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Separation of palladium and silver from E-waste leachate: effect of nitric acid concentration on adsorption to Thiol scavenger

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ABSTRACT

The development of recovery techniques for metals present in low concentrations in E-waste, such as silver and palladium, is important from the aspect of the circular economy. Adsorption of palladium and silver was studied in detail in a batch process with silica-based Thiol scavenger from nitric acid leachate of waste printed circuit boards (PCBs). High adsorption efficiencies of Pd(II) and Ag(I), >97%, were reached in nitric acid concentrations below 3 mol L⁻¹. At higher acid concentrations, adsorption efficiency of Ag(I) decreased drastically which enables the separation of Ag(I) and Pd(II) based on nitric acid concentration in sample solution. Pd(II) and Ag(I) followed pseudo 2nd order kinetic model with fast adsorption with contact times of 60 and 30 min, respectively, in all studied acid concentrations. Adsorption followed Langmuir isotherm reaching highest loading capacities of 199 mg g⁻¹ for Ag(I) and 105 mg g⁻¹ for Pd(II) in 1 mol L⁻¹ nitric acid media, after which loading capacities decreased while nitric acid concentration increased. Thiourea-based desorption agents were most effective for desorption with >80% desorption efficiencies for Ag(I) and 55 - 88% efficiencies for Pd(II) in a one-step desorption. However, separation of Pd(II) and Ag(I) is not entirely possible in desorption step, hence the highest separation between Pd(II) and Ag(I) was found with two-step adsorption in which Pd(II) and Ag(I) were separated initially at adsorption step based on nitric acid concentration, followed by desorption step with acidic thiourea solution.

1. Introduction

Efficient recovery of metals from E-waste is becoming more and more critical due to the increasing use and discarding of various electronic devices. E-waste contains a broad range of materials including metals, plastics, and steel [1], and due to the high concentrations of precious metals, the most valuable part of E-waste is printed circuit boards (PCBs), including capacitors and solder [2,3]. However, PCBs contain also hazardous materials, such as flame retardants and heavy metals, which cause challenges in recycling. Fortunately, innovative removal techniques have already been developed for hazardous materials from E-waste to minimize the environmental impacts of recycling processes [4–6]. E-waste can consist of various weight percentages of base metals and up to 3300 mg kg⁻¹ of silver, 1000 mg kg⁻¹ of gold, and 210 mg kg⁻¹ of palladium [2]. Recycling of silver is made challenging by the relatively low market price compared to other precious metals, while the low and varying concentration of palladium in different types of PCBs make recovery of palladium challenging. Hence, development of new cost-effective recycling techniques for palladium and silver are

needed.

When hydrometallurgy is used for recovery of palladium and silver, leaching of waste PCBs is a necessary step to gain the metals into aqueous solution before separation. Leaching of silver and palladium from pretreated waste PCBs has previously been studied with different leaching agents, including mineral acids and thiourea based leaching agents. Nitric acid has been found to be effective in leaching of silver, with efficiencies over 80%, by using low nitric acid concentration of 3 - 4 mol L⁻¹ and short leaching times of less than 2 hours [7–9]. With similar leaching conditions, palladium has also been leached effectively using nitric acid with over 95% leaching efficiencies from waste PCBs [10] and multi-layer ceramic capacitors [11,12]. However, low leaching efficiencies of palladium [9] and silver [10] with nitric acid leaching have also been reported in some publications. Benefit of nitric acid leaching is that other precious metals are poorly soluble in nitric acid media [13] and palladium can be separated already in the leaching step from the other precious metals (i.e. Au, and Pt). Leaching of palladium and silver has also been studied with a broad range of various other leaching agents, like thiourea-based leachates [14–16] and other mineral acids

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[17–19].

Silver and palladium are present in relatively low concentrations in waste PCB leachates; hence, adsorption is an attractive technique for effective recovery. Additionally, the metal matrix of leachates is complex and varying, with high concentrations of e.g. copper, lead and tin when nitric acid is used for dissolution of waste PCBs. Traditionally, silver has been precipitated as a chloride salt, which has been found to be efficient due to the low solubility of silver chloride [7,9,12,20]. Non-commercial cellulose-based adsorbent has been used successfully for adsorption of silver and palladium in nitric acid media, with up to 5 mol L⁻¹ acid concentration [21]. Additionally, thiol-functionalized adsorbent has been studied for adsorption of silver and efficient adsorption was found at pH range 2.0 - 5.4 [22]. Ion exchange of silver, with commercial adsorbents, has been studied in various matrices, i.e. cyanide leachate [23] and pH-adjusted waste waters [24,25]. However, commercial adsorbents have rarely been used for adsorption of silver from nitric acid media.

Adsorption and separation of palladium from various waste waters containing nitric acid has been studied widely, since palladium is one of the fission products in nuclear reactors [26–28]. Adsorption of palladium has been found to be efficient with non-commercial silica-based adsorbents [26,29], chitin-based adsorbent [30], and persimmon-based PPF resin [13] in low nitric acid concentrations or using adjusted pH. In higher nitric acid concentrations, up to 5 mol L⁻¹, various non-commercial silica [27,28] and cellulose-based [21] adsorbents have shown high adsorption efficiencies for palladium. In samples containing chloride, non-commercial thiol-functionalized silica adsorbent [31] but also commercial ion-exchange resins [32,33] have been mainly studied for palladium adsorption. Since the selected leaching agent significantly affects the leaching efficiency as well as the selection of separation method and adsorbent, these two steps need to be considered together in a recovery process.

In the present study, a commercial silica-based Thiol scavenger was studied for adsorption of palladium and silver from real waste PCB leachates with varying nitric acid concentrations. Adsorption isotherms, kinetical parameters, and selectivity were studied in a broad acid concentration range for both metals to estimate the effect of acid concentration to adsorption parameters, but also for separation efficiency of these metals. Finally, desorption of silver and palladium was determined with several eluents to gain maximum separation.

2. Experimental

2.1. Nitric acid leaching of PGM-rich waste PCB fraction

A waste PCB residue after sulfuric acid and hydrogen peroxide leaching step from authors' previous publication was used as a sample material in the present study [34]. Based on literature, nitric acid was selected as a leaching agent due to its high leaching efficiency for silver and palladium and low leaching efficiency for other precious metals. The dry residue was leached either with 6 or 8 mol L⁻¹ nitric acid (made from 67%, puriss p.a., Sigma Aldrich). The leaching was performed using 100 g L⁻¹ pulp density and 4 hours leaching time at room temperature (21°C) with magnetic stirring. The solid residue was separated by filtration (Macherey-Nagel MN615, 185mm diameter) from the leachate. Diluted leachate was used as a sample solution throughout experiments in this study Table 1.

Table 1
Range of metal concentrations (mg L⁻¹) in nitric acid leachates.

	Ag	Pd	Al	Cu	Fe	Ni	Pb	Zn	Au	Pt	Sn
6 or 8 mol L ⁻¹ Nitric acid	6 - 25	2.9 - 4.7	170 - 250	1900 - 4900	35 - 55	50 - 90	640 - 670	60 - 110	<LOD	<LOD	170 - 470

2.2. General procedure of experiments

SiliaMets® Thiol metal scavenger (SiliCycle inc., Canada) is a silica-based scavenger containing thiol as a functional group. The manufacturer provided a loading capacity of 1.30 mmol L⁻¹ (138 mg g⁻¹ for palladium and 140 mg g⁻¹ for silver) and particle size of 40-63 µm for the batch used (Lot number: 164340) in this study.

Sample solutions for adsorption experiments were prepared by dilution of nitric acid leachate to 1 - 7 mol L⁻¹ concentrations, with additions of palladium and silver (Palladium: Atomic absorption modifier solution 10 000 mg L⁻¹ Pd(NO₃)₂ in 15% HNO₃, PerkinElmer/Merck, & Silver: 10 000 mg L⁻¹ AgNO₃ solution prepared from solid AgNO₃ ≥99.5%, VWR). General procedure of adsorption experiments, throughout this study, was to weight 50 mg of SiliaMets® Thiol scavenger into beaker, which was contacted with 7.5 or 10 ml of sample solution (S/L-ratio 1:15 or 1:20). Contact was performed under room temperature (21°C) with magnetic stirring using 2 hours contact time. Sample was filtered (Whatman 41), rinsed with ultrapure water (Type 1, resistivity of 18.2 MΩ cm, Synergy®, MilliQ) followed by preparation to volume of 25 ml.

Adsorption experiments were performed in 1 - 7 mol L⁻¹ nitric acid with 30 mg L⁻¹ addition of palladium and silver. Adsorption efficiencies of silver and palladium were calculated with Eq. 1

$$\text{Adsorption efficiency (\%)} = \frac{n(\text{initial}) - n(\text{after})}{n(\text{initial})} \cdot 100\% \quad (1)$$

where n(initial) is an initial quantity of analyte in solution and n(after) is the quantity in moles in solution after contact time. Separation factor, S_F, is defined in Eq. 2, where n(Pd/Ag, adsorbed) and n(adsorbed metals) are adsorbed quantities of palladium or silver and other metals, respectively.

$$S_F (\text{Pd} / \text{Ag}) = \frac{n(\text{Pd/Ag, adsorbed})}{n(\text{adsorbed metals})} \quad (2)$$

Enrichment factor, EF, of adsorption process is shown in Eq. 3, which is defined with palladium/silver concentration in scavenger (Q_{Ag/Pd}) and in sample solution (C_{Ag/Pd}), and similarly, concentrations of other elements in scavenger (Q_{el}) and in sample solution (C_{el}).

$$EF = \frac{(Q_{\text{Ag/Pd}}/Q_{\text{el}})_{\text{Scavenger}}}{(C_{\text{Ag/Pd}}/C_{\text{el}})_{\text{sample}}} \quad (3)$$

Desorption experiments were performed similarly to loading experiments, with 10 ml of desorption solution and 50 mg of loaded Thiol scavenger (S/L-ratio 1:20). However, contact time was increased to 6 hours to gain equilibrium of the system. In desorption experiments, used reagents were supplied by Sigma Aldrich with purity of Puriss. p.a. except for sodium hydroxide (Fisher chemicals, ≥97%).

2.3. Kinetics

Adsorption kinetics were studied for silver in 1, 2, and 3 mol L⁻¹ and palladium in 1, 3, and 6 mol L⁻¹ nitric acid concentrations. Concentrations of silver and palladium were adjusted to 200 and 100 mg L⁻¹, respectively, in the sample solutions. Contact times of 3 - 30 min were used for all silver experiments and palladium in 1 mol L⁻¹ acid concentration experiments, while 15 - 120 min contact times were used for palladium in 3 and 6 mol L⁻¹ acid concentrations. Each experiment was repeated 3 times (n=3) to study the repeatability of the experiments.

Results were given as a mean and standard deviation of replicates for each concentration.

Adsorption kinetics were estimated with linear form of Lagergren pseudo-first-order kinetic and pseudo-second-order kinetic models in Eqs. 4 and 5 using terms Q_e equilibrium loading, Q_t loading at time t (min), k' 1st order rate constant, and k'' 2nd order rate constant.

$$\ln(Q_e - Q_t) = \ln(Q_e) - k' t \quad (4)$$

$$\frac{1}{Q_e^2 k''} + \frac{t}{Q_e} = \frac{t}{Q_t} \quad (5)$$

Kinetic data was fitted also to the linear form of 1st order kinetic model in Eq. 6 where k' is a rate constant and C_0 and C_t are initial concentration and concentration at time t (min). Elovich model, in Eq. 7 was also studied for kinetic data, where a and b are initial adsorption rate and the desorption constant.

$$\ln\left(\frac{C_t}{C_0}\right) = -k' t \quad (6)$$

$$Q_t = b \ln(ab) + b \ln(t) \quad (7)$$

These models are widely used in literature to estimate the kinetics of adsorption in various batch experiments [21,28,30,35].

2.4. Adsorption isotherms

Adsorption isotherms of Thiol scavenger were studied at different nitric acid concentrations: between 1 - 3 mol L⁻¹ for silver and 1 - 7 mol L⁻¹ for palladium. Sample solutions were prepared with additions of analyte to gain 200 - 1000 mg L⁻¹ concentrations. Experiments were performed with a minimum of 3 replicates and results were reported with a mean and standard deviation. Experimental data were fitted to Langmuir [36] and Freundlich [37] linear models in Eqs 8 and 9.

$$\frac{C_c}{Q_e} = \frac{1}{Q_m} C_c + \frac{1}{b Q_m} \quad (8)$$

$$\ln(Q_e) = \frac{1}{n} \ln(C_c) + \ln(K_F) \quad (9)$$

In eq. 8 and 9, Q_e is equilibrium loading in mg g⁻¹, C_c equilibrium concentration of the sample in mg L⁻¹, Q_m is experimental maximum loading and b is Langmuir constant (L mg⁻¹). K_F is a constant indicating adsorption capacity and n is also constant, which indicates adsorption intensity in Eq. 9.

2.5. Analytical methods

Metal concentrations in solutions were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer, Optima 8300), following a similar procedure to authors previous study [34] with minor modifications, which are shown in section S.1 in SI. *Aqua regia* digestion was performed for solid samples (shown detailed Section S.1 in SI), to determine metal concentrations in loaded scavenger. Solid state analytics were performed with Fourier transformation infrared spectrometer (FT-IR, Thermo Scientific Nicolet iS50 FT-IR), Raman microscope (Thermo scientific, DXR Raman microscope, used parameters shown in SI table S.4) and scanning electron microscope with an energy dispersive x-ray spectrometer (SEM-EDS, Zeiss EVO-50XVP SEM and Bruker Quantax 400 ED). IR-spectra library of manufacturer was used for identification of IR peaks.

3. Results and discussion

3.1. Effect of acid concentration on adsorption efficiency and selectivity

Palladium and silver adsorption efficiency to Thiol scavenger was

studied at 1 - 7 mol L⁻¹ nitric acid concentrations. In Fig. 1.A, high adsorption efficiencies are gained for Pd in all used acid concentrations, however, for Ag, the efficiency starts to decrease when acid concentration is 4 mol L⁻¹, being only 20% at the highest studied acid concentration of 7 mol L⁻¹. Based on fittings of Hydra Medusa software [38], palladium occurs as a Pd²⁺ ion in all studied nitric acid concentrations, while Ag⁺ ion is the major component until 2 mol L⁻¹, after which soluble AgNO₃ complex is the predominant component for silver (figures presented in SI section S.2). Since AgNO₃ complex has no charge, adsorption of this complex does not occur to the Thiol scavenger, decreasing the Ag adsorption efficiency dramatically in higher nitric acid concentrations. Hence, it is evident that nitric acid concentration has a higher impact on efficiency of Ag(I) than Pd(II).

Additionally, Pd(II) and Ag(I) start to get separated after 4 mol L⁻¹ nitric acid concentration, when Pd(II) adsorbs still effectively to the Thiol scavenger, while high Ag(I) concentration remains in the sample solution. This would enable their separation in the adsorption step, by recovery of mainly Pd(II) by using a higher nitric acid concentration of 6 - 7 mol L⁻¹, after which efficient recovery of Ag(I) could be possible in the second adsorption step, by diluting the nitric acid leachate to below 3 mol L⁻¹ concentration. When a lower nitric acid concentration is used, both metals are adsorbed efficiently to the Thiol scavenger, and no separation occurs, and the separation of metals could be done in the desorption stage of the recovery process.

Adsorption of competing metal ions was studied with two nitric acid concentrations, 6 mol L⁻¹ and 2 mol L⁻¹, to estimate the selectivity of Thiol scavenger in different concentrations. In Fig. 1.B, Pd(II) is adsorbed from 6 mol L⁻¹ nitric acid media with high efficiency of 96.5%, while Cu, Pb, Sn, and Ag(I) are adsorbed in lower quantities with efficiencies below 5%. Metal concentrations in loaded scavengers were verified with SEM-EDS analysis shown in Section S.2 in SI. Separation and enrichment factors of Pd(II) were 3.1 and 58.5 over studied metals (with addition of 30 mg L⁻¹), respectively, indicating good separation and enrichment. Both Ag(I) and Pd(II) were adsorbed effectively with 97.5 and 100% efficiencies from 2 mol L⁻¹ nitric acid media, respectively, shown in Fig. 1.C, while copper and tin were adsorbed with approx. 15% efficiencies. Since both metals were adsorbed efficiently from 2 mol L⁻¹ nitric acid media, the separation factor for Ag(I) was only 0.9, while enrichment factor of silver was 19.1 (with addition of 30 mg L⁻¹) in adsorption step, hence selective desorption would hence be needed to separate the metals from each other when using this acid concentration. A two-step adsorption process is also an attractive option for separation of the metals: Pd(II) is adsorbed from 6 or 7 mol L⁻¹ acid media followed by dilution and adsorption of Ag(I) from 1 - 3 mol L⁻¹ acid media.

Effective adsorption of palladium [31] and silver [22] has previously been reported with thiol-functionalized adsorbents, but these experiments have been done only in below 1 mol L⁻¹ nitric acid media. In the present study, nitric acid concentration had a minor effect on adsorption efficiency of Pd(II), and a similar trend has also been reported for several adsorbents in the literature [21,27,28] However, for some adsorbents, the adsorption efficiencies of palladium have been reported to decrease in milder nitric acid media [13,29]. Decreased silver adsorption efficiencies, while nitric acid concentration increases, have been reported for dithiocarbamate-functionalized cellulose [21], which is compatible observation with this study. In previous publications, increased formation of palladium [13] and silver [21] nitrate complexes have been presented to be one reason for decreased adsorption efficiencies of palladium and silver in higher nitric acid concentrations. This supports our findings for decreased silver adsorption; however, formation of palladium nitrate complex is unlikely in the present study due to the high adsorption efficiencies of palladium found up to 7 mol L⁻¹ acid concentration.

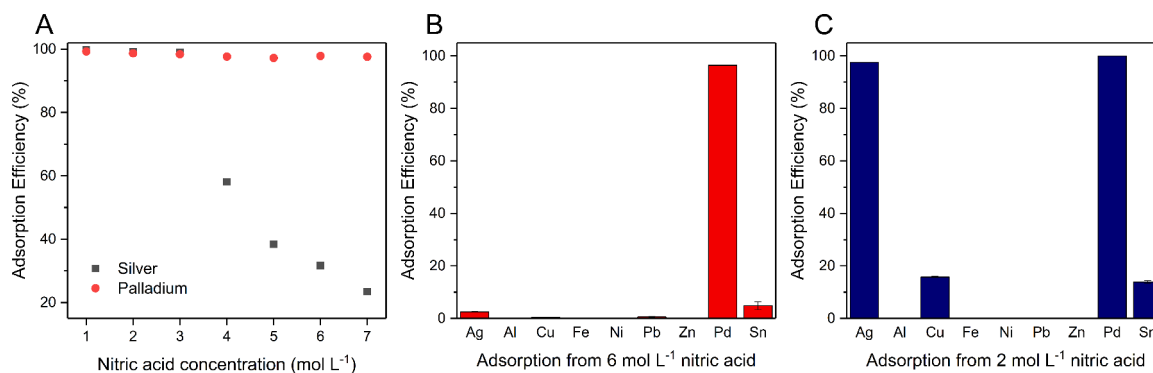


Fig. 1. A: Adsorption efficiencies of Ag(I) and Pd(II) to Thiolo scavenger (addition of 30 mg L⁻¹ for Ag and Pd) B: Adsorption efficiencies in 6 mol L⁻¹ nitric acid with additions of Pd (100 mg L⁻¹) and Ag (400 mg L⁻¹) C: Adsorption efficiencies in 2 mol L⁻¹ nitric acid with addition of Ag (130 mg L⁻¹) and Pd (30 mg L⁻¹).

3.2. Kinetical studies of Ag(I) and Pd(II)

The kinetics of Pd(II) and Ag(I) adsorption were studied in different acid concentrations, to evaluate the reaction kinetics and possible effect of nitric acid concentration. Ag(I) loading was found to approach equilibrium in only 15 min, as seen in Fig. 2, whereas reaction of Pd(II) proceeds slower, and contact time of 60 min is needed for the reaction to approach equilibrium in studied metal concentrations. Pseudo 2nd order kinetical model, in Eq. 5, described accurately experimental data of both metals with high correlations ($R^2 > 0.98$), while other models correlations varied broadly (R^2 0.72-0.87 for silver(I) and R^2 0.86-0.97 for Pd (II)), which are presented in section S.4 in SI. Pseudo 2nd order kinetical model indicates that reaction between surface and metal ion is the rate limiting step in adsorption of Pd(II) and Ag(I). Relatively small particle size of scavenger (40-63 μm) may account for fast kinetics of Pd(II) and Ag(I) in the studied acid concentrations.

Parameters of pseudo 2nd order kinetical model fittings are shown in tables 2 and 3 for Pd(II) and Ag(I), respectively. One replicate of Ag(I) k'' value in 1 mol L⁻¹ acid concentration was found to be a statistical outlier based on the Grubbs test (detailed calculations are shown in section S.4 in SI), hence it was removed from experimental data. Calculated equilibrium constants, Q_e , were similar with experimental data, which verify good fitting between experimental data and pseudo 2nd order kinetical model. Rate constants of Ag(I) were higher than Pd (II) in all studied concentrations, hence adsorption process of Ag(I) is more rapid, which agrees with data in Fig. 2. The highest pseudo 2nd

Table 2

Correlation coefficients of pseudo 2nd order kinetical model and k'' (min g mg⁻¹) and Q_e (mg g⁻¹) values from the pseudo 2nd order kinetical model for Ag(I) in various nitric acid concentrations. Results are shown as a mean and standard deviation of replicates.

Nitric acid (mol L ⁻¹)	Pseudo 2 nd order k''	Q_e	R^2
1	0.025 ± 0.009	45.0 ± 4.6	0.9993 ± 0.0008
2	0.039 ± 0.010	43.7 ± 3.9	0.9995 ± 0.0005
3	0.028 ± 0.011	38.8 ± 0.4	0.9967 ± 0.0025

Table 3

Correlation coefficients of pseudo 2nd order kinetical model and k'' (min g mg⁻¹) and Q_e (mg g⁻¹) values from the pseudo 2nd order kinetical model for Pd(II) in various nitric acid concentrations. Results are shown as a mean and standard deviation of replicates.

Nitric acid (mol L ⁻¹)	Pseudo 2 nd order k''	Q_e	R^2
1	0.015 ± 0.006	21.1 ± 1.0	0.9958 ± 0.0024
3	0.019 ± 0.011	22.6 ± 1.1	0.9950 ± 0.0079
6	0.006 ± 0.003	24.3 ± 1.6	0.9824 ± 0.0220

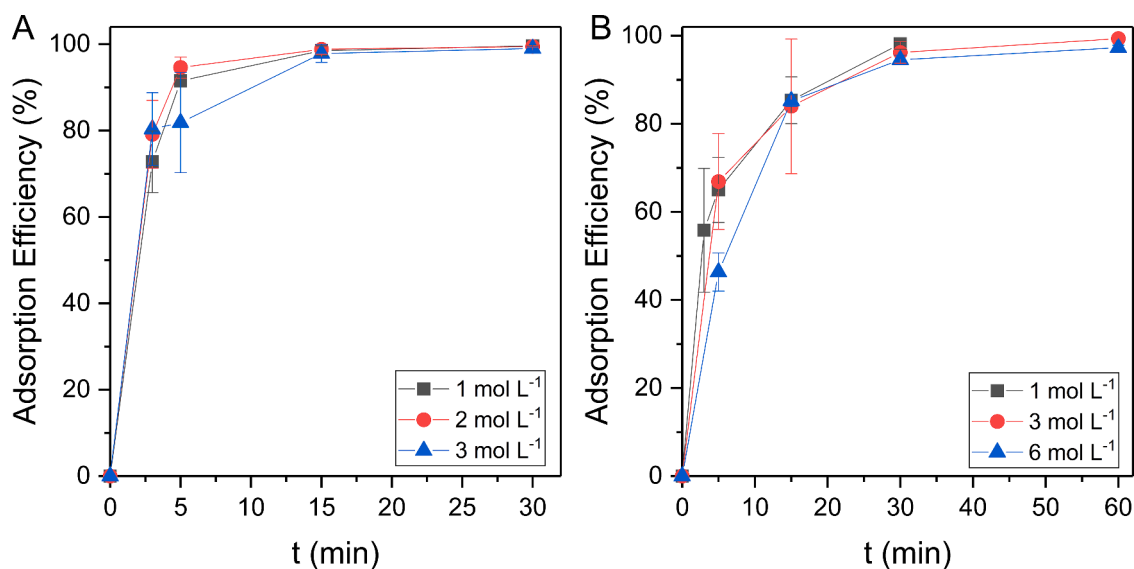


Fig. 2. Adsorption efficiencies of A: Ag(I) and B: Pd(II) as function of contact time in studied acid concentrations.

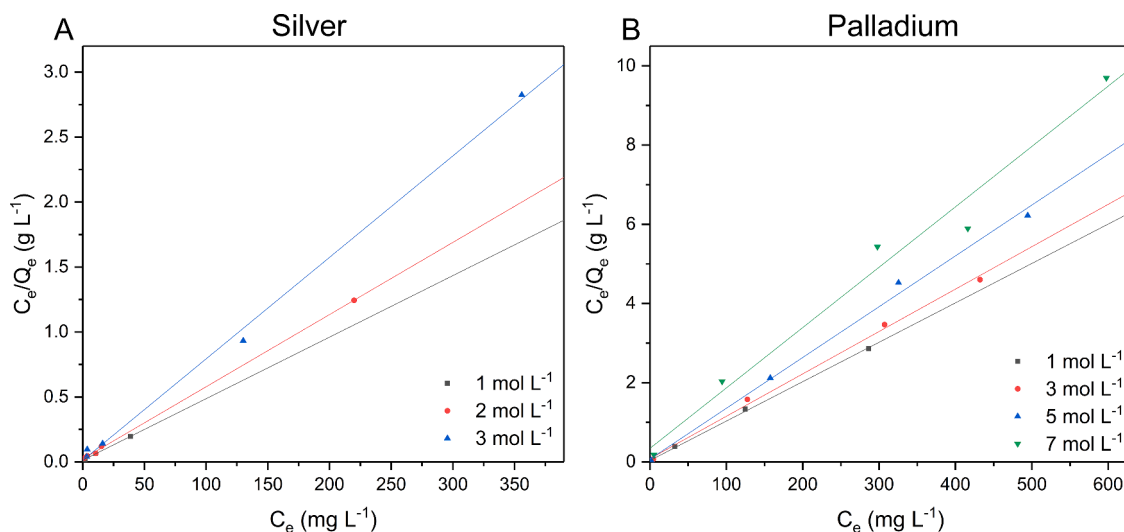


Fig. 3. Linear fittings of Langmuir model in various concentrations for A: Ag(I) and B: Pd(II). Fittings are presented for one replicate; fittings of all replicates are shown in section S.5 in SI.

order rate constant was found for Ag(I) ($k = 0.0390 \pm 0.0103 \text{ g min mg}^{-1}$) in 2 mol L^{-1} and for Pd(II) ($k = 0.0186 \pm 0.0110 \text{ g min mg}^{-1}$) in 3 mol L^{-1} nitric acid at room temperature (21°C). However, when $2 - 3 \text{ mol L}^{-1}$ acid concentration with the highest rate constants is used, separation factor between palladium and silver remains low, and the adsorption process is not very selective. In this case, selective desorption is needed to separate the metals from each other.

3.3. Effect of acid concentration to adsorption isotherms

The loading capacity of Ag(I) and Pd(II) to Thiol scavenger was studied in $1 - 3 \text{ mol L}^{-1}$ and $1 - 7 \text{ mol L}^{-1}$ nitric acid concentrations, respectively, to estimate the effect of acidity on adsorption isotherms. Langmuir model (Eq. 8) expressed accurately the experimental data of Pd(II) and Ag(I), with high correlations, as can be seen from Fig. 3 and tables 4 and 5, while fit of Freundlich model (Eq. 9) was poor for both metals (R^2 0.60-0.98). Linear fittings and parameters of studied models are shown in SI section S.5. Langmuir adsorption model indicates that both metals adsorb through monolayer adsorption with similar adsorption energy of adsorption sites. Decrease of Langmuir constants, b shown in tables 4 and 5, indicates that Ag(I) and Pd(II) ions' interaction

with surface gets weaker when nitric acid concentration increases. However, it should be noted that standard deviations in Ag(I)'s Langmuir constants are high.

The highest Langmuir loading capacities, 199 mg g^{-1} and 105 mg g^{-1} , were found in 1 mol L^{-1} nitric acid media for Ag(I) and Pd(II), respectively, and this indicates that Ag(I) ions adsorb to one adsorption site while Pd(II) ions adsorb to two adsorption sites. Adsorption of Ag(I) and Pd(II) is reduced while nitric acid concentration increases, which can be seen from decreased Langmuir adsorption capacities of both metals. Several factors affect negatively to loading capacity of Ag(I) and Pd(II) while nitric acid concentration increases. Based on Raman measurements, Thiol scavenger starts to oxidize after 3 mol L^{-1} acid concentration (with 4 hours contact time) due to the lack of thiol group peak at $\sim 2580 \text{ cm}^{-1}$ (spectra shown in section S.3 in SI). Decomposition of thiol groups was found to be 10% when acid concentration increases up to 7 mol L^{-1} , based on analysis with ICP-OES and SEM-EDS (shown in SI section S.3). These two factors will decrease the loading capacity in higher nitric acid concentrations. Langmuir constant decrease as a function of acid concentration for both studied metals, indicating decreased interaction between adsorbent surface and metal ions in higher acid concentrations. Lastly, formation of AgNO_3 complex will

Table 4

Calculated parameters for Ag(I) adsorption in $1 - 3 \text{ mol L}^{-1}$ acid concentrations from Langmuir linear fittings and correlation coefficients for Langmuir fittings. Results are shown as a mean and standard deviation of replicates.

Nitric acid (mol L^{-1})	Number of replicates	Q_m (mg g^{-1})	b (L mg^{-1})	R^2
1	4	198.9 ± 44.1	0.31 ± 0.17	0.9954 ± 0.0048
2	4	170.3 ± 21.0	0.22 ± 0.98	0.9972 ± 0.0025
3	3	131.5 ± 25.8	0.09 ± 0.56	0.9973 ± 0.0020

Table 5

Calculated parameters for Pd(II) adsorption in $1 - 7 \text{ mol L}^{-1}$ acid concentrations from Langmuir linear fittings and correlation coefficients for Langmuir fittings. Results are shown as a mean and standard deviation of replicates.

Nitric acid (mol L^{-1})	Number of replicates	Q_m (mg g^{-1})	b (L mg^{-1})	R^2
1	3	104.7 ± 5.8	0.21 ± 0.06	0.9987 ± 0.0003
2	3	97.6 ± 5.7	0.18 ± 0.07	0.9962 ± 0.0054
3	3	87.2 ± 10.4	0.30 ± 0.25	0.9984 ± 0.0015
4	3	86.7 ± 2.4	0.12 ± 0.08	0.9971 ± 0.0033
5	3	77.2 ± 10.2	0.10 ± 0.06	0.9931 ± 0.0047
6	3	75.1 ± 3.3	0.039 ± 0.004	0.9865 ± 0.0035
7	3	61.4 ± 6.2	0.034 ± 0.010	0.9802 ± 0.0099

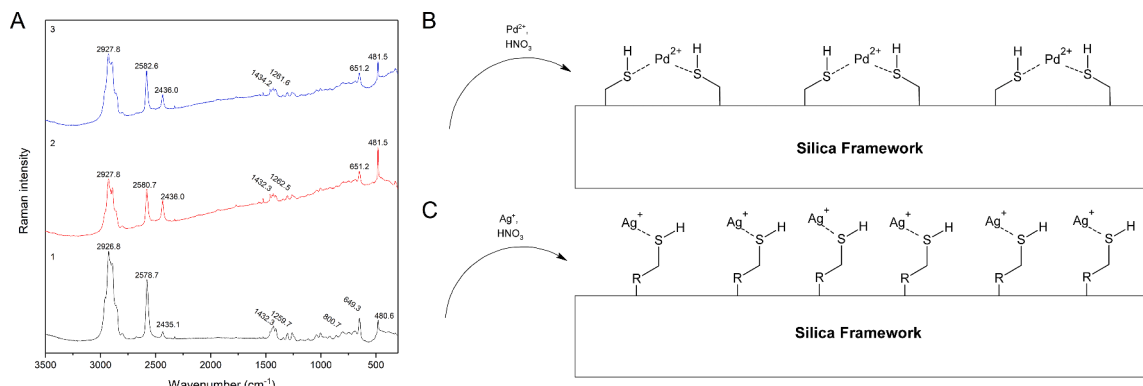


Fig. 4. A: Raman spectra of (1) fresh, (2) silver loaded (1 mg g⁻¹) and (3) palladium loaded (1 mg g⁻¹) Thiol scavenger, B: Proposed adsorption mechanism of palladium C: Proposed adsorption mechanism of silver.

Table 6

Desorption efficiencies of Pd(II) and Ag(I) with various eluents for loaded Thiol scavenger, from 2 and 6 mol L⁻¹ nitric acid media.

	Desorption from 2 mol L ⁻¹ HNO ₃ Ag(I) Efficiency (%)	Pd(II) Efficiency (%)	Desorption from 6 mol L ⁻¹ HNO ₃ Ag(I) Efficiency (%)	Pd(II) Efficiency (%)
1 mol L ⁻¹ HCl	1.4	0.0	20.9	1.8
3 mol L ⁻¹ HCl	4.7	0.0	49.5	3.7
1 mol L ⁻¹ H ₂ SO ₄	0.3	0.0	6.4	0.0
3 mol L ⁻¹ H ₂ SO ₄	0.4	0.0	5.7	0.0
0.3 mol L ⁻¹ Thiourea	60.6	3.3	64.5	7.2
0.5 mol L ⁻¹ Thiourea	82.6	6.4	86.6	7.2
7 mol L ⁻¹ HNO ₃	43.2	0.0	13.1	0.5
0.3 mol L ⁻¹ HCl + 0.3 mol L ⁻¹ Thiourea	101.8	94.7	95.7	57.4
0.3 mol L ⁻¹ HNO ₃ + 0.3 mol L ⁻¹ Thiourea	102.6	107.5	104.5	78.8
0.3 mol L ⁻¹ NaOH + 0.3 mol L ⁻¹ Thiosulfate	107.6	49.4	90.5	87.5

also decrease adsorption efficiency of Ag(I), while Pd(II) occurs as Pd²⁺ ion in studied nitric acid concentration range.

For palladium, adsorption capacities of several silica-based adsorbents have been reported, with 61 and 76 mg g⁻¹ loading capacities, in 2 and 3 mol L⁻¹ nitric acid media [27,28]. The highest adsorption capacity for palladium has been reported for functionalized cellulose, with loading capacity of 460 mg g⁻¹ in 0.2 mol L⁻¹ hydrochloric acid, while adsorption efficiencies were high also in nitric acid media [21]. Adsorption capacities of Ag(I) have been studied rarely in as acidic conditions as presented in this study. For functionalized cellulose adsorbent, loading capacity of Ag(I) has been reported as 1078 mg g⁻¹ from 0.2 mol L⁻¹ nitric acid, however adsorption efficiencies of Ag(I) decreased in higher acid concentrations [21], hence adsorption capacity of adsorbent may decrease also. Higher loading capacities of various adsorbents have been reported, however, using adjusted pH for Ag(I) [24,25] and palladium [13,29]. The rapid decrease of adsorption efficiencies in more concentrated acid media prevents effective usage of those adsorbents in the studied conditions.

3.4. Adsorption mechanisms of Ag(I) and Pd(II)

Adsorption mechanism of Pd(II) and Ag(I) was studied with solid state analytical methods, including FT-IR and Raman. FT-IR spectra are shown in SI section S.2, where IR-Peaks at area of 1500 - 400 cm⁻¹ correspond with reported IR-spectra of silica gel, which is consistent with the silica-matrix of the used Thiol scavenger. Thiol group S-H stretch reported in previous publications at ~2600 cm⁻¹ area [22,31] was not detected in this study even for the unused scavenger. This is due to the weakness of the S-H stretch, and the fact that there are only ~3 wt

% of thiol groups in the studied scavenger.

However, S-H stretch at ~2580 cm⁻¹ area is strong in Raman, hence, the determination of thiol group is possible before and after adsorption using Raman spectroscopy. To prevent excess emission from loaded metals, spectra were determined from loaded scavengers with only 1 mg g⁻¹ of Ag(I) and Pd(II) loaded in 2 and 6 mol L⁻¹ nitric acids, respectively. In Fig 4.A, Thiol group is present also after adsorption; however, peak has moved slightly to higher wavenumbers, which indicates interaction between thiol group and adsorbed metal (Ag(I) or Pd(II)). As can be seen, Thiol peak was found in adsorption step of palladium from 6 mol L⁻¹ nitric acid, with optimized 60 min contact time, which indicate that adsorption process is faster than oxidation of thiol group in 6 mol L⁻¹ nitric acid media. Other Raman peaks, in Fig. 4.A, have been specified in section S.3 in SI. Moreover, Ag(I) interacts with one thiol group, while Pd(II) interacts with two thiol groups based on adsorption isotherms (determined in section 3.3), and in conclusion, the proposed adsorption mechanism of Ag(I) and Pd(II) to the Thiol-scavenger is presented in Fig 4.B and C. In previous studies, silver [22] and palladium [31] have been found to adsorb to the thiol group via the sulfur atom, which correspond the results of this study. XPS measurements are also commonly used for mechanism studies, however, XPS was not possible in this study due to the decomposition of the thiol scavenger by x-ray radiation during XPS measurements.

3.5. Desorption of Pd(II) and Ag(I) from Thiol scavenger

Desorption of Pd(II) and Ag(I) was studied with 10 different solutions to find efficient desorption agent, but also to increase separation of Ag(I) and Pd(II) from each other. In addition, Thiol scavenger, loaded from

two different acid concentrations, were studied to estimate the effect of adsorption conditions to the desorption step. Acidic thiourea and basic thiosulfate solutions were selected for desorption experiments, since they have been used for palladium [26,27,31] and silver [39] desorption with efficiencies of 65 - 98% from various adsorbents. Desorption experiments were performed with two materials, which were used to estimate selectivity of Thiol scavenger from 2 and 6 mol L⁻¹ nitric acid media (see section 3.1).

Loadings of studied Thiol scavengers were approximately 23 and 4 mg g⁻¹ of Ag(I) and Pd(II) from 2 mol L⁻¹ nitric acid media, while Pd(II) loading was 15 mg g⁻¹ and Ag(I) 2 mg g⁻¹ from 6 mol L⁻¹ nitric acid media. Even though the major metal loaded to the scavenger changes in different acid concentrations, both loaded adsorbents contained Ag(I) and Pd(II), hence, efficient separation is needed in desorption step. In table 6, basic thiosulfate was the most efficient desorption agent for Pd(II) and Ag(I); however, strong bases, like sodium hydroxide, may dissolve silicates, hence usage of thiosulfate is not reasonable for desorption from the aspect of scavenger reuse. Ag(I) desorbed fully by using acidic thiourea solutions; and similarly, desorption efficiencies of Pd(II) were high at 60 - 108%. Hence, separation of Pd(II) and Ag(I) is not possible with these desorption solutions. The desorption efficiency of metals was not significantly affected by the different acid concentrations in the adsorption step, or the slightly different metals concentrations in the loaded scavengers.

Maximum separation of Ag(I) and Pd(II) could be achieved using a two-step desorption process, where 0.5 mol L⁻¹ thiourea desorbs Ag(I) effectively with minor concentration of Pd(II), after which acidic thiourea solution would be employed for desorption of Pd(II). However, desorption of Ag(I) with thiourea is not complete and the remainder of Ag(I) could desorb with Pd(II) in second step resulting mixture of Pd(II) and Ag(I) in acidic thiourea solution. As a result, two-step adsorption is needed to gain highest separation of Pd(II) and Ag(I).

Copper was found as the main impurity adsorbed into Thiol scavenger from 2 mol L⁻¹ nitric acid media with 12 mg g⁻¹ loading, while concentrations of other impurities were below 1 mg g⁻¹. Additionally, total concentration of impurities was below 2 mg g⁻¹ in Thiol scavenger loaded from 6 mol L⁻¹ nitric acid. Impurities were desorbed efficiently with thiourea and thiosulfate solutions, as well as acid solutions, with over 80% efficiencies (shown in SI section S.6). A washing step for desorption of impurities with e.g. 3 mol L⁻¹ HCl before desorption of Ag(I) and Pd(II) could be employed to increase the purity of palladium and silver in the desorption process.

Pd(II) could be adsorbed effectively from high nitric acid concentrations, e.g. 6 mol L⁻¹ media (shown in sections 3.1. and 3.3.), with fairly good separation already over Ag(I) and impurities studied. This enables usage of nitric acid with a broad acid concentration range in leaching step to gain maximum leaching rate of Pd(II) before adsorption step with Thiol scavenger. Effective desorption of Pd(II) can be achieved with high purity using various desorption agents. On the other hand, Ag(I) could be adsorbed efficiently only from low nitric acid concentration (< 3 mol L⁻¹, shown in sections 3.1. and 3.3.), which limits concentration of nitric acid in the leaching step. Low nitric acid media causes poor separation of Pd(II) over Ag(I) and other studied metals, hence efficient desorption steps are needed to separate Ag(I) and Pd(II). Additionally, Purity of Pd(II) and Ag(I) solutions could be increased with washing step of loaded scavenger using e.g. 3 mol L⁻¹ HCl before desorption step of Pd(II) and Ag(I).

4. Conclusions

Adsorption of Ag(I) and Pd(II) to silica-based Thiol scavenger in waste PCB nitric acid leachate media is discussed in detail in this study. Pd(II) adsorption was efficient with over 95% efficiency, even in high acid concentrations of up to 7 mol L⁻¹, while adsorption efficiency of Ag(I) started to decrease in higher acid concentrations than 3 mol L⁻¹, from 97% to 24%. The separation and enrichment factors of Pd(II) were

determined to S_F(Pd) 3.1 and EF 58.5 in 6 mol L⁻¹ nitric acid, while for Ag(I), separation factor of 0.9 and enrichment factor of 19.1 were determined from 2 mol L⁻¹ nitric acid. Hence, stepwise separation of these metals was feasible based on modification of acid concentration. Both metals studied followed a pseudo 2nd order kinetical model, hence rate limiting step is chemisorption for both metals. Optimized contact times, with over 95% adsorption efficiencies, were 60 minutes for Pd(II) and 30 minutes for Ag(I) in studied concentrations. Copper, lead, and tin were determined as impurities during the adsorption of both metals. With two-step adsorption, Pd(II) and Ag(I) were separated effectively into two separate adsorbent phases in different acid concentrations.

Langmuir adsorption model fitted well to experimental data in each concentration for Ag(I) and Pd(II), which indicates monolayer adsorption of the studied metals. Langmuir adsorption capacities of Thiol scavenger were highest in 1 mol L⁻¹ nitric acid media. Ag(I) capacity was found to be 199 mg g⁻¹ and it decreased by 34% until 3 mol L⁻¹ acid concentration, while Pd(II) capacity was found to be 105 mg g⁻¹ and it decreased by 59% until 7 mol L⁻¹. Dissolution and oxidation of Thiol scavenger was found in higher acid concentrations, which decreased the Langmuir's loading capacity slightly. Formation of AgNO₃ was proposed to affect negatively to the adsorption efficiency and Langmuir capacity of Ag(I), however, formation of nitrate complex was not observed for Pd(II).

Desorption of Ag(I) and Pd(II) can be done efficiently with acidic thiourea solutions, with over 80% efficiencies, but separation of these metal cannot be achieved in desorption step; hence, two-step adsorption is a beneficial choice. Additionally, adsorbed base metal impurities can be removed with diluted mineral acids before desorption of studied metals. In the present study, commercial silica-based scavenger was utilized successfully for adsorption of Ag(I) and Pd(II), with determination of adsorption isotherms and kinetical models, in nitric acid media. Results give new insight into recycling of palladium and silver from waste PCBs and will support the development of the circular economy of metals.

CRedit authorship contribution statement

Joona Rajahalmi: Conceptualization, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Siiri Perämäki:** Conceptualization, Supervision, Writing – review & editing. **Ari Väisänen:** Conceptualization, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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