



Article **Application of Ion Exchange for Recovery of Noble Metals**

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Abstract: The production of noble metals has started to shift towards using different types of wastes. The leaching solutions collected during the processing of waste have low concentrations of noble metals; therefore, it forces the use of sorption methods in recovery technology. This work focused on recovering noble metals with a technological solution, obtained during the processing of waste from refining processes. The research consisted of a set of experiments using a batch method that enabled determination of the parameters of the process and selection of the leading resins. Sorption isotherms were determined and kinetic studies were conducted, along with the preliminary elution tests with the use of different eluents. Cementation experiments were the final part of the research. During the experiments, it was concluded that the leading resins for the sorption of noble metals were Puromet MTS9200, Puromet MTS9850, and Lewatit K 6362. The volume ratio $V_r:V_s = 1:10$ and the reaction time 15–30 min could be used as basic conditions to conduct the experiments in the column; the solution of thiourea in hydrochloric acid can be used as an eluting agent from which noble metals could be cemented using powder zinc.

Keywords: noble metals; PGM; ion exchange; sorption; resins; metal recovery; waste management

1. Introduction

Noble metals, such as platinum, palladium, rhodium, and gold, are some of the most valuable elements due to their exceptional properties, such as high chemical and thermal resistance, which directly leads to their wide applicability in the electrical, jewelry, and automotive industries [1–4]. Due to their scarcity in the deposits naturally occurring in the Earth's crust, the current manufacturing tendency is slowly shifting to obtaining them from secondary raw materials, e.g., automotive catalysts, computer parts, and other electronic equipment [5–7]. Recovering noble metals from such sources is not an easy task, due to the similarity of their properties and the presence of other metals such as copper, iron, and zinc, which often hinder the recovery process [8,9]. The leaching solutions obtained in the process of dissolution of wastes have low concentrations of noble metals, which makes using traditional methods such as selective precipitation or extraction practically ineffective. Therefore, to be able to recover noble metals from those solutions sorption technologies have to be introduced into the process.

Ion exchange has been researched in noble metal recovery technology for quite some time due to a number of advantages, such as the low cost of exploitation, low energy consumption, the possibility of regenerating the resins, long life span of the resins, price, selectivity, high efficiency, and the simple process apparatus [10]. Over the years, many resins have been researched in terms of noble metal recovery from different types of solutions, mostly synthetic ones [11–15]. Although conducting experiments using a premade synthetic solution provides a large database of information helping to plan further tests,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). introducing industrial solutions very often results in uncovering another set of problems for the researchers to resolve before being able to use the tested materials in the real processes. Currently, more research is focusing on recovering PGM and gold from industrial-like solutions instead of synthetic ones [16,17]. Nevertheless, many more tests have to be conducted to obtain a knowledgeable database that would be able to quickly and easily transfer laboratory experiments to the industry.

Therefore, the aim of this research is to examine the applicability of the commercial ion exchange resins in the technology of recovery of noble metals, such as platinum, palladium, rhodium, and gold, from a technological solution. The solution used in the experiments came from the leaching of different types of waste obtained from the refining processes of noble metals, hence its complex composition. Many publications concentrate on obtaining elements from one type of waste, e.g., automotive catalysts, WEEE (Waste of Electrical and Electronic Equipment), or computer elements, which is undoubtedly important, although not a lot of attention is paid to obtaining noble metals from the waste produced during the refining process. The technological solution used in the experiments came from leaching of that type of waste.

2. Materials and Methods

2.1. Materials

Puromet MTS9200, Purolite MTS9850, and Puromet MTS9100 were supplied by Purolite (King of Prussia, PA, USA); Lewatit MonoPlus TP 214 and Lewatit K 6362 were provided by Lanxess Energizing Chemistry (Cologne, Germany). Depending on the functional group, they are strong or weak basic ion exchangers and are supplied in a form of spherical beads. Their main characteristics are reported in Table 1.

Name	Туре	Functional Group	Ionic Form	Matrix	Company
Puromet MTS9200	weak base	isothiouronium	H ⁺ form	polystyrenic crosslinked with divinylbenzene	
Puromet MTS9850 Puromet MTS9100	-	polyamine amidoxime	FB form	polyacrylic crosslinked with divinylbenzene	Purolite
Lewatit MonoPlus TP 214	weak base	thiourea	-	polystyrenic	Lanxess
Lewatit K 6362	strong base	quaternary ammonium salt, type I	Cl ⁻ form		

Table 1.	Resins	used	in	the	research.
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Noble metal concentrates and wastes (e.g., filters and precipitates) were supplied by the Łukasiewicz Research Network-Institute of Non-Ferrous Metals (Łukasiewicz-IMN, Gliwice, Poland) and used as the sources of metals for the technological solution. Nitric acid (65%, AR, Avantor, Gliwice, Poland) and hydrogen peroxide (30%, AR, Avantor, Gliwice, Poland) were applied for leaching of the waste materials and concentrates. Hydrochloric acid (35–38%, AR, Avantor, Gliwice, Poland) was used for the leaching, conditioning, and elution experiments. Ammonium thiocyanate and thiourea (AR, Avantor, Gliwice, Poland) were applied for the elution experiments. Zinc powder was supplied by the Łukasiewicz-IMN (Gliwice, Poland) and used for the cementing of noble metals from eluates. Distilled water (<2 μ S/cm) was used in the experiments. A rotary shaker (330 rpm; CERTOMAT MO II, Sartorius, Göttingen, Germany) was used to mix the solutions and resins.

The technological solution used in the research (belonging to the Łukasiewicz-IMN) was obtained from the concentrates and precipitates produced during the refining process of noble metals, containing low percentages of them. Below we present a simplified scheme of the noble metal refining process developed by the Łukasiewicz Research Network-Institute of Non-Ferrous Metals, the Centre of Hydroelectrometallurgy (Figure 1).



Figure 1. Simplified scheme of the noble metal refining process conducted in the Łukasiewicz Research Network-Institute of Non-Ferrous Metals.

The refining steps, such as filtration, precipitation, concentration, or reduction, generate a large amount of waste, including waste solutions, filters, precipitates, or concentrates, all of which contain low concentrations of noble metals. Such materials were leached with a mixture of hydrochloric acid, nitric acid, and hydrogen peroxide, and the solution obtained during this process was used in the following experiments.

Tables 2 and 3 show the composition of the solution obtained by the semiquantitative analysis and quantitative analysis.

Aside from the noble metals (such as platinum, palladium, rhodium, and gold), the solution also contained significant amounts of copper and zinc, which are often found in the industrial solutions [8].

The results from Table 3 were used as the basic parameters of the technological solution.

Composition [mg/dm ³]							
Pt	Pd	Rh	Au	Mg	Al	Р	
142	182	77	12	$0.\bar{4}$	<5	<25	
К	Ca	Sc	Ti	\mathbf{V}	Cr	Mn	
98	11	< 0.5	< 0.5	41	3	< 0.5	
Fe	Со	Ni	Cu	Zn	Ga	Ge	
25	2.5	<2.5	69	36	3	0.1	
As	Se	Br	Rb	Sr	Y	Zr	
16	<5	<50	< 0.5	< 0.5	< 0.05	< 0.5	
Nb	Mo	Ru	В	Be	Ag	Cd	
< 0.05	< 0.5	0.2	2	< 0.5	3.1	3.9	
In	Sn	Sb	Te	Ι	Cs	Ba	
2.5	5.6	< 0.05	0.1	<50	< 0.5	< 0.5	
La	Ce	Pr	Nd	Sm	Eu	Gd	
< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
Tb	Dy	Ho	Er	Tm	Yb	Lu	
< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
Hf	Ta	W	Re	Os	Ir	Li	
< 0.05	< 0.05	0.1	1.5	< 0.5	< 0.05	< 0.5	
Na	Hg	T1	Pb	Bi	Th	U	
20	<0.5	< 0.05	5.7	4.2	< 0.05	< 0.05	

Table 2. Composition of the technological solution obtained by the semiquantitative analysis.

Table 3. Composition of the technological solution obtained by the quantitative analysis.

Concentration [mg/dm ³]						
Pt	Pd	Rh	Au	As	Zn	
674	601	215	44	33	159	
Cu	К	Na	V	Ca	Fe	
241	<0.5	49	<0.5	6	4	

2.2. Methods

2.2.1. Conditioning of the Resins

The resins were conditioned with 10% (w/w) HCl. This stage was conducted to ensure that all the functional groups were activated and, therefore, were able to exchange ions.

The measured by volume amounts of chosen resins were submerged in distilled water and stirred for about 20 min, to remove any physical contamination. The resins were filtered and 10% HCl was added in a 1:1 volume ratio ($V_{resin}:V_{HCl}$). The mixture was stirred at room temperature for about 1 h and then filtered. The resins were then washed with distilled water, until the pH of the washing water was around 5. Resins prepared this way were used in the further experiments.

2.2.2. Batch Experiments

First, from a larger group of ion exchangers, a smaller number of resins was selected to be used in the further research. In this stage, 5 resins were bought, and 3 were selected for the following experiments based on the noble metal recovery of the initial tests.

The yields were calculated according to the formula:

$$SY = \frac{C_i - C_f}{C_i} \times 100\%$$
(1)

SY—sorption yield (recovery), %; C_i = initial concentration of the metal in the solution, mg/dm³; and C_f—final concentration of the metal in the solution, mg/dm³.

In total, 50 cm³ of technological solution was added to 10 cm³ of resin and the mixture was stirred for an hour at room temperature ($V_r:V_s = 1:5$, V_r —volume of the resin, vs.— volume of the solution). At the end of the process, the resin was filtered and the solution

analyzed. The same experiment was conducted for every resin. The selected resins were then used in the next stage of research.

For each resin, the sorption isotherm was plotted. For this purpose, the sorption of platinum, palladium, gold, and rhodium was studied under more detailed batch experiment conditions; different volumes of resins (10–60 cm³) were mixed with different volumes of technological solution (30–100 cm³) to conduct experiments with different V_r:V_s ratios. The mixtures were stirred in the rotary shaker for 1 h. These sorption processes were repeated for each selected resin.

Kinetic studies were also conducted during which the resins were mixed with the technological solution for various durations (5–60 min), using $V_r:V_s = 1:2$ ratio.

The samples of resins were then used to check how many steps were needed to obtain technological solution with the concentrations of noble metals $< 5 \text{ mg/dm}^3$, which could be treated as a waste. The resins were mixed with the technological solution in the volume ratio of V_r:V_s = 1:10 for 30 min. After the designated time the mixture was filtered, part of the solution was analyzed, and the rest was mixed with a fresh batch of conditioned resin, still in the same conditions. The process was repeated six more times.

2.2.3. Elution Experiments

Resins samples from the tests with different ratios were used in the elution tests with different eluents using a batch method. The eluents were as follows: 10% HCl, 2 mol/dm³ ammonium thiocyanate, 2 mol/dm³ ammonium thiocyanate in 10% HCl, and 1 mol/dm³ thiourea in 2 mol/dm³ HCl.

The samples were washed with distilled water until the water pH was around 5. The resins were then contacted with the eluents for 1 h in the volume ratio of $V_r:V_s = 1:5$. At the end of the process, the resins were filtered and the solutions analyzed.

The yields were calculated according to the formula:

$$EY = \frac{C_f}{C_i} \times 100\%$$
 (2)

EY—elution yield (recovery), %; C_i —initial concentration of the metal in the resin, mg/dm³; and C_f —final concentration of the metal in the solution, mg/dm³.

2.2.4. Cementation Experiments

We mixed together the solutions after the elution experiments using 1 mol/dm³ thiourea in 2 mol/dm³ HCl. These were used for the cementation experiments using Zn powder.

Four different amounts of zinc (0.1 g, 0.5 g, 1.0 g, and 2.0 g) were added separately to 20 cm³ of eluate and then each was stirred for 1 h using a rotary shaker. The residues were then filtered and the solutions analyzed.

The yields were calculated according to the formula:

$$CY = \frac{C_i - C_f}{C_i} \times 100\%$$
(3)

CY—cementation yield (recovery), %; C_i —initial concentration of the metal in the solution, mg/dm³; and C_f —final concentration of the metal in the solution, mg/dm³.

2.2.5. Analytical Methods

The analyses were carried out by the Łukasiewicz Research Network-Institute of Non-Ferrous Metals, the Department of Analytical Chemistry (Gliwice, Poland). The concentrations of platinum, palladium, rhodium, and gold in the collected solution samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; NexION 300D, PerkinElmer, Waltham, MA, USA). Copper and zinc were analyzed via Flame Atomic Absorption Spectroscopy (FAAS; SOLAAR S4, Thermo, Waltham, MA, USA). The semiquantitative analysis was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; NexION 300D, PerkinElmer, Waltham, MA, USA). The average error of the method was between 10% and 20%, depending on the dilution of the samples and the concentration of noble metals.

3. Results and Discussion

3.1. Batch Experiments

3.1.1. Selection of the Ion-Exchange Resins

Sorption yields of the ion exchange resins selection experiments are presented in Table 4.

		Puromet MTS9200	Puromet MTS9850	Puromet MTS9100	Lewatit MonoPlus TP 214	Lewatit K 6362
	Pt	99.08	99.04	74.18	99.86	99.55
	Pd	99.98	99.98	97.95	99.97	99.80
Comption reald [0/]	Rh	80.19	80.28	43.26	74.60	70.79
Sorption yield [%]	Au	92.73	91.82	96.36	99.77	99.77
	Cu	8.71	8.30	27.88	99.17	7.68
	Zn	20.75	19.50	23.40	69.31	81.13

Table 4. Sorption yields of the individual elements after the preliminary sorption studies.

In addition to platinum, palladium, rhodium, and gold, copper and zinc were taken into account during the selection process, because they are the most common impurities present in industrial solutions directed to the ion-exchange process. Their concentration in the solution was high; therefore, they could influence the sorption process.

According to the data in Table 4, it was possible to recover noble metals with a high yield, oscillating even around 99%. It is common knowledge that platinum, palladium, and gold are the metals that easily undergo ion exchange, while rhodium is the hardest one to sorb on resins [12]. This is visible in the results in Table 4 because the sorption yields of Pt, Pd, and Au were around 99%, whereas rhodium could only be recovered with the yield around 70%.

The main factor eliminating specific resins from further tests was the uptake of copper and zinc in comparison to the rest of noble metals. That is because the resins chosen for specific industrial processes should be selective, even in a complex solution that could be fed into the technology. Heeding this line of thinking, Lewatit MonoPlus TP 214 was immediately excluded from further research (Zn yield = 69.31%, Cu yield = 99.17%). Puromet MTS9100 was also rejected due to the lower intake of Pt (yield = 74.18%) and Rh (yield = 43.26%) in comparison to the other ion-exchange resins. The remaining resins— Puromet MTS9200, Puromet MTS9850, Lewatit K 6362—were then used in the more specific and detailed batch experiments.

It is also worth noting that the concentration of Pd and Au in the post-process solution was $<5 \text{ mg/dm}^3$. Thus, this type of solution could be used to recover rhodium and platinum and later treated as a waste.

3.1.2. Sorption Isotherms

Figure 2 shows the correlation between the sorption yields of the individual noble metals and the volume ratio of the process ($V_r:V_s$).

It is noticeable that platinum, palladium, and gold can be recovered with the yields around 99% in almost every case. The only exception is the behavior of gold while using Puromet MTS9850. In this case, Au behaves like Rh, so the sorption yields raise with the higher resin to solution volume ratio. Rhodium can be recovered with the yield around 90% only using the higher ratios ($V_r:V_s = 1:1$ or 2:1), which is not a condition that can be used in any industrial technology. This means that the process needs to be refined, possibly with the addition of another step of recovering rhodium. Changing the parameters of the



inputted solution is also not excluded. Specific sorption isotherms were determined and are presented in Figure 3.

Figure 2. Sorption yields of the individual noble metals in relation to the volume ratio of the phases used in the experiments (V_r:V_s): (a) Puromet MTS9200, (b) Puromet MTS9850, and (c) Lewatit K 6362.

According to the isotherms shown in Figure 3, not all of them obeyed the laws of typical Langmuir or Freundlich isotherms—two of most popular and known models [17–19].

The most exceptional case was gold, where the plot was only moderately similar to the traditional isotherm while using Puromet MTS9850. The reason for that could be the quick way the gold undergoes the ion exchange process, so even in lower volume ratios its concentration in the resin is too high to determine the isotherm. However, it is also possible that the ion exchange of gold transpires not according to Langmuir or Freundlich isotherm laws. Nevertheless, the results confirmed the theory that gold was the first one to undergo the ion exchange process. In every example, it was possible to recover gold with a high yield, leaving only trace amounts in the solution (~0.1 mg/dm³), which is an amount impossible to recover.



Figure 3. Sorption isotherms (T = 20 °C); for (**a**) platinum, (**b**) palladium, (**c**) rhodium, and (**d**) gold; C_e—concentration of the metal in the solution in equilibrium, R_e—concentration of the metal in the resin in equilibrium.

The graphs for platinum and palladium were relatively similar, with points of palladium isotherm being closer to lower concentrations of this element in the post-process solution. In every example it was possible to recover palladium with a high yield, leaving only trace amounts in the solution (~0.5 mg/dm³). In the case of platinum, the process became more problematic due to the lessening amount of free space, which could recover the remaining metals from the solution after gold and palladium. It results in slightly lower yields of the platinum sorption and the overall process. Near the lower volume ratios, platinum remained in the solution in concentrations greater than 5 mg/dm³, which means that additional steps of processing and recovery need to be undertaken.

The classic isotherms were visible only in the graphs related to rhodium. It was the last element to undergo the ion-exchange process. Similar to platinum, the process was hindered by the amount of free functional groups, but also the inert character of the element.

Nevertheless, in most cases satisfactory results could be obtained by conducting the ion-exchange process with the ratio of $V_r:V_s = 1:10$, which is a ratio that can be used on an industrial scale.

3.1.3. Kinetic Studies

Diagrams showing the relation between the time and the sorption yields are presented below. The ratio $V_r:V_s = 1:2$ was chosen due to the fact it allowed maximization of the

recovery of all noble metals in the process, which was conducted for 1 h. After the experiment, neither gold nor palladium were analyzed in the solution.

Figure 4 clearly shows that in terms of platinum, the time does not influence the sorption yields to a high extent [17]. At almost every point of time, the yield was above 98%. However, to obtain the solution with the Pt concentration below 5 mg/dm^3 , the process needs to be conducted for at least 15 min.



Figure 4. The dependence of the sorption yields on the process time for platinum and rhodium ($V_r:V_s = 1:2$, RT) for (**a**) Puromet MTS9200, (**b**) Puromet MTS9850, and (**c**) Lewatit K 6362.

In the case of rhodium, Figure 4 presents mostly upward trends (for Puromet MTS9200 and Lewatit K 6362). In no case was the reaction yield above 90%, although the trend would indicate that obtaining such a result would be possible only after conducting the process for a long enough time, taking into account the possibility of sorbing other elements remaining in the solution. For all three resins, after 15 min the sorption yield was above 80%, which is an optimistic result, one that could be used later in dynamic studies.

3.1.4. Determination of the Sorption Yield Depending on the Number of Process Steps

The possibility of obtaining the post-process solution, by increasing the number of steps, consisting of less than 5 mg/dm^3 of each metal was checked. The results are presented in Table 5 and Figure 5.

			Number of Steps						
			1	2	3	4	5	6	7
Metal concentration [mg/dm ³]	Puromet	Rh	109.0	67.8	53.4	44.4	29.4	24.0	19.5
	MTS9200	Pt	36.5	2.2	-	-	-	-	-
	Puromet	Rh	58.4	34.9	25.7	23.2	13.8	10.7	8.4
	MTS9850	Pt	14.1	4.0	-	-	-	-	-
	Lewatit	Rh	91.5	53.5	35.2	25.8	-	-	9.2
	K 6362	Pt	4.9	2.4	-	-	-	-	-

Table 5. Concentration of Rh and Pt in the post-process solution depending on the number of sorption steps.



Figure 5. The dependence of the sorption yields of rhodium on the number of ion-exchange process steps for (**a**) Puromet MTS9200, (**b**) Puromet MTS9850.

The results presented in Table 5 show that it is possible to recover platinum after two steps to the level of 5 mg/dm³ remaining in the post-reaction solution. In the case of rhodium, even conducting seven steps with a fresh batch of resin on the same solution did not result in a post-reaction solution with a concentration of Rh below 5 mg/dm³.

The sorption yield of rhodium decreased with the number of steps, and it stabilized at the same value after the fourth step. In both examples, there is a visible sudden increase in the yield in the 5th step, but it may be because steps 5–7 were researched at a later time than the previous ones. This would mean that, in the meantime, new complexes of rhodium formed in the solution, ones that could more easily undergo the ion-exchange process. However, it also could be the results of a measurement error due to a different time of the conducted analysis.

In all experiments, rhodium was the hardest element to be recovered, due to its inert character. In acidic solutions, especially in the aqueous chloride solutions, it forms a series of complexes, such as: $[RhCl_6]^{3-}$, $[Rh(H_2O)Cl_5]^{2-}$, $[Rh(H_2O)_2Cl_4]^-$ or $[RhCl_6]^{2-}$ [20]. Even though rhodium can exist in a tetravalent oxidation state, it more often appears in the chloride solutions in a trivalent oxidation state, therefore forming the aforementioned variety of aqua-complexes. The noble metals complexes have a specific tendency to create ion pairs with ion exchangers, according to: $[MCl_6]^{2-} > [MCl_4]^{2-} >> [MCl_6]^{3-} > aqua-complexes.$ In accordance with this series, rhodium is the last one to undergo the ion exchange process, hence its low sorption yields in the experiments [21,22].

3.2. Elution

In the elution experiments, four types of eluents were researched: 10% HCl, 2 mol/dm³ ammonium thiocyanate, 2 mol/dm³ ammonium thiocyanate in 10% HCl, and 1 mol/dm³ thiourea in 2 mol/dm³ HCl. The results of the research are presented in Table 6.

		Metal	10% HCl	2 mol/dm ³ AT	2 mol/dm ³ AT in 10% HCl	1 mol/dm ³ TU in 2 mol/dm ³ HCl
		Pt	0.15	0.15	1.84	41.28
	Puromet	Pd	0.17	0.34	0.69	63.11
	MTS9200	Rh	1.04	0.52	4.18	7.31
		Au	2.35	2.35	4.71	47.08
Election		Pt	0.16	0.47	2.91	61.20
	Puromet	Pd	5.94	1.40	2.33	81.79
yields [%]	MTS9850	Rh	0.51	0.51	0.68	0.51
		Au	2.39	2.39	3.19	74.15
		Pt	0.54	4.86	1.69	35.66
	Lewatit K	Pd	2.42	0.15	0.32	37.97
	6363	Rh	19.88	22.08	10.12	11.93
		Au	2.07	2.07	4.31	20.70

Table 6. Elution yields (AT-ammonium thiocyanate, TU-thiourea).

The further recovery of noble metals from the resins is not an easy task as is clearly visible in Table 6 [11]. Only the solution of 1 mol/dm³ thiourea in 2 mol/dm³ HCl showed promising results in terms of elution of PGMs and gold. Nevertheless, the recovery depends on the previously used resin. The best results were obtained for Puromet MTS9850 and Puromet MTS9200. The high results of the recovery of rhodium could be caused by its small initial concentration in the resin. Therefore, a small amount of rhodium freed to the solution would give significant results.

The low elution yields could be also the result of conducting the experiments using the batch method, whereas dynamic studies are believed to give better outcomes. Another reason could be the character of the eluting agent. In case of thiourea, which has a high selectivity towards noble metals. according to the theory of hard and soft acids and bases. The metals are released when the negatively charged chlorides in noble metal anionic complexes are fully replaced by neutral thiourea [23]. The process continues until the complexes are positively charged or neutral. It is fully possible that this state was not reached [24]. Another reason is the character of the resins' functional groups. Both Puromet MTS9200 and Puromet MTS9850 are weak base resins, containing isothiouronium or polyamine functional groups. In comparison, Lewatit K 6362 is a strong base resin, containing quaternary ammonium salt as the functional group. In the case of weak base exchangers, the process of sorption can be reversed by changing the acid concentration (hence, the use of less acidic thiourea). The deprotonation does not happen as easily in strong base resins, from which metals can be eluted using large amounts of eluting agents containing competing agents [20]. Therefore, the elution yield of Lewatit K 6362 could be increased by increasing the amount of eluting solution, although it is not a method that could be used in industry, due to the hazardous character of thiourea. In the case of Puromet MTS9200 and Puromet MTS9850, the elution yields could be increased by lowering the acid concentration.

3.3. Cementation

The cementation experiments were conducted to examine the possibility of obtaining noble metal concentrates. The results are presented in Table 7.

Cementation with zinc powder is a well-known method of metal recovery from acidic solutions [25–29]. Increasing the amount of Zn to the same amount of acidic thiourea solution caused the pH to increase, which is a natural phenomenon. The concentration of dissolved zinc increased to a specific point and further on decreased. Therefore, the amount necessary for cementation has dissolved and the solubility equilibrium has been reached. There is no reason to add more zinc powder.

	1	2	3	4
m _{0Zn} [g]	0.0996	0.5064	1.0000	2.0000
m _{fZn} [g]	0.0135	0.0302	0.1538	0.8865
_	Pt 0.444	Pt 0.987	Pt 0.367	Pt 0.065
	Pd 0.960	Pd 0.879	Pd 0.477	Pd 0.084
Concentrate composition [%]	Rh 0.187	Rh 0.083	Rh 0.016	Rh 0.003
-	Au 0.225	Au 0.101	Au 0.020	Au 0.003
	Zn 98.184	Zn 97.950	Zn 99.120	Zn 99.845
pН	0.00	0.12	5.82	6.00

Table 7. Cementation experiment results with the use of zinc powder; m_{0Zn} —initial mass of zinc powder, m_{fZn} —final mass of zinc powder.

Figure 6 confirms the theory that the cementation yield increased with the addition of Zn powder. After adding 1g of Zn, the recovery reached 99%. The plot stabilized after reaching a specific point, which was also confirmed by the results visible in Table 6. Cementation with the use of zinc powder from the thiourea acidic solution is a good method of recovering noble metals.



Figure 6. The dependence of noble metal cementation yields [%] on the amount of zinc added to the solution [g].

3.4. Comparison with Other Research

It is difficult to compare the results of one's own work with already published results, as every type of research has a different approach to the experiments and the results. Table 8 shows the results of the experiments conducted in the most similar conditions.

Fable 8. Comparison of this study's results with other published results [10,13,1]	.4].
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	This Study's Results	Comparison [13,16,17]			
Puromet MTS9200					
Type of solution	Technological solution	Synthetic solution [13]			
Sorption studies	$\begin{array}{c} Pt \ 97.0\% \\ pH = 0.24, \ V_r = 10 \ mL, \ vs. = 100 \ mL, \\ t = 1.0 \ h, \ T = 20 \ ^\circ C \end{array}$	$Pt \sim 91.0\% \label{eq:phi} Pt = 0.50, m = 0.05 \; g, V = 50 \; mL, t = 1.5 \; h, T = 25 \; ^{\circ}C$			
Kinetic studies	Equilibrium time = 5 min pH = 0.24, V _r = 10 mL, vs. = 20 mL, T = 20 $^{\circ}$ C	Equilibrium time = 10 min pH = 1, m = 0.05 g, V = 50 mL, T = 25 $^{\circ}$ C			
Elution studies	$\label{eq:ctube} \begin{array}{l} Pt \ 41.0\% \\ C_{TU} = 1 \ mol/dm^3 \ in \ 2 \ mol/dm^3 \ HCl, \\ V_r = 10 \ mL, \ vs. = 50 \ mL, \ t = 1 \ h, \ T = 20 \ ^\circ C \end{array}$	$\label{eq:CTU} \begin{array}{l} Pt \sim 41.0\% \\ C_{TU} = 0.6 \mbox{ mol}/\mbox{dm}^3, \mbox{ m} = 0.05 \mbox{ g}, \mbox{ V} = 50 \mbox{ mL}, \mbox{ t} = 1 \mbox{ h}, \mbox{ T} = 25 ^{\circ}\mbox{C} \end{array}$			

	This Study's ResultsComparison [13,16,17]			
	F	Puromet MTS9850		
Type of solution	Technological solution	Synthetic solution [16]	Process leach solution [16]	
Sorption studies	Pt 98.0% Pd 99.9% Rh 74.4%	Pt 75.6% Pd 52.3% Rh 94.8%	Pt 81.6% Pd 58.8% Rh 87.8%	
	$V_r = 10 \text{ mL}, \text{ vs.} = 100 \text{ mL}, \text{ t} = 1 \text{ h}$	V _r = 5 mL, vs. =	200 mL, t = 24 h	
Kinetic studies	Equilibrium time = $15-30$ min V _r = 10 mL, vs. = 20 ml	Equilibrium $V_r = 5 \text{ mL}$	time = 30 min vs. = 200 ml	
Elution studies	$\begin{array}{c} Pt \ 61.0\% \\ Pd \ 81.0\% \\ Rh \ 0.5\% \\ C_{TU} = 1 \ mol/dm^3 \ in \ 2 \ mol/dm^3 \ HCl, \\ V_r = 10 \ mL, \ vs. = 50 \ mL, \ t = 1 \ h \end{array}$	Pt 70.0% Pd 93.0% Rh 7.0% $C_{TU} = 1 \text{ mol/dm}^3 \text{ in 2 mol/dm}^3 \text{ HCl},$ $V_r = 5 \text{ mL}, \text{ vs.} = 50 \text{ mL}, t = 5 \text{ h}$		
	F	Puromet MTS9850		
Type of solution	Technological solution	Synthetic s	olution [17]	
Sorption studies	$\begin{array}{c} Pt \ 98.0\% \\ Rh \ 74.0\% \\ C_{HCl} \sim 1 \ mol/dm^3, \ V_r = 10 \ mL, \\ V_s = 100 \ mL, \ t = 1 \ h, \ T = 20 \ ^\circ C \end{array}$	Pt 89.0% Rh 94.0% $C_{HCl} = 1 \text{ mol}/dm^3$, $m_r = 0.1-0.2 \text{ g}$, vs. = 10.0-20.0 m t = 24 h, T = 20 °C		
Kinetic studies	Equilibrium time = $15-30$ min V _r = 10 mL, vs. = 20 ml	Equilibrium $m_r = 0.1 g$,	time = 30 min vs. = 10 ml	
Elution studies	$\begin{array}{c} {\rm Pt} 61.0\% \\ {\rm Rh} 0.5\% \\ {\rm C_{TU}} = 1 \; {\rm mol}/{\rm dm}^3 \; {\rm in} \; 2 \; {\rm mol}/{\rm dm}^3 \; {\rm HCl}, \\ {\rm Vr} = 10 \; {\rm mL}, \; {\rm vs.} = 50 \; {\rm mL}, \; {\rm t} = 1{\rm h} \end{array}$	Pt 94.0% Rh 94.8% $C_{TU} = 1 \text{ mol/dm}^3 \text{ in}$ 2 mol/dm ³ H ₂ SO ₄	Pt 63.1% Rh 97.4% $C_{TU} = 1 \text{ mol/dm}^3 \text{ in}$ 2 mol/dm ³ KOH	

Table 8. Cont.

The results presented in this work are promising, as they are similar or in some cases superior in comparison with the results presented in other work.

4. Conclusions

The ion-exchange process was investigated to discover the applicability of commercially available resins in the recovery of noble metals from a technological solution, obtained from the leaching of waste produced during the refining process of noble metals. After the conducted experiments, it can be concluded that:

- The best resins for the sorption of noble metals are Puromet MTS9200, Puromet MTS9850, and Lewatit K 6362. Among the resins, Puromet MTS9200 and Lewatit K 6362 should be used for solutions with a higher concentration of gold (due to the lower gold sorption yields in the isotherm experiments for Puromet MTS9850), and Puromet MTS9850 and Lewatit K 6362 should be used in processes, which need to be conducted using fewer ion exchange steps (due to the lower recovery of noble metals after one step for Puromet MTS9200);
- 2. The volume ratio $V_r:V_s = 1:10$ and reaction time of 15–30 min could be used as the basic conditions for conducting the experiments using a dynamic method;
- 3. The solution of thiourea in hydrochloric acid could be used as the eluent to recover noble metals;
- 4. From the acidic thiourea eluates, noble metals can be recovered as concentrates using cementation with zinc powder;
- 5. In case of Lewatit K 6362, to obtain a concentrate with a high concentration of noble metals, the resin must be burned and then leached.

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