

Selective Recovery of Palladium from Used Aqua Regia by Hollow Fiber Supported with Liquid Membrane

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(Received 28 April 2003 • accepted 21 July 2003)

Abstract—This research study was aimed at recovering palladium from used aqua regia by means of a hollow fiber thoroughly supported with liquid membrane. The liquid membrane, consisting of two extractants—thioridazine•HCl and oleic acid-solubilized in chloroform—was used to coat the microporous hollow fiber throughout. Sodium nitrite, a stripping agent, which was fed through the shell side, flowed counter-currently with the feed solution fed via the tube side. The following factors were investigated: the concentrations of the two extractants and of sodium nitrite, the pH of used aqua regia, the flow rates of both the feed and stripping solution, and the number of runs in the hollow fiber module. It was found that after a 30-minute operation, 29.10% of palladium ion was optimally recovered at 0.0005-M thioridazine and 0.05-M oleic acid. With reference to the precious metals recovered, the following order was recorded: Pd(II) > Pt(IV) > Cu(II) > Au(III). It was observed that synergistic extraction could be gained at the concentration level of the extractants, regulated in the experiment. The liquid membrane system had long-term stability and even after the third run, it could still recover palladium up to 65%.

Key words: Palladium, Recovery, Hollow Fiber, Liquid Membrane, Synergistic Extraction

INTRODUCTION

Environmental problems are among the most crucial issues facing the world today. Hence, it is deemed appropriate that indepth research studies must be carried out to help find ways either to eliminate or lessen the problems. One good example is the recycling of industrial wastewater so that it becomes environmentally friendly and, at the same time, precious metals can be recovered and reused in the industry. This will certainly enhance the industry's production process and reduce its costs.

Palladium, known as a precious or noble metal, has been increasingly used in various industries [Rizvi et al., 1996], for instance, automotive industries, electronics industries, and those producing dental tools, ornaments, wear-resistant alloys, and petrochemical and catalyst processes [Kakoi et al., 1996]. Due to its related properties, however, the ordinary separation of palladium from other noble metals cannot be efficiently achieved [Tavlarides et al., 1987]. Solvent extraction, which has been well known for some time now, is usually used as a metal recovery process on an industrial scale. Nevertheless, there are several disadvantages that cause the solvent extraction process to be less efficient. The key obstacles include its limitation of extractability, sheer bulk of solvent consumption, multi-staged operations, relatively slow extraction rate, and extensive mass-transfer area requirements. With the development of so-called liquid membranes, the above obstacles disappear. In addition, using a liquid-membrane process requires only a small amount of power.

Recently, several researchers have focused their attention on the applications of various liquid-membrane processes in palladium recovery - bulk liquid membrane [Rizvi et al., 1996; Farhadi and

Shamsipur, 2000], emulsion liquid membrane [Kakoi et al., 1996, 1997; Tavlarides et al., 1987], and flat-sheet-supported liquid membrane [Fu et al., 1995, 1997; Antico et al., 1994; Rovira and Sastre, 1998]. However, few studies have been done on the application of hollow-fiber supported by liquid membrane that contains two types of extractants. In the past, the findings of most research studies of this nature could not be applied for a large scale and multi-component metal ions in source phase. Unlike the past research studies, this indepth laboratory experiment was aimed at the recovery of palladium from palladium-rich, used aqua regia by using a hollow-fiber thoroughly supported with a liquid membrane that contains two kinds of extractants. It is hoped that this contribution will be of benefit not only for work in laboratories but also for genuine application of the process in industries.

EXPERIMENTAL

1. Reagents

Reagent-grade thioridazine•HCl, TRHCl (Sigma-Aldrich Co., Ltd.) and oleic acid (Carlo Erba Co., Ltd.) used as the organic liquid membrane, were dissolved in analytical grade chloroform solvent (APS Chemical Ltd.). Sodium nitrite (APS Chemical Ltd.) was used as the stripping agent. Greatest Gold & Refinery Ltd. (Thailand) kindly supplied the palladium-rich, used aqua regia. All other chemicals, which were of highest purity, came from Merck. Doubly deionized water was used throughout the experiments.

2. Apparatus

Extraction and stripping processes occurred within the Liqui-Cel® Liquid/Liquid Extraction System (Hoechst Celanese Corporation, model Cat. #5PCM-106), which contained many hollow fibers (model Celgard® x-30 240Microporous Polypropylene). The atomic absorption spectrophotometer used for the measurement of metal

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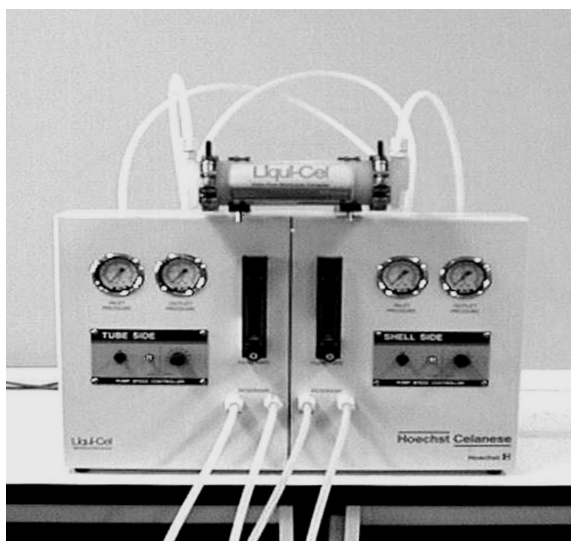


Fig. 1. Extraction apparatus of hollow fiber supported with liquid membrane.

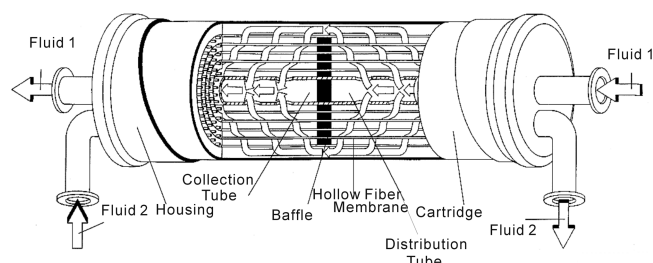


Fig. 2. Hollow fiber module.

concentration in the aqueous phase was a Varian® AA-Spectra Ten-plus instrument. The atomic absorption measurements were carried out under the recommended conditions for each metal ion. The pH values of solutions were measured by a digital pH meter (Jenco, model 60).

3. Procedure

All experiments were carried out at ambient temperature. First, a liter of chloroform liquid membrane, containing 0.0005 M thioridazine•HCl and 0.05 M oleic acid, was fed into the tube side and shell side. It was left for 30 minutes to make sure that the liquid mem-

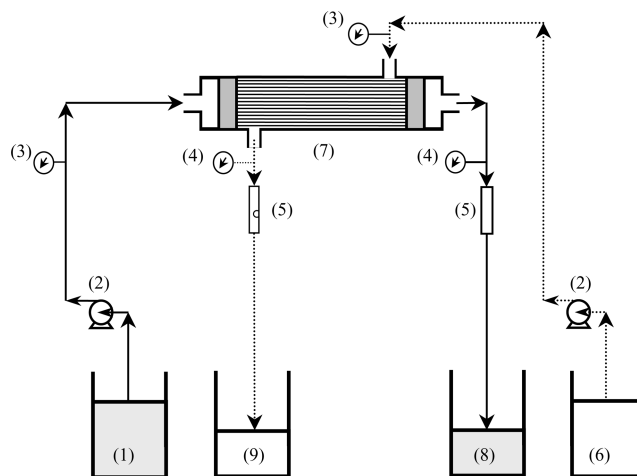


Fig. 3. The characteristics of operation.

- | | |
|---------------------------|-----------------------------------|
| (1) Feed tank | (6) Stripping solution tank |
| (2) Pump | (7) Hollow fiber supported module |
| (3) Inlet pressure gauge | (8) Raffinate tank |
| (4) Outlet pressure gauge | (9) Concentrated solution tank |
| (5) Flow meter | |

brane impregnated all the hollow fiber pores. In order to prevent the concentration polarization, used aqua regia, filtered with the filter papers (Whatman 42) by a vacuum pump, was diluted 100 times with doubly deionized water. The pH of source phase was adjusted to 2 with sodium hydroxide. Then 5 liters of used aqua regia was fed through the hollow fiber and 5 liters of sodium nitrite was simultaneously pumped in around the hollow fiber. The flow rate of both streams was 100 ml/min. The operating time lasted 30 minutes. Determination of the metal ion concentration in both aqueous phases was carried out by AAS. Detailed conditions are included in the graphs of the text. The illustrative example of operation is shown in Fig. 3.

RESULTS AND DISCUSSION

1. The Effects of TRHCl Concentration

The mass-transfer mechanism of palladium ion through the liquid membrane is shown in Fig. 4. The reaction of PdCl_4^{2-} ion in the feeding solution and TRHCl in the liquid membrane yields a stable complex compound [Deshmukh and Kharat, 1976; Gowda and

Table 1. The characteristics of hollow fiber

Characteristics	Dimensions
Fiber type	Polypropylene
Fiber internal diameter	240 μm
Fiber outer diameter	300 μm
Effective pore size	0.05 μm
Hollow fiber porosity	30 %
Maximum transmembrane differential pressure	4.2 Kg/cm ² (60 psi)
Effective surface area	1.4 m ² (15.2 ft ²)
Effective area/volume	29.3 cm ² /cm ³ (74.4 m ² /m ³)
Maximum operating temperature	1 °C to 60 °C
Housing size	8×28 cm (2.5×8 inch)

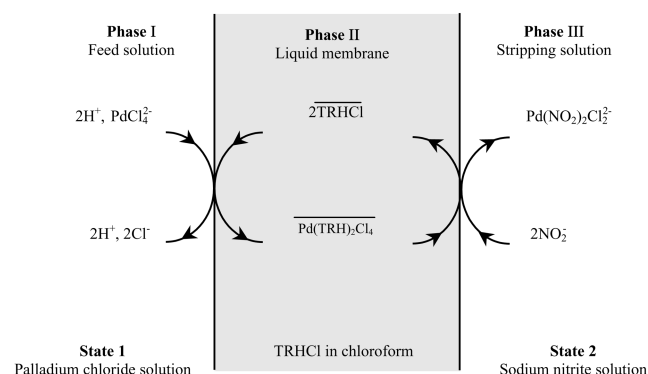
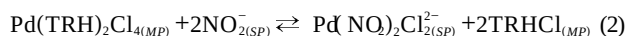
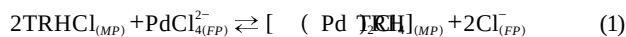


Fig. 4. Transport mechanism of palladium ion in liquid membrane.

Padmaji, 1978; Gowda et al., 1997]. Then the formed complex compound diffuses itself from the liquid-membrane phase to the stripping-solution phase with a concentration gradient as a driving force. It reacts with the stripping agent to form a complex compound of $[\text{Pd}(\text{NO}_2)_2\text{Cl}_2]^{2-}$. TRHCl is released and, with a concentration gradient as a driving force, diffuses back to the feeding-solution phase [Yi, 1995]. The mechanism of these chemical reactions repeatedly occurs as in the following illustrations.



The effects of TRHCl concentration can be determined by varying the concentration of TRHCl and keeping the amount of other constituents constant. The results are shown in Fig. 5 and Fig. 6. From Fig. 5, when the concentration of TRHCl increases from 0.000125 M to 0.0005 M, the metal ions dissolved in used aqua regia are increasingly extracted. This phenomenon is consistent with Henry Louis Le Chateliers theory. The extraction sequence of the metal

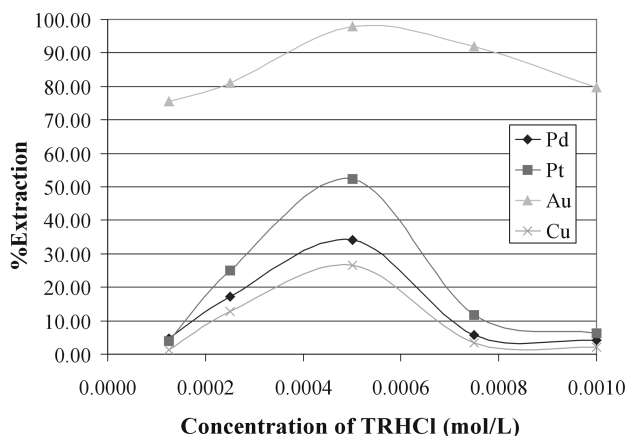


Fig. 5. The effect of TRHCl concentration on the extraction of metal ion. Feed: pH 2. Liquid membrane: 0.05 M oleic acid in chloroform. Strip: 0.03 M NaNO_2 .

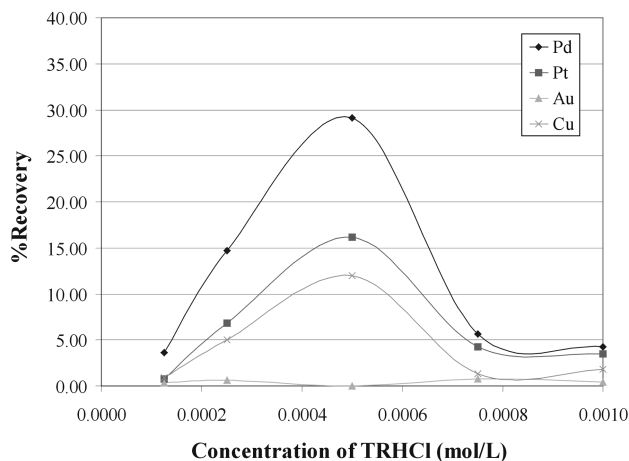
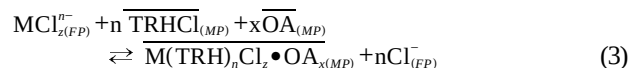


Fig. 6. The effect of TRHCl concentration on the recovery of metal ion. Feed: pH 2. Liquid membrane: 0.05 M oleic acid in chloroform. Strip: 0.03 M NaNO_2 .

ions can be shown as the following: $\text{Au(III)} > \text{Pt(IV)} > \text{Pd(II)} > \text{Cu(II)}$. This is so because the gold ion can interact with only one mole of TRHCl extractant, whereas the other metal ions can do with two moles of TRHCl extractants. The other metal ions can be transcribed by the following equation of TRHCl and oleic acid (OA) extractants.



Note: MCl_z^{n-} can be replaced by PdCl_4^{2-} , PtCl_6^{2-} , and CuCl_4^{2-} .

This equation is called “synergistic extraction” [Ramakul and Pancharoen, 2003]. Because Pt(IV) has ionic radius longer than Pd(II) and Cu(II), Pt(IV) can appear more in the synergistic extraction [Jeong and Ju, 2002; Farbu et al., 1974; Mathur, 1983].

When the concentration of TRHCl extractant is over 0.0005 M, the metal ions can be decreasingly extracted. This is so because the viscosity of liquid membrane solution increases [Patthaveekongka, 1999]. Another possible reason is the combination of TRHCl extractants that occur in the third phase. It may hinder the diffusion of met-

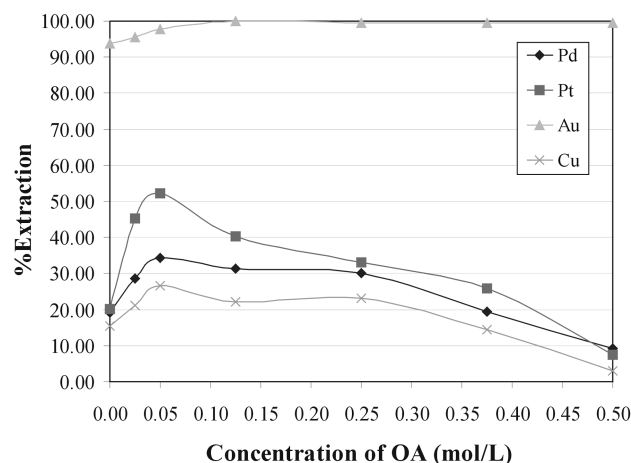


Fig. 7. The effect of OA concentration on the extraction of metal ion. Feed: pH 2. Liquid membrane: 0.0005 M TRHCl in chloroform. Strip: 0.03 M NaNO_2 .

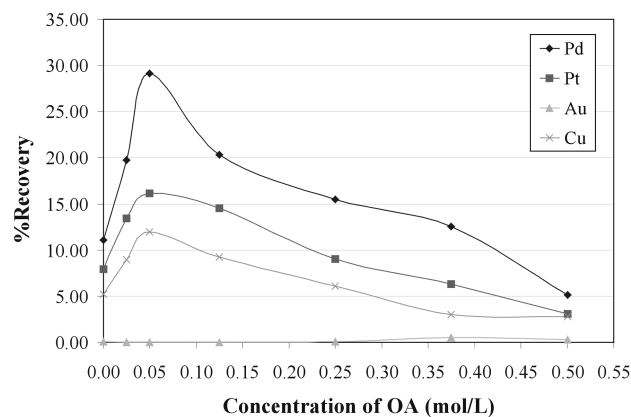


Fig. 8. The effect of OA concentration on the recovery of metal ion. Feed: pH 2. Liquid membrane: 0.0005 M TRHCl in chloroform. Strip: 0.03 M NaNO_2 .

al ions [Tarlarides et al., 1987].

As for the stripping (see Fig. 6), it is found that the optimized concentration of TRHCl extractant is 0.0005 M when Pd(II) is stripped best. It is so because it can interact with the stripping solution, NaNO_2 , better than the other metal ions [Farhadi and Shamsipur, 2000].

2. The Effects of Oleic Acid Concentration

The effects of oleic acid (OA) concentration were investigated by keeping the TRHCl concentration constant at 0.0005 M. The results are shown in Fig. 7 and Fig. 8. In Fig. 7, it is found that the metal ions can be increasingly extracted when the OA concentration increases from 0.00 M to 0.05 M. This is because synergistic extraction occurs, and as a matter of fact oleic acid can improve the efficiency of TRHCl extractant [see Eq. (3)]. Another possibility is that the OA forms an inverse micelle [Rosen, 1978; Myers, 1988] inside, and at the same time the carrier molecules may be trapped. The TRHCl may then be easily transported across the liquid membrane inside the inverse micelle.

When the OA concentration is over 0.05 M, the metal ions are decreasingly extracted. This is because the viscosity of liquid membrane increases or else OA and TRHCl extractants may self-interact. This phenomenon is called "Antagonism," as illustrated by the following equation [Mathur, 1983]:



As for the stripping in Fig. 8, it is found that the optimized OA concentration is 0.05 M, at which palladium ion can be stripped the most.

3. The Effects of the pH of Feed Solution

The influence of the pH of the feed solution on the efficiency of Pd(II) recovery was studied with the 0.5 to 2.2 pH range, adjusted by sodium hydroxide. The results are shown in Fig. 9.

In Fig. 9, when the pH of feed solution increases from 0.5 to 2.0, the recovery efficiency of metal ion also increases. A decrease of concentration of Cl^- ion results in an increase of extraction of metal-TRHCl complex within the liquid membrane [see Eq. (1)]. But at a higher pH, Pd(II) is almost diminished. This is because the complex $\text{Pd}(\text{TRH})_2\text{Cl}_4$ is stable in strongly acidic media [Gowda et al., 1975, 1997]. Thus, the maximum palladium recovery occurs at pH

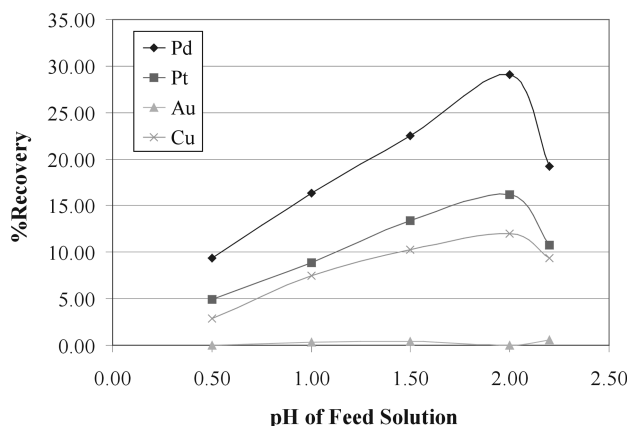


Fig. 9. The effect of pH of the feed solution on the recovery of metal ion. Liquid membrane: 0.0005 M TRHCl and 0.05 M of OA in chloroform. Strip: 0.03 M NaNO_2 .

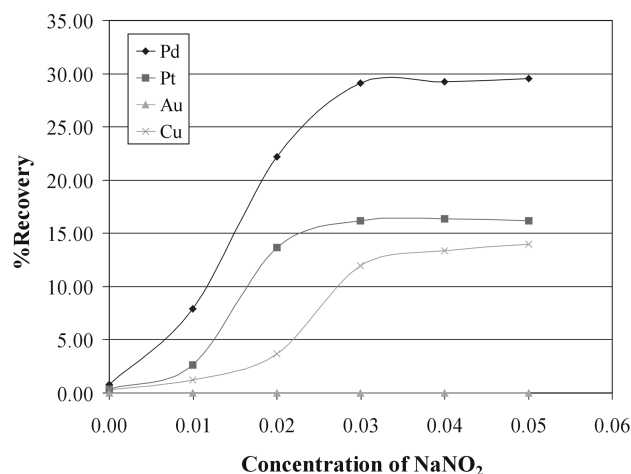


Fig. 10. The effects of NaNO_2 concentration in the receiving phase. Feed: pH 2.0. Liquid membrane: 0.0005 M TRHCl and 0.05 M OA in chloroform.

of about 2, while at some lower or higher pH values a decrease of transport efficiency is observed.

4. The Effects of NaNO_2 Concentration in the Receiving Phase

Farhadi and Shamsipur [2000] found the use of NO_2^- ion as the stripping ligand in the receiving phase caused a large enhancement in the efficiency and selectivity of Pd^{2+} ions, while the presence of other receiving agents such as thiourea, SCN^- , $\text{S}_2\text{O}_3^{2-}$, and EDTA resulted in a pronounced decrease in the efficiency of palladium transport. Thus, in this research the use of NaNO_2 as the stripping agent was investigated and the results are shown in Fig. 10. Pd(II) is about 30% recovered within the 0.03 to 0.05 M NaNO_2 range with the optimized concentration of NaNO_2 is 0.03 M.

5. The Effects of the Number of Runs through Hollow Fiber Module

In the liquid membrane system, the solutions containing the expensive carrier - TRHCl for this research - could be used by various industries to reduce operating costs and improve process efficiency. Therefore, the possibility of a number of runs through the hollow fiber module was investigated. Fig. 11 shows the effects of the number of runs through the hollow fiber module on the recovery of pal-

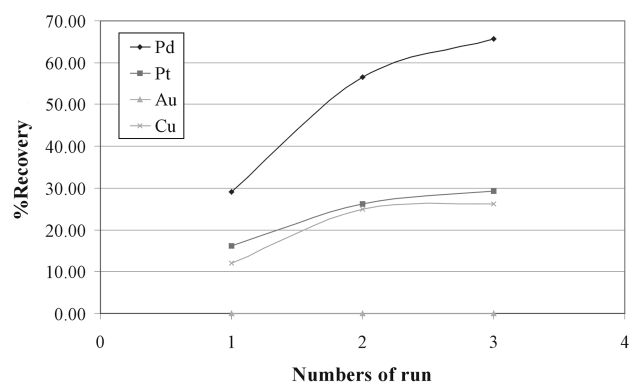


Fig. 11. The effects of the number of runs through hollow fiber module. Feed: pH 2.0. Liquid membrane: 0.0005 M TRHCl and 0.05 M OA. Strip: 0.03 M NaNO_2 .

ladium. It increases sharply as the number of runs increases. This is because palladium ion can be stripped more with NaNO_2 than any other metal ion. In addition, this liquid membrane system has good stability. Although it underwent 3 runs continuously, it could still recover palladium up to 65%.

CONCLUSION

It can be concluded that the hollow fiber supported with liquid membrane extraction system can separate and/or recover palladium ions from used aqua regia. The liquid membrane was produced by mixing two kinds of extractants - TRHCl & OA - together. Then, it was dissolved in an organic solvent - chloroform. These two extractants reinforce each other and make extraction become more efficient. The so-called synergistic extraction state occurs when the concentration of TRHCl equals 0.0005 moles, and OA, having been dissolved in chloroform, equals 0.05 moles. The appropriate pH of the feed solution and the concentration of sodium nitrite in the stripping solution must be at 2 and 0.03 moles respectively.

The results clearly indicate the potential use of hollow fiber supported with liquid membrane to help extract many different kinds of precious metals both for commercial purposes and for the purpose of environmental conservation. It can also be applied to the separation of herbal substances that usually exist naturally in low content. This would be most beneficial for the making of cosmetics, health foods and pharmaceutical products.

ACKNOWLEDGMENT

The authors wish to thank the Graduate School from Chulalongkorn University for granting a partial research fund and also thank The Greatest Gold & Refinery Ltd. (Thailand) for supply of used aqua regia.

NOMENCLATURE

M : mole
OA : oleic acid
TRHCl : thioridazine•HCl

Subscripts

FP : feed phase
MP : membrane phase
n, x, z : among mole balance
SP : stripping phase

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