Extraction Potential of Tantalum from Spent Capacitors Through Bioleaching

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Abstract

Tantalum (Ta) is the one of the most critical elements according to the European Commission. There is limited research on tantalum recovery from secondary sources such as waste electrical and electronic equipment (WEEE), bottom ash and by products of the industrial activities. In this study, the recovery potential of tantalum from spent tantalum capacitors was tested using bioleaching under the biomining concept. Three different kinds of microorganisms were tested for tantalum recovery, which were *Pseudomonas putida* (DSM No. 6125), *Bacillus subtilis* (DSM No. 1088532), and *Penicillium simplicissimum* (DSM No. 1078). It turned out that *P. simplicissimum* has the ability to leach tantalum from wasted tantalum capacitors. The maximum leaching rate was 1.25 g Ta per kg sample, 0.67% of Ta could be extracted after a period of 14 days. An unknown species achieved the highest leaching rate (9.88 g Ta / kg sample, extraction rate of 5.31%) for 15 days, at 25 ℃ and 150 rpm, bulk density of 0.1%, but the isolation and identification failed. The potential of tantalum recovery by bioleaching is demonstrated, however, further research needs to be carried out.

1 Introduction

Tantalum is a hard, blue-gray transition metal with high corrosion-resistance. Tantalum is highly conductive of heat and electricity, and is easily fabricated, in addition to having a very low coefficient of thermal expansion [1]. These features of tantalum result in a very wide application. It can be used in the instruments for preparation of inorganic acids, and its service life could be ten times longer than that of stainless steel. In chemical, electronics and electrical industries, tantalum can also be used to take the place of some precious metals, and thus reduce the cost. Tantalum is also a kind of biological metal. It can be used as orthopedic and surgical material, and silk, to reconnect broken nerves. Tantalum carbide is very hard, and has a high melting point (3880℃), so it can be used for cutting tools and drills. Tantalum oxide is used for the manufacturing of advanced optical glass and catalysts [1].

More than half of the total tantalum is used for tantalum capacitors. Tantalum capacitors are widely used in communication equipments, digital audio and video products, computers, automotive electronics and the defense industry. The characteristics of tantalum capacitors are attractive. Ueberschaar et al. [2] reported the average tantalum content per mass printed circuit board (PCB) and product (Figure 1). In addition, elemental composition of tantalum capacitors were identified by Ueberschaar et al. [2] (Figure 2). Compared with traditional aluminum capacitors, tantalum capacitors are more stable. The leakage current is much lower, as is capacitor heating, which might have some influence on the service life. In addition, the failure rate of tantalum capacitors is also lower [3, 4].

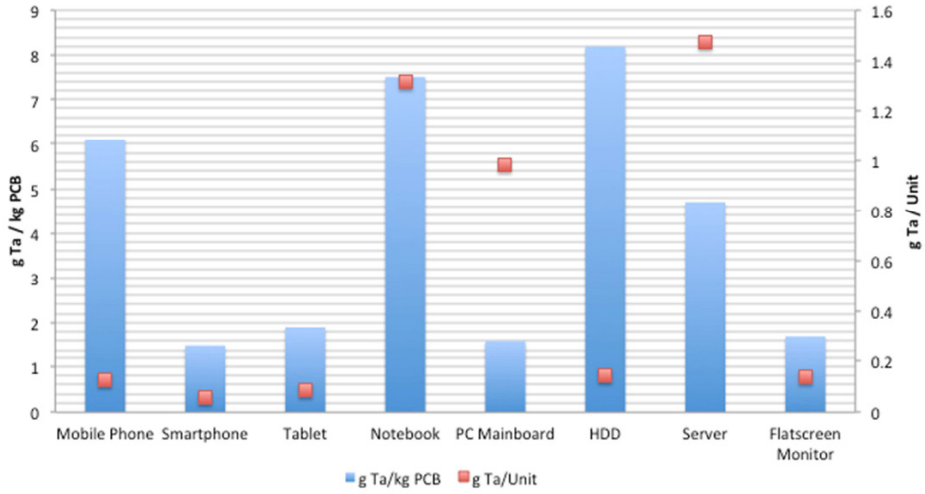


Figure 1. Average Ta content of the PCB and product (adapted from [2])

A. Pehlken et al. (Eds.), *Cascade Use in Technologies 2018*,
https://doi.org/10.1007/978-3-662-57886-5_7

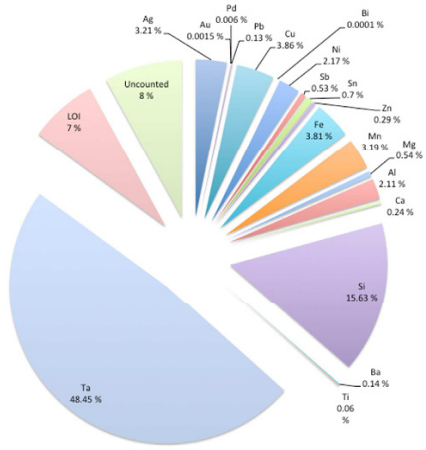


Figure 2. Elemental composition of tantalum capacitors (LOI: Loss of Ignition) (adapted from [2])

1.1 Reserves and production

According to United States Geological Survey (USGS), the global reserves of tantalum are larger than 100,000 tons, of which about 62% are found in Australia and about 36% in Brazil [5]. The largest two tantalum deposits are both in Australia. In 2014, the global tantalum mineral production was 1200 tons, of which the production from Rwanda accounts for half of the total production (600 tons). Figure 3 shows the global tantalum mineral production in 2014 [5].

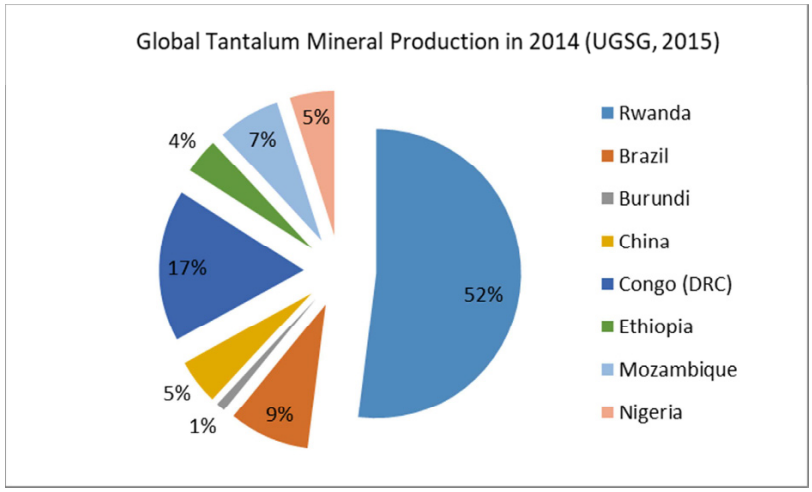


Figure 3. Global tantalum production in 2014 [5]

1.2 Recovery of Tantalum from WEEE

In WEEE or e-waste, most of the valuable substances are found in PCBs [6]. Precious and scarce materials account for only a small percentage of the total weight, but with enough recycling value. Tantalum accounts for about 0.0157% of the total weight of a computer and is mostly found in capacitors [7]. Since the production of tantalum has not been stable in price and the quantity, the recovery of tantalum from WEEE (mainly used capacitors) is becoming a serious issue. There is a general trend towards miniaturization and the use of less tantalum per capacitor; therefore, the quantity of tantalum powder per tantalum wire has been decreasing [2]. As a result of this situation the implementation of a recycling process for tantalum from waste capacitors may not be sustainable [2]. Nowadays, about 15% to 20% of the total tantalum production is from waste recycling processes [8]. The normal tantalum recovery process is quite complex, especially for the metal cladding liquid tantalum capacitors. Electrolysis or aqua regia degradation has to be applied first to remove the

metal clad, followed by sodium reduction or carbon reduction for deoxidation, and electron beam smelting is applied as the last step (Figure 4-A). In addition, for chip capacitors, after the separation process which removes plastic and wires, sodium hydroxide, nitric acid and hydrochloric acid should be applied step by step to leach and remove tin, silver and manganese, then sodium reduction and electron beam smelting are applied (Figure 4-B) [8-10].

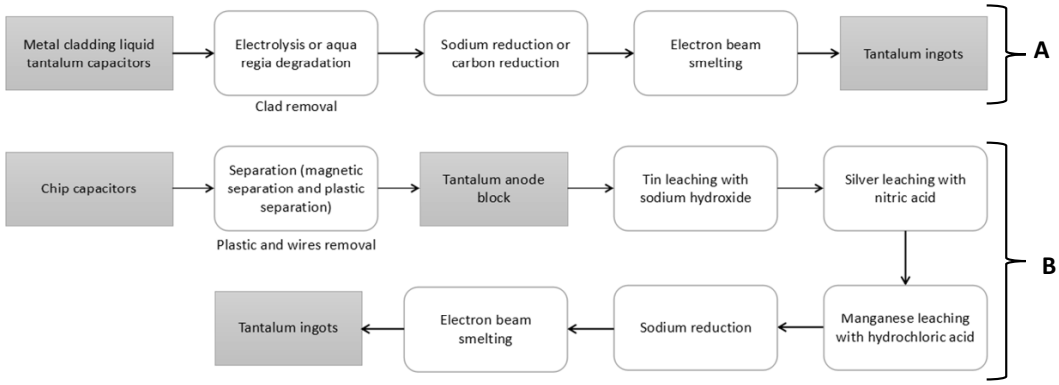


Figure 4. Tantalum recovery process for the metal cladding liquid tantalum capacitors (A), for chip capacitors (B) [8, 9]

1.3 Aims of the study

As mentioned before, bioleaching processes are already widely used in the mining industry. A lot of designs and innovative ideas are still at lab scale. There is only limited research on the recovery of precious metals (PMs) and rare earth elements (REEs) from WEEE using biomining process. But rough ideas are already given. For example, Gurung et al. [11] carried out gold and silver recovery through biomining from spent mobile phones, and achieved a maximum recovery rate of 72.33% for gold and 85.91% for silver. Kucuker [6] reported that PMs and REEs could be recovered from WEEE using biomining process such as bioleaching and biosorption. So the possibility of applying biomining to the recovery of tantalum, which is more or less alike to precious metals and rare earth elements, has already been shown. The aim of this study is to test the bioleaching method for the recovery of tantalum from spent capacitors. Three different microorganisms (*Pseudomonas putida* (DSM No. 6125), *Bacillus subtilis* (DSM No. 1088532), and *Penicillium simplicissimum* (DSM No. 1078)) were studied.

2 Methods and Materials

2.1 Characterization of the Sample of Spent Tantalum Capacitors

The tantalum capacitor samples were obtained from WEEE and were milled into powder. A special acid digestion with hydrofluoric acid (HF) was carried out in order to measure the tantalum content in the sample using the EU standard method EN 13656 (Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3), and hydrochloric (HCl) acid mixture for subsequent determination of elements) [9]. 0.5 g of milled tantalum capacitor samples were taken, and filled into each plastic digestion vessel. The samples were pre-humidified with a few drops of deionized water. An acid mixture of 6 mL HCl, 2 mL HNO_3 and 2 mL HF was filled into each digestion vessel. In the next step, the digestion vessels were closed, put into the microwave oven and the digestion program was applied according to the DIN EN 13656 method.

The microwave-assisted digestion was finished, the samples were cooled and the digestion vessels were opened. To avoid potential harm to the analysis devices, the hydrofluoric acid was neutralized by building up a complex with boric acid. 650 mg boric acid was added into each vessel (e.g. 22 ml 4 % (m/m) solution). The vessels were closed and heated again in the microwave at 300 W for 3 min.

Afterwards the vessels were cooled down. To deal with the particles remaining in the vessels, the solution could be either centrifuged or filtrated. The solution was first analyzed qualitatively with energy dispersive X-ray fluorescence (EDXRF) and then quantitatively analyzed with Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

2.2 Bioleaching Experiments

Three different microorganisms were chosen for the bioleaching experiment: *Pseudomonas putida* (DSM No. 6125), *Bacillus subtilis* (DSM No. 1088), and *Penicillium simplicissimum* (DSM No. 1078). All three species were ordered from Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ) [12]. Two mediums (Medium 1 and Medium 2) were prepared for the cultivation of microorganisms and the bioleaching experiment. Medium 1: 5.0 g

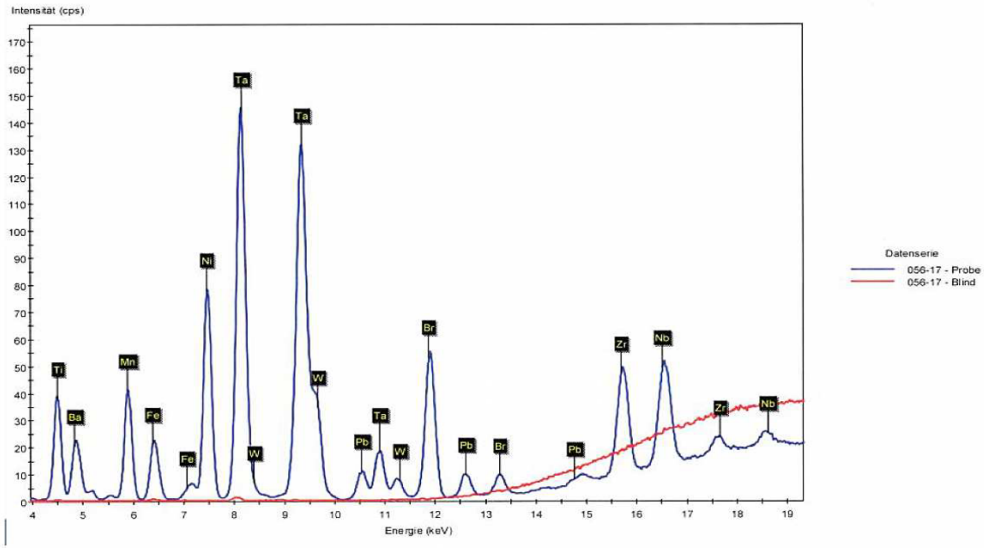
peptone and 3.0 g meat extracts were added into 1000 ml distilled water, and the pH value was adjusted to 7.0. Medium 2: 200 g scrubbed and sliced potatoes were boiled in 1000ml water for 1 hour. The mixture was then sieved, and 20 g glucose was added into every 1000ml sieved infusion. Both mediums were autoclaved before further operations. *Pseudomonas putida* (DSM No. 6125) and *Bacillus subtilis* (DSM No. 1088) were cultivated in Medium 1 at 28 ℃, 150 rpm, and *Penicillium simplicissimum* (DSM No. 1078) was cultivated in Medium 2 under room temperature (about 20-23 ℃), 150 rpm, for 48 hours. A test was carried out to check the potential of bioleaching of tantalum with the chosen microorganisms. Before the test, a literature survey was carried out, aimed at figuring out suitable bioleaching conditions for the test experiment. Two-step bioleaching was chosen as a test method. Tantalum capacitors were grinded into particles with a size of about 0.5 mm. 100 ml of each culture were poured into 250 ml flasks, and 0.1 g tantalum capacitor particles were added into each flask, to achieve a bulk density of 0.1%. Every test was duplicated, and 3 comparative tests were carried out, with 100 ml deionized water, pure Medium 1, pure Medium 2, and 0.1 g tantalum capacitor particles. The mouths of the flasks were covered by cotton to ensure a good aeration. All 9 flasks were cultivated under room temperature (about 20-23 ℃) and 150 rpm. To ensure mixing conditions, all the flasks were shaken slightly by hand for 1 min. 5 ml samples were taken from each flask on the 7th and 15th day for the measurement of tantalum ion concentration.

3 Results and Discussion

3.1 Characterization of the Tantalaum Capacitors

In Figure 5, the qualitative analysis result of the tantalum capacitor sample by the EDXRF analysis is shown. From the spectrum, Ta, Ti, Ba, Fe, Mn, Nr, W, Pb, BR, Zr, Nb and Ag (out of the diagram) can be detected from the sample. The Tantalum content measurement was carried out in the central laboratory for chemistry analytics in the Hamburg University of Technology (TUHH), following the standard method DIN EN 13656. The Ta content in the representative sample was 185.9 g Ta / kg sample.

Figure 5. The elemental composition of the Ta-capacitor sample by EDXRF



According to the literature, the content of tantalum in Ta capacitors could be around 40%. But from the spent Ta capacitors the characterization showed that the content of tantalum was 18.59%. Instead, the wasted Ta capacitors contained quite high percentages of Fe, Cu, Ni, and Pb. Since the capacitors were sorted from wasted PCBs, it is certain that the collected capacitors contained a certain amount of wires and impurities. As the capacitors are small and hard to be recognized, some other types of capacitors, such as Ni capacitors and Al capacitors might be mixed together with Ta capacitors. This can explain the low content of Ta and high content of other metals in the wasted Ta capacitors.

3.2 Bioleaching Tests

The results of the bioleaching experiments are given in Table 1. In the bioleaching experiments, tantalum essentially cannot be leached out by *Pseudomonas putida* (DSM No. 6125, maximum leaching rate: 0.33 g Ta / kg sample, Ta extraction rate of 0.18%) and *Bacillus subtilis* (DSM No. 1088, maximum leaching rate: 0.34 g Ta / kg sample, Ta extraction rate of 0.18%) even under favorable growth conditions. *Penicillium simplicissimum* (DSM No. 1078) has the ability to leach tantalum, but the leaching rate was still limited (maximum leaching rate: 1.25 g Ta/ kg sample, extraction

rate of 0.67%). An unknown species achieved the highest leaching rate (9.88 g Ta / kg sample, Ta extraction rate of 5.31% in 15 days, and 28.65 g Ta / kg sample, Ta extraction rate of 15.41% after 70 days), at 25 ℃ and 150 rpm, bulk density 0.1%, but the isolation and identification of this species failed. The unknown species which contaminated the flasks in the prior experiments achieved the highest leaching rate. As reference group Medium 2 was the contaminated group, the unknown species could possibly be a kind of fungi. The problem is the isolation of the unknown species failed, which means the microorganisms in the contaminated flasks were already dead after the cultivation period for bioleaching. The contamination was successfully repeated for one more time. However, this is an endless loop, because by the time the leaching result turns out that the contamination occurred by the right species, the culture is already dead. This leads to a very high identification cost for the species, as metagenome sequencing plus the data analysis have to be done to identify the species.

As the content of tantalum in PCBs was extremely low, the exact percentage-leaching rate cannot be calculated. With regards to the low content of tantalum in PCBs, it is not commercially acceptable to recover tantalum as a single metal directly from PCBs without a combination with other metal recovery processes, but as the bioleaching process also has the ability to leach out a high percentage of base metals (copper, nickel, aluminum and manganese), the combined multi-metal recovery process can be taken into account. Tantalum is a very stable metal element which cannot be leached even by aqua regia, and there is almost no current existing literature on tantalum bioleaching. As the pioneer of this kind of research, this study started from zero. The potential of bioleaching is clearly shown. As the bioleaching process does not require and produce highly toxic and highly corrosive chemicals, the downstream processes, including metal removing from liquid phase and waste water treatment, would also be much simpler. The research in tantalum recovery by bioleaching is interdisciplinary, and needs very close cooperation between different labs and institutes, especially for unexpected situations, as in this case, for example, the contamination of the reference group. The identification of unknown microorganisms (Denaturing Gradient Gel Electrophoresis, DGGE, for example) needs special equipment and expertise, so it took time and labor to contact and cooperate with another institute (Technical Microbiology, TUHH). In addition, funding is needed for further identification processes.

Table 1. Results of the bioleaching experiments

Bulk density 0.1%	**Leaching rate of Ta (%)**		**Bulk density 1%**	**Leaching rate of Ta (%)**	
Leaching agent	**7th day**	**15th day**	**Leaching agent**	**7th day**	**15th day**
Medium 1	ND	0.091	Medium 1	0.002	0.019
Medium 129	2.495	5.314	Medium 129	0.168	0.389
P. simplicissimum 1	0.295	0.672	*P. simplicissimum 1*	0.123	0.293
P. simplicissimum 2	0.398	0.591	P. simplicissimum 2	0.115	0.249
P. putida 1	0.155	0.172	*P. putida 1*	0.006	0.021
P. putida 2	ND	0.177	*P. putida 2*	ND	0.026
B. subtilis 1	0.016	0.102	*B. subtilis 1*	ND	0.017
B. subtilis 2	0.166	0.182	*B. subtilis 2*	ND	0.037

ND: under detection limit

For bioleaching experiments, prior research shows that smaller particle size of raw materials, low bulk density and better growth conditions may have the potential to achieve higher leaching rates. It is also recommended to test more different microorganism types and species, and different leaching processes (for example, spent medium leaching). Current existing literature also figured out the possibility to use mixed cultures (with different microorganisms) in bioleaching. This is already applied in gold mining, but for tantalum it still needs more effort. Genetic modification might also be helpful to increase the leaching rate. The research done by TUHH has certainly figured out the potential of tantalum recovery by bioleaching, as the research is still in its infancy.

4 Conclusion

The result of the tantalum recovery trial by bioleaching from tantalum capacitors turns out to be negative. Tantalum essentially cannot be leached out by *Pseudomonas putida* (DSM No. 6125, maximum leaching rate: 0.33 g Ta / kg sample, extraction rate of 0.18%) and *Bacillus subtilis* (DSM No. 1088, maximum leaching rate: 0.34 g Ta / kg sample, extraction rate of 0.18%) even under favorable growth conditions. *Penicillium simplicissimum* (DSM No. 1078) has the ability to leach tantalum, but the leaching rate was still limited (maximum leaching rate: 1.25 g Ta / kg sample, extraction rate of, 0.67%). An unknown species achieved the highest leaching rate (9.88 g Ta / kg sample, extraction rate of 5.31%), at 25 ℃ and 150 rpm, bulk density 0.1%, but the isolation and identification failed. Since there is no current existing literature that has directivity in the field of tantalum bioleaching, it is difficult to choose the species for experiment, as there are different kinds of microorganisms which can produce acid and have the potential for bioleaching. This means it might be constly to find out a suitable species. However, researchers focus on species which might be helpful while studying the mechanism of tantalum bioleaching. On the other hand, genetically modified organisms might be the best choice to increase the bioleaching rate of tantalum. However, this only feasible after the mechanism of tantalum leaching is totally clarified. Tantalum cannot be leached out even by aqua regia, so a high leaching rate must be caused by the

synergy of several different organic or inorganic substances. It might be quite hard to figure out the actual mechanism, and the genetic modifying even after the mechanism is clarified, since the research will take a huge amount of time, and needs cross-sectoral cooperation.

5 Zusammenfassung

Tantal wird von der Europäischen Kommission als hoch kritisches Element eingestuft, dennoch existieren bisher kaum Forschungsarbeiten zur Rückgewinnung von Tantal aus Sekundärquellen wie Elektro- und Elektronikaltgeräten, Schlacke und Nebenprodukten industrieller Aktivitäten. In diesem Beitrag wird das Rückgewinnungspotenzial von Tantal aus verbrauchten Tantalkondensatoren durch Bioleaching untersucht. Hierfür wurden die drei verschiedenen Mikroorganismen *Pseudomonas putida* (DSM No. 6125), *Bacillus subtilis* (DSM No. 1088532), und *Penicillium simplicissimum* (DSM No. 1078) getestet. Es stellte sich heraus, dass *P. simplicissimum* Tantal aus gebrauchten Tantalkondensatoren auslaugen konnte. Die höchste Auslaugungsrate betrug hierbei 1,25g Tantal pro kg Versuchsmaterial, und nach einer Periode von 14 Tagen konnten 0,67% Tantal extrahiert werden. Eine unbekannte Spezies erreichte die höchste Auslaugungsrate (9,88 g Ta / kg Versuchsmaterial, Extraktionsrate von 5,31%) bei 15 Tagen, 25℃, 150 rpm und einer Lagerungsdichte von 0,1%, jedoch sind Isolation und Identifizierung fehlgeschlagen. Das Potenzial der Tantalrückgewinnung durch Bioleaching konnte gezeigt werden, es sind jedoch weitere Forschungen notwendig.

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