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# Enhanced bioleaching of Cr and Ni from a chromium-rich electroplating sludge using the filtrated culture of *Aspergillus niger*

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ABSTRACT

Electroplating sludge is classified by environmental agencies as a hazardous waste, the disposal of which can be a serious environmental concern. In the present study, the recovery of Ni and Cr from chromium-rich electroplating sludge was conducted using the filtrated culture of *Aspergillus niger* for the first time. Pulp density, leaching temperature, and leaching duration were identified as variables affecting the recovery optimization. Leaching temperature of 66 °C, leaching duration of 1 day, and pulp density of 10 g/L were found as the optimal conditions. Under optimum conditions, Cr and Ni recoveries were 53% and 95.7%, respectively. Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure tests showed that electroplating sludge was effectively detoxified by bioleaching. The kinetic studies demonstrated that the leaching proceeded with one stage kinetics for Cr and two stages kinetics for Ni. Cr recovery was controlled by interface transfer and diffusion across the product layer. Also, the first stage of Ni leaching was controlled by interface transfer and diffusion across the product layer, and the second stage of Ni leaching was a mixed-control mechanism and both diffusion through the product layer and chemical reaction were involved. Eventually, the results of this study represent the filtrated culture of *Aspergillus niger* has the ability to recover metals from electroplating sludge and detoxify it.


## 1. Introduction

The heavy metal content of the soil is significantly increasing worldwide due to industrial, mining, agricultural, and domestic activities. These metals are non-biodegradable and consistent environmental contaminants. The toxicity of heavy metals is mainly caused by metals interfering with enzymes and metabolic system inhibition (Bahaloo-Horeh et al., 2018; Ren et al., 2009). Extensively used in the industry, electroplating generates significant amounts of waste, which is mostly in form of wastewater and contains large amounts of chromium, zinc, copper, nickel, cadmium, and other heavy metal ions with high toxicity. This wastewater is treated by chemical precipitation, neutralization, and ion exchange and converted to a slurry, called “electroplating sludge”.

The annual amount of produced electroplating sludge is approximately 150,000 tons in the EU (Magalhães et al., 2005) and nearly 1.3 million wet tons in the U.S. (Li et al., 2010a). More than 100,000 tons of precious heavy metals in form of electroplating sludge are wasted in China per annum (Li et al., 2010a). Moreover, high levels of metals are accumulated in electroplating sludge more significantly than those of ores (Wang et al., 2018; Zhou et al., 2019). The greater source of concern is that the conventional treatment methods of electroplating sludge (e.g., land-filling, ocean-dumping, incineration, stabilization, or solidification) are not appropriate disposal methods, and they may lead to the secondary severe pollution. That is why the electroplating sludge poses extremely harmful threats to human health and is classified as a hazardous waste by environmental agencies (Magalhães et al., 2005; Wang et al., 2018; Zhou et al., 2019). Consequently, due to the massive production of electroplating sludge at the world level, it must be cleaned in terms of economic and environmental viewpoints by recovering the heavy metals.

Currently, electroplating sludge is treated by different technologies such as acid leaching (Li et al., 2010a), immobilization of heavy metals by fixatives (Asavapisit et al., 2005), and bacterial bioleaching (Rastegar et al., 2014). Among these methods, bioleaching has received widespread attention over other similar methods because of its attractive features (Muddanna and Baral, 2019). Low cost and energy consumption, environmental friendliness, operational simplicity, and proper recovery are among the features that make bioleaching a green and desirable process (Naseri et al., 2019). Bioleaching is a bio-hydrometallurgical process based on microorganisms’ ability to convert insoluble solid materials into soluble and extractable elements. Bacteria and fungi are

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the pioneering microorganisms, widely used and studied by different cellular and chemical mechanisms for bioleaching from various sources (Bahaloo-Horeh and Mousavi, 2017; Biswas et al., 2013).

*Aspergillus niger* is one of bioleaching's most commonly used fungi. It is used in organic acid productions such as citric acid, oxalic acid, and gluconic acid. These biogenic organic acids are the most critical lixiviants for leaching of heavy metals from minerals and solid wastes (Biswas et al., 2013; Muddanna and Baral, 2019; Ren et al., 2009). One of the appealing advantages of the organic acids as leaching agents is that the recovery can occur in gently acidic conditions (pH 3–5). Moreover, microorganisms emit organic acids with low molecular weight in soil and plant phytosphere in natural ecosystems, thus these acids are biodegradable (Ousmanova and Parker, 2007). Unlike inorganic acids, organic acids are less toxic to most natural species due to complexing capacity of organic acids, which reduces the toxic metal concentrations. Besides, these biogenic organic acids produced by microorganisms are less harmful to the environment than synthetic lixiviants (Muddanna and Baral, 2019). The organic acid chemical synthesis is not effective because of the costly raw materials and complex methods with low yields. Unlike the chemical processes, the microbiological synthesis is a more elegant method with fewer overheads (Bahaloo-Horeh and Mousavi, 2017).

Bioleaching of heavy metals can be conducted in two methods: 1) the waste is added to the medium containing fungi, and they are in direct contact and 2) the fungi are allowed to generate organic acids to the highest amount that is attainable and filtrated. Then, the solid waste is added to the fungal filtrated culture which is considered to be desirable for industrial use. In the fungal filtrated culture method, the solid waste is not contaminated by microbial biomass, and also the fungi can be recycled. In addition, in the absence of waste, the fermentation process can be individually optimized. And in the absence of microbes and cell wall harm due to toxicity of waste, there is no constraint for exerting the high pulp densities. Thus, higher pulp densities can be achieved as compared to bioleaching in the presence of fungi (Rasoulnia and Mousavi, 2016).

However, no reports are available on the use of fungal filtrated culture for remediation of metals from electroplating sludge, and most bioleaching studies have only focused on the bacterial bioleaching. Therefore, this study was planned to explore the potential of biogenic organic acids of *A. niger* filtrated culture for the solubilization of metals from electroplating sludge. The present study investigated the simultaneous recovery of Cr and Ni from electroplating sludge via fungal filtrated culture of *A. niger*. The main drawback of bioleaching is its slow kinetics (Muddanna and Baral, 2019). With this in mind, we attempted to minimize the bioleaching duration and maximize the Cr and Ni recoveries while considering the leaching temperature, pulp density, and bioleaching duration as input variables in the design of experiments (DOE). Therefore, the optimization was conducted via the central composite design of response surface methodology (CCD-RSM). Moreover, the toxicity of electroplating sludge was evaluated before and after bioleaching. Finally, a kinetic study was undertaken to define the leaching process rate-controlling step.

## 2. Materials and methods

### 2.1. Electroplating sludge preparation

For this study, the electroplating sludge was sampled from Baragh Metal-plating Industries located at Tehran, Iran. The sludge was air-dried at room temperature before using. The prepared powder was ground and then sieved by vibrator shifter with mesh 200 to obtain a homologous mixture with particle size less than 75 μm employed for all following tests. Prior to each test, the electroplating sludge was autoclaved at 121 °C for 15 min.

### 2.2. Characterization of the electroplating sludge

Chemical digestion and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) were used to analyze the elemental composition. In this regard, 0.2 g of sample was added to the platinum crucible containing 1 g of the mixture of $LiBO_2$ and $Li_2B_4O_7$ and heated to 1000 °C for 1 h. Then, the melted material was dissolved in 100 mL of 5 wt% $HNO_3$ solution. This solution was then analyzed using ICP-OES. Multi-element standard (Merck) was used for calibration standards of ICP-OES. Also, the initial pH value of the sludge sample was determined (the details are reported in Supplementary Information (S1)).

Table S1 shows the result of the metal content. As seen, the concentrations of Cr and Ni in electroplating sludge are high. As for their environmental pollution and economic interest (9000 $/ton for Cr and 14000 $/ton for Ni (Survey, 2018)), the recovery of Cr and Ni is the principal purpose of this study.

The phase structure of electroplating sludge was determined by X-ray diffraction (XRD) analysis (Fig. S1).

### 2.3. Microorganism and preparation of spore suspension

*A. niger* (PTCC 5010) was obtained from the Iranian Research Organization for Science and Technology (IROST) in Tehran, Iran. The fungus was cultivated on 39 g/L potato dextrose agar (PDA) plates at 30 °C. Spores were washed from one-week-old cultures using sterile distilled water. To prepare suitable spores suspension (nearly $10^7$ spores/mL), the spores were numbered under a phase-contrast microscope (Standard 25, Zeiss, Germany) using a Neubauer counting chamber (depth of 0.1 mm and an area of 0.0025 $mm^2$).

#### 2.3.1. Selection of suitable culture medium for A. niger strain

To select an appropriate culture medium for *A. niger*, four culture media (PDB, Bosshard, Czapek dox broth, and modified Czapek dox broth) were studied. The composition of each culture medium was propounded in Table S2. To assess pH change, each culture medium was inoculated with 1 mL of spore suspension/100 mL of medium and incubated in a shaker (30 ± 1 °C, 130 rpm) for 11 days. Before inoculation, the sucrose medium was autoclaved at 121 °C for 15 min. The pH of each culture medium was measured daily until the $11^{th}$ day.

#### 2.3.2. A. niger pure culture

In order to define the growth characteristics of *A. niger* and obtain fungal filtrated culture with the maximum amount of organic acids, the measuring of pH, organic acid concentration, and dry weight biomass were monitored in regular time intervals within 25 days. To this end, 1 mL of spore suspension was added to 100 mL medium culture in 250 mL Erlenmeyer flasks and was shaken at 30 °C and 130 rpm. Furthermore, in the defined days, the medium was filtered through a 0.2 μm Whatman filter paper, and the residue was used to calculate the dry weight biomass. Also, the filtrate pH and organic acid concentrations excreted by fungi were measured. During the process, the amount of evaporated water was being expiated by measuring the weight of Erlenmeyer flasks and adding sterile distilled water. To analyze the organic acid concentration in the filtrate, High-Performance Liquid Chromatography (HPLC) was used. After appointing the day when acid production is highest, the culture medium was filtered via a filter press, through 0.2 μm Whatman filter paper in order to supply fungal filtrated culture for employing in subsequent bioleaching experiments.

### 2.4. Bioleaching experiment

Bioleaching tests were accomplished in batch mode. In all experiments, the desired amount of electroplating sludge (g) was added to 250 mL Erlenmeyer flasks containing 100 mL prepared fungal filtrated culture and incubated in desired temperature and duration at 160 rpm. The amounts of the pulp density (10–50 g/L), leaching temperature (30–70 °C), and bioleaching duration (1–13 day) were specified by DOE for each experimental test. Metals released during incubation were measured using ICP-OES after the sample was filtered to remove solid material.

### 2.5. Toxicity tests

Different testing procedures have been recommended and accomplished by various regulatory agencies to evaluate the toxicity of waste. In the United States of America, the Environmental Protection Agency (USEPA) has suggested Toxicity Characteristic Leaching Procedure (TCLP) (Fallis, 1992) and Synthetic Precipitation Leaching Procedure (SPLP) (US EPA, 1994). TCLP test mimics the waste under landfilled conditions, and SPLP simulates the effect of rainfall on leaching of waste if landfilled under laboratory test conditions. In the TCLP analysis, the electroplating sludge before and after the bioleaching was mixed in 1:20 solid-to-liquid ratio with a sodium acetate-acetic acid buffer solution and placed in a shaker for 18 h at 30 rpm. The SPLP analysis is similar to TCLP; however, the extraction fluid is replaced with nitric/sulfuric acid mixture. These two methods were selected to study the toxicity of electroplating sludge before and after bioleaching and then compare with their regulatory limits in each test to categorize wastes as hazardous or not.

### 2.6. Apparatus

An orbital shaker-incubator (Wise Cube, South Korea) was used to fix the temperature and rotating speed during the bioleaching process. The dissolved concentrations of both Cr and Ni were analyzed using ICP-OES (Spectro Arcos, Germany). The evaluation of organic acid concentration spattered in the medium was conducted using HPLC (Agilent Technologies, USA). The method of measurement was reported in Supplementary Information (S3). To monitor the pH variations of medium, a digital multi-meter (CP-500L, ISTEK, Korea) was used. The crystal mineralogical composition of the electroplating sludge was indicated by XRD (X'Pert MPD, Philips, and Netherland) with Co Kα radiation. The applied tube voltage was 40 kV with a tube current of 40 mA. The powder was scanned from 5 to 90° range using a 0.02° step size. To demonstrate chemical structure, functional groups, and bonds of electroplating sludge, the Fourier transform infrared spectroscopy (FTIR) (Perkins-Elmer; USA) was applied. FTIR tests were performed at room temperature within the range of 400–4000 $cm^{-1}$. Samples were prepared by pressing the mixture of electroplating sludge and KBr powders. The variation in surface morphology and elemental distribution of electroplating sludge particles before and after the process was assessed by Field Emission Scanning Electron Microscope (FESEM) working at 30 kV and mapping analysis (TESCAN MIRA3, Czech Republic), respectively. The sample was placed on adhesive carbon tubes and then covered with a 30 nm gold film. Brunauer–Emmett–Teller (BET) analysis (Belsorp-mini, BEL Japan Inc.) was used to differentiate the variation of electroplating sludge surface area before and after bioleaching. Before performing BET tests, the samples were degassed at 150 °C for 5h and then cooled to room temperature. Filtration of fungal culture medium in order to prepare fungal filtrated culture was performed with filter press, including pressure vessel (Sartorius, SM 17530) and pressure filter holder (Sartorius, Type 16275).

### 2.7. DOE and optimization

Response surface method (RSM) consists of a set of mathematical and statistical techniques to investigate the dependence of the response on factors, evaluate the multiple factors, and determine the optimal response. A famous second-degree model is commonly used in RSM to the related response of interest and associated control variables:

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

Where Y is the predicted response, $X_i$ and $X_j$ are input variables, $\beta_0$ is the constant coefficient, $\beta_i$ is the linear coefficients, $\beta_{ii}$ is the quadratic coefficients, $\beta_{ij}$ is the interaction coefficients, K is the number of factors studied and optimized in the experiments, and ε is the random error (Khuri and Mukhopadhyay, 2010). In this study, CCD was employed to study and optimize the process variables. CCD is the most common design used in RSM, which can fit a full quadratic model. CCD consists of three parts: 1) $2^k$ factorial design whose factors' levels are coded as −1 and 1, 2) Axial part, which consists of 2k points. Two points were selected for each factor at a distance of α from the center and 3) $c_p$ center points. Therefore, the total number of experiments was calculated by $2^k + 2k + c_p$ (Khuri and Mukhopadhyay, 2010).

Many factors affect the recovery rate of metals from waste. The maximum metal recovery may be attained when some of these parameters are considered and optimized. In the present study, temperature, pulp density, and bioleaching duration were optimized as independent factors to probe their relative or interactive effects on the Cr and Ni recoveries as the responses and to obtain maximum recovery of both metals. These three independent factors were analyzed, 18 tests were generated for them (including four replicates of the central point). Besides, the α value was considered 2. The software Design-Expert (version 11.1.0.1) was employed to design and analyze the experiments. The levels of the factors are reported in Table S3. It should be noted since organic acids, and different fungal metabolites would decompose at temperature upper than 80 °C, all tests were conducted below 80 °C (Biswas et al., 2013).

## 3. Results and discussion

### 3.1. Selection of suitable culture medium for A. niger strain

The most suitable medium for the bioleaching process is the medium with the highest concentration of acid production. From Fig. 1, in PDB and modified-Czapek dox broth, pH goes up during 11 days incubation. This increase represents the inability of *A. niger* to produce organic acids in these media and the secretion of intracellular metabolites with an alkaline buffer origin (Bahaloo-Horeh et al., 2016). However, the pH has a downward trend in Czapek dox broth and Bosshard. The considerable pH reduction is for Czapek dox broth, which decreases from 7.1 to 2.1.

Furthermore, the titration of 20 mL filtered culture of each medium was conducted using 0.1 N NaOH and phenolphthalein as an indicator at the end of the $11^{th}$ day. The amounts of consumed NaOH were 16, 0.8, negligible, and 14 mL for Czapek dox broth, modified Czapek dox broth, PDB, and Bosshard, respectively. As seen, the most significant quantity of NaOH was consumed by Czapek dox broth. So, the Czapek dox broth was selected as the optimum culture medium for *A. niger* and used in the next steps.

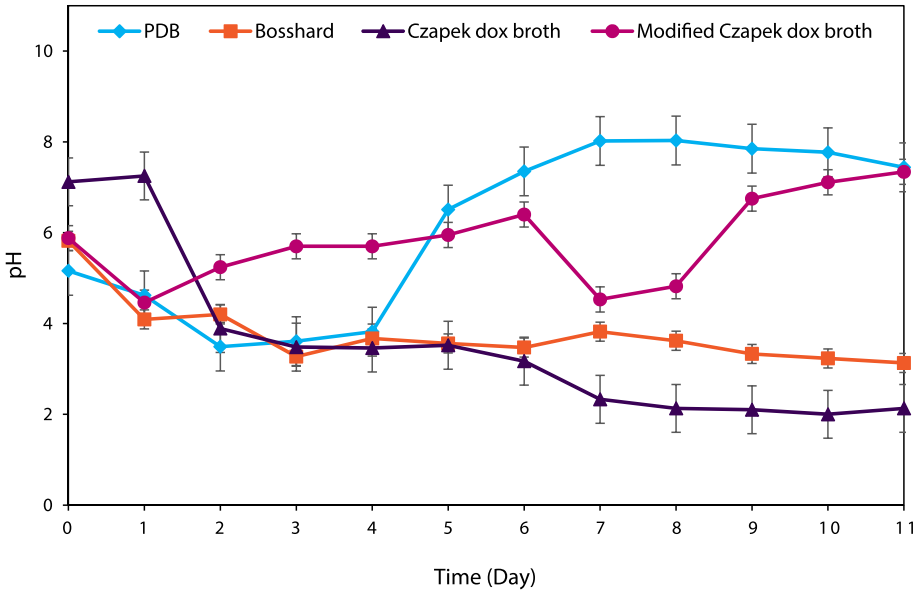


**Fig. 1.** Variations of pH with time for PDB, Bosshard, Czapek dox broth, and modified Czapek dox broth culture media.

### 3.2. Determination of growth characteristics and acid production

Fig. 2 shows the changes in pH, biomass dry weight, and the amount of organic acid secreted by *A. niger* during 25 days. After 3 days of fungal growth, the abrupt increase in biomass dry weight from 0.9 to 4.8 g/L and sudden decrease in pH from 6.7 to 4, represent the entry of fungi to logarithmic growth phase and the release of organic acids (oxalic acid, citric acid, gluconic acid, and malic acid), especially oxalic acid. Generally, during 25 days of *A. niger* growth, the highest amount of organic acid production is related to oxalic acid. The concentration of the carbon source is an important parameter in the type of organic acid production. In this work, the low sucrose concentration (30 g/L) resulted in an increased production of oxalic acid. In low levels of carbon source, the amount of citric acid production decreases, and oxalic acid production increases (Bahaloo-Horeh and Mousavi, 2017). It has been reported that sugar concentrations between 100 and 140 g/L are suitable conditions to produce citric acid which is not produced in concentrations below 25 g/L (Xu et al., 1989).

Oxalic acid can be produced over three various pathways in *A. niger* (Fig. 3): (1) The cytoplasmic pathway; (2) TCA (Krebs) cycle; and (3) the glyoxylate cycle. In case of cytoplasmic pathway, cytosolic oxaloacetate is hydrolyzed to oxalate and acetate by oxaloacetate hydrolase. This pathway is the established route of oxalate biosynthesis on glucose as a carbon source. In case of the TCA and glyoxylate pathways, pyruvate is first oxidized into acetyl-CoA. For the TCA pathway, which occurs in the mitochondria, oxalic acid is produced through the cleavage of oxaloacetate by the oxaloacetate hydrolase, as in the cytoplasmic pathway. The glyoxylate pathway occurs in glyoxysomes when citrate is used as the carbon source. In this case, oxalic acid is produced through glyoxylate oxidation. Oxalate is produced via hydrolysis of citrate into glyoxylate by the glyoxylate dehydrogenase (Palmieri et al., 2019).

Another significant parameter in the production of oxalic acid is pH. It has been reported that oxalate production is induced by *de novo* near neutral pH. At this pH, the concentration of intracellular oxaloacetate increases, which in turn induces oxaloacetate hydrolase enzyme (Bahaloo-Horeh et al., 2016).

The maximum concentration of acid production occurred on the 14$^{th}$ day, equivalent to 12600 mg/L oxalic acid, and the amount of other organic acids is negligible. Hence, the 14$^{th}$ day is proper for the preparation of fungal filtrated culture. In the following days, due to reduced nutrients and consequently reduced fungal growth, as well as the possibility of acid intake by the microorganism, and the reaction or conversion to other metabolites in the culture medium, the amount of acid in the culture medium reduced (Hassan et al., 2015).

### 3.3. DOE and optimization

The experiments, which proposed by CCD and the responses are listed in Table S4. Applying CCD, the following second-order quadratic model was generated for both the Cr and Ni recovery. The coded factors are represented in Eqs. (2) and (3), where Y is the predicted recovery of metals as the response. A, B, and C show the temperature (°C), pulp density (g/L), and bioleaching duration (day), respectively.

$$Y_{Cr\%} = 14.27 + 1.14A - 10.70B + 1.38C - 0.0862AB + 0.0263AC - 1.07BC - 0.77A^2 + 3.72B^2 - 0.41C^2 \quad (2)$$

$$Y_{Ni\%} = 68.33 + 6.19A - 9.45B + 5.34C - 4.26AB + 0.0875AC - 2.39BC - 1.23A^2 + 1.65B^2 + 1.42C^2 \quad (3)$$

According to the equations, pulp density (B) with the highest coefficient has a profound effect on the recovery of Cr and Ni. The negative sign in the pulp density coefficient illustrates that the level of recovery increases. It is also understood that both temperature (A) and bioleaching duration (C) have a positive effect on the recoveries of both metals but they have a more intensive impact in Ni recovery of electroplating sludge.

The values obtained from experiments and empirical models were compared and data is reported in Fig. S2.

The analysis of variance (ANOVA) was applied to define the competency and statistical significance of the model (Tables S5 and S6). These results help us judge the satisfaction of the model. The results and discussions are indicated in Supplementary Information (S5).

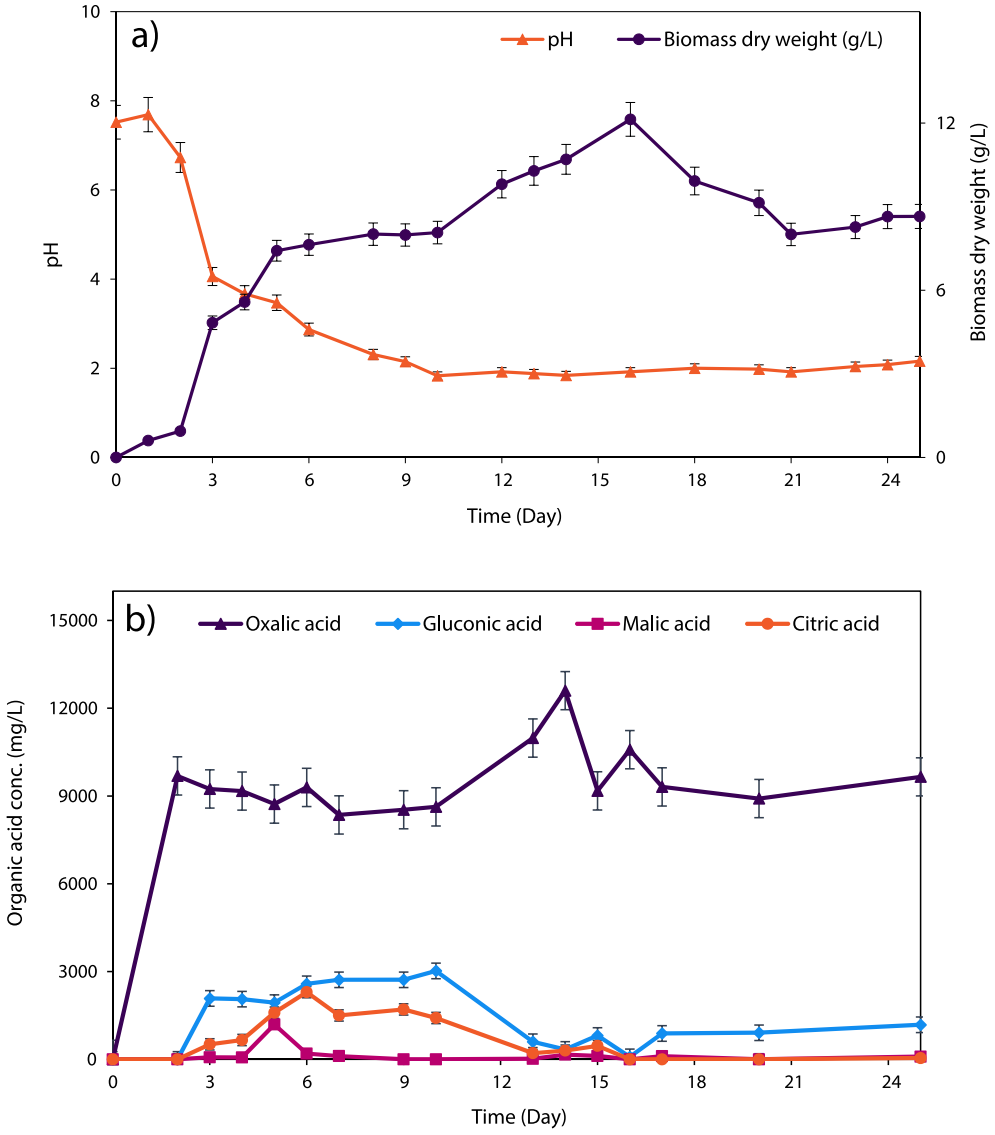


**Fig. 2.** Changes in (a) fungal dry weight and pH and (b) concentration of organic acids over time for *A. niger* pure culture.

### 3.3.1. Cr recovery graphs

Fig. 4(a, b, and c) represents the effects of pulp density and temperature on Cr recovery at bioleaching durations of 1, 7, and 13 days. As seen, at a constant bioleaching duration, the recovery of Cr declines as pulp density increases and temperature decreases. At higher pulp densities, the recovery is not affected by temperature. As predicted by the Cr model, the negative impact of rising pulp density is much greater than the positive effect of temperature rise. The decrease in recovery with increasing pulp density has also been reported by Ting (Wu and Ting, 2006) and Amiri (Amiri et al., 2011). Adding electroplating sludge to the fungal filtrated culture, containing a fixed amount of organic acids, reduces the availability of metal oxides to organic acids following a decrease in the formation of ionic and hydrogen bonds and Van der Waals forces. Therefore, this reduction results in a decrease in the formation of metal-acid complexes and the recovery efficiency from electroplating sludge (Biswas et al., 2013; Biswas and Bhattacharjee, 2014). Increasing the bioleaching duration from 1 day to 7 days causes a change in the maximum recovery of Cr and its region. The recovery almost becomes independent of temperature as bioleaching duration increases to 13 days (Fig. 4(c)). In this case, the duration is long enough for the reaction to occur and the effect of temperature is covered.

Fig. S3 (a, b, and c) presents the effects of bioleaching duration and pulp density on Cr recovery at 30, 50, and 70 °C. As can be seen from Fig.s3 (a and b), with increasing the temperature from 30 °C to 50 °C at 10 g/L pulp density and 7 days bioleaching duration, the Cr recovery increases from 42% to 50%. However, changing the temperature from 50 °C to 70 °C (Fig. S3 (c)) does not have a significant effect on Cr recovery at similar conditions. At high temperatures (50 and 70 °C), the Cr recovery is independent of changes in temperature.

### 3.3.2. Ni recovery graphs

Fig. S3 (d, e, and f) represents the effects of bioleaching duration and pulp density on Ni recovery at different constant temperatures. As shown in Fig. S3 (d), Ni recovery is 79% at 30 °C, pulp density of 10 g/L, and duration of 13 days. Increasing temperature from 30 °C to 50 °C (Fig. S3 (e)), in the same conditions (13 days and 10 g/L), increases the Ni recovery to 100%. At a temperature of 70 °C (Fig. S3 (f)), Ni recovery was 100% at 10 g/L pulp density and 1 day duration. Evidently, at high temperatures, Ni recovery is relatively

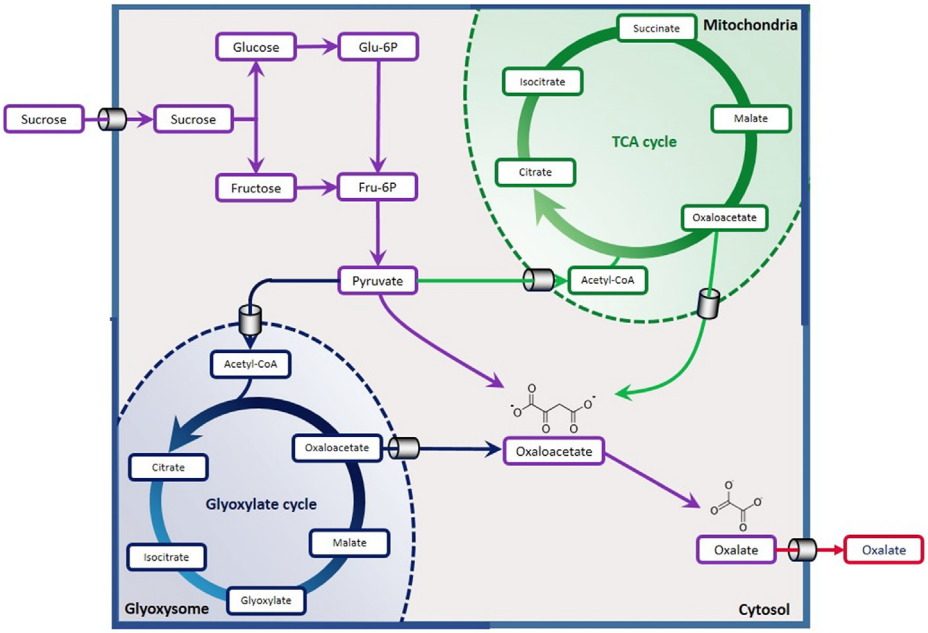


**Fig. 3.** Oxalic acid pathway in *A. niger*.

independent of bioleaching duration and maximum recovery obtains on the first day. This suggests that Ni recovery is strongly dependent on temperature, rather than bioleaching duration.

The enhanced dissolution of metals, which occurs at elevated temperatures, is due to an increasing transfer of the reactants to the interface of the heterogeneous reaction sites, which results in high diffusion of constituent components (Biswas et al., 2013). Similar results have also been reported for the effect of temperature on metal recovery by Jadhav (Jadhav et al., 2016) and Li (Li et al., 2010b). According to their results, at high temperatures, acid dissociation is an endothermic reaction and releases more hydrogen ions in solution, which increases the rate of leaching.

Fig. 4(d and e, and f) indicates the effects of temperature and pulp density on Ni recovery at bioleaching durations of 1, 7, and 13 days. As can be seen in Fig. 4(d), it is possible to achieve the recovery of 95% at 65 °C and pulp density of 10 g/L in the bioleaching duration of 1 day. In other words, the maximum recovery of Ni can be obtained in the shortest durations at elevated temperatures, which again verifies the endothermic nature of the current process (Asghari and Mousavi, 2014). With increasing bioleaching duration from 1 day to 7 and 13 days (at a pulp density of 10 g/L), we can achieve 95% recovery at 50 °C and 40 °C, respectively.

### 3.3.3. Optimum condition and confirmation test

As was noted, bioleaching suffers from long leaching duration. Thus, the main purpose of this optimization is achieving maximum recovery of both Cr and Ni from electroplating sludge simultaneously at the minimum bioleaching duration. In these circumstances, the statistical models suggest a temperature of 66 °C, pulp density of 10 g/L, and minimum leaching duration of 1 day as the optimum conditions that lead to maximum recoveries of Cr (53%) and Ni (95.7%). Under these conditions, the model demonstrates prediction values, low and high 95% confidence intervals (CI) (see Table 1). Two experiments were conducted in optimal conditions to clarify the results of the model prediction. The data is illustrated in Table 1. The validity of the model is assessed and confirmed by comparing experimental values with low and high confidence intervals.

### 3.3.4. Comparison of the performance of this work to other leaching approaches

As can be seen in Table 2, the significant content of Cr (279400 mg/kg) in electroplating sludge and high recovery of both metals, distinguish the present work from the rest. Although some studies have been worked on electroplating sludge at high pulp densities, the total amount of Cr in their waste was lower than the total amount of Cr in the optimum pulp density used in this study. As mentioned, the main disadvantage of bioleaching in comparison to chemical leaching is its slow kinetics and a long time to reach maximum metals recovery. As can be seen evidently, the bioleaching duration in this work reduced dramatically (1 day) in comparison with other bioleaching processes. Certainly, when compared to chemical leaching processes performed with strong inorganic acids such as sulfuric acid, the leaching time obtained in this work is higher. However, the application of bioleaching with biogenic organic acid produced by *A. niger* still appeared promising. Because unlike the inorganic acids that damage the environment, organic acids are less toxic and no further downstream processing may be required before disposal.

## 3.4. FESEM, mapping analysis, FTIR, and BET assessment before and after bioleaching

To examine how the bioleaching progresses in terms of appearance, the changes on particle surfaces were investigated before and after the bioleaching process under optimal conditions. Photomicrographs of electroplating sludge are represented at 5 μm magnification in Fig. 5.

When the great proportion of solid is a soluble part of that, the perfect erosion of solid particles can take place (Calgaro et al., 2015). Therefore, high recovery of metals from electroplating sludge may cause extreme erosion of the primary structure, increase in porosity, and the formation of rough surfaces. This phenomenon creates new surfaces for the reaction (Naseri et al., 2019) and indicates the effective activity of the fungal metabolic, especially oxalic acid.

Also, as shown in Table 3, BET analysis demonstrates that there

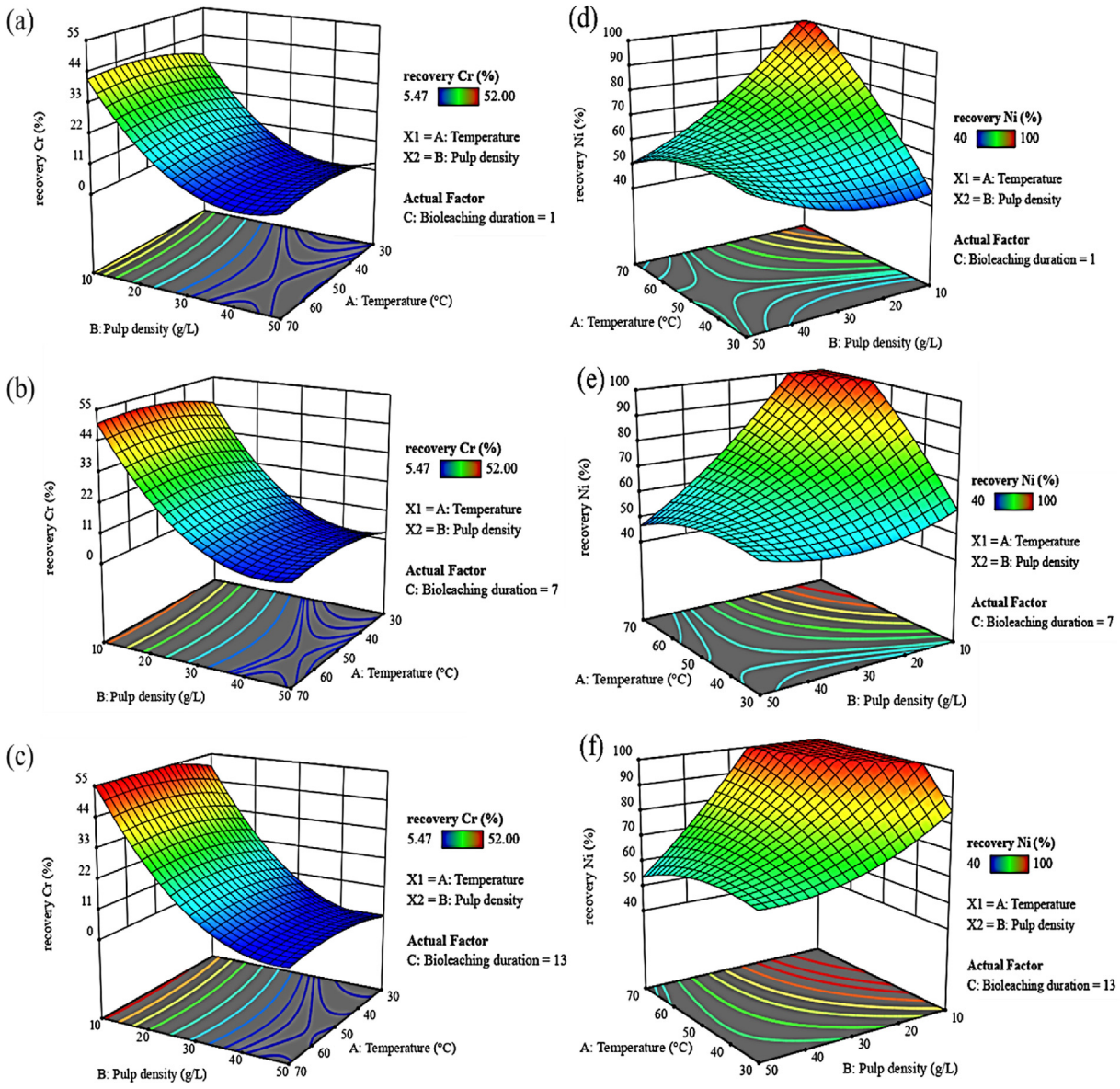


**Fig. 4.** Effect of temperature and pulp density at bioleaching durations of (a) 1, (b) 7, and (c) 13 days for Cr recovery, and at bioleaching durations of (d) 1, (e) 7, and (f) 13 for Ni recovery.

**Table 1**
The optimal conditions and confirmation results.

| Response | Purpose | Prediction (%) | 95% CI low | 95% CI high | Confirmation test (%) |
|---|---|---|---|---|---|
| Cr recovery | maximize | 45.9 | 31.1 | 52.8 | 53 |
| Ni recovery | maximize | 99.7 | 76.9 | 121.8 | 95.7 |

was a change in the specific surface area (48.688–67.053 $m^2/g$), pore size (32.97–27.741 nm), and pore volume (0.4013–0.465 $cm^3/g$) through the bioleaching process. The data indicate an increase in porosity of electroplating sludge after bioleaching, and confirm the results were obtained from SEM analysis.

Mapping analysis was displayed in Fig. 5 ($b_1$ and $c_1$). From this figure, it can be seen that the distribution of both metals decreases through the bioleaching process. So, it has been found that fungal filtrated culture can successfully extract Cr and Ni from electroplating sludge and confirm the previous results.

Moreover, as shown in Fig. S4, FTIR was employed to identify the existence, nonexistence, and the type of chemical bonding for electroplating sludge before and after bioleaching. The results and discussions are provided in Supplementary Information (S6).

### 3.5. Prediction of environmental implication by toxicity tests

The TCLP and SPLP tests were carried out to assess the potential risk of electroplating sludge before and after bioleaching. According to results (Fig. 6), it is evident that the concentration of Cr and Ni in

**Table 2**
Comparison of metal recoveries from electroplating sludge and process conditions in this study with other published studies.

| Leaching type | Leaching agent | Content of raw sludge (mg/kg) | Pulp density (g/L) | Time | Metals recovery | Reference |
|---|---|---|---|---|---|---|
| Bioleaching | *Acidithiobacillus ferrooxidans* | Ni: 20160 | 10 | 20 day | Ni: 84.4% | Prabhu and Baskar (2015) |
| Bioleaching | *Acidithiobacillus ferrooxidans* | Cr: 212<br>Ni: 729 | 20 | 20 day | Ni: 93%<br>Cr: 34% | Bayat and Sari (2010) |
| Bioleaching | *Acidithiobacillus ferrooxidans* | Cr: 290000<br>Ni: 2000 | 9 | 7 day | Cr: 55.6%<br>Ni: 58.2% | Rastegar et al. (2014) |
| Chemical leaching | Sulfuric acid | Cr: 29000<br>Ni: 26000 | 4 | 40 min | Cr: Ni: 97.6% | Ozdemir and Piskin (2011) |
| Bioleaching | *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans* | Cr: 80740<br>Ni: 37340 | 1.5 | 7 day | Cr: negligible<br>Ni: 40% | Yan et al. (2008) |
| Bioleaching | Microbial mixture | Cr:17900<br>Ni: 8000 | 150 | 1 day | Cr: 90.3%<br>Ni: >95.6% | Zhang et al. (2020) |
| Combination of chemical leaching and bioleaching | *Acidithiobacillus ferrooxidans*, sulfuric acid | Cr: 155000<br>Ni: 8500 | 80 | 9 h (acid leaching) + 60 h (bioleaching) | Cr: 80.9% and Ni: 65.8% (with acid leaching) + 6.0% Cr and 11.7% Ni (additional extraction by bioleaching) | Wu et al. (2020) |
| Chemical leaching | Sulfuric acid | Cr: 154800<br>Ni: 8846 | 80 | 24 h | Cr: 97.4%<br>Ni: 75.6% | Wu et al. (2019) |
| Bioleaching | *A. niger* | Cr: 279400<br>Ni: 1900 | 10 | 1 day | Cr: 53%<br>Ni: 95.7% | This study |

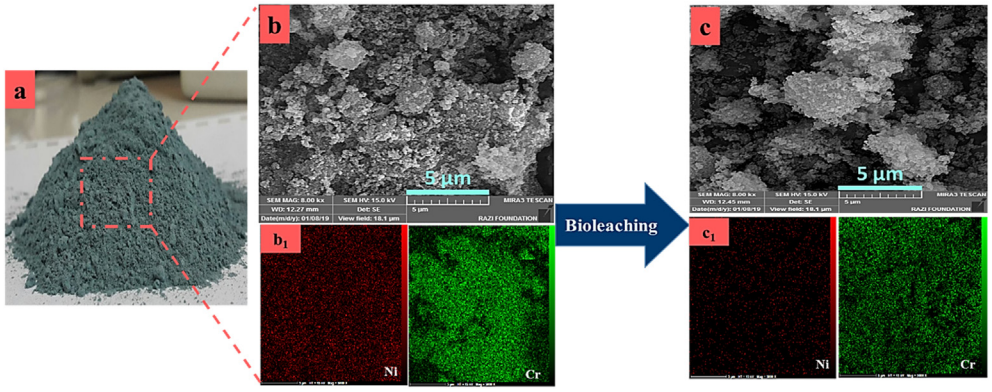


**Fig. 5.** The (a) camera image, (b) SEM image, and ($b_1$) mapping analysis of electroplating sludge before bioleaching; (c) SEM image and ($c_1$) mapping analysis of electroplating sludge after bioleaching.

**Table 3**
BET analysis of electroplating sludge before and after bioleaching.

| | Surface area ($m^2/g$) | Pore size (nm) | Total pore volume ($cm^3/g$) |
|---|---|---|---|
| Before bioleaching | 48.688 | 32.97 | 0.4013 |
| After bioleaching | 67.053 | 27.741 | 0.465 |

two tests of raw electroplating sludge was up to regulatory levels. On the contrary, the concentration of both metals in solid residue after bioleaching treatment was reduced to the well below the threshold limits and meets the limit value that is accepted for landfill or can be reused in construction material safely. It could be concluded that the Cr and Ni remaining in the solid residue have an unleachable form and could not be released by fungal filtrated culture under the mentioned condition. Therefore, it is noteworthy that the fungal filtrated culture of *A. niger* can successfully detoxify the electroplating sludge.

### 3.6. Kinetic study

To define the kinetic mechanisms of Ni and Cr dissolution from electroplating sludge, the reacted fractions of metals are plotted versus time and linearized for different models at optimal conditions of 66 °C and 10 g/L pulp density during 1 day. The best provided-fit across models for the selected data will be selected as the rate-controlling step based on $R^2$ values.

In this work the shrinking core model, the stochastic model, and modified-shrinking core are investigated and introduced in Supplementary Information (S7). All of these models are presented in Table 4.

Fig. 7 outlines the Cr and Ni recovery versus time in 1 day. It is clear that the leaching of Cr completes gently until t = 12 h and remains static until the end of the process. Therefore, it ratifies that the whole leaching process is controlled by a solitary mechanism. The conversion of Cr(x) was plotted versus time for Eqs. (4)–(8)

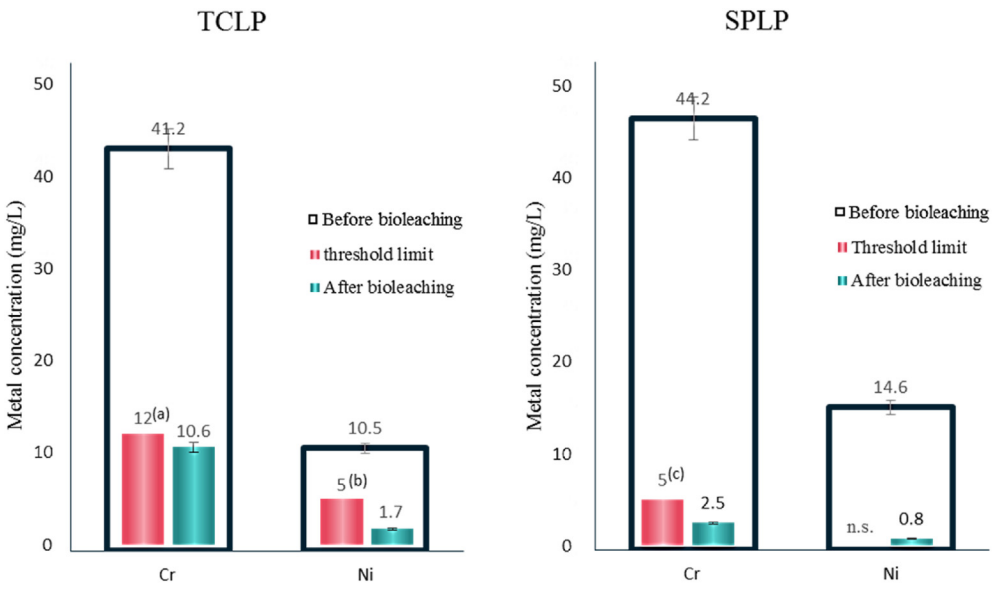


**Fig. 6.** Results of TCLP and SPLP tests for electroplating sludge before and after bioleaching.

(presented in Table 4) to estimate the mechanism of the reaction.

According to Ni recovery at different times (Fig. 7), there is a marked drop in the slope and notable different leaching rates, suggesting that there may be a change in a mechanism. Furthermore, testing a single equation on the experimental data for the whole of the leaching period failed to provide a uniform trend and revealed sharp changes after t = 5 h. This would appear to indicate that a single mechanism cannot explain the kinetic behavior of the whole leaching process. Thus, it can be reasonably assumed that the Ni leaching kinetics is a two-stage process. Based on Fig. 7, the first stage occurs before t = 5 h and the second stage after t = 5 h. Consequently, the different models should be separately evaluated for the divided stages.

It should be noted that in Eqs. (4)–(8), the part which is a function of x is calculated and plotted versus time for the first stage of the leaching process. It is worthwhile noting that these equations are the solved forms of the differential equations with the initial condition of x = 0 at t = 0. The data for the second stage does not

**Table 4**
Kinetics models proposed for electroplating sludge dissolution.

| Model ($x = 0$ **at** $t = 0$) | Eq. no. | Controlling step |
|---|---|---|
| **Shrinking core model** | | |
| $kt = x$ | 4 | Diffusion through liquid film |
| $kt = 1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)$ | 5 | Diffusion through ash layer |
| $kt = 1 - (1-x)^{\frac{1}{3}}$ | 6 | Chemical reaction |
| **Modified shrinking core model** | | |
| $kt = \left(\frac{1}{(1-x)^{\frac{1}{3}}} - 1\right) + \frac{1}{3}\ln(1-x)$ | 7 | Interface transfer and diffusion across the product layer |
| **Stochastic model** | | |
| $kt = (1-x)^{-2/3} - 1$ | 8 | Chemical reaction control |
| **Model ($x = x_1$ at $t = t_1$)** | **Eq. no.** | **Controlling step** |
| **Shrinking core model** | | |
| $k(t - t_1) = x - x_1$ | 9 | Diffusion through liquid film |
| $k(t - t_1) = 1 - 3\left(\frac{1-x}{1-x_1}\right)^{\frac{2}{3}} + 2\left(1 - (1-x_1)^{\frac{1}{3}}(x - x_1)\right)$ | 10 | Diffusion through ash layer |
| $k(t - t_1) = 1 - \left(\frac{1-x}{1-x_1}\right)^{\frac{1}{3}}$ | 11 | Chemical reaction |
| **Modified shrinking core model** | | |
| $k(t - t_1) = \left((1-x)^{-\frac{1}{3}} - (1-x_1)^{\frac{-1}{3}}\right) + \frac{1}{3}\ln\left(\frac{1-x}{1-x_1}\right)$ | 12 | Interface transfer and diffusion across the product layer |
| **Stochastic model** | | |
| | 13 | Chemical reaction control |

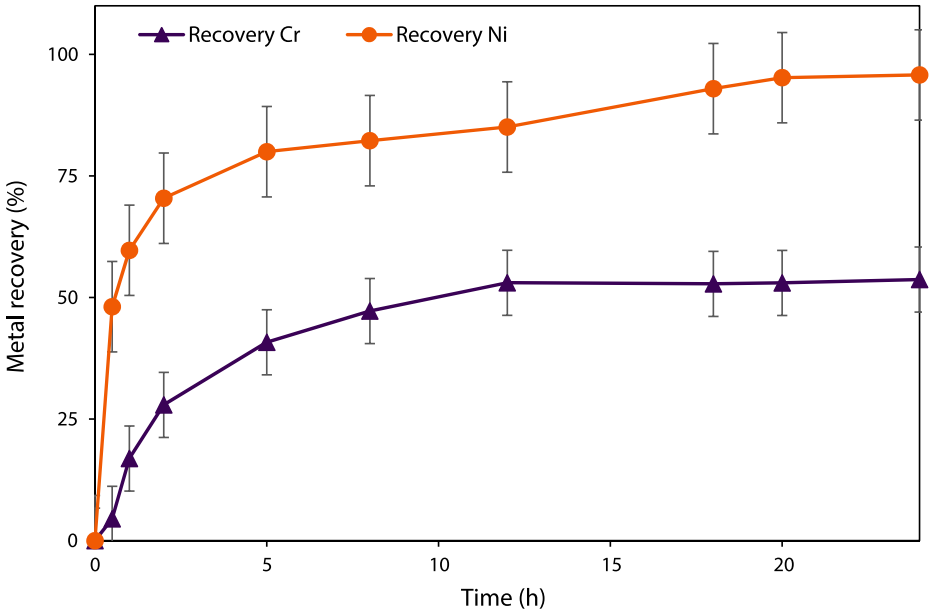


**Fig. 7.** Metals recovery versus time at 66 °C and pulp density of 10 g/L for 24 h.

satisfy this condition. The second stage begins from t = 5 h rather than t = 0, and conversion is not zero and its value from Fig. 7 should be considered as the initial condition. Hence, the initial condition should be adjusted for the second stage data set and the primary differential equation should be resolved to satisfy the new initial condition. To present a general form of these equations with the general initial condition, the primary differential equations are resolved analytically with the general condition of $x = x_1$ at $t = t_1$. Plotting the F(x) against ($t-t_1$) will lead to origin-crossing lines, which is similar to f(x)-t plots in the first stage. These models with new initial conditions proposed as Eqs. (9)–(13) in Table 4.

Table 5 shows the result of fitting experimental data for both metals. According to data, there is a satisfactory agreement between Eq. (7) and experimental data for Cr recovery, thus the interfacial transfer and diffusion across the product layer would control the Cr recovery in the whole bioleaching course. Besides, Eq. (7) has the best correlation for the first stage of Ni recovery, too. Therefore, in the first 5 h of Ni recovery (first stage), the interfacial transfer and diffusion across the product layer is a rate-controlling mechanism. As it is evident, the correlation coefficients in the second stage of Ni recovery for Eqs. (9)–(11) are too close and make it impossible to differentiate which rate-controlling mechanism prevails. In this case, it is possible to combine three steps and consider all three mechanisms simultaneously as Eq. (14). In this method, the value of $\theta_F$, $\theta_P$ and $\theta_R$ are shares of each mechanism in the bioleaching of Ni in the second stage. In this approach, these constants are quantified via the constrained least square technique through multi-linear regression analysis. This technique can be described as Eqs. (15) and (16) (Nazemi et al., 2011). The calculation of the values of $\theta_F$, $\theta_P$ and $\theta_R$ can be obtained by any optimization approach. This minimization problem was solved and the obtained values of $\theta_F$, $\theta_P$, and $\theta_R$ are 0, 9.56, and 2.21 (h), respectively. This fit gives an $R^2$ of 0.97 with experimental data. It can be concluded that bioleaching of Ni is a mixed-control mechanism in the second step and both diffusions through the product layer and chemical reaction models play important roles in controlling Ni recovery after t = 5 h.

$$t - t_1 = \theta_F(X - X_1) + \theta_P\left(1 - 3\left(\frac{1-X}{1-X_1}\right)^{\frac{2}{3}} + 2\left(1 - (1-X_1)^{\frac{1}{3}}(X - X_1)\right)\right) + \theta_R\left(1 - \left(\frac{1-X_1}{1-X}\right)^{\frac{1}{3}}\right) \quad (14)$$

$$\phi = \sum_i \left[\theta_F(X_i - X_1) + \theta_P\left(1 - 3\left(\frac{1-X_i}{1-X_1}\right)^{\frac{2}{3}} + 2\left(1 - (1-X_1)^{\frac{1}{3}}(X_i - X_1)\right)\right) + \theta_R\left(1 - \left(\frac{1-X_1}{1-X_i}\right)^{\frac{1}{3}}\right) - (t_i - t_1)\right]^2 \quad (15)$$

$$\text{Min } \phi \quad \text{subjected to } \theta_F,\ \theta_P \text{ and } \theta_R > 0 \quad (16)$$

### 3.7. Future prospects

Nowadays, the bioleaching technique is an efficient, economical, and environmental substitute for recovering metals from industrial waste. In this approach, using of biogenic organic acid as an

**Table 5**
Correlation coefficients ($R^2$) of the kinetics models for Cr and Ni.

| Eq. no. | Cr | Ni- first stage | Eq. no. | Ni- second stage |
|---|---|---|---|---|
| 4 | 0.71 | 0.57 | 9 | 0.96 |
| 5 | 0.97 | 0.93 | 10 | 0.96 |
| 6 | 0.79 | 0.71 | 11 | 0.95 |
| 7 | 0.99 | 0.99 | 12 | 0.90 |
| 8 | 0.89 | 0.90 | 13 | 0.82 |

innovative solution responds to issues connected to conventional metal recycling methods. However, most studies on fungal leaching of industrial waste have been conducted on a laboratory scale. Therefore, broad pilot-scale researches should be carried out to evaluate the applicability of the process on the industrial scale. Also, future works will focus on solving some major challenges associated with bioleaching of waste (e.g., electroplating sludge) to make this process more cost-effective industrial process: (1) increasing the pulp density (ratio of solid to liquid); (2) finding new approaches for strain improvement to increase the biogenic organic acids production; and (3) finding a cheap nutrient source for microbes.

## 4. Conclusion

This study investigated the ability of organic acids produced by *A. niger* in leaching of Cr and Ni from electroplating sludge. It also studied the culture media of PDB, Bosshard, Czapek dox broth, and modified Czapek dox broth and Czapek dox broth reduced pH from 7.1 to 2.1. Thus, Czapek dox broth was selected as the optimum culture medium for *A. niger*. Furthermore, growth characterization assessment results that the maximum amount of organic acids was obtained at the $14^{th}$ day of *A. niger* fermentation (12600 mg/L oxalic acid). Due to bioleaching optimization, maximum recoveries of Cr (53%) and Ni (95.7%) were obtained under the optimal condition of 10 g/L pulp density, 66 °C leaching temperature, and minimum leaching duration of 1 day using fungal filtrated culture. Also, FESEM and mapping analysis of the initial electroplating sludge and bioleached residue demonstrated the efficacy of fungal metabolites in the leaching of electroplating sludge metals. TCLP and SPLP tests highlighted that Cr and Ni in raw electroplating sludge had surpassed maximum regulatory levels. On the contrary, the concentration of both metals in solid residue after bioleaching treatment was reduced to the well below the threshold limits and meets the limit value that is accepted for landfill or can be reused in construction material safely. The leaching of Cr completes until hour 12 and remains static until the end and its kinetics is single-stage and controlled by interfacial transfer and diffusion across the product layer. The kinetics of Ni leaching shows a two-stage process. In the first stage (before hour 5), interfacial transfer and diffusion across the product layer is a rate-controlling mechanism. For the second stage (after hour 5), the constrained least square technique is employed through multi-linear regression analysis because of too close correlation coefficients, and revealed that bioleaching of Ni in the second stage is a mixed-control mechanism and both of diffusion through the product layer and chemical reaction models play a role.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Sima Nikfar:** Investigation, Writing - original draft, Data curation, Formal analysis. **Alireza Parsa:** Investigation, Formal analysis, Methodology. **Nazanin Bahaloo-Horeh:** Investigation, Methodology, Conceptualization, Writing - review & editing. **Seyyed Mohammad Mousavi:** Writing - review & editing, Project administration, Funding acquisition, Supervision.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.121622.

## References

Amiri, F., Yaghmaei, S., Mousavi, S.M., 2011. Bioleaching of tungsten-rich spent hydrocracking catalyst using *Penicillium simplicissimum*. Bioresour. Technol. 102, 1567–1573.
Asavapisit, S., Naksrichum, S., Harnwajanawong, N., 2005. Strength, leachability and microstructure characteristics of cement-based solidified plating sludge. Cement Concr. Res. 35, 1042–1049.
Asghari, I., Mousavi, S.M., 2014. Effects of key parameters in recycling of metals from petroleum refinery waste catalysts in bioleaching process. Rev. Environ. Sci. Biotechnol. 13, 139–161.
Bahaloo-Horeh, N., Mousavi, S.M., 2017. Enhanced recovery of valuable metals from spent lithium-ion batteries through optimization of organic acids produced by *Aspergillus niger*. Waste Manag. 60, 666–679.
Bahaloo-Horeh, N., Mousavi, S.M., Baniasadi, M., 2018. Use of adapted metal tolerant *Aspergillus niger* to enhance bioleaching efficiency of valuable metals from spent lithium-ion mobile phone batteries. J. Clean. Prod. 197, 1546–1557.
Bahaloo-Horeh, N.B., Mousavi, S.M., Shojaosadati, S.A., 2016. Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using *Aspergillus niger*. J. Power Sources 320, 257–266.
Bayat, B., Sari, B., 2010. Comparative evaluation of microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge. J. Hazard Mater. 174, 763–769.
Biswas, S., Bhattacharjee, K., 2014. Fungal assisted bioleaching process optimization and kinetics: scenario for Ni and Co recovery from a lateritic chromite overburden. Separ. Purif. Technol. 135, 100–109.
Biswas, S., Dey, R., Mukherjee, S., Banerjee, P.C., 2013. Bioleaching of nickel and cobalt from lateritic chromite overburden using the culture filtrate of *Aspergillus niger*. Appl. Biochem. Biotechnol. 170, 1547–1559.
Calgaro, C.O., Tanabe, E.H., Bertuol, D.A., Silvas, F.P.C., Espinosa, D.C.R., Tenório, J.A.S., 2015. Leaching processes. In: Electronic Waste: Recycling Techniques, pp. 39–59.
Fallis, A., 1992. Toxicity characteristic leaching procedure, method 1311. In: Journal of Chemical Information and Modeling, pp. 1689–1699.
Hassan, R., El-Kadi, S., Sand, M., 2015. Effect of some organic acids on some fungal growth and their toxins production. Int. J. Adv. Biol. 1–11.
Jadhav, U., Su, C., Hocheng, H., 2016. Leaching of metals from printed circuit board powder by an *Aspergillus niger* culture supernatant and hydrogen peroxide. RSC Adv. 6, 43442–43452.
Khuri, A.I., Mukhopadhyay, S., 2010. Response surface methodology. Wiley Interdiscip. Rev. Comput. Stat. 2, 128–149.
Li, C., Xie, F., Ma, Y., Cai, T., Li, H., Huang, Z., Yuan, G., 2010a. Multiple heavy metals extraction and recovery from hazardous electroplating sludge waste via ultrasonically enhanced two-stage acid leaching. J. Hazard Mater. 178, 823–833.
Li, L., Ge, J., Wu, F., Chen, R., Chen, S., Wu, B., 2010b. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. J. Hazard Mater. 176, 288–293.
Magalhães, J.M., Silva, J.E., Castro, F.P., Labrincha, J.A., 2005. Physical and chemical characterisation of metal finishing industrial wastes. J. Environ. Manag. 75, 157–166.
Muddanna, M.H., Baral, S.S., 2019. A comparative study of the extraction of metals from the spent fluid catalytic cracking catalyst using chemical leaching and bioleaching by *Aspergillus niger*. J. Environ. Chem. Eng. 7, 103335.
Nazemi, M.K., Rashchi, F., Mostoufi, N., 2011. A new approach for identifying the rate controlling step applied to the leaching of nickel from spent catalyst. Int. J. Miner. Process. 100, 21–26.
Naseri, T., Bahaloo-Horeh, N., Mousavi, S.M., 2019. Bacterial leaching as a green approach for typical metals recovery from end-of-life coin cells batteries. J. Clean. Prod. 220, 483–492.

Ousmanova, D., Parker, W., 2007. Fungal generation of organic acids for removal of lead from contaminated soil. Water Air Soil Pollut. 179, 365–380.
Ozdemir, O.D., Piskin, M.B., 2011. Temperature effect on sulfuric acid leaching of galvanic sludge. Int. Rev. Chem. Eng. 3, 123–124.
Palmieri, F., Estoppey, A., House, G.L., Lohberger, A., Bindschedler, S., Chain, P.S.G., Junier, P., 2019. Oxalic acid, a molecule at the crossroads of bacterial-fungal interactions. In: Advances in Applied Microbiology, pp. 49–77.
Prabhu, S.V., Baskar, R., 2015. Detoxification of electroplating sludge by bioleaching: process and kinetic aspects. Pol. J. Environ. Stud. 24, 1249–1257.
Rasoulnia, P., Mousavi, S.M., 2016. V and Ni recovery from a vanadium-rich power plant residual ash using acid producing fungi: *Aspergillus niger* and *Penicillium simplicissimum*. RSC Adv. 6, 9139–9151.
Rastegar, S.O., Mousavi, S.M., Shojaosadati, S.A., 2014. Cr and Ni recovery during bioleaching of dewatered metal-plating sludge using *Acidithiobacillus ferrooxidans*. Bioresour. Technol. 167, 61–68.
Ren, W.X., Li, P.J., Geng, Y., Li, X.J., 2009. Biological leaching of heavy metals from a contaminated soil by *Aspergillus niger*. J. Hazard Mater. 167, 164–169.
Survey, U.S.G., 2018. Usgs Comodities 2018. U.S. Geological Survey., Reston, VA.
US EPA, 1994. Method 1312: synthetic precipitation leaching procedure (SPLP). In: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods; SW-846, pp. 1–30.
Wang, M., Gong, X., Wang, Z., 2018. Sustainable electrochemical recovery of high-purity Cu powders from multi-metal acid solution by a centrifuge electrode. J. Clean. Prod. 204, 41–49.
Wu, H.Y., Ting, Y.P., 2006. Metal extraction from municipal solid waste (MSW) incinerator fly ash - chemical leaching and fungal bioleaching. Enzym. Microb. Technol. 38, 839–847.
Wu, P., Zhang, L., Lin, C., Xie, X., Yong, X., Wu, X., Zhou, J., Jia, H., Wei, P., 2020. Extracting heavy metals from electroplating sludge by acid and bioelectrical leaching using *Acidithiobacillus ferrooxidans*. Hydrometallurgy 191, 105225.
Wu, P., Zhang, L., Liu, Y., Xie, X., Zhou, J., Jia, H., Wei, P., 2019. Enhancing Cu-Zn-Cr-Ni Co-extraction from electroplating sludge in acid leaching process by optimizing $Fe^{3+}$ addition and redox potential. Environ. Eng. Sci. 36, 1244–1257.
Xu, D.B., Kubicek, C.P., Röhr, M., 1989. A comparison of factors influencing citric acid production by *Aspergillus niger* grown in submerged culture and on filter paper. Appl. Microbiol. Biotechnol. 30, 444–449.
Yan, S., Zhang, T., Li, M., Nan, Y., Cao, L., 2008. Bio-leaching of heavy metals from electroplating sludge by *Thiobacillus*. Ecol. Environ. 17, 1787–1791.
Zhang, L., Zhou, W., Liu, Y., Jia, H., Zhou, J., Wei, P., Zhou, H., 2020. Bioleaching of dewatered electroplating sludge for the extraction of base metals using an adapted microbial consortium: process optimization and kinetics. Hydrometallurgy 191, 105227.
Zhou, W., Zhang, L., Peng, J., Ge, Y., Tian, Z., Sun, J., Cheng, H., Zhou, H., 2019. Cleaner utilization of electroplating sludge by bioleaching with a moderately thermophilic consortium: a pilot study. Chemosphere 232, 345–355.