Supplementary Information

Recovery of platinum from spent automotive catalytic converters by leaching with aluminium-based salts solutions

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1. SACC characterization

Table S1. SEM-EDS mass composition for milled SACC before burning. (Bruker Nano GmbH microscope).

Element	Si	Al	Mg	S	O	P
Composition (wt%)	19.92	19.98	6.89	0.95	52.17	0.08

Table S2. Metal concentration of the water after washing pretreatment of SACC (S/L ratio = 1/10 w/w, T = 363 K, t = 6h).

Element	Fe	Ni	Zn	Ce
Composition ($mg \cdot L^{-1}$)	1.14 ± 0.11	0.58 ± 0.04	6.90 ± 0.22	24.90 ± 0.87

2. Extraction

2.1. Alternative leaching media

The SACC leaching was performed employing initially different solutions already reported for Pt extraction: 6 M HCl, 1 M HCl + 3.8 M NaCl [14] and 60.5 wt % $AlCl_3 \cdot 6H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$. [31] The tests were performed with the SACC only milled. The conditions are present in **Table S3**. For the two HCl based systems, in contrast to the procedures described in the original article,[14] both leaching tests were conducted without microwave assistance, using conventional heating instead. For the aluminium salts mixture, extra water was added beyond the optimal conditions previously identified [31] to ensure complete dissolution of the salts at room temperature, reaching a concentration of hydrated salts of 60.5 wt %.

Table S3. Conditions used in the preliminary tests of alternative media for leaching of SACC.

Leaching Solution	S/L ratio w/w	T (K)	Rotation (rpm)	t (h)	Observation
6 M HCl	35	363	350	6	-
1 M HCl + 3.8 M NaCl	35	363	350	6	-
60.5 wt % $AlCl_3 \cdot 6H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$	35	363	350	6	$AlCl_3 \cdot 6H_2O$/ $Al(NO_3)_3 \cdot 9H_2O$ ratio = 1 w/w

2.2. Al Salts leaching optimization

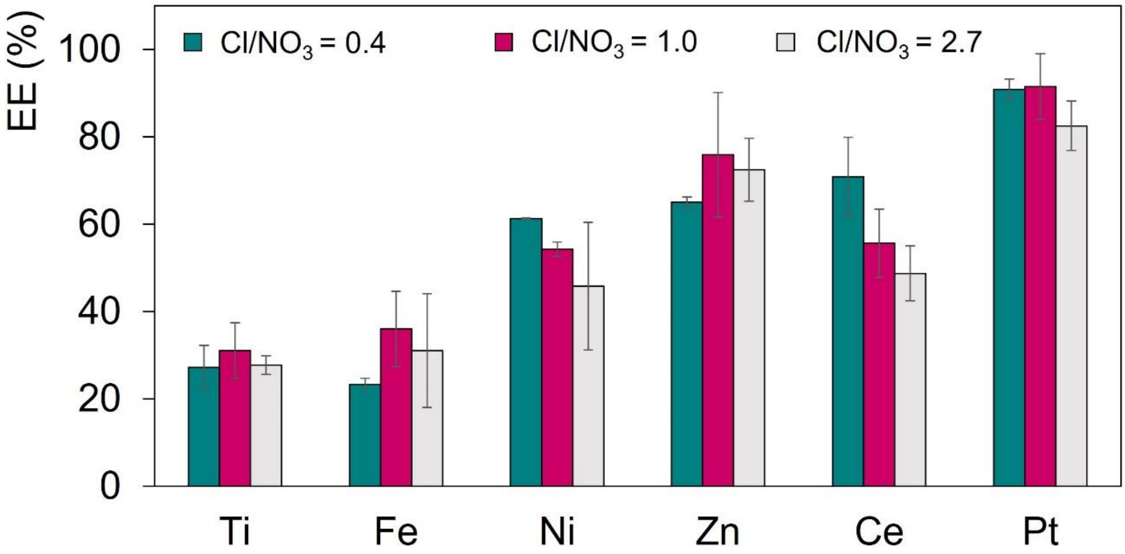

Figure S1. The effect of salts mass ratio between $AlCl_3·6H_2O/Al(NO_3)_3·9H_2O$ (Cl/NO_3) for the dissolution of metals from SACC pretreated powder. ([salts]= 44 wt%, S/L ratio = 1/35 w/w, T = 363 K, t = 6h).

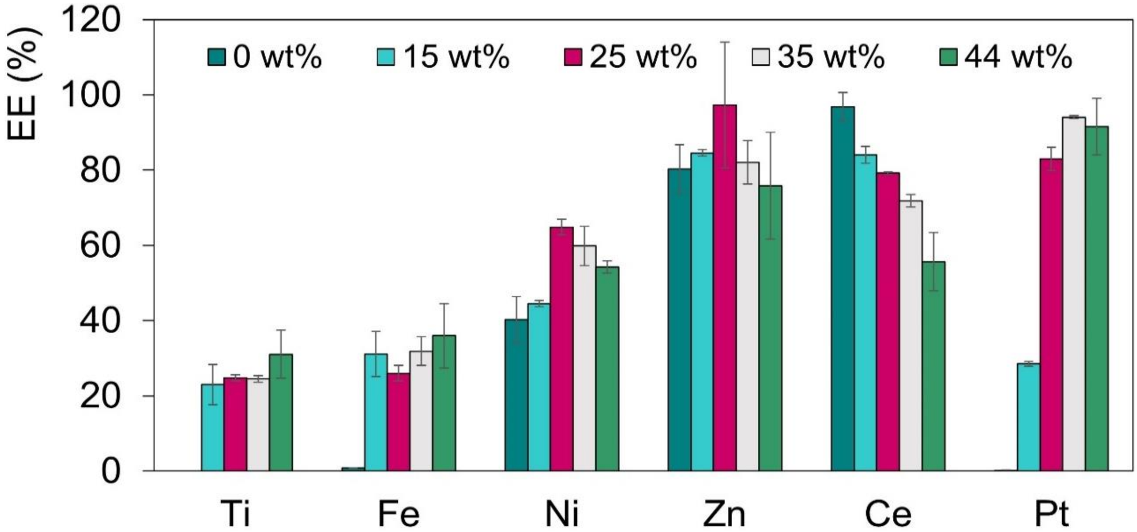

Figure S2. The effect of salts mass concentration for the dissolution of metals from SACC pretreated powder (Cl/NO_3= 1, S/L ratio = 1/35 w/w, T = 363 K, t = 6h).

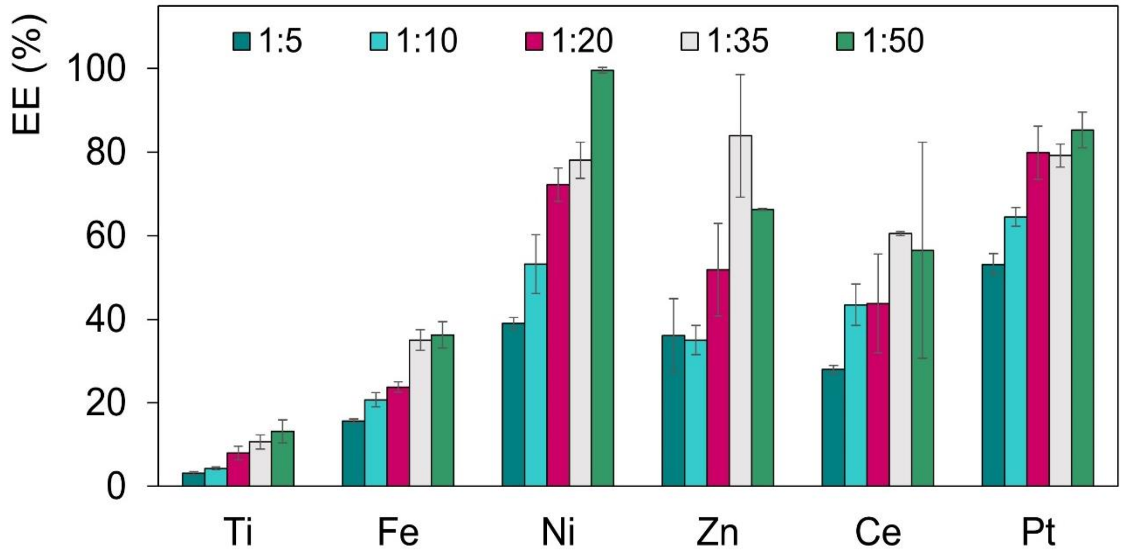

Figure S3. The effect of solid-to-liquid ratio for the dissolution of metals from SACC pretreated powder ([salts] = 35 wt%, Cl/NO_3 = 1, T = 363 K, t = 6h).

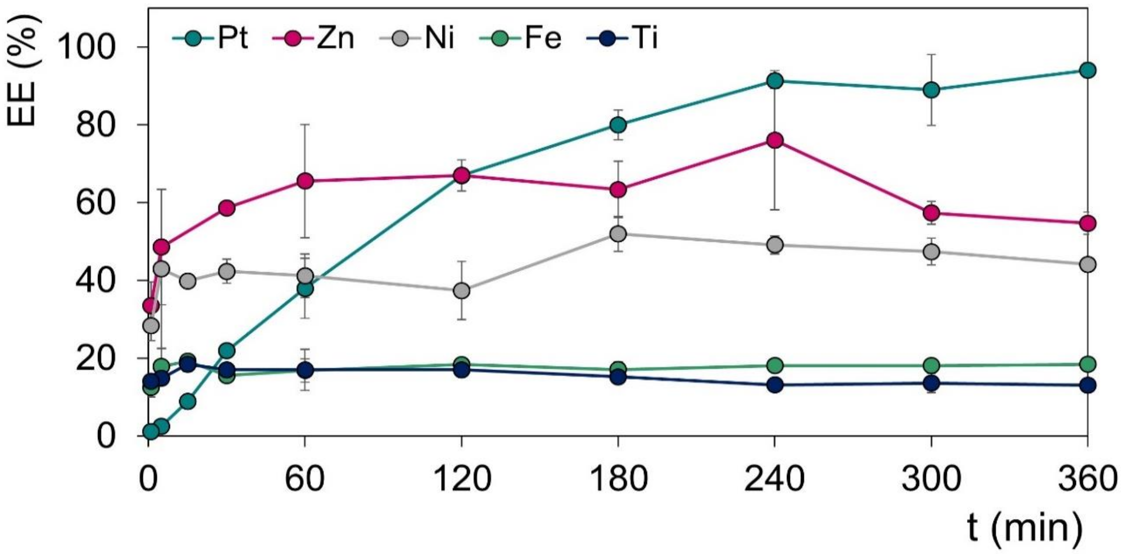

Figure S4. The effect of contact time for the dissolution of metals from SACC pretreated powder ([salts] = 35 wt%, Cl/NO_3 = 1, S/L ratio = 1/20 w/w, T = 363 K).

2.2.1. Mechanism of Pt extraction on leaching

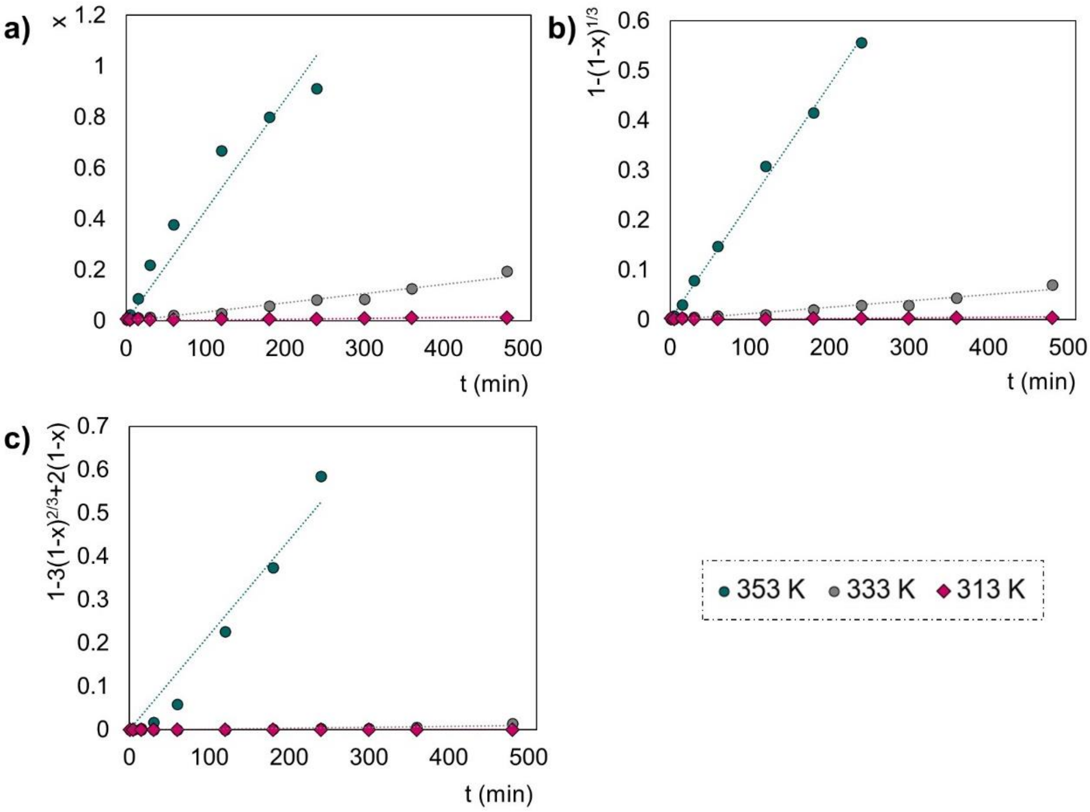

Figure S5. Linear fits using different shrinking core models for Pt dissolution at different temperatures: (a) layer mass transfer control model. (b) surface chemical reaction control model. (c) residual layer diffusion control model. ([salts] = 35 wt%, $Cl/NO_3 = 1$, S/L ratio = 1/20 w/w).

2.3.1 Activation energy (E_a) determination

To calculate the activation energy of the leaching process using the empirical Arrhenius law (Equation 12), reaction rate constants were determined at various temperatures. The surface chemical reaction model provided the best fit for the data, and the rate constants derived from this model (**Table 3**) were used for the calculations. By plotting a graphic of $\ln k \; vs \; \frac{1}{T}$ and fitting a curve, the slope corresponding to E_a /R, was obtained (**Figure S6**), allowing for the subsequent calculation of the E_a..

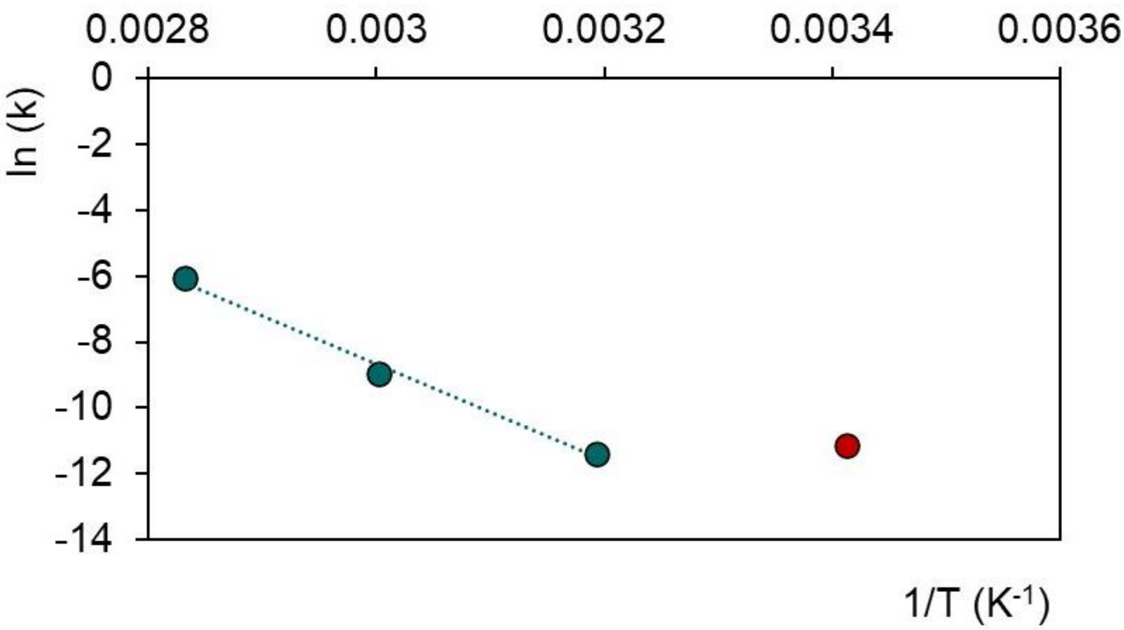

Figure S6. Linear Arrhenius law plot for the calculation of the activation energy of Pt extraction. Red dot represents an outlier behavior at 293 K and was not considered for linearization. ([salts] = 35 wt%, $Cl/NO_3 = 1$, S/L ratio = 1/20 w/w).

3. Purification

3.1. Adsorption

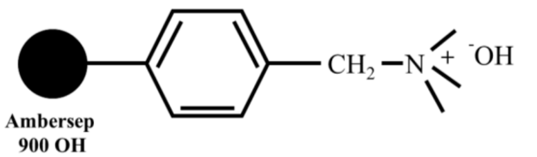

Figure S7. Scheme of the general structure of the Ambersep® 900 resin.

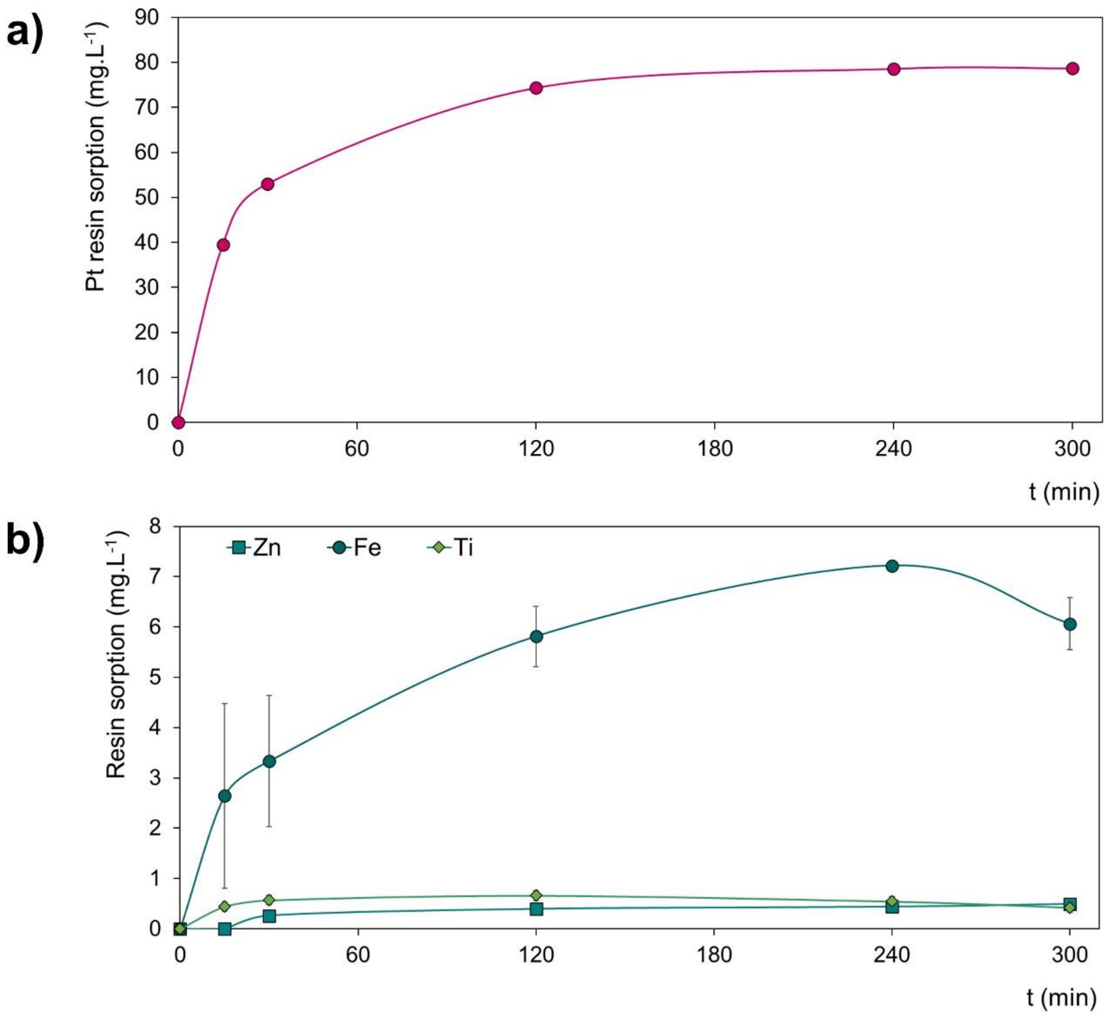

Figure S8. HNO_3 treated resin sorption in function of time: (a) for Pt and (b) for the other adsorbed metals (R/L = 1/100 w/w, room temperature).

3.2. Resin water wash after adsorption

The purpose of the water wash was to maximize the purity of Pt and the results are illustrated in **Figure S9**. The desorption of metals from the treated resin by the water wash (A) was calculated using equation (S2):

$$A\ (\%) = \frac{C_a}{C_f} \cdot 100 \quad \text{(S2)}$$

where C_f ($mg \cdot L^{-1}$) is the metal concentration in the resin and C_a ($mg \cdot L^{-1}$) is the metal concentration in the water resultant from the wash subtracting the values for a blank with just water.

It is important to consider that Ni and Ce were not initially adsorbed by the resin in quantifiable amounts while Fe and Zn are present in low concentrations, around 1 $mg \cdot L^{-}$

[1], which can introduce some degree of imprecision in their quantification. This imprecision may account for the high error bars observed in certain sorption rates or values exceeding 100%. Despite using a blank sample of water to correct the desorption values, slight variations in water composition between samples could also contribute to these discrepancies.

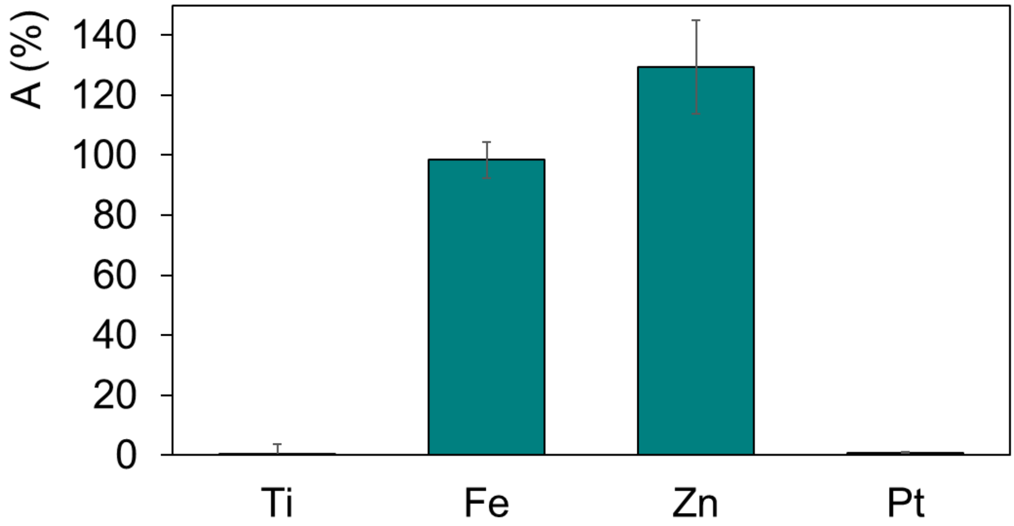

Figure S9. Desorption of metals from treated Ambersep® 900 applying a water wash (R/L = 1/100 w/w, room temperature, 80 rpm vertical rotation, t = 1 h).

3.3. Metal elution from resin

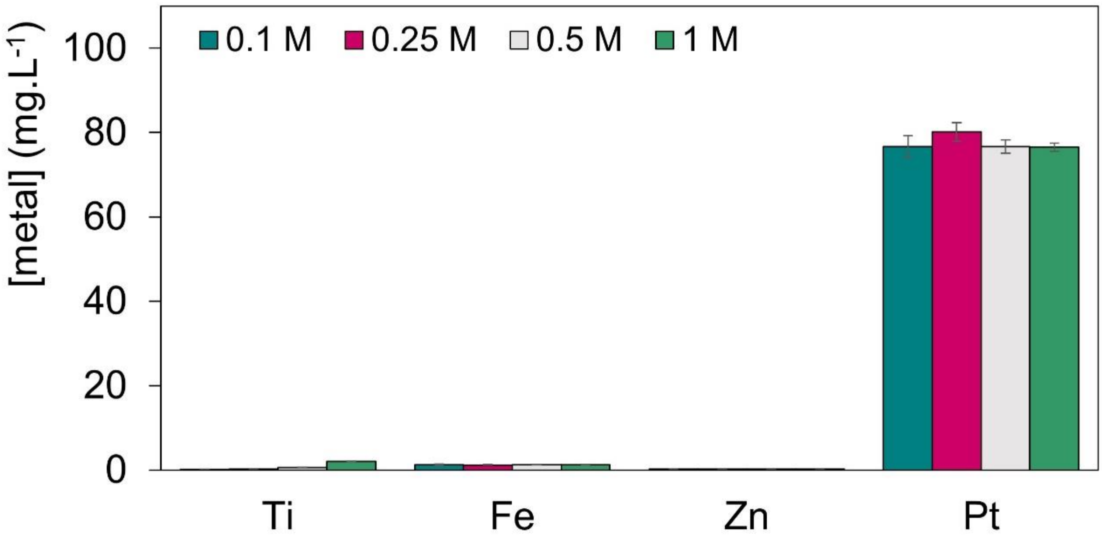

Figure S10. Pt recovery from loaded Ambersep® 900 using different concentrations of thiourea (R/L = 1/100 w/w, room temperature, t = 2 h).

4. Scale-up

4.1. Extraction

In the scale up the experiments the leaching solution volume was increased from 2 mL to 120 m. In the setup, it was essential to apply mechanical agitation with a thermal bath. A significant discrepancy between the values obtained for 2 ml and 120 ml after 4 h of reaction was observed. Mass transfer effects are evident in the larger system, with values approaching the plateau only after 8 h of leaching (**Figure S11**). The reuse of leaching solution was also analysed, and the results are show in **Figure S12.**

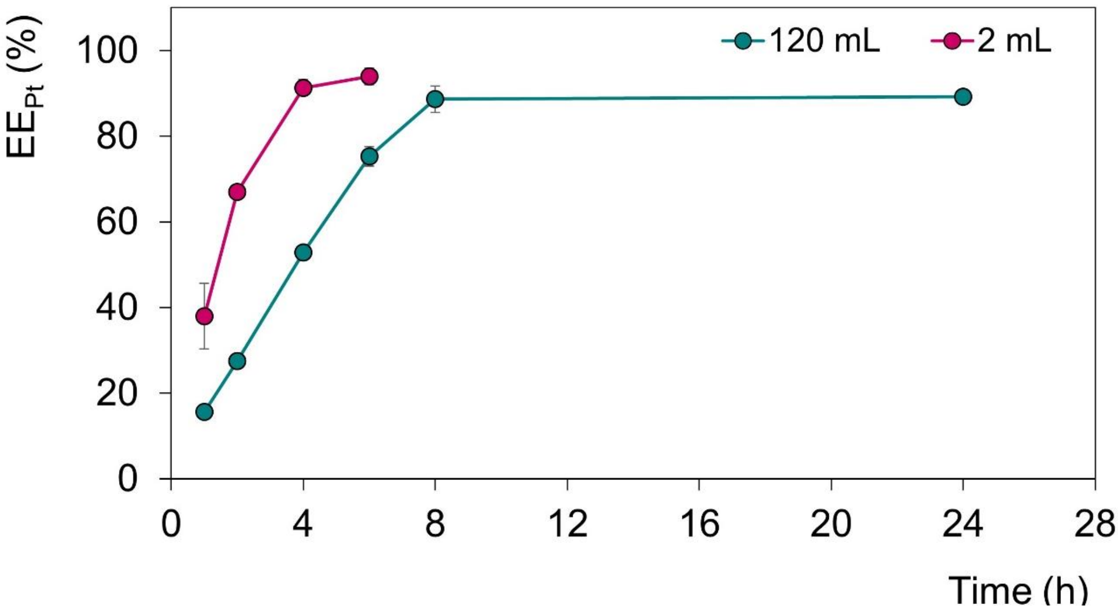

Figure S11. The effect of solution volume on Pt extraction efficiency in leaching with Al salts ([salts]= 35 wt%, Cl/NO_3=1, S/L ratio = 1/20 w/w, T = 363 K).

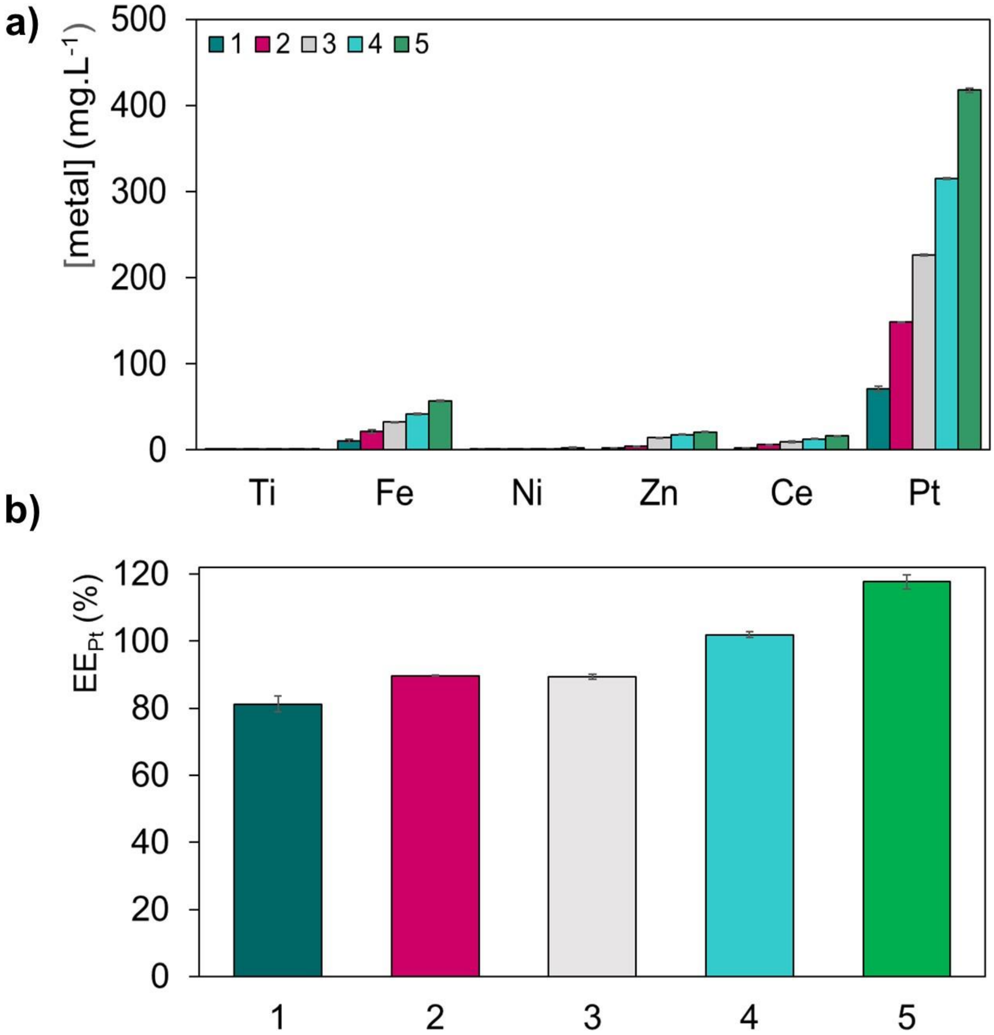

Figure S12. Analysis of the 5 cycles of leaching on (a) metal extraction and (b) Pt extraction efficiency. ([salts] = 35 wt %, Cl/NO_3 = 1, S/L ratio = 1/20 w/w, 350 rpm, T = 363 K, t = 24h).

For the adsorption, after 24 h, Pt reached 405 mg.L^{-1}, corresponding to 97% of the initial concentration with a selectivity of 83% among the quantified metals. The resin sorption ratio (q) for Pt reached 36.65 mg.g^{-1}, as can be seen in **Figure S*13***.

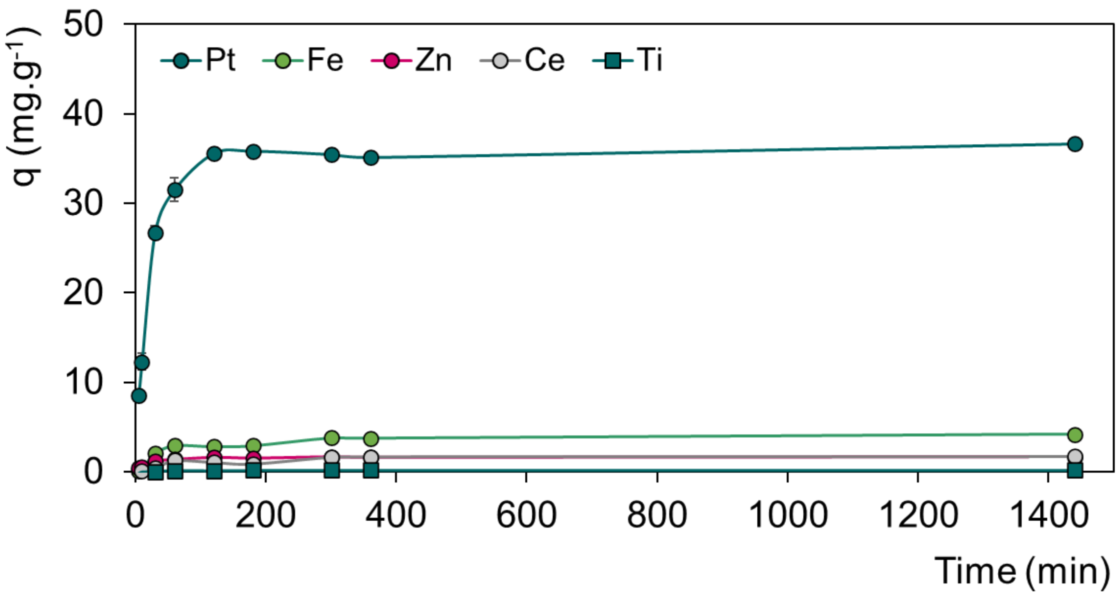

Figure S13. Kinetics analysis of adsorption of leaching solution after five cycles in Ambersep® 900 (R/L = 1/100 w/w, room temperature, leaching volume = 120 mL).

4.2. Purification

4.2.1. Resin water wash after adsorption

In the sequence, a water wash was performed in the resin. Once again, the water wash effectively removed a substantial portion of Fe (70 %) and Zn (83%) while retaining nearly 100% of the Pt adsorbed. Unlike the first water wash, it was possible to observe the desorption of Ni (7%) and Ce (52%), since these metals were present in quantifiable quantities in the concentrated leachate (**Figure S14**). The desorption of metals from the resin by the water wash (A) is shown in **Figure S14**. It is also essential to consider the reduction of the degree of imprecision in the quantification because the metal concentrations were higher, leading to lower proportional error bars and no sorption rates exceeding 100% as in the first scenario.

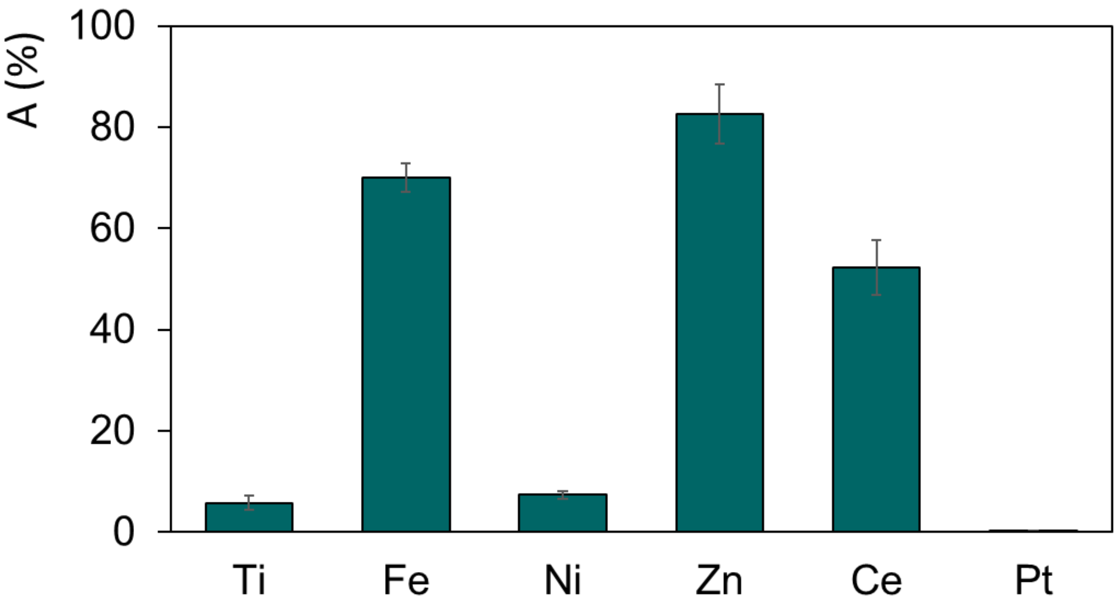

Figure S14. Water desorption of metals from Ambersep® 900 that was in contact with concentrated leaching solution (R/L = 1/100 w/w, room temperature, t = 1 h).

4.2.2. Pt elution from resin

The stripping of Pt from the resin with concentrated leachate was tested with various concentrations of thiourea solutions: 0.10 M, 0.50 M, and 1.00 M (**Figure S15**). Pt continues to be extracted with hight selectivity (95-97%). However, the concentration of thiourea has a more pronounced effect on increasing the desorption of Pt compared to the process with only one cycle leachate. As a compromise, a 0.5 M thiourea was used in the scaled-up process.

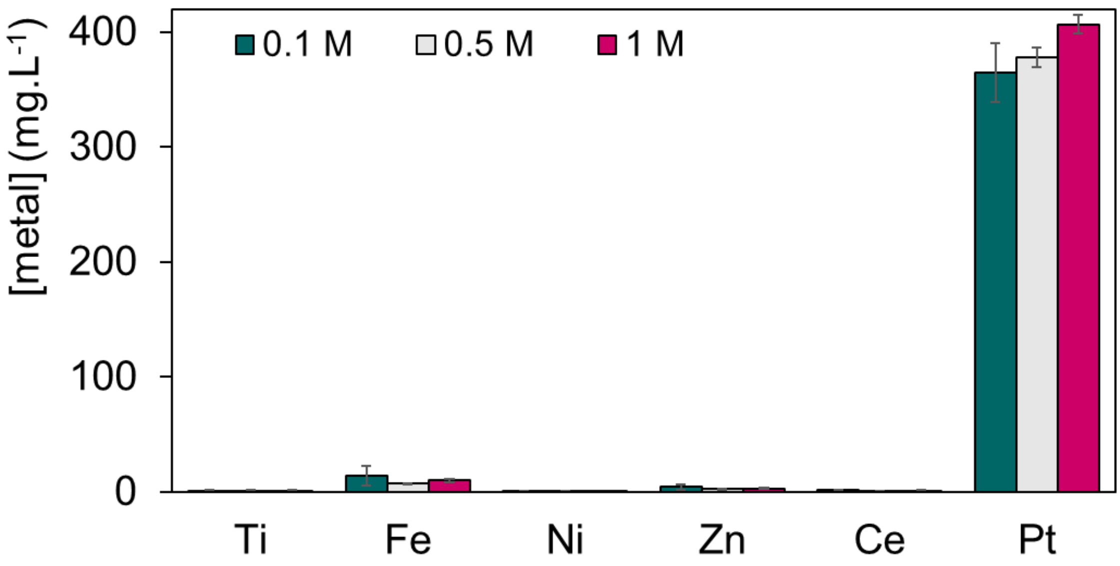

Figure S15. Pt recovery using different concentrations of thiourea from charged Ambersep® 900 that was in contact with scaled-up leaching solution (R/L = 1/100 w/w, room temperature, t = 24 h).