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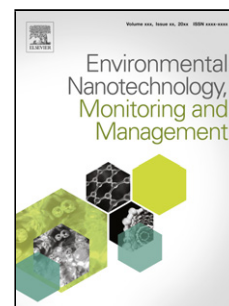
Title: Chemo-biohydrometallurgy—A hybrid technology to recover metals from obsolete mobile SIM cards

Author: Aditya Sahni Anil Kumar Sudhir Kumar

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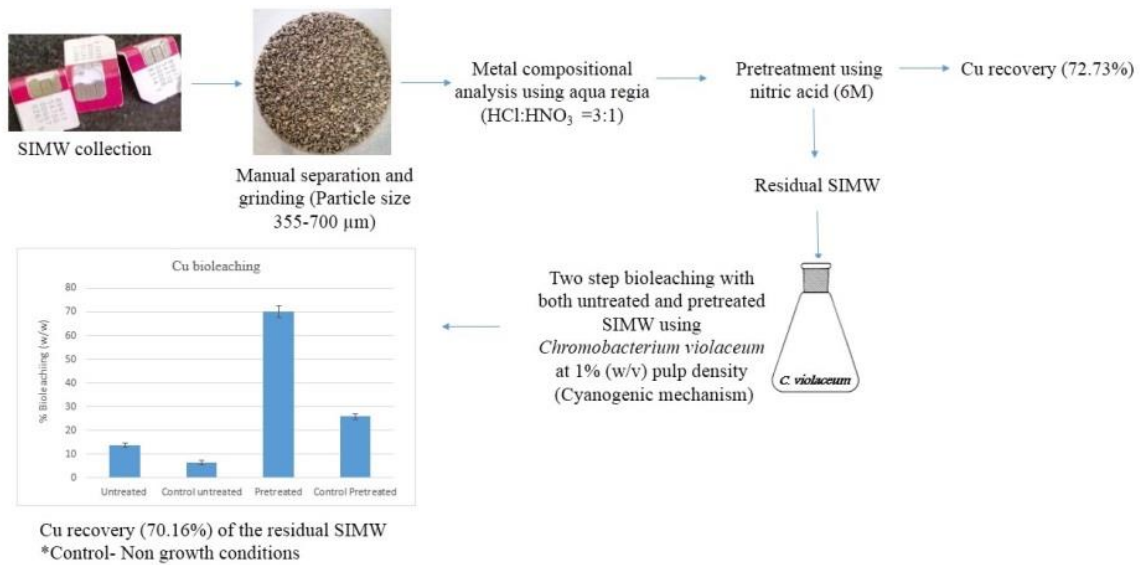
**Title: Chemo-biohydrometallurgy-A hybrid technology to recover metals from obsolete mobile SIM cards**

**Authors:** Aditya Sahni, Anil Kumar and Sudhir Kumar\*

Department of Biotechnology and Bioinformatics, Jaypee University of Information Technology,  
Waknaghat, Solan - 173234, Himachal Pradesh, India

\*Corresponding author ([sudhir.syal@juit.ac.in](mailto:sudhir.syal@juit.ac.in))

## Graphical Abstract



**HIGHLIGHTS**

- SIM waste (SIMW) like Computer Printed Circuit Boards (CPCB) is a source of precious metals.
- Chemo-biohydrometallurgy promotes recovery of Cu and other metals from SIMW.
- Bioleaching coupled with acidic pretreatment yielded high recovery of Cu from SIMW
- SIMW have potential to be used in recycling industry and can lower burden on natural resources which needs serious consideration.
- Higher Cu percentage of SIMW is a hindrance in recovery of other metals like Au.

## Abstract

The exponential increase in the cellular networking and advancement in the related technology has led to an increase in obsolete SIM cards. Elemental composition of obsolete SIM waste (SIMW) of particle size 355-700 $\mu$ m was 75.84% Cu, 0.42% Au, and 0.01% Ag. SIMW can be used to extract valuable metals. A chemo-biohydrometallurgy approach was employed for metals recovery from SIMW. Bioleaching experiments were performed in 150 ml Erlenmeyer flasks with 50 ml of Luria broth medium at pH 9, glycine concentration 5 g/L, rpm 150, temperature 30° C and pulp density 10g/L. Two step bioleaching of untreated SIMW using *Chromobacterium violaceum* yielded poor metals mobilization of copper (13.79%), gold (0.44%) and silver (2.55%). Acidic pretreatment of SIMW recovered 72% of copper, as its high concentration cause hindrance for leaching and solubilization of other metals like Au, and Ag. Subsequent, two-step bioleaching of pretreated SIMW at alkaline pH using *Chromobacterium violaceum* solubilized 70.61% of the remaining Cu within 4 days of incubation period. Therefore, a hybrid technology can be applied to efficiently recover Cu and other metals from SIMW. To the best of authors' knowledge, this is the first report of using hybrid technology to leach out Cu and other metals from SIMW.

**Keywords:** Bioleaching, *Chromobacterium violaceum*, SIM waste, e-waste, Chemo-biohydrometallurgy

## 1. Introduction

Electronic waste (e-waste comprises) of discarded electronic appliances of which computers and mobile phones are disproportionately abundant pose new environmental challenges and threats. (Pradhan and Kumar, 2014; Robinson, 2009). Most of the electronic waste is a complex mixture of precious metals (Ag, Au, and Pt); base metals (Cu, Al, Ni, Si, Zn and Fe); toxic metals (Hg, Be, Cd, Cr, As, Sb and Bi) along with halogens and combustible substances such as plastics and flame retardants (Wu et al., 2016). However, complex composition and increasing volumes of e-waste, along with difficulties in treating it, are the cause of concern. Therefore, recycling of electronic waste is an important subject not only for waste management but also for the recovery aspect of valuable materials.

A subscriber identity module or subscriber identification module (SIM) card is an integral part of mobile telephony ([https://en.wikipedia.org/wiki/Subscriber\\_identity\\_module](https://en.wikipedia.org/wiki/Subscriber_identity_module)). The exponential increase in the cellular networking and advancement in the related technology has led to an increase in obsolete SIM cards which are regarded as enriched source of precious metals, especially copper and gold. Waste SIM cards are being produced/generated from electronic gadgets especially mobile phones, therefore may be considered in e-waste category. Upcoming SIM less technology is seen as a long term solution to this problem, but the implementation of the same will increase the number of obsolete SIM in near future. Obsolete mobile SIM cards with its significant metals content, is recognized as a new emerging and fast growing waste stream and could be considered as a secondary ore for copper, gold etc.

In this context, recycling of e-waste is required for hazardous waste minimization and resource recovery (Raghupathy and Chaturvedi, 2013). Presently traditional hydrometallurgical and pyrometallurgical processes are in place to extract metals, but the intensive cost and toxic by-products are barriers (Man et al., 2013). In contrast, bioleaching process such as cyanogenic leaching is commercially exploitable technology applicable for metal extraction from electronic waste and low grade ores (Brandl et al., 2001; Ilyas and Lee, 2014; Natarajan and Ting, 2015; Pradhan and Kumar, 2012; Shah et al., 2015). Cyanogenic bacteria produces cyanide at early stationary phase of their growth, which acts as lixiviant during cyanogenic bioleaching of metals (Natarajan and Ting, 2015; Pradhan and Kumar, 2012). Enhanced metals recovery by cyanogenic bacteria is favorable at alkaline pH due to increase in total cyanide ions available for bioleaching (Chi et al., 2011; Natarajan and Ting, 2015). Researchers used cyanogenic bacteria like *Chromobacterium violaceum*, *Pseudomonas aeruginosa*, *Bacillus megaterium*, *Pseudomonas fluorescens* and leached significant amount of gold and copper from metal containing solid waste of computer printed circuit boards (CPCBs) (Arshadi and Mousavi, 2015; Brandl et al., 2008; Faramarzi et al., 2004; Natarajan and Ting, 2014; Pham and Ting, 2009; Tay et al., 2013). Therefore, the present work focused on bioleaching of Cu and Au at alkaline pH from metals containing solid waste of SIM card origin using *Chromobacterium violaceum*. To the best of author knowledge this is the first attempt on metals recovery from e-waste of SIM cards origin.

## 2. Materials and Methods

### 2.1 Procurement and metal content analysis of SIMW

Obsolete mobile SIMW were procured from M/S Vicky Communications, Sanjauli, Shimla and local shops nearby Jaypee University, Solan, Himachal Pradesh, India. SIM cards were weighed on digital weighing balance and the individual mass of single SIM card was 0.410g. These SIM cards were manually sorted into metal parts, crushed, ground and sieved. Metallic part of each SIM cards varied in mass from 0.040 to 0.055g and the weight of plastic body of SIM card was 0.360 to 0.370g. To analyze chemical composition one gram of SIM waste with particle size 355-700  $\mu\text{m}$  was dissolved in 100 mL of aqua regia ( $\text{HCl}:\text{HNO}_3 = 3:1$ ) by refluxing in a round-bottom flask at 100 °C for 1 hr (Ilyas et al., 2007). The solution was allowed to cool and the volume was made up to 100 mL with deionized water followed by filtration through 0.45  $\mu\text{m}$  glass fiber filters (Pall Life Sciences) to guarantee particle-free suspensions. Dissolve metal ions were analyzed using atomic absorption spectrophotometry (Perkin Elmer AAnalyst 400) at the following wavelengths (nm): Ag (328.1), Au (242.8) and Cu (324.8) (Pradhan and Kumar, 2012). Prior to the bioleaching experiment, the SIM waste was sterilized by autoclaving at 121°C for 15 minutes.

### 2.2 Pretreatment and Recovery of Cu

The copper was leached out from SIM e-waste using 6 M nitric acid. The metal particles were added to 6 M nitric acid at room temperature and was efficiently mixed. SIM card metal particles were added incrementally to the nitric acid to prevent excessive frothing due to the production of nitric oxide gas. The mixture was centrifuged and the residue was washed with deionized water and re-centrifuged. The cycle was repeated until traces of blue-green copper nitrate were no longer visible. The pretreated SIM metal pellet was finally removed, dried and weighed to constant mass (Natarajan and Ting, 2014). The leachate as well as dry pellet of e-waste, were further subjected to metal content analysis using aqua regia ( $\text{HCl}:\text{HNO}_3 = 3:1$ ).

### 2.3 Bacterial growth conditions and two step bioleaching

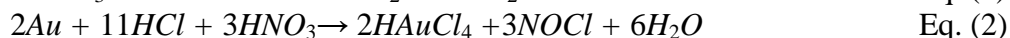
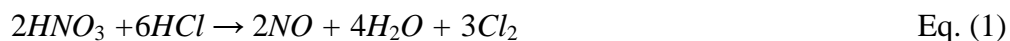
*Chromobacterium violaceum* (MTCC-2656) was taken from culture repository of Jaypee University Waknaghat, Solan, HP; earlier procured from Institute of Microbial Technology,

Chandigarh, India. A two-step bioleaching process was followed, since bacterial growth and cyanide production is inhibited due to the toxicity of e-waste in one step process (Brandl et al., 2001; Mishra and Rhee, 2010; Natarajan and Ting, 2014). Bioleaching experiments were carried out in 150 ml Erlenmeyer flasks with 50 ml of Luria Broth (LB) medium at pH 9, glycine concentration 5 g/L, rpm 150, temperature 30° C and pulp density 10g/L. The flasks were autoclaved at 121 °C and 15 psi pressure for 15 min. *Chromobacterium violaceum* was inoculated into experimental flasks and 0.5 g of sterilized e-waste (SIM powder, 1% (w/v) was added after 2 days of incubation to ensure maximum growth. After e-waste addition, the experimental flasks were incubated for another 7 days (Pradhan and Kumar, 2012). A separate control was run in parallel for a period of 7 days i.e. a flask containing SIM waste without bacteria to see the effect of media on metal mobilization. The leachate obtained was analyzed for the presence of metal ions (Atomic Absorption Spectrophotometer), final pH (Eutech, pH Testr30) of the medium and microbial growth in terms of total protein content by the micro-biuret method as per protocol mentioned in (Pradhan and Kumar, 2012).

### 3. Results and discussion

#### 3.1 Chemical content analysis and pretreatment of SIM waste

The chemical composition of SIM waste was represented in Table 1. The concentration of copper, and gold was 75.84%, and 0.42%, respectively; higher than the concentration reported in waste CPCBs (Arshadi and Mousavi, 2015; Brandl et al., 2001; Ilyas et al., 2007; Natarajan and Ting, 2014; Shah et al., 2015; Yazici and Deveci, 2014). Aqua regia dissolves Au, forming soluble complex i.e. Chloroauric acid is shown in equation (1) & (2) (Cui and Zhang, 2008); whereas Cu dissolution is presented in equation (3).

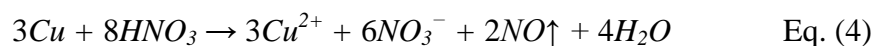


The concentration of silver (0.01%) in SIMW was significantly lower than silver (0.33%) present in waste CPCBs (Theo, 1998). Other metals like Fe, Zn, Ni, Co and Cr were also present in significant quantity (Table 1). Metals chip pasted on the plastic part of SIM can be easily detached manually and provides a selective advantage to remove and recycle plastics over e-



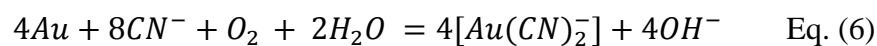
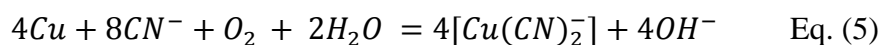
waste of CPCBs origin. The high concentration of metals brings it in the category of “artificial mines” or “enriched metals resource” which needs special attention to recover precious metals.

Majority of metals (Zn, Fe, Au, Ag, Ni and Cu) present in e-waste forms stable complexes with cyanide (Faramarzi et al., 2004), however higher concentration of copper causes hindrance in recovery of gold (Mudder et al., 2001; Natarajan and Ting, 2014). Thus, SIM waste was added to nitric acid to recover copper and other metals, and the residual waste was subjected for bioleaching to promote gold cyanidation. Pretreatment with acid lead to 72, 61.78, 54.83 and 53.15% of Cu, Ni, Fe and Cr recovery without significantly altering the concentration of Au (Table 1). Nitric acid mediated dissolution of Cu is presented in equation (4). Our results corroborated with the study of (Natarajan and Ting, 2014), reported nearly 80% removal of copper.



### 3.2 Bioleaching of untreated and pretreated SIM waste using *Chromobacterium violaceum*

Two-step bioleaching of metals was done using both untreated and pretreated SIMW to enhance the metals solubilization by reducing the toxic effects of metals. Copper mobilization (13.79%) was recorded in majority as compared to gold (0.44%) and silver (2.55%) (Fig.1 & 2). This may be due to high concentration (75.84%) of copper present in the untreated SIMW which consumed the lixiviant produced by bacteria (Mudder et al., 2001) and Au ( $E^0_{\text{Au}^{3+}/\text{Au}}$ : 1:52 V) is nobler than copper ( $E^0_{\text{Cu}^{2+}/\text{Cu}}$ : 0.34 V) (Chi et al., 2011); resulted in poor metal mobilization. Bioleaching of Cu using *Chromobacterium violaceum* depends on the amount of cyanide produced. Cu forms various complexes with cyanide like  $[\text{Cu}(\text{CN})_2^-]$ ,  $[\text{Cu}(\text{CN})_3^-]$  and  $[\text{Cu}(\text{CN})_4^-]$ , depending on the pH and other conditions. However, Au bio-dissolution forms dicyanide anions (Liang et al, 2014) and can be represented by following chemical reactions:



Overall poor metal mobilization was observed in case of untreated SIMW (Fig. 2). During bioleaching with untreated and pretreated SIMW, an increase in metals (0.72% of Au and

70.16% of Cu) mobilization was observed up to 4<sup>th</sup> day of incubation and thereafter no significant increase was observed up to seventh day. Ag mobilization was recorded maximum (2.86%) at 2<sup>nd</sup> day. The low mobilization of Au and Ag was due to the presence of high amount of Cu (20.68%) present even after pretreatment in the SIMW. The results contrast with previous studies (Arshadi and Mousavi, 2015; Brandl et al., 2008; Faramarzi et al., 2004; Natarajan and Ting, 2014; Natarajan and Ting, 2015; Pradhan and Kumar, 2012) on metals mobilization from waste CPCBs, where metals mobilization gradually increase up to 7<sup>th</sup> day of incubation period. This might be due to the presence of higher metals concentration in SIMW compared to waste CPCBs, which enhanced toxicity stress to bacteria in the shake flasks. Figure (2) revealed Cu mobilization in control flask for both untreated and pretreated SIMW. Similar findings were reported from e-waste of the CPCBs (Natarajan and Ting, 2014).

During chemo-biohydrometallurgical process the major secondary waste generated is residual e-waste with reduced metal concentrations; finally disposed off through TSDF (Treatment, Storage, and Disposal Facilities). Whereas pyrometallurgical treatment releases harmful brominated and chlorinated di-benzo furans and dioxin in the atmosphere (Pradhan and Kumar, 2012). Other than this majority of e-waste is recycled using hydrometallurgical methods to recover metals. This produces toxic gases and water which are highly poisonous for environment as well as human health (Robinson, 2009).

### 3.1.1 Bacterial growth estimation and pH analysis

Bacterial growth was measured in terms of total cellular protein and provides an estimate of growth in the shake flask (Ilyas et al., 2007; Pradhan and Kumar, 2012). From the results of Fig. 3, it was clear that *C.violaceum* was able to grow at alkaline pH (9.0) in the presence of SIMW of 355-700  $\mu\text{m}$  (1% w/v). The trend of bacterial growth was measured after addition of SIMW (both untreated and pretreated) for 2<sup>nd</sup>, 4<sup>th</sup>, and 7<sup>th</sup> day, respectively. A slight decrease in bacterial growth from 2<sup>nd</sup> to 4<sup>th</sup> day was observed with pretreated SIMW, whereas growth was inhibited significantly from 2<sup>nd</sup> to 4<sup>th</sup> day in case of untreated SIMW. Further increase in incubation period up to the 7<sup>th</sup> day resulted in decreased bacterial growth for both pretreated and untreated SIMW. Comparatively, higher bacterial growth was observed from the flasks containing pretreated waste as compared to the untreated one (Fig. 3). This shows that

pretreatment reduces the toxicity stress and bioleaching was better at lower SIMW concentration (1% w/v).

The decrease in the pH of the medium for initial 2 days without SIMW (data not shown) was attributed to the bacterial acidification process for the conversion of organic compounds, particularly glycine into carboxylic acids such as glyoxylic, cyanofornic, and oxalic acids (Liang et al., 2014). After SIMW addition; pH was measured at 2<sup>nd</sup>, 4<sup>th</sup>, and 7<sup>th</sup> day, respectively. Results of Fig. 4 revealed an increase in the final pH up to the 4<sup>th</sup> day for both untreated (9.36) and pretreated (9.39) SIMW. The increase in pH was due to the formation of metals cyanide complex (Pradhan and Kumar, 2012) and decreased pKa of HCN from 9.3 to 8.3 in the presence of salts (Faramarzi et al., 2004). However, by the end of the 7th day, pH dropped to a level of 9.1 (approx.) in both the cases. This may also correspond to decreased bacterial growth and thereby poor HCN production.

## Conclusions

The present study examined chemical composition, pretreatment and bioleaching of Cu, Au and Ag from SIMW using *Chromobacterium violaceum* at alkaline pH. Chemical analysis of SIMW showed higher metals concentration than present in waste CPCBs. The higher concentration of metals inhibited bacterial growth and reduces metal bioleaching. Pretreatment with nitric acid recovered majority of copper and remaining bulk was leached out through cyanogenic bioleaching. However, bioleaching did not prove to be an efficient way to leach out gold from SIMW in the presence of high proportion of other metals like copper. A hybrid technology like chemo-biohydrometallurgy proved to be effective to recover significant amount of Cu from SIMW. Direct bioleaching is recommended only when the metals concentration in the waste is low. For gold mobilization from SIMW, chemical treatment with aqua regia found to be an efficient and more suitable process. Finally, it is concluded that metals at such high concentration in SIM waste have potential to be used in recycling industry.

**Acknowledgement:** Authors thankful to Jaypee University of Information Technology for providing resources and infrastructure facility.

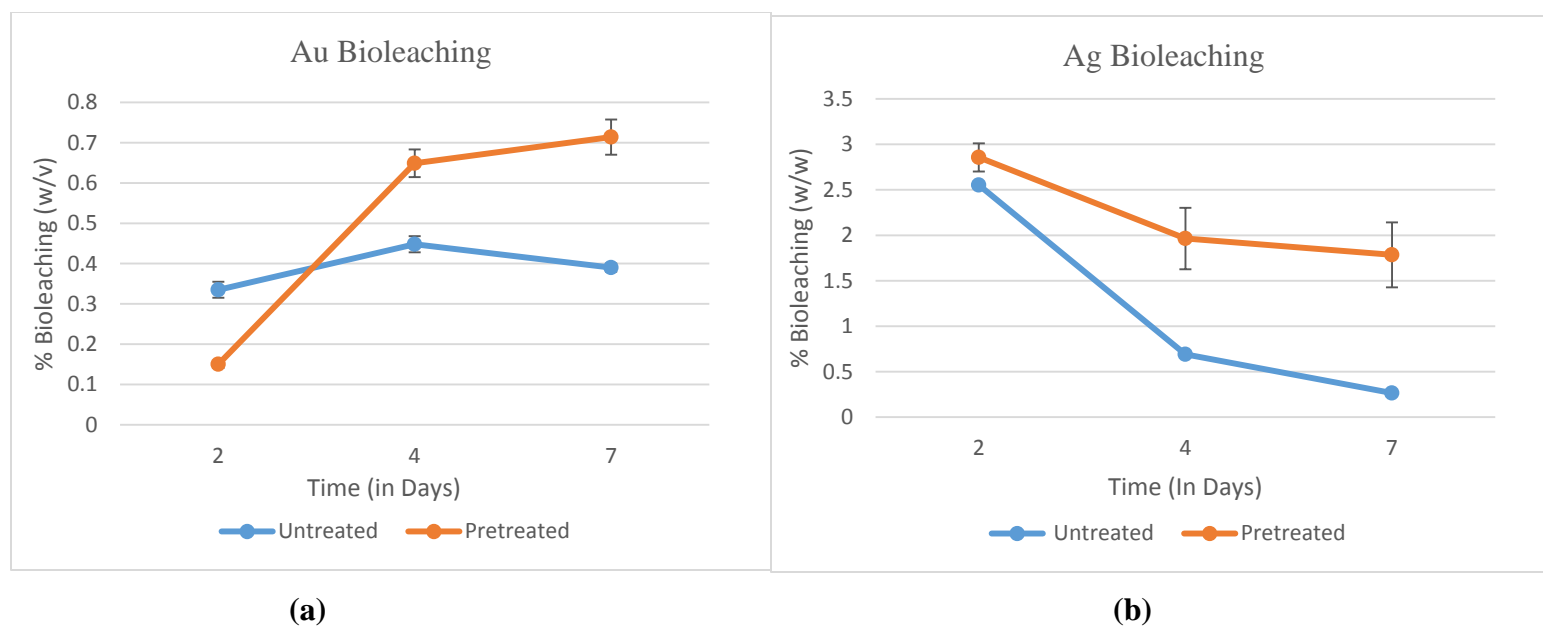
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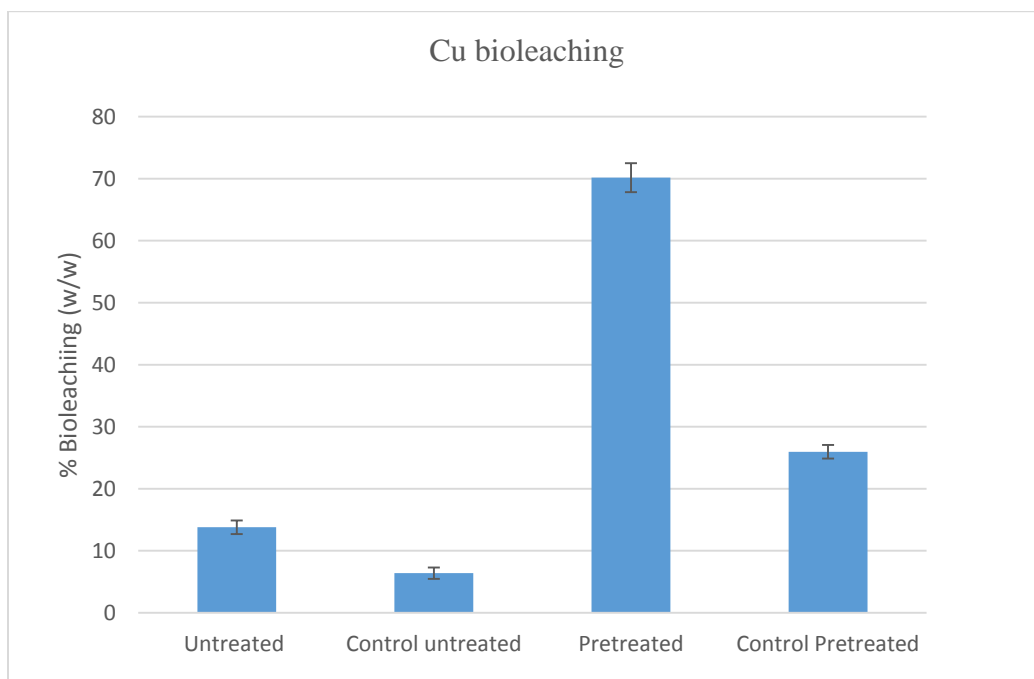
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**Table 1.** Chemical composition of pretreated and untreated SIM waste using acid digestion by aqua regia

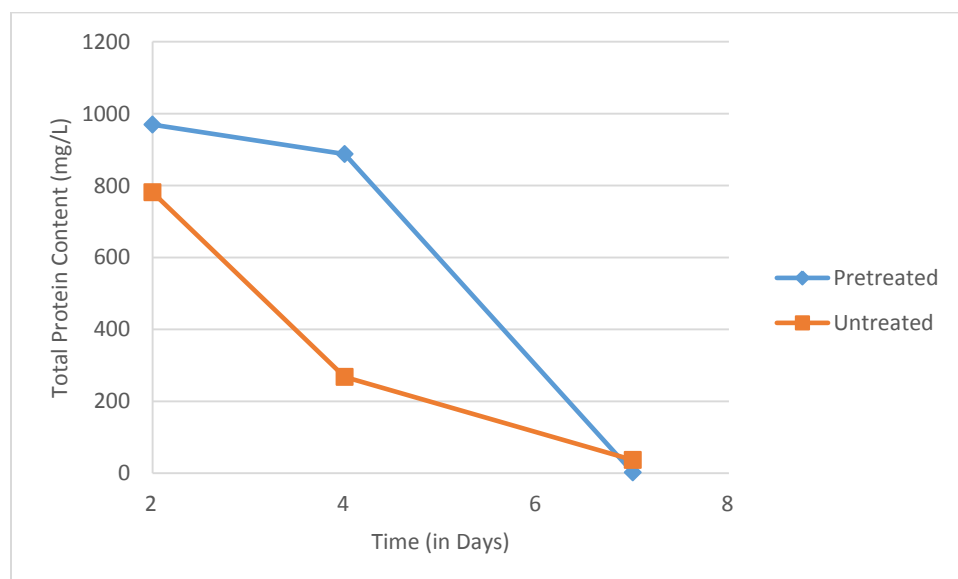
<b>Metals</b>	<b>Untreated (% w/w)</b>	<b>Pretreated (% w/w)</b>	<b>% Removal with pretreatment</b>
Cu	75.84±0.53	20.68±0.14	72.73
Ni	3.17±0.022	1.21±0.008	61.78
Fe	1.28±0.009	0.58±0.004	54.83
Au	0.42±0.003	0.40±0.008	4.80
Ag	0.01±0.003	0.01±0.0008	-
Cr	0.50±.004	0.23±0.002	53.15
Co	0.02±0.0001	0.02±0.0001	16.67
Zn	0.06±0.0004	0.06±0.0004	-



**Fig. 1** Metals recovery through bioleaching of untreated and pretreated SIMW: (a) Au; (b) Ag. Data presented in the Figure is mean of those obtained from duplicate experiments.

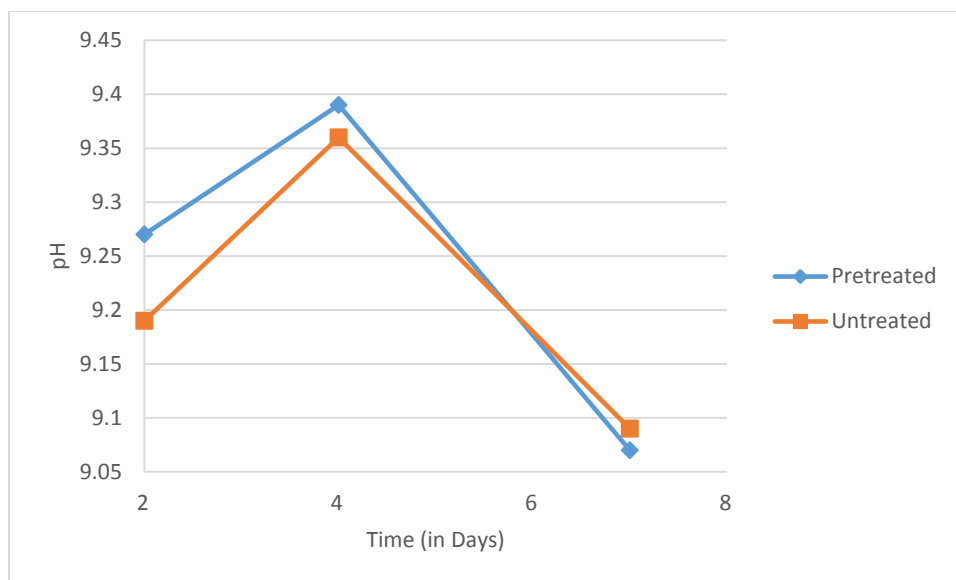


**Fig. 2** Bioleaching of Cu from untreated and pretreated SIMW using *Chromobacterium violaceum*



**Fig. 3** Bacterial growth (total cellular protein) during bioleaching of untreated and pretreated SIMW





**Fig. 4** Change in pH during two step bioleaching of untreated and pretreated SIMW