Integration of selectrodialysis and solvent impregnated resins for Zn(II) and Cu(II) recovery from hydrometallurgy effluents containing As(V)

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ABSTRACT

The main challenge for copper smelters is to ensure product quality under the constant increase in impurities (As, Se, Mo, Co, Zn, Sb, and Pb) in copper ores that has occurred over the years. The presence of toxic elements, such as As(V), in acidic streams rich Cu(II) and Zn(II) (pH 2.0–2.5) limits the valorisation of both metals. In this study, a novel combination of the following two ion-exchange-based processes were proposed: i) membrane selectrodialysis (SED) for the selective separation of Zn(II)/Cu(II) from As(V) and ii) impregnated ion-exchange (IX) resins for the selective separation of Zn(II) from Cu(II). The selective separation of As(V), which is present in solution as H_3AsO_4/$H_2AsO_4^-$, is achieved using a combination of monocharge and non-monocharge selective cation-exchange membranes to avoid the co-precipitation of As(V) when IX resins are used for Cu(II)/Zn(II) recovery. This combination of processes represents the novelty of the present study since it could be used in hydrometallurgical industries to remove As(V) and, at the same time, to valorize two value-added metals [Cu(II) and Zn(II)]. At the moment, only single-stage processes have been proposed. Using SED, a Cu(II)/Zn(II)-rich stream [97±2% Cu(II) and 82±3% Zn(II)] was obtained, and 60±4% of As(V) was removed from the initial feed stream. Then, the separation of Zn(II) from Cu(II) was proposed using Lewatit VP OC 1026 resin at pH=2.2 and 4.3, respectively. In this IX resin process, it was possible to recover about 70±3% of Zn(II) and 98±2% of Cu(II) and to concentrate Zn(II) and Cu(II) around 30- and 23-times, respectively.

Keywords: ion-exchange, metallurgical industry, metal recovery, circular economy, resource efficiency, copper and zinc

1. INTRODUCTION

Copper (Cu) and zinc (Zn) are considered the most consumed non-ferrous metals obtained in the extractive metallurgy industry using either pyrometallurgy, hydrometallurgy, or electrometallurgy processes. Pyrometallurgy is one of the most important processes, providing about 75–80% copper by flash smelting. On the other hand, zinc world output (90–95%) is obtained by means of hydrometallurgy processes [1,2]. However, during metallurgical activities, liquid (e.g., streams) and solid (e.g., slags) waste are produced, rich in copper and zinc, among other impurities. In this sense, the management of metallurgical industries is essential to reduce water and solid pollution [3–5].

Metallurgical process effluents are mainly composed of copper and zinc, which could be used as secondary resources for metal recovery, although current management options are complex [6]. Furthermore, the presence of elements, such as As(V), Sb, and Bi, in acidic streams rich Cu(II) and Zn(II) (pH 2.0–2.5) limits the valorisation of both metals. From a chemical point of view, these non-metal elements could be present as oxyanions. In this sense, when cation-exchange processes are used for the separation of As(V) from Cu(II)/Zn(II) streams or when anion-exchange resins are used for the selective removal of the As(V)-oxyanion, the formation of Cu(II) and Zn(II)-arsenates on the impregnated ion-exchange (IX) resin beds limits their effective separation and subsequent valorisation [7]. Similar limitations have been reported using solvent extraction or selective precipitation [1,8,9]. Recently, membrane-based processes have also been used to separate, concentrate, and purify metallurgical and hydrometallurgical streams [10–16].

Much attention has been devoted to novel membrane technology based on electrodialysis (ED), namely selectrodialysis (SED), which exhibits remarkable potential

in oxyanion recovery, such as phosphate from wastewaters [17–19] and concentrated industrial brines [20,21] and heavy metal recovery from acidic streams [22]. This technology uses standard and mono-selective membranes to separate different charged ions when electrical current is applied [23]. Moreover, SED improves the separation performance of standard ED configurations [24,25].

On the other hand, the most common processes for the removal of heavy metals from wastewaters are IX [26–31] and sorption [32–36] processes. The later process presents limitations for hydrometallurgical applications, such as its relatively low sorption capacity, low selectivity for metal ions, poor mechanical stability, fouling, and wash-water requirements when used for high-grade applications. Unlike most competing sorption processes, IX resins present more advantages (e.g., they do not require complex pH adjustment during the process). Miron et al. [28] investigated two types of resins (Purolite C 106 and Purolite PPC 104) for the removal of Cu(II) and Zn(II) from metal finishing or mineral processing industry streams, concluding that both resins achieved efficient metal-ion recovery. Taute et al. [37] evaluated the use of di(2-ethylhexyl) phosphoric acid (D_2EHPA)-impregnated resin and amino-phosphonic acid resins for the selective removal of Zn(II) from Cu(II), obtaining a maximum loading capacity of 17.0 mg Zn(II)/g resin at pH=2.7–3.1. Moreover, removal of Zn(II) from industrial waste liquors by D_2EHPA-impregnated resins was also studied by Simpson et al. [38]. It is remarkable that one of the main disadvantages of impregnated resins are their extractant losses, although they have been reduced by improvements in the manufacturing processes. Moreover, these losses are minimized if the acidity of the aqueous stream (sorption, elution, and wash liquors) is maintained below pH=4 [39]. Furthermore, a new family of more effective chelating resins, especially under low pH values, based on

bispicolylamine functional groups attached to a polystyrene divinylbenzene matrix have been commercialized in the last decade (e.g., Purolite S960 or Dowex M-4195) [40–42].

Finally, the retention of Zn(II) over Cu(II) at lower pH values provides the possibility of achieving separation of both metal ions by IX resins, and it provides single ion-rich streams that could be processed using electrowinning technologies [43,44].

Therefore, the aim of this work was to separate arsenic and recover copper and zinc from non-ferrous metallurgical industry streams by a new combination of technologies based on two ion-exchange processes: (i) SED and (ii) IX resins.

2. MATERIALS AND METHODS

Figure 1 shows the experimental processes carried out in this article, focussed on the separation of arsenic (toxic impurity) from acidic metallurgical streams [mainly composed of Cu(II) and Zn(II)] by means of SED. Then, the obtained As(V)-rich solution could be treated properly for external disposal due to the toxic behaviour of the arsenic. On the other hand, after SED treatment a Cu(II)/Zn(II)-rich stream was also obtained. Afterwards, ion-exchange resins were used to separate and concentrate Cu(II) from Zn(II) in order to reuse both streams in the copper and zinc metallurgical industries, respectively, following the circular economy concept proposed by the European Union (EU) [45,46]. Therefore, the practical applicability of this study is the integration of these two ion-exchange processes in metallurgical industries in order to solve two main challenges: (i) the removal of impurities [e.g., As(V)] in copper smelters through SED and (ii) the selective separation and concentration of Cu(II) and Zn(II) using resins. As a consequence, metallurgical industries could implement these sustainable ion-exchange processes to obtain copper and zinc deposits with low arsenic content.
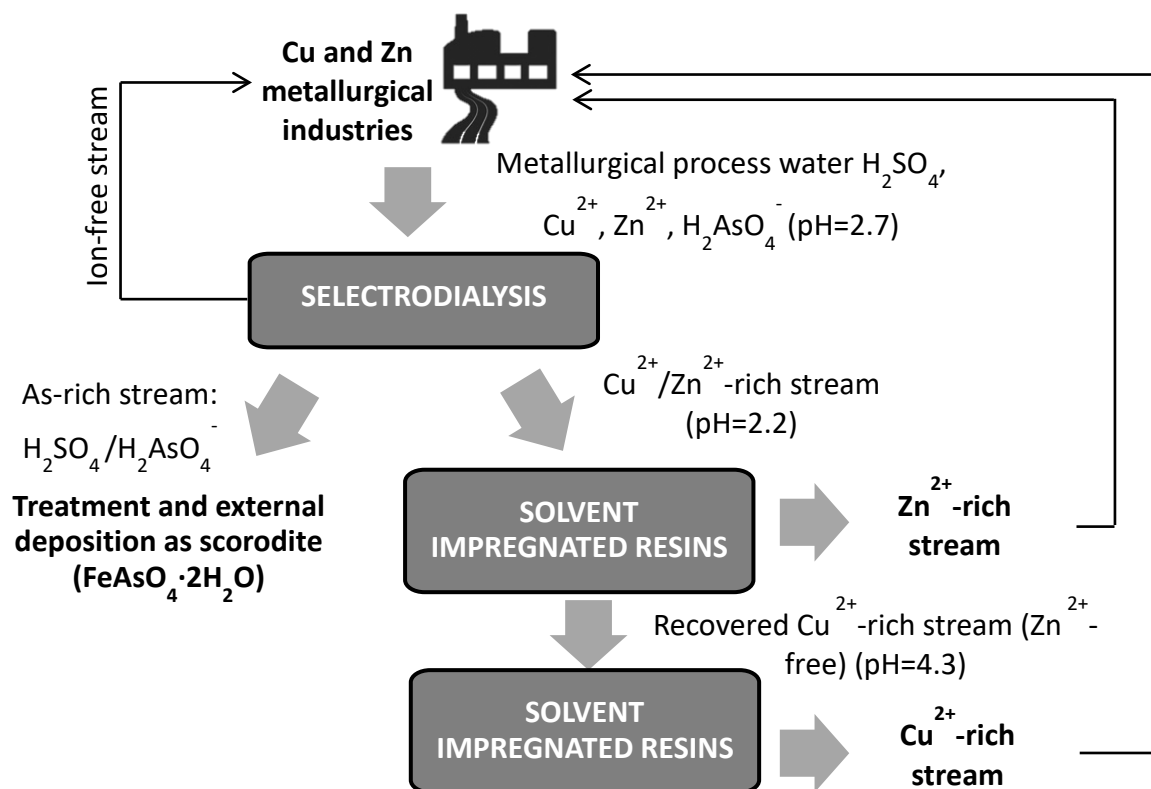
Figure 1. Flowchart proposed in this study for Cu(II) and Zn(II) recovery and As(V) removal from metallurgical streams following the circular economy strategy.

2.1. Materials and reagents

Anhydrous copper sulphate ($CuSO_4$), zinc sulphate monohydrate ($ZnSO_4 \cdot H_2O$), sulfuric acid (H_2SO_4), and sodium sulphate (Na_2SO_4) were supplied by Panreac. Sodium arsenate dibasic heptahydrate (Na_2HAsO_4) was purchased from Sigma-Aldrich. All reagents were of analytical quality (PA-ACS-ISO).

Membranes used for SED experiments were supplied by Fujifilm Manufacturing Europe B.V (Netherlands). The following two ion-exchange resins were used for IX tests: (i) Purolite S960, which is a chelating resin composed of a bis-picolylamine group, purchased from Purolite, and (ii) Lewatit VP OC 1026, which is a solvent-impregnated resin containing the extractant agent D2EHPA, supplied by Lanxess.

2.2. Selectrodialysis (SED) set-up for arsenic removal

SED experiments were conducted using a conventional ED lab-scale set-up (ED 64-004) supplied by PCCell (Germany) whereas membranes were supplied by Fujifilm Manufacturing Europe B.V (Netherlands), with an active area of 64 cm^2 per membrane. In this case, a standard anion-exchange membrane (AEM), standard cation-exchange membrane (CEM), and monovalent selective cation-exchange membrane (MVC) were placed between two electrodes following the sequence AEM-MVC-CEM (3 membrane trios), previously proposed by Reig et al. [22]. Furthermore, the following four streams were used in the SED system: (i) a feed solution mimicking an acidic metallurgical stream, (ii) 3 mM H_2SO_4 as the initial Cu(II)/Zn(II)-rich product, (iii) 3 mM H_2SO_4 as the initial As(V)-rich product, and (iv) 1 mM Na_2SO_4 as the electrode rinse solution. The solution mimicking an acidic stream, obtained from a confidential copper metallurgical industry, contained 1.65 mM Cu(II), 0.73 mM Zn(II), and 1.13 mM As(V) from $CuSO_4$, $ZnSO_4$, and Na_2HAsO_4, respectively, with a pH close to 2.2.

The initial volume of each stream was 2 L, pumped at 15 L/h for the feed stream and the Cu(II)/Zn(II)-rich and As(V)-rich products, while the electrode rinse solution was pumped at 90–100 L/h. A constant voltage of 7 V was applied at 25ºC for all experimental tests since this was the maximum allowed voltage with this membrane configuration.

Samples collected during the experiments were analysed by inductively coupled plasma (ICP) to determine Cu(II), Zn(II), and As(V) concentrations in each stream during the operational time. Data are reported as the mean ± standard deviation of duplicate determinations.

2.3. SED process efficiency

The separation efficiency of SED process was evaluated by using two concepts: (i) energy consumption and (ii) faradic yield [22]. Energy consumption (E_c) was calculated as kWh per kilogram (kg) of the product, according to the following equation (1):

$$Ec\left(\frac{kWh}{kg\ product}\right)$$
$$= \frac{(V_{Cell} * I * t)/1000}{v_{tank} \cdot C_{product} - v_{tank,0} \cdot C_{product,0}} \tag{1}$$

where V_{cell} (V) and I (A) are the voltage and current applied in the ED stack, respectively; t (h) is the operation time; $v_{tank,0}$ and v_{tank} are the tank volume (L) at initial time "0" and at time "t", respectively; and $C_{product,0}$ and $C_{product}$ are the product concentration (kg/L) at initial time "0" and at time "t", respectively.

On the other hand, the faradic yield for the product was calculated according to the following equation (2):

$$\varphi\ (\%) = \frac{z * F\left(C_i * v_{tank} - C_{i,0} * v_{tank,0}\right)}{\int_0^t I(t)dt * n} * 100 \tag{2}$$

where z is the ion charge [neutral substance (acid, salt), $z=1$; ion, $z=$ion charge; in this case $z=2$]; F is Faraday's constant (96500 C/mol); C_i and $C_{i,0}$ are the ion concentration (mol/L) at time "t" and initial time "0", respectively; $v_{tank,0}$ and v_{tank} are the tank volume (L) at t=0 and t=t, respectively; I is the current applied (A); t is the operation time (s); and n is the number of cell pair/trios used (3 in this case).

2.4. Ion-exchange resins set-up for copper and zinc recovery

The following two types of configurations were used for the ion-exchange process with the resins: (i) a batch configuration to conduct kinetic and pH studies and (ii) a fixed-

bed configuration to carry out individual separation of Cu(II) and Zn(II). Furthermore, two ion-exchange resins were used, Purolite S960 and Lewatit VP OC 1026.

2.4.1. Metal kinetic performance: Time to attain equilibrium

Batch kinetic experiments were performed in tubes with 0.5 g of each resin and 20 mL of Cu(II)/Zn(II)-rich stream from the SED process, containing Cu(II) (1.55±0.02 mM) and Zn(II) (0.61±0.09 mM) at pH=2.2. Experiments were done by shaking the samples at 200 rpm using a Heidolph Reax 2 overhead shaker (Germany) at room temperature (25ºC) for 30 min. Samples were withdrawn sequentially at certain time intervals and analysed by ICP to determine Cu(II) and Zn(II) concentrations in each sample over time. Data are reported as the mean ± standard deviation of duplicate determinations.

2.4.2. Effect of initial solution pH

Batch experiments were carried out at the same solid-to-liquid ratio (1:40 w/v) used in the kinetic study but with the ion-exchange time set at 2 h and the pH varied between the following values: -0.5, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0. Two hours were enough to attain equilibrium because after 30 min of the kinetic study constant values were achieved. The pH was adjusted using 1 M NaOH or 1 M H_2SO_4, and it was measured with a pH meter (GLP 22, Crison, Spain). Once equilibrium was attained, samples were filtered and Cu(II) and Zn(II) content was analysed by ICP. Data are reported as the mean ± standard deviation of duplicate determinations.

2.4.3. Column experiments

Glass columns (1 cm diameter × 7 cm height) were packed with 2.75 g of resin. Then, the Cu(II)/Zn(II)-rich stream from SED was pumped at 2 mL/min using a Miniplus 3 peristaltic pump (Gilson, USA) in an open-loop configuration to obtain Cu(II) and Zn(II) breakthrough curves at 25ºC. Samples were obtained over time using an FC 204 fraction collector (Gilson, USA), and metal concentrations were determined by ICP.

The batch experiments determined the pH value that was used in the column experiments (maximum ion exchange). After each ion-exchange process, the elution step was necessary to recover and concentrate the metals previously exchanged with the IX resins. The elution was carried out with 1 M H_2SO_4 at a flow rate (0.5 mL/min) four times lower than the ion-exchange process.

Data are reported as the mean ± standard deviation of duplicate determinations.

2.5. Operational parameters for the ion-exchange process with resins

The bed volume (BV) can be defined as the free volume in a fixed-bed column, described by the following equation (3) [47]:

$$BV = \frac{Q \cdot t_{1/2}}{V_b} \tag{3}$$

where BV is the bed volume (dimensionless), Q is the flow rate (mL/min), $t_{1/2}$ is the inflection point in the breakthrough curve (min), and V_b is the volume of the reactive bed (mL). Furthermore, V_b was defined by the following equation (4):

$$V_b = \pi \cdot r^2 \cdot h_b \cdot \varepsilon \tag{4}$$

where r is the internal radius of the column (cm), h_b is the length of the resin bed (cm), and ε is the porosity. Finally, the porosity was calculated by following the equation (5):

$$\varepsilon = \frac{Q \cdot t_{1/2}}{V_{column}} \tag{5}$$

where Q is the flow rate (mL/min) and V_{column} is the total column volume (mL).

On the other hand, the sorbed metal mass during the ion-exchange process was determined by integrating the area above the breakthrough curve for each metal. As C/C_0 represents the outlet concentration, a simple mass balance defines the sorbed concentration as $1-C/C_0$. Therefore, the adsorbed mass can be obtained from the following equation (6):

$$m_{ads} = C_0 \int_0^{V_{sat}} \left(1 - \frac{C}{C_0}\right) dV \tag{6}$$

where m_{ads} is the adsorbed metal mass (mg), C_0 is the feed concentration (mg/L), and V_{sat} is the total volume of solution that passed through the column at the saturation point (L). Therefore, resin sorption capacity (Q_{ads}, mg metal/g resin) was calculated afterwards by the following equation (7):

$$Q_{ads} = \frac{m_{ads}}{m_{res}} \tag{7}$$

where m_{ads} is the mass of the sorbed metal (mg) and m_{res} is the resin mass in the column (g).

Regarding the elution process, the metal concentration in the elution stream is defined according to the following equation (8):

$$m_{elu} = \int_0^{V_p} C \ dV \tag{8}$$

where C is the measured metal concentration (mg/L), V_p is the volume of the eluent required for total metal desorption (L), and m_{elu} is the eluted metal mass in the elution stream (mg). Thus, the resin elution capacity (Q_{elu}, mg metal/g resin) was calculated by the following equation (9):

$$Q_{elu} = \frac{m_{elu}}{m_{res}} \qquad (9)$$

where m_{elu} is the mass of the eluted metal (mg) and m_{res} is the resin mass in the column (g).

Consequently, the total percentage of metal recovery can be established by the relationship between sorption capacity and elution capacity of the resin. This parameter (metal recovery percentage, %) is calculated by the following equation (10):

$$Metal\ recovery\ (\%) = \frac{Q_{elu}}{Q_{ads}} \cdot 100 \qquad (10)$$

Lastly, the concentration factor (CF) of the ion-exchange separation stage was determined for each metal ion by the following equation (11):

$$CF = \frac{C_{elu}}{C_0} \qquad (11)$$

where C_{elu} is the metal concentration in the elution stream and C_0 is the metal concentration in the Cu(II)/Zn(II)-rich stream from SED used in the ion-exchange process.

2.6. Analytical analysis

ICP with optical emission spectrometry (OES) (Agilent 5100) or mass spectrometry (MS) (Agilent 7800) was used to determine element concentrations in mg/L or µg/L, respectively. Commercial metal standards were used to generate calibration curves.

3. RESULTS AND DISCUSSION

3.1. Cu(II) and Zn(II) separation from As(V) by SED

Once the initial feed solution, mainly composed of 1.65 mM Cu(II), 0.73 mM Zn(II), and 1.13 mM As(V) (from $CuSO_4$, $ZnSO_4$, and Na_2HAsO_4, respectively, with a pH close to 2.2), was fed into the SED stack and when current was applied, ions started to migrate through the membranes to the electrodes. The conductivity of each sample was measured in-line in order to check its evolution over time. As expected, the conductivity of the electrode rinse solution was constant during the experimental test [22,48], and the concentrations of Cu(II), Zn(II), and As(V) were below 0.002 mM. The evolution of Cu(II), Zn(II), and As(V) concentration in each stream [Cu(II)/Zn(II)-rich, As(V)-rich, and feed] is depicted in **Figure 2**.
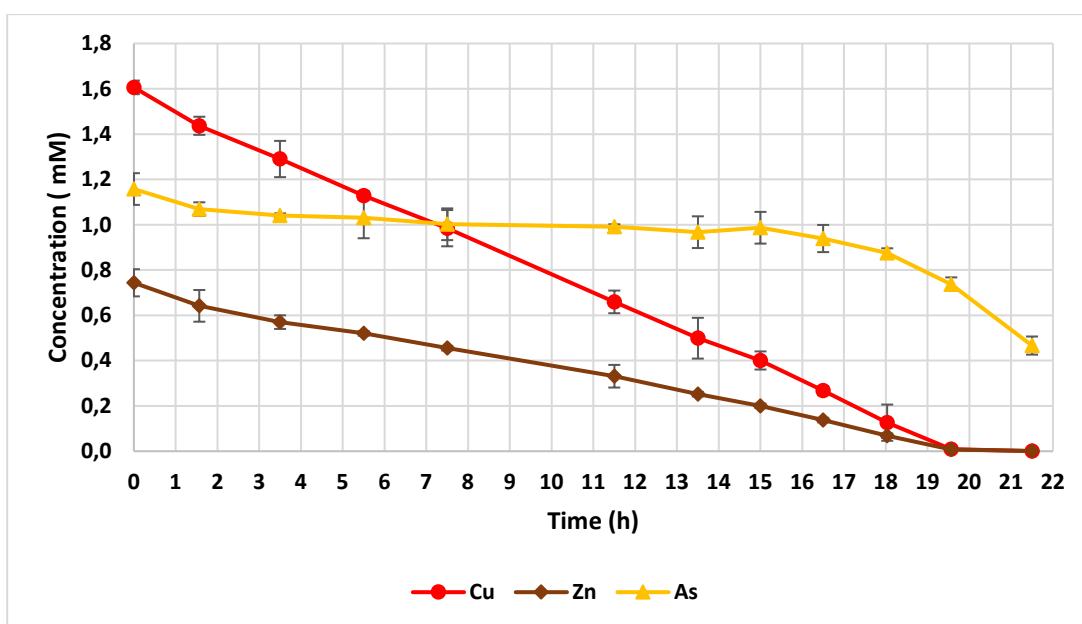
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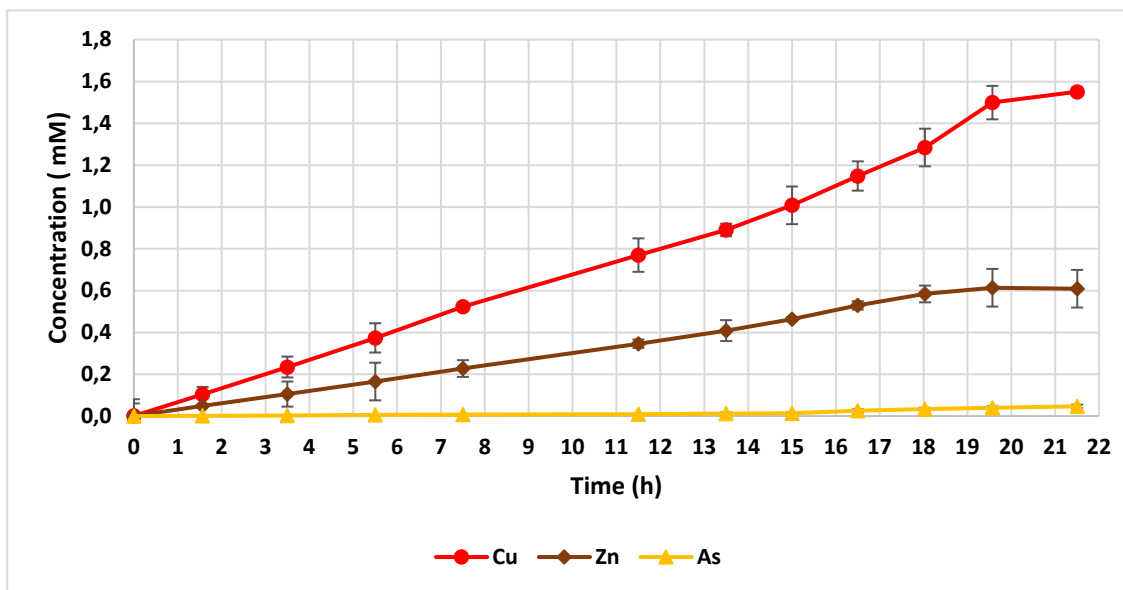
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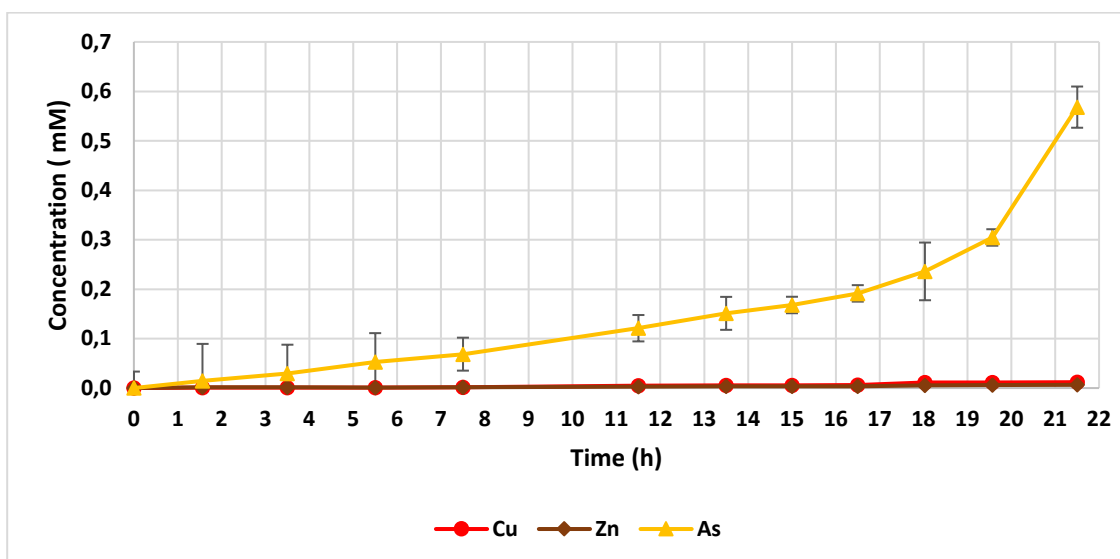
c)

Figure 2. Evolution of Cu(II), Zn(II), and As(V) concentration over time in the a) Cu(II)/Zn(II)-rich, b) As(V)-rich, and c) feed streams.

As shown in **Figure 2a** and **Figure 2b**, the initial Cu(II), Zn(II), and As(V) concentrations for the Cu(II)/Zn(II)-rich and As(V)-rich streams were zero since at the beginning of the experiments these streams contained 3 mM H_2SO_4. However, when

current was applied and ion migration took place in the SED cell, only Cu(II) and Zn(II) ions were concentrated in the Cu(II)/Zn(II)-rich stream (up to 1.55±0.02 and 0.61±0.09 mM, respectively) (**Figure 2a**), whereas As(V) was the only ion that increased its concentration in the As(V)-rich stream (up to 0.57±0.04 mM) (**Figure 2b**). After 22 h of operation, the As(V) concentration in the Cu(II)/Zn(II) stream (**Figure 2a**) and the Cu(II) and Zn(II) concentrations in the As(V)-rich compartment (**Figure 2b**) were almost zero [0.047±0.008 mM As(V), 0.012±0.002 mM Cu(II), and 0.007±0.001 mM Zn (II), respectively].

Figure 2c shows that the ion concentrations decreased over time in the feed stream. Cu(II) and Zn(II) concentrations decreased sharply from the beginning of the experiment to the end. In fact, the Cu(II) concentration decreased from 1.61±0.03 mM to 0.0004±0.0001 mM, whereas the Zn(II) concentration decreased from 0.74±0.06 mM to 0.0013±0.0008 mM. However, total deconcentration of As(V) in the feed stream was not reached over the experimental time [59.7% As(V) removal], while Cu(II) and Zn(II) reached around 99.8% removal for both ions. It is important to point out that the ionic migration flux is the most relevant phenomenon that takes place in the SED stack, although there are also undesired ions and water transports that could affect the membrane selectivity and, thus, change the expected results, reducing the efficiency of the process [23,49].

All in all, it was proven that SED allowed for the separation of Cu(II) and Zn(II) (as a mixture of $CuSO_4$ and $ZnSO_4$) from As(V) (as Na_2HSO_4). Ion recovery from the initial feed solution into its respecting product streams was 96.6% and 81.9% for Cu(II) and Zn(II) in the Cu(II)/Zn(II)-rich stream, respectively, whereas only 49.1% of the initial As(V) was recovered in the As(V)-rich stream. Moreover, energy consumption (**Figure**

3) and faradic yield (data not shown) profiles were also calculated over the experimental time.
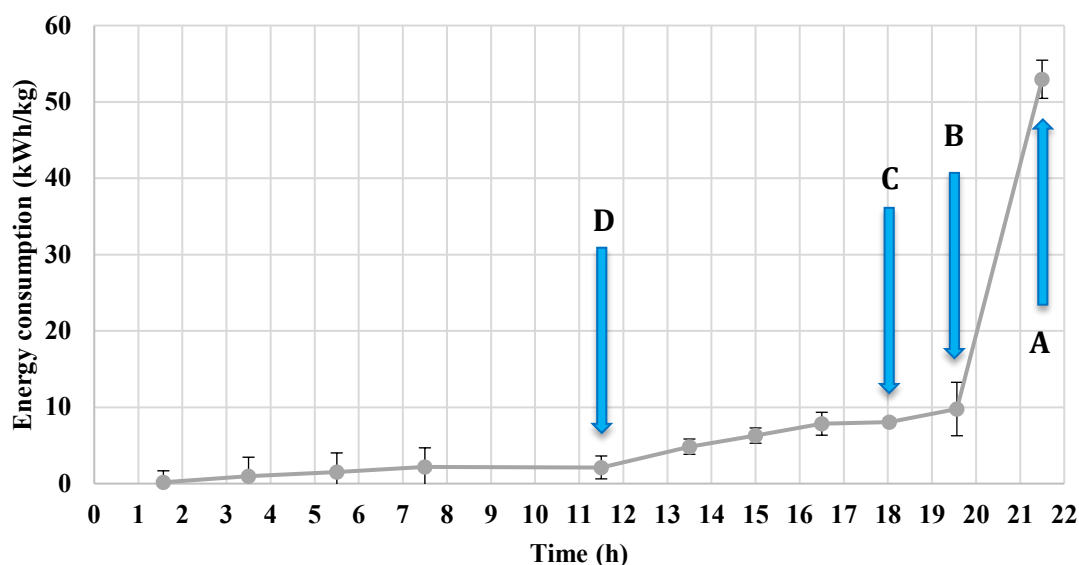

Figure 3. Energy consumption evolution over time by selectrodialysis (SED).

As plotted in **Figure 3**, the energy consumption profile can be divided into the following four different sections depending on the experimental time: A (21.5 h), B (19.6 h), C (18 h), and D (11.5 h). Taking into account the entire experiment (section A), the energy consumption increased from 0.2±1.5 to 53.0±2.5 kWh/Kg Cu(II)+Zn(II). The rapid increase in the final section was due to the plateau reached for Cu(II) and Zn(II) concentrations in the Cu(II)/Zn(II)-rich stream (see **Figure 2a**). This behaviour, in which energy consumption increased drastically, was already detected when the concentration was established at a constant value over time [50]. On the other hand, the faradic yield was observed to be inversely proportional to the energy consumption curve, obtaining high values (above 70%) when the energy consumption was low [around 2 kWh/kg Cu(II)+Zn(II)].

Therefore, to determine the optimal time to stop the experiment, with low energy consumption and high Cu(II)/Zn(II) recovery, **Table 1** shows the average energy consumption and the Cu(II)/Zn(II) recovery obtained in each section.

Table 1. Energy consumption and Cu(II)/Zn(II) recovery in the Cu(II)/Zn(II)-rich stream depending on the operational time.

Section	Time range (h)	E_c average [kWh/kg Cu(II)+Zn(II)]	Cu(II)/Zn(II) recovery
A	0–21.5	8.8	89.2±10.4
B	0–19.6	4.4	87.9±7.7
C	0–18.0	3.8	79.2±1.0
D	0–11.5	1.4	47.2±1.0

As seen in **Table 1**, it is necessary to establish a compromise between energy consumption and the Cu(II)/Zn(II) recovery achieved in each section. In this case, section B (19.6 h) was found to be optimum to achieve acceptable energy consumption [4.4 kWh/kg Cu(II)+Zn(II)], whereas recovering 87.9% of the initial concentration of Cu(II) and Zn(II) in the Cu(II)/Zn(II)-rich stream. This energy consumption value is in agreement with that reported by Ye et al. (2018), who used the same membrane configuration (AEM-MVC-CEM), applying 7 V to the SED stack. In the aforementioned study, the aim of the work was to fraction magnesium ions from seawater for struvite recovery, and the energy consumption under the mentioned conditions was 5.4 kWh/kg $MgCl_2$ [51].

Finally, **Table 2** gives an overview of the Cu(II), Zn(II), and As(V) concentrations obtained after the SED experiment in each stream in comparison with the initial feed concentration from the metallurgical industry.

Table 2. Overall Cu(II), Zn(II), and As(V) concentrations in each stream after the SED process.

Stream		Ion concentration (mM)		
		Cu(II)	**Zn(II)**	**As(V)**
Initial	Feed from metallurgical industry	1.61±0.03	0.74±0.06	1.16±0.07
Produced	Diluate	$4.37E^{-4} \pm 1.01E^{-4}$	$1.34E^{-3} \pm 8.02E^{-4}$	0.47±0.04
	As(V)-rich	$1.19E^{-2} \pm 2.27E^{-3}$	$6.51E^{-3} \pm 9.10E^{-4}$	0.57±0.04
	Cu(II)/Zn(II)-rich	1.55±0.02	0.61±0.09	0.05±0.01

As seen in **Table 2**, the diluate stream obtained from SED contained As(V), as well as the As(V)-rich stream. For this reason, both streams were mixed for external treatment, reacting with iron and disposed as scorodite, which is a hydrated iron arsenate mineral ($FeAsO_4 \cdot 2H_2O$) [52–54]. On the other hand, the Cu(II)/Zn(II)-rich stream contained mainly copper and zinc, which must be separated for reuse.

3.2. Cu(II) and Zn(II) recovery using chelating/impregnated ion-exchange resins

After the SED process, the Cu(II)/Zn(II)-rich stream (containing 1.55±0.02 mM Cu and 0.61±0.09 mM Zn at pH=2.2) was treated with resins to recover and separate Cu(II) and Zn(II). Afterwards, both ions could be reused in copper and zinc metallurgical industries, respectively.

3.2.1. Kinetic performance

The kinetic profiles, represented as C/C_0 versus time, are depicted in **Figure 4**. For Purolite S960 (**Figure 4a**), reaching the equilibrium with the Zn(II) exchange reaction was faster than Cu(II) since it was reached after 15 min, while 30 min were needed for

Cu(II). In terms of capacity, Purolite S960 showed higher affinity for Cu(II) than Zn(II) because the removal was 90% for Cu(II) and 40% for Zn(II) after 30 min.

Figure 4b shows that Zn(II) equilibrium was attained after 25 min using Lewatit VP OC 1026. In addition, Zn(II) retention was reached at C/C_0=0.5 after 3 min, meaning that the adsorption process was very fast. Also, it was possible to remove 80% of Zn after 30 min.

Under the acidity conditions of pH=2.2, Cu(II) was not extracted and its kinetic performance was not reached (see **Figure 4b**). It was concluded that this resin had higher selectivity for Zn(II) than Cu(II). Moreover, this result is in concordance with previous studies. For instance, Simpson et al. [38] tested Lewatit VP OC 1026 for Zn(II) recovery and reported that this resin has great selectivity for zinc.
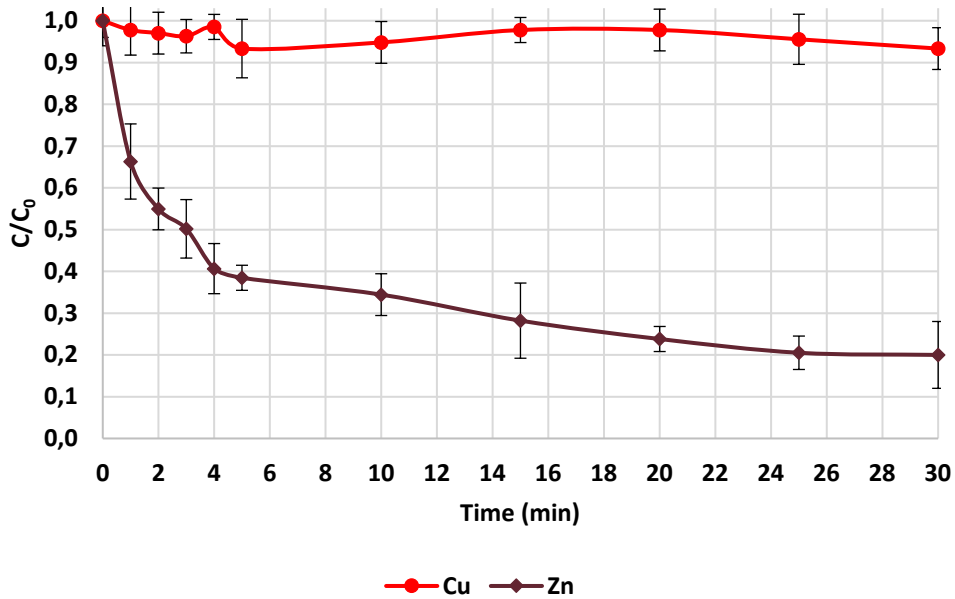
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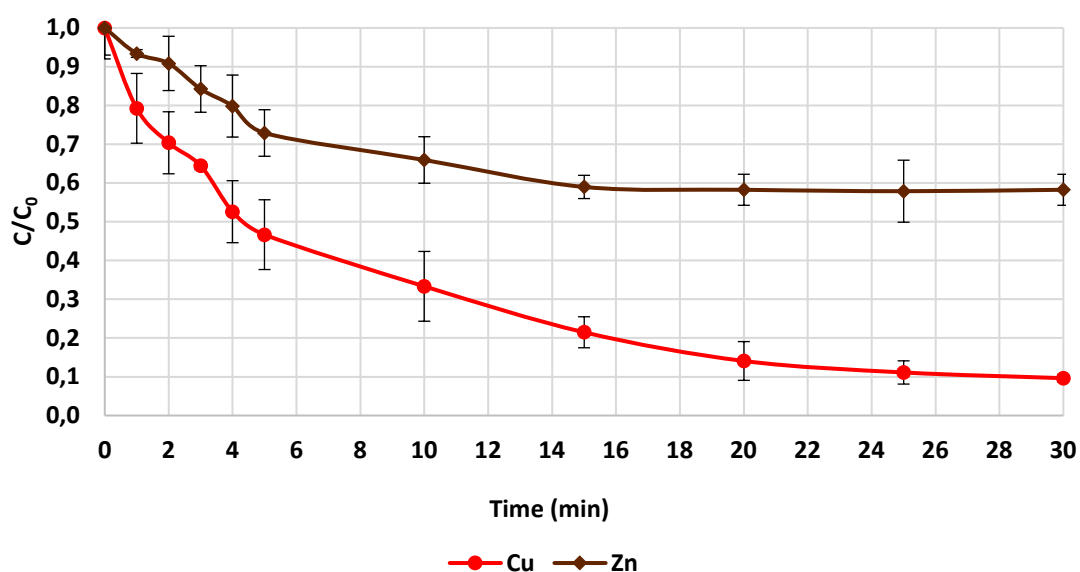
b)

Figure 4. Ion-exchange kinetic curves for Cu(II) and Zn(II) retention using a) Purolite S960 and b) Lewatit VP OC 1026 resins, respectively.

From the kinetic studies, it can be concluded that Lewatit VP OC 2016 seems to be the most appropriate resin for Cu(II) and Zn(II) separation if using only one resin since both concentration curves [for Cu(II) and Zn(II)] during the ion-exchange process indicate different sorption capacities (**Figure 4b**) than when Purolite S960 is used (**Figure 4a**). In fact, Juang et al. [55] also used Lewatit VP OC 1026 resin for Cu(II) and Zn(II) recovery from aqueous sulphate solutions. Although, they observed that Lewatit VP OC 1026 was more selective for the retention of zinc.

### *3.2.2. Cu(II)/Zn(II) retention performance: Equilibrium dependence on solution acidity*

The metal retention dependence on equilibrium is shown in **Figure 5**. As seen in **Figure 5a**, when using Purolite S960 maximum Cu(II) retention was reached at pH$\geq$1.0

(97±1%), whereas maximum Zn(II) retention of 60±2% was obtained at pH values of 2.5–5.0, fixing the ion-exchange time at 2 h. Moreover, it was observed that copper retention drastically changed with pH, varying between –0.5 and 0.5. After a pH of 0.5, it remained constant at a high retention percentage. In the case of zinc, at the first pH value (between –0.5 and 0.5) differences in the adsorption were not observed and only a pronounced change was observed when the pH was higher than 1, achieving maximum retention at pH=3.5.

Considering that the aim was to maximize the recovery of one metal and not to alter the other, the optimum pH range for Cu(II) separation would be between 0.5 and 1.0. In this scenario, the highest recovery of Cu(II) is expected, while less than 6–10% of Zn(II) would be extracted.

On the other hand, the pH effect on the metal retention capacity using the Lewatit VP OC 1026 resin is depicted in **Figure 5b**. It shows that the maximum retention of Zn(II) is greater than 98±1% at pH≥2.5. Moreover, maximum Cu(II) retention took place at pH=3.5 (around 94±1%). With this resin, both metals presented the same tendency in their breakthrough curves as a function of pH (between –0.5 and 1.0). However, after pH>1.0, zinc retention was faster than copper, and only copper retention was observed with pH≥2.0. In this case, the optimal pH value to obtain the highest selectivity for Zn(II) (between 84–98%) was 2.0–2.5, while the Cu(II) retention in this pH range was about 3–28%. Additionally, as the pH increases, for instance, to pH=3.5, the retention of Cu(II) was also greater (94%).
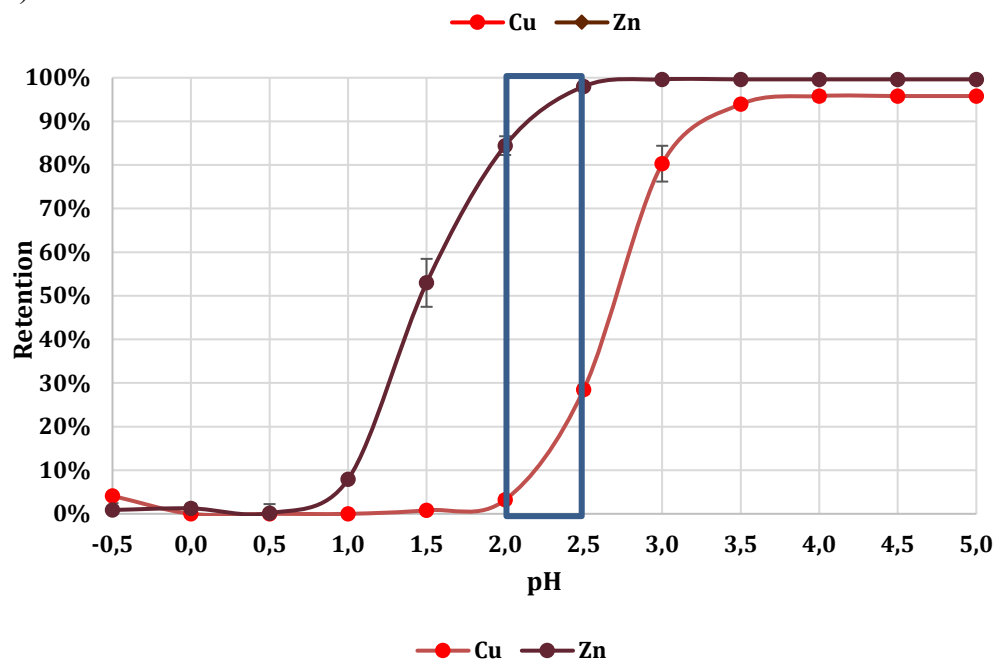
a)
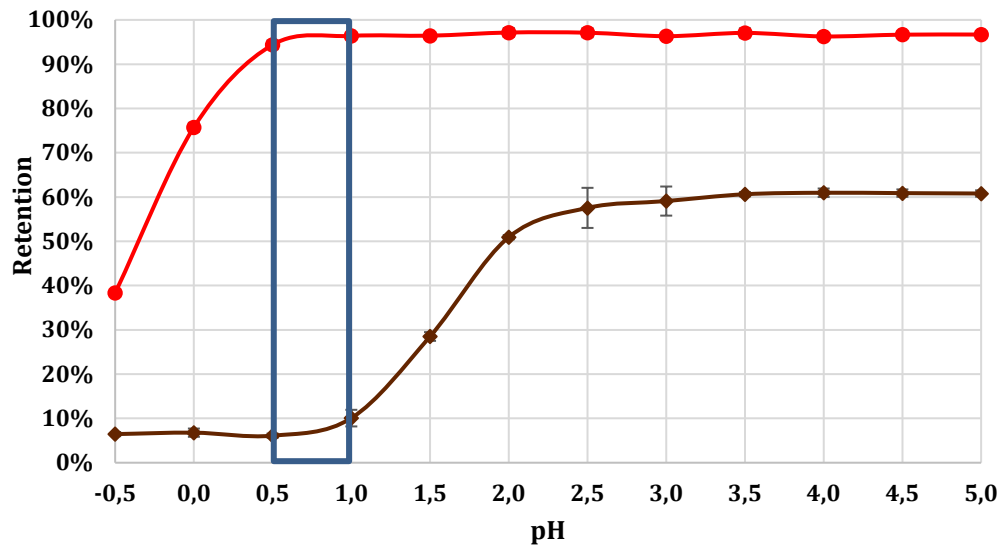
b)

Figure 5. Retention dependence of Cu(II) and Zn(II) as a function of the initial pH for a) Purolite S960 and b) Lewatit VP OC 1026 resins, respectively, at different pH values.

Taute et al. [37] and Cortina et al. [56] observed that the maximum Zn(II) loading capacity was obtained at pH values around 2.5 when using Lewatit VP OC 2016 resin. In the present work, for both tested resins it was observed that metal retention depends on

the working pH, following a typical S-shape function. In both cases, two pH windows could be found (**Figure 5**), with blue rectangles, where it was possible to extract one of the studied ion-metals (retention >90%) whereas the co-retention of the second one was below 10%. In the case of Purolite S960, Cu(II) could be extracted from solutions at pH 0.5, while for Lewatit VP OC 1026 Zn(II) could be extracted at a pH value around 2.2.

On the other hand, taking into account the regeneration step in both resin options, the regeneration of Cu(II) using an acid usually produces regeneration efficiencies of <60%, and complexing extractants with NH_3 have been proposed. Otherwise, Zn(II) and Cu(II) regeneration from Lewatit VP OC 1026 could be carried out with H_2SO_4 solutions, with recoveries higher than 95% [40]. Accordingly, experiments in column configuration with Purolite S960 resin were discarded in order to avoid reagent consumption correcting the pH since the Cu(II)/Zn(II)-rich stream from the SED process presents pH values higher than 0.5. Contrarily, the Lewatit VP OC 1026 resin allows for working at higher pH windows (between 2.0 and 5.0).

Therefore, the Cu(II)/Zn(II)-rich stream from SED was treated in a fixed-bed configuration without changing the pH (around pH=2.2) by the Lewatit VP OC 1026 resin, since at this pH the highest Zn(II) recovery was achieved (**Figure 5b**). Once Zn(II) was recovered, the Cu(II)-rich stream (free of Zn(II)) was also treated with Lewatit VP OC 1026 resin but at pH=4.3 in order to achieve the highest Cu(II) recovery. The overall scheme of these column experiments for separating both ions in a consecutive manner is represented in **Figure 6**.
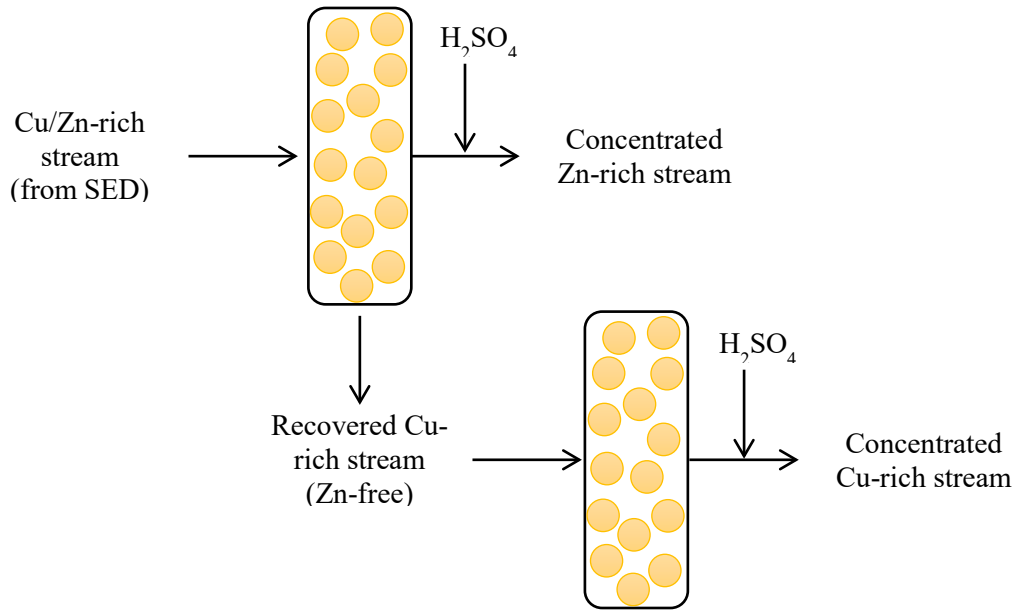
Figure 6. Scheme of column experiments for Cu(II) and Zn(II) recovery.

The proposed experimental design is in accordance with work reported by Juang et al. [55], where the pH for zinc recovery varied between 2.2 and 3.5 and for copper the recovery varied from 3.0 to 5.5.

3.2.3. Fixed-bed assays

The ion-exchange evolution of the Cu(II)/Zn(II)-rich stream from the SED process by the selected resin is plotted in **Figure 7a**. The Cu(II) concentration increased until reaching the maximum sorption at 55 BV (where $C/C_0=0.99$), indicating that Cu(II) was not well-adsorbed by the resin under these experimental conditions. Afterwards, the evolution of the Cu(II) concentration profile was constant over time.

On the other hand, the concentration of Zn(II) remained constant in C/C_0 values up to 96 BV, but an increase after this point was detected, where the resin began to become saturated with Zn(II). $C/C_0=0.5$ was achieved after around 160 BV, and finally at 224 BV the resin was totally saturated by Zn(II) (**Figure 7a**). It is important to mention

that Cu(II) and Zn(II) recovery by solvent-impregnated resins have not been widely studied. For this reason, due to the novelty of the present study, few works can be found in the literature reporting results for Cu(II) and Zn(II) recovery. Taute et al. [37] studied Zn(II) and Cu(II) recovery, apart from other metals, using the same resin tested in this study. Their feed solution contained 45.0 mg/L of Zn(II) [0.7 mM Zn(II)] at a pH around 2.5, which is comparable with the initial feed composition from SED [0.6 mM Zn(II)]. In that case, the authors reported that Zn(II) was also exchanged by Lewatit VP OC 2016, while Cu(II) was not able to be adsorbed by the resin.

The sorption capacities of the first column for Cu(II) and Zn(II) recovery were 3.3±0.4 mg/g resin and 15.9±2.7 mg/g resin, respectively. These values indicate that Zn(II) was more sorbed than Cu(II) with these operation conditions. Moreover, the Zn(II) sorption capacity by Lewatit VP OC 1026 obtained in this work is similar to that reported by Taute et al. [37], where 17.0 mg Zn(II)/g resin was achieved for the Zn(II) capacity.
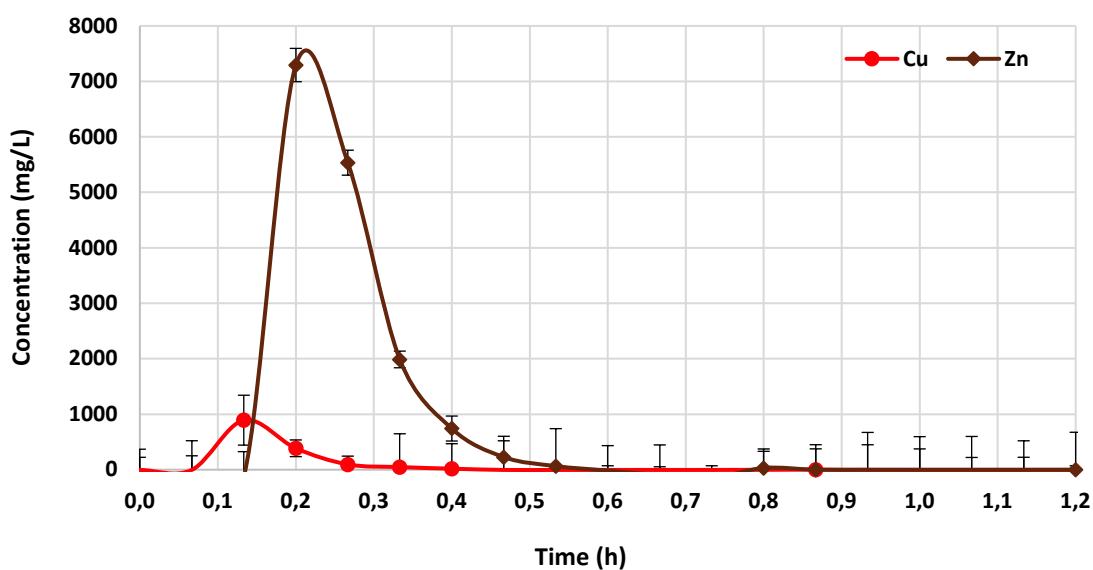
a)
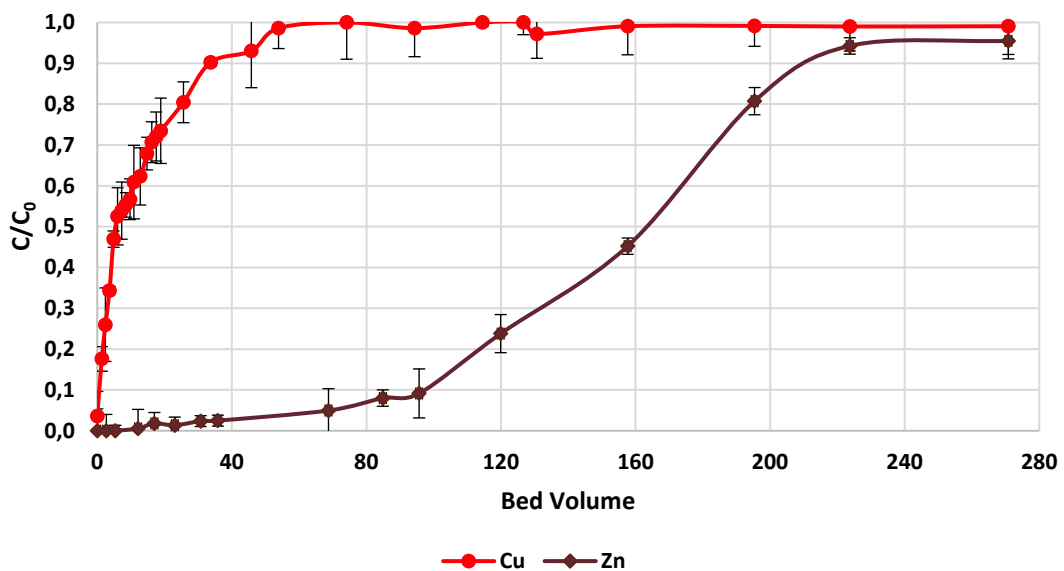
b)

Figure 7. Evolution curves for a) ion-exchange and b) elution processes for Zn(II) recovery from sorption experiments using Lewatit VP OC 1026.

Regarding the elution process (**Figure 7b**), it was observed that the total recovery of Zn(II) took 0.5 hours, achieving a maximum peak of 7300 mg/L of Zn(II). In the same figure, it is seen that part of the copper that was initially retained by the resin was also recovered, presenting a maximum peak close to 890 mg/L after 0.13 hours of elution. In this sense, it was possible to recover 29.0±2.1% and 68.7±4.8% of Cu(II) and Zn(II), respectively, with a concentration factor of 3.8±0.4 for Cu(II) and 29.5±3.0 for Zn(II). Previous work reported total Zn(II) recovery after around 0.8 hours also using H_2SO_4, with a maximum elution peak of 6800 mg Zn(II)/L [37].

On the other hand, **Figure 8a** shows the Cu(II)-rich stream [almost free of Zn(II)] ion-exchange evolution over time. From the first moment, copper was continuously reteined by the resin since it does not have a flat zone in the breakthrough curve. This is due to the change in pH of the stream (at pH=4.3), which causes maximum Cu(II) recovery by the Lewatit VP OC 1026 resin. $C/C_0=0.5$ was achieved after about 24 BV,

and finally the Lewatit VP OC 1026 resin was saturated by Cu(II) after 70 BV (C/C_0=1); whereas the C/C_0 value of Zn(II) was zero due to its concentration being lower than the detection limit of ICP (30 µg/L).

The sorption capacities of the second column for Cu(II) and Zn(II) recovery were 4.2±0.5 mg/g resin and 0.4±0.1 mg/g resin, respectively.

The complete elution of Cu(II) was carried out after 0.25 hours, reaching a maximum value of 2340 mg/L and achieving a recovery percentage of 97.5±2.5% with a concentration factor of 22.6±1.5 (**Figure 8b**). In addition, a small recovery of Zn(II), close to 220 mg/L, was registered (recovery of 96.5±0.7%) because even though Zn(II) was not detected during the sorption experiment, the concentration effect of the elution process allows for its detection during this stage.
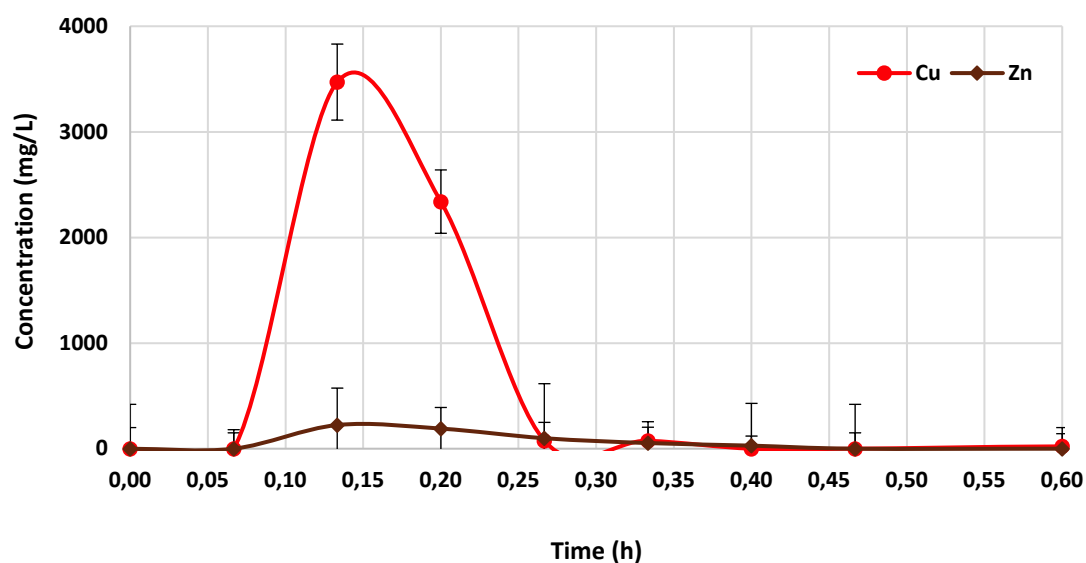
a)
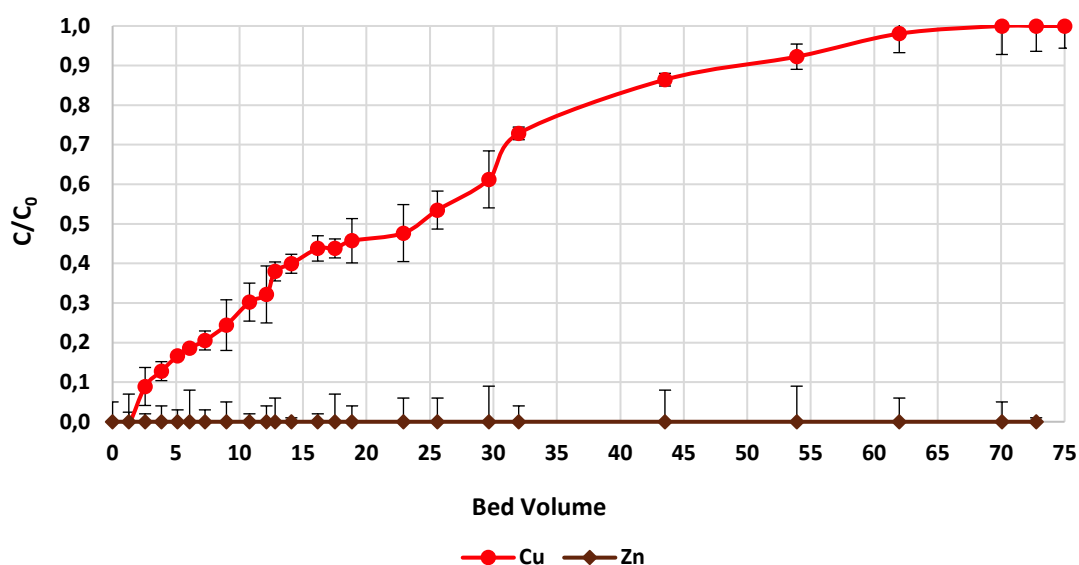
b)

Figure 8. Evolution curves for a) ion-exchange and b) elution processes for Cu(II) recovery from sorption experiments using Lewatit VP OC 1026.

Overall, the versatility of the Lewatit VP OC 1026 resin allowed for separation of zinc and copper. On the one hand, in the first ion-exchange step, this resin was used for the recovery of zinc from the Cu(II)/Zn(II)-rich stream from the SED process at pH=2.2. Then, increasing the pH of the Cu(II)-rich stream (free of Zn(II)) up to 4.3, the Lewatit VP OC 1026 resin allowed, in a second ion-exchange step, the recovery of copper.

4. CONCLUSIONS

Results showed that it was possible to separate metal cationic forms of Cu(II) and Zn(II) from As(V) oxyanions ($H_2AsO_4^-$) using SED technology. From the initial feed stream, $97\pm2\%$ and $82\pm3\%$ of Cu(II) and Zn(II), respectively, were recovered in the Cu(II)/Zn(II)-rich stream. Then, the Cu(II)/Zn(II)-rich stream was used to feed the IX process with resins in order to separate and concentrate both metallic ions, which can be reused in copper and zinc metallurgical industries. The IX process with resins allowed

for recoveries of around 70±3% for Zn(II) and 98±2% for Cu(II), and it concentrated Zn(II) and Cu(II) by 30 and 23 times, respectively, by means of an impregnated resin (Lewatit VP OC 1026) containing an acidic organophosphorus extractant with an operating cycle of retention/regeneration.

Therefore, the application of a new hybrid ion-exchange process based on SED-IX resins could be a potential process for arsenic separation and recovery of valuable non-ferrous metals (copper and zinc) from hydrometallurgical waters to achieve a circular economy strategy in these industries.

ACKNOWLEDGMENTS

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