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Fungal leaching of valuable metals from a power plant residual ash using *Penicillium simplicissimum*: Evaluation of thermal pretreatment and different bioleaching methods

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ABSTRACT

Each year a tremendous volume of V-Ni rich ashes is produced by fuel oil consuming power plants throughout the world. Recovery of precious metals existing in these ashes is very important from both economic and environmental aspects. The present research was aimed at investigating bioleaching potential of *Penicillium simplicissimum* for the recovery of metals from power plant residual ash (PPR ash) using different bioleaching methods such as one-step, two-step, and spent-medium bioleaching at 1% (w/v) pulp density. Furthermore, the effects of thermal pretreatment on leaching of V, Ni, and Fe, as major elements present in PPR ash, were studied. Thermal pretreatment at various temperatures removed the carbonaceous and volatile fraction of the ash and affected the fungal growth and metal leachability. The highest extraction yields of V and Ni were achieved for the original PPR ash, using spent-medium bioleaching in which nearly 100% of V and 40% of Ni were extracted. The maximum extraction yield of Fe (48.3%) was obtained for the pretreated PPR ash at 400 °C by spent-medium bioleaching. In addition, the fungal growth in pure culture was investigated through measurement of produced organic acids via high performance liquid chromatography (HPLC). Chemical leaching experiments were performed, using commercial organic acids at the same concentrations as those produced under optimum condition of fungal growth (5237 ppm citric, 3666 ppm gluconic, 1287 ppm oxalic and 188 ppm malic acid). It was found that in comparison to chemical leaching, bioleaching improved V and Ni recovery up to 19% and 12%, respectively. Moreover, changes in physical and chemical properties as well as morphology of the samples utilizing appropriate analytical methods such as XRF, XRD, FTIR, and FE-SEM were comprehensively investigated.

1. Introduction

Vanadium and nickel are two precious metals which have many industrial applications. Vanadium is an important by-product with numerous physical properties such as high tensile strength, fatigue resistance and toughness. Thus it is used as an additive to titanium alloys, an alloying element in steel and iron industry, or a catalyst in chemical and polymer industries. Nickel, an important metal existing in nature as sulfides and oxides, is also employed in stainless steel and super alloys production industries because of its corrosion resistance property (Biswas et al., 2013; Mohammadreza et al., 2014; Moskalyk and Alfantazi, 2003; Navarro et al., 2007).

Since common vanadium content of processed ores is usually less than 2% and it is not present in high concentrations in minerals, many industrial sub-products such as converter and smelter slag, or spent catalysts, have been investigated and used for recovery of vanadium (Navarro et al., 2007; Vitolo et al., 2000).

It is interesting to know that another source of vanadium is the ash produced in power plants as a result of incomplete combustion of fuel oil. Chemical composition of these ashes may vary, depending on the applied fuel oil composition and its combustion method, the operation mode of boiler units, and the utilized reagents for neutralizing the washing waters of the thermal power plants. Generally, these ashes are characterized by a high content of vanadium, nickel, iron, aluminum, silicon, sulfur and non-burnt carbon. Among these metals Ni and V are the most valuable ones (Al-Ghouti et al., 2011; Navarro et al., 2007; Tsygankova et al., 2011).

Among the types of fuels that are combusted in thermal power plants in Iran, fuel oil is ranked second after natural gas. For instance, approximately 14,462 million liters of fuel oil have been consumed in 2012; consequently, this high consumption of fuel oil

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is estimated to result in production of almost 40,000 tons of ashes (NIORDC, 2012; Tsai and Tsai, 1998).

It is of utmost importance to recover metals from these ashes not only because of their economic values (for the valorization of V and Ni) but also for environmental considerations (Navarro et al., 2007). In fact, indiscriminate disposal of these solid wastes containing a variety of toxic heavy metals is threatening to the environment and public health, because in aqueous environment these hazardous constituents can be easily leached and lead to a secondary pollution of soil and water (Lee and Pandey, 2012; Xu and Ting, 2009).

Biotechnological leaching processes, which in many cases are more cost efficient, simpler, and more environmentally friendly than their chemical counterparts, have been proposed as a promising technology useful either to recover valuable metals from industrial metal-rich wastes or to detoxify them for a less hazardous disposal (Brandl and Faramarzi, 2006; Bredberg et al., 2004).

In bioleaching, a variety of microorganisms including different species of bacteria and fungi are used to mobilize and leach metals from solid materials. The most common bacteria utilized in bioleaching belong to the *thiobacilli* genus, and therefore, *acidophilic* species such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* have been extensively studied (Arshadi and Mousavi, 2015; Ijadi Bajestani et al., 2014; Chen and Lin, 2010; Haghshenas et al., 2009; Wang et al., 2009).

Additionally, some species of fungi belonging to genera *Penicillium* and *Aspergillus* have been successfully employed in bioleaching of various heavy and valuable metals from solid wastes like spent catalysts, electronic scraps, red mud, and municipal waste incineration fly ash, indicating their potential in recovery of metals (Amiri et al., 2011; Bosshard et al., 1996; Brandl et al., 2001; Qu et al., 2013; Wu and Ting, 2006; Xu and Ting, 2009).

Fungal leaching is based on four major mechanisms as follows: (a) acidolysis (the most important mechanism) in which solubilization of metal occurs resulting from production of organic acids; (b) complexolysis where the metals form complexes with the excreted organic acids or amino acids; (c) redoxolysis in which the reduction of metal is mediated by organic acids; and (d) bioaccumulation where the mycelium acts as a sink for the metal ions (Bosshard et al., 1996).

The ash produced in power plants as a consequence of combustion of heavy fuel oil still has a high fraction of carbonaceous and volatile part. It should be noted that the fuel oil (not the ash) is burned and the ash is the collected residue in the furnace pipes and funnels. In comparison to the direct bioleaching of the original PPR ash, its thermal pretreatment could have some advantages, including: 1- reducing the carbonaceous and volatile impurities of PPR ash which are considered to be a growth inhibitory factor to the fungus; 2- increasing the vanadium content of PPR ash and thus having a liquor with a higher concentration of vanadium at the end of bioleaching; and 3- lower acid consumption and consequently reaching a higher yield in the stage of precipitation of vanadium (Vitolo et al., 2001). Moreover, another advantage of preliminary roasting of the PPR ashes is the possibility of recovering the heat of combustion of their carbonaceous fraction. Vitolo et al. (2001) investigated the effects of thermal pretreatment of heavy oil fly ash on chemical leaching of vanadium in a temperature range of 650–1150 °C. However, no studies have been done on fungal leaching of V and Ni from PPR ashes and the effects of their thermal pretreatment.

Therefore, in this study the fungus *Penicillium simplicissimum*, which produces high amounts of organic acids (citrate, gluconate, oxalate), has been selected to accomplish bioleaching experiments. The PPR ash was burned at four different temperatures (200, 400, 600, 800 °C) for 2 h. Bioleaching of the pretreated ash samples as well as the original one was performed, using one-step, two step, and spent-medium leaching in order to compare the methods and examine the effects of pretreatment on metal leaching yields. In addition, changes in physical properties and surface characteristics of the original, pretreated, and bioleached samples were comprehensively investigated by appropriate analytical methods.

2. Materials and methods

2.1. Preparation of V-Ni rich PPR ash

PPR ash was provided from a thermal power plant located in Iran, and was screened through 75 μm sieves. The screened PPR ash was heat treated at temperatures of 200, 400, 600 and 800 °C for two hours in an electrical furnace (Wisetherm FP, *DAIHAN* Scientific, South Korea) so as to prepare the pretreated samples. Higher temperatures were not investigated because volatilization of V and fusion and formation of Ni-V compounds may have occurred beyond 950 °C, which could adversely affect the recovery of vanadium (Vitolo et al., 2001).

2.2. Fungi inoculum preparation and growth conditions

P. simplicissimum fungus (PTCC 5129) was purchased from the Iranian Research Organization for Science and Technology (IROST) in lyophilized form. The fungus was activated and cultivated on PDA (potato dextrose agar) Petri dishes. Seven days after incubation of the cultures at 30 °C, the spores were washed off from the surface of PDA plates, using sterilized distilled water. The number of spores was counted by means of a standard hemocytometer chamber, and subsequent to adjusting, a multiple of 10^7 spores was inoculated to bioleaching medium with the following composition: sucrose (100 g/l), $NaNO_3$ (1.5 g/l), KH_2PO_4 (0.5 g/l), $MgSO_4{\cdot}7H_2O$ (0.025 g/l), KCl (0.025 g/l), and yeast extract (1.6 g/l) (Bosshard et al., 1996).

2.3. Analytical procedures

The composition of original PPR ash and the pretreated samples was determined via X-ray fluorescence (XRF; PW2404, Philips, The Netherlands). To investigate the effect of thermal pretreatment of PPR ash on chemical state and metal compounds phases, X-ray diffraction (XRD; X'Pert MPD, Philips, The Netherlands) and Fourier transform infrared spectroscopy (FTIR; PerkinElmer, Frontier, USA) analyses were applied. The concentrations of excreted organic acids by the fungus in pure cultures (citric, gluconic, oxalic and malic acids) were analyzed by high performance liquid chromatography (HPLC; Sykam, MACHERY-NAGEL, Germany) at 210 nm with a 250 × 4.6 mm, Nucleodur C18 ec, 5 μm column, and a DAD UV–Vis detector. In order to detect the acids, 20 μl of each of the HPLC-grade organic acids solutions were injected into the column as standards. Surface characteristics of the pretreated and original PPR ash along with the bioleached samples were determined, utilizing field emission scanning electron microscope (FE-SEM; HITACHI S-4160, Japan). The samples provided for the above-mentioned analyses were dried at room temperature. Having completed the bioleaching period and filtering of the flasks through 0.22 μm syringe filters, metal ion concentrations in filtrate were analyzed, using inductively coupled plasma optical emission spectrometer (ICP-OES; Vista-pro, Australia). Increases in metal concentrations as a result of pretreatment and medium evaporation losses during bioleaching period were considered when calculating the metal recoveries. Biomass and PPR ash residue on the filter paper were transferred to a pre-weighed container and were dried in an oven at 80 °C for 24 h. Subsequently, the dried residue was burned at 500 °C for 4 h to determine the biomass dry weight