Recovery of platinum from spent catalysts by liquid–liquid extraction in chloride medium

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ABSTRACT

This work examines a hydrometallurgical route for processing spent commercial catalysts (Pt and PtSnIn/A$_2$O$_3$) used in Brazilian refineries for recovery of the noble metal with less final wastes generation. Samples were initially pre-oxidized (500 °C, 5 h) in order to eliminate coke. The basis of the present route is the partial dissolution of the pre-oxidized catalyst in aqua-regia. Temperature and time necessary to dissolve all platinum were optimized in order to reduce the operation severity and aluminum solubilization. All platinum and 16–18 wt.% of aluminum were dissolved at 75 °C in 20–25 min. Separation of platinum from the acidic solution was accomplished by solvent extraction. The best extractant (>99 wt.%) was Aliquat 336 (a quaternary ammonium salt) in one stage (A/O phase ratio = 1, v/v). Platinum was stripped (>99.9 wt.%) in one stage (A/O phase ratio = 1, v/v) with aqueous sodium thiosulfate (≥ 0.75 mol L^{-1}). Black platinum was obtained from this solution via reduction with magnesium or ascorbic acid.

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1. Introduction

Cracking and reforming catalysts are extensively used in refining and petrochemical industries. When these catalysts deactivate due to coke deposits they are regenerated and replaced periodically by fresh catalysts. But their lifetime is limited; when regeneration is no longer possible the so-called spent catalyst are usually treated in order to recover the noble metal present.

The petroleum and petrochemical industries produce considerable amounts of spent catalysts containing platinum and other precious and rare metals every year. Spent catalysts are classified by the North-American Environmental Protection Agency (EPA) as a hazardous waste because they may be pyroforic, spontaneously combustible and release toxic gases. Although spent catalysts correspond to about 4 wt.% of its overall waste, they are among the dangerous wastes generated in petroleum refineries [1,2].

The platinum group metals (PGMs) are the main active ingredients of these catalysts. Their excellent selective and activity towards reactants and resistance to oxidation at high temperatures make them very effective catalysts. The high cost of platinum and its extensive use in catalysis, electronic and electric devices, jewelry, medical instruments, dental equipment and space materials has made the recovery of this metal from spent sources a viable

and cost effective alternative. Platinum demand in 2003/2004 was higher than the world supply [3]. Although the demand decreased 2.3% in 2008, platinum supply decreased 4.2% [4]. This metal is also a very rare element in Earth's crust; the worldwide reserves are concentrated in only two regions, Siberia and South Africa. Although the amount of this metal in a commercial catalyst is approximately 1 wt.%, it corresponds to the main cost of this product [5,6]. Therefore, recycling of spent catalysts is an attractive way to lower the catalyst cost [7].

There are many recovery methods of platinum and other PGMs from spent catalysts, including automobile catalytic converters. However, the fraction recovered from such secondary sources reaches only about 40% of the overall amount [8]. At present, research is mainly conducted under mild experimental conditions. In many cases, a preliminary step is performed, mainly coke burning under controlled conditions [6,9–11]. This step "cleans" the catalyst surface, thus reducing losses of recoverable metals by physical blocking. Care must be taken to avoid coke ignition during pretreatment, thus forming refractory compounds that are difficult to solubilize in the leaching medium. The goal is to reduce the noble metal to metal state while the other catalyst components, particularly the support, are dissolved in an appropriate medium such as aqueous NaOH or non oxidizing acids. Most ordinary recovery methods reported in literature are based on full dissolution of the sample in an acidic oxidative medium (particularly aqua-regia) [12]. The concentration of the oxidizing agent must be high enough to oxidize the noble metal to an ionic form so that it can

Table 1
Chemical analysis (wt.%, dry basis) of the fresh and spent catalysts.

		Pt	Sn	In	Al	Fe	C
Pt/Al$_2$O$_3$	Fresh	0.37	–	–	50.60	0.05	3.5
	Spent	0.35	–	–	52.80	0.02	–
PtSnIn/Al$_2$O$_3$	Fresh	0.37	0.41	0.26	48.30	0.15	5.0
	Spent	0.39	0.42	0.28	50.82	0.03	–

be complexed by halide ions. Acidity must be sufficient to activate the complexation reactions. After this step, platinum recovery is performed by chemical or electrochemical routes. Some processes replace aqua-regia by aluminum chloride solutions with low concentration of nitric acid [12]. The idea is to reduce corrosivity of the leaching solution. However, all these routes generally produce considerable amounts of final wastes due to the complete solubilization of the catalyst, which is undesirable when hazardous wastes are processed.

Another group of processes employs the cyanide leaching method [13]. However, such processes are considered inadequate within environmental and economical terms [14].

Extraction of metals with extractants dissolved in organic solvents has been gaining importance since the 1990s. It has been reported that extraction (and separation) of PGMs by liquid–liquid extraction (LLE) is a very difficult task because their chemistry is very similar [15]. The high price of PGMs, the increasing demand of such metals in commercial and technological applications, the low amounts in natural ores and the deficit in PGMs supply have been stimulating research on the use of LLE techniques to recover them from primary and secondary sources.

Some extractants for platinum from spent samples or standard chloride solutions have been reported in the last years, but these extractants fall into only two basic groups: (i) organophosphorus compounds such as tributyl phosphate (TBP) [16], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) [17], try-octyl phosphine oxide (Cyanex 921) [6,18] and bis(2,2,4-trimethyl-pentyl)monothiophosphinic acid (Cyanex 302) [19]; (ii) amines such as tri-octyl/decylamine (Alamine 308) [15], tri-octyl/decylamine (Alamine 336), [16,20] mixtures of trioctylamine and tridecylamine [21] and ammonium quaternary salts such as Aliquat 336 [22]. Amines are of interest because Pt can be extracted without the interference of metals such as Fe and Al [15,20].

The recovery of extracted Pt(IV) from an organic phase by ordinary stripping methods is usually a difficult step, particularly when the concentration is low. Crystallization of (NH$_4$)$_2$PtCl$_6$ has been known as an efficient and effective method of isolating Pt(IV) [23], provided concentration of the noble metal is high enough to reach K_{sp} of this salt. It can be readily decomposed by calcination or gaseous reduction at high temperature; sponge-like Pt metal is the final product [20]. Other studies use stripping with Na$_2$S$_2$O$_3$ [21] or thiourea [15,19,22] in a single stage.

As a conclusion, PGMs extraction and recovery from organic phase is worth exploring. The presence of other possible interfering metals and parameters such as acidity, concentration of complexing agents and PGMs may play an important role on the behavior of the extraction process. This work presents a hydrometallurgical route for processing spent Pt-containing catalysts in aqua-regia. Pt solubilization was attempted with simultaneous minimized Al solubilization, thus reducing final wastes generation. The acidic solution obtained was submitted to LLE procedures for platinum. The residual aqueous solution was also processed in order to recover other metals present. Attention was also paid to the final wastes generated. The overall route present in this work was compared to those presented in the literature for spent Pt-containing catalysts.

2. Experimental

2.1. Catalysts

Two commercial spent catalysts were employed in this study: a monometallic Pt/Al$_2$O$_3$ and a multimetallic PtSnIn/Al$_2$O$_3$. Both were kept in their original forms (spheres d = 1.5 mm). Chemical analysis data of fresh and spent catalysts are presented in Table 1. Both samples were used in catalytic reforming units. Spent samples were oxidized in a furnace (500 °C, 1 atm, 5 h, 1 °C min^{-1}) to eliminate coke and water. The roasted mass was cooled down in the furnace and transferred to a dessicator before running the experiments.

2.2. Leaching procedure

Aqua-regia was used as the leaching agent. It oxidizes platinum according to the following reaction:

$$8H^+ + 8Cl^- + 2NO_3^- + Pt \rightarrow PtCl_6^{2-} + 4H_2O + 2NOCl \qquad (1)$$
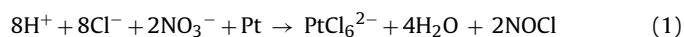
The volume of aqua-regia employed was 4 mL g^{-1} sample (liquid/solid ratio = 4), which was the minimum amount to cover all catalyst. In contrast to most literature procedures, the next step was to dissolve quantitatively all platinum with simultaneous low aluminum solubilization. Leaching was performed with manual or slow magnetic stirring (50 rpm) in order to avoid catalyst fragmentation, thus reducing exposure of aluminum to the leachant. Two experimental parameters were varied: time (5–30 min) and temperature (25–100 °C). After the experiments, the insoluble matter was separated from the liquid phase by filtration, washed with water (10 mL g^{-1} Pt/Al$_2$O$_3$; 20 mL g^{-1} PtSnIn/Al$_2$O$_3$) and dried 150 °C for 2 h. Washing waters were added to the leachate. All experiments were run in triplicate, and data obtained were within ±3%.

2.3. Extraction and stripping procedures

Platinum extraction was carried out using several extractants (5–15 vol%) dissolved in deodorized kerosene: Alamine 304 (tridodecylamine); Alamine 336 (tri-octyl/decylamine); Aliquat 336 (methyl-trioctyl/decylammonium chloride), D2EPA (bis-2-ethyl-hexylphosphoric acid) and TBP (tributylphosphate). The experiments were performed at 25 °C with equal volumes of aqueous and organic phases (O/A = 1, v/v). The influence of the acidity of the leachate on platinum extraction was also examined: it was kept as such or the leachate was diluted with water (1:1, v/v). Platinum concentration in the aqueous and organic phases was determined in order to calculate the distribution ratio, D (D = [Pt]$_{org}$/[Pt]$_{aq}$).

Platinum stripping from the organic phase was investigated using various aqueous solutions (O/A = 1, v/v): HCl (1 or 12 mol L^{-1}); NaCl (1 or 2 mol L^{-1}); NaHSO$_3$ (1 mol L^{-1}); Na$_2$CO$_3$ (3 mol L^{-1}); NH$_4$OH (15 mol L^{-1}); (NH$_4$)$_2$CO$_3$ (1.5 mol L^{-1}), Na$_2$S$_2$O$_5$ (1 mol L^{-1}), Na$_2$S$_2$O$_4$ (1 mol L^{-1}) and Na$_2$S$_2$O$_3$ (0.5–1 mol L^{-1}). In the last three cases pH was adjusted to 9 by adding 12.5 mol L^{-1} NaOH in order to avoid decomposition of the anion with release of toxic gases (SO$_2$). The stripping efficiency ([Pt]$_{aq}$/[Pt]$_{org}$ × 100) was determined. All

Table 2
Leaching of platinum and aluminum from Pt/Al_2O_3 and $PtSnIn/Al_2O_3$ catalysts (75 °C, 4 mL aqua-regia.g^{-1} catalyst).

Time (min)	Pt leached (wt.%)		Al leached (wt.%)	
	Pt/Al_2O_3	$PtSnIn/Al_2O_3$	Pt/Al_2O_3	$PtSnIn/Al_2O_3$
10	80.1	54.9	13.0	11.5
15	95.5	80.1	14.1	13.4
20	99.9	90.4	16.0	16.3
25	99.8	99.9	19.2	18.0
30	–	100.0	–	18.7

Table 3
Time for full platinum leaching from Pt/Al_2O_3 and $PtSnIn/Al_2O_3$ catalysts at various temperatures (4 mL aqua-regia g^{-1} catalyst).

Temperature (°C)	Time for full Pt leaching (min)		wt.% Al leached	
	Pt/Al_2O_3	$PtSnIn/Al_2O_3$	Pt/Al_2O_3	$PtSnIn/Al_2O_3$
25	>120	>200	Not determined	Not determined
50	42	52	15.5	17.0
75	20	25	16.0	18.0
80	18	22	16.5	19.0
90	14	18	18.5	22.0
100	12	15	23.5	27.5

Table 4
Textural properties of Pt/Al_2O_3 and $PtSnIn/Al_2O_3$ catalysts.

Parameter	Pt/Al_2O_3			$PtSnIn/Al_2O_3$		
	Fresh	Spent	Leached*	Fresh	Spent	Leached*
Pore volume ($mL\,g^{-1}$)	0.34	0.27	0.50	0.32	0.22	0.48
BET surface area ($m^2\,g^{-1}$)	130	120	148	133	117	152

* After coke burning and leaching with aqua-regia

Table 5
Elements concentration in the leachates.

Catalyst	Acidity ($mol\,L^{-1}$)	Pt ($g\,L^{-1}$)	Cl^- ($mol\,L^{-1}$)	In ($g\,L^{-1}$)	Sn ($g\,L^{-1}$)
Pt/Al_2O_3	3.44	1.04	1.40	–	–
$PtSnIn/Al_2O_3$	1.19	0.73	0.49	0.66	0.30

experiments described in this section were run in triplicate and data obtained were within ±5%.

Recovery of platinum as black platinum was tried using reducing agents: zinc, magnesium, Dewarda alloy (45 wt.% aluminum, 50 wt.% copper and 5 wt.% zinc) and ascorbic acid under mild heating (40 °C) and stirring (100 rpm). The reducing agent was added slowly.

2.4. Processing of the leachate after platinum extraction

Soluble aluminum (Pt/Al_2O_3) was recovered by direct neutralization with 12.5 mol L^{-1} NaOH. pH was adjusted to 6.5–7.0. In the case of the multimetallic sample, soluble aluminum, tin and indium were precipitated together by the same procedure.

2.5. Analytical methods

Metal concentrations in the aqueous phases were determined by atomic absorption spectrometry (PerkinElmer AAS 3300). The following wavelengths were employed: platinum, 265.9 nm; tin, 286.3 nm; indium, 303.9 nm; aluminum, 396.2 nm. The following detection limits were determined experimentally: 1 mg L^{-1} (aluminum and tin), 0.5 mg L^{-1} (indium and platinum). The concentration of platinum in the organic phase was estimated by mass balance. Acidity of leachates was determined by potentiometry using an Ag/AgCl reference electrode (Orion 2AI3-JG). Chloride concentration was determined by an ion-selective electrode (Orion 9417-BN). Textural properties (surface area and total pore volume) of fresh, spent and leached samples were determined by N_2 adsorption at −196 °C (BET method–Micromeritics Gemini III 2375). Phase identification of the catalysts before and after platinum leaching was performed by X-ray diffraction (XRD) analysis (Shimadzu XRD 6000) by continuous scanning method at 20 mV and 40 mA, using Cu Kα as the radiation source.

3. Results and discussion

3.1. Influence of time and temperature on catalyst leaching with aqua-regia

At 25 °C platinum leaching was very low, regardless of time of contact. Therefore, heating was necessary to speed up the process. Platinum was fully solubilized (Table 2) at 75 °C after 20 min (Pt/Al_2O_3) or 25 min ($PtSnIn/Al_2O_3$). The longer time for the multimetallic catalyst was observed in the temperature range studied (25–100 °C, Table 3). This difference is probably due to the presence of tin in the multimetallic catalyst, since its oxide (SnO_2) slowly dissolves in strong acidic medium, thus making platinum leaching somewhat slower.

Temperatures lower than 75 °C slightly decreased aluminum leaching but time for full platinum leaching more than doubled (Table 3). On the other hand, as expected, platinum solubilization was much faster when temperature was raised up to 100 °C, since the activation energy decreased [14]. However, it is not

worth working at this temperature. Aluminum leaching considerably increased (Table 3). Therefore, it appears that working at 75 °C allows a full platinum leaching in a reasonable time without excessive aluminum leaching.

Data of Tables 2 and 3 demonstrate that it is not necessary to solubilize all support in order to bring all platinum into solution. This is an advantage since less amounts of acidic solution are necessary, less final wastes are generated and platinum recovery from the leachate is easier. These arguments were also reported in a recent research [24].

The solid/liquid ratio (4) employed in this study was enough to dissolve platinum, thus avoiding an excess of reactant; otherwise, more aluminum would be brought into solution. Platinum leaching sharply decreased when the liquid/solid ratio was below 4. A similar conclusion was found in a previous study [20] although platinum content in the samples examined is higher than those in the present study.

Textural properties of the leached catalysts are presented in Table 4, and are compared to those of fresh and spent samples. Since catalyst leaching is a surface process, it is not surprising that such properties are higher in leached samples. The lowest values for the spent samples are due to coke deposits. The leached samples are very rough and easily crumbled. Fig. 1 shows the aspect of the spent leached catalyst without platinum compared to the corresponding spent and pre-oxidized sample. The visual effect is clear.

The leached catalyst may be a raw material for Al recovery or co-processed (mineralizing raw material) according to the Directory No. 264/99 from the National Brazilian Environmental Council (CONAMA) [25].

Table 5 presents some features of the leachates (after addition of washing waters). More than 95 wt.% of indium was fully dissolved but only 50 wt.% of tin was solubilized. Acidity and Cl^-/Pt(IV) concentrations are higher for Pt/Al_2O_3 leachates because water consumption during washing of leached catalyst was lower.
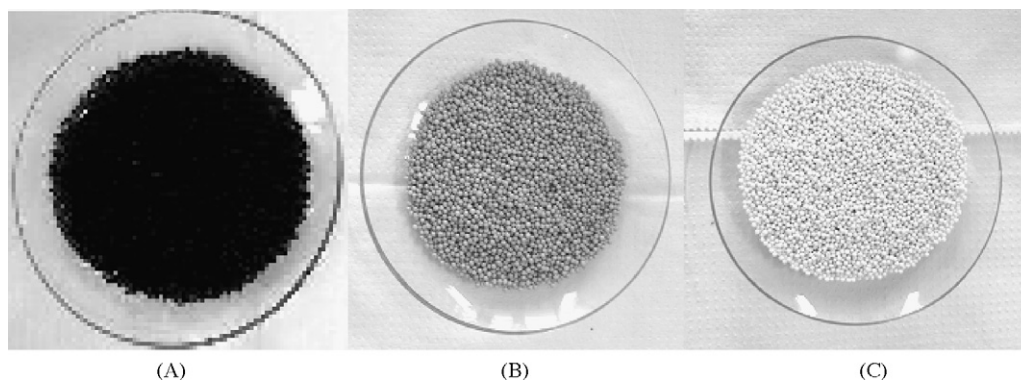
Fig. 1. Visual aspect of the spent catalysts before (a) and after (b) pre-oxidizing, and after (c) partial leaching (Pt removal).

Leachates are yellow due to $PtCl_6^{2-}$ ions. Fig. 2 presents XRD data of the spent pre-oxidized multimetallic catalyst before and after platinum leaching. The crystalline structure of the support remained the same (γ-alumina). This is also the structure of the support of the Pt/Al_2O_3 catalyst after platinum leaching.

3.2. Platinum extraction

Extraction of platinum was negligible with D2EPA and TBP. Even when the original acidity was doubled (by adding HCl) or reduced to 50% of the initial value (after adding water) no platinum was found in the organic phase. Pure TBP did not extract the noble metal in the original acidity of the Pt/Al_2O_3 catalyst, which is close to experimental conditions reported in literature [16].

The amines extracted platinum when acidity was between $1 \, mol \, L^{-1}$ and $2 \, mol \, L^{-1}$. In the original acidity, extraction of platinum in the Pt/Al_2O_3 leachate was low. Therefore dilution with water (1:1, v/v) was necessary. When acidity was below $1 \, mol \, L^{-1}$ platinum extraction was drastically reduced. This last result agrees with data of Lee et al. [22] with standard $PtCl_4$ solutions ($0.1 \, g \, L^{-1}$). On the other hand platinum extraction was high up to $5 \, mol \, L^{-1}$ HCl [22]. In our case, protonation of amines was found when acidity was higher than $3 \, mol \, L^{-1}$, leading to emulsification, and this may account for the difference observed, since concentration of the amine is much lower in their study.

Table 6 presents data for the tertiary amines employed in this study. Equilibrium time was about 5 min in both leachates. D values of each amine are the same for both leachates. Alamine 336 was a better extractant, specially in higher concentrations.
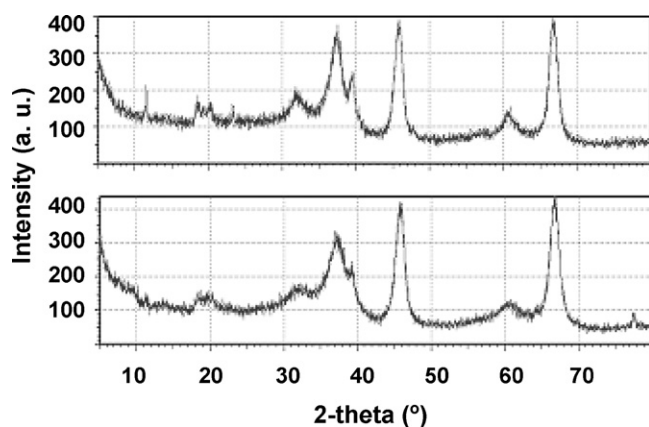
Table 6
D_{Pt} values for Alamine 304 and Alamine 336 (A/O = 1:1, v/v, 25 °C, 1 stage).

Amine concentration in kerosene (vol%)	D_{Pt} Alamine 304	D_{Pt} Alamine 336
5	2.6	2.8
10	3.4	5.3
15	4.1	24.0

Fig. 3 shows that 96 wt.% of platinum was extracted by 15 vol% Alamine 336 in kerosene in one stage. Except for the concentration of the amine, these results are comparable to those of Barakat and Mahmoud [20].

Data for Aliquat 336 are presented in Fig. 4. The quaternary ammonium salt was a better extractant than Alamine 336. D_{Pt} for Aliquat 336 was 15 (5 vol%), 36 (10 vol%) and 249 (15 vol%). Platinum recovery reached 99.4 wt.% in one stage. The organic phase became yellow, whereas the aqueous phase was almost colorless. This result is very good but it must be pointed that platinum concentration in the leachates is very low ($0.5-0.7 \, g \, L^{-1}$). The behavior of Alamine 336 and Aliquat 336 for platinum extraction needs further studies for a better understanding. The quaternary ammonium salt has a permanent positive charge, thus forming salts over a wider pH range than tertiary amines [22]. Protonation of tertiary amine is necessary prior to the extraction step [15]. The acidity of the leachate and extractant concentration was the same in the experiments. Therefore it appears that it is easier to form the complex $[(C_8H_{17})_3/(C_{10}H_{21})_3CH_3N^+]_2PtCl_6$ (which is extracted to the organic phase [26]) when Aliquat 336 is employed. It is known that

Fig. 2. XRD pattern of the spent pre-oxidized PtSnIn/Al$_2$O$_3$ catalysts before (above) and after (below) platinum leaching with aqua-regia. The peaks represent γ-alumina phase.
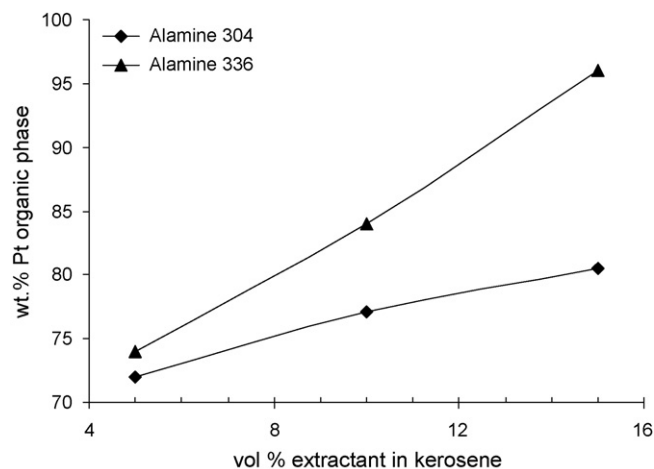

Fig. 3. Amount (wt.%) of Pt extracted by Alamine 304 and 336 (25 °C, A/O = 1:1 (v/v), equilibrium time 5 min, one stage).
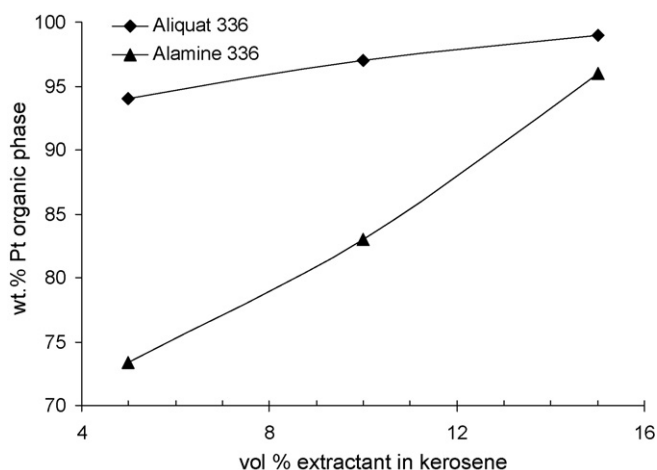
Fig. 4. Amount (wt.%) of Pt extracted by Alamine 336 and Aliquat 336 (25 °C, A/O = 1:1 (v/v), equilibrium time 5 min, one stage).

zinc and cadmium are better extracted by quaternary ammonium salts than tertiary amines in chloride medium [27].

3.3. Platinum stripping

The equilibrium time was 5 min and no contraction/expansion of both phases was observed. Among the several stripping solu-

tions tested, only $Na_2S_2O_3$ (0.5–1 mol L^{-1}) and $Na_2S_2O_4$ (1 mol L^{-1}) in pH 9 stripped the noble metal. In this process reduction of Pt(IV) to Pt(II) takes place. $Na_2S_2O_3$ gave the best results since platinum was stripped in one stage provided concentration is $\geq$0.75 mol L^{-1}. Below this value, two stages were necessary. 1 mol L^{-1} $Na_2S_2O_4$ required three stages. Literature [21] has reported a one-stage platinum stripping in an organic phase containing a mixture of 10 vol% trioctyl/tridecylamine in kerosene with 1 mol L^{-1} $Na_2S_2O_3$. Platinum stripping with simultaneous reduction of the noble metal can be described by the following equation:

$$5H_2O + S_2O_3{}^{2-} + 4PtCl_6{}^{2-} \rightarrow 2SO_4{}^{2-} + 4PtCl_4{}^{2-} + 8Cl^- + 10H^+ \quad (2)$$
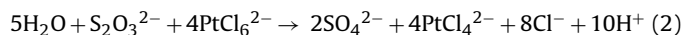
This reaction explains the decrease of pH during stripping. The initial pH (9) was lowered to 7.5–8.0. Under these conditions $S_2O_3{}^{2-}$ does not decompose to gaseous SO_2 and elemental S.

0.75–1.0 mol L^{-1} $Na_2S_2O_3$ can treat three organic solutions containing platinum before recovery of the noble metal (Section 3.4). On the other hand, the extraction and recovery of platinum was not significantly changed after five successive extraction and stripping cycles using the same Aliquat 336 organic solution.

3.4. Recovery of platinum metal

Mild heating ($\approx$40 °C) was required to accomplish platinum reduction in short time; this is easily followed by disparition of the greenish color of Pt(II) (about 5 min for all reducing agents). The noble metal was recovered as a black fine precipitate. Final solution
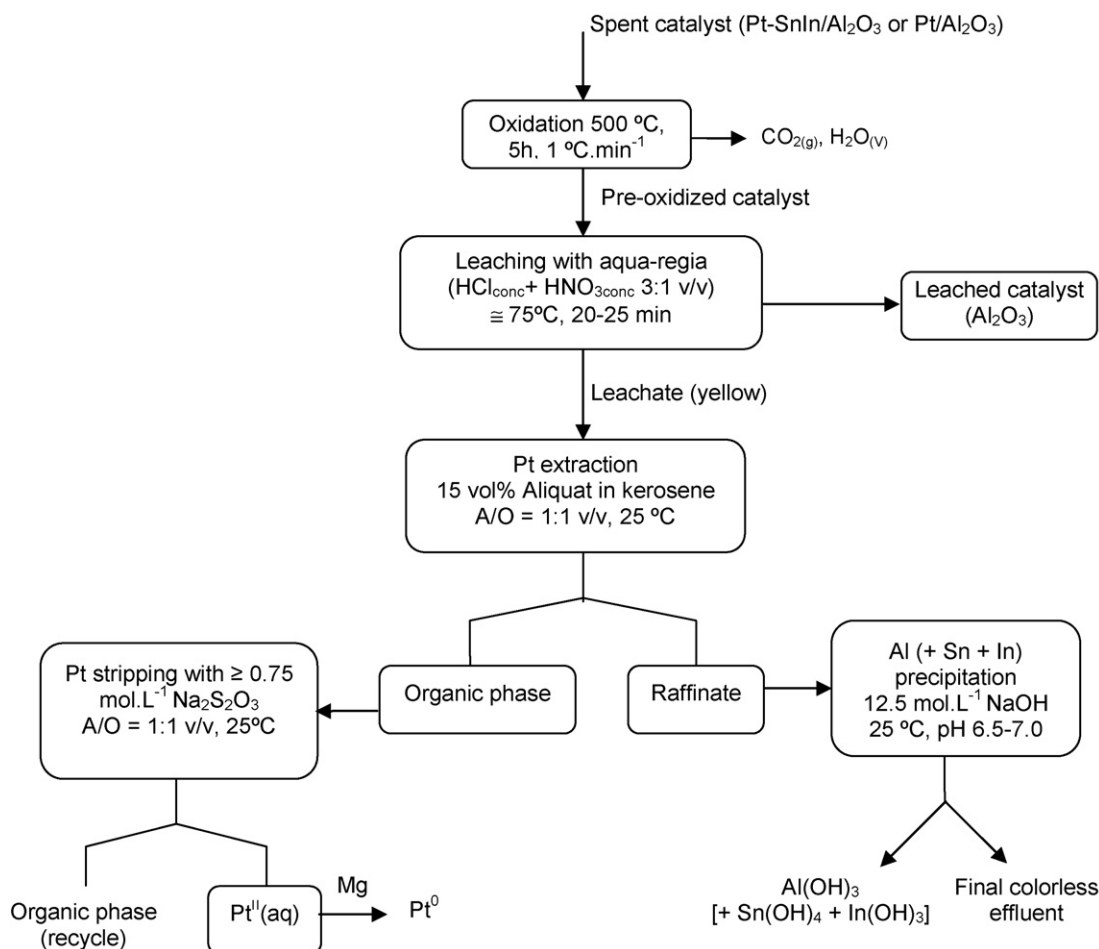

Fig. 5. General scheme for processing of spent Pt/Al$_2$O$_3$ and PtSnIn/Al$_2$O$_3$ catalysts after pre-oxidation and partial leaching with aqua-regia.

is colorless. Magnesium and ascorbic acid are preferable because they do not generate final toxic wastes and also avoid additional steps such as filtration after neutralization of the final solution. Chemical qualitative analysis of the final solution [28,29] suggests that the remaining thiossulfate ions were oxidized to sulfite/sulfate species by oxygen:

$$H_2O + S_2O_3{}^{2-} + O_2 \rightarrow 2SO_3{}^{2-} + 2H^+ \tag{3}$$

$$SO_3{}^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4{}^{2} \tag{4}$$
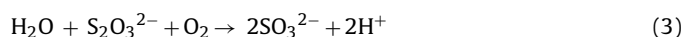
pH of the final solution was lowered from 7.5–8.0 to around 7.0, which accounts to oxidation of thiossulfate as described above. This solution was treated with H_2O_2 in order to eliminate the sulfite ions (reaction (5)). The treated solution can be discarded according to the Brazilian Directory No. 357/2005 from the CONAMA [30].
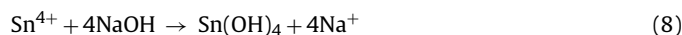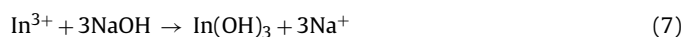
$$SO_3{}^{2-} + H_2O_2 \rightarrow SO_4{}^{2-} + H_2O \tag{5}$$

3.5. Recovery of soluble aluminum and other metals

When pH of the raffinate was adjusted to 6.5–7.0 with 12.5 mol L^{-1} NaOH aluminum precipitated as hydroxide:

$$Al^{3+} + 3NaOH \rightarrow Al(OH)_3 + 3Na^+ \tag{6}$$

If indium and tin were present (multimetallic catalyst), they precipitated as follows:

$$In^{3+} + 3NaOH \rightarrow In(OH)_3 + 3Na^+ \tag{7}$$

$$Sn^{4+} + 4NaOH \rightarrow Sn(OH)_4 + 4Na^+ \tag{8}$$

The amounts of these metals precipitated agree with their concentration in the leachate as shown in Table 5. More than 95 wt.% of indium present in the sample was recovered in this precipitate. Also, the aluminum recovered in this step corresponds to the amount solubilized in the leaching step (Table 2). No attempt was performed to separate these three metals in the precipitate.

The neutralized effluent is colorless and metals concentration is below 1 mg L^{-1} (The amounts of aluminum, indium and tin are below the detection limit of the analytical method employed in this study), and meets the requirements of the Directory No. 357/2005 from the National Brazilian Environmental Council (CONAMA) for final disposal [30]. It is basically composed by a mixture of aqueous NaCl and NaNO$_3$ salts.

Fig. 5 presents the overall processing scheme of the leachates developed in this work.

4. Conclusions

This study demonstrates that it is not necessary to dissolve all spent catalyst in order to recover the noble metal present, thus reducing consumption of reactants and generation of final wastes. Full platinum solubilization in aqua-regia can be accomplished in short time (20–25 min) at 75 °C with simultaneous low aluminum leaching (less than 20 wt.%). Other metals eventually present in the catalyst may be almost fully (indium) or partially solubilized (tin).

Under our experimental conditions Aliquat 336 (15 vol% in kerosene) extracted more than 99 wt.% of platinum in one stage at 25 °C with an A/O phase ratio equal to 1 (v/v). No other metals were extracted. Platinum was quantitatively stripped with Na$_2$S$_2$O$_3$ (0.5–1.0 mol L^{-1}), with simultaneous reduction from Pt(IV) to Pt(II), in one stage at 25 °C with an A/O phase ratio equal to 1 (v/v). Platinum metal was obtained in short time (5 min) after addition of a reducing agent such as magnesium or ascorbic acid at 40 °C.

Taking into account our data and previous literature results, more research is necessary to better understand the behavior of LLE of noble metals such as platinum. The nature and composition of the sample, as well as leaching, extraction and stripping conditions seem to affect the feasibility of noble metals recovery from secondary sources by LLE techniques.

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