Recovery and separation of valuable metals (copper and zinc) from acidic mine waters by ion-exchange resins

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Abstract

Mining wastewaters, containing heavy metals such as copper (Cu) and zinc (Zn), have a huge impact on the environment due to they are not biodegradable and tend to bioaccumulate in plants or living organisms. Therefore, in this work the performance of ion-exchange and solvent-impregnated resins were compared for the separation and recovery of valuable metals (Cu, Zn) from acidic mine waters (AMW). Lewatit 207 as an ion-exchange resin, and an impregnated resin containing Di-2-ethylhexylphosphate, named Lewatit 1026, were evaluated for extract both metal ions. Additionally, the metal extraction was determined as a function of pH (from 1 to 5) when an AMW was used to carry out the experiments. Batch experiments results showed that best extraction of Zn was obtained using Lewatit 1026 being around 96% (pH=2.5-3); whereas Lewatit 207 performance was optimum for Cu extraction (about 99%) at pH=3-4. Moreover, using a fixed-bed configuration column, it was possible to separate and concentrate Zn (10 times) and Cu (40 times) by using Lewatit 1026 and 207, respectively. Overall, the application of an ion-exchange process showed a great potential in the recovery of valuable metals from mine waters to promote a circular economy scheme in the metallurgical industries.

Keywords: Mining wastewaters; metal recovery; ion-exchange process

1. Introduction

Water processes with toxic metals (e.g. Cd, Cr, Hg, Ni, Pb, Cu, Zn, among others) and non-metals (e.g. As, Se) from hydrometallurgical industries and mine sites cause environmental pollution (Hubicki and Kołodyńska, 2012). Therefore, in this work, an ion-exchange (IX) process, through IX resins and solvent-impregnated resins (SIRs), was proposed as an alternative technique for the separation and recovery of valuable metals, like Cu and Zn, from acidic mine waters (AMW) and to valorise them in a circular economy scheme (Kirchherr et al., 2017; European Comission, 2015). The metal extraction of the resin was firstly evaluated from pH 1 to 5 using a batch operation system and then the recovery process was studied in a fixed-bed configuration set-up.

2. Experimental methods

2.1. Lewatit resins

The resins used in this work consisted of Lewatit VP OC 1026 and Lewatit TP 207. Before use, Lewatit TP 207 was converted into Na^+ form by washing the resin sequentially with 1 M NaOH solution and distilled water (until pH = 7), whereas Lewatit VP OC 1026 was not converted because it is a SIR resin.

2.2. Acidic mine waters

The AMW was composed by Al (363±7 mg/L), Ca (501±10 mg/L), Cu (300±6 mg/L), Fe (109±3 mg/L), Mg (1996±40 mg/L), Mn (196±4 mg/L), Cd (2.4±0.1 mg/L) and Zn (790±16 mg/L) with a pH = 2.7. Before experiments, Fe and Al were removed by oxidation with H_2O_2 and sequentially pH was raised to precipitate them. In a first stage, 1 mL of H_2O_2 30% (v/v) per litre of AMW was added to oxidize Fe(II) to Fe(III). Afterwards, Fe was precipitated as $Fe(OH)_3$ by increasing the pH up to 3.7-3.8 using NaOH 2 mol/L. Additionally, once the Fe was precipitated, the pH was raised up to 4.8 for Al removal, and finally the sample was filtered.

2.3. Batch and column experiments

Batch experiments were carried out at 25ºC to treat 20 mL of AMW with 5 g of resin for SIRs and around 2 g for Lewatit TP 207 to have the same IX resin capacity, at a stirring speed of 150 rpm. At different time intervals (0, 30, 60, 90 and 120 min) and pHs (1, 1.5, 2, 2.5, 3 and 5), samples of the AMW were collected, and the copper and zinc concentrations were measured by Atomic Absorption Spectrometry (AANALYST 200 SNGL W/D2 from PERKIN ELMER) in order to determine the best resin for the extraction of each metal.

Afterwards, a fixed-bed configuration was used to carry out the metal extraction in a column set-up (ion-exchange and elution steps) in order to separate and also concentrate both ions of interest (Cu and Zn), following the scheme proposed in Figure 1.

3. Results and discussion

The experimental results obtained under different pH conditions in batch experiments, after 120 min of the IX process, showed that the SIR, Lewatit 1026, had higher selectivity for Zn than Cu (96% Zn extraction and 22% Cu extraction at optimal pH 2.5-3), while the behaviour of the IX resin (Lewatit 207) was the opposite, Cu was more retained than Zn (99% Cu extraction and 80% Zn extraction at optimal pH 3-4).

Then, two columns were used to separate and concentrate Zn and Cu. On the one hand, Lewatit 1026 was used to valorise the Zn from AMW, and then Lewatit 207 to recover the Cu.

It was possible to extract Zn (23.3 ± 2.2 mg Zn/g resin) and also to concentrate around 10 times by the elution process. Once the Zn was removed from the initial AMW, the feed sample pH was adjusted at 3.5 before being treated by the second column set-up, but using Lewatit 207 resin. Cu was the most extracted compound by Lewatit 207 resin, obtaining an adsorption capacity of 37.8 ± 2.1 mg Cu/g resin and being able to concentrate it around 40 times by the elution process.

4. Conclusions

Based on the results obtained in this work, the utilization of an IX process could represent an interesting and eco-friendly alternative to other techniques used for metal separation. The results demonstrated that it was possible to separate valuable metals from AMW by IX process. SIRs (Lewatit 1026) were the best candidates for Zn removal; whereas IX resins, like Lewatit 207, provided the highest selectivity for Cu. By means of this technique, it was possible to recover separately Zn (23.3 mg Zn/g resin) and Cu (37.8 mg Cu/g resin) from AMW and also concentrate them by concentration factors of 10 and 40 for Zn and Cu, respectively.

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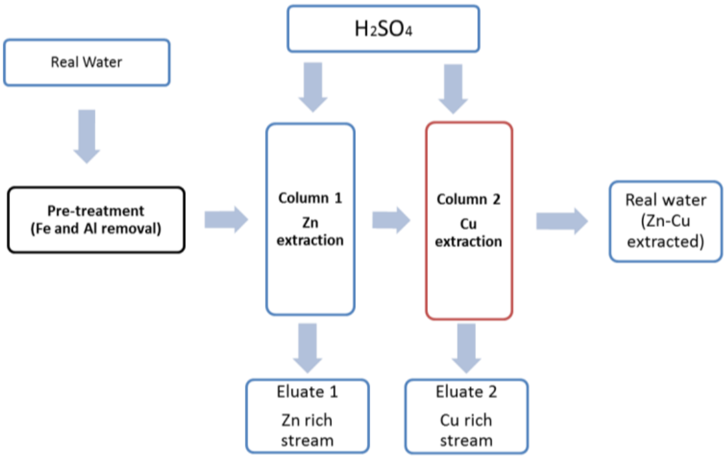

Figure 1. Zn and Cu separation and recovery process flow sheet

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