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Recovery of Platinum and Palladium from Spent Automotive Catalysts: Study of a New Leaching System Using a Complete Factorial Design

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Abstract: The recovery of materials and energy from end-of-life products is increasingly a fundamental factor in the sustainable development of various countries. Recovering metals from different types of waste is not only a practice in support of the environment, but is also a profitable economic activity. For this reason, exhausted automotive catalysts can become renewable sources of critical raw materials such as Pt, Pd, and Rh. However, recovering Pt and Pd from spent catalysts through an efficient, economical, and green method remains a challenge. This article presents a new leaching process for the hydrometallurgical recovery of Pt and Pd from exhausted automotive catalysts. The leaching solution consists of an aqueous mixture of hydrochloric acid, two organic acids (citric acid and acetic acid) and hydrogen peroxide. A complete factorial plan on two levels (2^k) was performed in order to evaluate the main effects of the analyzed factors and their interactions. The factors that were presumed to be the most influential on the leaching of Pt and Pd were the concentrations of the different reagents and the reaction time. The optimal circumstances for achieving the largest recovery (over 80% Pt and 100% Pd) were achieved using the following conditions: a concentration of HCl of 5 M, a concentration of H_2O_2 of 10% wt./vol., a concentration of $C_2H_4O_2$ of 10%vol./vol., and a reaction time of 3 h.

Keywords: automotive catalyst; platinum and palladium recovery; hydrometallurgical process; leaching; factorial plan

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1. Introduction

Platinum and palladium are part of the class of materials called Platinum Group Metals (PGMs), together with rhodium, iridium, osmium and ruthenium. PGMs are used in numerous strategic sectors and are among the elements that the European Union has classified as Critical Raw Materials (CRMs), that is, all those raw materials that are economically and strategically important and that have a high supply risk.

The most remarkable application of these metals is certainly in catalysis, both in oil-refining processes, in various petrochemical processes, and in the control of gaseous emissions from gasoline engines and diesel vehicles. PGMs are also widely used in electronics to produce numerous electrical components, such as computer hard drives, capacitors or plasma display screens. Currently, the production of hydrogen electrolytically is increasingly a reality; in this field, PGMs are essential for creating high-performance electrolyzers [1].

The use of these metals is so vast that PGMs can be found both in the medical field, for example, to produce pacemakers or cancer-fighting drugs, and in automobile manufacturing (oxygen sensors, airbags and others). This wide range of applications is linked to the various properties of PGMs, which, to date, have no adequate substitutes that can provide the same performance [2,3].

The growing demand for these metals has led to a significant increase in the price of PGMs (except Pt price) in the last ten years, up until the COVID-19 epidemic, as shown in Figure 1. The recent global COVID-19 crisis caused a dramatic decrease in the price of PGMs [4,5].

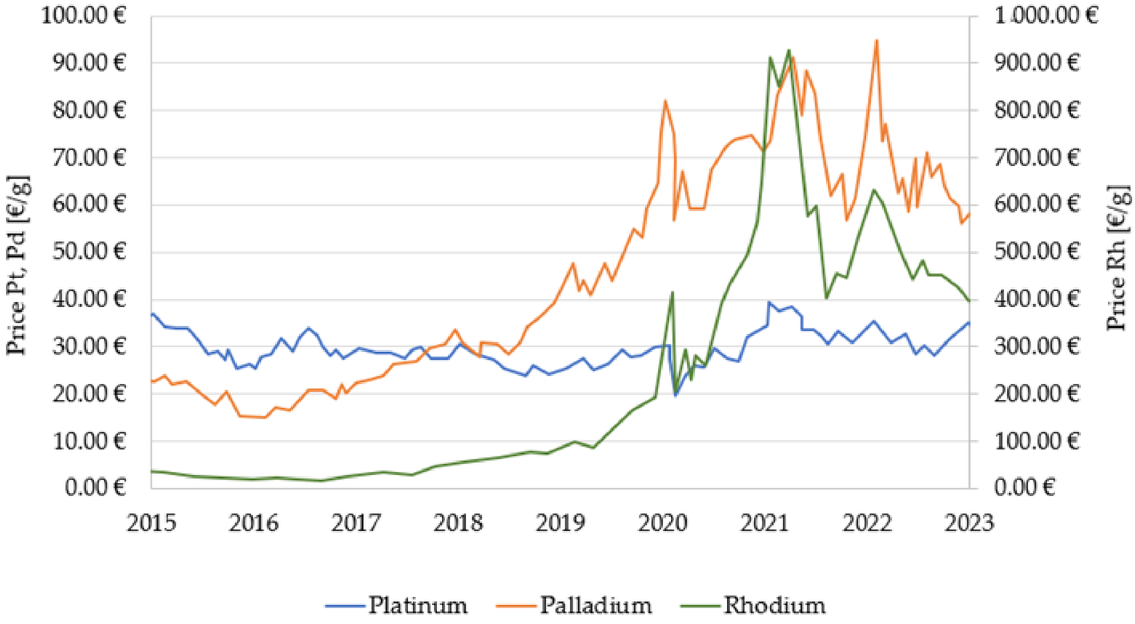

Figure 1. Trend in PGM prices from 2015 to 2023 [4].

Mineable deposits of PGMs are scarce, with their production amounting to around 400 ton/y [6] and their primary deposits being in South Africa, Zimbabwe, the USA, Canada and Russia. For this reason, there is increasing interest in the use of secondary sources, such as exhausted catalysts, electrical and electronic devices, or other end-of-life products. Furthermore, in secondary sources, there are concentrations of PGMs that even exceed the concentrations in natural sources. Generally, the concentration of PGMs in mineral sources is around 2–10 ppm; on the contrary, in a secondary source such as the automotive catalytic converter (ACC), concentrations of PGMs are about 0.1–0.3 wt.% [7]. Recovering these metals from end-of-life products not only allows primary sources to be safeguarded, but also environmental pollution to be reduced. For example, in order to obtain 1 kg of platinum from primary minerals, approximately 400 tons of waste is generated, while the same amount of platinum can be recovered by recycling 2 tons of Spent Automotive Catalysts (SACs) [8].

The recovery of PGMs from SACs can be performed both by pyrometallurgical and hydrometallurgical processes. Despite being the most efficient methods for the recovery of PGMs, pyrometallurgical or fusion processes are commonly energy-intensive and therefore are influenced by considerable gaseous emissions [9]; in addition, harmful reagents are consumed and potentially dangerous solid waste streams are produced. For all these reasons, hydrometallurgical processes have been preferable in the recovery of metals from solid matrices in recent decades.

One of the most delicate phases of the hydrometallurgical process is leaching. Numerous leaching systems have been studied regarding the recovery of PGMs, and a common component of these systems is the use of acid leaching solutions [1,10–14]. In many extraction systems, an oxidizing agent, such as hydrogen peroxide, is typically added to increase the yield of the target metal [12,15]. Various process intensification techniques have been developed in order to further enhance metal extraction yields, such as microwave-assisted leaching [16] or ultrasonic tanks [17]. One such variant of classical leaching, which has been the subject of numerous studies, involves the use of microorganisms to facilitate oxidation and complexation reactions [7,18].

With this study, we want to propose a new leaching system for the recovery of Pt and Pd from SACs that allows a reduction in the amount of hydrochloric acid used. In order to perform this operation, some of the hydrochloric acid was replaced with organic acids, such as citric and acetic acid, which are milder compared to mineral acids such as sulfuric or hydrochloric acid. By using these organic acids, less severe conditions can be employed, thus minimizing the risk of corrosion and the need for expensive materials in the construction of the reactor.

All this is reflected in a decrease in the overall environmental impact of the process. In this regard, the combined use of some organic acids with hydrochloric acid and hydrogen peroxide was evaluated. The process proposed in this document involves using a leaching solution composed of hydrochloric acid (HCl)/citric acid ($C_6H_8O_7$)/acetic acid ($C_2H_4O_2$)/hydrogen peroxide (H_2O_2). The current research utilizes a statistical approach that has not been found in the literature related to this topic. In fact, it presents a complete factorial plan that can be used to investigate the effect of different parameters and their interaction on the recovery yield of Pd and Pt.

2. Materials and Methods

Generally, SACs are characterized by an alumina ceramic matrix (Al_2O_3), on which active sites containing Pt, Pd and Rh are present [19]. In this case, to proceed with a hydrometallurgical treatment, the dimensions of the material must be reduced in advance. For this reason, the grinding of the SAC was carried out using a planetary ball mill. In Figure 2, it is possible to see the photographic aspect of the SAC before and after the grinding.

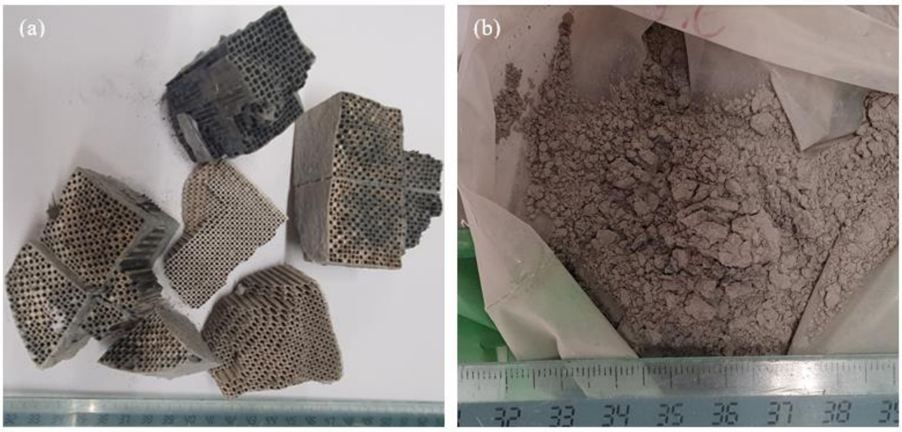

Figure 2. Spent automotive converter before (**a**) and after grinding (<500 µm) (**b**).

Then, the chemical analysis was performed for Pt and Pd determination within the initial sample. For the study carried out, the recovery of rhodium was not considered. The material was chemically attached with aqua regia, and the solution was analyzed through ICP-OES (Agilent 5100). The achieved values are reported in Table 1.

Table 1. Pt and Pd concentration within the SAC sample.

Replications Number	Pt [g/kg]	Pd [mg/kg]
I	3.67	5.74
II	3.65	5.68
III	3.54	5.78
Average	3.62	5.73
St. Dev.	0.07	0.05

X-ray diffraction analysis was used for the identification of the different components of the powdered catalyst. The instrument used for the XRD analysis was an X'Pert PRO powder and film diffractometer. The XRD diffractogram of the spent catalyst is presented in

Figure 3. Several articles in the literature identify cordierite as the main component of this type of material; cordierite is a magnesium aluminosilicate that performs the supporting function (3–35% MgO, 32–35 Al_2O_3, 45–51 SiO_2 e 2–12% Fe_2O_3) [5]. The catalyst that was used in this experimental work had three mixed compounds: cordierite, SiO_2 and Pt nanoparticles. The absence of Pd in the XRD can be explained based on the lower concentration (i.e., 3670 mg/kg vs. 5.74 mg/kg).

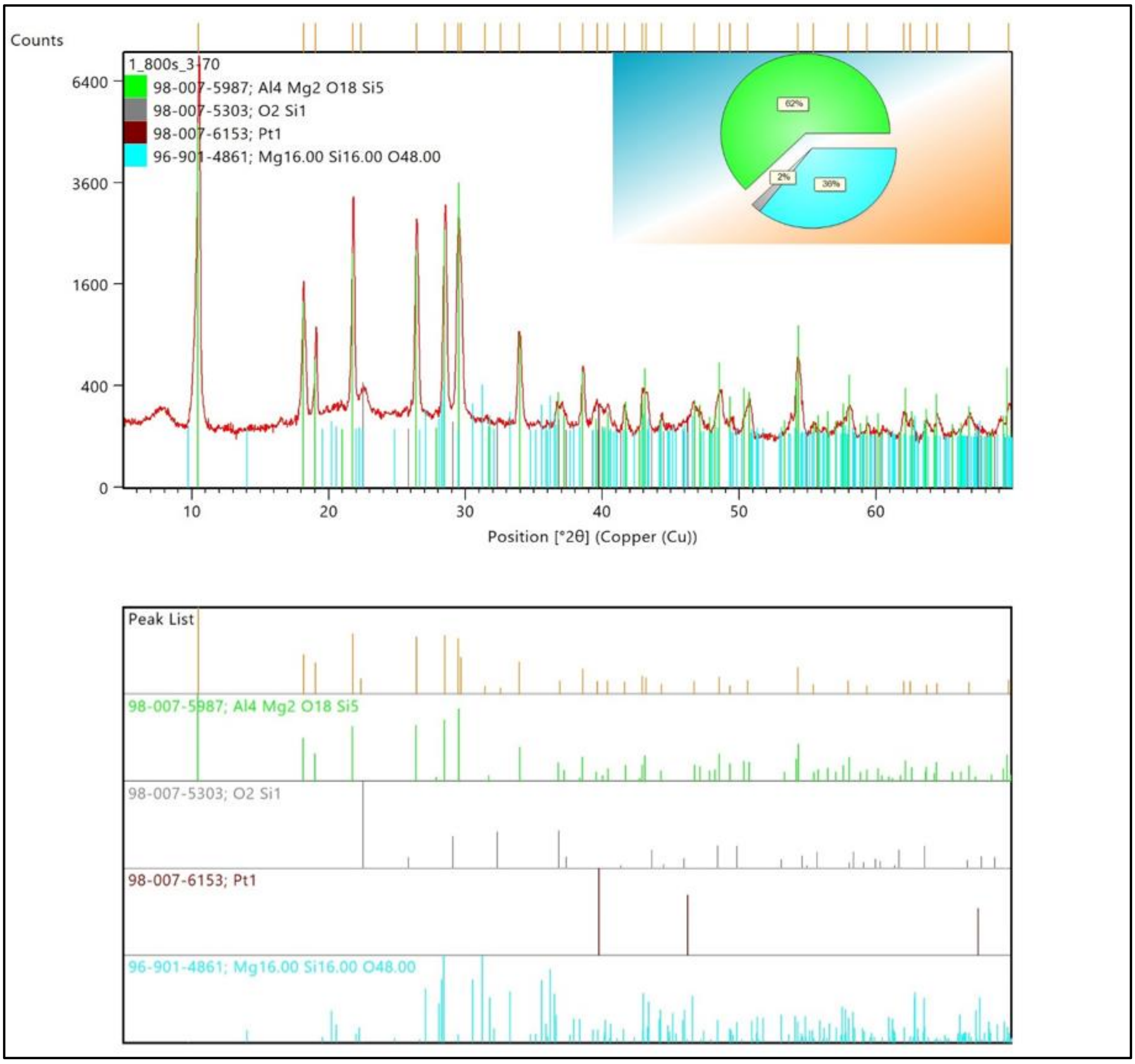

Figure 3. X-ray diffraction patterns of the spent automotive converter.

After milling, the catalyst sample was subjected to granulometric analysis. Four sieves with opening sizes of 212, 125, 53 and 40 µm were used. The determined granulometric distribution is reported in Figure 4.

The determined particle distribution revealed that about 50% of the material had a size within the range of 125–212 µm.

A full factorial plan with two levels and five independent variables was designed. The investigated factors and levels are reported in Table 2. In total, 35 runs were performed (factorial plan 2^5 + 3 central point replications).

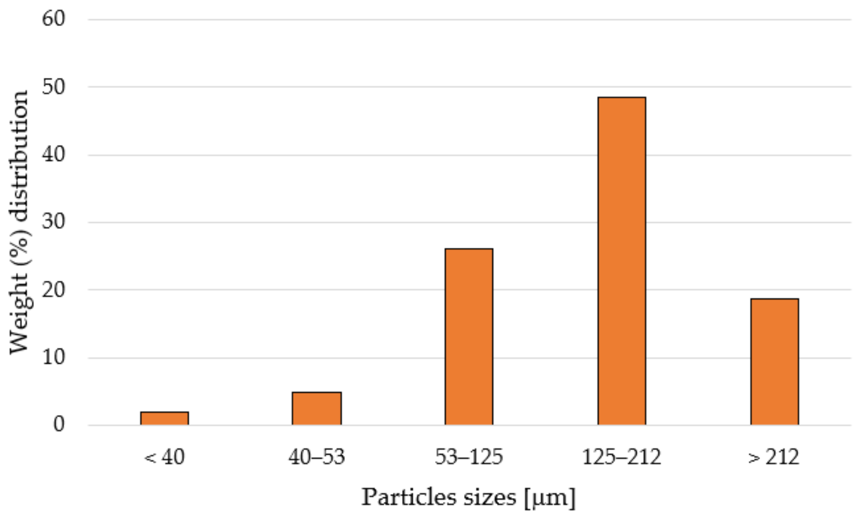

Figure 4. Particles size distribution for catalyst sample after milling.

Table 2. Factors and levels for Pd and Pt recovery from SAC.

Factors			**Levels**		
			–	**0**	**+**
A	HCl concentration	[mol/L]	3	4	5
B	H_2O_2 concentration	[% wt./vol.]	1	5.5	10
C	$C_6H_8O_7$ concentration	[% wt./vol.]	0	5	10
D	$C_2H_4O_2$ concentration	[% vol./vol.]	0	5	10
E	Time	[h]	1	2	3

For each test described above, 5 g of solid and 50 mL of leaching solution were used. In this way, the solid–liquid ratio was kept constant at the value of 10%. For each test, the leaching solution was first prepared in a 250 mL conical flask, and then the solid was added. The solution was prepared by adding the different chemicals to the water in the following order: hydrochloric acid, acetic acid, citric acid and finally hydrogen peroxide. The leaching temperature was maintained at 25 ± 2 °C and the rotation speed at 250 rpm.

Once the expected reaction time had elapsed, the two phases were separated using vacuum filtration. The residual solid was washed with 15 mL of distilled water (*WW*) to remove the solution remaining in the material's pores. ICP-OES then analyzed the resulting leach liquor (*LL*) and *WW* in order to determine their Pt and Pd content. In this way, it was possible to determine the extraction yield of the leaching process for each element using Equation (1).

$$E(\%) = \frac{c_{LL} \cdot V_{LL} + c_{WW} \cdot V_{WW}}{m_s \cdot \omega_s}, \quad (1)$$

where c_{LL} [mg/L] is the concentration of the metal in *LL*, V_{LL} [L] is *LL* volume, c_{WW} [mg/L] is the concentration of the metal in *WW*, V_{WW} [L] is the volume of *WW*, m_s [mg] is the mass of the SAC used for the test and ω_s is the weight percentage of the reference metal in the solid (the average value of the three chemical attacks carried out for the characterization of the material).

Once the recovery yield of Pt and Pd was determined, an analysis of variance (ANOVA) was carried out to evaluate which variations recorded in the responses were significant compared to the variations caused by experimental error. For this reason, the effects on the response for each test were calculated using the Yates algorithm. Once the effect on the response for the generic test i was known, it was possible to determine the quadratic sum (SS_i) with Equation (2).

$$SS_i = \frac{\text{Effect}_i^2}{n^k}, \tag{2}$$

where k is the number of factors analyzed and n is the number of levels. Note that by using SS_i, it is possible to find the square mean MS_i:

$$MS_i = \frac{SS_i}{\nu_i}, \tag{3}$$

where ν_i is the degree of freedom of parameter i (factor or interaction). The three replications at the central point allow for an estimation of the experimental error and, therefore, variance in the error of MS_e:

$$MS_e = \frac{\sum_{i=1}^{R}(y_i - \overline{y})}{R-1}, \tag{4}$$

where y_i is the response of replication I, R is the number of replications and $\overline{y}$ is the mean value of the response of the three replications. We proceed through statistical tests assuming that there is equality between the variability; this is due to the factor linked to the experimental error and the rejection of the hypothesis in the case of significance greater than 95%. In this sense, for each test, the significance of the variation in the response of the generic factor can be calculated:

$$s_i(\%) = \left[1 - F\left(\frac{MS_i}{MS_e}, \nu_i, \nu_e\right)\right] \cdot 100, \tag{5}$$

where s_i is the significance of the factor i, F is the Fisher distribution for the ratio between the square means, ν_i is the degree of freedom associated with the numerator and therefore with the factor analyzed (1 for each test as there are no replications), and ν_e is the degree of freedom associated with the denominator and therefore with the experimental error [20].

3. Results and Discussions

The main reactions that take place during the involved leaching systems [9] are as follows:

$$H_2O_2 + 2HCl = Cl_2 + 2H_2O \qquad \Delta G(21\ ^\circ C) = -23.550\ \text{kcal/mol} \tag{6}$$
$$Cl_2 + C_2H_4O_2 = C_2H_3ClO_2 + HCl \qquad \Delta G(21\ ^\circ C) = -23.760\ \text{kcal/mol} \tag{7}$$
$$C_2H_4O_2 + H_2O_2 = C_2H_4O_3 + H_2O \qquad \Delta G(21\ ^\circ C) = -23.760\ \text{kcal/mol} \tag{8}$$
$$2HCl + 2H_2O_2 + C_2H_4O_2 = C_2H_4O_3 + 3H_2O + Cl_2 \qquad \Delta G(21\ ^\circ C) = -83.862\ \text{kcal/mol} \tag{9}$$
$$2C_2H_4O_3 + 4HCl + Pt = PtCl_4 + 2H_2O + 2C_2H_4O_2 \qquad \Delta G(21\ ^\circ C) = -95.136\ \text{kcal/mol} \tag{10}$$
$$2H_2O_2 + 4HCl + Pt = PtCl_4 + 4H_2O \qquad \Delta G(21\ ^\circ C) = -86.441\ \text{kcal/mol} \tag{11}$$
$$2C_2H_3ClO_2 + 2HCl + Pt = PtCl_4 + 2C_2H_4O_2 \qquad \Delta G(21\ ^\circ C) = -36.943\ \text{kcal/mol} \tag{12}$$
$$C_2H_4O_3 + 2HCl + Pd = PdCl_2 + H_2O + C_2H_4O_2 \qquad \Delta G(21\ ^\circ C) = -64.370\ \text{kcal/mol} \tag{13}$$
$$H_2O_2 + 2HCl + Pd = PdCl_2 + 2H_2O \qquad \Delta G(21\ ^\circ C) = -60.023\ \text{kcal/mol} \tag{14}$$
$$C_2H_3ClO_2 + HCl + Pd = PdCl_2 + C_2H_4O_2 \qquad \Delta G(21\ ^\circ C) = -12.712\ \text{kcal/mol} \tag{15}$$

The solutions produced as a result of the leaching tests and the washing waters of the solid were analyzed using ICP-OES in order to determine the Pt and Pd content. Table 3 shows the different parameters of the complete factorial design. Table 4 shows the results obtained and the related recovery yields calculated in Equation (1).

Table 3. Summary of important parameters.

-	-	Pt	Pd
Factors	k	5	5
Levels	n	2	2
Variance error	MSe	1.85	1.18
Degree of freedom error	ve	2	2

Table 4. Results of Pt and Pd leaching according to the factorial plan.

Run	Run Code	HCl [mol/L]	H_2O_2 [%wt./vol.]	$C_6H_8O_7$ [%wt./vol.]	$C_2H_4O_2$ [%vol./vol.]	Time [h]	LL Concentration [mg/L]		WW Concentration [mg/L]		Recovery (%)	
							Pt	Pd	Pt	Pd	Pt	Pd
1	1	3	1	0	0	1	17.41	0.21	8.18	0.10	5.71	43.59
2	a	5	1	0	0	1	85.71	0.33	44.11	0.16	30.45	73.31
3	b	3	10	0	0	1	21.37	0.23	11.19	0.04	7.14	42.90
4	ab	5	10	0	0	1	85.32	0.33	40.81	0.15	28.08	68.01
5	c	3	1	10	0	1	13.58	0.22	6.87	0.11	3.98	38.36
6	ac	5	1	10	0	1	56.42	0.29	30.88	0.15	17.01	51.79
7	bc	3	10	10	0	1	16.36	0.23	8.83	0.12	4.92	41.12
8	abc	5	10	10	0	1	64.44	0.30	32.57	0.14	19.25	52.94
9	d	3	1	0	10	1	18.04	0.25	9.78	0.12	5.43	44.26
10	ad	5	1	0	10	1	180.03	0.43	82.56	0.21	53.22	76.27
11	bd	3	10	0	10	1	30.09	0.31	14.50	0.13	9.91	63.12
12	abd	5	10	0	10	1	63.12	0.30	32.55	0.11	24.52	70.45
13	cd	3	1	10	10	1	21.78	0.26	10.66	0.17	7.19	57.19
14	acd	5	1	10	10	1	138.92	0.35	72.83	0.11	46.43	68.70
15	bcd	3	10	10	10	1	28.56	0.28	14.02	0.14	9.44	58.59
16	abcd	5	10	10	10	1	174.76	0.39	88.24	0.18	61.89	86.00
17	e	3	1	0	0	3	33.73	0.28	14.94	0.12	10.97	57.19
18	ae	5	1	0	0	3	135.89	0.35	61.36	0.16	44.32	72.19
19	be	3	10	0	0	3	34.18	0.29	14.63	0.12	11.06	58.94
20	abe	5	10	0	0	3	145.12	0.41	67.12	0.18	47.51	84.05
21	ce	3	1	10	0	3	23.71	0.22	9.97	0.10	8.96	53.01
22	ace	5	1	10	0	3	135.78	0.32	62.30	0.16	51.90	78.12
23	bce	3	10	10	0	3	34.34	0.27	12.83	0.09	12.42	60.89
24	abce	5	10	10	0	3	149.06	0.34	86.21	0.19	55.65	79.65
25	de	3	1	0	10	3	39.00	0.32	16.70	0.11	13.91	70.17
26	ade	5	1	0	10	3	200.55	0.44	95.71	0.21	72.63	100.58 *
27	bde	3	10	0	10	3	32.96	0.28	0.28	0.28	10.23	74.21
28	abde	5	10	0	10	3	221.62	0.48	115.49	0.23	81.33	109.79 *
29	cde	3	1	10	10	3	28.00	0.26	14.59	0.12	10.28	59.15
30	acde	5	1	10	10	3	201.50	0.40	99.22	0.20	73.31	92.07
31	bcde	3	10	10	10	3	41.54	0.28	18.15	0.12	14.40	61.10
32	abcde	5	10	10	10	3	284.78	0.44	113.03	0.23	88.01	89.70
33	I	4	5.5	5	5	2	64.93	0.32	29.10	0.13	22.59	69.33
34	II	4	5.5	5	5	2	57.61	0.32	25.48	0.13	20.00	69.33
35	III	4	5.5	5	5	2	59.10	0.31	26.54	0.13	20.57	67.45

* values higher than 100% are due to experimental error.

The significance of the variation in the response for each factor and for each interaction is calculated using Equation (5). Figures 5 and 6 report the effects of significant factors and interactions.

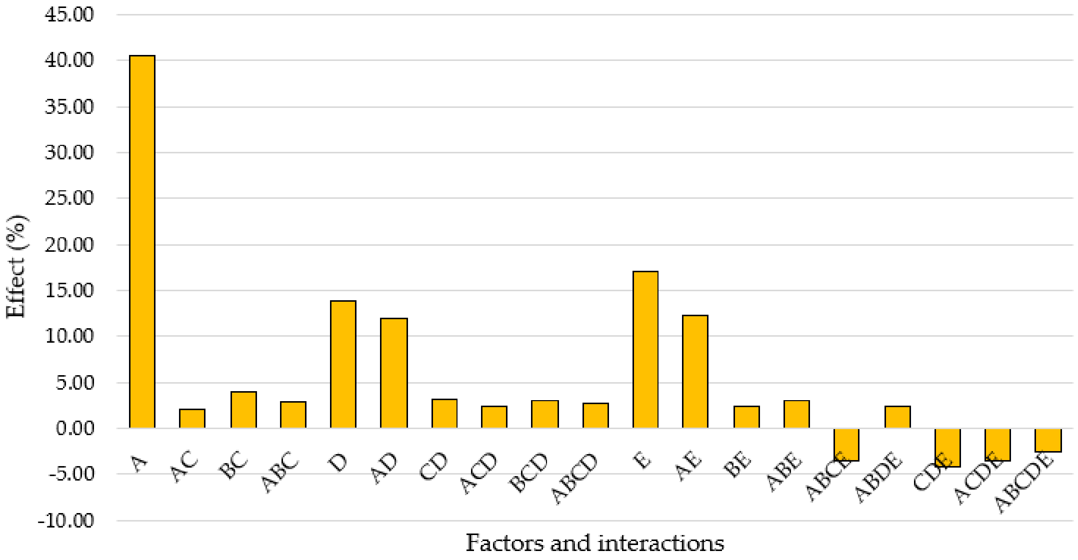

Figure 5. Main factors and their interaction effects on Pt leaching.

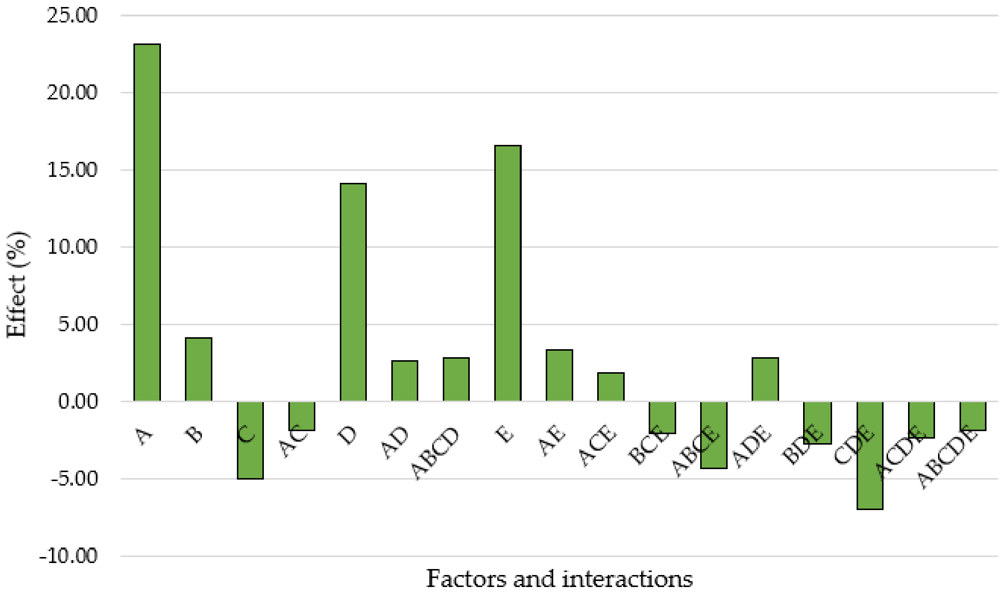

Figure 6. Main factors and their interaction effects on Pd leaching.

Due to the numerous significant interactions, a new count was performed, neglecting the replications and confusing the variations in the fourth and fifth-order interactions with the experimental error.

In this sense, it is possible to define the empirical error variance as the average of the MSi of the interactions of the highest degree. Figures 7 and 8 report the effects of the significant factors and the interactions calculated using this new method.

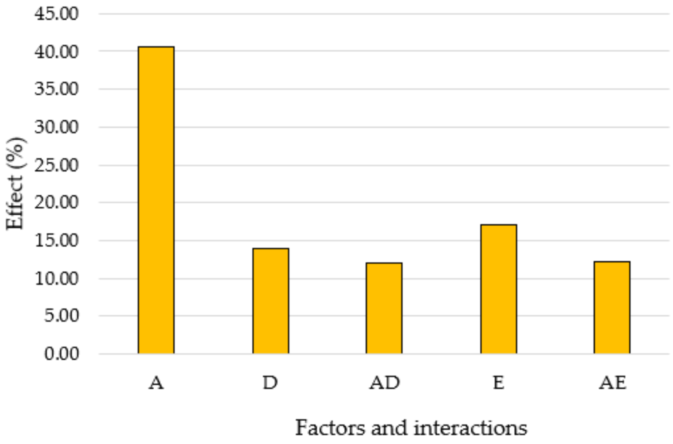

Figure 7. Main factors and their interaction effects on Pt leaching (new method).

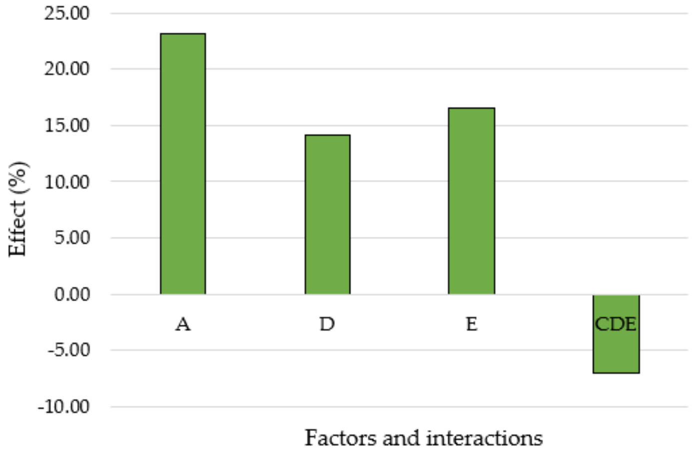

Figure 8. Main factors and their interaction effects on Pd leaching (new method).

3.1. Influence of Hydrochloric Acid

Between nitric acid, sulfuric acid and hydrochloric acid, the latter is the most efficient acid for the dissolution of the platinum group of metals [21]. The main parameter that influences the recovery yield of both elements is the concentration of hydrochloric acid (parameter A). The significance was greater than 99% for both elements, positively affecting leaching yields. Increasing its concentration from 3 to 5 M results in a 40% increase in Pt recovery, and the same factor determines an increase of about 23% for the Pd.

Several studies in the literature confirm that the increase in the concentration of hydrochloric acid leads to an increase in the leaching yields of Pt and Pd. This occurs because PGMs find greater stability in solution as chloride complexes, except for Rh. In addition, a high concentration of chloride ions also improves the dissolution and oxidation efficiency of metals. A high concentration of HCl (>3 mol/L) is usually required for the maximum recovery of PGMs [22–24]. The interaction of this factor with time (AE) also had a significant positive effect, leading to an improvement in the recovery of more than 12%, which is typical of relatively slow reaction kinetics. Another significant positive effect was the second-order interaction between factor A and factor D (the concentration of acetic acid). The increase in the concentration of both reagents determined an increase of over 12% for Pt and 3% for Pd.

The effects of the second-order interactions on the Pt recovery yield are shown in Figure 9.

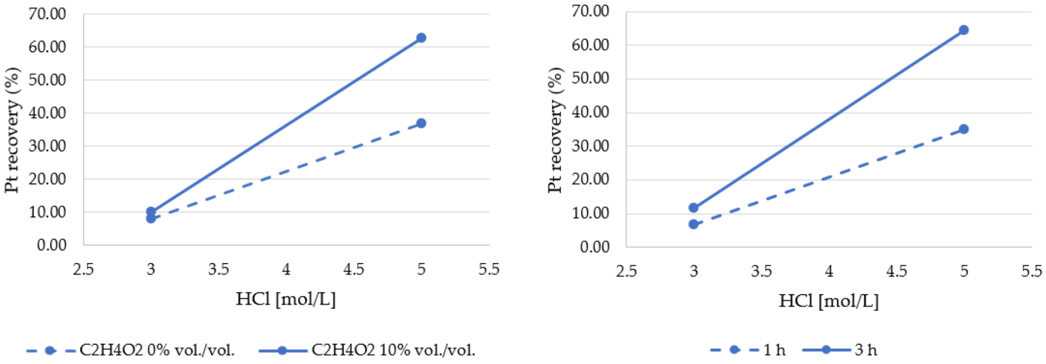

Figure 9. Effects of second-order interactions on the Pt recovery yield.

The only third-order significant interaction with the second calculation method is the CDE interaction (interaction between hydrochloric acid, acetic acid and reaction time). The increase in all three factors leads to a decrease of about 7% in the recovery yield of the Pd and has no significant effects on the Pt. All the other third-order interactions are non-significant with the second calculation method, due to low MS_i values. For this reason, the variation recorded in the responses is confused with the effect due to the experimental error. Interactions higher than the third order were used to estimate MS_e and, therefore, are not significant to the response.

3.2. *Influence of Hydrogen Peroxide*

The study showed that the effect of H_2O_2 was not significant on the extraction yield of the reference metals. Usually, hydrogen peroxide promotes leaching thanks to its strong oxidizing power. However, in the case examined, the addition of the oxidant did not lead to an increase in the extraction yields. This behavior can be explained if we consider the HCl: H_2O_2 ratio. Studies in the literature show the possibility of obtaining high recovery yields (>95%) with leaching systems containing HCl and H_2O_2, with the oxidizing agent in a 10 HCl: 1 H_2O_2 solution [25].

The lower level chosen for the concentration of H_2O_2 in the factorial plane coincides precisely with the ratio indicated above. For this reason, the further increase in hydrogen peroxide did not lead to significant increases in the recovery yields.

3.3. *Influence of Organic Acids*

The effect caused by the increase in citric acid in the leaching solution was not significant on the recovery yields of Pt and Pd. On the contrary, a positive significant factor was the presence of acetic acid. This reagent improves the leaching of Pt and Pd by about 14%. This behavior can be explained by considering that acetic acid can act as a complexing agent, forming complexes with PGMs that enhance their solubility in solution. This effect can be further enhanced by adding an oxidizing agent such as hydrogen peroxide or oxygen to the solution, which promotes the formation of soluble PGM complexes.

3.4. *Influence of Time*

The leaching time was also a significant critical factor in the recovery of both metals (significance > 98%). Its increment from 1 to 3 h produced a rise in the recovery efficiency of about 17% for both elements. Other studies in the literature show how the recovery yield with similar leaching systems significantly increases even up to 5 h from the start of the reaction [22,26].

4. Conclusions

The current study made it possible to analyze a new leaching system for the recovery of Pt and Pd from spent automotive catalysts. The developed process is more sustainable from an environmental point of view than the numerous leaching processes proposed in the literature for the treatment of this type of material. In fact, the use of organic acids allows for high recovery yields with a lower consumption of hydrochloric acid. XRD analysis confirmed the presence of cordierite and platinum in the material examined. The chemical attack using aqua regia made it possible to determine, respectively, for Pt and Pd, the concentrations of 3.62 ± 0.21 g/kg and 5.73 ± 0.15 mg/kg.

The largest amounts of Pt and Pd were leached with a mixture of HCl, H_2O_2, $C_6H_8O_7$, and $C_2H_4O_2$. Hydrochloric acid is the most positive and significant factor in recovering both precious metals.

Run 28 was the best run in terms of the recovery yield of both elements. In this case, the recovery of Pt was greater than 80% and the recovery of Pd was total.

Based on the obtained results, future research could optimize the entire leaching phase of the proposed hydrometallurgical process. This would maximize the yields of both materials without the excessive consumption of time, material, and energy.

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