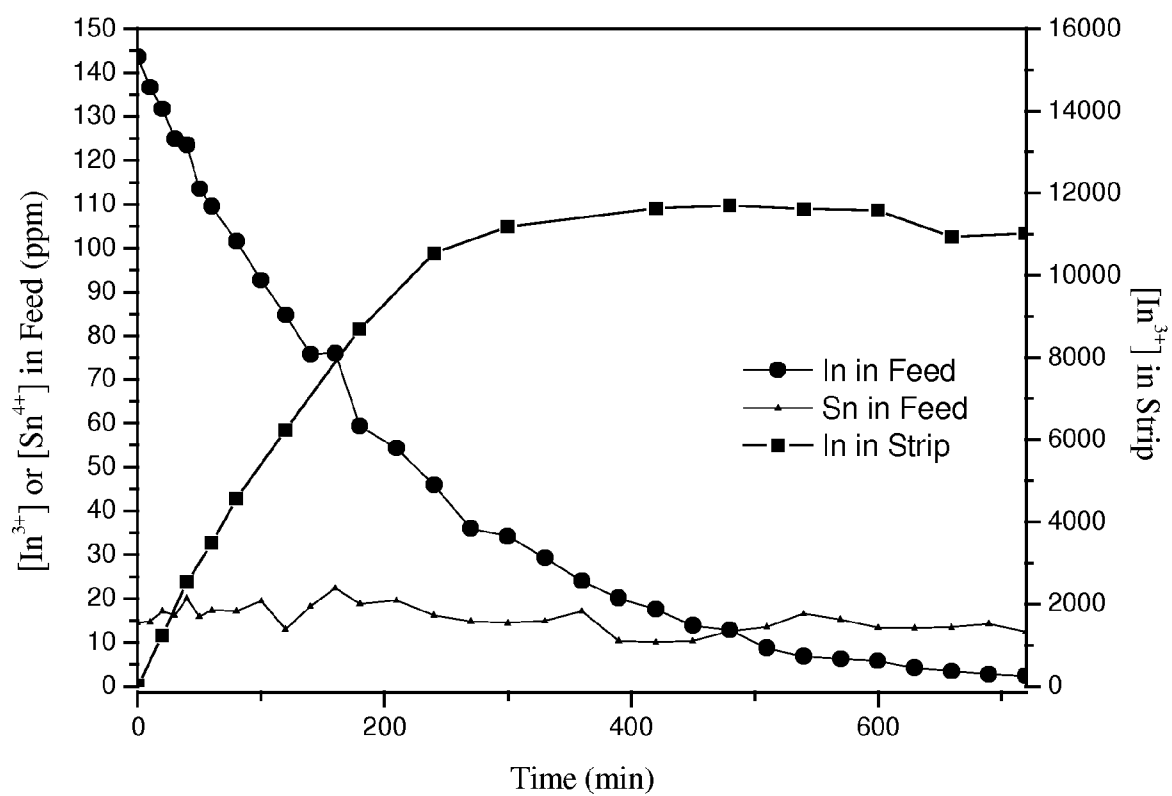
**Figure 2**

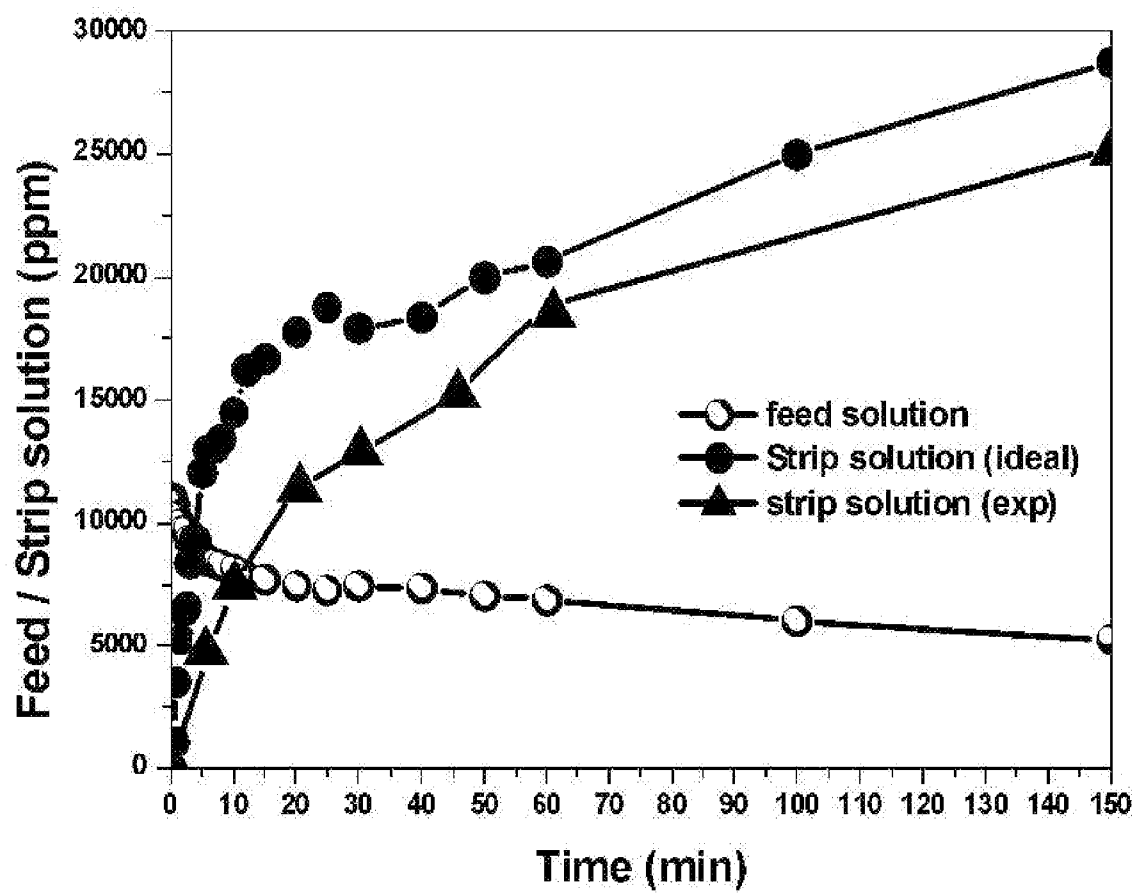
**Figure 3**

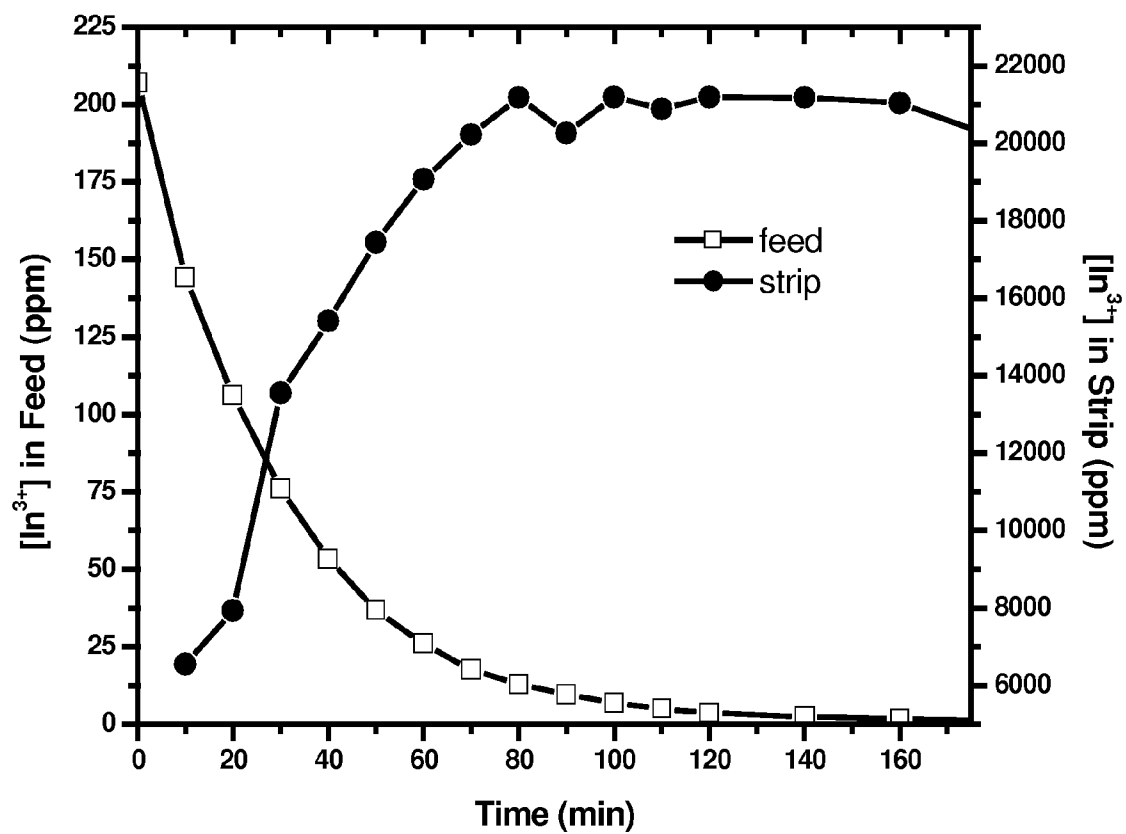
**Figure 4**

**Figure 5**

**Figure 6**

**Figure 7**

**Figure 8**

**Figure 9**

INDIUM RECOVERY BY SUPPORTED LIQUID MEMBRANE WITH STRIP DISPERSION

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to the removal and recovery of indium from feed solutions, such as process streams and waste waters, using supported liquid membrane technology.

[0003] 2. Description of the Prior Art

[0004] Liquid membranes combine extraction and stripping, which are normally carried out in two separate steps in conventional processes such as solvent extractions, into one step. A one-step liquid membrane process provides the maximum driving force for the separation of a targeted species, leading to the best clean-up and recovery of the species (W. S. Winston Ho and Kamalesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992).

[0005] There are two types of liquid membranes: (1) supported liquid membranes (SLMs) and (2) emulsion liquid membranes (ELMs). In SLMs, the liquid membrane phase is the organic liquid imbedded in pores of a microporous support, e.g., microporous polypropylene hollow fibers (W. S. Winston Ho and Kamalesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992). When the organic liquid contacts the microporous support, it readily wets the pores of the support, and the SLM is formed.

[0006] For the extraction of a target species from a feed solution, the organic-based SLM is placed between two aqueous solutions—the feed solution and the strip solution where the SLM acts as a selective membrane for the transport of the target species from the feed solution to the strip solution. The organic liquid in the SLM contains an extractant, a diluent which is generally an inert organic solvent, and sometimes a modifier, and it is immiscible in the aqueous feed and strip streams.

[0007] SLMs have been investigated to remove metals, radionuclides, and rare earth metals from aqueous feed solutions in the scientific and industrial community. The removal of metals, including copper, zinc, cadmium, and palladium, with SLMs has been described (N. Aouad, G. Miquel-Mercier, E. Bienvenue, E. Tronel-Peyroz, G. Jerninet, J. Juillard, and P. Seta, "Lasalocid (X537A) as a Selective Carrier for Cd(II) in Supported Liquid Membranes," *J. Membrane Sci.*, 139, 167-174 (1998); J. A. Daoud, S. A. El-Reefy, and H. F. Aly, "Permeation of Cd(II) Ions through a Supported Liquid Membrane Containing Cyanex-302 in Kerosene," *Sep. Sci. Technol.*, 33, 537-549 (1998); J. Vander Linden and R. F. De Ketelaere, "Selective Recuperation of Copper by Supported Liquid Membrane (SLM) Extraction," *J. Membrane Sci.*, 139, 125-135 (1998); M. E. Campderros, A. Acosta, and J. Marchese, "Selective Separation of Copper with LIX 864 in a Hollow Fiber Module," *Talanta*, 47, 19-24 (1998); M. Rovira and A. M. Sastre, "Modelling of Mass Transfer in Facilitated Supported Liquid-Membrane Transport of Palladium(II) Using Di-(2-ethylhexyl)Thiophosphoric Acid," *J. Membrane Sci.*, 149, 241-250 (1998); J. C. Lee, J. Jeong, J. T. Park, I. J. Youn, and H. S. Chung, "Selective and Simultaneous Extractions of Zn and Cu Ions by Hollow Fiber SLM Modules Containing HEH(EHP) and LIX84," *Sep. Sci. Technol.*, 34, 1689-1701 (1999); F. Valenzuela, C. Basualto, C. Tapia, and J. Sapag, "Application of Hollow-Fiber Supported Liquid

Membranes Technique to the Selective Recovery of a Low Content of Copper from a Chilean Mine Water," *J. Membrane Sci.*, 155, 163-168 (1999)).

[0008] On the removal of radionuclides, Dozol et al. (J. F. Dozol, N. Simon, V. Lamaare, H. Rouquette, S. Eymard, B. Tournois, D. De Marc, and R. M. Macias, "A Solution for Cesium Removal from High-Salinity Acidic or Alkaline Liquid Waste: the Crown Calix[4]arenes", *Sep. Sci. Technol.*, 34, 877-909 (1999)) have described the use of the extractant, Calix[4]arenes monocrown or biscrown, blocked in 1,3 alternative cone conformation, in SLMs for the removal of cesium from high-salinity acidic or alkaline liquid waste. Kedari et al. (C. S. Kedari, S. S. Pandit, and A. Ramanujam, "Selective Permeation of Plutonium (IV) through Supported Liquid Membrane Containing 2-Ethylhexyl 2-Ethylhexyl Phosphonic Acid as Ion Carrier", *J. Membrane Sci.*, 156, 187-196 (1999)) have studied the selective permeation of plutonium (IV) through a SLM containing 2-ethylhexyl 2-ethylhexyl phosphonic acid as the ion carrier.

[0009] On the extraction of rare earth metals, Yaftian et al. (M. R. Yaftian, M. Burgard, C. B. Dieleman and D. Matt, "Rare-earth Metal-ion Separation Using a Supported Liquid Membrane Mediated by a Narrow Rim Phosphorylated Calix [4]arene," *J. Membrane Sci.*, 144, 57-64 (1998)) has reported the use of SLMs for europium, lanthanum, neodymium, praseodymium, and gadolinium.

[0010] One disadvantage of SLMs is their instability due mainly to loss of the membrane liquid (organic solvent, extractant, and/or modifier) into the aqueous phases on each side of the membrane (A. J. B. Kemperman, D. Bargeman, Th. Van Den Boomgaard, H. Strathmann, "Stability of Supported Liquid Membranes: State of the Art", *Sep. Sci. Technol.*, 31, 2733 (1996); T. M. Dreher and G. W. Stevens, "Instability Mechanisms of Supported Liquid Membranes", *Sep. Sci. Technol.*, 33, 835-853 (1998); J. F. Dozol, J. Casas, and A. Sastre, "Stability of Flat Sheet Supported Liquid Membranes in the Transport of Radionuclides from Reprocessing Concentrate Solutions", *J. Membrane Sci.*, 82, 237-246 (1993)). The prior art has attempted to solve this problem through the combined use of SLM with a module containing two sets of hollow fibers, i.e., the hollow-fiber contained liquid membrane (W. S. Winston Ho and Kamalesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992). In this configuration with two sets of microporous hollow-fiber membranes, one carries the aqueous feed solution, and the other carries the aqueous strip solution. The organic phase is contained between the two sets of hollow fibers by maintaining the aqueous phases at a higher pressure than the organic phase. The use of the hollow-fiber contained liquid membrane increases membrane stability, because the liquid membrane may be continuously replenished. However, this configuration is not advantageous because it requires mixing two sets of fibers to achieve a low contained liquid membrane thickness.

[0011] In ELMs, an emulsion acts as a liquid membrane for the separation of the target species from a feed solution. An ELM is created by forming a stable emulsion, such as a water-in-oil emulsion, between two immiscible phases, followed by dispersion of the emulsion into a third, continuous phase by agitation for extraction. The membrane phase is the oil phase that separates the encapsulated, internal aqueous droplets in the emulsion from the external, continuous phase (W. S. Winston Ho and Kamalesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992). The species-

extracting agent is contained in the membrane phase, and the stripping agent is contained in the internal aqueous droplets. Emulsions formed from these two phases are generally stabilized by use of a surfactant. The external, continuous phase is the feed solution containing the target species. The target species is extracted from the aqueous feed solution into the membrane phase and then stripped into the aqueous droplets in the emulsion. The target species can then be recovered from the internal aqueous phase by breaking the emulsion, typically via electrostatic coalescence, followed by electroplating or precipitation.

[0012] The use of ELMs to remove metals, rare earth metals, and radionuclides from aqueous feed solutions has also been pursued in the scientific and industrial community. The ELMs for the removal of metals, including cobalt, copper, zinc, nickel, mercury, lead, cadmium, and silver, and for the removal of rare earth metals, including europium, lanthanum, and neodymium, have been described in detail (W. S. Winston Ho and Kamallesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992). The removal of metals including cobalt, nickel, cadmium, mercury, and lead with ELMs has been reported quite a lot in the literature (B. Raghuraman, N. Tirmizi, and J. M. Wiencek, "Emulsion Liquid Membranes for Wastewater Treatment. Equilibrium Models for Some Typical Metal-Extractant Systems," *Environ. Sci. Technol.*, 28, 1090-1098 (1994); T. Kakko, M. Goto, K. Sugimoto, K. Ohto, and F. Nakashio, "Separation of Cobalt and Nickel with Phenylphosphonic Acid Mono-4-tert-octylphenyl Ester by Liquid Surfactant Membranes," *Sep. Sci. Technol.*, 30, 637-657 (1995); R. S. Juang and J. D. Jiang, "Recovery of Nickel from a Simulated Electroplating Rinse Solution by Solvent Extraction and Liquid Surfactant Membrane," *J. Membrane Sci.*, 100, 163-170 (1995); H. Kasaini, F. Nakashio, and M. Goto, "Application of Emulsion Liquid Membranes to Recover Cobalt Ions from a Dual-component Sulphate Solution Containing Nickel Ions," *J. Membrane Sci.*, 146, 159-168 (1998); S. Y. B. Hu and J. M. Wiencek, "Emulsion-Liquid-Membrane Extraction of Copper Using a Hollow-Fiber Contactor," *AIChE J.*, 570-581 (1998)).

[0013] On radionuclides, the removal of strontium, cesium, technetium, and uranium has also been described in detail by Ho and Sirkar (W. S. Winston Ho and Kamallesh K. Sirkar, eds., *Membrane Handbook*, Chapman & Hall, New York, 1992). The extraction of strontium with the ELM technique has been investigated (I. Eroglu, R. Kalpakci, and G. Gunduz, "Extraction of Strontium Ions with Emulsion Liquid Membrane Technique," *J. Membrane Sci.*, 80, 319-325 (1993)).

[0014] One disadvantage of ELMs is that the emulsion swells upon prolonged contact with the feed stream. This swelling causes a reduction in the stripping reagent concentration in the aqueous droplets which reduces stripping efficiency. It also results in dilution of the target species that has been concentrated in the aqueous droplets, resulting in lower separation efficiency of the membrane. The swelling further results in a reduction in membrane stability by making the membrane thinner. Finally, swelling of the emulsion increases the viscosity of the spent emulsion, making it more difficult to demulsify. A second disadvantage of ELMs is membrane rupture, resulting in leakage of the contents of the aqueous droplets into the feed stream and a concomitant reduction of separation efficiency. Raghuraman and Wiencek (B. Raghuraman and J. Wiencek, "Extraction with Emulsion Liquid Membranes in a Hollow-Fiber Contactor", *AIChE J.*, 39, 1885-1889 (1993)) have described the use of microporous

hollow-fiber contactors as an alternative contacting method to direct dispersion of ELMs to minimize the membrane swelling and leakage. This is due to the fact that the hollow-fiber contactors do not have the high shear rates typically encountered with the agitators used in the direct dispersion. Additional disadvantages include the necessary process steps for making and breaking the emulsion.

[0015] Thus, there has been a need in the art for an extraction process which maximizes the stability of the SLM membrane, resulting in efficient removal and recovery of metals, radionuclides, penicillin, and organic acids from the aqueous feed solutions. Ho recognized the need and invented the combined supported liquid membrane/strip dispersion process for the removal of chromium (W. S. Winston Ho, "Supported Liquid Membrane Process for Chromium Removal and Recovery", U.S. Pat. No. 6,171,563 (2001)), metals (W. S. Winston Ho, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Radionuclides and Metals", U.S. Pat. No. 6,328,782 (2001); W. S. Winston Ho, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Metals", U.S. Pat. No. 6,350,419 (2002)), radionuclides (W. S. Winston Ho, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Radionuclides and Metals", U.S. Pat. No. 6,328,782 (2001); W. S. Winston Ho, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Radionuclides", U.S. Pat. No. 6,696,589 (2004)), and penicillin and organic acids (W. S. Winston Ho, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Penicillin and Organic Acids", U.S. Pat. No. 6,433,163 (2002)). The synthesis of dialkyl monothiophosphoric acid extractants for the combined supported liquid membrane/strip dispersion process for the removal of metals has been reported (W. S. Winston Ho and Bing Wang, "Combined Supported Liquid Membrane/Strip Dispersion Process for the Removal and Recovery of Metals: Dialkyl Monothiophosphoric Acids and Their Use as Extractants", U.S. Pat. No. 6,291,705 (2001)). But, none of these patents by Ho disclose the use of the combined supported liquid membrane/strip dispersion process for the removal and recovery of indium.

[0016] Thus, there is a need in the art for an extraction process which maximizes the stability and effectiveness of the SLM membrane for the efficient removal and recovery of indium from the aqueous feed solutions.

SUMMARY OF THE INVENTION

[0017] The present invention relates to a process for the removal and recovery of indium from a feed solution using a combined SLM/strip dispersion.

[0018] In one embodiment, the present invention relates to a process for the removal and recovery of indium from a feed solution which comprises the following steps. First, a feed solution containing indium is passed on one side of the SLM embedded in a microporous support material and treated to remove the indium by the use of a strip dispersion on the other side of the SLM. The strip dispersion can be formed by dispersing an aqueous strip solution in an organic liquid, for example, using a mixer. Second, the strip dispersion, or a part of the strip dispersion, is allowed to stand, resulting in separation of the dispersion into two phases: the organic liquid phase and the aqueous strip solution phase containing a concentrated indium solution.

[0019] The continuous organic phase of the strip dispersion readily wets the pores of a microporous support to form a stable SLM. The process of the present invention provides a number of operational and economic advantages over the use of conventional SLMs or solvent extraction.

[0020] Thus, it is an object of the present invention to provide an SLM process for the removal and recovery of indium which provides increased membrane stability.

[0021] It is another object of the invention to provide an SLM process having high indium removal and recovery.

[0022] It is yet another object of the present invention to provide an SLM process having improved recovery of indium to provide a concentrated strip solution of indium.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 is a schematic representation of the combined supported liquid membrane/strip dispersion of the present invention for the recovery of indium.

[0024] FIG. 2 is an enlarged view of the schematic representation of the combined supported liquid membrane/strip dispersion of the present invention for the recovery of indium.

[0025] FIG. 3 shows the indium concentrations in the feed and strip solutions as a function of time for the feed solution containing 200 ppm In^{3+} in pH 1 H_2SO_4 of 15.5 L. The strip dispersion was prepared by mixing together 0.12 L (120 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing 0.6M di(2-ethyl-hexyl)phosphoric acid (D2EHPA) and 2 vol % dodecanol in Isopar-L.

[0026] FIG. 4 shows the indium concentrations in the feed and strip solutions as a function of time for the feed solution containing about 180 ppm In^{3+} in pH 1 HNO_3 of 1 L. The strip dispersion was prepared by mixing together 0.12 L (120 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing 0.6M D2EHPA and 2 vol % dodecanol in Isopar-L. Also shown are the indium concentrations in the feed solutions for the original feed solutions containing about 190 ppm In^{3+} in pH 1 H_2SO_4 and 160 ppm In^{3+} in pH 1 HCl, all with the same feed volume of 1 L and the same strip dispersion.

[0027] FIG. 5 depicts the indium concentrations in the feed solutions originally containing about 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ as a function of time for 0.2M, 0.6M and 1M D2EHPA concentrations. Each of the strip dispersions was prepared by mixing together 0.1 L (100 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing the specified D2EHPA concentration and 2 vol % dodecanol in Isopar-L.

[0028] FIG. 6 depicts the indium concentrations in the feed and strip solutions as a function of time for the feed solution containing 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ of 15.5 L. The strip dispersion was prepared by mixing together 0.12 L (120 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing 0.6M D2EHPA and 2 vol % dodecanol in Isopar-L.

[0029] FIG. 7 shows the indium concentrations in the feed and strip solutions as a function of time for the ITO feed solution of 15.5 L containing about 140 ppm In^{3+} at pH 0.9. The strip dispersion was prepared by mixing together 0.12 L (120 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing 0.6M D2EHPA and 2 vol % dodecanol in Isopar-L. Also shown is the tin concentration in the feed solution as a function of time.

[0030] FIG. 8 depicts the indium concentrations in the feed and strip solutions as a function of time for the residual

electrolyte feed solution of 0.5 L containing about 11000 ppm In^{3+} at pH 1. The strip dispersion was prepared by mixing together 0.1 L (100 ml) of the strip solution of 5M HCl and 0.9 L (900 ml) of the organic solution containing 0.6M D2EHPA and 2 vol % dodecanol in Isopar-L. In this figure, both the indium concentration in the strip solution obtained experimentally, i.e., strip-exp, and that calculated from the feed concentration based on the material balance, i.e., strip-ideal (the ideal case), are included.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0031] The present invention relates to a process for the removal and recovery of indium from a feed solution, such as waste waters or process streams. This new process employs a combination of a supported liquid membrane (SLM) and a strip dispersion.

[0032] In one embodiment, the present invention relates to a process for the removal and recovery of indium from a feed solution which comprises the following steps. First, a feed solution containing indium is passed on one side of the SLM embedded in a microporous support material and treated to remove the indium by the use of a strip dispersion on the other side of the SLM. The strip dispersion can be formed by dispersing an aqueous strip solution in an organic liquid, for example, using a mixer. Second, the strip dispersion, or a part of the strip dispersion, is allowed to stand, resulting in separation of the dispersion into two phases: the organic liquid phase and the aqueous strip solution phase containing a concentrated indium solution.

[0033] While any SLM configuration may be employed in the process of the invention, the preferred configuration employs a hollow fiber module as the liquid membrane microporous support. Such hollow fiber modules consist of microporous hollow fibers arranged in a shell-and-tube configuration. In the present invention, the strip dispersion is passed through either the shell side of the module or the tube side of the module, and the aqueous feed solution containing indium for extraction is passed through the opposing side of the module. The use of the hollow fiber system in the combined SLM/strip dispersion process allows constant supply of the strip dispersion as shown in FIG. 1, ensuring a stable and continuous operation.

[0034] For the purposes of the invention, strip dispersion is defined as a mixture of an aqueous phase and an organic phase. The aqueous phase of the dispersion comprises an aqueous strip solution, while the organic phase comprises an extractant or extractants in an organic liquid. The dispersion is formed by the mixing of the aqueous and organic phases as shown in FIG. 1. This combination results in droplets of the aqueous strip solution in a continuous organic phase. The dispersion is maintained during the extraction process due to the flow of the dispersion through a membrane module, e.g., a hollow-fiber module. The continuous organic phase of the strip dispersion readily wets the hydrophobic pores of the microporous hollow fibers in the module, forming a stable liquid membrane.

[0035] FIG. 2 shows an enlarged view of a schematic representation of the SLM with strip dispersion of the present invention. A low pressure, P_a , which is typically less than approximately 2 psi, is applied on the feed solution side of the SLM. The pressure P_a is greater than the pressure, P_o , on the strip dispersion side of the SLM. This difference in pressure prevents the organic solution of the strip dispersion from

passing through the pores to come into the feed solution side. The dispersed droplets of the aqueous strip solution in a typical size of about 80 to about 800 micrometers and are orders of magnitude larger than the pore size of the microporous support employed for the SLM, which is in the order of approximately 0.03 micrometer. Thus, these droplets are retained on the strip dispersion side of the SLM and cannot pass through the pores to go to the feed solution side.

[0036] In this SLM/strip dispersion system, there is a constant supply of the organic membrane solution, i.e., the organic phase of the strip dispersion, into the pores. This constant supply of the organic phase ensures a stable and continuous operation of the SLM. In addition, the direct contact between the organic and strip phases provides efficient mass transfer for stripping. The organic and strip phases can be mixed, for example, with high-shear mixing, to increase the contact area between the two phases.

[0037] Once removal of indium is complete, the mixer for the strip dispersion is stopped, and the dispersion is allowed to stand until it separates into two phases, the organic membrane solution and the concentrated strip solution. The concentrated strip solution containing indium is the product of this process.

[0038] The feed solution includes, but is not limited to, waste waters or process streams containing indium.

[0039] The microporous support employed in the invention is comprised of, for example, microporous polypropylene, polytetrafluoroethylene, polyethylene, polysulfone, polyethersulfone, polyetheretherketone, polyimide, polyamide, polyaramide, or mixtures thereof. The preferred microporous supports are microporous polypropylene and polytetrafluoroethylene hollow fibers.

[0040] The aqueous portion of the strip dispersion comprises an aqueous acid solution, such as a mineral acid. Examples of mineral acids useful in the present invention include, but are not limited to, hydrochloric acid (HCl), sulfuric acid (H₂SO₄), nitric acid (HNO₃), and acetic acid (CH₃COOH). The acid is present in a concentration between about 0.1 M and about 18 M. The preferred concentration for the acid solution is between about 1 M and about 6 M.

[0041] The continuous organic liquid phase into which the aqueous strip solution is dispersed contains an extractant or extractants. The extractant is capable of extracting indium contained in the feed solution. Typical extractants which are known in the art for extraction of indium from waste waters or process streams may be employed in the present strip dispersion.

[0042] The extractants include dialkyl phosphoric acids and alkyl phenylphosphonic acids. The dialkyl group of the dialkyl phosphoric acid is paraffinic (saturated) and has from 6 to 26 carbon atoms. The dialkyl phosphoric acids are selected from the group consisting of di(2-ethyl-hexyl)phosphoric acid (D2EHPA), di(2-butyl-octyl)phosphoric acid, di(2-hexyl-decyl)phosphoric acid, di(2-octyl-decyl/2-hexyl-dodecyl)phosphoric acid, di(2-octyl-dodecyl)phosphoric acid, di(hexyl)phosphoric acid, di(heptyl)phosphoric acid, di(octyl)phosphoric acid, di(nonyl)phosphoric acid, di(decyl)phosphoric acid, di(undecyl)phosphoric acid, di(dodecyl)phosphoric acid, di(tridecyl)phosphoric acid, di(tetradecyl)phosphoric acid, di(pentadecyl)phosphoric acid, di(hexadecyl)phosphoric acid, di(heptadecyl)phosphoric acid, di(octadecyl)phosphoric acid, di(nonadecyl)phosphoric acid, di(decadecyl)phosphoric acid, di(undecadecyl)phosphoric acid, di(dodecadecyl)phosphoric acid, di(tridecadecyl)phosphoric acid, di(tetradecadecyl)phosphoric acid,

di(pentadecadecyl)phosphoric acid, di(hexadecadecyl)phosphoric acid, and mixtures thereof. The preferred dialkyl phosphoric acid is di(2-ethyl-hexyl)phosphoric acid (D2EHPA).

[0043] The alkyl group of the alkyl phenylphosphonic acid is paraffinic (saturated) and has from 6 to 26 carbon atoms. The alkyl phenylphosphonic acids are selected from the group consisting of 2-butyl-1-octyl phenylphosphonic acid (BOPPA), 2-hexyl-1-decyl phenylphosphonic acid, 2-octyl-1-decyl/2-hexyl-1-dodecyl phenylphosphonic acid, 2-octyl-1-dodecyl phenylphosphonic acid, hexyl phenylphosphonic acid, heptyl phenylphosphonic acid, octyl phenylphosphonic acid, nonyl phenylphosphonic acid, decyl phenylphosphonic acid, undecyl phenylphosphonic acid, dodecyl phenylphosphonic acid, tridecyl phenylphosphonic acid, tetradecyl phenylphosphonic acid, pentadecyl phenylphosphonic acid, hexadecyl phenylphosphonic acid, heptadecyl phenylphosphonic acid, octadecyl phenylphosphonic acid, nonadecyl phenylphosphonic acid, decadecyl phenylphosphonic acid, undecadecyl phenylphosphonic acid, dodecadecyl phenylphosphonic acid, tridecadecyl phenylphosphonic acid, tetradecadecyl phenylphosphonic acid, pentadecadecyl phenylphosphonic acid, hexadecadecyl phenylphosphonic acid, and mixtures thereof. The preferred alkyl phenylphosphonic acid is 2-butyl-1-octyl phenylphosphonic acid (BOPPA).

[0044] The organic liquid of the present strip dispersion optionally comprises a hydrocarbon solvent or mixture. The hydrocarbon solvent or mixture has a number of carbon atoms per solvent molecule ranging from 6 to 18, preferably from 10 to 14. The hydrocarbon solvent includes, for example, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, isodecane, isoundecane, isododecane, isotridecane, isotetradecane, isoparaffinic hydrocarbon solvent (with a flash point of 92° C., a boiling point of 254° C., a viscosity of 3 cp (at 25° C.), and a density of 0.791 g/ml (at 15.6° C.)) or mixtures thereof.

[0045] The organic liquid of the present strip dispersion optionally contains a modifier to enhance the complexation and/or stripping of the target species. The modifier can be, for example, an alcohol, a nitrophenyl alkyl ether, a trialkyl phosphate or mixtures thereof. The alcohol can be, for example, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol or mixtures thereof. The nitrophenyl ether can be, for example, o-nitrophenyl octyl ether (o-NPOE), o-nitrophenyl heptyl ether, o-nitrophenyl hexyl ether, o-nitrophenyl pentyl ether (o-NPPE), o-nitrophenyl butyl ether, o-nitrophenyl propyl ether or a mixture thereof. The trialkyl phosphate can be, for example, tributyl phosphate, tris(2-ethylhexyl)phosphate or mixtures thereof.

[0046] The organic liquid of the present strip dispersion comprises about 2 volume % to about 100 volume % (approximately 0.05M to 3M) extractant and about 0 volume % to about 20 volume % modifier in a hydrocarbon solvent or mixture. More preferably, the organic liquid of the present strip dispersion comprises about 5 volume % to about 40 volume % extractant and about 1 volume % to about 10 volume % modifier in a hydrocarbon solvent or mixture. Even more preferably, the organic liquid comprises 5 volume % to about 40 volume % extractant and about 1 volume % to about 10 volume % dodecanol in an isoparaffinic hydrocarbon solvent or in n-dodecane. All percentages are by volume unless specified otherwise.

[0047] The present invention has several advantages over conventional SLM technology for removal and recovery of

indium from aqueous feed solution. These advantages include increased membrane stability, reduced costs, increased simplicity of operation, improved flux, and improved recovery for indium.

[0048] The present invention provides a constant supply of the organic membrane solution into the pores of the hollow fiber support for removal and recovery of indium from aqueous feed solution. This constant supply results in an SLM which is more stable than conventional SLMs, ensuring stable and continuous operation. This constant supply also eliminates the need for recharging membrane modules, which is required with conventional SLMs. Further, it eliminates the need for a second set of membrane modules for use during recharging of the first set of membrane modules. Thus, the present invention decreases not only operational costs but also the initial capital investment in the system. The present invention also increases simplicity of the removal operation.

[0049] The present invention provides direct contact between the organic/extraction phase and aqueous strip phase. Mixing of these phases provides an extra mass transfer surface area in addition to the area given by the hollow fibers, leading to extremely efficient stripping of the target species from the organic phase. This efficient stripping enhances the flux for the extraction of indium.

[0050] The present invention comprises a new type of SLM for removal and recovery of indium, and it provides increased flexibility of aqueous strip/organic volume ratio. This flexibility allows the use of a smaller volume of aqueous strip solution to obtain a higher concentration of the recovered indium in the aqueous strip solution. The concentrated strip solution is a valuable product for resale or reuse.

[0051] This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. To the contrary, it is to be clearly understood that reading the description herein may suggest various other embodiments, modifications, and equivalents to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

EXAMPLES

General Procedure

[0052] In all of the following examples, the supported liquid membranes (SLMs) with trip dispersion were used to extract indium from an aqueous feed solution to an organic solution, in which an aqueous strip solution was dispersed to continually strip the extracted indium. The SLM system consisted of a hollow-fiber membrane module (Liquid-Cel®, extra-flow 2.5×8, Membrana-Charlotte, USA), a feed solution tank, a feed pump (model 7592-50, Cole-Parmer, USA) to drive the feed solution into the polypropylene hollow fibers in the module, a strip dispersion tank with a mixer (SS-NZ-1000, Eyela, Japan) to well disperse the aqueous strip solution in the organic solution, and another pump (model 7553-70, Cole-Parmer, USA) to drive the water-in-oil dispersion into the shell side of the module. The hollow-fiber module was 6.35 cm (2.5 inches) in diameter and 20.3 cm (8 inches) in length, and it had a membrane surface area of 1.4 m².

[0053] All of the following examples were run in the counter-current mode with the feed solution passing through the tube side of the microporous polypropylene hollow fiber module whereas the strip dispersion passing through the shell side of the module. Indium in the feed solution was extracted

to the organic solution in the membrane module, and the extracted indium was stripped into the dispersed strip solution both in the module and in the dispersion tank.

[0054] The aqueous feed solution, containing indium, was placed in the feed tank that was agitated by a magnetic stirring bar at a rate of 300 rpm. The strip solution, 5M HCl aqueous solution, was dispersed with a 2-bladed paddle (8.5 cm in diameter) at a rate of 300 rpm in the organic solution containing D2EHPA (Merck) as the extractant for indium in Isopar-L (ExxonMobil). The concentration of D2EHPA in Isopar-L was 0.6 M (20.5 vol %) for most of the experiments we performed unless specified otherwise. The organic solution also contained 2 vol % of 1-dodecanol (Merck), unless specified otherwise, as the modifier for the extractant. The total volume of the organic solution was 0.90 L (900 ml), and that of the strip solution was 0.12 L (120 ml) unless specified otherwise. Both of the feed and dispersion tanks were thermostated at 25° C.

[0055] The process was first started by passing the feed solution through the tube side of the hollow fiber module. After the hollow fibers were filled with the feed solution, the water-in-oil dispersion was pumped into the shell side of the module. To prevent the organic phase from passing through the pores of the hollow fibers into the feed solution, the pressure in the tube side was maintained at a positive pressure, i.e., 4 to 5 psi higher than that in the shell side unless specified otherwise. Both the feed and dispersion solutions were pumped from the tanks to the module and then recycled back to the tanks. The pumping rate for both streams was kept at 1 L/min.

[0056] During each experiment, samples from the feed and strip solutions were taken at certain timed intervals. The strip dispersion samples were allowed to stand until phase separation occurred. The aqueous phase from the strip dispersion sample was then collected. The aqueous phase samples from the strip dispersion samples and the feed solution samples were then analyzed to determine the indium concentrations by using an atomic absorption spectrophotometer (GBC 906, GBC, Australia) unless specified otherwise (for example, using an inductively coupled plasma (ICP) spectrometer).

[0057] Experiments with different feed compositions and volumes were carried out to investigate the performance of the process of SLM with strip dispersion. The performance maybe expressed in terms of indium recovery and concentrations in both the treated feed and strip solutions.

Example 1

[0058] Feed Solution with 200 ppm In³⁺ in pH 1 H₂SO₄ of 15.5 L.

[0059] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L.

[0060] Strip=5M HCl, 0.12 L

The feed solution contained 200 ppm In³⁺ in pH 1 H₂SO₄, and it had a volume of 15.5 L. The organic solution was 0.6M di(2-ethyl-hexyl)phosphoric acid (D2EHPA) and 2 vol % dodecanol in Isopar-L, and it had a volume of 0.9 L. The strip solution was 5M HCl with a volume of 0.12 L. A strip dispersion was prepared by mixing together 0.12 L (120 ml) of the strip solution and 0.9 L (900 ml) of the organic solution as described in the general procedure above. The feed solution containing about 200 ppm In³⁺ was pumped into the tube side of the polypropylene hollow fiber module. The strip dispersion was fed into the shell side of the hollow fiber module. Samples of the feed and strip solutions were collected at

certain timed intervals as described in the general procedure above and analyzed by atomic absorption spectrophotometry. The indium concentrations in the feed and strip solution samples as a function of time are listed in Table 1. The results are shown in FIG. 3. Both the table and figure show that the SLM process with strip dispersion can produce the strip solution with a very high indium concentration of greater than 20000 ppm.

TABLE 1

Time (min)	Feed (ppm)	Time (min)	Strip (ppm)
0	200.2	0	0
5	172.0	10	4459
10	141.5	20	8996
15	125.9	30	12191
20	105.9	40	15037
25	90.07	50	17364
30	79.76	60	18851
35	65.73	70	20580
40	49.63	80	21386
45	48.40	90	21100
50	41.26	100	22337
55	34.82	110	22641
60	29	120	23528
70	21.71	140	22808
80	14.62	160	22203
90	9.48	180	22758
100	5.09	200	21742
110	2.94		
120	0.32		
130	0		
140	0		
150	0		
160	0		
170	0		
180	0		
195	0		
200	0		

Example 2

[0061] Feed Solution with about 180 ppm In³⁺ in pH 1 HNO₃ of 1 L.

[0062] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L.

[0063] Strip=5M HCl, 0.12 L.

The experimental procedure for this example was the same as that described in Example 1 except the feed solution with about 180 ppm In³⁺ in pH 1 HNO₃ of 1 L was used instead of the feed solution with 200 ppm In³⁺ in pH 1 M H₂SO₄ of 15.5 L. The indium concentrations in the feed and strip solution samples as a function of time are listed in Table 2. The results are also shown in FIG. 4.

TABLE 2

Time (min)	Feed (ppm)	Time (min)	Strip (ppm)
0	181.9	0	0
1	89.5	5	1034
3	16.8	10	1246
5	0	15	1315
		20	1305
		25	1337
		30	1282

TABLE 2-continued

Time (min)	Feed (ppm)	Time (min)	Strip (ppm)
		40	1280
		50	1325
		60	1315

Example 3

[0064] Feed Solution with about 190 ppm In³⁺ in pH 1 H₂SO₄ of 1 L

[0065] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0066] Strip=5M HCl, 0.12 L

The experimental procedure for this example was the same as that described in Example 1 except the feed solution with about 190 ppm In³⁺ in pH 1 H₂SO₄ of 1 L was used instead of the feed solution with 200 ppm In³⁺ in pH 1 M H₂SO₄ of 15.5 L. The indium concentrations in the feed solution samples as a function of time are listed in Table 3. The results are also shown in FIG. 4 for comparison. Both the table and figure show that the results for this example using the feed solution with pH 1 H₂SO₄ were very similar to those for Example 2 using the feed solution with pH 1 HNO₃ while the other conditions were essentially the same.

TABLE 3

Time (min)	Feed (ppm)
0	191.6
1	99.01
2	53.77
3	25.17
5	0

Example 4

[0067] Feed Solution with about 160 ppm In³⁺ in pH 1 HCl of 1 L

[0068] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0069] Strip=5M HCl, 0.12 L

The experimental procedure for this example was the same as that described in Example 1 except the feed solution with about 160 ppm In³⁺ in pH 1 HCl of 1 L was used instead of the feed solution with 200 ppm In³⁺ in pH 1 M H₂SO₄ of 15.5 L. The indium concentrations in the feed solution samples as a function of time are listed in Table 4. The results are also shown in FIG. 4 for comparison. Both the table and figure show that the results for this example using the feed solution with pH 1 HCl were very similar to those for Example 2 using the feed solution with pH 1 HNO₃ and Example 3 using the feed solution with pH 1 H₂SO₄ while the other conditions were essentially the same.

TABLE 4

Time (min)	Feed (ppm)
0	156.6
1	87.98
3	29.48

TABLE 4-continued

Time (min)	Feed (ppm)
5	8.27
7	0.72
10	0

Example 5

[0070] Feed Solution with about 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ of 1 L

[0071] Condition: Organic Solution=0.2M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0072] Strip=5M HCl, 0.1 L

The experimental procedure for this example was the same as that described in Example 1 except (1) the feed solution with about 200 ppm In^{3+} in pH 1, 2 wt % H_2CO_4 (oxalic acid) of 1 L was used instead of the feed solution with 200 ppm In^{3+} in pH 1 M H_2SO_4 of 15.5 L, and (2) 0.2M D2EHPA was used instead of 0.6M, and (3) the volume of the strip solution used was 0.1 L (100 ml) instead of 0.12 L (120 ml). The indium concentrations in the feed solution samples as a function of time are listed in Table 5. The results are also shown in FIG. 5.

TABLE 5

Time (min)	Feed (ppm)
0	208.0
1	194.9
3	189.7
5	183.8
7	176.5
10	167.2
15	150.0
20	128.7
25	124.2
30	111.7
40	87.16
50	69.80
60	55.66
72	40.14
80	30.03
90	21.90
100	16
110	13.48
120	10.98
130	9.58
140	8.35
155	7.05
160	6.11
170	4.67
190	2.89

Example 6

[0073] Feed Solution with about 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ of 1 L

[0074] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0075] Strip=5M HCl, 0.1 L

The experimental procedure for this example was identical to that described in Example 5 except 0.6M D2EHPA was used instead of 0.2M, i.e., the experimental procedure was similar to that for Example 1. The indium concentrations in the feed

solution samples as a function of time are listed in Table 6. The results are also shown in FIG. 5 for comparison. Both the table and figure show that the results for this example using the 0.6M D2EHPA were much better than those for Example 5 using 0.2M D2EHPA.

TABLE 6

Time (min)	Feed (ppm)
0	205.7
1	169.3
3	137.1
5	107.2
7	86.34
10	60.57
15	31.99
20	13.82
25	3.99
30	0

Example 7

[0076] Feed Solution with about 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ of 1 L

[0077] Condition: Organic Solution=1M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0078] Strip=5M HCl, 0.1 L

The experimental procedure for this example was identical to that described in Example 5 except 1M D2EHPA was used instead of 0.2M, i.e., the experimental procedure was similar to that for Example 1. The indium concentrations in the feed solution samples as a function of time are listed in Table 7. The results are also shown in FIG. 5 for comparison. Both the table and figure show that the results for this example using the 0.6M D2EHPA were better than those for Example 6 using 0.6M D2EHPA and much better than those for Example 5 using 0.2M D2EHPA. These results indicated that 0.6M D2EHPA was suitable and effective for the extraction of indium from the feed solution containing the oxalic acid.

TABLE 7

Time (min)	Feed (ppm)
0	194.2
1	141.5
3	109.6
5	81.82
7	59.68
10	34.33
12.5	18.34
15	10.85
17.5	6.28
20	0

Example 8

[0079] Feed Solution with 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_2\text{O}_4$ of 15.5 L

[0080] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0081] Strip=5M HCl, 0.12 L

The experimental procedure for this example was identical to that described in Example 1 except the feed solution with 200 ppm In^{3+} in pH 1, 2 wt % $\text{H}_2\text{C}_{2l}\text{O}_4$ was used instead of that in

pH 1 H_2SO_4 . The indium concentrations in the feed and strip solution samples as a function of time are listed in Table 8. The results are also shown in FIG. 6. Both the table and figure show that the SLM with strip dispersion can recover and concentrate indium in the strip solution with 18000 ppm or higher from the feed solution containing the oxalic acid.

TABLE 8

Time (min)	Feed (ppm)	Time (min)	Strip (ppm)
0	200.1	0	0
5	196.6	10	1057
10	190.7	20	2209
15	185.5	30	3253
20	180.1	40	4399
25	179.0	50	5560
30	172.9	60	6399
35	169.3	70	7181
40	163.2	80	7965
45	158.6	90	8078
50	153.4	100	10162
55	148.9	110	10953
60	144.4	120	11491
70	137.6	140	12445
80	129.5	160	13741
90	124.9	180	14744
100	116.5	200	15453
110	112.0	220	16166
120	105.0	240	16762
130	99.03	270	17308
140	93.15	330	18200
150	88.31	360	17725
160	83.72	390	18258
170	80.51	420	18320
180	75.44	450	18342
195	70.85	480	18274
200	67.99	510	18272
210	66.24	540	18662
220	62.07	570	17853
240	55.45	600	17168
255	51.75	630	17127
270	47.97	660	17305
285	43.52		
300	39.39		
315	36.43		
330	34.09		
345	31.97		
360	29.08		
375	26.32		
390	24.23		
405	21.68		
420	20.54		
435	17.99		
450	17.01		
465	15.19		
480	14.16		
500	11.97		
510	12.21		
540	9.74		
560	8.23		
570	7.57		
600	6.16		
630	5.98		
660	4.48		

Example 9

[0082] ITO Feed Solution with about 140 ppm In^{3+} and pH 0.9 of 15.5 L

[0083] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0084] Strip=5M HCl, 0.12 L

The experimental procedure for this example was identical to that described in Example 1 except the ITO (indium tin oxide)

feed solution with about 140 ppm In^{3+} and pH 0.9 was used instead of that with 200 ppm In^{3+} in pH 1 H_2SO_4 . The indium concentrations in the feed and strip solution samples as a function of time are given in Table 9. The results are also shown in FIG. 7. Both the table and figure show that the SLM with strip dispersion can recover and concentrate indium in the strip solution with 11000 ppm or higher from the ITO feed solution. Also given in this table are the tin concentrations in the feed solution samples as a function of time and those in the strip solution samples at the beginning and end of the experiment. Also shown in the figure are the tin concentrations in the feed solution samples as a function of time. These results indicate that the tin was hardly extracted from the feed solution and nor concentrated in the strip solution. Thus, the SLM with strip dispersion was effective for the removal and recovery of indium from the ITO feed solution.

TABLE 9

Feed			Strip		
Time (min)	In (ppm)	Sn (ppm)	Time (min)	In (ppm)	Sn (ppm)
0	143.5	14.52	0	0	0
10	136.6	14.67	20	1240	—
20	131.7	17.15	40	2538	—
30	124.8	16.11	60	3485	—
40	123.4	19.97	80	4564	—
50	113.4	15.79	120	6222	—
60	109.5	17.28	180	8692	—
80	101.4	17.13	240	10532	—
100	92.53	19.39	300	11177	—
120	84.62	12.99	420	11631	—
140	75.69	18.2	480	11695	—
160	75.94	22.28	540	11606	—
180	59.28	18.81	600	11581	—
210	54.21	19.60	660	10932	—
240	45.84	16.17	720	11018	20
270	35.88	14.71			
300	34.15	14.42			
330	29.21	14.83			
360	23.93	17.00			
390	20.03	10.33			
420	17.43	9.97			
450	13.81	10.30			
480	12.71	12.51			
510	8.71	13.50			
540	6.76	16.48			
570	6.19	15.20			
600	5.72	13.31			
630	4.12	13.29			
660	3.32	13.45			
690	2.64	14.23			
720	2.26	12.34			

Example 10

[0085] Residual Electrolyte Feed Solution with about 11000 ppm In^{3+} and pH 0.9 of 0.5 L

[0086] Condition: Organic Solution=0.6M D2EHPA, 2 vol % dodecanol in Isopar-L, 0.9 L

[0087] Strip=5M HCl, 0.1 L

The experimental procedure for this example was identical to that described in Example 1 except the residual electrolyte feed solution with about 11000 ppm In^{3+} and pH 1 was used instead of that with 200 ppm In^{3+} in pH 1 H_2SO_4 . The indium concentrations in the feed and strip solution samples as a function of time are given in Table 10. In this table, both the indium concentration in the strip solution obtained experimentally, i.e., strip-exp, and that calculated from the feed

concentration based on the material balance, i.e., strip-ideal (the ideal case), are included. The results are also shown in FIG. 8. Both the table and figure show that the SLM with strip dispersion can recover and concentrate indium in the strip solution with 25000 ppm or higher (strip-exp) from the feed solution of residual electrolyte.

TABLE 10

Time (min)	Feed (ppm)	Strip-ideal (ppm)	Time (min)	Strip-exp. (ppm)
0	11018	0	0	0
0.5	10798	1103	6	4738
1	10309	3545	10	7412
1.5	9966	5261	20	11440
2	9723	6476	30	12791
2.5	9690	6641	45	15170
3	9335	8414	60	18783
3.5	9154	9321	150	25206
4	9154	9321		
5	8605	12068		
6	8422	12981		
7	8403	13076		
8	8329	13448		
10	8121	14488		
12	7775	16214		
15	7687	16658		
20	7460	17789		
25	7269	18745		
30	7437	17908		
40	7337	18404		
50	7019	19998		
60	6897	20606		
100	6022	24980		
150	5262	28779		

[0088] Examples 1 to 10 have demonstrated that D2EHPA is an effective extractant in the supported liquid membranes (SLMs) with strip dispersion for the removal and recovery of indium from various aqueous feed solutions. These results of the SLMs with strip dispersion for indium are very much different from those for the metals and radionuclides disclosed in Ho's patents mentioned earlier (U.S. Pat. Nos. 6,291,705, 6,328,782, 6,350,419, 6,696,589) where D2EHPA was ineffective. Thus, these results disclosed in this present invention are unexpected in view of the prior art disclosed in the Ho's patents.

Example 11

2-Butyl-1-Octyl Phenylphosphonic Acid (BOPPA) Extractant

[0089] Feed Solution with 200 ppm In^{3+} in pH 1 H_2SO_4 of 1 L

[0090] Condition: Organic Solution=0.6M BOPPA, 2 vol % dodecanol in Isopar-L, 0.8 L

[0091] Strip=5M HCl, 0.12 L

The experimental procedure for this example was similar to that described in Example 1 except the extractant of 0.6M 2-butyl-1-octyl phenylphosphonic acid (BOPPA; C12 alkyl group) was used instead of that of 0.6M D2EHPA. The indium concentrations in the feed and strip solution samples as a function of time are given in Table 11. The results are also shown in FIG. 9. Both the table and figure show that the SLM with strip dispersion can effectively recover and concentrate indium in the strip solution with 20000 ppm or higher from the feed solution.

TABLE 11

Time (min)	Feed (ppm)	Time (min)	Strip (ppm)
0	173.6	0	0
5	137.5	5	1044
10	98.2	10	1584
15	69.2	15	2207
20	48.5	20	2567
25	32.1	25	2849
30	20.4	30	3010
40	9.7	40	2940
50	3.0	50	3125
60	1.4	60	3021
120	0.1	120	3130

What is claimed is:

1. A combined supported liquid membrane (SLM)/strip dispersion process for the removal and recovery of indium from a feed solution containing the indium comprising

(1) treating a feed solution containing indium on one side of the SLM embedded in a microporous support material to remove the indium by the use of a strip dispersion on the other side of the SLM, the strip dispersion being formed by dispersing an aqueous strip solution in an organic liquid comprising an extractant using a mixer; and

(2) allowing the strip dispersion or a part of the strip dispersion to separate into two phases, the organic liquid phase and the aqueous strip solution phase containing a concentrated indium solution.

2. The process of claim 1, wherein the feed solution is treated to remove indium to a concentration of 5 parts per million (ppm) or lower.

3. The process of claim 1, wherein the aqueous strip solution of the strip dispersion comprises an acid.

4. The process of claim 3, wherein the acid is selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, acetic acid, and mixtures thereof.

5. The process of claim 1, wherein the organic liquid of the strip dispersion further comprises a modifier in a hydrocarbon solvent or mixture.

6. The process of claim 1, wherein the organic liquid of the strip dispersion comprises about 2 volume % to about 100 volume % extractant and about 0 volume % to about 20 volume % modifier in a hydrocarbon solvent or mixture.

7. The process of claim 6, wherein the organic liquid of the strip dispersion comprises about 5 volume % to about 40 volume % extractant and about 1 volume % to about 10 volume % modifier in a hydrocarbon solvent or mixture.

8. The process of claim 5, wherein the modifier is selected from the group consisting of alcohols, nitrophenyl alkyl ethers, trialkyl phosphates, and mixtures thereof.

9. The process of claim 8 wherein the alcoholic is selected from the group consisting of hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, and mixtures thereof.

10. The process of claim 8 wherein the nitrophenyl alkyl ether is selected from the group consisting of o-nitrophenyl octyl ether (o-NPOE), o-nitrophenyl heptyl ether, o-nitrophenyl hexyl ether, o-nitrophenyl pentyl ether (o-NPPE), o-nitrophenyl butyl ether, o-nitrophenyl propyl ether, and mixtures thereof.

11. The process of claim 8, wherein the trialkyl phosphate is selected from the group consisting of tributyl phosphate, tris(2-ethylhexyl)phosphate, and mixtures thereof.

12. The process of claim 5, wherein the hydrocarbon solvent is selected from a group consisting of n-decane; n-undecane; n-dodecane; n-tridecane; n-tetradecane; isodecane; isoundecane; isododecane; isotridecane; isotetradecane; isoparaffinic hydrocarbon solvent having a flash point of 92° C., a boiling point of 254° C., a viscosity of 3 cp at 25° C., and a density of 0.791 g/ml at 15.6° C.; and mixtures thereof.

13. The process of claim 1, wherein the microporous support material is selected from the group consisting of polypropylene, polytetrafluoroethylene, polyethylene, polysulfone, polyethersulfone, polyetheretherketone, polyimide, polyamide, polyaramide, and mixtures thereof.

14. The process of claim 1, wherein the microporous support material is polypropylene.

15. The process of claim 1, wherein the extractant comprises a dialkyl phosphoric acid.

16. The process of claim 15, wherein the dialkyl group of the dialkyl phosphoric acid is paraffinic (saturated) and has from 6 to 26 carbon atoms.

17. The process of claim 15, wherein the dialkyl phosphoric acid is selected from the group consisting of di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2-butyl-octyl)phosphoric acid, di(2-hexyl-decyl)phosphoric acid, di(2-octyl-decyl/2-hexyl-dodecyl)phosphoric acid, di(2-octyl-dodecyl)phosphoric acid, di(hexyl)phosphoric acid, di(heptyl)phosphoric acid, di(octyl)phosphoric acid, di(nonyl)phosphoric acid, di(decyl)phosphoric acid, di(undecyl)phosphoric acid, di(dodecyl)phosphoric acid, di(tridecyl)phosphoric acid, di(tetradecyl)phosphoric acid, di(pentadecyl)phosphoric acid, di(hexadecyl)phosphoric acid, di(heptadecyl)phosphoric acid, di(octadecyl)phosphoric acid, di(nonadecyl)phosphoric acid, di(decadecyl)phos-

phoric acid, di(undecadecyl)phosphoric acid, di(dodecadecyl)phosphoric acid, di(tridecadecyl)phosphoric acid, di(tetradecadecyl)phosphoric acid, di(pentadecyl)phosphoric acid, di(hexadecadecyl)phosphoric acid, and mixtures thereof.

18. The process of claim 15 wherein the dialkyl phosphoric acid is di(2-ethyl-hexyl)phosphoric acid (D2EHPA).

19. The process of claim 1 wherein the extractant comprises an alkyl phenylphosphonic acid.

20. The process of claim 19 wherein the alkyl group of the alkyl phenylphosphonic acid is paraffinic (saturated) and has from 6 to 26 carbon atoms.

21. The process of claim 19 wherein the alkyl phenylphosphonic acid is selected from the group consisting of 2-butyl-1-octyl phenylphosphonic acid (BOPPA), 2-hexyl-1-decyl phenylphosphonic acid, 2-octyl-1-decyl/2-hexyl-1-dodecyl phenylphosphonic acid, 2-octyl-1-dodecyl phenylphosphonic acid, hexyl phenylphosphonic acid, heptyl phenylphosphonic acid, octyl phenylphosphonic acid, nonyl phenylphosphonic acid, decyl phenylphosphonic acid, undecyl phenylphosphonic acid, dodecyl phenylphosphonic acid, tridecyl phenylphosphonic acid, tetradecyl phenylphosphonic acid, pentadecyl phenylphosphonic acid, hexadecyl phenylphosphonic acid, heptadecyl phenylphosphonic acid, octadecyl phenylphosphonic acid, nonadecyl phenylphosphonic acid, decadecyl phenylphosphonic acid, undecadecyl phenylphosphonic acid, dodecadecyl phenylphosphonic acid, tridecadecyl phenylphosphonic acid, tetradecadecyl phenylphosphonic acid, pentadecadecyl phenylphosphonic acid, hexadecadecyl phenylphosphonic acid, and mixtures thereof.

22. The process of claim 19 wherein the alkyl phenylphosphonic acid is 2-butyl-1-octyl phenylphosphonic acid (BOPPA).

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