

Process for the separation and recovery of palladium and platinum from spent automobile catalyst leach liquor using LIX 84I and Alamine 336

B. Ramachandra Reddy^{a,*}, B. Raju^a, Jin Young Lee^b, Hyung Kyu Park^b

^a Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Uppal Road, Hyderabad 500607, India

^b Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), 92 Gwahang-no, Yuseong-gu, Daejeon 305-350, Republic of Korea

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ABSTRACT

Spent catalysts from automobile industry contain environmentally critical and economically valuable metals such as Pt, Pd, Fe, Ni, Mn, and Cr. In this paper, we present a process for the selective separation and complete recovery of palladium (Pd) and platinum (Pt) from hydrochloric acid leach liquors of spent automobile catalyst employing solvent extraction method. Typical composition of leach liquor used for the present study contains (mg/L): Pd-150, Pt-550, Mn-500, Ni-1000, Fe-1500, Cr-100 and 3 M HCl. Selective separation of Pd from the leach liquor is achieved with 0.5 vol.% LIX 84I (2-hydroxy-5-nonylacetophenone oxime in a mixture with a high flash point hydrocarbon diluent) in kerosene at an aqueous to organic (A/O) ratio of 3 in 2 stages, with an enrichment factor of three. Quantitative stripping of Pd from loaded organic is achieved with 0.5 M thiourea and 1 M HCl. Co-extraction of Fe and Pt with 5 vol.% Alamine 336 (tertiary amine of mixed tri-octyl/decyl amine) in kerosene followed by selective scrubbing of Fe with dilute HCl and complete stripping of Pt from loaded organic was proposed with 0.5 M thiourea and 0.1 M HCl. Purity of Pd and Pt strip solutions are 99.7%. Finally, the present process can solve environmental related issues and at the same time recover valuable metals in pure form.

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1. Introduction

The main mineral sources of the platinum group metals (PGMs) are the copper-nickel ores, Sperrylite (platinum arsenide, PtAs₂), cooperite (platinum sulfide, PtS). The huge volume of nickel-copper ore processing makes the PGMs extraction profitable in spite of their low concentration in these ores. The PGMs are increasingly used in industry for various purposes such as dental applications, in electronic and electrical devices, in Jewellery and as catalysts, mainly in automobile exhaust emission control catalysts. Catalysts after a certain period of active life get deactivated and at this stage it is considered as a waste. Spent catalysts are harmful to the environment due to the presence of soluble/leachable organic and inorganic compounds [1,2] and as such their disposal in landfills is restricted. Recycling and recovery of spent automobile catalysts continues to provide a growing secondary source of PGMs production. Worldwide efforts are being made to recover and refine palladium (Pd) and platinum (Pt) from different spent materials [3], by an efficient and cost effective method. Furthermore, the potential environmental hazards of spent industrial and automotive catalysts call for putting

an emphasis on recovery and recycling policies for these waste materials.

Hydrometallurgical leaching of spent automobile catalysts with mineral acids in the presence of additives results in leach liquors containing free acid about 2–3 M, and precious metals and impurities such as Cr, Mn, Fe and Ni [4–7]. Traditional PGMs recovery methods involve physical treatment, acid dissolution, chemical separation and refining [8]. Recovery of PGMs are reported by classical precipitation methods [9,10] with a relatively poor selectivity, numerous unit operations, recycle streams and refining steps. On the other hand, hydrometallurgical leaching followed by solvent extraction (SX) separation of metals offer a number of advantages over the classical precipitation methods due to their higher selectivity, scrubbing step to achieve high metal purity, and complete removal of metals is possible through the use of multi-stage extraction [11].

Literature survey revealed that the solvent extraction of PGMs, in particular of Pd and Pt, have been reported extensively by many researchers from chloride media, mostly from synthetic solutions at low metal concentrations employing extractants such as TBP [12] amines [13–18], oximes [19–21], thio-phosphoric acid [22], phosphonic acid [23], thiophosphonic acid [24,25], TIBPS [26], sulphoxides [27–29]. Most of these studies report extraction behavior, temperature and extracted species. There are no reports on separation and recovery of Pd and Pt from hydrochloric acid leach solutions of spent automobile catalysts.

* Corresponding author. Tel.: +91 40 27193169; fax: +91 40 27160921.

E-mail addresses: drbrcreddy.iict@yahoo.com, brcreddy@iict.res.in (B.R. Reddy).

In this paper, we report the solvent extraction separation and recovery of Pd and Pt from a hydrochloric acid leach liquor of spent automobile catalyst by a simple, cost effective and environmental friendly process. Leach liquor used in this work, contain Pd and Pt ions along with base metal impurities such as Fe, Cr, Mn, Ni and 3 M HCl. Optimisation of process parameters include effect of extractant concentration, aqueous to organic phase ratio (A:O), counter-current extraction simulation (CCES), scrubbing, screening of stripping reagents, counter-current stripping simulation (CCSS) and flow sheet of the process.

2. Experimental

2.1. Apparatus

A PerkinElmer Atomic Absorption Spectrophotometer (AAS), model A 300 and Thermo fisher inductive coupled plasma optical emission spectrometer (ICP-OES), model IRIS Intrepid II XDL, was used to determine the metal ions in the aqueous solutions. A Wrist action shaker (Acmas Technocracy Pvt. Ltd, India) was used for extraction experiments and Digisun make digital pH meter (Model 707) was used for measurement of pH of the aqueous solution.

2.2. Reagents

Spent two way automobile catalyst sample used in the present study was first generation catalyst containing Pt and Pd, which was used 30 years ago for small cars. Leaching of spent catalyst was carried out with aquaregia followed by nitrate removal from leach liquor by heating.

Aqueous feed solution similar to leach liquor generated by the processing of spent two way automobile catalyst (1st generation automobile catalyst), containing Pd and Pt (PdCl₂, PtCl₂ Alfa Aesar, Johnson Matthew Company, London.) and other base metal impurities, Cr, Mn, Ni and Fe was prepared from respective metal salts (A.R grade K₂Cr₂O₇, MnCl₂·4H₂O from S.d fine-Chem Limited, NiCl₂·6H₂O from Loba Chemie Pvt.Ltd, and FeCl₃ (anhydrous) Finar chemicals Limited, India.) dissolved in Analar grade 3 M HCl. LIX 84I (2-hydroxy-5-nonylaceto-phenone oxime in a mixture with a high flash point hydrocarbon diluent) and Alamine 336 (tertiary amine of mixed tri-octyl/decyl amine) supplied by Cognis, Ireland were used as such without any purification. Distilled kerosene (b.p.: 160–200 °C), mostly aliphatic (96.2%), was used as diluent. Shakeout experiments were carried out in reagent bottles. All other chemicals were A.R grade.

2.3. Solvent extraction procedure

Suitable volumes of aqueous and organic phases (10 mL) were contacted for 5 min (initial experiments showed that equilibrium was reached with in 1 min) in reagent bottles. The phases were separated, Pt and Pd metal concentrations in the aqueous were determined by ICP-OES and Fe, Cr, Mn and Ni were determined by AAS. All the experiments were carried out at room temperature (30 ± 1 °C). The distribution ratio, *D*, was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From the *D* values, the percentage extraction ($%E = D \times 100 / (D + (V_{aq}/V_{org}))$) where *V*_{aq} and *V*_{org} are the volumes of aqueous and organic phases, respectively, and separation factor ($\beta = D_{M1}/D_{M2}$), *M*₁ represents Pd and *M*₂ represents other metals (Pt, Cr, Mn, Fe and Ni), were calculated. Experiments are conducted in duplicate and the percentage extraction of metals varied with in 3%. Initial tests on stripping of Pd with thiourea at O/A ratio of 1 and Pt at O/A ratio >1 showed hydrolysis of metal in strip solutions. As a result acidified thiourea was used for stripping studies of Pd and Pt from loaded organic phases and the strip

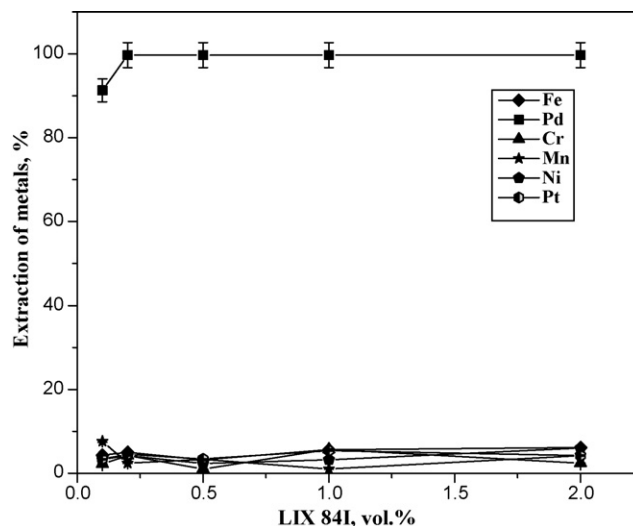


Fig. 1. Effect of LIX 84I concentration on the extraction of palladium and other metals. Palladium: 150 mg/L; HCl: 3 M.

solutions were analyzed for metal contents by ICP-OES after proper dilution, in order to determine the stripping efficiency of Pt and Pd.

3. Results and discussion

3.1. Separation and recovery of palladium

3.1.1. Variation of LIX 84I concentration on the extraction behavior of metals

The extraction behavior of Pd and other metals has been carried out with LIX 84I of different concentrations varied from 0.1 to 2 vol.% in kerosene. Quantitative extraction of Pd is possible with ≥0.2 vol.% LIX 84I, whereas the percentage extraction of other metals varied from 1 to 6% (Fig. 1). The corresponding Separation factor ($\beta = D_{Pd}/D_{mix}$) values of Pd increased from 50.7 to 2658.4 with increasing extractant concentration from 0.1 to 0.5 vol.% and decrease thereafter, due to increase in the percentage co-extraction of other metals (Table 1). 0.5 vol.% LIX 84I was chosen for the construction of extraction isotherm. Accordingly, McCabe–Thiele plot was obtained for the extraction of Pd with 0.5 vol.% LIX 84I at A:O ratios from 1:2 and O:A ratios from 1:7 (Fig. 2). The plot clearly suggests that 2 stages are required for quantitative separation of Pd at A/O ratio of 3, thereby showing possible enrichment of Pd concentration during extraction stage by 3 times. In order to confirm the extraction isotherm a prediction, a two stage counter-current extraction simulation test was conducted at A/O ratio of 3 and analysis of raffinate indicated 0.3 mg/L Pd, corresponding to an extraction efficiency of 99.8% (Fig. 3). Analysis of loaded organic phase contains 449.1 mg/L Pd and about 5 mg/L of other metals.

LIX 84I was used for the separation of Pd and Pt from associated metals like Fe, Cu, Ni, Zn, Al from synthetic solutions containing 1 g/L each of Pd and Pt. With 0.15 M LIX 84I Pd was extracted along with Cu around 2 pH. Aqueous phase pH increased to 9 with

Table 1
Separation factor of palladium with LIX 84I.

| | LIX 84I, vol.% | | | | |
|--------------------------|----------------|--------|--------|--------|--------|
| | 0.1 | 0.2 | 0.5 | 1.0 | 2.0 |
| <i>D</i> _{Pd} | 10.5 | 332.3 | 332.3 | 332.3 | 332.3 |
| <i>D</i> _{mix} | 0.207 | 0.197 | 0.125 | 0.216 | 0.223 |
| $\beta = D_{Pd}/D_{mix}$ | 50.7 | 1636.1 | 2658.4 | 1492.1 | 1445.3 |

$$D_{mix} = D_{Pt+Cr+MnNi}$$

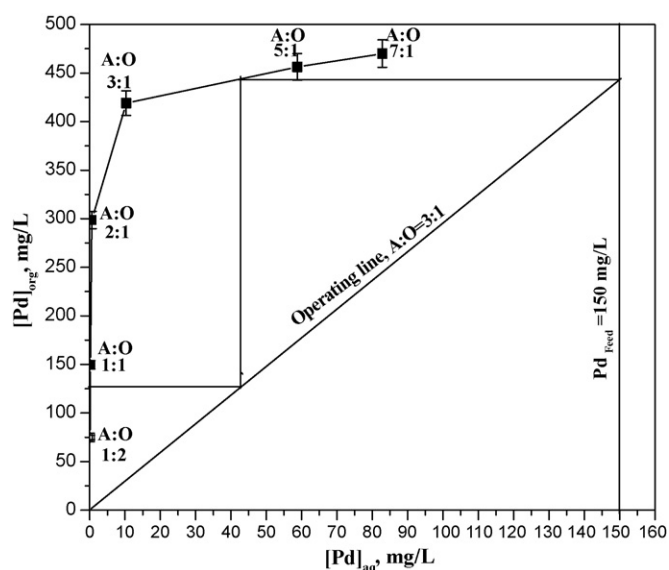


Fig. 2. McCabe–Thiele plot for palladium extraction. Organic: 0.5 vol.% LIX 841; aqueous (mg/L): Pd-150, Pt-550, Cr-100, Mn-500, Fe-1000, Ni-1000; HCl: 3 M.

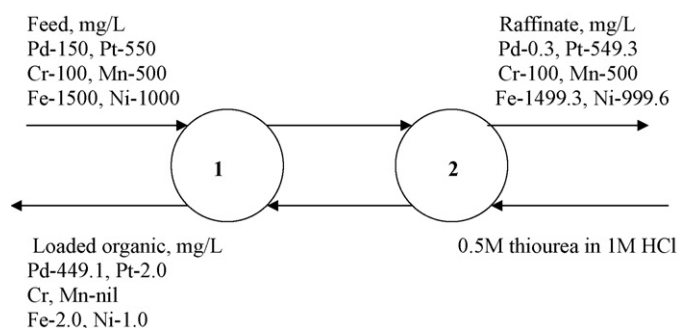


Fig. 3. Two stage counter-current extraction simulation for palladium. Pd: 150 mg/L; LIX 841: 0.5 vol.%; A/O ratio: 3.

liquor ammonia and Pt was extracted along with Ni and Zn. Scrubbing step with dilute H_2SO_4 was applied to remove the Cu, Ni and Zn impurities from loaded organic phases [20]. Under the present experimental conditions Pd of extraction with 0.5 vol.% LIX 841, the process is very selective for Pd and the co-extraction of other metals is negligible.

3.1.2. Stripping of Pd from loaded organic phase

Stripping studies of Pd from loaded organic phase was carried out with different concentrations (0.1 M, 0.5 M and 1 M) of thiourea and HCl separately and in combinations as presented in Table 2. Stripping Pd with HCl alone is nil. On the other hand, combination of HCl from (1–2 M) and thiourea (0.1–1 M) in different concentration gave Pd stripping efficiency of 100%. Using 0.5 M thiourea and 1 M HCl, stripping of Pd from loaded organic was carried out at O/A ratios from 1 to 10 (Table 3). It was observed that Pd stripping was

Table 2
Effect of stripping reagents on Palladium stripping from loaded organic.

| [HCl], M | Pd stripping, % | [HCl], M | [Thiourea], M | Pd stripping, % |
|----------|-----------------|----------|---------------|-----------------|
| 0.1 | 0 | 1.0 | 0.1 | 100 |
| 0.5 | 0 | 1.0 | 0.5 | 100 |
| 1.0 | 0 | 1.0 | 1.0 | 100 |
| 2.0 | 0.3 | 2.0 | 0.1 | 99.5 |
| 3.0 | 0.3 | 2.0 | 0.5 | 99.8 |
| 5.0 | 1.0 | 2.0 | 1.0 | 99.9 |

Table 3
Effect of phase ratio on stripping of palladium from loaded organic containing 449.1 mg/L palladium.

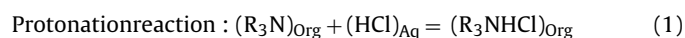
| A:O ratio | Pd in SO, mg/L | Pd stripping efficiency, % |
|-----------|----------------|----------------------------|
| 1:1 | 1.85 | 99.6 |
| 1:2 | 1.85 | 99.6 |
| 1:3 | 1.85 | 99.6 |
| 1:5 | 2.55 | 99.4 |
| 1:7 | 2.55 | 99.4 |
| 1:10 | 3.82 | 99.1 |

>99% even at highest O/A ratio of 10. A two stage stripping test was conducted at O/A ratio of 5 for seven cycles. Analysis of combined SO contains 1.5 mg/L Pd corresponding to a stripping efficiency of 99.7%. The overall enrichment of Pd during extraction and stripping steps was 15 times.

3.2. Separation and recovery of platinum from palladium raffinate

3.2.1. Effect of Alamine 336 concentration on platinum extraction

Extraction of platinum from palladium raffinate with Alamine 336 of different concentrations (1–5 vol.%) individually showed third phase formation. As a result, 2 vol.% TBP was used as phase modifier. Results of extractant variation on percentage extraction of Pt are presented in Fig. 4. With increasing Alamine 336 concentration from 1 to 5 vol.%, extraction of Pt and Fe increases, whereas the extraction of Mn, Ni and Cr was <1%. For example, with 5 vol.% extractant concentration, the extraction of Pt and Fe was 99.7% and 99%, whereas Mn, Ni and Cr was 0.6, 0.9% and zero, respectively. The results clearly suggest that Alamine 336 extracts Pt and Fe simultaneously in 3 M HCl. Pt and Fe exists in 3 M HCl as anionic species such as H_2PtCl_6 and $HFeCl_4$, their mechanism of extraction follows anion exchange type with the formation of $(R_3NH^+)_2PtCl_6^{2-}$ and $(R_3NH^+)FeCl_4^-$ complexes into the organic phase as given by Eqs. (1)–(3) [30,31,32]. Further, the results of Pt extraction by Alamine 336 suggest a scrubbing step is necessary to remove the co-extracted Fe from organic phase. Alamine 336 reacts with HCl by protonation reaction to form chloride species:



where the subscripts (Org) and (Aq) represent the organic and aqueous phases, respectively.

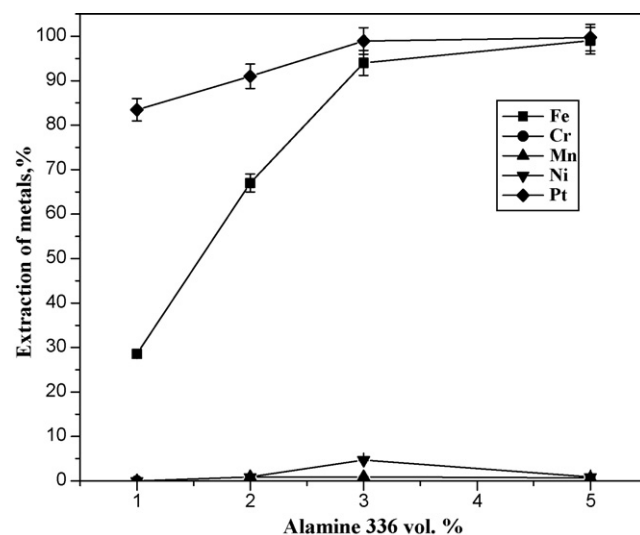


Fig. 4. Effect of Alamine 336 concentration on the extraction of platinum and other base metals (Cr, Mn, Fe and Ni). Platinum: 550 mg/L; HCl: 3 M.

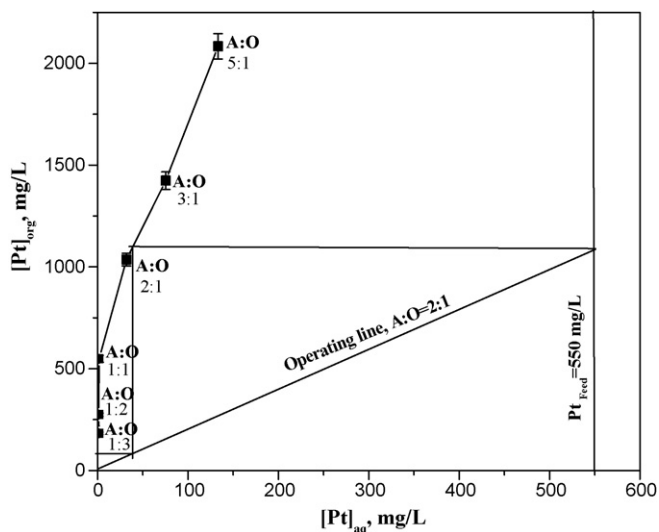
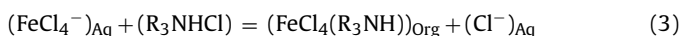


Fig. 5. McCabe–Thiele plot for platinum extraction. Organic: 5 vol.% Alamine 336; aqueous (mg/L): Pt-550, Cr-100, Mn-500, Fe-1000, Ni-1000; HCl: 3 M.

Pt (IV) and Fe (III) extraction can be represented by ion exchange mechanism:



In a similar study on the extraction of Pt and Fe from 0.01 to 10 M HCl solutions with 10 vol.% TOA in kerosene, it was reported that the extraction of Pt is quantitative in the entire acid range, whereas the extraction of Fe increases with acid and reaches quantitative around 1–5 M acid. Around 0.01 M acid clear separation of Pt from Fe and quantitative co-extraction of Pt and Fe was reported in the acid range 1–5 M acid [3]. In the present study on Pt separation from palladium raffinate, similar behavior of co-extraction of Pt and Fe was observed, leaving Cr, Mn and Ni in aqueous solution.

3.2.2. Extraction isotherm of platinum

To find out the theoretical number of stages and possibility of enriching the Pt concentration in the loaded organic phase during extraction stage, the extraction isotherm was obtained by contacting the raffinate with 5 vol.% Alamine 336 at different A:O phase ratios from 1 to 3 and O:A phase ratios from 1 to 5 (Fig. 5). From the extraction isotherm, it was observed that, at A/O phase ratio of 2, complete extraction efficiency of Pt is achievable in two stages. Considering the present Pt extraction efficiency in single stage, phase ratio and minimum stages are required for complete recovery of Pt, an A/O phase ratio of 2 was selected in order to recover Pt in two counter-current stages.

3.2.3. Counter-current extraction simulation studies for platinum extraction

To confirm McCabe–Thiele predictions, a two stage counter-current extraction simulation (CCES) test was carried out at A/O phase ratio of 2 using 5 vol.% Alamine 336. The aqueous and organic outlet streams were collected after the third cycle onwards and analyzed for metal values. The combined raffinate contain 0.95 mg/L Pt, corresponding to 99.8% extraction (Fig. 6). The co-extraction of Fe was 99.3%. The generated loaded organic contains 1098.1 mg/L Pt and 2978.8 mg/L Fe. Scrubbing step is necessary to remove the co-extracted Fe impurity from loaded organic phase.

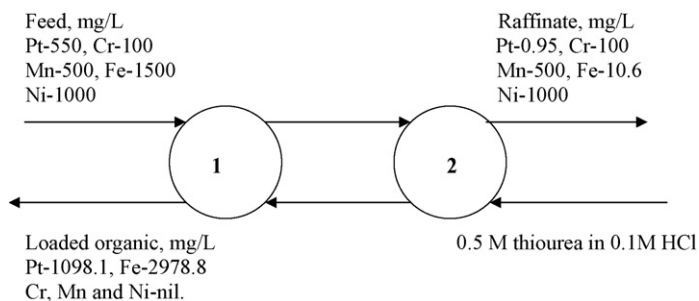


Fig. 6. Two stage counter-current extraction simulation for platinum. Pt: 550 mg/L; Alamine 336: 5 vol.%; A/O ratio: 2.

Table 4

Effect of HCl and H₂SO₄ concentration on iron scrubbing from loaded organic containing 1098.1 mg/L platinum and 2978.7 mg/L iron.

| [HCl], M | Fe scrubbing, % | [H ₂ SO ₄], M | Fe scrubbing, % |
|---------------------|-----------------|--------------------------------------|-----------------|
| 0.0001 ^a | 98.7 | 0.01 | 65.8 |
| 0.0001 ^b | 96.7 | 0.1 | 71.6 |
| 0.0001 | 84.4 | 0.5 | 66.5 |
| 0.001 | 78.7 | 1.0 | 70.3 |
| 0.01 | 74.3 | 2.0 | 73.5 |
| 0.01 ^a | 84.7 | – | – |
| 0.1 | 58.9 | – | – |
| 0.5 | 33.5 | – | – |
| 1.0 | 19.9 | – | – |
| 2.0 | 6.8 | – | – |

^a A:O = 2:1.

^b A:O = 1.5:1.

3.2.4. Scrubbing of Fe from loaded organic phase

Fe scrubbing from loaded organic containing Pt and Fe was carried out with HCl and H₂SO₄ as scrubbing reagents in the range from 0.0001 M to 2 M. The results are presented in Table 4. In case of HCl, scrubbing efficiency of Fe from loaded organic decreased with increase in acid concentration, whereas with H₂SO₄, it did not vary much. Further increase in A/O phase at a given acid concentration increases the scrubbing efficiency of Fe. Finally, a two stage counter-current scrubbing of Fe from loaded organic was carried at A/O phase ratio of 1.5 using 0.0001 M HCl. Analysis of scrubbed loaded organic indicated 2.2 mg/L of Fe, corresponding to 99.93% Fe scrubbing efficiency. The scrubbed loaded organic con-

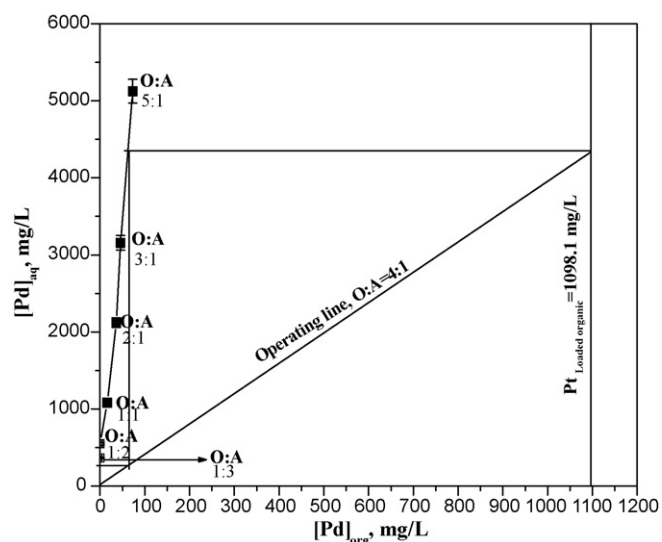


Fig. 7. McCabe–Thiele plot for platinum stripping; Platinum in loaded organic: 1098.1 mg/L.

Table 5
Stripping of platinum from loaded organic phase.

| [HCl], M | [Thiourea], M | Pt stripping, % | [HCl], M | [Thiourea], M | Pt stripping, % |
|----------|---------------|-----------------|----------|---------------|-----------------|
| 0.1 | – | 0 | – | 0.5 | 99.4 |
| 0.5 | – | 0.2 | 0.1 | 0.5 | 98.5 |
| 1.0 | – | 0.2 | 0.3 | 0.5 | 94.9 |
| 2.0 | – | 0 | 0.5 | 0.5 | 92.6 |
| 4.0 | – | 0 | 1.0 | 0.5 | 90.2 |
| – | 0.1 | 65.7 | 2.0 | 0.5 | 52.1 |
| – | 0.3 | 84.5 | 4.0 | 0.5 | 22.9 |

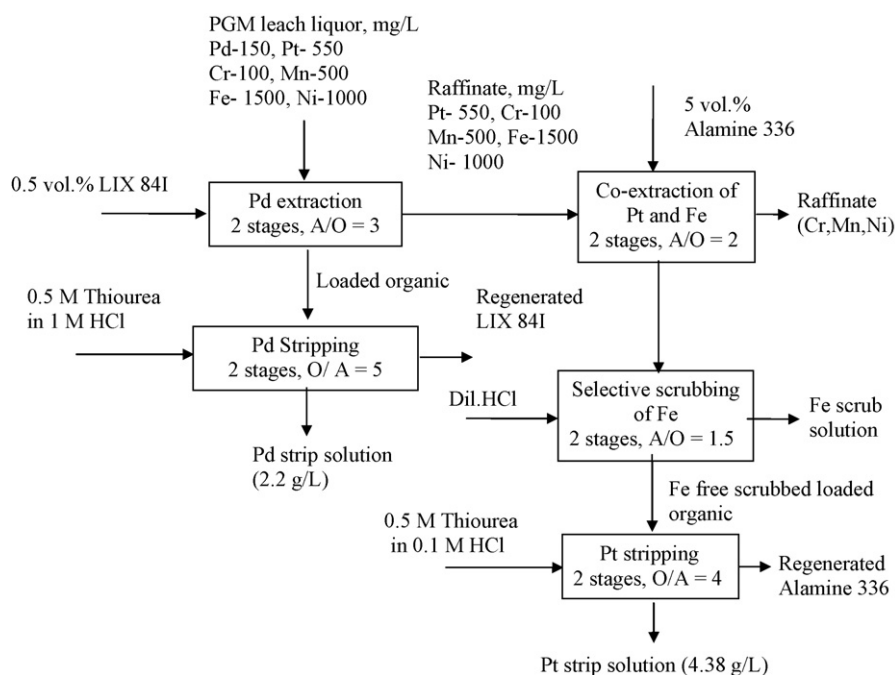


Fig. 8. Flow sheet of the process for the solvent extraction separation and recovery of Pd and Pt from chloride leach liquor of spent automobile catalyst.

taining platinum was used for the generation of platinum stripping conditions.

3.2.5. Screening of reagents for stripping of platinum from scrubbed loaded organic

Single stage stripping of platinum from scrubbed loaded organic containing 1098.1 mg/L Pt with HCl in the range from 0.1 to 4 M was zero, whereas with thiourea it increases with increase in thiourea concentration and reaches to >99% at 0.5 M (Table 5). However, stripping of Pt from at higher O/A ratios >1 resulted hydrolysis of metal. As a result, acidified thiourea of different concentrations was tested and found that a combination of 0.1 M HCl and 0.5 M thiourea gave >99% stripping efficiency in single stage.

3.2.6. Stripping isotherm and counter-current stripping simulation of platinum from loaded organic

In order to find out the extent of enrichment possible and also theoretical number stages required at a chosen O/A phase ratio, the stripping isotherm was obtained at different O:A ratios using the strip feed (0.5 M thiourea and 0.1 M HCl) and loaded organic. The McCabe–Thiele plot (Fig. 7) indicates that quantitative stripping of Pt is achievable in two CCSS at O/A phase ratio of 4. To confirm the stripping isotherm prediction data, a two stage CCSS test was carried out at O/A phase ratio of 4. Spent organic contains 3 mg/L Pt, corresponding to 99.7% stripping efficiency. The overall enrichment of Pt during extraction–stripping stages was 8 times with a purity of 99.7%. The overall process for the separation and recovery of Pd and Pt is presented in Fig. 8.

4. Conclusions

Separation and recovery of Pd from the leach liquor with 0.5 vol.% LIX 84I in kerosene gave selective extraction of Pd leaving Pt and other metals in the raffinate. Stripping of Pd from loaded organic was achieved with acidified low thiourea concentration. Extraction of Pt from the raffinate with 5 vol.% Alamine 336 in kerosene showed quantitative co-extraction Fe and Pt. Scrubbing of Fe from loaded organic was achieved with dilute HCl. Finally, Pt was stripped with acidified thiourea in 2 stages. The present process generates high concentration of Pd and Pt with 99.7% purity. Based on the results, complete flow sheet of the process for the separation and recovery of Pd and Pt is presented from spent automobile catalyst chloride leach solution.

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