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Porous 3D Printed Scavenger Filters for Selective Recovery of Precious Metals from Electronic Waste

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Abstract

Selective Laser Sintering (SLS) 3D printing technique was used to fabricate highly porous ion scavenger filters for recovery of Pd and Pt from electronic waste. The scavengers were printed by using a mixture of polypropylene with 10 wt-% of type-1 anion exchange resin as the printing material. Porosities and the flow-through properties of the filters were controlled by adjusting the SLS printing parameters. The cylinder-shaped filters were used in selective recovery of the target metals, Pd and Pt, from acidic leachate of electronic waste simply by passing the solution through the object at room temperature. Under such conditions, the scavenger filters were able to capture Pd and Pt with high efficiency and selectivity from a complex solution of metal ions that contained up to 100 times higher concentrations of other metals, such as copper. By using the Pd/Pt scavenger together with previously reported, highly selective nylon based Au scavenger, the most precious metals *i.e.* Au, Pd and Pt could all be recovered from the electronic waste leachate in a single flow-through process. One of the main advantages of the employed printed scavengers is that all recovered metals can be easily extracted from the filters as separate fractions by using aqueous solutions of thiourea or

diluted nitric acid. After removal of the captured metals, the scavengers are reusable without significant loss in their ion capturing performance.

Introduction

Development of 3D printing techniques has enabled the preparation of chemically and/or physically functional materials and devices.^[1] Fascinating examples have been reported where the potential, industrially relevant applications range from antimicrobial composites to catalytically active materials and even light emitting diodes.^[2] Advances in printing material development have opened the field for intriguing discoveries such as new energy storage devices or drug delivery systems.^[3] Typically, these products have been obtained by utilizing printing techniques such as stereolithography, extrusion-based methods or inkjet printing.^[1a, 4] The chemical activity is often obtained only via post processing the printed object.^[2b, 5] In most of these cases, the porosity, and thus the specific surface area, of the printed material itself is low and cannot be adjusted.

In powder-based printing methods, *e.g.* selective laser sintering (SLS), small, typically 50-100 μm , particles are fused together by laser. This allows, at least up to a point, control over the porosity of the material by fine-tuning the printing parameters including laser power, exposure time, printing temperature and cooling rate.^[6] When the particles are sintered in such a way that only their surfaces are partially melted, a solid structure containing accessible voids between the sintered grains is obtained. Such porous materials can be utilized directly in chemical applications. For example, if a porous column is printed, a fluid (liquid or gas) can flow through the object, interacting with the surface of the partially fused particles. When this type system is compared to a column packed with loose particles, the advantages are obvious. First of all, as the positions of the particles are fixed, they cannot be rearranged by the flowing fluid. Thus, any unwanted channeling is prevented. Second, the porosity can be adjusted,

which can be utilized in controlling the back-pressure of the object. Third, the possibilities to design the shape, interior structure and the size of the object are almost limitless due to the printing technique. Hence, if the printing material is chemically active, the object can be used as a chemically functional device. In principle, the potential applications of such devices are limited only by the chemical functionality of the printing material.

We have recently published a study concerning recovery of gold from acidic leachate of Waste Electrical and Electronic Equipment (WEEE) by using pure nylon (polyamide 12, PA) based 3D printed scavenger object. Herein, we extend this approach to a hybrid printing material consisting of polypropylene and type-1 anion exchange resin. The goal was to develop a 3D printed scavenger filters for recovering Pd and Pt from WEEE leachate and to show that even very low concentrations of metals can be cost-effectively and selectively captured by using simple, reusable scavenger devices.

Results and Discussion

To prepare 3D printed functional filters with precious metal scavenging properties, swollen beads of additive **1** (type-1 anion exchange resin, Dowex 21K) were dried at 90 °C overnight and grinded to a fine powder in a ball mill. The chemically active resin (10 wt-%) was mixed with readily available and easily printable polypropylene (PP), which was chosen as the supporting matrix for the chemically active component. The mixture was then used to print filters with desired shape, size (5 mm tall disc with 16.5 mm diameter) and porosity (see the Experimental section) by using Sharebot SnowWhite SLS 3D printer. The final filters were analyzed using microscopic techniques and X-Ray tomography.

Scanning electron microscopy (SEM) is commonly utilized to acquire information about the porosity and composition of novel materials. Unfortunately, non-conducting samples, like

organic polymers, are known to have notable charging problem during SEM experiments. This charging effect can be reduced, for example, by image post-processing or by coating the sample with metal, but important information about surface structure could be lost during the treatment. Thus, imaging of insulating samples is challenging using standard electron microscopic methods. In helium ion microscopy (HIM) imaging is based on usage of positive He ions when the aforementioned charge problem can be circumvented by utilization of charge compensating low voltage electron beam (a flood gun), enabling the imaging of insulating samples.^[7] Hence, the surfaces of the printed objects were thoroughly investigated using HIM (**Figure 1**). By inspecting the images acquired from the break surfaces of PP/resin filter (**1-PP**) (**Figure 1**, left), it is evident that the filters are highly porous throughout the sample. In general, the material appears to be composed of polypropylene beads partially sintered together forming a macroporous structure. Extensive melting of the polymer beads is not observed either in printed pure PP (supplementary **Figure S1**) or **1-PP**. When zooming in, the particles of anion exchange resin additive **1** can be seen firmly attached to the surface of sintered polypropylene (**Figure 1**, middle). However, the additive is not encapsulated by the polypropylene matrix. The active resin is thus available for chemical interactions. In addition to overall porosity, using SLS technique different density material can be printed in a single object enabling fabrication of entirely functioning products with solvent impermeable edges and chemically active interior (**Figure S2**).

Detailed and comprehensive information about the the interior structure of the objects and the distribution of the active component was acquired using X-ray tomography (**Figure 1**, right). The overall porosity of the objects was established from the high estimated porosity percent (~32 %). The pore size distribution is relatively even, as the diameter of most of the pores falls between 20 and 60 micrometers (**Figure S3**). The data obtained from this analysis demonstrates that the inside structure of the filters corresponds to the HIM images and, even

more importantly, that the active material (Dowex 21K) is evenly distributed over the whole object.

The chemical performance of the printed scavengers was evaluated by using a synthetic test solution containing 100 mg L⁻¹ of Ni, Zn, Fe and Cu and 50 mg L⁻¹ of Al, Cr, Pb and Sn along with 5 mg L⁻¹ of Pd and Au and 1 mg L⁻¹ of Pt in 5% *aqua regia*. The chosen composition mimics the metal ratio in an average sample of an *aqua regia* dissolved Printed Circuit Board (PCB) waste.^[8] Synthetic test solution was used due to the fact that the metal concentrations in true WEEE leachates vary considerably depending on the actual waste material. Hence, analysis of a well-defined synthetic mimic solution is needed for estimating the true capacity and the overall performance of the printed scavengers. It should also be noted that the main part of the metal scavenging experiments with 1-PP Pd/Pt scavenging hybrid material were conducted with a test solution without two key components, Ag and Au, found in electronic waste. From authentic PCB waste, silver can precipitate in presence of chloride, hence it was not included in any of the test solutions. Similarly, gold can be removed completely and selectively by using the 3D printed nylon scavenger prior to 1-PP filter (see below and **Table S4**).^[8] Hence, the synthetic test solution mimics the leachate after removal of Au and Ag. The scavengers were also tested with authentic WEEE solutions, which were prepared by using ultrasound assisted *aqua regia* leaching to dissolve metals from crushed PCB waste. The efficiency of the scavenger was determined by analyzing the metal content of the solution before and after it was passed through the filter. In all experiments, 8 mL of metal solution were passed through three separate 5 mm thick cylinder-shaped 1-PP filters with a diameter of 16.5 mm. This was carried out by placing the tightly fitting filters into a 10 mL syringe and pressing the solution gently through them (**Figure S4**).

For the synthetic test solution over, 96 % of Pd and 98% of Pt were captured from the solution with high selectivity. The most concentrated metal ions, such as aluminium, iron and copper were not retained by the filter while about 50 % of Sn and 10-22 % of Pb and Zn were initially adsorbed (**Figure 2**). However, practically all of zinc and lead as well as most of tin and traces of other metals trapped inside the filters during experiments could be easily removed by subsequent water washes (6 times 8 ml), and only a small amount of tin remained as the main impurity. Excellent efficiency and selectivity for capturing Pd and Pt was also obtained when an authentic WEEE leachate was used instead of the synthetic test solution. These results are summarized in the supplementary data (**Table S6**).

By using a sequence of nylon filters and the **1-PP** filters, the most valuable metals, *i.e.* Au, Pt and Pd, could be captured selectively even from an authentic WEEE solution (**Figure 3**). In this process, the solution was first passed through gold scavenging filters (pure 3D printed nylon) followed by a set of **1-PP** filters. Over 98 % of Au could be removed from the authentic WEEE solution with three 5 mm thick nylon filters with a diameter of 16.5 mm, and over 79 % of Pd and 89 % of Pt could be captured by using three subsequent **1-PP** hybrid filters.

Both Au and Pd/Pt scavengers are fully reusable as the recovered metals can be removed from the filters without destroying their ability to capture ions. Because Au and Pd/Pt were captured in discrete filters, the stripping could be performed separately to produce cleaner end-products. Au was extracted from the nylon filter by using 7 M nitric acid as reported earlier.^[8] Pd and Pt were removed from **1-PP** hybrid filter one-by-one with thiourea solutions. Pd was extracted first with 0.1 M aqueous thiourea followed by extraction of Pt with 0.3 M aqueous thiourea solution (**Table S2**). Total of about 83 and 85 % of adsorbed Pd and Pt, respectively, were recovered with thiourea washes (see the experimental section). This

process allowed separation and isolation of Pd and Pt as separate fractions. In the end, the residual Sn, also trapped by the **1-PP** (see above), was removed also as a separate fraction by using 4.5 M nitric acid. Unlike nylon scavenger for Au, which was ready to be re-used immediately after removal of the captured metal, the **1-PP** filters needed to be regenerated with 0.1 M hydrochloric acid before reuse. However, neither the stripping of the metals nor the regeneration of the filters caused significant reduction in adsorption efficiency (**Table S3**). Maximum adsorption capacity of the **1-PP** filters was studied by passing 10 ml of solution containing 400 mg L⁻¹ of Pd and Pt in 5 % *aqua regia* through one 5 mm filter five times (**Table S5**). Pd and Pt scavenging capacity of the filters was calculated to be about 11 wt-% relative to the mass of the additive in the filter. Performance of the 3D printed filter was compared with similar weight (520 mg) of powderous, non-printed mixture of type-1 anion exchanger resin (Dowex 21K) and polypropylene. The powder mixture was stirred in 10 ml of concentrated Pd/Pt solution and the maximum capacity was found to be *ca.* 13 wt-%. The results show that printing decreases the maximum capacity of the resin only slightly, again highlighting the high porosity of the objects and the availability of the chemically active component **1**.

Conclusions

The presented results clearly demonstrate that SLS 3D printing can be utilized to fabricate porous but still rigid chemically functional objects. These objects can be printed by using a hybrid material such as **1-PP** in which the chemically active component is printed together with easily printable supporting matrix. The results also show that the printing does not destroy the chemical functionality of the active component. The **1-PP** filters introduced in this paper can be used as effective and selective scavengers for Pd and Pt from complex mixtures of metal ions such as acidic leachate of WEEE waste. The captured metals can be removed from the scavenger filter in a stepwise manner, enabling the separation of Pd and Pt as

individual fractions. After removal of the metal ions, the objects can be regenerated, which makes them fully re-usable.

Although we have used WEEE leachate as an example, the scavengers could also be used to capture metal ions from various other source materials. In a broader scope, the concept of using functional printing materials could be extended even beyond scavenging of ions. By developing new, chemically active printing materials it is possible to open entirely new chapter in design of chemically functional devices for various chemical processes.

Experimental Section

Chemicals and solvents: Synthetic solutions used were prepared from PerkinElmer spectroscopy standards (1000 mg L⁻¹). Polymers used for 3D printing were purchased from Advanc3d Materials. Dowex 21K, thiourea, nitric acid ($\geq 65\%$) and hydrochloric acid ($\geq 37\%$) were purchased from Merck. High purity water of 18.2 M Ω cm resistivity was used throughout the experiments. Water was purified using Elga Purelab Ultra.

Sample preparation: Synthetic solution containing 100 mg L⁻¹ of Ni, Zn, Fe and Cu and 50 mg L⁻¹ of Al, Cr, Pb and Sn along with 5 mg L⁻¹ of Pd (and Au for a solution for synthetic test with gold, see **Table S4**) and 1 mg L⁻¹ of Pt in 5% *aqua regia* was prepared by using PerkinElmer spectroscopy standards. Synthetic solution used for capacity tests containing 400 mg L⁻¹ of Pd and Pt in 5% *aqua regia* was also prepared using PerkinElmer spectroscopy standards. The authentic WEEE solution was prepared by ashing milled printed circuit boards for 4 hours at 950 °C. 1 g of the ashed WEEE was placed in a 50 ml centrifuge tube and 10 ml of *aqua regia* was added. Ultrasound assisted leaching was conducted at 25 °C by performing six three-minute cycles. Pressure was released from the tubes between the cycles. Elma Elmasonic P was used as the ultrasound bath. Samples were filtered using Whatman 41 filter papers and diluted in 1:5 ratio before being used for adsorption tests. Detailed descriptions of

HIM imaging, X-ray tomography and ICP-OES measurements can be found from Supporting Information.

Metal recovery and stripping: Recovery experiments were conducted by placing three 5 mm thick and 16.5 mm diameter tightly fitting filters in a 10 ml syringe. Before the adsorption tests, were prepared by passing 8 ml of water through them. 8 ml of the synthetic or authentic solution was then pushed through the filters and metal concentrations were measured before and after the adsorption experiment. To consider the amount of solution trapped in the objects, the final metal concentrations were compared to those of solution that had been passed through a syringe containing three 5 mm thick and 16.5 mm diameter pure PP filters. Hence, the recovery efficiency was calculated as the percentage difference in metal concentrations between initial solution (synthetic or authentic) passed through the pure PP filters and the concentration detected after 1-PP treatment. After water washes, recovery efficiency (**Table S1**) was obtained by adding the concentrations present in water wash fraction to the metal concentrations left in the solution after the treatment with 1-PP and by comparing this value to the initial metal concentration of untreated synthetic solution.

Stripping tests were performed by using filters that had been used for recovery tests with synthetic solution. First, six washing cycles were performed by using water (5 times 8 ml), followed by four 8 ml washes of 0.1 M thiourea. Next, four 8 ml washes of 0.3 M thiourea were conducted, followed by four 8 ml washes of 4.5 M nitric acid. Finally, filters were regenerated by passing through 16 ml of 0.1 M hydrochloric acid. All experiments presented in this paper were performed in triplicate.

Capacity experiment was conducted by placing one 5 mm thick and 16.5 mm diameter filter in 10 ml syringe and passing 10 ml of the synthetic solution containing 400 mg L⁻¹ of Pd and Pt in 5 % *aqua regia* through the filter for five times. Results of this experiment were compared to the result received by stirring the same weight (520 mg) of powder used for manufacturing the filters with 10 ml of the same synthetic solution for 30 minutes.

3D printing: Filters were designed using FreeCad v. 0.16 and sliced by using Slic3r v 1.2.9. Printing was done using ShareBot SnowWhite SLS 3D-printer. 0.1 mm layer thickness was used for all 3D printed objects. For PP and 1-PP, the used laser power was 40 % with a rate of 60000 (2400 mm s⁻¹). Build plate temperature of 119-123 °C was used. For nylon, laser power of 40 % with a rate of 64000 (2560 mm s⁻¹) was used. Build plate temperature was set to 160-163 °C for the duration of the print.

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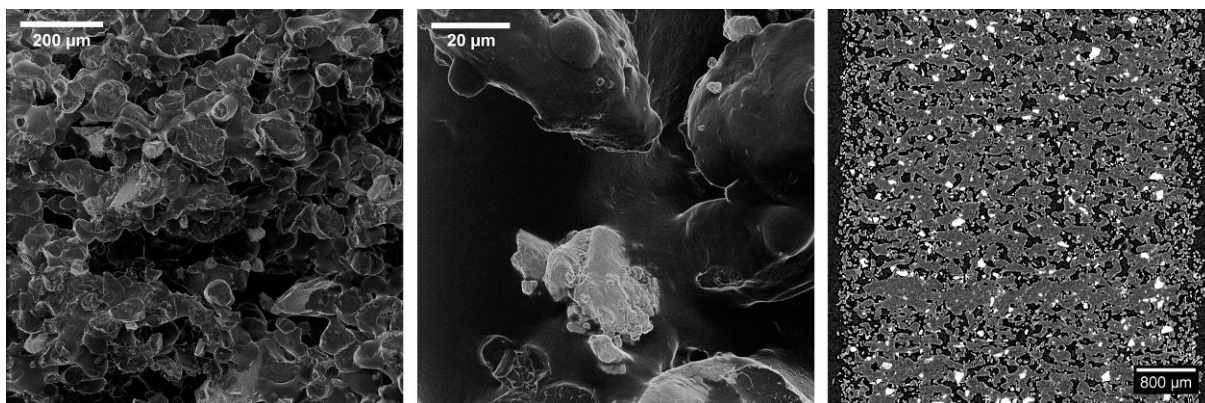


Figure 1. HIM image of break surface of **1-PP** (left), zoomed in view of **1-PP** (middle) and X-ray tomography image of **1-PP** showing the additive in white and supporting polypropylene in grey (right).

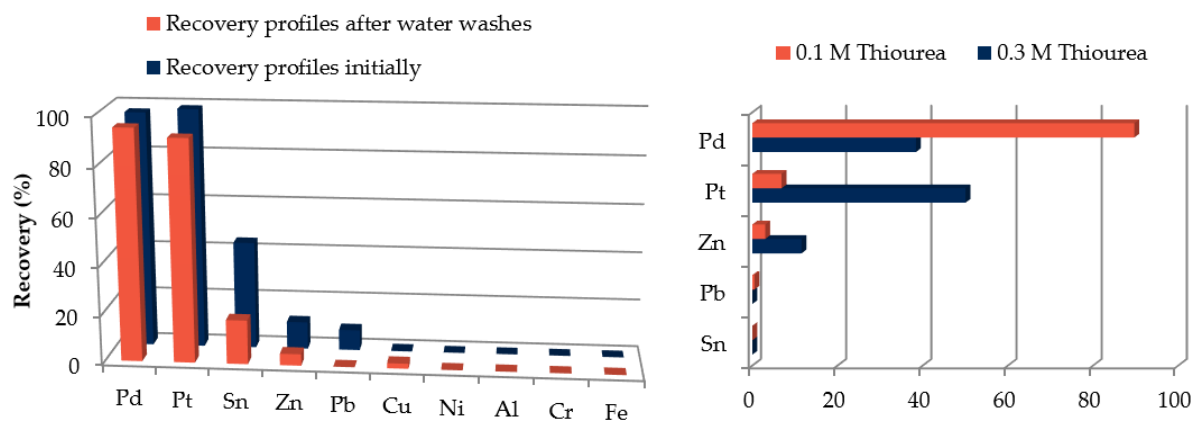


Figure 2. Recovery profiles after treatment with three **1-PP** 5mm filters (left) and compositions of stripping solutions (right).

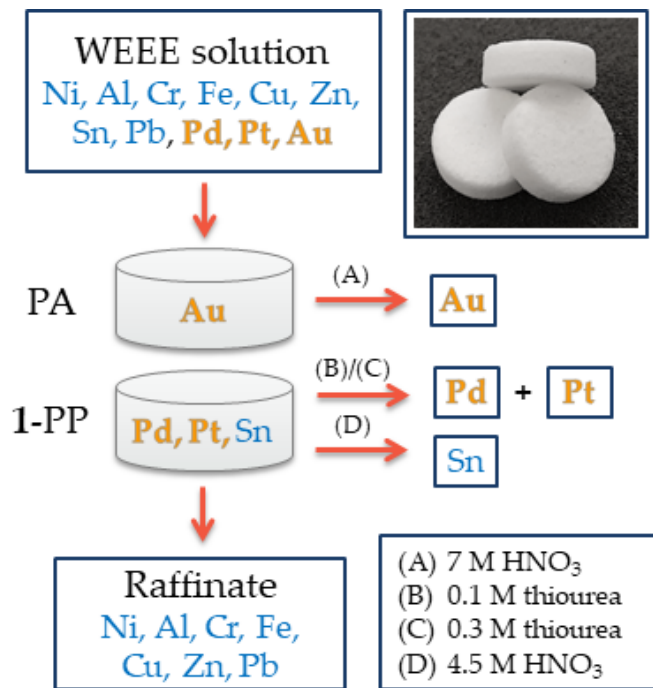


Figure 3. Complete route for extraction and stripping of gold and platinum group metals from WEEE solution using PA and 1-PP filters.