

## **Extraction of rhodium from platinum solutions in presence of aluminum chloride with tri-octylphosphine oxide in toluene**

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### **ABSTRACT**

Solvent extraction of rhodium(III) and platinum(IV) in 2 M hydrochloric acid with tri-octyl phosphine oxide (TOPO) was found to be substantially changed after addition of aluminium chloride to the aqueous solution. The extraction of the two metal ions was as low as 45 and 22 %, respectively, in absence of AlCl<sub>3</sub>. Rh(III) extraction drastically increased with increasing AlCl<sub>3</sub> concentration to reach > 95% in 2M, while that of Pt(IV) sharply decreased to reach almost 0.0 in 0.5 M. This behavior may be related with steric effect created by interaction between AlCl<sub>3</sub> as Lewis acid and chloro species of metal ions as Lewis bases. These findings have been utilized to separate Rh from Pt in a real leach liquor originally contains AlCl<sub>3</sub>. The extraction of Rh reached about 57% after 3 hours, while that of Pt was neglected along with time. Nearly quantitative extraction of Rh(III) was obtained by increasing HCl concentration to 3 M for only 2 min mixing time. Rh(III) was stripped from TOPO and precipitated in 2 M KOH.

**Keywords:** Solvent Extraction, Platinum, Rhodium, Separation, Recovery, stripping, Tri-octyl phosphine oxide, TOPO.

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### **INTRODUCTION**

Platinum group metals (PGMs) are in extensive use for catalysis reactions, electronic devices, space materials, etc. The PGMs are increasingly employed for the manufacture of auto exhaust catalysts. The high cost and increasing demand has prompted the recovery of PGMs from spent catalysts and low grade ores. The separation and purification of these metals from their solutions is one of the difficult areas in precious metals refining, mainly due to their complex solution chemistry [1,2]. Solvent extraction is a promising separation technique based on the control of the type of metal species in aqueous phase in presence of some additives [3] Several publications are found dealing with solvent extraction of PGMs from chloride media using different organic reagents such as Tributyl phosphate (TBP), trioctyl amine (TOA) [4] and others. A series of organophosphorous compounds have been marketed under the trade name of Cyanex (272, 301, 302) as acidic extractants for metal ions, and Cyanex (921, 923, 925) as neutral extractants [5,6] which are found to be superior extractants for precious metals. Existence of several number of species makes the quantitative removal and separation of Rh salts difficult, and careful control of solution conditions is essential. To date, no industrial solvent extraction system has been published for Rh. The more classical methods used for its recovery are inefficient, because these techniques are based on several precipitation/dissolution stages to achieve the desired degree of purity.

Pt(VI) and Rh(III) form varieties of chloro-complexes in acidic chloride media. Anionic, neutral and cationic chloro species can be formed depending on the chloride ion concentration. Pt(VI) and Rh(III) are known to mostly extracted into the organic solutions in the form of anionic species. These anions can be considered as Lewis bases in

aqueous solution. On the other hand,  $\text{AlCl}_3$  is known as a strong Lewis acid and can easily interact with these Lewis bases. Therefore, addition of  $\text{AlCl}_3$  to the aqueous solution of these metal ions may affect their extraction.

Aluminium chloride have been used as an alternative to hydrochloric acid for leaching PGMs from spent catalysts [7]. In a separate study, we have examined this technique where almost all Pt and Rh could be dissolved out of a dust waste accumulated in nitric acid production plant, in a mixture of 2 M  $\text{AlCl}_3$  and 2 M  $\text{HNO}_3$  [8]. The leach solution contains Pt and Rh and other impurities. The aim of the present work is concentrated on extraction and separation of Pt and Rh from their solution that obtained from  $\text{AlCl}_3$ - $\text{HNO}_3$  leaching of the Pt dust. Cyanex 921 (tri-octylphosphine oxide, TOPO) will be used as organic phase based on its tendency for the extraction of Pt and Rh from their pure solutions.

## MATERIALS AND METHODS

### Sample collection and leaching

A 1Kg of platinum dust have been collected from reactors of nitric acid production in The Egyptian Chemical Industries Company - KIMA. The dust contained mainly iron oxides,  $\text{SiO}_2$ , Pt and Rh. A 5 gm dust sample was leached with a solution of 2M  $\text{AlCl}_3$  and 2M  $\text{HNO}_3$  at boiling conditions for 45 min., with a solid/liquid ratio of 1 : 200 g/ml. Both Pt and Rh dissolved quantitatively. A stock leach solution of about 1L was prepared and used for separation of Pt and Rh by solvent extraction. The metal concentrations in this solution are shown in Table 1. This leach liquor contained 550 ppm Pt(IV) and 50 ppm Rh(III) where the main metallic impurity, other than Al, is Fe (430 ppm).

Table 1: Metal concentrations in leach liquor of platinum dust

Metal	Pt	Rh	Fe	Ni	Cr	Cu	Mn	Al
ppm	550	50	430	26	15	5.6	4.8	2*

\* Molar concentration

### Reagents

Cyanex 921 (Fluka) was used as organic extractant without further purification. The active component of Cyanex 921 is tri-octylphosphine oxide, TOPO, 90%, (see Fig.1). Different concentrations of Cyanex 921 were prepared by dissolving appropriate amounts of Cyanex 921 in toluene (ADWIC). Analytical grade hydrochloric acid, 37% (Panreac), with different concentrations, was used as an aqueous medium in solvent extraction experiments. Different concentrations of tin(II) chloride solution were prepared by dissolving  $\text{SnCl}_2$  (MERCK) in minimum amount of HCl and diluting with doubly distilled water. Perchloric acid, 70% (GR, LOBA CHEMIE PVT. LTD., INDIA), was mixed with hydrochloric acid in different concentrations for stripping of Pt. Potassium hydroxide, (MERCK), was dissolved in doubly distilled water and used in precipitation stripping of Rh.

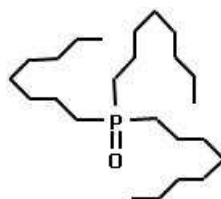


Figure 1. Chemical structure of tri-octyl phosphine oxide, TOPO

### Procedure

**Extraction:** A 10 ml of aqueous phase was prepared by mixing 5 ml of the leach solution containing Pt & Rh with 5 ml of doubly distilled water or with 5 ml HCl of the desired concentration. Stannous chloride ( $\text{SnCl}_2$ ) with required concentration was added to the latter 5 ml when desired. The organic phase was prepared by dilution of TOPO with toluene to the desired concentration. In a sealed 50 ml glass bottle, the 10 ml of the aqueous phase was shaken with equal volume (or otherwise mentioned) of the organic phase in water bath shaker (model GFL 1083) at  $30^\circ\text{C}$  for the desired time. After elapse of extraction time, the two phases were allowed to separate and the metal ion concentration in the aqueous phase was determined using Atomic Absorption Spectrometer (AAS) model Perkin Elmer A Analyst 200, and the metal concentration in the organic phase was calculated by mass balance of the metal before and after extraction. The metal extraction percentage was calculated as follows:

$$\text{Extraction efficiency \%} = \frac{[M]_i - [M]_a}{[M]_i} \times 100$$

where  $[M]_i$  is the initial metal concentration in the aqueous phase, and  $[M]_a$  is the metal concentration in the aqueous phase after extraction.

*Stripping:* Aqueous solutions of KOH or of HCl/HClO<sub>4</sub> mixture with the desired concentrations were used for stripping of Rh and Pt from their organic loaded solutions, respectively. A 10 ml (or otherwise mentioned) of the loaded organic phase was shaken with 10 ml of the aqueous phase in a sealed 50 ml glass bottle using. After elapse of stripping time, the two phases were allowed to separate and the metal ion concentration in the aqueous phase was determined by AAS. The stripping efficiency was calculation as follows:

$$\text{Stripping efficiency \%} = \frac{[M]_s}{[M]_i - [M]_a} \times 100$$

where  $[M]_s$  is the metal concentration in the strip aqueous phase after stripping.

## RESULTS AND DISCUSSION

### Effect of aluminum chloride on solvent extraction of Pt and Rh

A series of experiments were carried out to demonstrate the effect of aluminum chloride addition to the aqueous solution on the extraction of Pt(IV) and Rh(III) with TOPO. Figure 2 shows the effect of increasing amounts of AlCl<sub>3</sub> (up to 2 M) on the extraction of Pt(IV) and Rh(III) from a synthetic solution containing 2M HCl into 150 mM TOPO in toluene. The extraction was conducted for 5 min with a liquid / liquid ratio of 1 / 1 at 30 °C. It can be seen from Fig. 2 that about 46% of Pt(IV) was extracted in absence of AlCl<sub>3</sub>, and the extraction sharply decreased to about 6% with increasing AlCl<sub>3</sub> concentration to 0.1 M. The Pt(IV) extraction further decreased at higher concentrations of AlCl<sub>3</sub> and became practically un-extracted at 0.5 M AlCl<sub>3</sub> and higher concentrations. On the other hand, the extraction efficiency of Rh was about 23% in absence of AlCl<sub>3</sub>, and this value significantly increased with increasing the AlCl<sub>3</sub> concentration, reached about 80% at 0.25 M AlCl<sub>3</sub> and further increased to 96 % at 2M AlCl<sub>3</sub>.

To confirm that the reason for the above extraction behavior of Pt(IV) and Rh(III) is only due to the presence of AlCl<sub>3</sub>, we examined the effect of increasing amount of AlCl<sub>3</sub> on the analytical measurements of these two metals by atomic absorption spectrometer (AAS). It is known that in some cases, background elements in aqueous solutions interfere with the measured elements. A series of solutions containing 40 ppm Pt(IV) and 40 ppm Rh(III) and different concentrations of AlCl<sub>3</sub> were prepared and the Pt and Rh contents were measured by AAS. The results showed that analytical measured values of Pt and Rh were between 39.79 and 40.15 ppm. Thus, AlCl<sub>3</sub> neither interfered with the measurements of Pt nor with that of Rh.

It is known that, extraction of metals into TOPO mostly followed the solvation mechanism. In general, the predominant Pt(IV) species in acidic chloride solutions is  $[\text{PtCl}_6]^{2-}$ . The low Pt(IV) extraction with TOPO can be explained on the bases of the low lability of the metal in the form of Pt(IV) due to the steric effect [9]. The trihalides (fluorides excepted) of aluminum are strong Lewis acids, and this is one of the most important aspects of their chemistry [10]. Therefore, aluminum chloride in the leaching solution is present in the form of  $[\text{AlCl}_4]^-$  anions, consequently, the Pt complex, might has the proposed form as  $[\text{Pt}(\text{AlCl}_4)_6]^{2-}$ . Thus, primarily keeping in mind the low lability of Pt(IV) species, according to this proposed mechanism, the steric effect established due to the presence of six  $[\text{AlCl}_4]^-$  anions related to the Pt species prevented the Pt complex to pack two cationic organic molecules around the single complex anion.

The speciation diagram of Rh chloride complexes at varying the chloride ion concentration was constructed using Stabcal software as shown in Figure 3, utilizing the free energy of these complexes shown in Table 2.

The species of Rh varies depending on the chloride ion concentration and the pH value. The general formula is  $[\text{RhCl}_{6-n}(\text{H}_2\text{O})_n]^{n-3}$ , where n varies from 0 to 6 [2] which in turn affect the Rh extraction efficiency. At high chloride concentration (> 2M) the dominant Rh species are  $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$  and  $\text{RhCl}_6^{3-}$ .

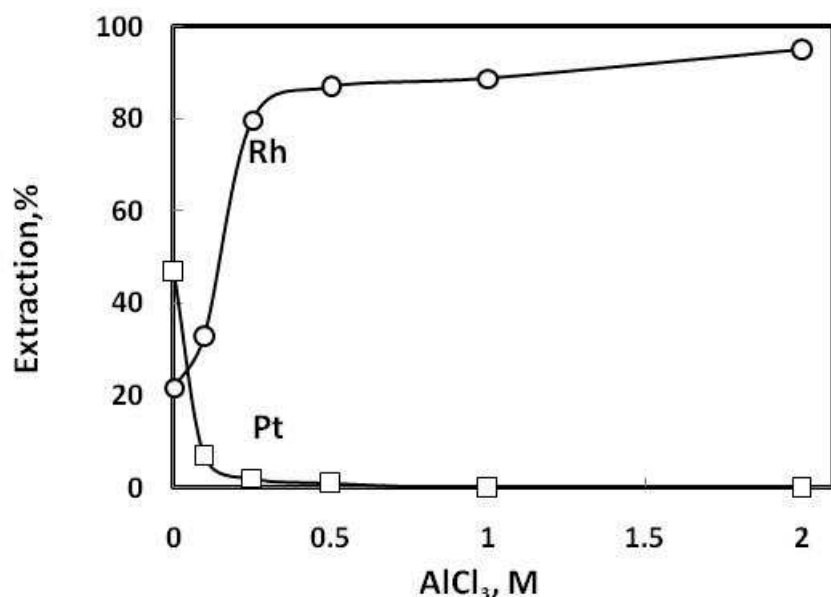


Figure 2. Effect AlCl<sub>3</sub> concentration on extraction of Pt(IV) and Rh(III) from synthetic solution. Aqueous phase : 40 ppm Pt and 40 ppm Rh in 2 M HCl. Organic phase : 150 mM TOPO in toluene. 5 min, L/L = 1/1, 30 °C

#### Effect of extraction time

Solvent extraction experiments were conducted to separate Pt and Rh from the aqueous leach solution of the platinum dust with 150 mM TOPO in toluene at 30 °C. The acidic leach liquor that produced from leaching of platinum dust (contained 550 ppm Pt, and 50 ppm Rh) was diluted with equal volume of double distilled water. Thus, the initial concentrations of Pt and Rh in the aqueous phase before the solvent extraction experiments were 275 ppm and 25 ppm, respectively. The aqueous solution also contained the residual amounts of AlCl<sub>3</sub> and HNO<sub>3</sub> those have been left in the aqueous phase after leaching of the platinum dust. Figure 4 shows the extraction behavior of Pt and Rh from this real leach solution as a function of time. It can be noticed that, the extraction percentage of Pt was neglected along with time even up to 180 min. However, the extraction of Rh gradually increased with time and reached 47% at 60 min and then very slowly increased. These results are in consistent with those obtained in Figure 2, where the presence of the residual amount of AlCl<sub>3</sub> in the leach liquor may be the reason for the suppression of Pt extraction and the simultaneous enhancement of Rh extraction. The unsatisfactory extraction of Rh may be related to the presence of Rh in the form of highly aquated complexes which are less labile [2].

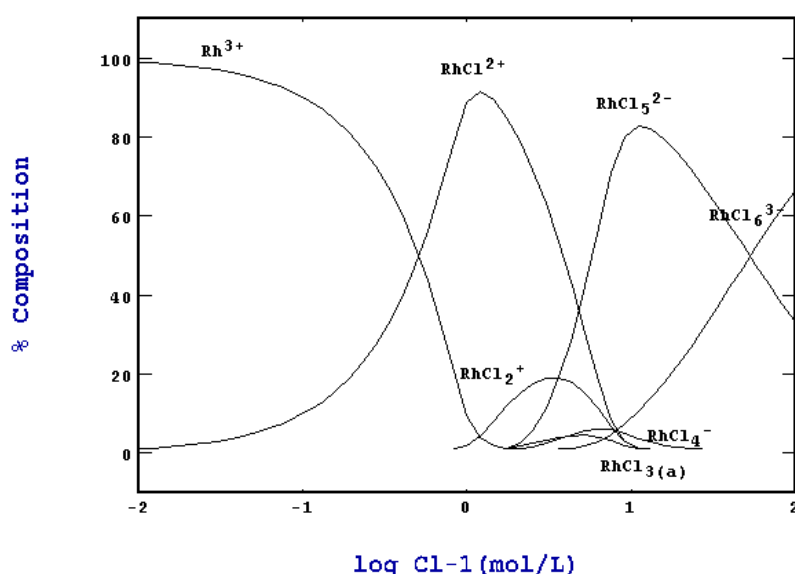


Figure 3. The calculated distribution graph of Rh species as a function of free chloride concentration

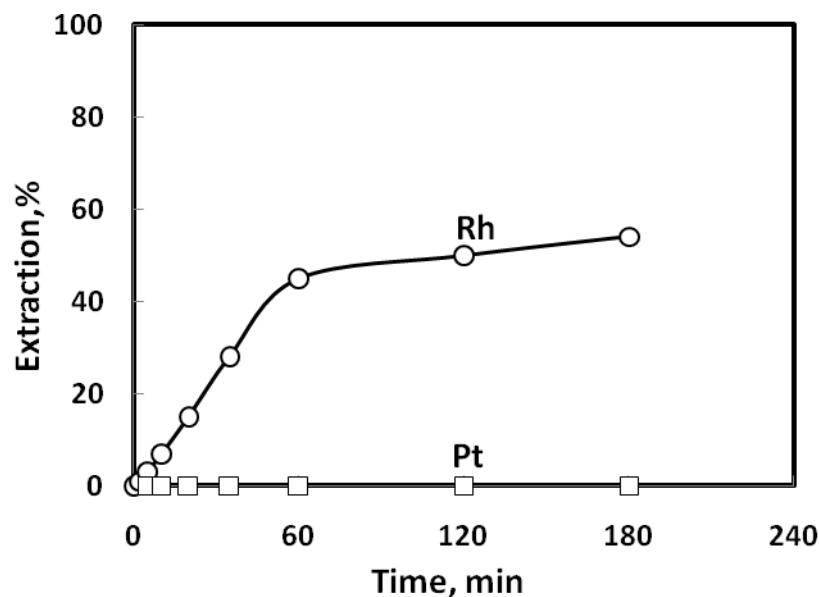


Figure 4: Effect of time on extraction of Pt and Rh from leach liquor. Organic phase: 150 mM TOPO in toluene. 30 °C and L/L = 1:1

Table 2: Free energy values of rhodium chloride complexes

Rhodium complex	Free energy (k cal/ mole)
Rh <sup>3+</sup>	52.45
RhCl <sup>2+</sup>	17.74
RhCl <sub>2</sub> <sup>+</sup>	-13.1294
RhCl <sub>3</sub>	-43.52
RhCl <sub>4</sub> <sup>-</sup>	-74.5886
RhCl <sub>5</sub> <sup>2-</sup>	-106.5529
RhCl <sub>6</sub> <sup>3-</sup>	-135.29

#### Effect of hydrochloric acid concentration

It has been stated that, the extraction behavior of the PGM changed completely at different hydrochloric acid concentrations due to the existence of different chloro-complexes chemistry. Firstly, the extraction of Pt and Rh from the leach liquor has been tested in the presence of 4 M HCl at different contact time, Figure 5. The extraction of Rh sharply increased with time and reached about 85% after only 2 min and remained at this high value at longer time. At high Cl<sup>-</sup> concentration such as 4M, the aquation ratio of Rh complexes decreased leading to enhancement of the extraction efficiency. On the other hand, the presence of a high HCl concentration of 4 M had no effect on the extraction of Pt; the extraction remained at < 0.01% even after 150 min.

Figure 6 shows the extraction of Pt and Rh as a function of hydrochloric acid concentration in the range from 0 to 5 M. Other parameters were kept constant as; 275 ppm Pt, 25 ppm Rh in AlCl<sub>3</sub> aqueous phase, 150 mM TOPO, 30 °C, liquid/liquid ratio 1:1, and contact time of 2 min. Increasing the hydrochloric acid concentration stabilizes the [AlCl<sub>4</sub>]<sup>-</sup> anions, therefore, steric effect still prevents Pt extraction to the organic phase as shown in Figure 6 according to the previously proposed mechanism. Increasing the hydrochloric acid concentration up to 3M, increased the Rh extraction up to 99.7%. This is due to the decreasing of Rh chloro- complexes aquation with increasing in HCl concentration, which makes it more labile and hence enhances its extraction to the organic phase. It has been found that anionic complexes of Rh are more labile than those of other PGMs, whereas the cationic and neutral complexes are quite inert. In other words, increasing HCl concentration enhances the formation of anionic chloro-complexes of Rh (RhCl<sub>4</sub><sup>-</sup>, RhCl<sub>5</sub><sup>2-</sup>, RhCl<sub>6</sub><sup>3-</sup>). This can explain the trend of increasing Rh extraction with increasing the HCl concentration in Figure 5. Increasing the hydrochloric acid concentration more than 3M, enhances the formation of RhCl<sub>6</sub><sup>3-</sup> with three negative charge, which were particularly difficult to be extracted due to steric effects. It being difficult to pack three cationic organic molecules around a single anion. From another point of view, extraction of Rh decreases at higher concentration of hydrochloric acid, due to the mass action effect of counter chloride ions [6].

liquid / liquid ratio was 1:1, the temperature was 30°C for 2 min. As can be seen in Figure 7, Rh extraction gradually increased with increasing TOPO concentration. Near to complete extraction of Rh can be achieved with TOPO concentration in the range from 150 mM to 300 mM. No any increase in Pt extraction was observed with increasing the TOPO in the studied concentrations.

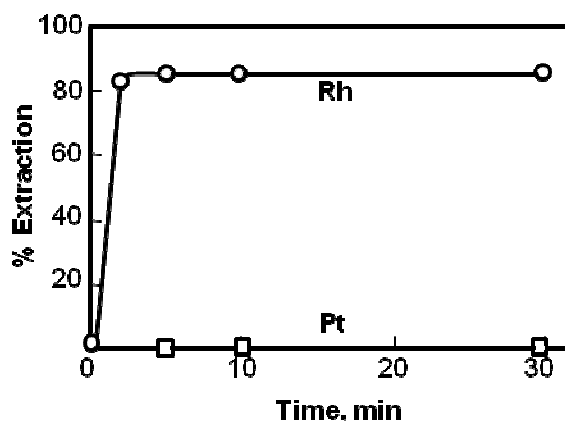


Figure 5: Extraction of Pt and Rh in 4M HCl org. phase, 150 mM TOPO & aq. phase, 275 ppm Pt, 25 ppm Rh & T 30 °C & l/l 1:1

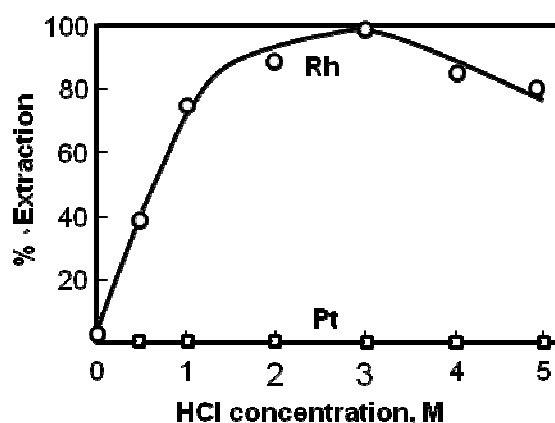


Figure 6: Effect of HCl concentration on extraction efficiency of Pt and Rh. organic phase, 150 mM TOPO, aqueous phase, 275 ppm Pt, 25 ppm Rh & T 30 °C & t 2min. & L/L = 1:1

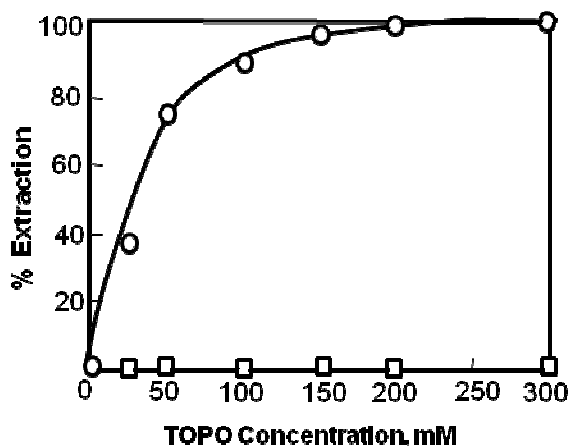


Figure 7: Effect of TOPO concentration on extraction of Pt and Rh. Aqueous phase: 3 M HCl, 275 ppm Pt, 25 ppm Rh. L/L ratio = 1:1 at 30°C for 2min

### Precipitation stripping of rhodium

Rhodium is known to form a yellow brown precipitate of a hydrolyzed species in alkaline solutions which is poorly extracted with organic reagents. Thus, utilizing alkaline solutions can be useful for Rh stripping from TOPO. Potassium hydroxide solution has been used here as a stripping precipitating agent for Rh from the loaded organic solution. Figure 8 shows the stripping efficiency of Rh as a function of potassium hydroxide concentration in aqueous phase. The experimental conditions were maintained constant at : liquid/ liquid ratio of 1:1, stripping time 5 min, at 30°C. The organic phase was loaded with 25 ppm Rh. It can be seen that, increasing the KOH concentration led to more removal of Rh from the organic phase with a maximum stripping efficiency (nearly 100%) at 2 M KOH.

Increasing the KOH concentration more than 2 M did not affect the stripping efficiency of Rh. It can be also seen from Figure 8 that the degree of Rh precipitation was also increased with increasing in KOH concentration up to 2M. Increasing in KOH concentration more than 4M led to the decrease in the amount of Rh hydroxide precipitate due to the dissolution of this in the excess KOH.

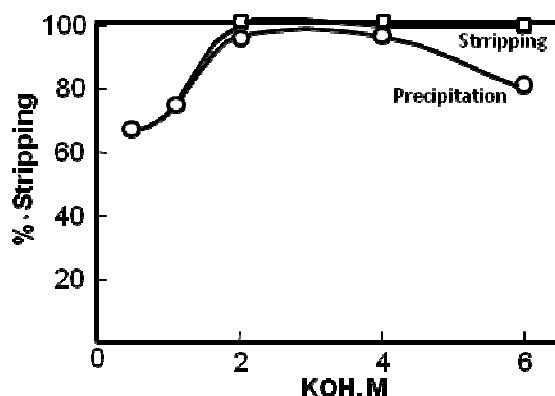


Figure 8: Stripping and precipitation efficiency of Rh as a function of KOH concentration. L/L ratio = 1:1, 5min, at 30 °C. The organic phase loaded with 25 ppm Rh

### CONCLUSION

Solvent extraction separation of Pt and Rh from acidic solution derived from leaching of Pt dust waste has been studied. The presence of aluminum chloride that is known as a strong Lewis acid, in the leaching solution retarded the extraction of Pt to the organic phase due to the steric effect but simultaneously enhanced the extraction of Rh. The extraction of Rh increased with increasing HCl concentration beyond 3 M. The loaded organic phase was treated with alkaline solution such as KOH for stripping of Rh.

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