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A Comparative Evaluation of Leaching Reagents of Platinum Group Metals from Spent Catalytic Converters Using Microwave Heating

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Platinum group metals (PGMs) are increasingly recycled from spent automotive catalysts due to their scarcity in nature. Many studies were developed using different leaching reagents to achieve greener benefits and reduce environmental pollution. This article reports for the first time a direct comparison of leaching reagents on the efficiency of PGMs using microwave (MW) assisted heating. The leaching system employed HCl with/without the addition of complexing (citric acid) or oxidizing agents (HNO_3, H_2O_2, NaClO, $NaClO_3$). It was shown that the 11.65 M HCl could leach all elements (94 % Pt, 82 % Pd and 74 % Rh) at 210 °C. The addition of oxidant(s) decreased the PGMs leaching efficiencies due to the formation of a protective oxide layer through surface passivation reaction. In some cases, the addition of complexing or oxidizing (H_2O_2) agents and a high leaching temperature (>180 °C) employed in the MW leaching could enhance PGMs leachabilities, particularly for Rh (>90 %). A detailed temperature study of the MW leaching demonstrated that HCl could obtain excellent recoveries (>90 %) for Pt and Pd at temperatures ≥ 150 °C. Therefore, this research illustrates that partially replacing the HCl with citric acid is a promising approach to achieve a greener and more efficient leaching process of PGMs.

1. Introduction

Current mining industries face challenges to meet global demand for platinum group metals (PGMs) due to their scarcity in natural resources.[1] Vehicle emission standards have been progressively tightened throughout the years, resulting in a major portion of PGMs being employed manufacturing of automotive catalysts.[2] Thus, there is a pressing need to actively recover PGMs from spent automotive catalysts (SACs) to address the relentless demand of these metals. Recycling PGMs from SACs could prevent hazardous waste disposal to the environment and minimize the search for new mining exploration, hence bringing benefits to the economy and environment. A catalytic converter consists of a ceramic carrier or monolith that has a honeycomb structure composed of cordierite ($2MgO.2Al_2O_3.5SiO_2$), alumina (γ-Al_2O_3), and together with the additives of CeO_2 and ZrO_2.[3] The active Pt, Pd and Rh catalytic particles (also referred to as PGMs) are dispersed on the washcoat layer which is responsible for the conversion of unburned hydrocarbons, CO and NO_x into less hazardous compounds (i.e., CO_2, H_2O, N_x, and O_2).[4]

Pyro- and hydro-metallurgy are two dominant techniques that have been employed effectively for the recovery of PGMs from SACs by different refining and metallurgy industries.[5] The pyrometallurgical smelting process involves mixing SACs with a flux agent (e.g., CaO) to remove impurities by forming slag and a suitable metal collector (e.g., Fe) to extract PGMs into an alloy phase under high-temperature conditions (2000 °C).[5] The process is fast and offers high extraction efficiency of PGMs although special equipment and high energy consumption are required to reach the desired temperature, resulting in a very high operational cost which hinders their industrial development.[6,7] The pyrometallurgical route produces a greater amount of greenhouse gases (CO_2) and chlorofluorocarbons (CFCs) and toxic gases (SO_2), hence, causing significant damage to the ozone layer.[8] In comparison with pyrometallurgy, hydrometallurgy is a more cost-effective and environmentally friendly approach that requires less energy demand due to the absence of high temperature operation.[9] It works by dissolving metals into strong mineral acids (HCl, HNO_3 or H_2SO_4). The process is easy-to-control and offers high selectivity which leads to a recovery of ~95 % of PGMs from SACs.[9]

Leaching PGMs in HCl has received extensive attention as it could facilitate the leaching of metals through their great capacity to form stable chloro-complexes ($PtCl_6^{2-}$, $PdCl_4^{2-}$ and $RhCl_6^{3-}$). The difference in the standard potential of

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PGMs in the absence and presence of chloride ions at standard conditions (25 °*C* and 1 atm) are listed in Table 1.[10]

Due to the high chemical inertness of PGMs, HCl could only achieve partial dissolution of metals in conventional leaching methods. PGMs could undergo chemical and physical changes by adsorbing oxygen onto their surface and undergoing oxidation to form oxides (PtO, PtO_2, PdO, PdO_2 and Rh_2O_3) under a certain high-exhaust temperatures (~1000 °C).[11] It is known that the PGM oxides are highly resistant against acidic attack, hence the addition of additives such as HNO_3, H_2O_2, NaClO, $NaClO_3$ or $C_6H_8O_7$ were often added to promote the leaching efficiency.[12–17] The leaching process is also dependent on the type of leaching techniques, particularly microwave (MW) leaching has been intensely studied by several authors[18–20] to significantly reduce energy and time consumption as well as enhance the leaching of PGMs from SACs. A list of PGMs leaching in different leaching systems is summarized in Table **S1** (Appendix A, Supplementary Material).

Many different chloro-leaching media have been widely investigated. However, to the best of our knowledge, which leaching solutions could achieve the highest PGMs leaching efficiency has yet to be answered. Hence, the purpose of this model study is to investigate and compare which leaching solution (i.e., HCl and HCl + complexing or oxidizing agents) will provide the highest amount of Pt, Pd and Rh from SACs. The dissolution of PGMs was carried out by using HCl as the fundamental acid system combined with another acid source (H_2SO_4), complexing agent (citric acid, $C_6H_8O_7$) or oxidant(s) (HNO_3, H_2O_2, NaClO, and $NaClO_3$). The concentrations of complexing and oxidizing agents were based on those reported in literature where $>90\%$ PGMs recoveries were achieved (Table **S1**, Supplementary Material). The experiments were performed using a closed MW-assisted acid leaching technique. This study also aims to determine the most cost effective, energy efficient and safest leaching approach to achieve high PGMs leaching efficiencies under MW heating conditions. Experiments were performed by investigating the effect of leaching temperatures.

Table 1. The standard potential of PGMs and chloro-PGMs.

Electrode chemical reaction	Electrode potential, E^0 (V)
$Pt^{2+} + 2e^- \rightleftharpoons Pt$	1.18
$Pd^{2+} + 2e^- \rightleftharpoons Pd$	0.951
$Rh^{3+} + 3e^- \rightleftharpoons Rh$	0.758
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt + 4Cl^-$	0.755
$PdCl_4^{2-} + 2e^- \rightleftharpoons Pd + 4Cl^-$	0.591
$RhCl_6^{3-} + 3e^- \rightleftharpoons Rh + 6Cl^-$	0.431

2. Experimental

2.1. Materials and Reagents

Two different SAC samples were used to study the PGMs leaching. The first sample was the spent car catalyst European reference material (CRM or ERM®-EB504a, BAM Germany) with values of 1414±9 mg kg^{-1} Pt, 1596±11 mg kg^{-1} Pd and 210±2 mg kg^{-1} Rh. This CRM was used to validate the methods and compare the results with those of the other sample (industrial sample) which was a crushed powder form of spent ceramic monoliths. It was provided by Hensel Recycling Australia PTY LTD (Melbourne, VIC) together with information of its PGM composition obtained by X-ray fluorescence, i.e., 221 mg kg^{-1} Pt, 2507 mg kg^{-1} Pd and 508 mg kg^{-1} Rh.

Concentrated HCl (36 %, Thermo Fisher), HNO_3 (70 %, Thermo Fisher), H_2SO_4 (98 %, Chem-supply), H_2O_2 (30 % w/w, Chem-supply), NaClO (8–12.5 %, Chem-supply), $C_6H_8O_7.H_2O$ (≥99 %, Chem-supply) and $NaClO_3$ (≥99 %, Sigma-Aldrich) were used in the preparation of six leachates with the following compositions: 75 % HCl-25 % HNO_3; 99.2 % HCl-0.8 % H_2O_2; 90 % HCl-0.5 % H_2O_2–0.5 % H_2SO_4; 79 % HCl-21 % $NaClO_3$; 97 % HCl-3 % NaClO; and 95 % HCl-3 % NaClO-2 % H_2O_2. The concentrations in all the leaching solutions are expressed in %(v/v). Deionized water (Merck Millipore, 18.2 MΩ cm) was used for the preparation of all standard solutions.

2.2. Chemical Characterization of the Spent Automotive Monolith Block and Powder

Electron microprobe analyser (EMPA, *JOEL JXA-8530F Plus*) was used for the characterization of the spent automotive monolith block to determine its chemical composition and metals distribution. Before analysis, the monolith block was mounted in *Epoxy* resin, followed by diamond polishing and carbon conductive coating to prevent electrons from accumulating and forming static cloud on the surface of the sample which tends to repel incoming beam of electrons, preventing the detection of signal.

To determine the exact chemical compositions of PGMs in the CRM and industrial sample, quantitative analyses were performed by using inductively coupled plasma optical emission spectroscopy (ICP-OES, *Agilent Technologies*, *5100*). All calibration standards (for Pt and Rh range of 0.05–5 g mL^{-1}; and for Pd range of 0.01–1 g mL^{-1}) and concentration of PGMs in the leaching solutions were quantitatively analysed by ICP-OES, using the wavelengths of Pt (214.423 nm), Pd (248.892 nm) and Rh (343.489 nm). The standard operating conditions of the ICP-OES were as follows: nebulizer gas flowrate: 0.70 L min^{-1}; plasma flowrate: 15.0 L min^{-1}; RF generator power: 1.20 kW; auxiliary gas flowrate: 1.20 L min^{-1}; viewing mode: axial.

2.3. Microwave Leaching

A microwave oven, Ethos Easy (Milestone, Sorisole, BG, Italy), was equipped with a high-pressure rotor with 15 PTFE-TFM vessels (SK-15 eT) of 100 mL. It allowed maximum temperature of 230 °C and maximum pressure of 100 bar. The microwave cavity was irradiated by two 950 W magnetrons working at 2.45 GHz. A contactless infrared sensor (T2) was used to control and monitor the internal temperature of all vessels. The desired temperature, microwave power and irradiation time could be adjusted by using the digital control program.

A spent catalyst sample to leaching solution ratio of 0.1 : 10 g mL^{-1} was added into each 100 mL PTFE-TFM vessels for the leaching experiments. The vessels were closed, and the spent catalyst materials were digested in high pressure microwave system with a two-stage heating program based on the study by Suoranta et al.[18] who achieved >90% PGMs leaching efficiencies in HCl solution: (1) ramping time of 15 min to 210 °C; (2) holding time of 10 min at 210 °C. All leaching processes were performed under 1800 W. After leaching, the solutions that appeared yellowish or orange-coloured were allowed to cool down to room temperature prior to opening of the vessels and were filtered using 0.45 µm syringe filter PES membrane. The solutions were made up to 50 mL by deionized water. The elemental PGM concentration in the leaching solutions were determined by ICP-OES. All experiments were run in triplicate.

For the optimization study, spent catalyst samples (0.1 g) were dissolved in 10 mL of leaching solutions using a microwave program of 15 min ramp + 10 min hold at four different temperatures (100, 150, 180 and 210 °C).

3. Results & Discussion

3.1. Composition of Spent Automotive Catalyst (SAC) Material

EMPA was employed to analyse the SAC materials. The detailed chemical compositions of the PGMs in the spent automotive monolith block (industrial sample) could not be obtained since the concentrations of the PGM elements were below the detection limits (~100 mg kg^{-1}) of the instrument. Though the results confirmed the presence of other metallic oxides (Al, Zr and Ce) on the surface of monolith as shown in Table 2. The EMPA images of the spent automotive monolith block are available in the Supplementary Material (Appendix B, Figure **S1**).

Table 2. Composition of the spent automotive monolith block (industrial sample) (n = 3).

Oxide	Al_2O_3	ZrO_2	CeO_2
Content±SD (%)	16±2	57±12	14±1

3.2. Leaching PGMs in HCl Solution

Experiments were conducted to investigate whether HCl could achieve high PGMs leaching under MW heating. The CRM and industrial sample were leached in 11.65 M (36%) HCl and both catalyst materials showed similar leaching behavior for Pt and Rh (Figure 1).

In CRM, the recoveries of 91 ± 13% Pt, 97 ± 13% Pd and 68 ± 13% Rh were obtained (Figure 1). The low Rh recovery was likely due to the chemical inertness of Rh and the presence of Rh oxides which are less amenable to dissolve in acidic media, hence slowing down the metal dissolution. This is also the similar to the industrial sample where good dissolution efficiencies were achieved for Pt (94 ± 20%) and Pd (82 ± 21%) and a moderate recovery for Rh (74 ± 22%). It is worth highlighting that different catalyst materials contain different elemental compositions; therefore, the leaching values were distinctive between the CRM and industrial sample.

3.3. Leaching PGMs in Various HCl-Oxidant(s) Solutions

The standard electrode potentials of oxidants are listed in Table 3. PGMs can be readily oxidized by a suitable oxidizing agent with a standard potential >0.74 V (Table 1). This is the first study where oxidizing agents such as HNO_3, H_2O_2, NaClO and $NaClO_3$ were chosen to compare and address the question of which acid-oxidizing agent(s) combination will

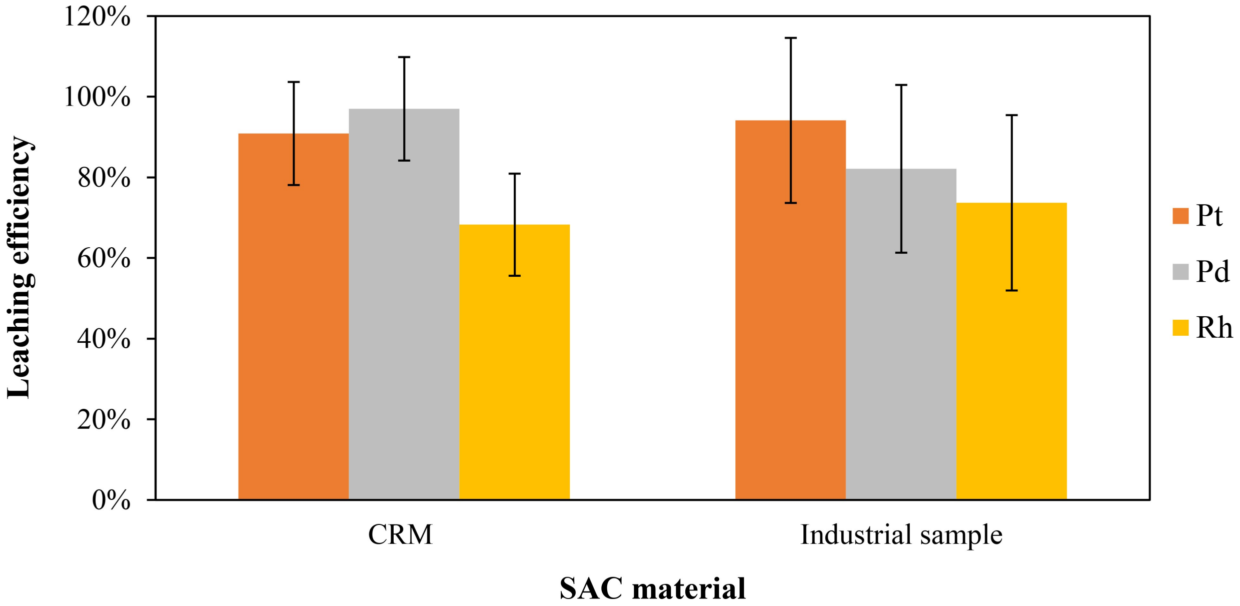


Figure 1. The leaching efficiencies of Pt, Pd and Rh from the CRM and industrial sample in 11.65 M (36%) HCl. Error bars are ± SD (n = 3).

produce the highest recoveries for the three elements. Amongst these oxidants, H_2O_2 has the strongest oxidizing power, 1.77 V. Thus, it can be expected that leaching solution containing H_2O_2 will achieve the highest PGMs leaching efficiency. The chemical reactions between PGMs and chloro-oxidizing agent(s) can be found in the Supplementary Material (Appendix C, Equations **1–33**).

The CRM and industrial sample were leached in HCl with the addition of oxidant(s) and both catalyst materials showed different leaching trends for PGMs (Figures 2A and B).

It is important to understand the chemical reactions associated with the MW leaching. As mentioned earlier, PGMs could exist in elemental and oxide forms. It is known that the metal oxides are less amenable to dissolve even in a strong acidic condition. The dissolution of Pt oxides could be enhanced under MW heating, in the presence of highly concentrated HCl (≥6 M) and in-situ generation of Cl_2 gas at temperatures ≥150 °C according to Equations (1)–(4).[10,19]

$$PtO_2 + 2H^+ + 2e^- \rightleftharpoons PtO + H_2O \; E^0 = 1.01\ V \quad (1)$$

$$PtO_2 + 4H^+ + 4e^- \rightleftharpoons Pt + 2H_2O \; E^0 = 1.00\ V \quad (2)$$

$$PtO + 2H^+ + 4Cl^- + Cl_2\ (aq) \rightleftharpoons PtCl_6^{2-} + H_2O \quad (3)$$

$$PtO_2 + 4H^+ + 6Cl^- \rightleftharpoons PtCl_6^{2-} + 2H_2O \quad (4)$$

The addition of oxidant(s) with electrode potentials, $E^0 > 1.02\ V$ could cause PdO to be further oxidized in the leaching media, resulting in recovery loss (Eq. (5)). MW-assisted chloride leaching (≥150 °C) could affect the Pd leaching by overcoming surface oxidation (Eq. (6)).[20]

$$PdO_2 + 2H^+ + 2e^- \rightleftharpoons PdO + H_2O \; E^0 = 1.02\ V \quad (5)$$

$$PdO + 2H^+ + 4Cl^- \rightleftharpoons PdCl_4^{2-} + 2H_2O \quad (6)$$

Moreover, molecules in the leaching solutions could absorb MW energy, causing them to vibrate, thus facilitating the rapid increase in temperature. Under these superheating induced by MW radiation, hot acid vapors and gaseous species (e.g., Cl_2, O_2, NOCl, NO and CO_2) are generated and encountered with the SAC material thereby enhancing the dissolution rate of Rh. To a certain extent, oxidized Rh is dissolved in the leaching system (Eq. (7)).[20]

$$Rh_2O_3 + 6H^+ + 12Cl^- \rightleftharpoons 2RhCl_6^{3-} + 3H_2O \quad (7)$$

As a result, good leaching efficiencies of 98±24% Pt, 103±30% Pd and 101±33% Rh were obtained for the CRM when using HCl-NaClO leaching solution (Figure 2A). Similar results were obtained upon the addition of H_2O_2 into the HCl-NaClO solution. The leaching system of HCl-H_2O_2 also gave high recoveries of 94±25% Pt, 99±25% Pd and 95±29% Rh. The addition of H_2SO_4 to the HCl-H_2O_2 solution gave similar PGMs recoveries. Thus, the H_2O_2 and H_2SO_4 are not required for the PGMs leaching. The HCl-HNO_3 system also gave high dissolution efficiencies of 93±11% Pt, 93±7% Pd and 87±15% Rh. The HCl-$NaClO_3$ gave the poorest PGMs recoveries (58±13% Pt, 61±13% Pd and 65±15% Rh) likely because of the highly oxidizing conditions which strongly favored the conversion of elemental PGMs to metal oxides (PtO, PtO_2, PdO, PdO_2 and Rh_2O_3), hence reducing PGMs leachabilities.

Table 3. Standard electrode potentials of oxidants.

Oxidant	Electrode chemical reaction	Electrode Potential, E^0 (V)	Ref
HNO_3	$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O$	0.96	[12]
H_2O_2	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.77	[14]
	$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$	0.68	
NaClO or $NaClO_3$	$Cl_2\ (aq) + 2e^- \rightleftharpoons 2Cl^-$	1.36	[15,16,21]
	$Cl_3^-\ (aq) + 2e^- \rightleftharpoons 3Cl^-$	1.42	
	$2HClO + 2H^+ + 2e^- \rightleftharpoons Cl_2\ (g) + 2H_2O$	1.63	

In the industrial sample, the HCl-HNO_3 system obtained the highest Pt, Pd and Rh recoveries of 120±11%, 103±11% and 122±13%, respectively (Figure 2B). The HCl-H_2O_2 leaching system achieved similar PGMs recoveries to the HCl-HNO_3 system. In the presence of H_2SO_4, the recoveries of Pt, Pd and Rh were 114±10%, 99±10% and 116±10%, respectively. The HCl-NaClO and HCl-NaClO-H_2O_2 leaching systems produced similar leaching results of 84±6% Pt, 72±6% Pd and 89±6% Rh, in the absence of H_2O_2, and 106±20% Pt, 91±21% Pd and 110±19% Rh, in the presence of H_2O_2. The Student's t-test showed that the experimental means were not statistically significantly different with or without the addition of H_2SO_4 to the HCl-H_2O_2 solution and H_2O_2 to the HCl-NaClO solution. These corrosive chemicals were not required for PGMs leaching from the industrial sample. The HCl-$NaClO_3$ also achieved good recoveries of PGMs.

From an environmental perspective, aqua regia (HCl-HNO_3) produces toxic gases such as NO and NOCl which could react with moisture in the air to form HNO_2 (well-known as an acid rain contributor), as described in Equations (8)–(10). Hence, HCl-H_2O_2 is a greener approach because the mixture only emits H_2 and Cl_2 gas, causing fewer negative impacts to the environment.

$$HNO_3\ (aq) + 3HCl\ (aq) \rightarrow NOCl\ (g) + Cl_2\ (g) + 2H_2O\ (l) \quad (8)$$

$$2NOCl\ (g) \rightarrow 2NO\ (g) + Cl_2\ (g) \quad (9)$$

$$NOCl\ (g) + H_2O\ (l) \rightarrow HNO_2\ (aq) + HCl\ (aq) \quad (10)$$

Lastly, the leaching system that recovered the highest amount of PGMs performed differently in both catalyst materials which was likely due to the difference in the oxidation states of PGMs (i.e., elemental or oxide) on the

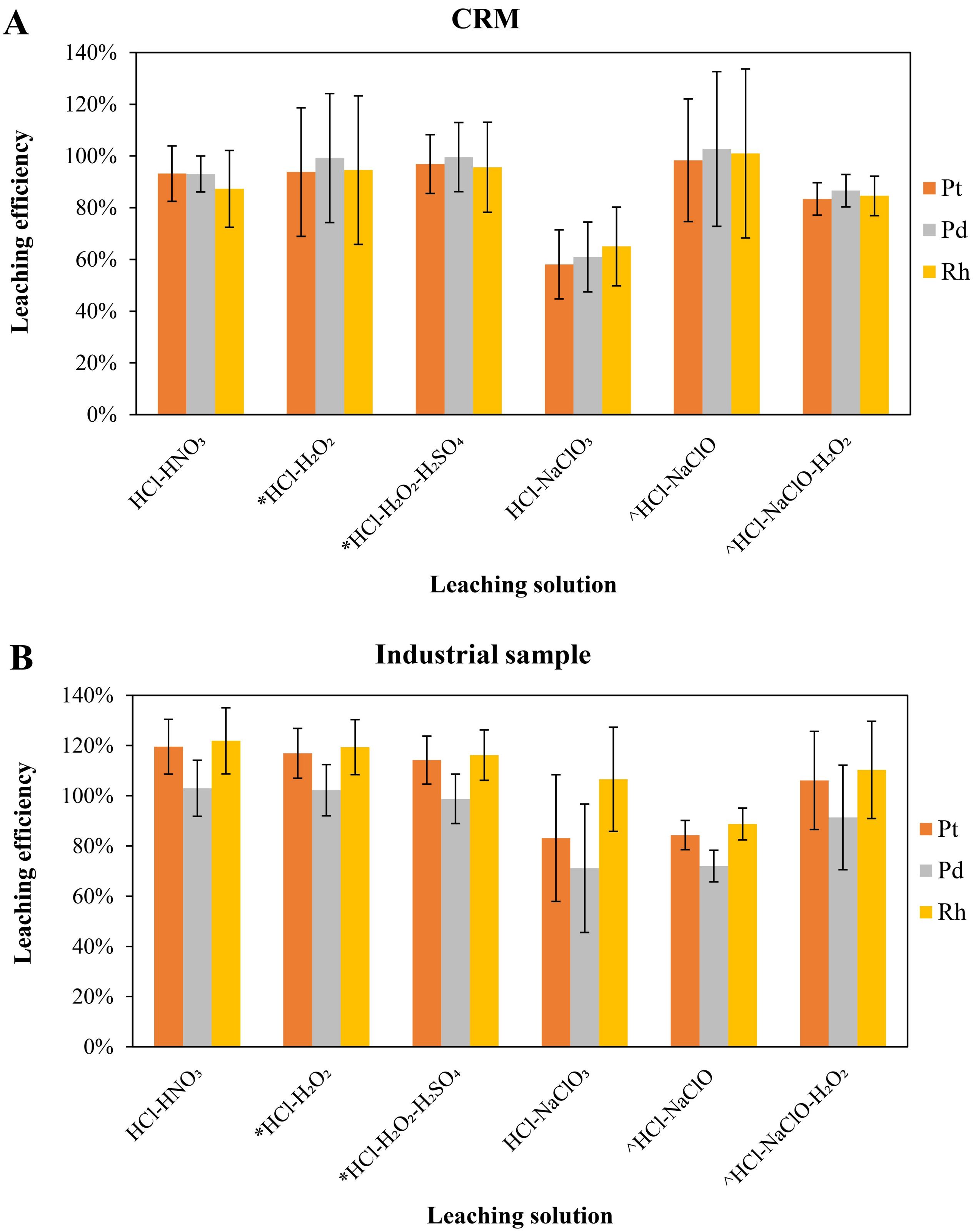


Figure 2. The leaching efficiencies of Pt, Pd and Rh from the CRM (**A**) and industrial sample (**B**) in different leaching systems. The Student's t-test was conducted at 95 % confidence level: * and ^ indicates that there was no significant difference for HCl-H_2O_2 *vs* HCl-H_2O_2-H_2SO_4 and HCl-NaClO *vs* HCl-NaClO-H_2O_2, respectively. Error bars are ± SD (n = 3).

monolith's surface. Furthermore, other elemental oxides (e.g., CeO_2 and ZrO_2) present on the monolith's surface which could be co-leached in the process, hence interfering in the leaching of PGMs and leading to lower PGMs recoveries.

3.3.1. Comparison of PGMs Leaching in HCl vs HCl-Oxidant(s) Solutions

A comparative study was conducted to investigate whether the addition of oxidant(s) into the HCl could improve PGMs dissolution efficiency.

For CRM, the results obtained by using HCl and HCl + oxidant(s) leaching solutions showed that there was no significant difference in the PGMs recoveries in the absence or presence of oxidant(s), except for the $NaClO_3$ addition, which led to recoveries lower by >30% for Pt and Pd due to the corresponding partial oxidation reactions. Thus, the addition of oxidant was not required for the leaching of PGMs from the CRM. Likewise in the case of industrial sample, the PGMs dissolution efficiencies were the similar with or without the addition of oxidant(s), except for the addition of HNO_3 which led to a 48% higher recovery of Rh than in the absence of oxidant (i.e., HCl).

Overall, the addition of oxidant(s) was not required to achieve an efficient PGMs leaching process from both catalyst materials.

3.4. Leaching PGMs in HCl-$C_6H_8O_7$ Solution

To achieve greener leaching process by minimizing the use of corrosive acids and reducing the emission of toxic gases (e.g., Cl_2, H_2, SO_2 and NO_x), an organic acid such as citric acid ($C_6H_8O_7$) was chosen to partly replace HCl by providing citrate ions for complexing reactions with PGMs. The CRM and industrial sample were leached in HCl-$C_6H_8O_7$ and similar leaching trends were obtained for Pt and Pd, while slightly different results were observed for Rh (Figure 3). The chemical reactions between PGMs and HCl-$C_6H_8O_7$ are listed in the Supplementary Material (Appendix C, Equations **34–36**).

For CRM, when $C_6H_8O_7$ was added into the HCl leaching solution, similar leaching efficiencies for Pt (88±4%) and Pd (86±2%) were obtained to those of a solution containing HCl only (Figure 3). On the other hand, the Rh recovery improved by 26% (i.e., 94±3%) upon the addition of $C_6H_8O_7$. In the industrial sample, the leaching efficiencies of Pt, Pd and Rh were 112±16%, 84±20% and 103±19%, respectively in the HCl-$C_6H_8O_7$ solution. These results were similar to those obtained with the HCl solution according to the Student's t-test.

In the presence of $C_6H_8O_7$, the Rh recovery from industrial sample was slightly different from those of the CRM which might be due to the difference in the PGM compositions (i.e., Rh could either exist in the elemental (Rh^0) or oxide (Rh_2O_3) form on the monolith's surface). The metal oxides are more difficult to dissolve in an acidic solution, resulting in no improvement of Rh recovery, particularly in the industrial sample. Another reason could be due to other metal oxides (CeO_2 and ZrO_2) present in the monolith which could be co-leached in the process thus reducing the efficiency of Rh dissolution.

3.4.1. Comparison of PGMs Leaching in HCl-Oxidant(s) vs HCl-$C_6H_8O_7$ Solutions

When HCl-oxidant(s) and HCl-$C_6H_8O_7$ solutions were used, the PGMs leaching efficiencies were not statistically different according to the Student's t-test. It is worth reminding that the use of $C_6H_8O_7$ is an eco-friendlier approach as it partly replaces the HCl, eliminates the use of aggressive and corrosive chemicals (e.g., HNO_3, H_2O_2, H_2SO_4, NaClO and

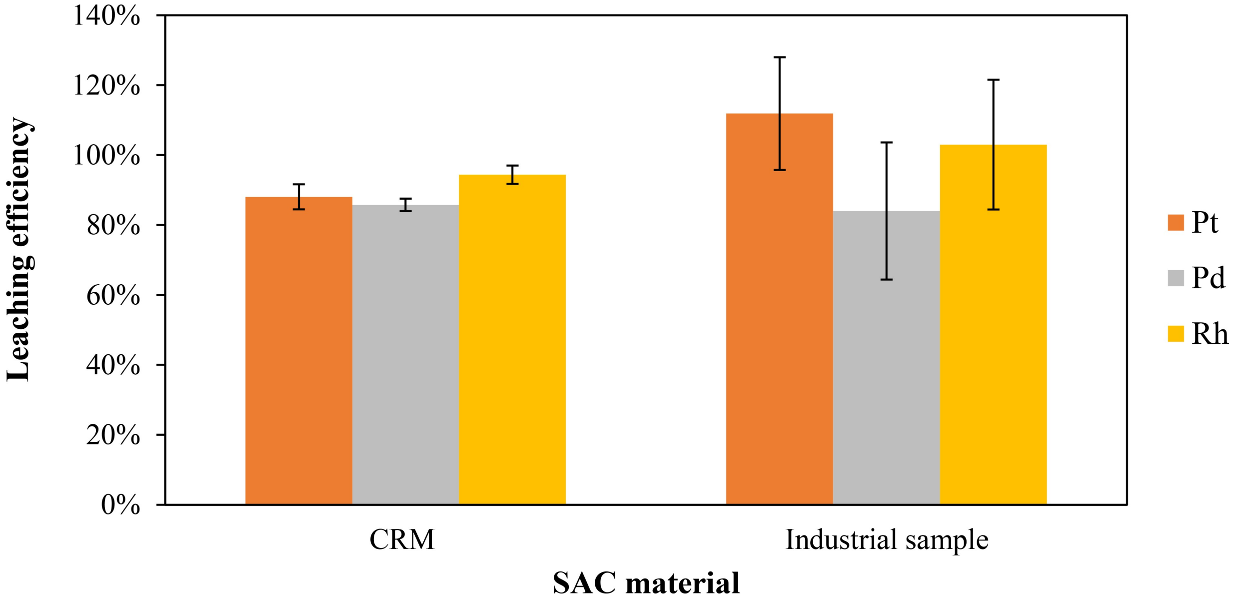
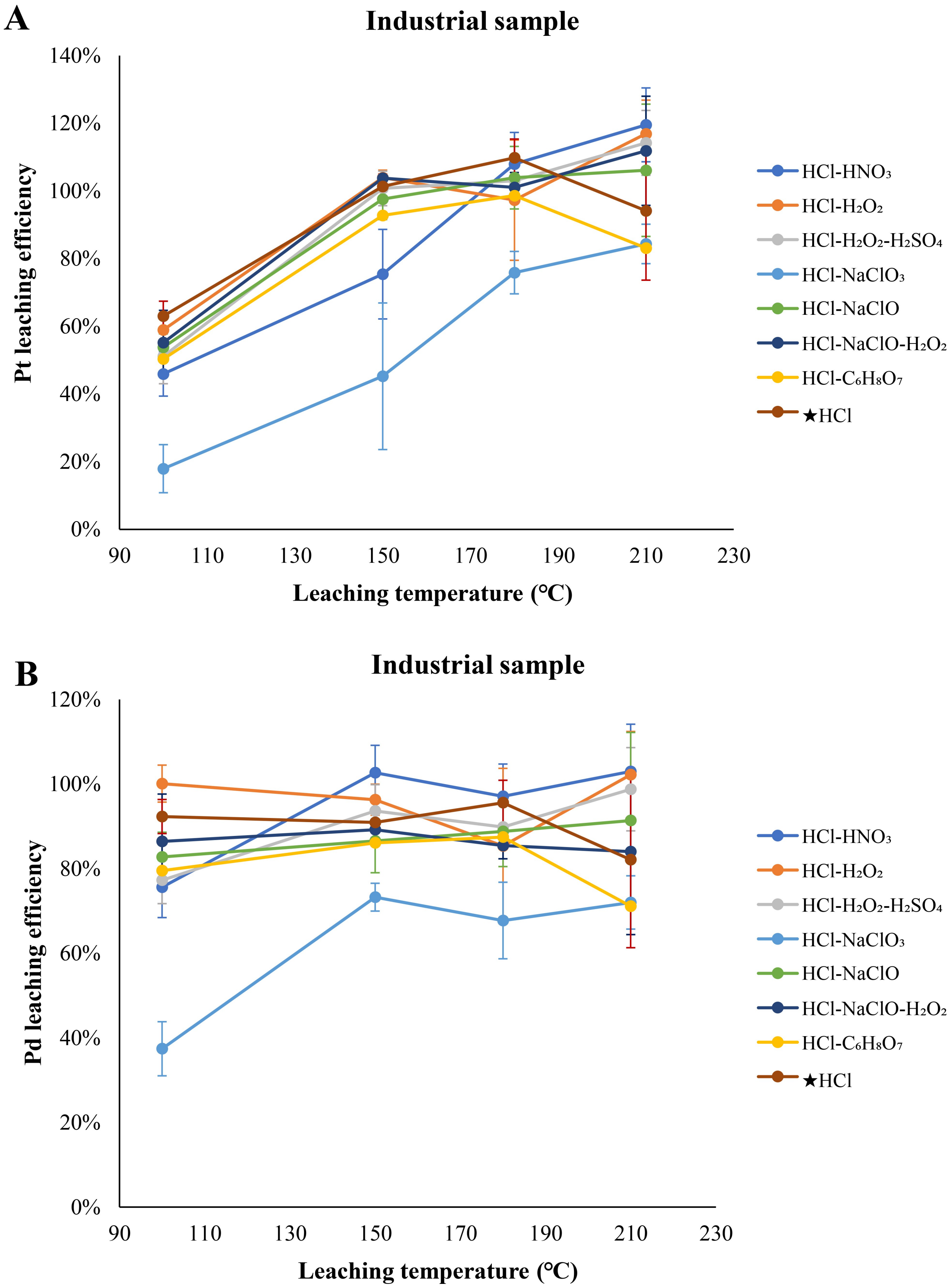


Figure 3. The leaching efficiencies of Pt, Pd and Rh from the CRM and industrial sample in 80% (v/v) HCl + 20% (v/v) $C_6H_8O_7$ solution. Error bars are ±SD (n = 3).


A
Industrial sample
Pt leaching efficiency
140%
120%
100%
80%
60%
40%
20%
0%
90
110
130
150
170
190
210
230
Leaching temperature (℃)
HCl-HNO$_3$
HCl-H$_2$O$_2$
HCl-H$_2$O$_2$-H$_2$SO$_4$
HCl-NaClO$_3$
HCl-NaClO
HCl-NaClO-H$_2$O$_2$
HCl-C$_6$H$_8$O$_7$
★HCl
B
Industrial sample
Pd leaching efficiency
120%
100%
80%
60%
40%
20%
0%
90
110
130
150
170
190
210
230
Leaching temperature (℃)
HCl-HNO$_3$
HCl-H$_2$O$_2$
HCl-H$_2$O$_2$-H$_2$SO$_4$
HCl-NaClO$_3$
HCl-NaClO
HCl-NaClO-H$_2$O$_2$
HCl-C$_6$H$_8$O$_7$
★HCl

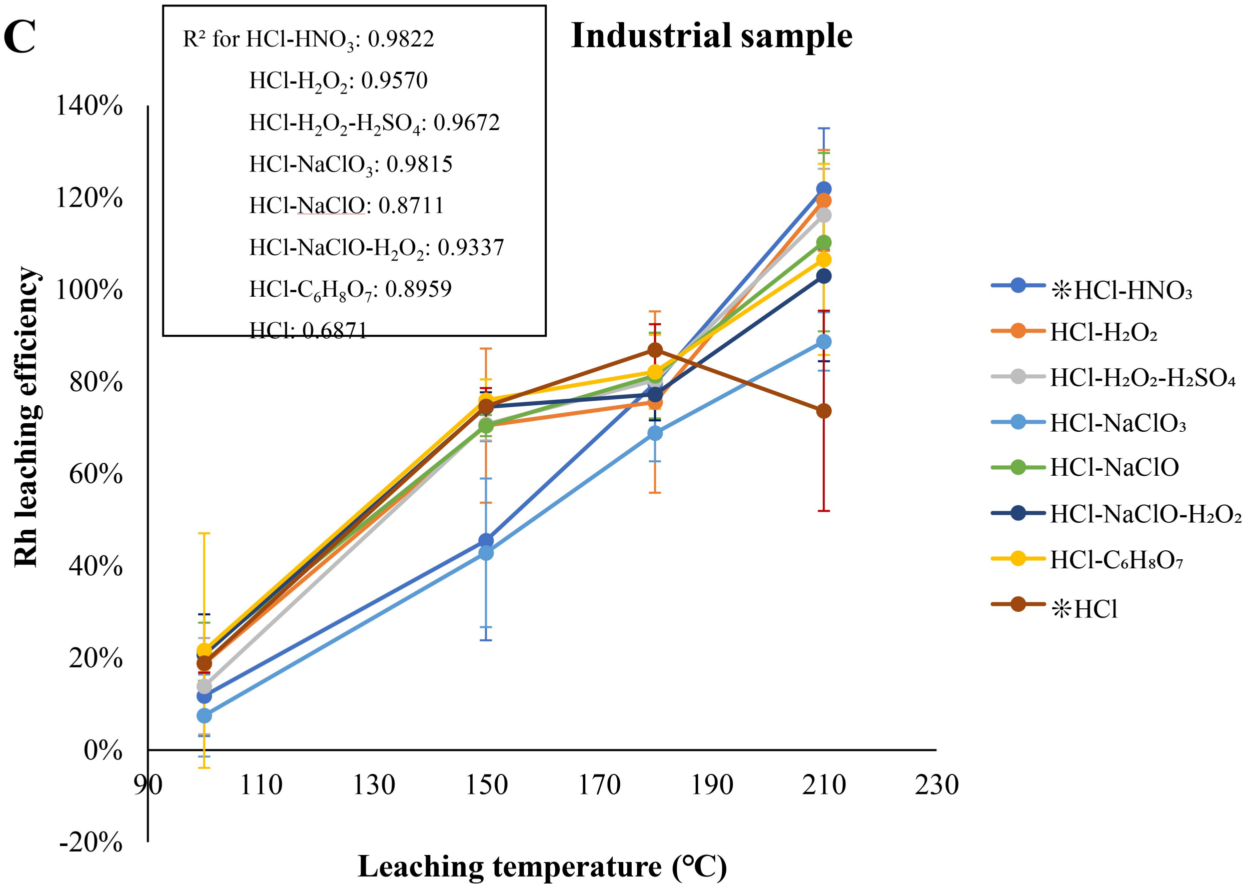


Figure 4. The leaching efficiencies of Pt, Pd and Rh in MW leaching from the industrial sample (**A**, **B**, and **C**) in different leaching systems at different temperatures for 25 min. Error bars are ± SD (n = 3). Student's t-test was conducted at 95 % confidence level: ★ indicates that there was no significant difference for the HCl leaching solution at 150 °C and 180 °C; and ❊ indicates that there was a significant difference for the HCl at 180 °C and the HCl-HNO_3 at 210 °C.

$NaClO_3$) and reduces the production of toxic gases (e.g., Cl_2, H_2, NOCl and SO_2).

3.5. Optimization of the Microwave-Assisted Leaching Method

3.5.1. Effect of Leaching Temperature

With respect to the economy and safety of the leaching process, it is important to determine the lowest possible dissolution temperature as well as achieving the highest leaching efficiencies of PGMs. The optimization experiments were performed in a two-steps microwave program, starting with a 15 min ramp followed by a 10 min holding time at temperatures of 100, 150, 180 or 210 °C in a S/L ratio of 0.1:10 g mL^{-1}. The CRM and industrial sample showed different recovery trends for PGMs.

For CRM, the HCl could achieve maximum recoveries of 103 ± 2 % Pt and 111 ± 2 % Pd at 150 °C (Appendix D, Figures **S2A** and **S2B**, Supplementary Material). While for Rh, poor to moderate leaching efficiencies (16–70 %) were observed as the temperature increased (Figure **S2C**, Supplementary Material). It is worth noting that the Rh recovery was similar in the absence or presence of oxidizing agent(s) at 210 °C. In contrast, the addition of $C_6H_8O_7$ improved Rh recovery from 73 ± 5 % at 180 °C to 94 ± 3 % at 210 °C. The experimental results confirmed that the Rh leaching kinetic was highly dependent on using a combination of a complexing agent and high leaching temperatures, facilitating the dissolution of Rh and Rh oxides, and thus leading to higher metal recovery.

For the industrial sample, the Pt leaching efficiencies increased upon increasing temperature except for the HCl and HCl-NaClO leaching solutions, where the highest Pt recoveries were reached at 180 °C and then decreased at higher temperatures (Figure 4A). The HCl leaching solution also achieved the highest recovery of 96 ± 5 % for Pd at 180 °C (Figure 4B). However, the Pt and Pd recoveries in the same solution at 150 °C and 180 °C were statistically similar. Thus, the use of a higher leaching temperature was not required. The HCl-H_2O_2 achieved the Pd highest recovery of 100 ± 4 % at 100 °C, and then decreased when > 100 °C, and afterwards increased to > 99 % at 210 °C. Such inconsistency might be due to the non-homogeneity of the catalyst material. The HCl-HNO_3 achieved maximum leaching efficiency of 103 ± 6 % Pd at 150 °C. While in the presence $C_6H_8O_7$ or NaClO obtained the highest Pd dissolution efficiencies at

180 °C. Other leaching systems such as HCl-H_2O_2-H_2SO_4, HCl-$NaClO_3$ and HCl-NaClO-H_2O_2 produced maximum Pd recovery at 210 °C. However, in comparison to the Pd recovery in the HCl leaching solution at 210 °C, there was no statistically significant difference in the recoveries in the absence or presence of oxidant(s) (i.e., H_2O_2-H_2SO_4, $NaClO_3$ or NaClO-H_2O_2). This indicates that the use of these corrosive chemicals was not required.

The average Rh leachabilities increased with increasing temperature in all the acid-complexing or oxidizing agents leaching systems (Figure 4C). HCl only could achieve a high Rh leaching efficiency of 87 ± 6 % at 180 °C. The results indicate that the addition of an oxidizing agent is not required for the dissolution of Pt, Pd and Rh at 180 °C. However, it is worth mentioning that the dissolution of Rh could be further improved by 32–35 % upon the addition of an oxidant (i.e., HNO_3 or H_2O_2) and applying a higher leaching temperature (210 °C).

From the above-mentioned results produced for two different catalyst samples, it can be concluded that the oxidation states of PGMs (i.e., elemental or oxides) cause a significant effect on metal dissolution. Amongst the three PGMs, Rh has the highest economic value.[2] Therefore, the addition of a complexing or oxidizing agent and a higher leaching temperature ($>$180 °C) should be taken into consideration to achieve an efficient and effective Rh leaching process. The leaching efficiency improves as the temperature in microwave instrument increases, suggesting the oxide forms of those catalyst require more energy to be dissociated into ions.

4. Conclusions

The present comparative model study demonstrated that the use of a chloro-leaching solution combination (i.e., HCl + complexing or oxidizing agents) was the key to achieving high PGMs leaching efficiency, particularly for different SAC materials. The MW-assisted leaching technique produced high PGMs recovery in a relatively fast leaching process (i.e., 25 min and $\geq$150 °C). The leaching solution containing HCl only showed that the in-situ generation of Cl_2 gas and O_2 in the air was sufficient to leach significantly large amounts of PGMs, therefore the addition of oxidant(s) was not necessary. However, challenges arose in the leaching of Rh as it formed a protective oxide layer on the monolith's surface during the service life of the catalytic converter and in the leaching process. This oxide layer hindered the efficient dissolution of the Rh in HCl solution, resulting in moderate recovery efficiency of 75 %. Thus, the addition of a complexing ($C_6H_8O_7$) or oxidizing (H_2O_2) agent and the use of a high leaching temperature ($>$180 °C) became essential in enhancing the Rh leaching rate. Importantly, the use of oxidizing agent(s) (i.e., HNO_3, H_2O_2, NaClO and $NaClO_3$) could pose greater environmental and safety risks as it increases the emissions of corrosive and flammable gases (i.e., Cl_2, NOCl, NO_x and H_2). The partial replacement of aggressive and corrosive chemicals (i.e., HCl) by $C_6H_8O_7$ has provided an alternative eco-friendlier (greener) PGMs leaching route. Future work should investigate whether partly replacing HCl with increasing concentration of $C_6H_8O_7$ could achieve similar or better metal recoveries. Finally, different organic acids should also be investigated as alternative leaching reagents to minimize the requirements of strong or harsh acidic conditions.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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