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Research article

Fungal bioleaching of WPCBs using *Aspergillus niger*: Observation, optimization and kinetics

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ABSTRACT

In this study, *Aspergillus niger* (*A. niger*) as an environmentally friendly agent for fungal bioleaching of waste printed circuit boards (WPCBs) was employed. D-optimal response surface methodology (RSM) was utilized for optimization of the bioleaching parameters including bioleaching method (one step, two step and spent medium) and pulp densities (0.5 g L^{-1} to 20 g L^{-1}) to maximize the recovery of Zn, Ni and Cu from WPCBs. According to the high performance liquid chromatography analysis, citric, oxalic, malic and gluconic acids were the most abundant organic acids produced by *A.niger* in 21 days experiments. Maximum recoveries of 98.57% of Zn, 43.95% of Ni and 64.03% of Cu were achieved based on acidolysis and complexolysis dissolution mechanisms of organic acids. Based on the kinetic studies, the rate controlling mechanism for Zn dissolution at one step approach was found to be diffusion through liquid film, while it was found to be mixed control for both two step and spent medium. Furthermore, rate of Cu dissolution which is controlled by diffusion in one step and two step approaches, detected to be controlled by chemical reaction at spent medium. It was shown that for Ni, the rate is controlled by chemical reaction for all the methods studied. Eventually, it was understood that *A. niger* is capable of leaching 100% of Zn, 80.39% of Ni and 85.88% of Cu in 30 days.

1. Introduction

Increase in population, the prompt technological improvements and developments in living standards have proliferated the demand for electrical and electronic equipment such as personal computers (PCs), TVs, MP3 players and cell phones (Awasthi et al., 2017; Iannicelli-Zubiani et al., 2016). Therefore, the increasing uses of electronic devices and diversity of products have boosted the amount of waste electrical and electronic equipment (WEEE) (Gomes et al., 2017). Based on United Nations (UNs) report, the amount of WEEE is going to reach to 50 million tons in 2018 (Gomes et al., 2017). Waste printed circuit boards (WPCBs) constitute 3–5 wt% of the WEEE by weight and are found to be the most important WEEE regarding the environmental restrictions and economic advantages of the valuable metals they contain (Kaya, 2017; Priya and Hait, 2017).

Waste printed circuit boards (WPCBs) consist of valuable metals with purity of more than that of minerals; i.e., 30% ($w.w^{-1}$) Cu, 10–20% ($w.w^{-1}$) Pb, 1–5% Ni ($w.w^{-1}$), 1–3% ($w.w^{-1}$) Fe, 1–3% ($w.w^{-1}$) Ag, 0.05% ($w.w^{-1}$) Au and 0.01% ($w.w^{-1}$) Pd (Kaya, 2017). On the other hand, due to the presence of toxic substances in WPCBs, land filling or incineration may lead to irremediable contaminations in the ecosystem (Cao et al., 2016; Jagannath et al., 2017). Thus, recycling of WPCBs with the target of removing hazardous contents of this waste streams has attracted attentions not only from the perspective of environmental regulations but also economical purpose (Kaya, 2017; Xiang et al., 2010; Zhu et al., 2011).

Bio-hydrometallurgy as an eco-friendly, inexpensive and feasible method has been used to eliminate the WPCBs and dissolve the metal contents of them by producing various organic acids resulting in formation of metal complexes at ambient temperature and pressure (Jagannath et al., 2017; Kim et al., 2016; Mirazimi et al., 2015). Effect of bacteria (*Acidithiobacillus ferrooxidans* (*A.f.*), *Acidithiobacillus thiooxidans* (*A.t.*)) and fungi (*Aspergillus niger* and

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Penicillium simplicissimum) on the recoveries of Cu, Sn, Al, Ni, Pb and Zn from WPCBs has been investigated (Arshadi and Mousavi, 2014; Brandl et al., 1999; Jadhav et al., 2016).

Despite the fact that extensive efforts have been devoted to investigate the effect of different bacteria in recovery of different metal species from WPCBs (Li et al., 2015; Liang et al., 2010), a few researchers have studied the effect of fungi on the recycling of metals from WPCBs. Brandl et al. (1999) investigated the effect of two types of bacteria (*A.f.* and *A.t.*) and fungi (*Aspergillus niger* and *Penicillium simplicissimum*) on the leaching efficiencies of Cu, Sn, Al, Ni, Pb and Zn. Results showed that both fungi are capable of dissolving 60% (w.w^{-1}) of Cu and Sn and 95% (w.w^{-1}) of Al, Ni, Pb and Zn. The tolerable limit of PD was investigated to be equal to 10 g L^{-1} and with further increase in PD, the microorganisms died. As a result, they concluded that the WPCB has certain toxicity to the microorganisms and growing the organisms in the absence of the wastes would lead to higher recoveries. Madrigal-Arias et al. (2015) used (*Aspergillus niger) A. niger* for bioleaching of precious metals from WPCBs obtained from mobile phones and PCs. In this study, fungi were incubated for 14 days in a rotary shaker at 280 rpm and 28 °C with different PD. Based on the results, the tolerable limit of Au for fungal activity was measured to be 50 mg L^{-1} (150 mg L^{-1} and 300 mg L^{-1} Au inhibited fungal growth) and at this condition about 87% (w.w^{-1}) Au, 29% (w.w^{-1}) Cu and 0.8% (w.w^{-1}) Ni could be leached. It was reported that organic acids such as citric acid are responsible for the metal recoveries and the key point of using fungi was its environmentally friendly and cost-effective operations. The weakness of fungi in dissolution of Ni was indicated. Another research using fungi was carried out by Jadhav et al. (2016) which employed a spent medium approach using *A. niger* and H_2O_2 at the same time to increase the bioleaching efficiency of WPCBs. The fungi were grown in sucrose medium for ten days at 120 rpm and 30 °C. The key points of their work were treating the WPCBs with NaOH (0.1 mol L^{-1} for 4–8 h at 150 rpm and 30 °C) prior to bioleaching and using H_2O_2 at leaching step. Based on the results, 100% of Cu, Al, Sn, Pb, B, Fe, Si, Mg, Ti, Ni, Sr, Zn, As, Mn, Co, Cd, Pd, Au and Ag were recovered at optimum condition (PD of 2 g L^{-1}, pretreated by NaOH and leached for 24 h using 100 mL of spent medium and 3.18% H_2O_2). It should be mentioned that using NaOH before bioleaching may lead to the loss of some valuable metals.

Considering aforementioned discussion and based on the lack of sufficient data about fungal bioleaching of WPCBs, a widespread study on the bioleaching of WPCBs using *A. niger* is still required. Accordingly, leaching by bacteria seems to be unlikable due to shortage of energy sources in the WPCBs; considering the fact that bacteria needs mainly iron and sulfur for their metabolisms, there is only little iron and no sulfur in the WPCB; therefore, they should be externally supplied in the case of using bacteria. Furthermore, bacteria needs initial pH adjustment and in some cases prolonged adaptions, which will affect the simplicity of the method. With respect to the fact that fungi has some benefits compared to bacteria; i.e., applicable in a wider range of pH (1.5–9.8) (Xu et al., 2014), quicker leaching rates (Wu and Ting, 2006), producing organic acids, selective metal leaching (Santhiya and Ting, 2006) and economic advantages (Pant et al., 2012), research on the fungal bioleaching as method to eliminate WPCBs is narrowly conducted by most of the researchers. Besides, the weakness of all bioleaching studies is the lack of detailed kinetics investigations.

In this study, recoveries of zinc (Zn), nickel (Ni) and copper (Cu) from WPCBs using *A. niger* as bioleaching agent were investigated to exclude toxic contents of these waste streams. The effect of PD (0.5–20 g L^{-1}) and bioleaching approaches (one step, two step and spent medium) on the recoveries of Zn, Ni and Cu were surveyed. For the first time, bioleaching parameters were optimized using D-optimal Response Surface Methodology (RSM) by means of Design Expert 7.0.0 (State-Ease Inc., Minneapolis, MN, USA) software. Besides, the interactions of the bioleaching parameters were studied and the results were interpreted. Since the kinetic aspects of the fungal bioleaching of WPCBs have not been studied before, the rate controlling mechanisms of the Zn, Ni and Cu dissolution were investigated.

2. Materials and methods

2.1. Approach overview

In this study, effect of two parameters (bioleaching approach and pulp density) on the fungal bioleaching of Zn, Ni and Cu from WPCBs was surveyed. After primary investigations, a set of experiments was designed by means of design expert 7 software, which led to determination of optimum conditions for recoveries of Zn, Ni and Cu. Then, based on the optimum conditions obtained in the previous step, kinetics of fungal bioleaching of Zn, Ni and Cu from WPCBs for all the bioleaching approaches (one step, two step, spent medium) was evaluated.

2.2. Sample preparation

The WPCBs of PCs from different manufacturers were used for this investigation. Primarily, they were cut into small pieces of approximately 5 × 5 cm^2 using bolt cutter, plastic components of the boards, capacitors and batteries were manually removed. Then, they were crushed (Moulinex, 276, France) and ground by a ball mill (planery ball mill, PM2400, Iran) and sieved into finer than 300 μm to prepare a homogeneous mixture. Afterward, to sterilize, the prepared sample was autoclaved at 121 °C for 20 min (Mulligan et al., 2004).

2.3. Analytical methods

To determine the composition of the initial sample, x-ray fluorescence (XRF, ARL 8420) was employed. Table 1 shows the results obtained from XRF analysis. To completely leach the initial sample, 0.5 g of the WPCBs were digested in 10 mL of aqua regia (HCl: HNO_3, 3: 1 ratio) using a hot plate at 60 °C for 2 h. In order to determine the Zn, Ni and Cu contents, the filtrate was analyzed by atomic

Table 1
XRF analysis of WPCB.

Component	Concentration (% w.w^{-1})	Component	Concentration (% w.w^{-1})	Component	Concentration (% w.w^{-1})
Na_2O	0.01	CaO	16.90	ZnO	0.49
MgO	0.54	TiO_2	0.65	Br	2.70
Al_2O_3	17.60	Cr_2O_3	0.03	SnO_2	1.80
SiO_2	39.90	MnO	0.04	Sb_2O_3	0.32
P_2O_5	0.31	Fe_2O_3	3.40	Au	0.02
SO_3	3.20	Co_3O_4	0.05	PbO	1.80
Cl	0.44	NiO	0.20		
K_2O	0.02	CuO	8.90		