CHAPTER 2

Experimental Details

2. Experimental details

2.1 Procurement of chemicals and materials

Several chemicals of analytical grade used in the present work were: nitric acid, sulfuric acid, hydrochloric acid (Molychem India Pvt. Ltd, India & Fisher Scientific, UK); sodium bromide (Loba chemie Pvt. Ltd, India); kerosene, tetrabutyl ammonium nitrate (Sigma-Aldrich); acetone , tetrathydrofuran, and ammonia solution (Loba chemie Pvt. Ltd, India); Chloroform (Sisco Research Laboratories Pvt. Ltd, India); (Acorga M5640 (Cytec India specialty chemicals & materials Pvt. Ltd., India); polyvinyl chloride (PVC)(Central Drug House (CDH) India,); Cellulose triacetate (CTA) (Cayman Chemical, USA) and distilled water. Obsolete mobile phones used in this work were collected from the local e-scrap vendors in Varanasi, India and also from the hostels of IIT(BHU), Varanasi, India.

2.2 Pre-treatment of WPCBs

2.2.1 Pre-processing

Initially, manual dismantling was used for separating WPCBs and other major components such as lithium ion batteries, screens and keyboard. Further, the heating gun (2000 W heat gun make '*Stanley Black and Decker India Pvt. Ltd'*) was used to remove the attached mounted electronic components such as capacitors, couplers, and diodes from WPCBs. The separated bare PCBs were further washed with warm water and then acetone to remove the dust and other contaminations such as any chemicals, stickers, and adhesive on the surface. The bare WPCBs were marked with horizontal and vertical lines using marking pens, and a shear cutter was used to cut them into different square sizes (1x1, 2x2 cm^2 as per the requirement). These WPCBs were shortened to prepare the feed material for the hammer milling ('*Ikon Instruments*', India).

2.2.2 Hammer milling and ultrasonic irradiation treatments of WPCBs

The measured quantity of pre-processed WPCBs of 1x1 cm^2 size was fed into the inlet chute of the hammer mill at actual feed rates (3kg/h) to obtain the fine powder. The WPCBs were crushed by the four swinging hammers concurrent impacts until the size was reduced to -16 BSS (British Standard Specification). The milled WPCBs were collected from the outlet chute and fitted at the bottom part of the hammer mill. The weighed amount of WPCBs powder was taken into a volumetric flask and mixed with 100mL of distilled water and tiny drops of acetone. Acetone enhances the hydrophilic nature of non-metallic fractions and helps properly mix with water. This volumetric flask was shaken manually to initiate the separation, and then it was put under an ultrasonic wave (Equipment supplied from *Neumann & Miller* ‘frequency: 40KHz, ultrasonic power: 60W). After 20 minutes of ultrasonic treatment at 30°C, black fibre/resins and other light particles were found to be floated on the upper part of the volumetric flask. Once the treatment was done, these floated particles on the top of the conical flask were washed out, and it was further filtered using filter paper. The concentrated metallic powder and separated non-metallic powder were then dried and sent for further characterization and processing. The proposed pre-treatment route has been shown in figure-2.1.

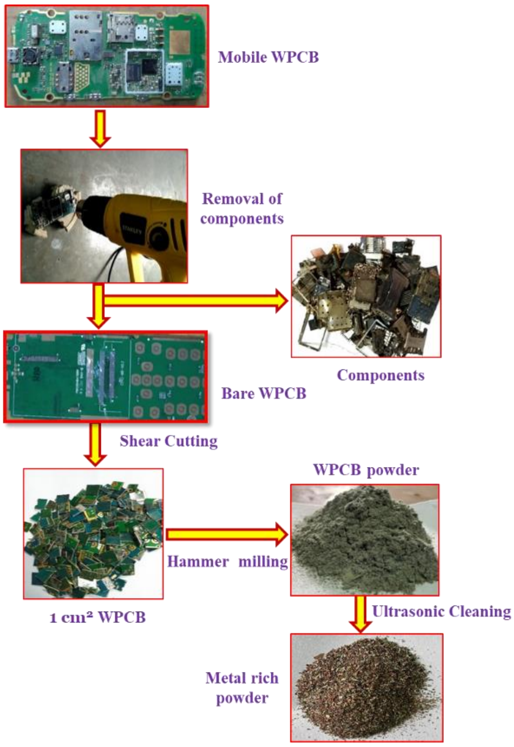

Figure 2.1-Schematic representation of proposed experimental procedure of WPCBs pre-treatment

2.2.3 Characterization and chemical analysis of WPCBs

WPCBs powder received after hammer milling and ultrasonically metallic rich powder was characterized by X-Ray diffraction instrument (XRD), Scanning electron microscopy (SEM). Moreover, Raw WPCBs powder and non-metallic fractions separated after the ultrasonic pre-treatment process has been characterized by Fourier Transform Infrared Spectroscopy (FTIR). In addition, inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) techniques have been employed to know the elemental concentrations in both raw WPCBs and metal-rich powder.

X-ray diffraction patterns of the Raw WPCBs and ultrasonically cleaned metallic rich fractions were recorded using an X-ray diffractometer (Malvern Panalytical Empyrean model) with Co-Kα of wavelength (λ) =1.789. 40 kV and 40 mA were the operational voltage and current, respectively. The scanning range was 3-90 degrees at 5 deg./min rate with 0.01 step size. The XRD analysis and the plot have been drawn with the help of Xpert high score and origin software.

Further, the powders of the WPCBs were examined using SEM attached with energy dispersive X-ray spectroscopy (EDS, FEI Nova Nano SEM 450) in order to notice the morphology and visualize the distribution of metallic and non-metallic fractions of powders. SEM images were recorded by EVO - Scanning Electron Microscope MA15/18 manufactured by Carl Zeiss Microscopy Ltd. Using sputtering, gold was applied to the samples to create a conductive surface. The images were recorded at 20 kV electron high tension (EHT) with secondary electrons as the signal for different magnifications.

The infrared (IR) spectrum of powders was documented with a Nicolet iS5 FT-IR Spectrometer (Thermo Electron Scientific Instruments LLC) in the transmission mode, in the range of 4000 to 500 cm^{-1}. The attenuated total reflection (ATR) sampling technique was used during the

FTIR analysis. The resolution was maintained at 4 cm^{-1}. FTIR analysis of raw WPCBs powder and separated non-metallic powder has been done to find out the different functional groups. The infrared spectrum of ultrasonically separated non-metallic fractions has been recorded in order to check possible changes during the ultrasonic treatment.

The raw WPCBs powder and separated metallic powder were digested in freshly prepared aqua regia to know the element concentrations. The complete dissolution of metallic powder was seen at 50 °C within 1h. However, plastics and glass/fiber particles from raw WPCBs remained as undissolved residues at the same dissolution parameters. The solution was then filtered and sent to AAS and ICP-MS. The different element concentrations of WPCBs powder has been measured by using AAS make '*Elico SL 194*' and ICP-MS make '*Agilent 7800*'.

2.3 Two stage leaching

2.3.1 Copper and Nickel leaching from WPCBs metallic fraction-1st Stage

The metal-rich fraction received after ultrasonic irradiation treatment has been treated with nitric acid for copper leaching. The leaching experiment was done in a three-necked flat-bottom flask (100, 250 mL). The three necks were used for connecting a condenser, thermocouple, and sampling, respectively. The heating was carried out on a magnetic stirrer with a hot plate setup (REMI 10 MLH; temperature accuracy of ±1°C) wherein the stirring was done with Teflon-coated magnetic stirrer (figure-2.2). A determined quantity of nitric acid (0.5-3.5 M) was transferred into the three-neck flask through the sampling neck and heated up to a leaching temperature (30-90°C). Once the set temperature was attained, the ultrasonically cleaned metallic powder was charged into the flask to preserve the pulp density (S/L ratio=1:20). The experiment was carried out over 30 to 180 min. Leach liquor are being withdrawn at different intervals. Once the experiment was over, the pregnant liquor was filtered. The filtrate and the liquor withdrawn during the experiments were then diluted and sent for analysis. The leaching efficiency of any metal is calculated based on eq.-2.1. All experiments were conducted in triplicate to ensure the accuracy of the results

$$\%\ Metal\ leaching = \frac{Wt\%\ of\ metal\ in\ leach\ liquor}{Wt\%\ of\ metal\ in\ feed\ samples} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

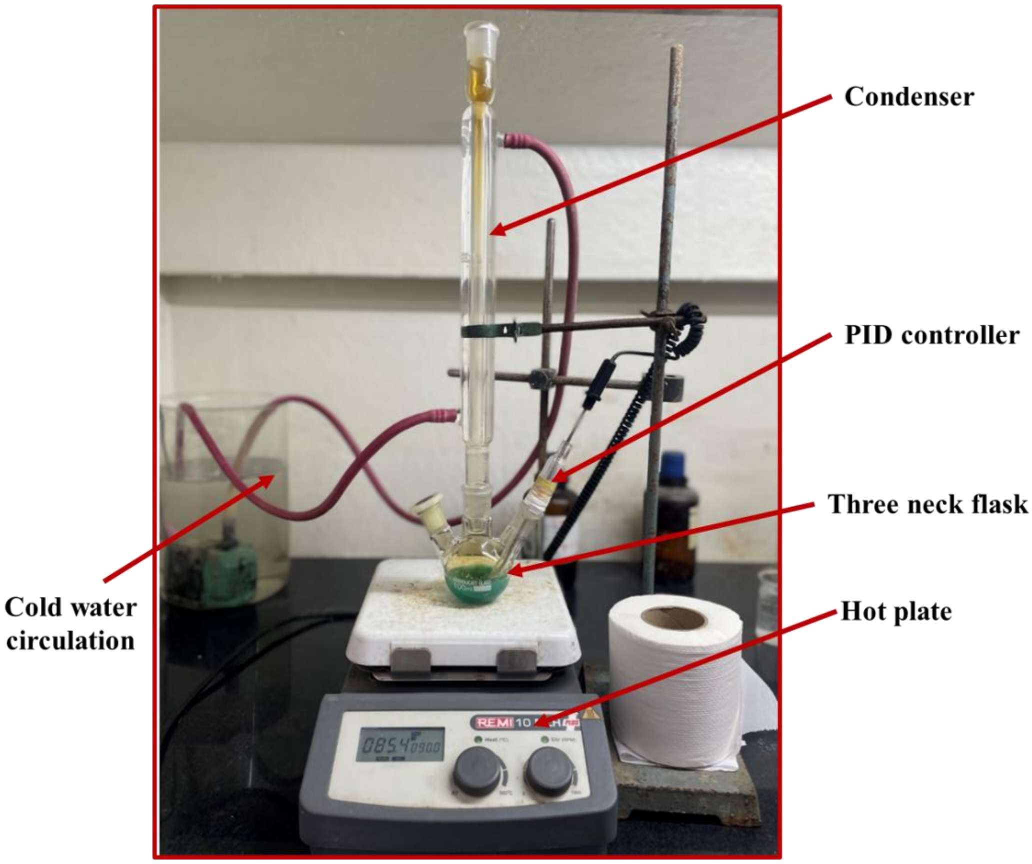

Figure 2.2- Photograph of leaching experiment setup

2.3.2 Experimental design for copper and nickel leaching

The optimization and validation of copper and nickel leaching parameters such as acid concentration, leaching time, and leaching temperature with nitric acid as a leaching reagent have been studied by the response surface methodology (RSM) of the design of experiments (DOE). All DOE studies were designed using the *Design-Expert*® *software, version 13, Stat-*

Ease, Inc. The metal-rich fraction received from the ultrasonic treatment was used as raw material for copper and nickel leaching. The stirring speed of 500 rpm and a pulp density of 50 g/L were kept constant during all the experiments.

In this work, a three-factor, three-coded level (low: -1, centered: 0, and high: +1) central composite design (CCD)-based RSM was used to verify the optimum conditions for the leaching of copper. Acid Concentration (A), time (B), and temperature (C) were taken as independent variables (factors), with copper leaching considered as response variables. By assuming that the optimized value is in-between them (Acid concentration: 0.5-3.5 M; Time: 30-180 min and temperature: 30-90°C), In a central composite design, alpha is the distance from a point that lies on any of the axes to the CCD cube centre.

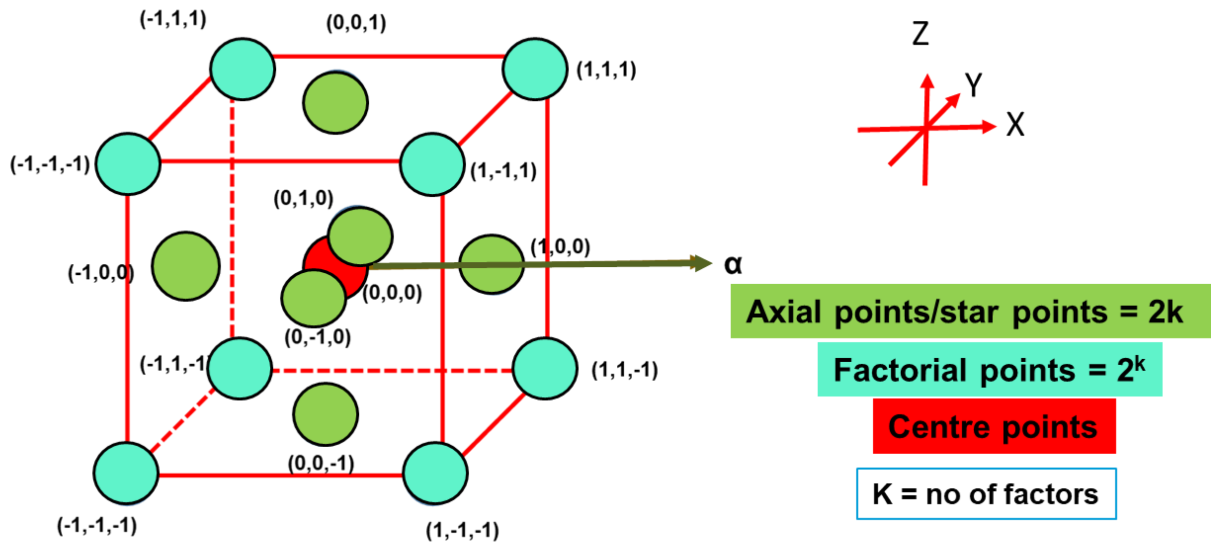

Figure 2.3- Generation of Central Composite Design (CCD) for three factors

The axial points are inside the cube if the alpha value is less than one (<1), on the cube's faces if the alpha value is equal to one (=1), and outside the cube if the alpha value is larger than one (>1). The axial points in this work are on the cube's faces, and alpha is set to 1. The lower and higher values of the factors in are therefore likewise equivalent to the -alpha and +alpha values as shown in table-2.1.

Table 2.1-RSM Parameters for copper and nickel leaching

Name of the factor	Units	Low(-1)	High (+1)	-alpha	+alpha
Acid Concentration (A)	M	0.5	3.5	0.5	3.5
Time (B)	min	30	180	30	180
Temperature (C)	°C	30	90	30	90

2.3.3 Gold leaching from stage-1 leach residue-2nd Stage

The residue of first stage leaching has been collected and oven dried and their chemical composition and morphology has been studied using SEM-EDS. Further, this residue was dissolved in the aqua regia to know the accurate metal content. The chemical analysis was done with Atomic Absorption Spectrophotometer (AAS) make Elico SL 194. The residue was subjected to a second stage leaching process where sulfuric acid and added halide salts (NaBr) were used at a variety of concentrations for the selective dissolution of gold and silver.

A determined quantity of H_2SO_4 and NaBr (0.5-3.5 M) was transferred into the three-neck flask through the sampling neck and heated up to a leaching temperature (30-65 °C). Once the set temperature was attained, the ultrasonically cleaned metallic powder was charged into the flask to preserve the pulp density (S/L ratio=1:20). The experiment was carried out over 30 to 90 min. Leach liquor are being withdrawn at different intervals. Once the experiment was over, the pregnant liquor was filtered. The filtrate and the liquor withdrawn during the experiments were then diluted and sent for analysis. The photographic representation 2nd stage leaching has been shown in figure-2.4. The leaching efficiency of gold and other metals can be calculated using eq-2.1.

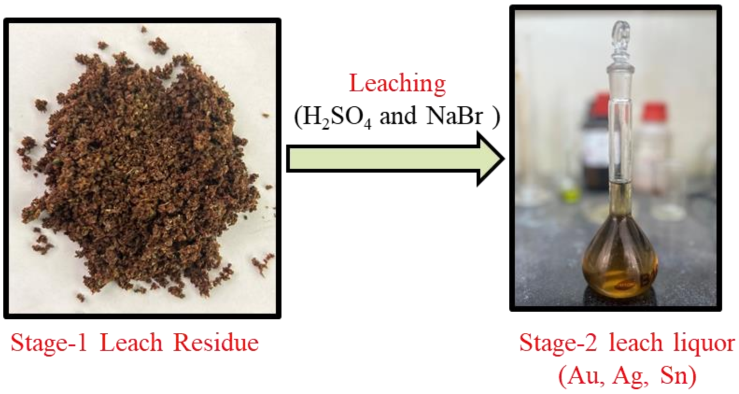

Figure 2.4- 2^{nd} Stage leaching of gold leach residue

2.4 Membrane synthesis and characterization

In the present study, the phase inversion method was employed for the fabrication of PIMs. PIMs were synthesized according to the previously reported practice by Sugiura and the team (Sugiura et al., 1989). a number of membranes with varying amounts of base polymer (PVC, CTA (molecular structure in figure-2.5)), and ACORGA M5640 and TBAN (molecular structure in figure-2.6) as carrier was dissolved in 15-20 mL Tetrahydrofuran and chloroform. The total weight of final mixture (base polymer+ carrier) was kept constant at 400 mg.

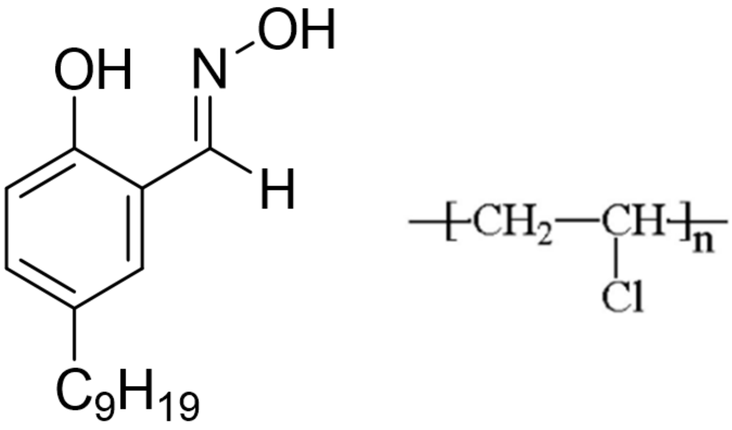

Figure 2.5-Molecular structure of ACORGA M5640 and PVC

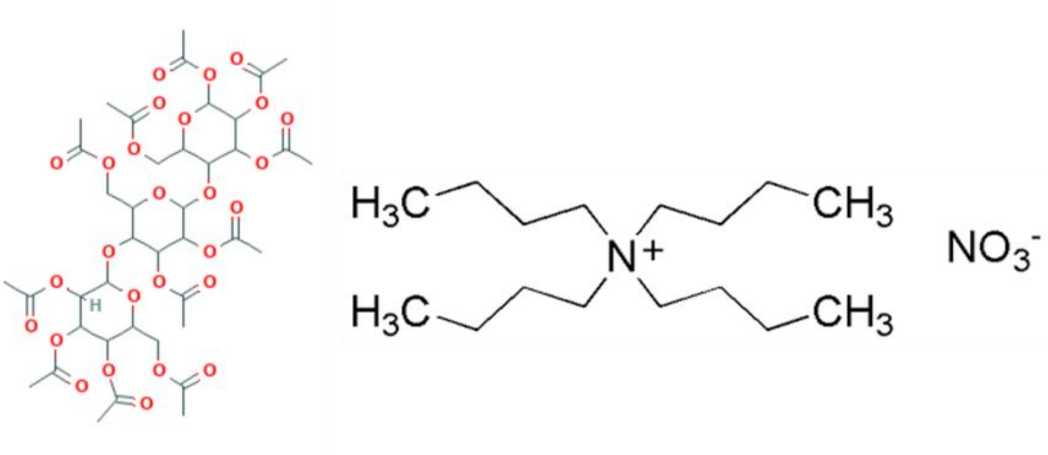

Figure 2.6- Molecular structure of CTA and TBAN

The dissolution was continued in a magnetic stirrer equipped hot plate at 400 rpm stirring speed until a homogeneous mixture was attained. The homogenous mixture was then dispensed into a 7.5 cm diameter petri dish. This petri dish was shielded with the glass funnel to avoid tarnishing with dust as shown in figure-2.7. The leisurely evaporation of solvent takes place for 16-24 h depending on the working temperature. Once the mixture was completely dried, a transparent thin-film was observed which then removed from the petri dish using a plucker. The PIMs were found as homogenous, flexible films having good strength. However, A few challenges in this process are encountered to maintain uniform thickness and to get transparent PIMs which will be discussed in detail in upcoming sections.

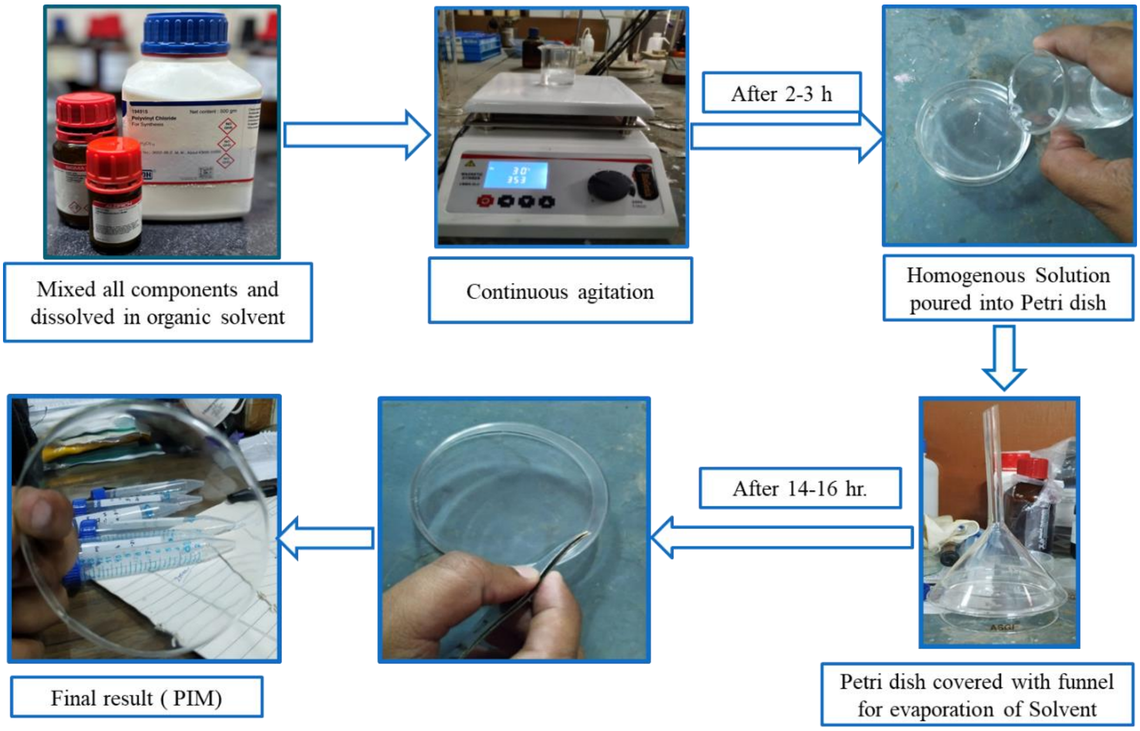

Figure 2.7-Schematic of the PIMs synthesis process on laboratory scale

The thickness of the prepared PIMs was measured by using Digimatic Micrometer (0-25mm) supplied by Mitutoyo, Japan. The average value of at least seven measurements from a single membrane was reported.

Infrared (IR) spectrum were documented with a Nicolet iS5 FTIR Spectrometer (Thermo Electron Scientific Instruments LLC) in the transmission mode, in the range of 4000 to 500 cm^{-1}. Attenuated total reflection (ATR) sampling technique was used during the FTIR analysis. The resolution was maintained to 4 cm^{-1}.

Next, SEM analysis was done in order to observe the morphology of PIMs. SEM images was recorded by EVO - Scanning Electron Microscope MA15/18 manufactured by Carl Zeiss Microscopy Ltd. The samples were coated with gold by sputtering in order to make conductive surface. The images were recorded at 20 kV electron high tension (EHT) with secondary electrons as signal for different magnifications.

An atomic force microscope (AFM) (NTEGRA Prima, NT-MDT Service & Logistics Ltd.), operated in tapping mode with 0.5Hz scan rate, was used for reviewing membrane surface morphology. 1cm x 1cm membrane pieces were analyzed for finding the micropores and to check the surface roughness of the membranes. The surface roughness of each membrane was calculated by using Nova PX software.

Finally, thermo-gravimetric analysis (TGA) was done on a TGA-50 thermo-gravimetric analyzer (Shimadzu (Asia Pacific) Pte Ltd). The synthesized membranes were heated from 25 to 800 °C at a rate of 10 °C /min under nitrogen atmosphere to get the results. The gas flow was maintained at 100 mL/min.

2.5 Preparation of feed phase for membrane transport studies

As the first step, recovery of copper by the solvent extraction route has been done using ACORGA M5640. The optimum parameters for copper recovery through leach liquor of metallic fractions was used from the previous work of our group (Rao et al., 2021b). The optimized parameters for solvent extraction step used are 30 vol% ACORGA M 5640, 1:1 organic to aqueous ratio, pH; 2.5 at 30°C temperature. Kerosene was used as organic phase and sulfuric acid was utilized for further stripping the copper from the loaded organic phase. The raffinate received from the SX step was utilized as feed phase for nickel recovery through the ACORGA M5640 based PIMs. The leach liquor of second stage was directly used as the feed phase for the gold recovery using TBAN based PIMs. The experimental route adopted for preparing feed phase for the nickel and gold recovery have been shown in figure-2.8 & 2.9 respectively.

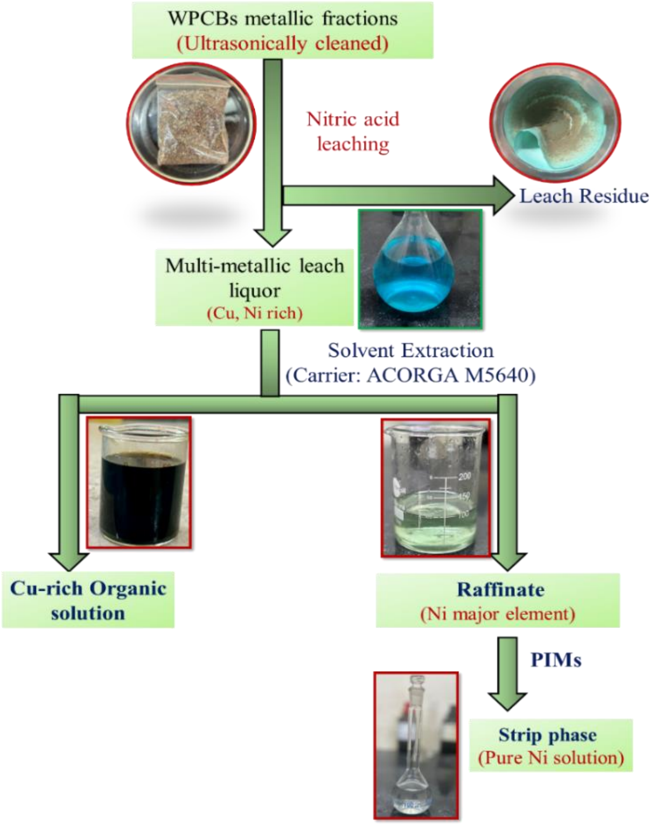

Figure 2.8-Experimental route adopted for preparing feed phase for the nickel recovery

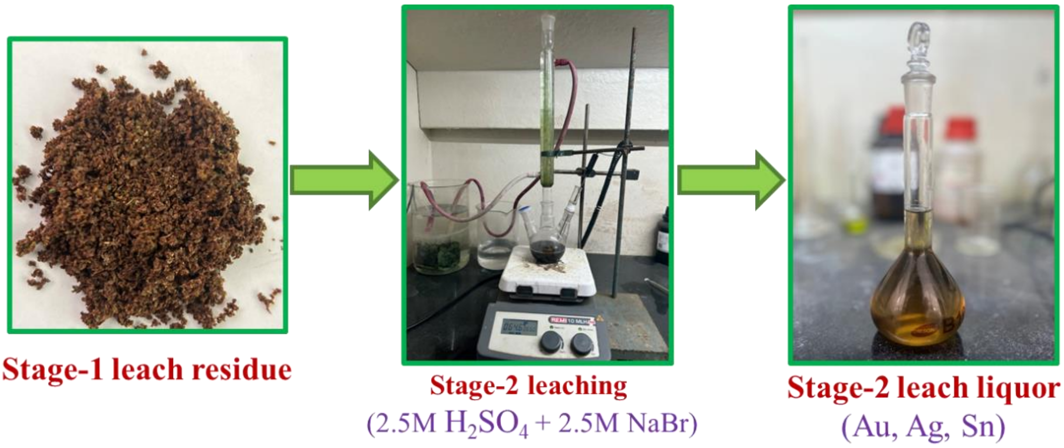

Figure 2.9-Experimental route adopted for preparing feed phase for the gold recovery

2.6 PIMs transport studies

The transport studies were conducted by sandwiching the prepared PIMs between two cell compartments as reported in previous works (Kavitha and Palanivelu, 2012b; Kubota et al., 2018b). The O rings were used for clamping the membrane between two cells as shown in figure 2.10. One of the compartment was filled by feed phase and other with strip phase. The volume of each compartment and effective membrane area were 90 cm^3 and 23.74 cm^2 (maximum capacity) respectively. Glass rod stirring with the help of electric motor (stirring speed; 550rpm) was maintained in both the compartment during the transport experiments. The transport trials were conducted at room temperature (27 °C).

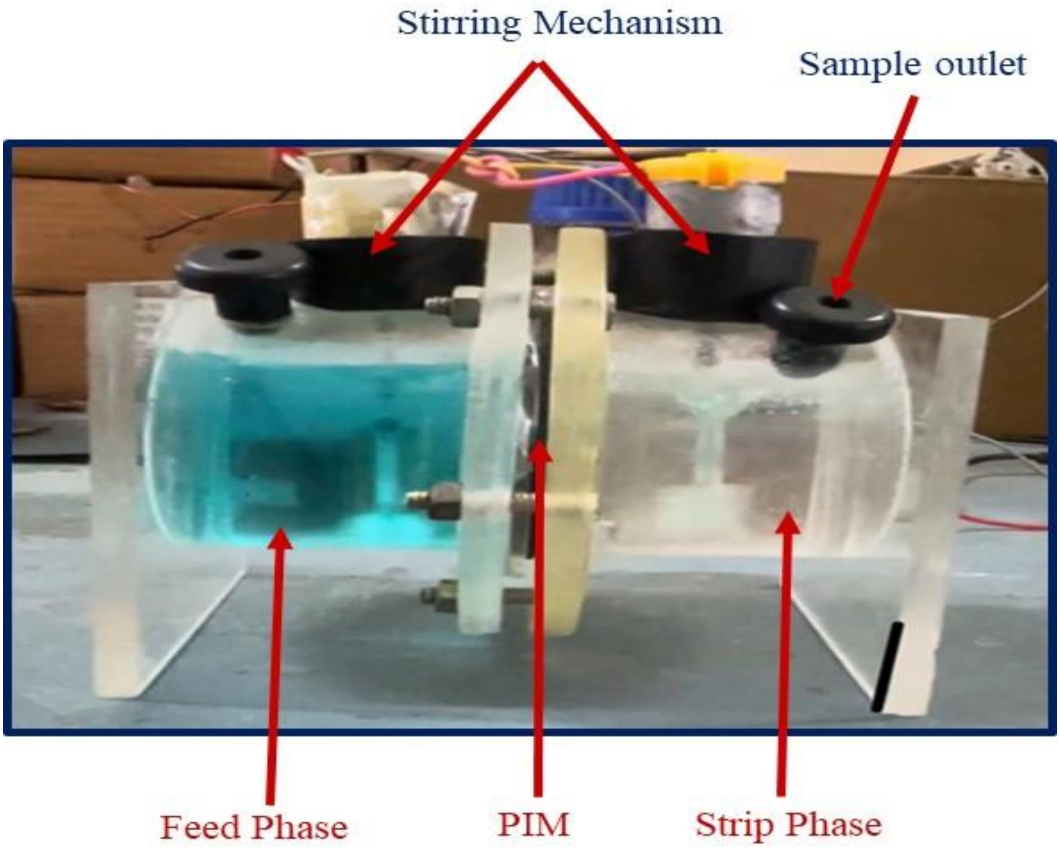

Figure 2.10-Photograph of the membrane transport cell

The metal ion concentration in both the feed and strip solutions were quantified at preselected intervals by removing 1mL samples, followed by Inductively Coupled Plasma Mass

Spectrometry (ICP-MS) manufactured by Agilent Technologies (model: Agilent 7800 ICP-MS mainframe) and Atomic absorption spectroscopy (AAS) manufactured by Elico (model: SL-194) analysis. All the transport experiments required for optimization was conducted at least twice.