



## Research article

# Bench scale microbial catalysed leaching of mobile phone PCBs with an increasing pulp density



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## ABSTRACT

The study reports the effect of increasing pulp density on the bio-catalyzed leaching of metals from waste mobile phone printed circuit boards. Mixed microbial consortia of iron and sulfur-oxidizing microorganisms were used for batch bioleaching at varying pulp density of 7%, 10% and 15% (w/v). The copper content in the feed material was 26.3% (w/w) and the prime focus was to recover maximum copper along with other minor metals, such as zinc, aluminum, and nickel. All the bioleaching experiments resulted with 98–99% of copper recovery together with reasonable extraction Zn, Al, and Ni. The optimum copper recovery from bioleaching experiments demonstrates the possibility of scaling up with high pulp density, which could be economical as well as eco-friendly.

## 1. Introduction

The waste generated in the form of waste mobile phones, computers, LCD screens, T.V., and other electronic devices compulsorily have an end of life (EOL) and termed as electronic waste (E-waste) [1]. The primary elemental composition of these electronic devices exists in printed circuit boards (PCBs) with a large number of base metals, precious metals, as well as rare earth metals [2]. A typical PCB contains 50–100 times higher gold, 7–200 times more PGEs (platinum group elements) and 50 times more copper in comparison of their ores/concentrates [3]. The mobile phone PCBs have been reported as high-grade material in contrast to other electronic devices [4]. Hence, the waste is considered as urban mines and has been treated by various established technologies such as physical separation, pyro, and hydrometallurgy for the metal recovery [5]. Different hydrometallurgical, as well as bio-hydrometallurgical process, have been reported till date for the recovery of base metals (Cu, Ni, Zn, etc.) as well as precious metals (Au, Ag, Pd, etc.) from waste PCBs. Despite the industrialization and worldwide acceptance of these technologies, each of the technique encompasses its benefits and

limitations.

Moreover, none of the techniques can independently fulfill process demand due to the complex nature of mineral or material to be processed. Thus, an integrated approach is being applied to recover the metal values from primary as well as secondary resources [6]. The extraction method plays a vital role during process design. Bio-hydrometallurgy is preferred over conventional methods for metal extraction due to (i) less energy consumption (ii) no dust and toxic gases formation (iii) no slag formation (iv) easy in operation (at room temperature and low-pressure conditions) (v) use of microorganisms instead of hazardous chemicals [7, 8]. The autotrophic, chemolithotrophs microorganisms such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* are widely used for the extraction of metals from various low/high-grade mineral sulfide ores/concentrates as well as oxidic wastes (industrial sludge, slag, mine tailings, electronic waste) [7, 9]. The microorganisms functions in a cooperative manner, the enhanced copper recovery have been widely reported in several studies using the mixed culture of iron and sulfur-oxidizing microbes [10, 11, 12]. Several bench-scale bioleaching studies have been carried out to determine the

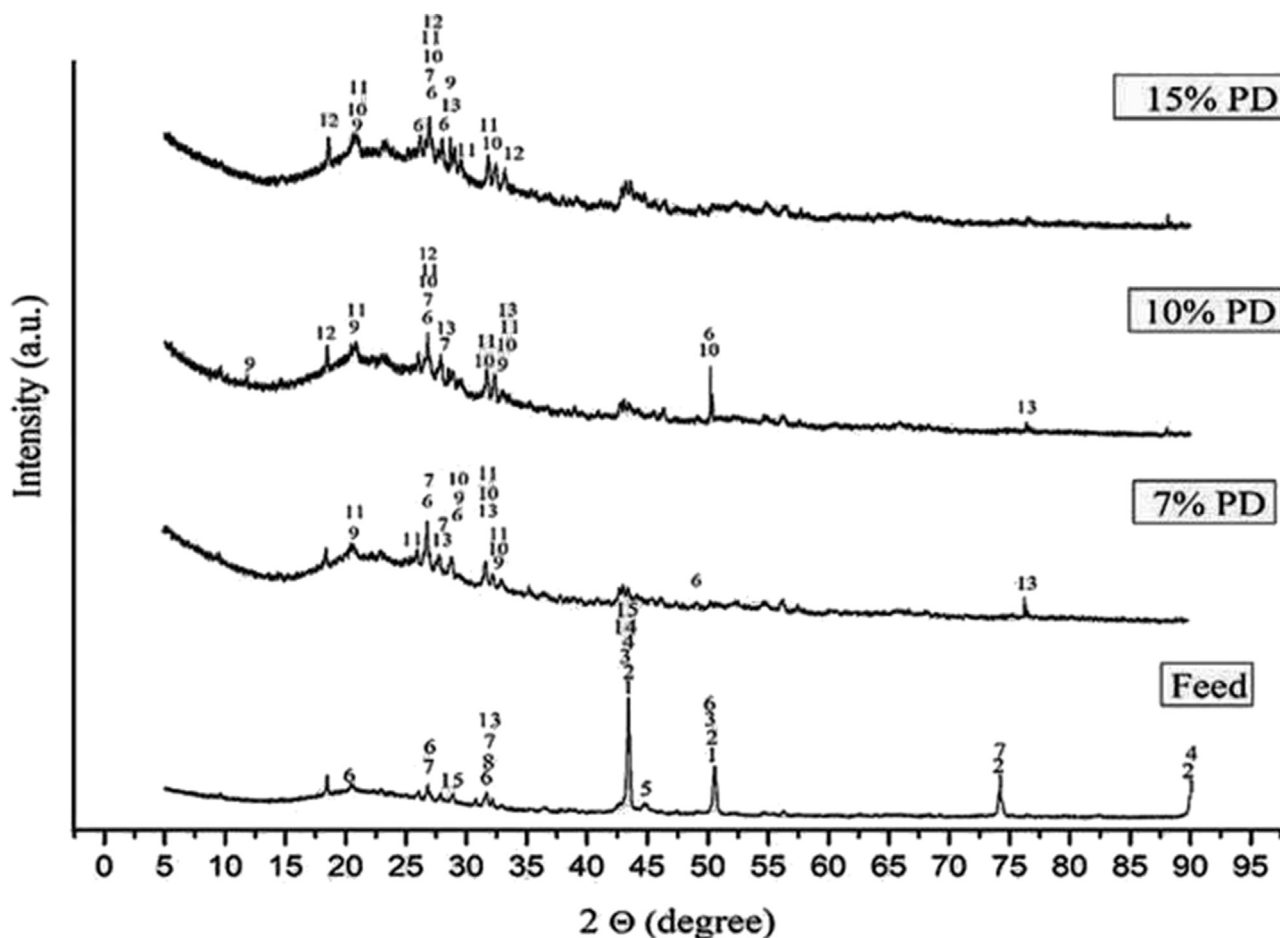
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- |  |   |
|--|---|
| 1. Copper metal ( $\text{Cu}^0$ )                                    | 9. Potassium jarosite ( $\text{KFe}[\text{SO}_4]_2[\text{H}_2\text{O}]$ ) |
| 2. Copper iron complex ( $\text{Cu}_{0.3}\text{Fe}_{0.7}$ )          | 10. Tin oxide ( $\text{SnO}$ )  |
| 3. Iron Nickel complex ( $\text{FeNi}$ )                             | 11. Titanium oxide ( $\text{Ti}_4\text{O}_7$ )                            |
| 4. Zinc metal ( $\text{Zn}^0$ )                                      | 12. Titanium oxide ( $\text{Ti}_3\text{O}_5$ )                            |
| 5. Iron Nickel complex ( $\text{Fe}_{0.9}\text{Ni}_{0.1}$ )          | 13. Silver Oxide ( $\text{Ag}_2\text{O}$ )                                |
| 6. Silicon oxide ( $\text{SiO}_2$ )                                  | 14. Iron Nickel Oxide ( $\text{Fe}_{0.25}\text{Ni}_{0.75}\text{O}$ )      |
| 7. Aluminum ortho silicate oxide $\text{Al}_2[\text{SiO}_4]\text{O}$ | 15. Cooper iron sulfide ( $\text{Cu}_{0.33}\text{Fe}_{0.67}\text{S}$ )    |
| 8. Calcium aluminosilicate ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ )  |   |

Fig. 1. XRD Diffractogram of Feed (mobile phone PCB) and bioleach residues (7,10 and 15% PD).

effects of process parameters such as the effect of pH,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  concentration, size fraction and pulp density on metal recovery from primary sulfide/oxide minerals as well as the secondary waste [13, 14, 15, 16]. The studies on bioleaching of the PCB are still on a laboratory scale [17, 18] and did not implement at an industrial level due to its low efficiency at higher feed concentrations such as toxic effects [19].

In contrast to the previously reported studies, the recent research on bioleaching suggests that base metal bioleaching from the waste at higher pulp densities is more economical [10, 20]. A recent study on microbial leaching of discarded cell phones has reported 99%, 56% and 29% recovery of Cu, Ni, and Zn respectively at 10% pulp density with pure iron oxidizers [17]. None of the studies reported Cu bioleaching at pulp densities more than 10%. The present study focuses bioleaching of base metals, i.e., Cu, Ni, Zn, and Al from waste mobile phone PCBs at higher pulp density (P.D.), i.e., 7%, 10% and 15% (w/v). The major challenge in bioleaching is to understand its process-dynamics and implementation on bench scale operations to scale-up for industrial

application. The present research work aims to determine the effect of increasing pulp density of mobile phone PCBs on microbial leaching by the mixed consortium of iron and sulfur-oxidizing microorganisms. This paper provides detailed insight into the changes in several process parameters during bioleaching.

## 2. Material and methods

### 2.1. Collection, pre-treatment, and analysis of waste mobile phones printed circuit boards (PCBs)

Waste mobile phones were collected from local electronic shops at Alwar, Rajasthan. The Printed Circuit Board (PCBs) were segregated from the waste mobile phones by the manual process and later crushed and ground at the Mineral Processing department of CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, India. The crushing of mobile phone PCBs was carried out in an impact crusher for ten cycles of

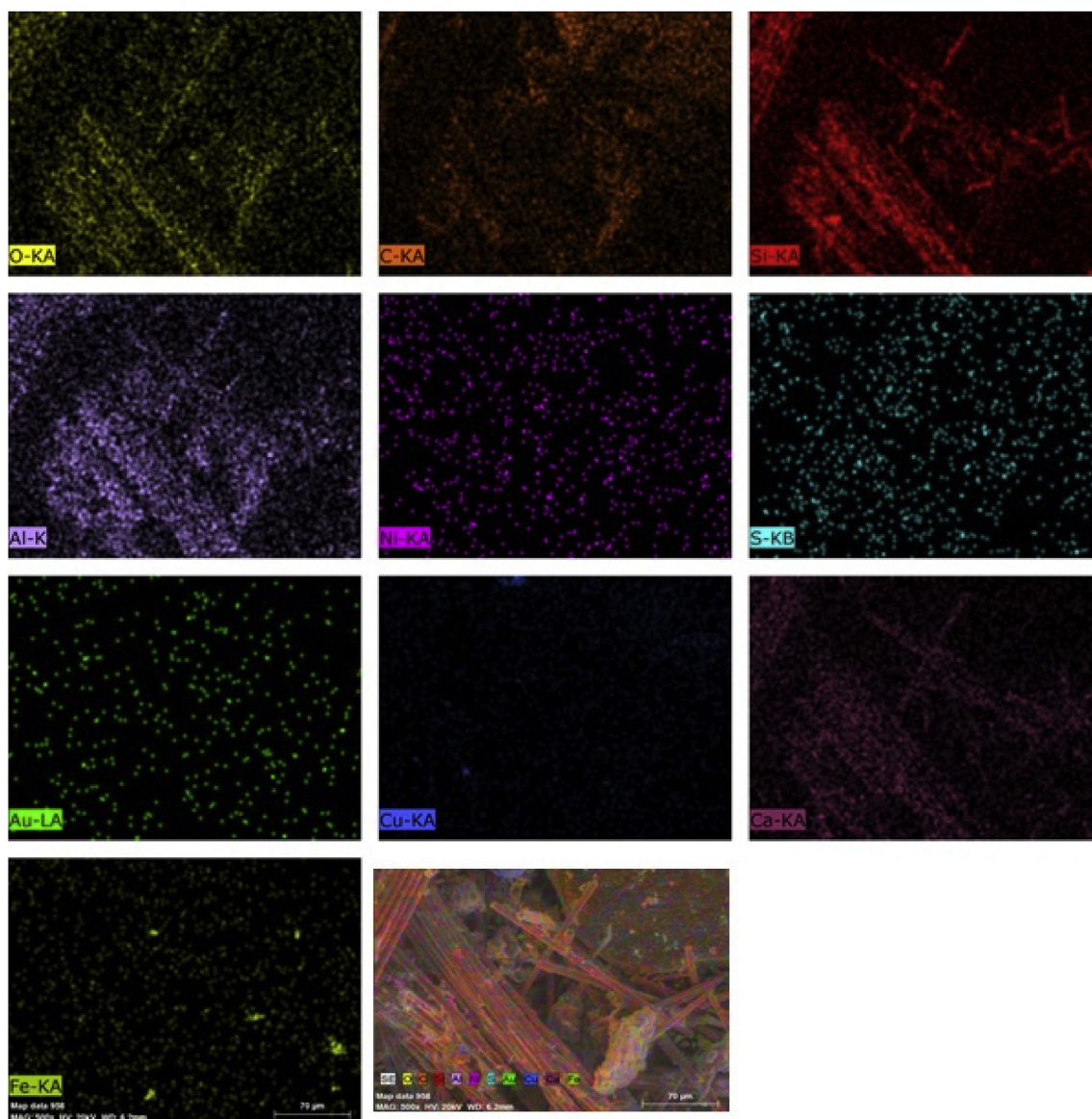


Fig. 2. Scanning Electron Microscope and Energy Dispersive X-ray (SEM-EDX) mapping of mobile phone PCB.

crushing and grinding. Final grind size upon sieving of the particles expressed as 80% passing ( $d_{80}$ ) was below 250 microns. Later the samples were mixed thoroughly and divided by a riffle sample divider until the desired amount of 70g, 100g, and 150g of the feed material was obtained for bioleaching experiments. Elemental analysis conducted by X-Ray Fluorescence analyzer (Bruker) on waste mobile phone PCBs ground material showed the presence of copper (Cu) 26.3% and silica (Si) 21.7% as major constituents, and relatively high amounts of calcium (Ca) 14.7%, bromine (Br) 9.6%, aluminium (Al) 6.1%, iron (Fe) 5.3% and barium (Ba) 4.31% together with lower content of tin (Sn) 3.1%, nickel (Ni) 1.4%, and zinc (Zn) 1.1% and other precious and rare earth element (REE) (Table 1). Mineralogical analysis of feed showed the significant peaks of Cu in the form of copper iron sulfide ( $\text{Cu}_{0.33}\text{Fe}_{0.67}\text{S}$ ), copper and iron complex ( $\text{Cu}_{0.3}\text{Fe}_{0.7}$ ), copper metal (Cu) along with the phases of Ni, Fe and Al (Fig. 1). The Scanning Electron Microscopy (SEM) images of ground waste mobile phone PCBs shows the metal distribution of a specific part in the sample. As the sample size of the feed material was below 250 microns, it was preferred to look into the depth of the sample to trace out the different complexes in their different arrangements at 30 microns. The SEM-EDX mapping shows the presence of various small-sized particles in rows. The same pattern of Si, oxygen (O) and Al

suggests the presence of aluminium oxide complexes, silicate minerals, and aluminosilicates (Fig. 2). The presence of these mineralogical phases can also be confirmed in X-ray diffraction (XRD) the of feed (Fig. 1). The small dotted arrangement patterns were found the same for Ni, and gold (Au) suggests that the Au is in a complex with Ni either in the form of sulfides or oxides. S, Cu, and Fe showed similar arrangement to each other, which indicate the presence of Cu mineral complex with Fe and sulfur; that can also be observed in XRD (Figs. 1 and 2).

## 2.2. Microbial culture

The microbial culture used in the bioleaching experiments were collected from the laboratory culture of Lulea University of Technology (Lulea, Sweden). The microbial culture was a mixed culture of chemolithotrophic, acidophilic mesophile consisting of Fe and S oxidizing microorganisms. Revealed from the Q-PCR analysis of Bioclear B.V., Netherlands. The microbial culture was dominated by *Acidithiobacillus ferrooxidans* (Fe & S - oxidizers), *Leptospirillum ferriphilum* (Fe-oxidizer) followed by *Acidithiobacillus caldus* (S-oxidizer), and with approximately the same amount of *Acidithiobacillus thiooxidans* (S-oxidizer), *Sulphobacillus* sp. (Fe-oxidizer) and *Ferroplasma* (Archaeal species, Fe-oxidizers).

**Table 1**  
Elemental analysis of feed (PCB) and bioleached residues.

Elements	Weight (%)			
	Feed (PCB)	7% PD residue	10% PD residue	15% PD residue
Cu	26.3	0.4	0.44	0.43
Si	21.7	30.2	28.2	26.4
Ca	14.7	17	15.4	17.6
Br	9.6	16	17.1	17.8
Al	6.1	2.5	1.72	2.4
Fe	5.3	3.9	2.52	2.9
Ba	4.3	8.8	7.12	6.9
Sn	3.1	4.0	11.1	10.2
Ni	1.4	1.2	0.44	0.8
P	1.2	3.1	2.89	2.3
Zn	1.1	0.3	ND*	0.2
S	0.8	2.3	2.83	2.6
Ti	0.8	2.6	2.02	1.7
Pb	0.7	2.1	2.44	2.4
Ag	0.4	0.1	1.4	1.2
Sb	0.3	0.3	0.69	0.5
Cr	0.3	0.7	0.51	0.51
Ta	0.3	0.7	0.29	0.3
Zr	0.2	0.6	0.42	0.4
Cl	0.2	0.5	0.024	0.6
K	0.1	0.2	0.14	0.2
Au	0.1	0.2	0.12	0.1

ND\*- Not detected.

The mixed microbial culture used in the experiment was grown in OK medium [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 3.0 gL<sup>-1</sup>; KCl, 0.1 gL<sup>-1</sup>; K<sub>2</sub>HPO<sub>4</sub>, 0.5 gL<sup>-1</sup>; MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.5 gL<sup>-1</sup>; Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 0.01 gL<sup>-1</sup>] supplemented with 22.4 gL<sup>-1</sup> ferrous sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O) as an iron source and 0.605 gL<sup>-1</sup> (2 mM) of potassium tetrathionate (K<sub>2</sub>S<sub>4</sub>O<sub>6</sub>) as a sulfur source and sub-cultured repeatedly prior to its use in the bioleaching experiment [21]. The culture was grown in a 2 L baffled glass reactor, with a working volume of 1 L (v/v). The pH was maintained at 1.50 ± 0.05 as it was an acidophilic microbial culture, and the temperature was maintained at 35 °C. The microbial growth analysis was carried out by regular measurement of pH, redox potential, Ferrous (Fe<sup>2+</sup>) ion and Ferric (Fe<sup>3+</sup>) ion concentration, total iron concentration, and viable cell count. The redox value of activated culture used for bioleaching was 700 mV, and the viable cell count of the inoculum used for 7% and 15% pulp density (P.D.) was 3.52 × 10<sup>7</sup> cells mL<sup>-1</sup> while 4.8 × 10<sup>6</sup> cells mL<sup>-1</sup> for 10% P.D. The reason for having good amount of viable cell count at high redox potential is due to the complete oxidation of ferrous iron to ferric by iron

oxidising microorganisms resulting with a high redox potential value. The sulfate concentration for OK media and inoculum was 7.28 gL<sup>-1</sup>, and 14.59 gL<sup>-1</sup> respectively, which were contributed by the total acid added media components, and sulfur oxidation. Several studies on the influence of sulphate ions on microbial activity have motivated to count the viable cells and understand the microbial dynamics [22]. Improvement in biodegradation process of either waste/waste water it is critical to control the process water carefully for a better understanding of the microbial system [23]. The total iron of the activated culture was 3.8 gL<sup>-1</sup>; the lesser amount of total iron was due to the formation of jarosite (XFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) precipitation, which is enhanced by the presence of monovalent cations present in the growth medium (Eq. 1).

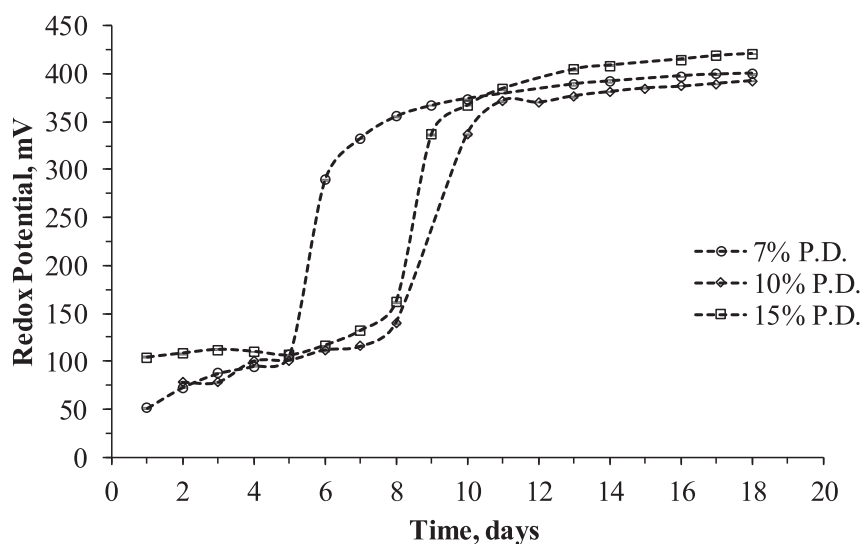


[X<sup>+</sup> = K<sup>+</sup>, Na<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, . . .]

Thus, the amount of total iron present in inoculum is necessary to estimate before initiating the experiment.

### 2.3. Analytical and instrumentation techniques

The pH measurements of the bioleaching solution during the experiments were carried out by a pH meter (Eutech). Calibration of the pH meter was done regularly with a three-point calibration using the standard buffers of pH 1.68, 4.0, and 7.0 and slope value ranged between 95–100. The oxidation-reduction potential (ORP) of the bioleaching solution was measured by an ORP meter having a platinum electrode with Ag v/s AgCl reference electrode. The Fe (II) concentration in the bioleaching experiment was estimated by a titrimetric method using cerium sulfate with 1, 10-phenanthroline as an indicator. The Fe (total) concentration of the bioleaching solution was measured by visible spectrophotometer at 510 nm. Whereas, the Fe (III) concentration of the bioleaching solution was calculated by subtracting concentration of Fe (II) from the Fe (Total). A turbidimetric method was used to determine the sulfate ion concentration of the bioleaching solution as per the procedure described in American Public Health Association, 1975 (APHA) [24]. The population dynamics study of the microorganisms was carried out by counting planktonic viable microbial cells by a bright-field microscope at 100X magnification on a Neubauer hemocytometer. The elemental composition of both feed and residues was carried out by X-Ray Fluorescence analyzer (XRF) (Bruker), whereas, Powder X-Ray Diffraction (PANalytical Powder XRD) determined the mineralogy. The samples for XRD were pulverized to ensure the homogeneity and the diffraction patterns



**Fig. 3.** Redox Potential profiles of bioleaching experiments (7, 10 and 15% PD). (The graph contains the values representing the mean ± Standard deviation of three replicates).

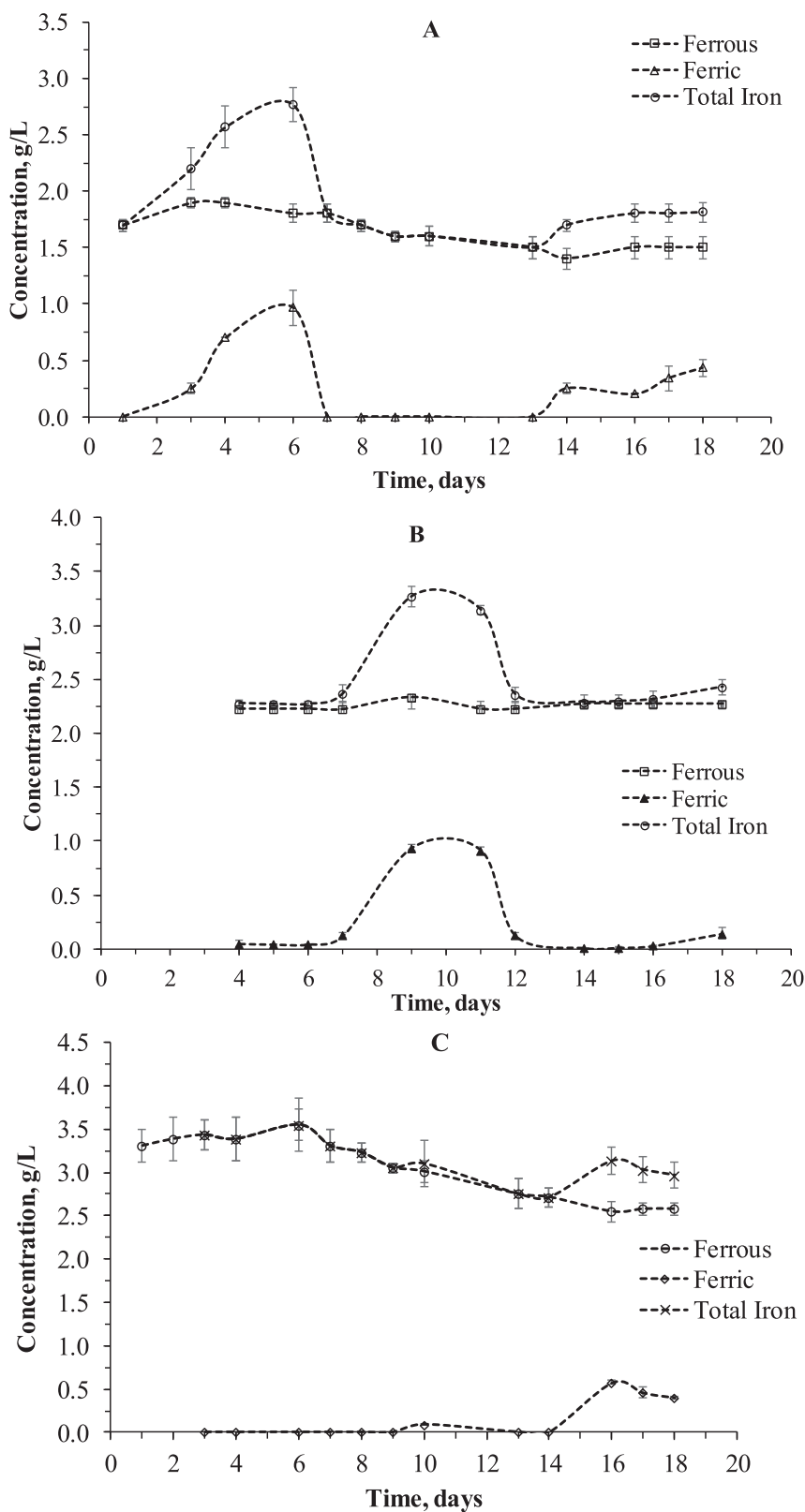


Fig. 4. Total iron/ferrous/ferric profile of PD A-7%, B-10% and C-15% (w/v) bioleaching experiments. (The graph contains the values representing the mean  $\pm$  Standard deviation of three replicates).

were measured at angles between  $10^\circ$  to  $90^\circ$  at a step size of  $0.02$  angle  $\text{sec}^{-1}$ . The crystalline phases were identified by using the joint committee for powder diffraction standards (JCPDS) file. The surface morphology, along with the mineralogy of the feed as well as the bioleach residue, was

studied by using SEM-EDX (Nova Nano FE-SEM 450 (FEI)). SEM studies together with Energy Dispersive X-Ray (EDX) studies were done for both feed and bioleach residue samples for further confirmation of the chemical composition and their mineralogy.

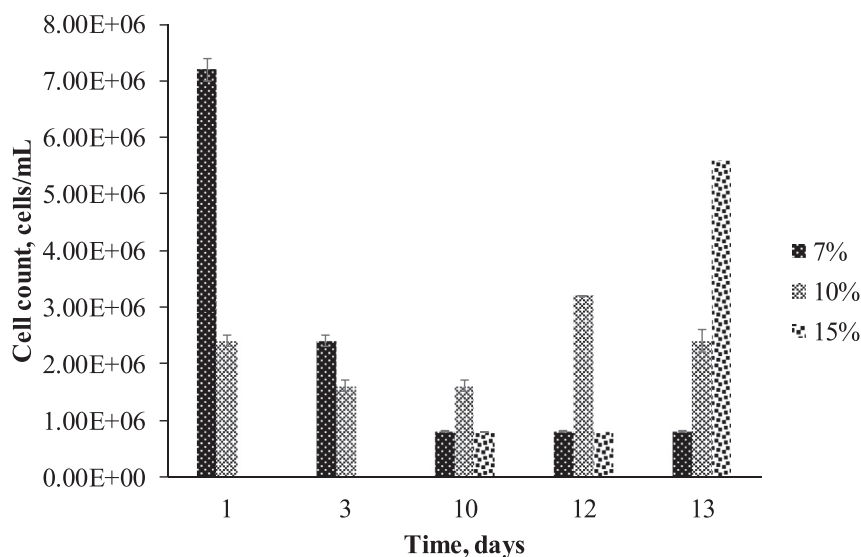


Fig. 5. Viable planktonic cell count profile of the bioleaching experiments with 7%, 10 % and 15% PD. (The graph contains the values representing the mean  $\pm$  Standard deviation of three replicates).

#### 2.4. Bioreactor set-up for bioleaching experiments

The bioreactor for all three bioleaching operations was of same configuration and material. All bioleaching experiments were carried out on a 2.5 L glass bioreactor with a working volume of 1 L (v/v). The stirring device in the bioreactor comprised of a mechanical overhead stirrer (IKA) and a flat blade turbine type impeller to ensure homogenous mixing of the bioleaching slurry with a stirring rate of 210 rpm. Two baffles were placed perpendicular to the wall of the reactor facing opposite at two extremes of the wall. Each baffle extended vertically from top to bottom of the bio-leaching slurry. The two baffles were used to avoid vortex formation in the bioreactor slurry, allowing homogenous mixing of the solid particles with the lixiviant. The temperature in the bioreactor was maintained at 35 °C by the help of a hot plate (IKA) placed beneath the reactor with desired temperature regulation.

#### 2.5. Bioleaching experiment

The working volume of batch bioleaching experiment was 1000 mL, which comprised of 900 mL (90% v/v) of OK growth medium and 100 mL (10% v/v) of inoculum (microbial culture). The bioleaching was carried out with increasing pulp density (P.D.), i.e., the weight of pulp or feed material per unit volume viz. 7, 10, and 15 (% w/v). Their effect on microbial growth and metal recovery was determined. The feed was added in the above mentioned 1000 mL solution after attaining the solution temperature of 35 °C. The pH of the bioleaching slurry was controlled at 1.5 with manual addition of 5M H<sub>2</sub>SO<sub>4</sub> daily from the start to the end of the experiment [25]. The cumulative acid addition in the batch experiment was monitored and recorded to calculate the volume of concentrated H<sub>2</sub>SO<sub>4</sub> required per ton of the feed material. The bioprocess dynamics of the experiment in batch operation was studied by measurement of pH and ORP values together with the concentration of Fe (II), Fe (III) and Fe (Total). The concentration of SO<sub>4</sub><sup>2-</sup>, Cu, Ni, and Zn were also measured along with planktonic viable microbial cell count in the bioleaching solution regularly. The experiments were continued until pH, ORP values, as well as all base metal concentration together with iron [Fe (II), Fe (III), and Fe (Total)] and sulfate concentration, was found to be stable or constant.

#### 2.6. Post-harvest processing

The bioleaching experiments were harvested by a solid-liquid separa-

tion by vacuum filtration using a water jet Aspirator Pump (Cole-Parmer). After separation of bioleached liquor (filtrate) the solid filter cake (bioleached residue) was thoroughly washed with a measured volume of deionized water, acidified to pH 1.5 with H<sub>2</sub>SO<sub>4</sub>. The bioleached residues were dried in a hot air oven at 60 °C for a few days until no change in the dry weight was observed. Further, the bioleach residues were ground and crushed via mortar and pestle and divided to smallest division by coning method to have replica samples for analysis. The residues were sent for chemical analysis by XRF and mineralogical analysis by XRD and SEM-EDX. The leaching yield was calculated based on elemental analysis of the feed and bioleach residue by XRF (Table 1) using the following formula (Eqs. (2), (3), and (4)).

$$M_f = M\% * f_w \quad (2)$$

$$M_{br} = M\% * f_{br} \quad (3)$$

$$L_y (\%) = \left(1 - \frac{M_{br}}{M_f}\right) * 100 \quad (4)$$

$M_f$  = metal content in the feed;  $M_{br}$  = metal content in bioleached residue;  $M\%$  = Metal percentage;

$L_y (\%)$  = Leaching Yield,  $f_w$  = weight of feed material,  $f_{br}$  = weight of bioleached residue.

### 3. Result and discussions

#### 3.1. Effect of increasing pulp density on ferrous/ferric bio-oxidation

The ferrous, ferric and total iron concentration profile during the bioleaching of 7% P.D. showed an initial increase in ferric ion concentration, followed by a balanced ferrous ferric cycle (Fig. 4A). The balanced ferrous ferric cycle here denotes to the simultaneous oxidation-reduction of ferrous/ferric. It has been reported that a balanced ferric-ferrous system is required for Cu mobilization from waste mobile phone PCBs [10]. The slow increase in the ORP value was also observed during the time period of 1–6 days in which complete copper recovery was attained. The increase in ORP and viable cell count during these days shows good microbial activity in the system (Figs. 3 and 5). In the middle of the investigation, a decrease in ferric ion concentration and pH emphasizes on the ferric reduction and jarosite formation. On the 10<sup>th</sup> day, a

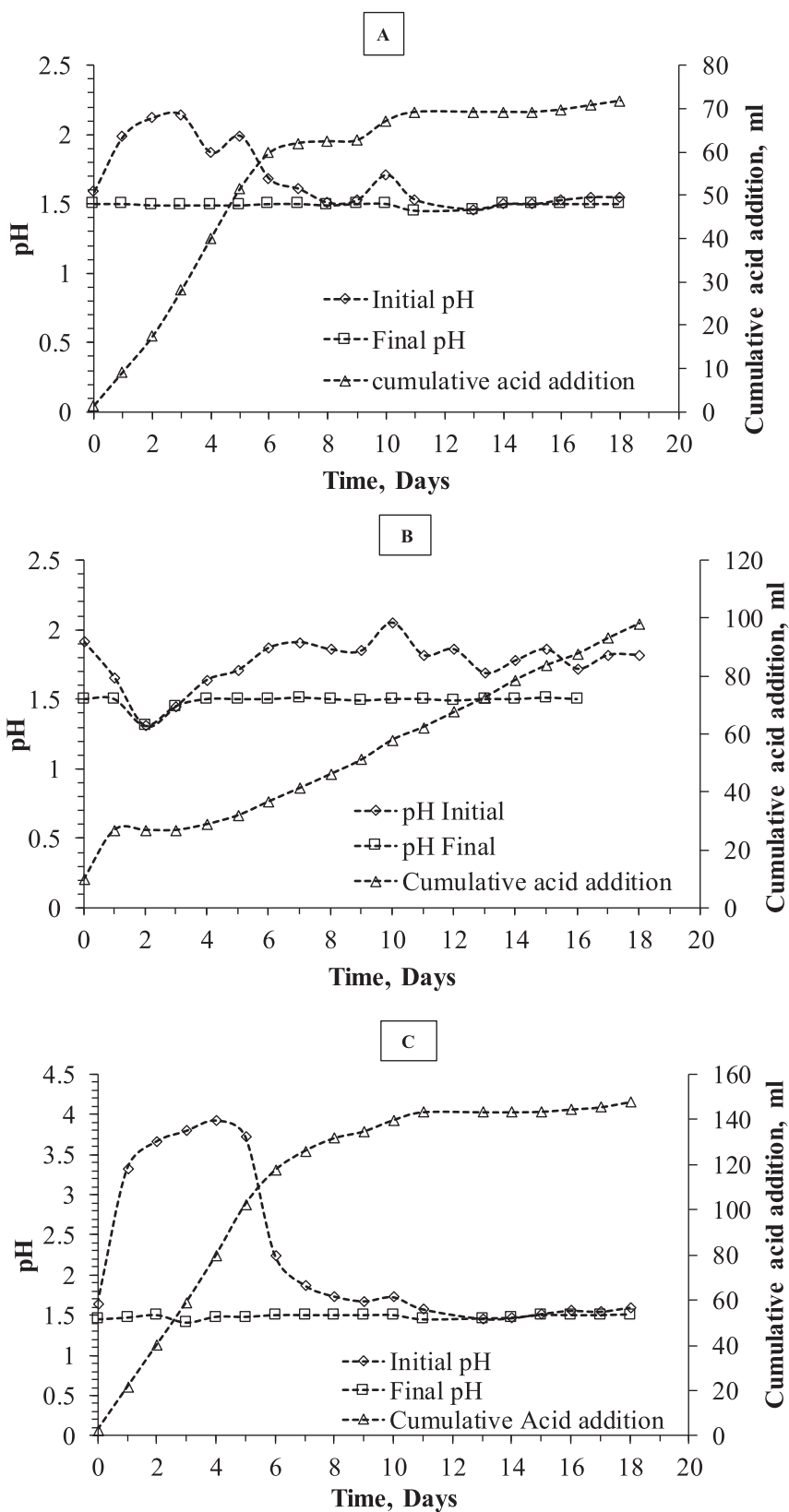
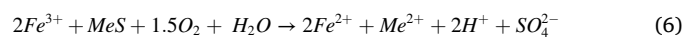


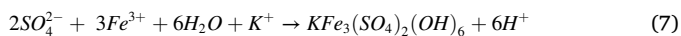
Fig. 6. pH profile of bioleaching experiment with 7% PD (A), 10% PD (B) and 15% PD (C).

slight increase in pH with an increased ORP value suggested that a simultaneous ferrous to ferric bio-oxidation was occurring. The following equations explain the changes in pH with the ferrous/ferric oxidation-reduction cycle and jarosite formation (Eqs. (5), (6), and (7)).



**Table 2**  
Summary table of all the experiments.

Process parameters/observations	7% PD	10% PD	15% PD
Feed weight, g	70	100	150
Bioleach residue weight, g	49.74	69.93	107.66
Weight loss, %	28.94	30.37	28.22
Acid consumption, kg conc. H <sub>2</sub> SO <sub>4</sub> /ton PCBs	422.44	430.08	457.053
Bioleach liquor volume, L	1.050	1.100	1.068



In 10% bioleaching study the ORP value was recovered from 140 mV to 330 mV on the 10<sup>th</sup> day (Fig. 3), which was also marked with the maximum ferric ion concentration in the system. The copper recovery during this period was 42% while the rest of copper was recovered after the 12<sup>th</sup> day of the experiment after achieving a redox value between 370-392 mV and a balanced ferrous/ferric ion profile (Fig. 4B). The viable cell count profile of 10% P.D. also shows an excellent microbial activity with the maximum viable cell count on the 12<sup>th</sup> day of bioleaching (Fig. 5).

In 15% P.D., the high amount of 5M acid added contributed to 73.96% of the copper recovery in the initial eight days. On the 9<sup>th</sup> day of the bioleaching experiment, the redox value was increased from 160 mV to 337 mV (Fig. 3), which denotes the microbial activity after an initial lag phase of 8 days. The addition of 15% solids in the medium makes the

slurry thick which negatively affects the microbial growth in the system as no viable cell count was detected during the initial eight days of the experiment (Fig. 5). The increase in ORP value along with decreasing total iron concentration and pH denotes that ferrous to ferric ion bio-oxidation and jarosite precipitation were simultaneous events (Figs. 3, 4C and 6C). The 82.17% copper was recovered till the 10<sup>th</sup> day of the experiment; on the same day, the visible viable cells were detected in the 15% P.D. bioleaching system (Fig. 6). The constant value of ferrous/ferric ion, pH, and redox after 16th day denotes the completion of bioleaching. The increased ferric ion concentration during the last few days with a slight increase in pH and cell count indicates ferrous to ferric bio-oxidation.

The waste mobile phone PCBs are a rich source of iron. Therefore, all the bioleaching experiments were carried out in iron-free medium so that the microorganisms can utilize the Fe from feed itself [19]. The ferrous concentration was calculated based on XRF analysis was 3.72 gL<sup>-1</sup>, 5.32 gL<sup>-1</sup>, and 7.92 gL<sup>-1</sup> in 7%,10%, and 15% P.D., respectively (Table 1). The redox value was between 300-450 mV in all the experiments (Fig. 3). A recent study stated that 450mV is a critical redox value for copper bioleaching above which the formation of jarosite passivation layer negatively affects the metal recovery [26]. The jarosite precipitation was minimum in 7% P.D. as the XRF analysis of bioleach residue and feed confirm 47.5% of 3.72 gL<sup>-1</sup> (iron in feed), i.e., 1.8 gL<sup>-1</sup> of iron was leached out in the bioleaching solution which was constantly present during the study as no external iron source was provided. The total iron profile during 10% as well as 15% P.D. bioleaching indicates jarosite

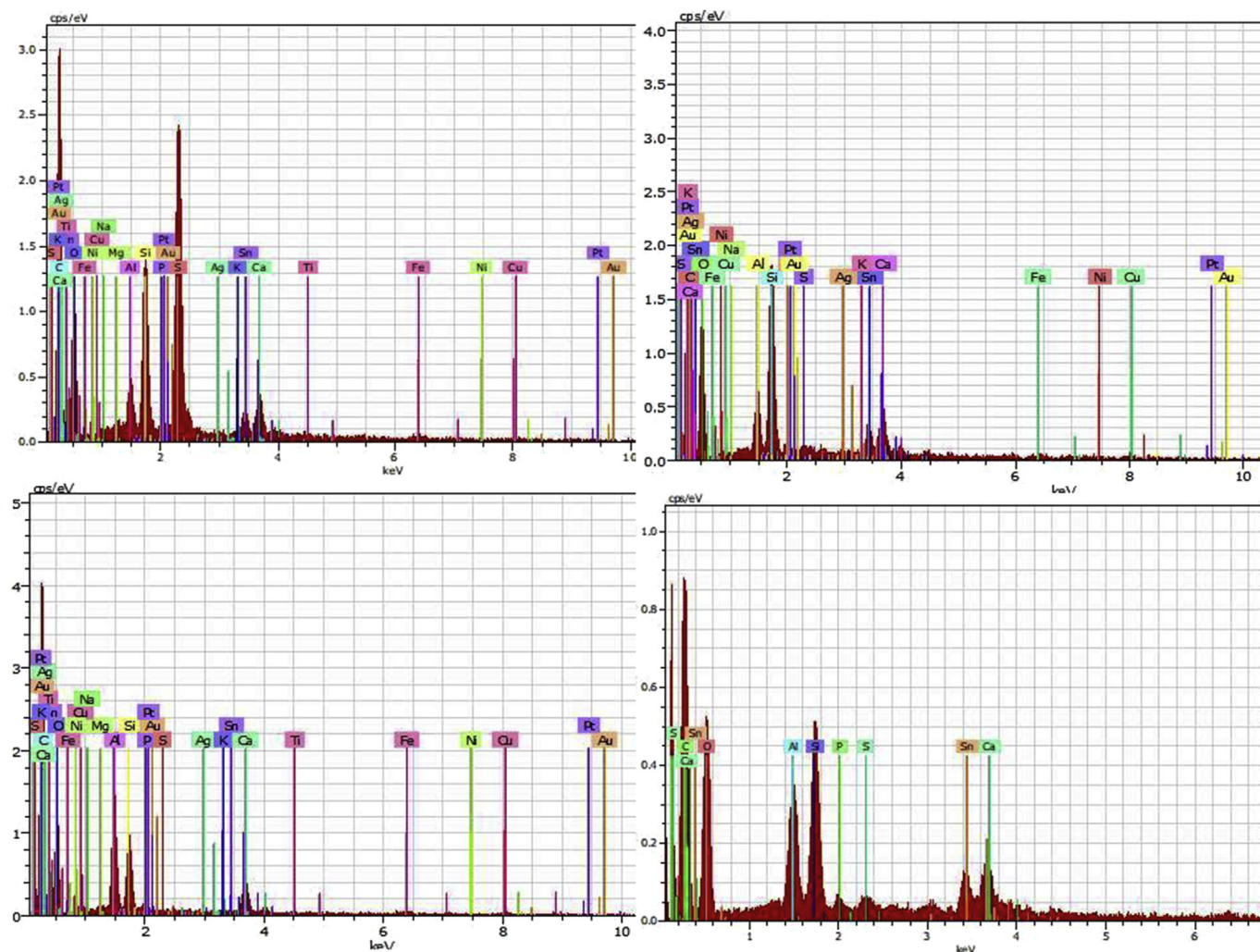


Fig. 7. Energy dispersive X-ray (EDX) graphs of A. feed (mobile phone PCB) and bioleached residues B. 7%, C. 10% and D. 15% (w/v) PD.



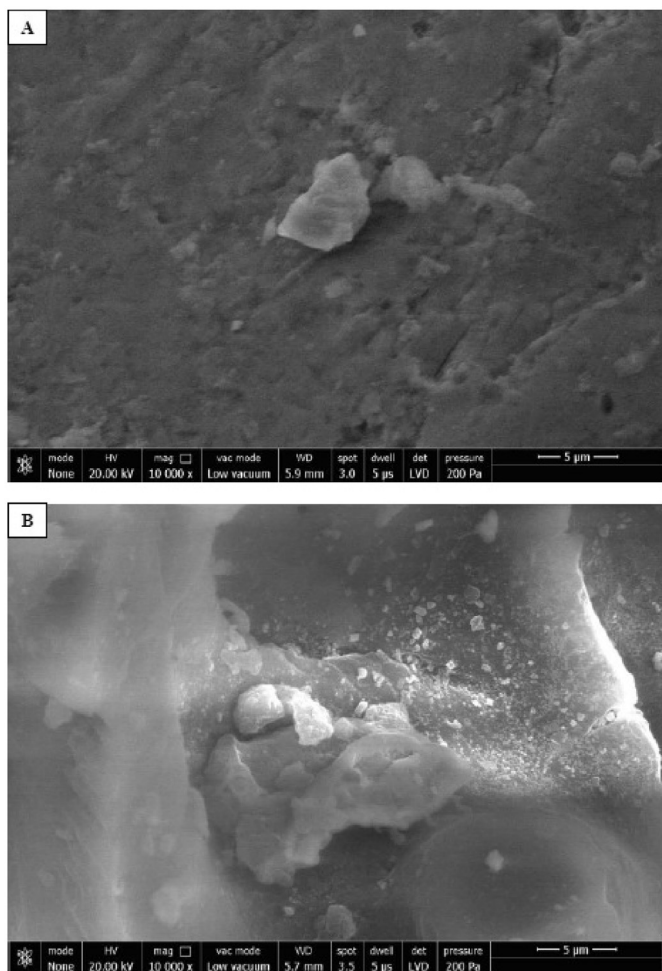


Fig. 8. Scanning Electron Microscopy (SEM) images of changes in morphology of A. feed (before bioleaching) and B. bioleached residue (after bioleaching).

precipitation as according to XRF analysis 67.01% and 61.01% of 5.32 gL<sup>-1</sup> and 7.98 gL<sup>-1</sup> (iron present in feed), i.e., 3.56 gL<sup>-1</sup> and 4.8 gL<sup>-1</sup> was leached out in the bioleaching system respectively, while only 2.4 gL<sup>-1</sup>

and 2.98 gL<sup>-1</sup> iron was detected at the end of the experiments. The jarosite precipitation was more likely with increasing pulp density as can be seen in comparative XRD diffractogram of feed and bioleach residues (Fig. 1).

### 3.2. Effect of increasing pulp density on pH

An increase in pH during the initial phase of bioleaching in all the experiments was due to increased alkaline nature and concentration of acid consuming gangue minerals and was highest in the experiment with 15% P.D [27]. Studies on soluble microbial products in sulphate radical mediated degradation are also widely studied, which has a correlation to sulphate chemistry and proton dissolution in the microbial system [28, 29]. The increase in pH on the 6<sup>th</sup> day of 7% P.D. was due to increased Fe<sup>3+</sup> ion concentration in the system (Fig. 6A) as the ferrous to ferric bio-oxidation is an acid consuming process (Eq. 5). However, the increased pH was balanced by the parallel phenomenon of reduction of ferric into ferrous to dissolve the metals ions at the same time in the system and resulted with a pH value of 1.68 which was later maintained at pH 1.5 by addition of 5M H<sub>2</sub>SO<sub>4</sub> (Fig. 5A). After 6<sup>th</sup> day of the experiment the solution pH was 1.5 thus to determine the activity of sulfur oxidizers the sulfate concentration in bioleaching medium was estimated and it was found that the sulfate concentration in 7% P.D. was 46.12 gL<sup>-1</sup> which was significantly high in comparison to the added amount of sulfate in the form of acid, 0K medium and inoculum which was 37.87 gL<sup>-1</sup>. The pH remained constant at 1.5 in the later days of the experiment, which indicated the completion of the process.

The pH in 10% bioleaching was showing an increasing trend during 7–12 days, and the highest value of pH 2.01 was marked on the 10<sup>th</sup> day of the experiment (Fig. 6B). The similar increasing trend of ferric ion concentration and ORP during the period suggests the ferrous to ferric bio-oxidation and a good microbial activity during the study. The minor fluctuations in pH were observed until the end of the experiment. A stable value of pH 1.82 at 17<sup>th</sup> day indicates less activity of sulfur-oxidizing microorganisms due to the sensitivity of *At. thiooxidans* at high metal ion concentration and P.D [11].

The pH of 15% P.D. was carefully monitored during the first few hours of the experiment, and 5M H<sub>2</sub>SO<sub>4</sub> was regularly added to prevent the ferric precipitation. On the 7<sup>th</sup> day, a decreased pH value of 1.88 was observed after which a controlled pH value between the range of 1.8–1.5 was noted (Fig. 6C). The reason for the decreased pH value here was different from P.D. 7 (% w/v). The sulfate concentration was deficient in

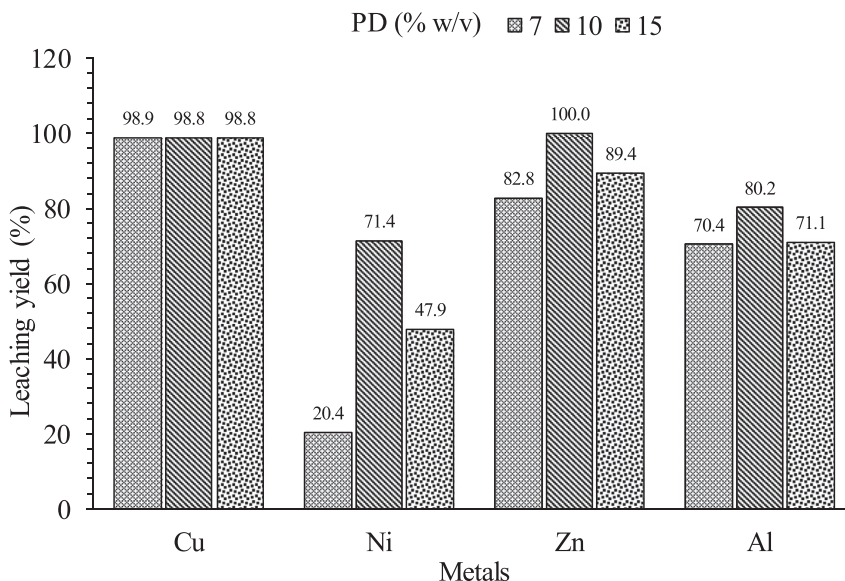


Fig. 9. X-ray Fluorescence (XRF) analysis of bioleaching experiments with 7%, 10% and 15% PD.

15% P.D., which shows less activity of S oxidizing microorganisms. The decrease in pH was due to jarosite formation; the decreasing total iron concentration profile during this period confirms the same. The total amount of acid consumption (kg per ton PCBs) were estimated for all the three bioleaching experiments (Table 2).

### 3.3. Chemical and mineralogical analysis

The changes in chemical composition, mineralogy and material surface before and after bioleaching was determined by the XRF, XRD and SEM-EDS analysis of feed as well as bioleach residues. The XRF analysis confirms the bioleaching of Cu, which was found as a trace element in the bioleach residues. Comparative SEM-EDX and XRD graphs of feed and bioleach residues show a high-intensity peak of Cu in the feed which was absent in all of three bioleached residues after Cu bioleaching. The elemental and mineralogical analysis of bioleached residues showed the increased concentration of Au and Ag, along with economically important element Ti after bioleaching. The calculations based on XRF data denotes that Ag was concentrated 80% in 7% P.D., and 100% in 10% and 15% P.D. bioleach residue. The concentration of Ti was 100, 79, and 52% in 7, 10, and 15% P.D., respectively (Table 1). The Au was concentrated by 17.78% in 7% P.D. bioleach residue. The XRD diffractogram of bioleach residues confirms the dissolution of Cu, Zn, Fe and Ni and concentration of Ag and Ti in the bioleach residue (Fig. 1). The peaks of Silver oxide (Ag<sub>2</sub>O), titanium oxide (Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>), tin oxide (SnO) and jarosite (KFe [SO<sub>4</sub>]<sub>2</sub>[H<sub>2</sub>O]) were observed in the residues. The comparative SEM-EDX micrographs of bioleach residue also show the peak of Au and Ag (Fig. 7). The SEM micrographs of PCB powder at 10000x magnification before and after bioleaching shows the significant change in the surface. The smooth surface of the powdered PCB material became disruptive and trenched post bioleaching, which indicates the proton and ferric attack (Fig. 8).

### 3.4. Effect of increasing pulp density on metal recovery

The bioleaching of Cu, which was the major element in the PCB sample, was high and did not influence by increasing pulp density. The Cu recovery was found to be 98.86%, 98.83%, and 98.81% in 7%, 10%, and 15% P.D. bioleaching experiment. Besides Cu, the recovery of other base metals such as Ni and Zn were also in considerable amount (Fig. 9). The recovery of Al was 70.40%, 80.20% and 71.05% in 7%, 10% and 15% PD respectively. According to a recent study, the Al recovery takes place before Cu bioleaching during the initial 24 h when the redox value becomes unstable due to fast consumption of Fe<sup>3+</sup> in comparison to the Fe<sup>2+</sup> re-oxidation [14]. An unstable redox potential value was also observed at the beginning of the experiment. The base metals i.e., Zn and Ni recovery were 82.83%, 100%, 89.37% and 20.39%, 71.44% and 47.9% in PD 7, 10 and 15 (% w/v) respectively. The less recovery of Ni in 7% P.D. was due to the early dissolution of Cu [30]. The less availability of lixiviants in 15% P.D. due to high solid to liquid ratio might be a reason behind the low-recovery of Ni.

## 4. Conclusion

The present study mainly focused on bioleaching of Cu; the major element (26.3%) in mobile phone PCB followed by Si, Ca, Al, Fe, Ni, and Zn. The Cu recovery was 98.9%, 98.8% and 98.8% in the ascending order of P.D., with similar weight loss (%) in all the three bioleaching experiments, i.e., 28.9%, 30.4%, 28.2%. It depicts that the increase in P.D. from 7% to 15% (w/v) did not hinder the Cu recovery. The recovery of Al and Zn was equally good in all the experiments. Except for Cu, Al, and Zn; Ni showed varied leaching behavior with varying P.D. The Ni recovery was only 20.39% and 47.9% in P.D. 7% and 15% (w/v). The less availability of lixiviants in 15% P.D. and early Cu dissolution in 7% P.D. experiments might be a reason behind the low-recovery of Ni. The precious metals such as Ag and Au and some other economically important metals, i.e., Ti

were concentrated in the bioleached residues. Other chemical treatments can further recover these metals. The study showed a balanced Fe<sup>2+</sup>/Fe<sup>3+</sup> concentration profile and an ORP value between 350-400 mV in all the three experiments which helped in Cu bioleaching. The solid (%), did not affect the viable cell count during 7%, 10% P.D. experiments while the 15% P.D. experiment was observed with an initial acclimatization period of 9 days for microbial growth. Acid consumption during 7%, 10% and 15% PD was 422.44, 430.08, 457.05 kg. ton<sup>-1</sup> respectively. Thus, it can be concluded that bioleaching with higher P.D. can be economically more feasible in terms of Cu recovery and acid consumption.

## Declarations

### Author contribution statement

Himanshi Garg, Neha Nagar, Ganapathy Ellamparathy: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Shivakumar Irappa Angadi, Chandra Sekhar Gahan: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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