Agromining of hyperaccumulator biomass: Study of leaching kinetics of extraction of nickel, magnesium, potassium, phosphorus, iron, and manganese from *Alyssum murale* ashes by sulfuric acid

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ARTICLE INFO

ABSTRACT

In the present study, a thorough investigation of the extraction rates and the extraction yields of 6 chemical elements (Ni, Mg, P, K, Fe and Mn) from *Alyssum murale* ashes is proposed. In this purpose, the impact of several parameters (temperature, stirring speed, acid concentration) on the extraction rates and on the extraction yields of each element was studied. Our first results showed that the acid leaching kinetics were neither limited nor controlled by external film diffusion. Depending on the chemical element, the impact of temperature and acid concentration were significant since the extraction yields and rates increased by increasing either the temperature or the acid concentration. All the data collected were of great consequence since it allows us to investigate and estimate the optimum conditions of selective leaching of nickel by using a Box-Behnken design of experiments. We also found that the nickel extraction rate can be perfectly estimated by the shrinking core model where only internal diffusion occurred; in this model, the apparent activation energy was estimated to be 60 kJ/mol and the nickel extraction rate is expressed by the following equation:

$$1 - 3(1 - X_{Ni})^{\frac{2}{3}} + 2(1 - X_{Ni}) = k_{d,s}t = 630.10^3 exp\left(-\frac{60.10^3}{RT}\right)t$$

1. Introduction

The metal recovery from secondary resources, such as metal-containing soils, has become an increasing interest especially since the global demand for metals has been increasing for the last few decades (van der Ent et al., 2015; Yellishetty et al., 2011). In this context, the interest of researchers on phytomining, now called agromining, which is a feasible superficial-contaminated remediation technique based on hyperaccumulator plants, has been growing for the 2 last past decades (Sarma, 2011; Sheoran et al., 2010; Vamerali et al., 2009).

Hyperaccumulator plants have been widely studied and present the specific property to achieve the bioaccumulation of heavy metals in their aerial parts (Chaney et al., 2007; Reeves, 2006; Tang et al., 2012; Verbruggen et al., 2009). In a Ni agromining context, huge volumes of Ni-containing secondary resources are available all over the world and at the same time, more than 400 Ni hyperaccumulator plants have been

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Table 1 – Range and values of parameters investigated in the leaching procedure. (* values kept constant when the effect of other parameters was investigated).

	Parameters	Range of values
Parameters investigation conditions	Acid concentration (mol/L)	1, 2*, 5
	Stirring speed (rpm)	100, 500*, 700
	Temperature (°C)	20, 40, 60, 90*
Design experiments conditions	Acid concentration (mol/L)	1 (−1),3 (0), 5 (+1)
	Temperature (°C)	20 (−1), 55 (0), 90 (+1)
	Time (min)	30 (−1), 75 (0), 120 (+1)

Table 2 – Chemical analysis of the washed ashes (*mg/g of dried ashes).

Component	Ca	Fe	K	Mg	Mn	Na	Ni	P
Concentration*	174	20	57	70	0.6	1.2	202	39
Stan. dev. (%)	4	5	4	4	3	4	3	3

identified and new species of tropical Ni hyperaccumulators were discovered recently (Bani et al., 2015; Sarma, 2011; Sheoran et al., 2010; Vamerali et al., 2009; van der Ent et al., 2015).

One possible path to recover Ni from such plants consists in drying and burning them to produce ashes which can be considered as bio-ores (Chaney et al., 2007; Zhang et al., 2014). These ashes can be processed by either pyrometallurgy or hydrometallurgy to produce Ni metal or catalysts for organic chemistry or Ni salts (Barbaroux et al., 2011; Barbaroux et al., 2012b; Zhang et al., 2014; Zhang et al., 2016). In this context, a patent was filed (Mercier et al., 2012) to supply a high valuable nickel salt (ANSH) from *Alyssum murale* thanks an innovating process based on the following stages: (i) dried Alyssum biomass is burnt to produce ashes, (ii) ashes are washed with water to remove potassium sulfate and (iii) leached with sulfuric acid. At this step, nickel is transferred into the leachate (with 6 other elements: Ca, Mn, Mg, Fe, P, K) and then (iv) ANSH is produced thanks a set of crystallization and purification steps. The acid leaching stage is a critical point in this process since the time and the costs needed in the crystallization and purification steps highly depend on the quality of the Ni leachate (Zhang et al., 2016).

To the best of our knowledge, the acid leaching of Ni-hyperaccumulator biomass ashes (as *Alyssum murale)* has never been investigated and no study has been published so far on the kinetics of Ni extraction of such ashes.

However, many studies have been published on kinetics of Ni extraction and the fate of Ni by acid leaching of some materials but only applied to industrial hazardous wastes or Ni-ores which are not produced from Ni hyperaccumulator biomass (Gharabaghi et al., 2013; Safarzadeh et al., 2009; Stopić et al., 2002). All these studies show that the Ni extraction kinetics follow a shrinking core model with internal diffusion for which the apparent activation energy associated are in the range of 10–70 kJ/mol.

Hence, the aim of this work was (i) to investigate the extraction kinetics of the 6 main chemical elements in *Alyssum murale* hyperaccumulator ashes which are alkali metals (K), alkali earth metals (Mg), transition metals (Fe, Mn, Ni) and non-metals (P) and, based on ANOVA analysis, (ii) to determine the optimal extraction conditions of Ni for which the relative concentration of Ni is the best since the presence of these other chemical elements may compromise the purity of ANSH, according to the process developed and described by Barbaroux et al. (2012b) and Zhang et al. (2016).

2. Material and methods

2.1. Materials

Washed ashes from Alyssum murale were used in this work. *Alyssum murale* plants were harvested, collected and dried in Albania in an ultramafic area near Pojskë (40°55′5″N; 20°38′55″E) in 2015. The plants were ground in an industrial grinder equipped with a 2 mm grid before the combustion. Biomass combustion was in an industrial biomass furnace (KWB Multifire MF2 D/ZI). The combustion temperature was measured with a K-type thermocouple (900 °C). The chemical and elemental composition of ashes before and after the leaching procedure were achieved (XRD, ICP-AES) and results are gathered in Table 2. Sulfuric acid from by Sigma Aldrich (95–97%) was used as leaching reagent. Hydrogen peroxide from VWR Chemicals (50% Rectapur) and nitric acid from Fisher Chemicals (67–69% Optima Grade) were used in the digestion step.

2.2. Leaching procedure

The leaching experiments were performed in a 1 L glass vessel equipped with a 2 bladed 50 mm propeller in PTFE for 60 min. A condenser was fitted on the vessel to avoid liquid evaporation and keep the solid mass fraction constant. Washed ashes (Houzelot et al., 2017; Zhang et al., 2016) and sulfuric acid were used with a solid mass fraction of 10% (s/s – 40 g of ashes and 360 g of acid) and the temperature was monitored by a heated oil bath. The impact of acid concentration, temperature, and stirring speed on Fe, Ni, K, P, Mn, and Mg extraction was investigated. The ranges of the values of those three parameters are gathered in Table 1. 40 g of ashes were introduced first and 360 g of preheated acid at the desire temperature were then filled in the vessel while stirring the bulk at the desire speed.

2 mL of solution were sampled at different time intervals, filtered (Phenomenex RC, 0.45 µm) and diluted in a 50 ml flask to perform elemental analysis (ICP-AES). Each experiment was replicated 3 times.

2.3. Analytical techniques

Solid samples (ca 0.15 g) were randomly collected and digested by adding 8.5 mL of nitric acid and 1.5 mL of hydrogen peroxide in a PTFE vessel. They were heated with a microwave furnace (Milestone Start D Microwave Digestion System Ethos 1) for 50 min with a set-point of 200 °C. The leachate was then diluted with deionized water in a 50 mL flask before elemental analysis by ICP-AES (Thermo ICAP6000).

The calibration of ICP-AES analysis was performed with PlasmaCAL custom standards (SCP Science) in a 5% vol. of HNO$_3$ matrix. Three replicates were achieved for each sample and a quality test was carried out every 10 measurements with a certified solution (PlasmaCAL, SCP Science). The analysis procedure (digestion and quantification) was controlled