

DEVELOPMENT OF NYLON 6 NANOFIBERS MODIFIED WITH CYANEX-272 FOR COBALT RECOVERY

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ABSTRACT

With a worldwide ever increasing demand for metals, particularly for the manufacture of electronics and batteries, there is not only a concurrent need to recover these materials from their subsequent waste streams but also a need to make advancements to do this via development of more efficient and eco-friendly processes for metal recovery; solid-phase extraction can be considered a promising alternative to conventional processes. This work studied the production of novel nanofibers modified with Cyanex 272 and their application in the recovery of cobalt present in aqueous solution. The nanofibers produced by forspinning were characterized by SEM, FT-IR, and TGA and the extraction of cobalt was evaluated by variation of the pH, solid:liquid (S:L) ratio, extraction time and Cyanex 272 content in the nanofibers. The best extraction efficiency was 99.96%, achieved under the following conditions: pH 8; (S:L) ratio of 1:200; 25% of Cyanex 272; Extraction time of 60 min. The maximum extraction capacity obtained was 15.46 mg Co/g of nanofiber and 70.15 mg Co/g of extractor. In successive reuse cycles, the results demonstrated that the extraction efficiency was maintained at over 85%. The findings showed that Nylon 6/Cyanex 272 nanofibers are a new robust and promising material for the recovery of heavy metals from aqueous solution, confirming that nanofibers have an

efficiency similar to conventional liquid-liquid extraction, without the disadvantage of volatile organic compounds emissions generated by the use of organic diluents.

1. Introduction

Cobalt is one of the 35 mineral considered critical to the economic, that has a supply chain vulnerable to disruption and a wide range of applications in various industrial processes and compounds. Either in the most varied functions as catalysts in petroleum refinery [1], in radiography and radiotherapy, and as an active component in drying formulations for oil paintings, or within manufacturing production, such as the cobalt special steel tools, magnetic alloys and superalloys that presents corrosion resistance, high-temperature resistance, grindability and workability [2].

Due to its properties, cobalt is also used in the manufacture of lithium-ion batteries [3] and alkaline [4]. The predominance of batteries in the portable power industry [5] and the geopolitical issues with the main primary sources of cobalt [1] hinder its extraction, and are two factors that drive the demand for the recovery and recycling of cobalt. Recycling presents itself as a solution to eliminate adverse environmental impact arising from inappropriate disposal and for recovery of these high value-added metals [6, 3]. The recovery of cobalt is also important during the treatment of various industrial wastewater [7].

However, the importance of cobalt recycling goes beyond the consequences of inappropriate disposal and metal reuse, the approach used during this recycling process is also very important. Considering that liquid-liquid extraction is extensively employed for the separation and extraction of metals and that the use of organic diluents can make this technique harmful to human health and the environment. Nanotechnology has attracted attention in the solid-phase extraction, because in addition to the advantages of shorter processing time and low intrinsic costs, it also ensures that there are no emissions of volatile organic compounds to the atmosphere [8].

The solid-phase extraction methods that are based on nanoscale fibers which provide a greater contact area, which is usually a disadvantage of solid-phase extraction compared to liquid-liquid extraction, in addition to benefits including high porosity and permeability, easy production, and simple regeneration [9, 10].

Currently, the most widely used method for nanofiber production is an Electrospinning technique that uses electrostatic forces. However, this method has some limitations such as low yield and wide diameter distribution of the nanofibers, in addition to the use of a high voltage power source [11]. In this study, the nanofibers were produced by using the Forcespinning® equipment [8], an alternative technology (centrifugal spinning) that is more efficient than the conventional Electrospinning.

Therefore, the aim of this work was to produce modified nanofibers for the recovery of cobalt from aqueous solutions by extraction. Nylon 6 nanofibers were modified with an organic extractant (Cyanex 272) using the centrifugal spinning technique. This synthesis of nanofiber modified combine the features of the extractant with a nanostructured supported material, that can be reused, reaching high percentage extraction using only small amounts of organic extractant. To the best of our knowledge, the use of nylon 6 nanofibers modified with Cyanex 272 has not been described in the literature yet.

2. Materials and methods

2.1 Materials

The nanofibers were prepared using Nylon 6 and formic acid (98%) obtained from Sigma-Aldrich (USA) and Neon Comercial, respectively. The commercial extractant bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) was obtained from Solvay (Brazil).

In the extraction and stripping steps, the aqueous solution was prepared using cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, analytical grade, Synth). The pH control of the solutions was performed using solutions of 0.05 M hydrochloric acid (HCl, Neon Comercial) and 0.05 M sodium hydroxide (NaOH, Vetec). The stripping was performed using a 1.5 M solution of hydrochloric acid (HCl 37%, Neon Comercial)

2.2. Characterization of the nanofibers

The synthesized materials were characterized in terms of several properties. The nanofiber morphology was observed using a VEGA-3 G (Tescan, Czech Republic) scanning electron microscope (SEM) equipped with a secondary electron (SE) detector for obtaining the images. Prior to analysis, the samples were sputter-coated with gold,

using a current of 20 mA for 90 s. The mean diameter of the nanofibers was determined from the SEM micrographs, using Image J software (NIH Image, USA).

Assays of mass loss during the polymers thermal degradation were determined by thermogravimetric analysis (TGA-50, Shimadzu). For TGA, approximately 6 mg of the sample was placed inside the alumina pans and heated from room temperature to 800 °C at a heating rate of 10 °C/min, under an inert atmosphere of analytical grade N₂, 5.0 (99.999% purity), and flow rate of 50 mL/min.

The functional groups present were identified by Fourier transform infrared spectroscopy (FT-IR) (Prestige 21210045, Shimadzu, Japan). All FTIR spectra were recorded in the range 400-4500 cm⁻¹ and were composed by 45 scans.

2.3. Experimental procedures

2.3.1. Preparation of the nanofibers

The nanofibers were prepared by mixing the required proportions of the Nylon 6 and the bis(2,4,4-trimethylpentyl)phosphinic acid extractant (Cyanex 272) in formic acid (98%), under magnetic stirring at 40 °C for 4 h, resulting in the formation of a homogeneous viscous solution [8, 12].

Nylon 6 nanofibers without the extractant were prepared using 25% (w/w) of polymer and 75% (w/w) of solvent [13]. The selection of the polymer was based on its high thermal resistance, stability, and mechanical resistance, enabling its reuse in several cycles.

In the case of the Nylon 6 nanofibers with the Cyanex 272 extractant, evaluation was made using different proportions of Cyanex 272 and polymer, with Nylon 6/Cyanex 272 ratios (% w/w) of 90/10, 75/15, 80/20 and 65/25, maintaining the same total amount of solvent (75 wt.%) used for the nanofibers without extractant.

The nanofibers were produced by the centrifugal technique using the Forcespinning® equipment (Model L1000-MS, FibeRio, U.S.A.), as shown in Figure 1. Approximately 2 mL of solution was fed to the spinneret, which was connected using needles (30 G ½”) at each end. The operating conditions were a rotation speed of 10,000 rpm and a 3 min spinneret reloading interval. The distance between the tip of the needle and the collector was fixed at 12.5 cm. The nanofibers were collected by a 4” collector

plate fitted with 16 metal panels. The experimental conditions were established in preliminary tests and using information provided from the literature [8, 12, 14].

2.3.2. Extraction and stripping

A solution was prepared with cobalt at a concentration of, approximately, 40 mg/L. The extraction experiments employed a heating plate with a magnetic stirrer (Fisatom, 752A) and a 50 mL beaker. They were performed using 20 mL of solution placed in contact with different masses of nanofibers, in order to provide the S:L ratio presented in Table 1. The experimental conditions were fixed at a temperature of 25 °C [12].

The extraction assays were performed in four steps, as shown in Table 1. The best condition obtained in each step was used in the subsequent experiments. In the first step, evaluation was made of the effect of different pH values on the Nylon 6/Cyanex 272 nanofibers extraction capacity, measured using a benchtop pH meter (Model pHB-500, ION). In the second step, different solid:liquid ratios (S:L, g/mL) were tested for the extraction of Co. In the step 3, the extraction conditions were applied differing the percentages of Cyanex 272 in the nanofibers for the metal extraction. Finally, in the fourth step, the contact time between the nanofibers and the solution was evaluated with the aim to achieve a higher extraction rate.

After the extraction, the nanofibers used in the best extraction conditions were placed in 15 mL (solid:liquid ratio of 1:150) of the stripping solution (1.5 M HCl), using a 50 mL Erlenmeyer flask, with agitation using a shaker/incubator (Model SL 222, Solab). The fixed experimental conditions during the entire stripping procedure were a temperature of 25 °C, agitation speed of 250 rpm and time of 30 minutes [14]. This procedure was repeated for three consecutive cycles, in order to determine the stability and to evaluate their reuse capacity.

The stripping solution (HCl) was used in a concentration of 1.5 M because at higher concentrations of HCl (≥ 2 M) degradation of the nanofibers and the disruption of the polymer chains could occur, causing a progressive loss of mass, as observed by da Silva [12]. All experiments were performed in triplicate, in order to ensure the reliability and reproducibility of the data.

The metal concentrations in the extraction and stripping aqueous phases were determined using flame atomic absorption spectrometry (Model 240FS AA, Agilent

Technologies) using a wavelength of 403.3 nm, slit width of 0.1 nm, acetylene fuel, and nitrous oxide support gas. All the analyses were performed using three replicates in order to ensure satisfactory precision.

The percentage extraction of the metals was obtained using Equation 1 and the extraction capacity (q_e) was determined using Equation 2 [14]:

$$\text{Extraction (\%)} = \frac{(C_0 - C_e)}{C_0} 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where, C_0 is the initial concentration of metal in the aqueous solution (mg/L), C_e is the final concentration of metal in the aqueous solution (mg/L), m is the mass of adsorbent (g) and V is the volume of the solution (L).

2.3.3. Cycles of extraction/stripping using the nanofiber

The Nylon 6/Cyanex 272 nanofibers capacity for reuse was evaluated with cycles of extraction and stripping, using the best experimental conditions established for the extraction steps. Three extraction and stripping cycles were performed to determine the stability and durability of the nanofibers [8, 12, 14]. In addition, SEM images were used to evaluate the wear of the Nylon 6/Cyanex 272 nanofibers after the extraction/stripping cycles.

3. Results and discussion

3.1 Characterization of the materials

3.1.1 FT-IR spectroscopy analysis

Infrared spectroscopy (FT-IR) was used to identify the main functional groups present in the samples and to confirm the presence of Cyanex 272 on the fiber surface. The spectra for pure Cyanex 272, the Nylon 6 nanofibers, and the Nylon 6/Cyanex 272 nanofibers are shown in Figure 2.

The spectrum for Cyanex 272 (Figure 2a) showed characteristic sharp bands centered at 959 and 819 cm^{-1} , assigned to P–O and P–O–C stretching vibration, that are characteristic of the organic extractant [15, 16]. Those bands were also present in the

spectrum for the modified nanofibers at 962 and 819 cm^{-1} , respectively. An intense band at 2955 cm^{-1} appears in the Cyanex 272 (Figure 2a) and also in the Nylon 6/Cyanex 272 (Figure 2c) spectrum, due to CH (methyl, methylene) stretching, confirming the organic extractor incorporation in the modified nanofibers [6]. C–H stretching bands of symmetric and asymmetric vibrations were observed at 2904 and 2870 cm^{-1} , respectively [17], the second one was also observed in the spectrum for the Nylon 6/Cyanex 272 nanofibers.

Figure 2b exhibits typical bands for Nylon 6 at wavenumbers of 3449 cm^{-1} (N-H stretching vibration), 1640 cm^{-1} (C=O stretching vibration, amide I), 1542 cm^{-1} (N-H bending vibration, amide II) and 1370 cm^{-1} (C-N stretching vibration, amide III) [18, 19, 20]. These bands were also present in the spectrum for the modified nanofibers.

The spectrum of the Nylon 6/Cyanex 272 nanofibers (Figure 2c) showed peaks at wavenumbers close to those observed for Cyanex 272 (Figure 2a) and the Nylon 6 nanofibers (Figure 2b). A band centered at 1169 cm^{-1} is observed in the Nylon 6/Cyanex 272 (Figure 2c) due to the P=O stretching, providing clear evidence of the presence of Cyanex 272 molecules onto the nanofibers [15].

These data provide strong evidence that Cyanex 272 is stably embedded in the Nylon 6 polymer, confirming that the addition of the extractor does not impair fiber formation. To the best of our knowledge, the possibility of doping Nylon 6 nanofibers with Cyanex 272 has not been described in the literature yet. So, the novelty of this work is the use of an extractant as important as Cyanex 272 in a more effective way, without the disadvantage of volatile organic compounds emissions, which makes this solid-phase extraction more ecofriendly when compared to the conventional liquid-liquid extraction method.

Also, from these data, it was obviously seen that chemical structures of functional groups of both Cyanex 272 and polymer supports maintained in the nanofiber mats. Therefore, the presence of Cyanex molecules onto the nanofiber webs was interpreted as linked only by intermolecular interactions, without the cleavage of any bonds between the functional groups, it is likely that the extractor become attached to the nanofibers by means of hydrogen bonds [6].

The interactions existing before and after metal extraction using the Nylon 6/Cyanex 272 nanofibers were also investigated using FT-IR. Figure 3 shows FT-IR

spectra of the Nylon 6/Cyanex 272 nanofibers, before and after the first cycle of extraction of Co using nanofibers with 25% of Cyanex 272, pH 8.0 and S/L ratio of 1:200.

The spectra showed that, the intensity of the peak at 962 cm^{-1} , attributed to P-OH stretching, decreased after the extraction process, indicating that the hydrogen atom was replaced by the metal ions during the cation exchange process [21]. Beyond that, the P=O bond stretching vibration at 1169 cm^{-1} in the Nylon 6/Cyanex 272 spectrum also decreased after the extraction process. This change could be explained by the formation of coordination interactions between the P=O groups of Cyanex 272 and the Co [22].

3.1.2 Thermogravimetric analysis (TGA)

The thermogravimetric (TGA) curves obtained for Nylon 6 and Nylon 6/Cyanex 272 (containing 25% of Cyanex 272) nanofibers, in the temperature range from 20 to 800 °C, are shown in Figure 4.

The initial thermal decomposition for both samples was around 5%, in the temperature ranges from 20 to 415 °C and from 20 to 230 °C for the Nylon 6 and Nylon 6/Cyanex 272 nanofibers, respectively, and it could be attributed to the loss of water and the loss of a small amount of solvent that remained in the polymer [23].

A thermal event between 230 and 400 °C was observed only for Nylon 6/Cyanex 272 nanofibers with a mass loss equivalent to 25%, which could be explained by the decomposition of Cyanex 272, given the extractor amount in the nanofiber and the temperature interval that is in agreement with the value reported for [17]. This event, together with the FT-IR results, confirmed the extractor presence in the modified material.

The next stage of thermal decomposition was quite substantial for both materials, occurring between 415 and 500 °C and between 400 and 500 °C for Nylon 6 and Nylon 6/Cyanex 272 nanofibers, respectively. These features were characteristic of the polymer and associated with Nylon 6 polymer complete decomposition [24, 12].

Finally, the temperature for the total mass loss of the Nylon 6/Cyanex 272 nanofibers and the Nylon 6 nanofibers was very similar, in both cases the degradation process stabilized at temperatures close to 500 °C, indicating a good thermal stability of the polymer [25].

3.1.3 Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS)

Figure 5 shows SEM images of the unmodified Nylon 6 nanofibers (a) and the Nylon 6/Cyanex 272 modified nanofibers (b). It can be seen, uniform structures were obtained in both nanofibers, with a long cylindrical structure and homogeneous surface, without identifiable beads or points of agglomeration along the structure.

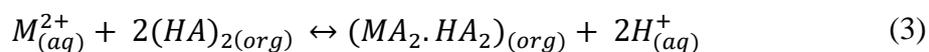
The average diameter of the Nylon 6 fibers ranged from 145 to 175 nm (Figure 5c), while for the Nylon 6/Cyanex 272 nanofibers were between 240 and 260 nm (Figure 5d). Therefore, the increase in the diameter of Nylon 6/Cyanex 272 nanofibers may have been a consequence of the impregnation process, caused by the increase in the viscosity of the solution due to the addition of Cyanex 272. The increase in the diameter of the nanofibers is associated with the increase in viscosity. [26, 27].

The elements distributions in the nanofiber was analyzed using SEM-EDS mapping of the Nylon 6/Cyanex 272 nanofibers after use in the metal extraction (Figure 6). The images indicated that the chemical elements were homogeneously distributed in the nanofibers. The distributions of carbon present in the Nylon 6 chains, are shown in Figure 6b. The oxygen present in the composition of Nylon 6 and Cyanex 272 was uniformly distributed on the nanofiber surface (Figure 6c). Figure 6d shows the distribution of phosphorus throughout the nanofiber structure, present in the composition of Cyanex 272 extractant, confirming that the extractor was evenly distributed throughout to the entire fiber. Finally, Figure 6e shows the element cobalt distributed on the nanofibers surfaces. The metal bonding occurred due to the Cyanex 272 incorporation in the Nylon 6 nanofibers, confirming the efficient extraction of the metals.

3.2 Metal extraction

3.2.1 Mechanism of the extraction process

According to the literature, the extraction equilibrium of metals M^{2+} (Co^{2+}) ions with a cation-exchange extractant such as Cyanex 272 in solution may be represented as Equation 3 [28, 22].



Where (HA)₂ refers to the hydrogen bonded dimeric form of the extractant (Cyanex 272). In nylon 6/Cyanex 272 nanofibers it is suggested that two phosphinic acids also deprotonate and coordinate to the Co, with the adoption of tetrahedral coordination geometries in the complexes formed [22]. Figure 7, shows the schematic structures of the extraction process. It is noteworthy that the nanofibers after extraction of Co²⁺ ions were blue in color supporting such a bidentate coordination of the Cyanex 272 to yield a blue tetrahedral Co²⁺ complex. Similar tetrahedral complexes are reported in the literature by Santanilla [29] for cyanex 272 complexes of Co²⁺ and blue Co²⁺ complexes in cyanex 272-PVC polymer inclusion membranes reported by Best [30].

3.2.2 Effect of pH

The influence of pH on cobalt extraction using the Nylon 6/Cyanex 272 nanofibers is shown in Figure 8 for extractions performed at pH 4, 5, 6, 7 and 8. The results showed that the metal extraction became more efficient as the pH increased, as expected for an acidic extractor, reaching values close to 90%. This results can be explained by the fact that the high H⁺ concentration at lower pH led to competition with the cobalt ions in the solution, preventing the Co²⁺ cations extraction [31, 14]. Therefore, for the conditions used in the tests, the optimum pH for extraction of cobalt using Nylon 6/Cyanex 272 nanofibers was pH 8. These values were in agreement with the work of Tait [32], where the extractions of cobalt increased as the pH increased, using the same extractant.

Figure 9 shows the chemical specification diagram for cobalt generated by the Hydra/Medusa software. The chemical speciation diagram indicated that, in an aqueous solution, the element cobalt can precipitate at pH values close to 9. Therefore, pH 8 was selected in the subsequent extraction assays, so precipitation was avoided, and the metal was in the cation Co²⁺ form.

3.2.3 Effect of S:L ratio

The influence of the S:L ratio on the extraction efficiencies of Co is presented in Figure 10. Higher Co extraction efficiency was obtained at lower S: L ratios, reaching nearly 90% efficiency for a ratio of 1:200. The maximum extraction capacity obtained was 15.46 mg of Co/g of nanofiber and 70.15 mg of Co/g of extractor for a ratio of 1:1000. Since, 2 moles of Cyanex 272 are needed to extract 1 mol of cobalt, the maximum theoretical extraction is 94.59 mg of Co/g of extractor, for nanofibers with 20% of Cyanex 272. Therefore, it is possible to conclude that, approximately, 74% of the employed

Cyanex 272 had involvement in the extraction, without neglecting the extraction performed by the pure Nylon 6 nanofibers.

The lower extraction percentages at higher S:L ratios were due to the high concentrations of metal ions in solution, which presumably exhausted the nanofiber capacity [33]. Since the aim was to achieve the highest metal extraction efficiency, the best extraction S:L ratio was considered as 1:200.

3.2.4 Effect of Cyanex (%) in the nanofibers

The effect of the Cyanex percentages in the nanofibers on the extraction process were determined at its optimum pH value, a contact time of 30 min, S:L ratio of 1:200 and by varying the Cyanex (%) from 10 to 25%. The results are shown in the Figure 11.

A progressive increase in the extraction efficiency is observed according to the amount of Cyanex 272 present in the nanofibers. The maximum percentage extraction was 96.55%, using the nanofibers containing 25% of extractor and 30 minutes of contact time. This behavior was also reported by Cadore [8] and Kolev [33]. In this way, the 25% Cyanex nanofibers were selected to continue the study.

Increasing the amount of Cyanex 272 in the nanofiber composition resulted in a decrease in the nanofiber production yield. That is why the production proved to be unfeasible when extractor contents above 25% were used. This behavior was also reported by Segala [14] and in the work of Nie [34] where it was observed that the polyacrylonitrile nanofiber diameter decreased, and the fibers became non-uniform and defective with an increase of the extractor content in the polymeric solution.

3.2.5 Effect of extraction time

To evaluate the effect of the extraction time in the process, the solution was kept in contact with a constant quantity of the modified nanofiber with 25% of Cyanex 272. The results are presented in the Figure 12.

After 30 minutes the extraction reached 96.55%, the maximum percentage extraction was 99.96% and was reached after 60 minutes of contact and remained constant at the time of 90 minutes. This behavior was also reported by Segala [14] where it was observed that there was a rapid increase in the first 30 min, after which the process became progressively slower, with equilibrium reached after around 60 min.

Finally, using the best conditions, an optimal percentage of extraction of 99.96%, an extraction capacity of 6.82 mg Co/g nanofibers and 21.58 mg Co/g extractor, were obtained. To the best of our knowledge, the use of nylon 6 nanofibers modified with Cyanex 272 has not been described in the literature yet. Although, polyacrylonitrile (PAN) nanofibers modified with Cyanex 272 were used in the study reported by Segala [14] for the recovery of gallium, where the maximum capacity of the PAN/Cyanex 272 nanofibers was 38.93 mg/g, and in the study reported by Martín [6] in the selective recovery of Europium and Yttrium, showing a maximum capacity of 200 and 400 mg/g for Y(III) and Eu(III), respectively. Also, Nylon 6/DEHPA nanofibers were used for metal recovery in the work of Da Silva [12] in the separation of zinc and nickel, where the best extraction efficiencies were 85.5% for Zn and 4.6% for Ni, and in the work of Cadore [8], where an indium extraction efficiency of around 74% was obtained.

3.2.6 The assessment of the unmodified nanofibers extraction efficiency

In this work, the ideal conditions selected for the Co extraction were: pH = 8; S:L ratio = 1:200 (g/mL); Cyanex (%) = 25%; Extraction time = 60 min. Using the best conditions, it was possible to obtain an optimal percentage of extraction of 99.96%, extraction capacity of 6.82 mg Co/g nanofibers and 21.58 mg Co/g extractor (without neglecting the extraction performed by the pure Nylon 6 nanofibers).

In order to evaluate the Cyanex 272 effect on the extraction capacity and the cobalt removal, Nylon 6 nanofibers without the extractor were used in the best conditions of extraction to allow comparison. The results are presented in Figure 13.

The tests showed that even the nanofibers without any extractor content have some capacity of cobalt extraction. Using Nylon 6 nanofiber in the best conditions, it was possible to obtain a percentage of extraction of 18.17% and extraction capacity of 1.42 mg Co/g nanofibers.

The removal of a small metal amount by the pure nanofibers was due to their physical and chemical characteristics, which favored extraction [35] presumably via coordination to either amide carbonyl groups of the Nylon 6 and any end groups that are accessible at the surface of the polymer. This behavior was also reported by Cadore [8] and Segala [14]. However, the extractor addition in the nanofibers showed a significant increase in the percentage of extraction, reaching nearly 100%.

3.3 Cobalt stripping

The stripping step was very important not only for the metal ions' recovery but also for recycling of the nylon 6/Cyanex 272 nanofiber materials. The ability to regenerate and reuse the nanofibers was studied using three sequential cycles of extraction and stripping.

The extraction and stripping efficiencies of the three cycles are shown in Figure 14. The results indicated that there was a small decrease in the metal extraction efficiency after the first cycle, which could have been due to the loss of a small portion of the extractor from the fibers, or a reduction of the extraction capacity due to the contact with HCl. However, the metal extraction has remained in the range of 85-99%, indicating that nylon 6/Cyanex 272 nanofibers are quite stable. The same happened to the stripping efficiency throughout the cycles, with values in the range 76-97%.

In a previous study of metals extraction using Nylon 6 nanofiber, no significant extractant loss was found after 10 extraction/stripping cycles [12]. These results suggested that nylon 6/Cyanex 272 nanofibers are quite stable and can be reused even after several cycles of operation.

To evaluate the efficiencies achieved in the three extraction/stripping cycles, the morphology of the nanofibers used only in the metal extraction steps was compared with those of the nanofibers after one and three extraction/stripping cycles using SEM images (Figure 15).

The images showed an increase of the nanofiber diameter, with values of between 215 and 320 nm after the first cycle (Fig. 15b) and between 225 and 340 nm after the third cycle (Fig. 15c). This increase was due to wear and agglomeration of the nanofibers during the extraction/stripping cycles, which was mainly caused by the HCl employed in the stripping step [12, 14].

Finally, another important point to consider is the effect of the stripping solution on the possible loss of Cyanex 272 from the nanofibers during these processes. For this aim, the presence of Cyanex 272 (phosphorous content) was quantified after the first and the third cycles of extraction/stripping using EDS analyses (Table 2).

Table 2: Chemical composition of the Nylon 6/Cyanex 272 nanofibers after one and three extraction/stripping cycles.

The results showed that there was a small loss of phosphorus after the three extraction/stripping cycles and that nanofibers could retain around 86% of the Cyanex 272 that is impregnated into the nanofibers after three stripping cycles. The findings confirmed that there is a strong interaction between the chains of the Nylon 6 and Cyanex 272 nanofibers that provides stability and Cyanex 272 agent fixation.

This incorporation resulted in highly efficient extraction/stripping of the Co. Proving that the Nylon 6/Cyanex 272 nanofibers can be considered a promising alternative for the recovery of metals from leaching solution, having excellent potential and good stability even after three extraction/stripping cycles. In addition to the advantages derived from shorter processing time and low intrinsic costs, this technique is not harmful to human health and the environment when compared to the conventional liquid-liquid extraction method, since there are not any emissions of volatile organic compounds to the atmosphere.

4. Conclusion

A novel Nylon 6/Cyanex 272 nanofiber with good extraction capacity of Co from aqueous solutions and excellent reuse potential was developed using the Forcespinning® technique. The nanofiber was fully characterized by SEM, FT-IR, and TGA, and it confirmed the impregnation of Cyanex 272.

The extraction was favored at pH 8 where using the best conditions for the Co extraction, that were a contact time of 60 min, and an S:L ratio of 1:200, it was possible to obtain a satisfactory percentage of extraction of 99.96%. Furthermore, the maximum extraction capacity obtained revealed that, approximately, 74% of the employed Cyanex 272 had involvement in the extraction.

Three sequential cycles of extraction and stripping demonstrated that Co can be recovered employing 1.5 M HCl, an S:L ratio of 1:150, and a contact time of 30 min, with high recovery rates (>76%), while the extraction efficiency was maintained over 85% and 80% of the organic extractant loaded into the nanofiber was retained.

Finally, the results showed that the Cyanex 272 offers stable use together with the polymer Nylon 6, confirming that this study provided an effective form of use for such an important extractant, without the disadvantage of environmental problems caused by volatile organic compounds emissions. Therefore, the Nylon 6/Cyanex 272 nanofiber can

be considered a promising alternative to separate heavy metals from wastewater, being able to recover almost 100% of the metal from aqueous solution and proving a quite stable reusability.

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Data Availability Statement

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

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