CHAPTER 2

EXPERIMENTAL DETAILS

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In the preceding chapter the various gaps within the existing literature concerning the processing of waste tantalum capacitors were identified and outlined in section 1.6. In order to address these identified gaps, the subsequent phase of experimental work was designed. Notably, a significant portion of prior research has leaned heavily on high-temperature methodologies, such as oxidation and pyrolysis, for disintegrating the outer mold resin of discarded tantalum capacitors. However, these high-temperature procedures are marked by their substantial energy consumption and adverse environmental repercussions. In an effort to mitigate these issues, a more accessible and cost-effective pre-processing technique was developed to separate the organic matter containing silica from waste tantalum capacitors.

Furthermore, the scope of research on tantalum recovery from waste capacitors is quite limited, with no prior investigation proposing a method for the sequential recovery of metals. The existing literature presents a complex array of procedures necessitating multiple stages for tantalum recovery. Therefore, the current study was designed to streamline the experimental process, aiming to recover a majority of the metals present in the initial raw material for maximum resource utilization using a minimal number of steps. A number of parameters were optimized throughout the recovery process to identify the most effective conditions for achieving maximum recovery of the targeted metals.

Following the establishment of this comprehensive recovery pathway, an economic evaluation was conducted to assess the viability of implementing the developed process within an industrial context. This assessment aimed to determine the practical feasibility and commercial potential of the proposed approach.

2.1 Procurement of raw materials

Tantalum capacitors (model D, 10 μF, 35 V, KYOCERA AVX) were obtained from a local capacitor supplier. Analytical grade reagents used in the present study were: sulphuric acid, nitric acid, hydrochloric acid (Molychem India Pvt. Ltd, India & Fisher Scientific, UK); sodium chloride, potassium hydroxide (G.S. Chemical testing lab & Allied industries, India); acetone (Fisher Scientific, India); ammonia solution (Loba Chemie Pvt. Ltd., India); Aliquat® 336 (Trioctylmethylammonium chloride), CYANEX272 (2,4,4,tri-methyl,pentyl-phosphinic acid), D2EHPA (Di-(2-ethylhexyl) phosphoric acid), kerosene (Sigma-Aldrich); toluene (Sisco Research Laboratories Pvt. Ltd, India); and distilled water.

2.2 Pre-processing and characterization of capacitors

The Tantalum capacitors were washed using double distilled water followed by washing in acetone to ensure removal of any dirt, grease and other contaminations. Individual capacitors were stroked manually using a ball-peen hammer to dismantle it into its components. Being brittle, the encapsulated resin part readily fragmented into small particles, isolating the metal coated tantalum anode and metallic terminal part (as shown in *Figure 2.1*). Based on the visual identification, undesired epoxy resin part was handpicked from the desired metallic faction.

For a rough approximation of composition of capacitor before and after removal of mold resin, it was subject to scanning electron microscopy (SEM) make *Zeiss Evo-18 Research 2045* with attached energy dispersive X-ray spectroscopy (EDS) make *FEI Nova Nano SEM 450.* The EDS results in *Figure 2.2*(a) were obtained on the mixture of broken metallic and non-metallic fractions, however, in *Figure 2.2*(b), the result was on metallic fraction only. For exact quantification of metals, capacitors before and after removal of epoxy resin were digested separately in a concentrated hydrofluoric acid (for tantalum analysis), in concentrated nitric acid (for silver analysis), and in freshly prepared aqua regia (HCl: HNO_3- 3: 1) (for the analysis of metals other than tantalum and silver, i.e. manganese, nickel, and iron) at 40°C, 70°C, and 70°C respectively. For this, initially the solution used for the digestion was taken in a three-necked flask, fitted with the condenser on the central neck, and heated using hot plate with magnetic stirrer setup with a PID controller and thermocouple arrangement. Once the desired temperature was attained, 2.5 gm of solid material was added into it while maintaining a pulp density of 50 g/l and reaction was continued at a constant stirring provided by PTFE coated magnetic stirrer. Once the dissolution was completed, each solution was cooled and filtered using filter paper (Whatman no. 42) to separate undissolved fraction. The filtered solution was then diluted to appropriate concentration range according to the detection limits of the atomic absorption spectroscopy (AAS) make *Elico SL 168* and inductively coupled plasma-mass spectroscopy (ICP-MS) make *Agilent 7800*. The non-metallic fraction was simply calculated using mass balance.

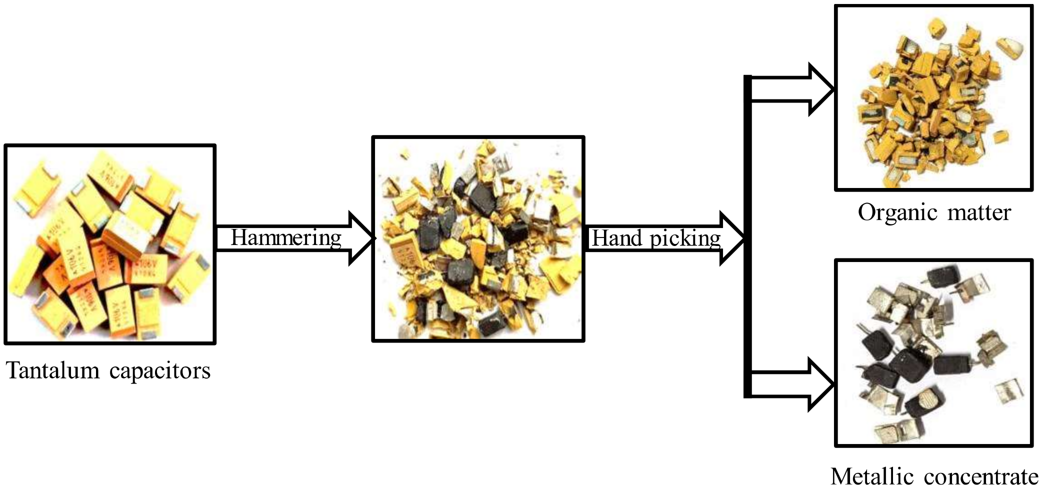
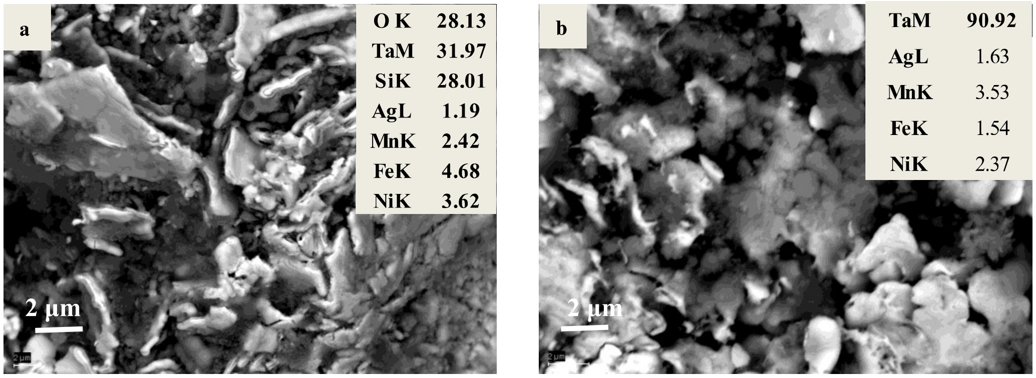


Figure 2.1 Pre-processing treatment of tantalum capacitors



a	
O K	28.13
TaM	31.97
SiK	28.01
AgL	1.19
MnK	2.42
FeK	4.68
NiK	3.62

b	
TaM	90.92
AgL	1.63
MnK	3.53
FeK	1.54
NiK	2.37

Figure 2.2 Morphology and compositional analysis of Ta-capacitor (a) before and (b) after pre-processing treatment obtained by SEM-EDS

The result of AAS/ICP-MS analysis is presented in *Table 2.1*. The tantalum accounted for 89% weight of the metal-rich part and 45% weight of the integral capacitor with silica resin. The concentration varies significantly with the manufacturing company and respective model number, as noted in the previous studies (W.-S. Chen et al., 2022; Niu et al., 2017b; Xia et al., 2021). In our case, the tantalum concentration in epoxy coated tantalum capacitor (ECTC) is 40-45%. This high concentration of superior grade tantalum in the capacitor made it an attractive secondary resource to recover the metal for a sustainable future supply. Besides tantalum, other metals were nickel, iron, manganese and silver with concentration of 0.7%, 0.05%, 4% and 1.2-1.6% respectively. The removal of silica required several steps for its complete elimination to obtain the tantalum-rich product (Mineta and Okabe, 2005). Separation of this silica along with the organic matter without mixing it with the inner tantalum-rich content would make the Ta-recovery process much simpler, obviating the need for the costlier and energy-consuming methods such as the pyrolysis, ionic liquid dissolution etc., employed in prior studies (Chen et al., 2019; Niu et al., 2017d, 2017e; Von Brisinski et al., 2014). We separated silica completely along with the organic matter from the metallic part of the tantalum capacitors using hammering and handpicking (gravity separation can be used at a larger scale). The tantalum-rich residue was subsequently treated by the hydrometallurgical route for recovery of tantalum.

Table 2.1 Composition of tantalum capacitor before and after removal of epoxy resin. ECTC- epoxy coated tantalum capacitor; ERTC- epoxy removed tantalum capacitor.

	Ta (wt%)	Ni (wt%)	Fe (wt%)	Ag (wt%)	Mn (wt%)	Epoxy resin and some minor elements (wt%)
ECTC	40-45	0.7	0.35	1.2-1.6	4	50-55%
ERTC	89	2.3	1.23	0.12	8.7	Nil

To visualize distribution of various metallic and non-metallic layers in a capacitor, it was halved using a disc cutter and the cross section was subsequently imaged using SEM. Each individual visually identifiable layer was then analysed with EDS to know the type of material from which it is made of. The individual components of the capacitor exposed after hammering, were also analysed using SEM-EDS.

2.3 Leaching of metal-rich fraction

For the recovery of tantalum, metal-rich part was leached under three different conditions viz. i) alkaline leaching (85% KOH), ii) single-stage acidic leaching (dil. HNO_3), and iii) two-stage acidic leaching (dil. HCl and HNO_3). Flowsheet of the overall process is shown in the *Figure 2.3*. Various parameters used under all three conditions are given in *Table 2.2*. The alkaline media should leach out tantalum in solution (G. J. P. Deblonde et al., 2019; H. Zhou et al., 2005), however, the acidic media should dissolve the non-tantalum metals in solution, leaving the tantalum in the residue (Theron et al., 2011). In two-stage leaching, the aim was to preferentially dissolve manganese and nickel in 1st stage using HCl as leaching reagent. Various parameters such as temperature, concentration of leaching reagent, pulp density, and time was optimized to select the most optimum parameters for dissolution of metals. The leach liquor thus obtained under optimum leaching condition was stored for subsequent recovery of metals. Whereas, the residue left behind after this, rich in tantalum, was dried in oven at 90°C overnight and then was analysed SEM-EDS to determine its composition. This residue was further subjected to 2nd stage leaching using

HNO_3 for dissolution of remaining silver and other minor metals and obtain purified tantalum in the residue.

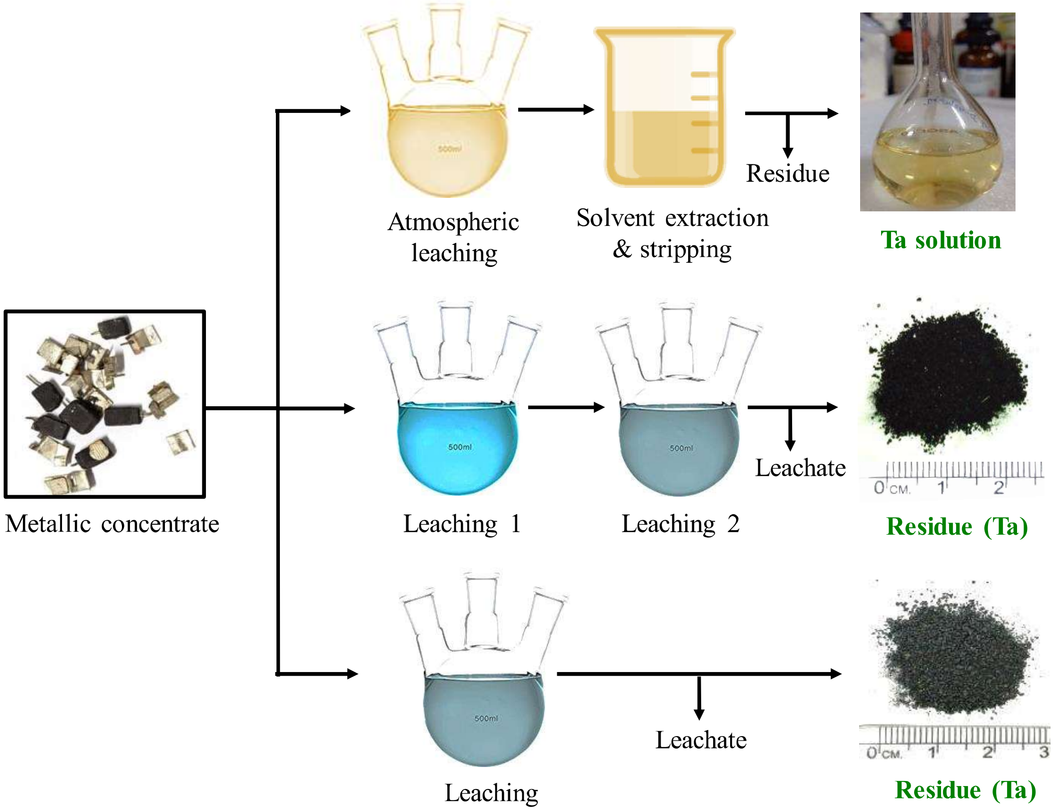


Figure 2.3 Flowsheet of tantalum recovery process

Table 2.2 A summary of the parameters used in the leaching of tantalum capacitors

Type of leaching	**Alkaline leaching**	**Single stage acidic leaching**	**Two-stage acidic leaching**	
			Stage-1 leaching	Stage-2 leaching
Leaching reagent	KOH	HNO_3	HCl	HNO_3
Pulp density	50 g/l	50 g/l	25-100 g/l	50 g/l
Concentration of leaching reagent	85% KOH	3 M	1-3 M	3 M
Reaction time	35 min	3 h	4 h	3 h
Temperature	160°C	40-80°C	30-70°C	50°C
Stirring speed	500 rpm	500 rpm	500 rpm	500 rpm

The schematic of set-up used for leaching is shown in *Figure 2.4*. All experiments were conducted in Teflon-coated hotplate with an automated PID controller and thermocouple arrangement. Leaching experiment was carried out in a 25 ml leaching medium in a three necked flask (100 ml capacity) which was heated to a pre-set temperature. Once the temperature reached the set value and remained stable, a fixed amount of solid sample was added slowly through side neck and the solution was stirred at 500 rpm using a magnetic stirrer. Once the reaction time was completed, the solution was filtered and leach liquor was diluted with distilled water and analysed using AAS and ICP-MS. All the experiments were performed in triplicate and the mean of the obtained value is presented in graphs with the error bars.

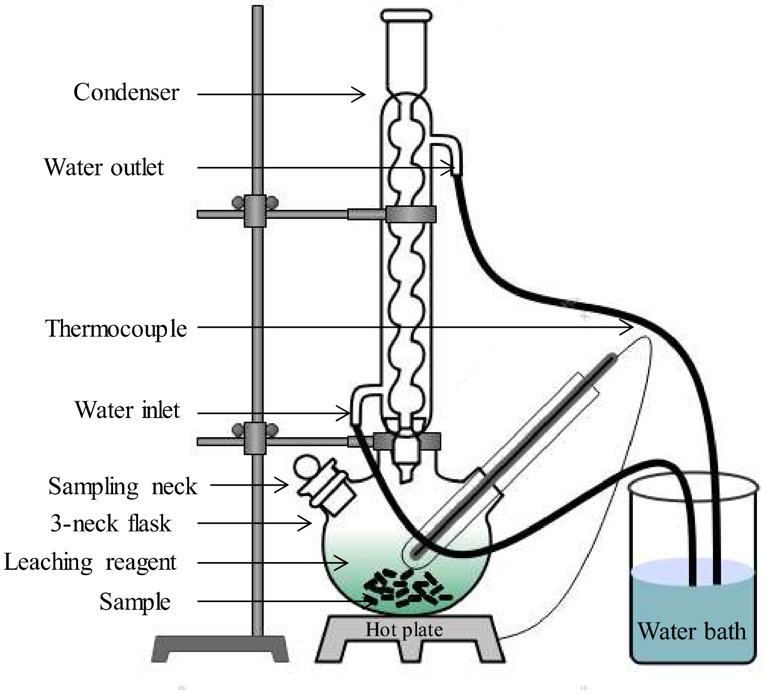


Figure 2.4 Experimental set-up used for leaching

Leaching efficiency of metals are calculated using the following formula (*Eq. 2.1*)

$$E = \frac{M_a - M_b}{M_a} \times 100\ \% \qquad (2.1)$$

where,

M_a= weight of metal into initial raw material, and

M_b= weight of metal into the residue after leaching

To identify the phases in the residue, X-ray diffraction analysis (XRD) was done using X-ray diffractometer make *Rigaku Ultima IV* with pixel 3D detector using Co-Kα (λ= 1.789 Å) radiation in 2θ angular range of 10° to 100°, at a scanning speed of 0.5°/min with increments of 0.02°. Phases were identified with the help of the ICDD PDF2 database. To further confirm the results obtained in XRD, the residue was subjected to SEM-EDS analysis.

2.4 Solvent extraction

2.4.1 Recovery of tantalum from alkaline leach liquor

Leach liquor from the alkaline leaching was diluted ten times and its pH was adjusted by drop wise addition of 2 M HCl. Once the target pH was reached, 5 ml solution was taken and was treated by solvent extraction for selective transfer of tantalum into an equal-volume of organic extractant (quaternary ammonium salt (Aliquat® 336) dissolved in toluene). Extraction was carried out at a temperature of 23°C, organic to aqueous ration of (o/a) 1:1, an agitation speed of 700 rpm for 30 min duration. After the reaction, the mixture was allowed to settle and the metal loaded organic phase was physically separated from the aqueous phase. The metal from the organic layer was back-extracted into an aqueous phase using 4 M nitric acid as stripping agent under the same experimental condition as solvent extraction. Aqueous phase from both the stages of extraction and the stripping was analysed using AAS and ICP-MS.

The extraction and back extraction (stripping) efficiency for the metal, M, for the reaction were calculated as follows (*Eq. (2.2) & (2.3)*):

$$\% \, Extraction = \frac{M_{org}}{M_{aq}} \times \frac{V_{org}}{V_{aq}} \times 100 \qquad (2.2)$$

where,

M_{org} = total concentration of M in the organic layer after the extraction

M_{aq} = total concentration of M in the aqueous layer before extraction

V_{aq} = volume of aqueous phase

V_{org} = volume of organic phase, and

$$\% \, Back \ extraction = \frac{M_{aq}}{M_{org}} \times \frac{V_{aq}}{V_{org}} \times 100 \qquad (2.3)$$

where,

M_{org} = total concentration of M in the organic layer before stripping

M_{aq} = total concentration of M in the aqueous layer after stripping

2.4.2 Recovery of manganese and nickel from 1st stage acidic leach liquor

The leach liquor obtained after 1st stage of acidic leaching, containing manganese, nickel, and other minor metals, was then subjected to solvent extraction to selectively recover manganese using D2EHPA and CYANEX272 as extractant diluted in kerosene. The pH of the aqueous phase was adjusted to a known value by adding 4 M ammonia solution and 2 M hydrochloric acid. A series of experiments were conducted to investigate the effect of different parameters, including temperature, pH of the aqueous phase, organic to aqueous (O/A) ratio, concentration of carrier, and time, as mentioned in *Table 2.3*, to select the best condition for maximum extraction of manganese with minimal impurity of nickel. Multi-stage extraction was also performed to ensure complete recovery of metal. The experiment included three-stage extraction with loaded organic phase from D2EHPA extraction and two-stage extraction with loaded organic phase from CYANEX272 extraction, under the optimized condition.

Table 2.3 A summary of the conditions investigated in the recovery of manganese using D2EHPA and CYANEX272 as carrier

Unit Operation	**Extraction**	**Extraction**	**Stripping**
Reagent for extraction or stripping	D2EHPA	CYANEX272	H_2SO_4, HNO_3 and HCl
Diluent	Kerosene	Kerosene	Distilled Water
Concentration	10-40 vol%	0.02-0.2 M	2-4 M
pH	2-4	2-4.5	-
O/A	1:5-5:1	1:4-4:1	1:1
Equilibration time	15-60 min	30 min	30 min
Temperature	35-45 °C	35-45 °C	30 °C
Stirring speed	700 rpm	700 rpm	700 rpm

Next, the loaded organic phase from CYANEX272 extraction was contacted with the different aqueous phases to select the best stripping reagent for manganese under the condition of O/A ratio unity, temperature 35 °C, stirring speed 700 rpm, contact time 30 min, and varying concentration of the aqueous phase. Flowsheet of overall extraction-stripping cycle in shown in *Figure 2.5*. After each contact, the mixture was allowed to settle down and then physically separated for subsequent analysis of the aqueous phase using AAS. To understand the bonding of functional groups of organic solvent mixed in kerosene before extraction and after extraction it was analysed by Fourier-transform infrared spectroscopy (FT-IR) make *FT-IR-4700, Jasco, Japan*.

All solvent extraction and stripping experiments were carried out in a 30 mL glass vial. A PTFE-coated hotplate with magnetic stirrer was used to provide the desired agitation. All the experiments were performed in triplicate and the mean of the obtained value is presented in graphs with the error bars.

It should be noted that the initial experiments throughout this thesis work were conducted using parameters optimized in previous research, which utilizing different initial raw materials. Once the initial experiment was completed with these parameters, they were systematically varied within a certain range. The effects of parameter variation were carefully considered to strike the right balance between efficiency and safety, prioritizing environmental responsibility throughout the process.

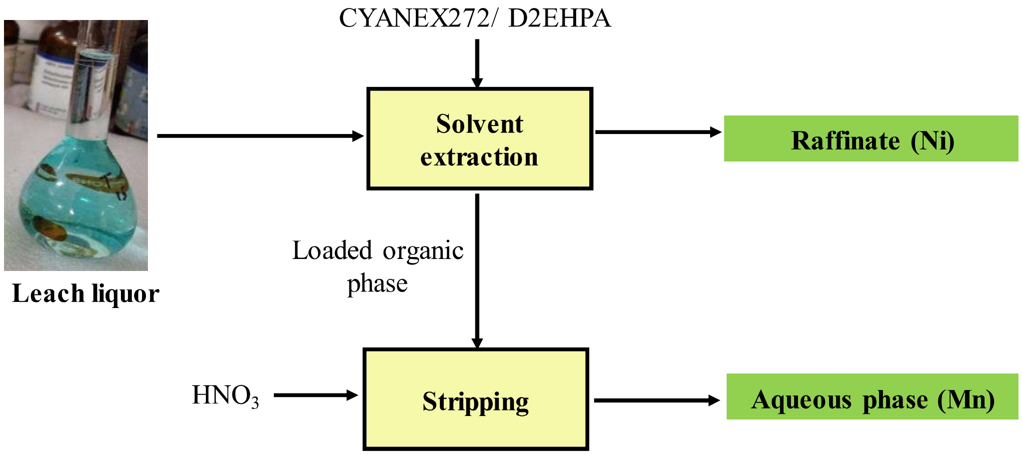


Figure 2.5 Flowsheet of extraction-stripping cycle from stage-1 (acidic leaching) leach liquor

2.5 Leaching of non-metallic-rich fraction

The non-metallic-rich fraction separated after pre-processing contained substantial amount of silver. To determine its composition, this fraction was separately digested in concentrated nitric acid and aqua regia and the solution obtained was filtered to separate undissolved non-metallic concentrate. The filtered solution was then diluted and analysed by AAS whose results are given in *Table 2.4*.

Table 2.4 Composition of non-metallic-rich fraction obtained after pre-processing

Elements	Concentration (wt %)
Ag	2.26
Mn	0.08
Non-metallic fraction	~96

To recover this silver, non-metallic-rich fraction was leached using 3 M HNO_3, at 500 rpm stirring speed, 50 g/l pulp density, under varying temperature (40-60°C), and 3 h reaction time. Samples were collected at regular intervals to study the effect of time and temperature on silver dissolution. The samples collected after each experiment was filtered, diluted with distilled water, and then analysed using AAS to calculate leaching efficiency of metal. The experiments were conducted using the set-up described in *Section 2.3* (shown in *Figure 2.4*).

2.6 Precipitation of silver

To recover silver from obtained leach liquor, chemical precipitation method was adopted. Here sodium chloride (NaCl) was used as a precipitation agent to precipitate silver in the form of silver chloride (AgCl). The amount of NaCl required for complete precipitation of silver was determined from stoichiometric calculation from the below equation (*Eq. 2.4*).

$$AgNO_3 + NaCl = AgCl + NaNO_3 \tag{2.4}$$

To conduct the experiment 50 ml of leach liquor was poured into the beaker and was kept at room temperature (25°C) on a ceramic top type digital hot plate with magnetic stirrer attached with a PID controlled temperature and thermocouple arrangement (Accuracy ± 1°C). Thereafter, for AgCl precipitation, NaCl was slowly added, under constant agitation to yield good mixing and avoid any accumulation, in 100% excess of stoichiometric calculation to ensure complete precipitation of silver. Precipitation was witnessed by the formation of white fine precipitate at the bottom of the beaker. This precipitate was filtered and dried in oven at 80°C overnight. The resulting dry powder was analysed by SEM-EDS to identify the elements present in it. To further confirm the phases, present in the precipitate, it was again characterized by XRD. The flowsheet representing various steps involved in recovery of silver is given in *Figure 2.6*.

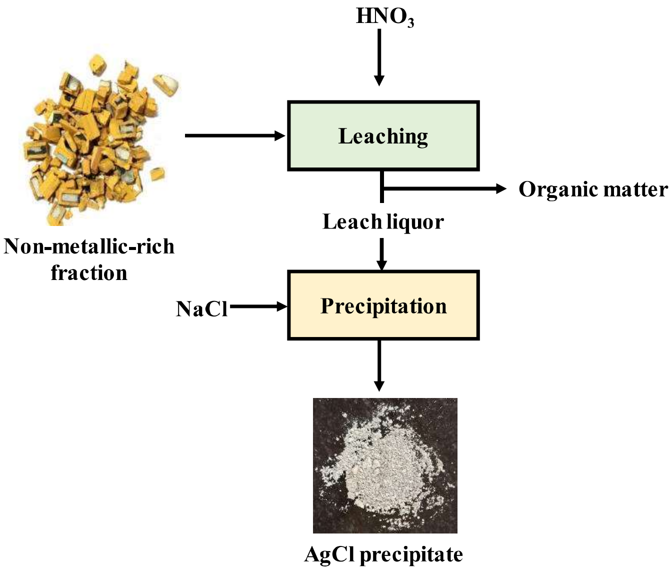


Figure 2.6 Steps involved in recovery of silver from non-metallic-rich fraction