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Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents

--Manuscript Draft--

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Abstract:	The exhaustion of Cu reserves minable and processable with the available technology is forcing the hydrometallurgical copper industry to seek alternative sources of Cu. Following circular economy principles, researchers' attention has focused on the recovery of valuable metals from the acidic waste streams generated. Nowadays, membrane technologies are being selected as the first alternative for the treatment and valorisation of such acidic waste streams. Among them, a new generation of high acidity resistance nanofiltration (NF) membranes offer the alternative for acid recovery while providing a metal-enriched stream. In this work, the extreme-acid resistant Duracid membrane was evaluated for the valorisation of different synthetic acidic waste streams from the hydrometallurgical Cu industry. These waters were characterised by a high acidity (pH 0.5–1.5) and the presence of Fe (11–14 g/L), Zn (0.7 – 1.4 g/L) and As (0.5–0.7 g/L), among others. Initially, the membrane was characterised by different techniques (SEM, FTIR-ATR, XPS). Experiments were performed under constant and varying permeate flux and feed water composition. Metals were effectively rejected (>90%), whereas H + easily permeated through the membrane. The experimental results were adjusted to the Solution-Electro-Diffusion-Film (SEDF) model to determine the membrane permeances to species. Empirical mathematical equations were developed and validated to express the dependence of permeances on solution composition. Finally, the prediction capability of the SEDF model, together with the developed empirical equations for the permeances, was proposed as a tool for designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry. The model predicted gypsum scaling onto the membrane and therefore anticipated the need of applying antiscalants.
Response to Reviewers:	Ref: CEJ-D-20-09918 Title: Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents Journal: Chemical Engineering Journal Dear Proff. Tejraj M Aminabhavi, Thank you for your invitation to resubmit our manuscript after addressing all reviewer comments. We have completed the review of your manuscript, and a summary of the raised comments and the comments and changes made could be found in the next pages below. We have considered all issues mentioned in the reviewers' comments, and we have outlined every change made point by point, and provide suitable rebuttals for any comments not addressed. The revised manuscript is now submitted for your consideration with all the corrections made. I look forward to receiving your comments. Kind regards, Julio Lopez Reviewers' comments: Reviewer #1: The manuscript with the title "Evaluation of an extreme acid-resistant sulphonamide

based nanofiltration membrane for the valorisation of copper acidic effluents" is about the characterization of the commercial nano filter (NF) membrane's (Duracid) ability to filter unwanted elements from highly acidic aqueous solutions. The manuscript also attempts to generate an empirical expression that can predict the amount of unwanted elements filtered by the membrane to the concentration of the unwanted elements in the aqueous solutions.

To be clear, the investigation of the Duracid ability to filter ions and other organic compounds from aqueous solutions is not novel and has been performed by various research works, thus lowering the value of this manuscript eventhough the manuscript target a different set of elements filtered. However, the inclusion of an empirical expression that can predict the amount of elements filtered is a novel and important idea that can aid the understanding of the dynamics of nano filtration process and enhance the knowledge in the area.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

For the manuscript to be accepted, a few issues needs to be improved.

(1) Typical in a lot of manuscript is the lack of clarity of the problem. While the manuscript does include sufficient background to the subject matter, the problem in the currently available technology or the knowledge gap is not clearly described. Please include the analysis on the available knowledge in predicting the amount of unwanted elements that will be filtered by nano filters and how this is still in sufficient such that a new empirical expression needs to be developed.

As indicated by the reviewer, the clarity of the problem has been defined at the end of the introduction. The main concern about NF membranes is to predict its behaviour properly as there are many parameters, such as solution composition, active layer properties and operation conditions, that influence their performance. In this work, we have been able to predict the performance of NF membranes properly by studying first the behaviour of an acid resistance membrane as the Duracid and then by developing analytical expressions that correlate that effect on membrane permeances.

(2) One of the stated goals of the research is to characterized the Duracid NF for the collections of copper and its derivative compounds from waste stream. In addition, the manuscript contains a lot of information about copper and its derivative compounds in the Introduction section. However, the solutions used for the filtration experiments contain only one copper containing solutions. Something is missing in between the discussion in the manuscript or in the experimental design.

As suggested by the reviewer, more information was provided in the introduction. Copper sulphides, such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S) and covellite (CuS), are used as raw materials in the copper hydrometallurgical industry. Mineral leaching is usually performed with sulphuric acid, accompanied by an oxidation (oxygen). The effluent will contain H_2SO_4, Cu^{2+} and other impurities, such as Fe and As, among others. Therefore, experiments were conducted only with Cu(II) as major component.

(3) The experimental setup is hard to be understood without a diagram. Please include a diagram to help with the description of the experimental setup as presented in section 2.1.

As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.

(4) On page 10, the description of the equations (1) and (2) should be proper; equation (1) describe the relation between flow and membrane permeance under virtual/transient/uncorrected concentrations, whereas equation (2) describe the relation between flow and membrane permeance at real/laboratory concentrations. Please fix the description of the equations. In addition, the whole mathematical moddeling is not sufficiently described. For example, why is the relation between flow and and memberane permeance at virtual/transient/uncorrected concentrations are needed? Why cannot the membrance permeance at real concentrations be measured/calculated directly from the experimental data?

As suggested by the reviewer, the section related to mathematical modelling was modified.

Equation 1 describes the transport of species in the concentration polarization layer. This concentration polarization layer is formed at the membrane boundary layer during the filtration process and implies an accumulation of solutes which causes higher osmotic pressures (i.e. low permeate flux) and a decrease in the rejections.

Instead, equation 2 shows the description of species transport across the membrane.

This one uses virtual concentrations, which are those in thermodynamic equilibrium with a sub-given point at the membrane. The use of virtual concentrations makes no necessary to provide more data about the membrane rather than membrane permeances. If virtual concentrations were not used, it would be necessary to characterise the membrane exhaustively to determine pore size, membrane charge, diffusion coefficient inside the membrane and distribution coefficients, among others. These experiments are carried out with single salts, and conditions can vary when treating a mixture of electrolytes, as in the present work.

Additionally, membrane permeances cannot be determined directly. The presence of concentration polarisation can make that the concentration of species at the boundary layer to be from 2 to 6 times higher than the bulk solution. Besides, the differences of transport of species generate an electric field inside the active membrane layer, which is hard to measure experimentally.

(5) On the results and discussion of the XPS results on page 13, the thickness of the active layer is claimed to be 250 nm. However, there is not enough evidence neither in the Figure 2 nor in other figures/tables/supplementary information to show that value. Please clarify how this value is obtained.

The active layer thickness was measured from the SEM images at x10000. Figure 2 was modified in order to show the active layer properly. As the literature is very scarce about Duracid membrane, specially from a characterization point of view, we were not able to provide results from others researchers.

(6) In section 4.4, the empirical expression is developed based on the amount of copper sulfate filtered. In an environment where other copper compounds are present, will the empirical expression still be valid? Please include some discussion on the validity fo the empirical expression when other copper species are present in the waste effluents.

The empirical expressions are only valid for Cu(II) and taking into account the composition of the treated solution in terms of total sulphate concentration. In any diiferent environment with other complexing ions (e.g. inorganic or organic), their rejection will be defined according to their nature and the membrane main tranport mechanisms. For each scenario, an empirical expression could be defined using the procedure developed in this work. As indicated by the reviewer, a discussion was added to the manuscript.

(7) In the conclusion section, the first paragraph, line 3 "...which revealed that the membrane was made of polysulphonamide..." should be changed to "...which suggested that the membrane was made of polysulphonamide...".

As indicated by the reviewer, the phrase was modified accordingly.

Reviewer #2:

Authors have present the Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents. i recommend the acceptance of this paper after the authors have carefully addressed my following comments.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

Abstract:

1. Page 2, Line 39: "Rmpirical" mathematical equations … what is the "Rmpirical" refer to?

As indicated by the reviewer, the typo was corrected to “Empirical”.

Introduction

2. Please has literature review on alternative methods for Cu recovery from high acidic effluent and What made you to choice nanomembrane methods compare to other methods such as adsorption by activated carbon? Some recommendation: Valorisation of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions, Microwave steam activation, an innovative pyrolysis approach to convert waste palm shell into highly microporous activated carbon.

As indicated by the reviewer, a section related to alternative methods for Cu recovery was added. The works suggested by the reviewer have been carefully revised and cited. We have selected nanofiltration membranes as they provide two streams: one containing a purified acid, and another one containing a high concentration of metals without the need for a regeneration step as with activated carbon. The research under development indicates that NF should be seen as a way just to reduce the amount of efluents (in terms of volume or flow) to be treated. A final stage using any sorption, ion-

exchange or selective precipitation stage will be needed as indicated by the reviewer.
3. Highlight the novel of your methods compares to other researchers of using nano-membrane as well.
As indicated by the reviewer, the novelty has been highlighted. The main concern about NF membranes is to predict its behaviour properly as there are many parameters, such as solution composition, active layer and operation conditions, that influences their performance. In this work, we have been able to predict the performance of NF membranes properly by studying first the behaviour of Duracid membrane and then by developing analytical expressions that correlate that effect on membrane permeances.
4. Why has Duracid NF membrane been selected? What is your main contribution to the model study?
Most of the commercial nanofiltration membranes are made of polyamide, which made the susceptible of suffernig hydrolysis at pH lower than 2. To overcome that issue, most of the main membrane producers (Hydranautics, Koch, GE) have developed membranes to cover the extreme acidic ranges(e.g. 5-20 wt. %) in the last decades. From the described providers, Duracid membrane can achieve higher concentration factors (rejections higher than 90%). In previous works, we have determined the performance of Hydranautics, Koch an even ceramic membranes (TiO2). However, they did not provided the requeriments needed to treat acidic waters (i.e. metal rejection, permeate purity). It should be also mentioned that there is scarce information on the description of mass transport processes with such type of membranes. Thus, a second important objective was the effort to increase the knowledge in this field.
Experimental setup
5. Please provide schematics diagram for better understanding
As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.
6. Please explain in detail "Three synthetic solutions (I, II and III)".
As indicated by the reviewer, the phrase was modified accordingly. The solutions correspond at the effluent from the solvent extraction stage at three different periods in a copper hydrometallurgical plant.
7. Please explain the experiment design/how do you experiment with detail.
As indicated by the reviewer, data about the experimental design was provided in the manuscript. The three solutions were treated with the Duracid membrane to evaluate the species rejection at different TMP, and therefore to determine the membrane permeances to species. After that, solutions I and III were treated at a constant TMP to evaluate the metal concentration factors, and therefore the prediction capabilities of the mathematical model. The experimental design was developed taking into account the experience of the research group in this field on the last decade and references have been provided.
Membrane characterisation
8. Please analyse and relate the membrane characterisation results to its applications.
As indicated by the reviewer, the results from membrane characterisation were related to its applications and the text has been modified appropriately.
9. Point the uniqueness of nano membrane compare to others membrane.
As indicated by the reviewer, the uniqueness of the membrane was compared to other commercial membranes. The discussion has been centred on their properties for having resistance in strongly acidic media.
Influence of solution composition
10. Page 14, line 14-17: the paragraphs is too short.
As indicated by the reviewer, the extension of the paragraph was enlarged.
Reviewer #4:
The manuscript deals with an interesting topic, being organized in alignment with a plethora of advanced analytical techniques. Besides, the outcomes unveil novel knowledge in the field of nanofiltration membrane technologies for the valorisation of copper acidic effluents. In this respect, the manuscript can be accepted for publication at the "Chemical Engineering Journal" after the consideration of the review comments suggested.
We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.
1) At the Abstract section, the "Rmpirical" can be changed to "Empirical".
As indicated by the reviewer, the typo was corrected.
2) Regarding the research objective of "designing a NF unit to valorise acidic streams

from the hydrometallurgical Cu industry", authors reported the co-presentation of Cu, Fe, Zn, and As. Therefore, authors are recommended to develop distinct subsections in which the following issues can be succinctly discussed:

a) Effect of ionic strength, referring to the competitive sorption of the other metals towards the main Cu recovery.

b) Effect of pH, involving the chemical bonds' development and their affection to the main Cu sorption mechanism and recovery.

c) Prospects of metals' recovery from the effluents, including a short discussion for each one from the aforementioned elements to be treated. Otherwise, authors could discuss whether the disposal of the waste stream containing these low amounts of impurities "as is" could be environmentally sustainable and ecologically safe.

Two or more extra subsections within the main section 4 are recommended.

As indicated by the reviewer, a paragraph regarding the recovery of Cu, Fe, Zn and As was added in Section 4.4. The influence of the described parameters have been taing into account on the modeling formulation stages.

The effect of ionic strength and pH is already discussed in section 4.2.1.

The pH can affect:

i)The membrane charge, making it more positive because of the higher protonation degree of amine groups. This implies that cations will be better rejected.

ii)The equilibrium bisulphate (HSO_4^-)/sulphate (SO_4^{2-}). Low pH values shift the equilibrium towards the formation of HSO_4^-, which is less rejected than SO_4^{2-} in agreement with dielectric exclusion.

The effect of ionic strength influences the equilibrium reactions in terms of activity coefficients.

3) The highlighted points can be enriched with numerical data and quantitative information, in order to strengthen the novelty of the analysis conducted.

As indicated by the reviewer, the highlights were modified accordingly. The main performamce indicators of Duracid membrane with hydrometallurgical acidic solutions have been stressed. Results of the modelling stage were directed to provide an exercise of predicting a filtration stage of a hydrometallurgical acidic solution.

4) The context of the circular economy involvement (and its key-worded inclusion) at the Cu recovery is intuitive and, in this respect, the theoretical background has to be solidified at the first paragraph of the Introduction section. Therefore, I recommend authors to consider indicative papers that I listed at the end of my review comments, which authors can consider and cite at the revised version of their study.

As indicated by the reviewer, the first paragraph has been solidified and the indicative papers has been considered and cited.

5) The underlined subheading-formats has to be removed and these subsections' can be numbered in alignment with the main headings. Similarly, the bold-typed Tables, Annex, Equations has to be changed to plain/normal typing.

As indicated by the reviewer, the underlined subheading formats, as well as the bold-type format, has been removed.

6) The section of mathematical modeling is poorly developed, thus, in depth explanation of the process and variables' functionality, it is needed. Particularly, the citing information has to be utilized in a more descriptive manner:

a) All variables can be accompanied by one explanatory sentence of functionality, values-range taken, and units' measured, where applicable.

b) All input and output of the Solution Electro-Diffusion Film (SEDF) model can be denoted in the form of a Table.

As requested by the reviewer, a depth explanation of the mathematical model and variables' functionality was provided.

7) There is a large portion of subheadings that are extended to more than two lines, thus, rephrasing and shortening them is needed. The narrative following can offer a fairly well description of the relevant issues/aspects studied.

As indicated by the reviewer, subheadings have been rephrased and shortened to avoid its extension to be more than two lines.

8) The narrative flow is structured mainly on membrane characterization and modeling presentation, being narrowed in discussing only Tables and Figures, whereas a synthesis and coherent discussion of the outcomes is actually missing. Therefore, authors are recommended to upgrade their analysis and verify/prove its significance by noting those shortcomings, limitations, and future developmental challenges of their analysis towards similar settings of environmental and interfacial/surface chemistry interest. Two or three cross-cited and descriptive argumentation are adequate and, to this end, literature refresh and update with the indicative list of published papers given

below, it can considered and cited.

As proposed by the reviewer, an up-grade of the analysis in the results and discussion section has been introduced. Intially, the cross-cited option to compare the performance with data published for Duracid membrane was not possible due to the scarce data found at the scientific level. Therefore, the performance of Duracid membrane was compared to other acid resistant membranes (MPF-34 and Hydracore 70pHT). It must be highlighted that there are not so much information about these two, specially in the modelling part as the membrane properties are so different to standard NF membranes (polyamide-based). Therefore, additionally references to cover this information have been provided.

9) The Conclusions section is out of scope since it is not a place to summarize the methodology adopted and the outcomes yielded but, based on them, authors are recommended to succinctly reiterate the drivers and the barriers concluded by the analysis. The current text content of the Conclusions section could be selectively retrieved and relocated to the aforementioned new paragraphs (review comment 7).

As indicated by the reviewer, the Conclussions section has been modified. The information has been relocated in Results and Discussion section. Accordingly, the conclusions section is devoted to the drivers and and barriers identified in this study.

10) The extensive notation of Tables' data in italics (where applicable) has to be revised in plain-normal typing, while the boxes of Figure 8 do not make sense, since their naming is missing.

As indicated by the reviewer, the notation of tables has been modified to plain-normal typing. Regarding Figure 8, each box represents one membrane module. A phrase was added to the caption to clarify it.

11) At citations of the References section other page-ranged are mentioned with the "pp." while others not. Check and revision is suggested in alignment with the journal's guidelines.

As indicated by the reviewer, the Journal’s Guidelines has been consulted. Accordingly, references from a chapter in a book include the term “pp”.

Zamparas, M., Kyriakopoulos, G.L., Drosos, M., Kapsalis, V.C., Kalavrouziotis, I.K., Novel composite materials for lake restoration: A new approach impacting on ecology and circular economy, (2020) Sustainability (Switzerland), 12 (8), art. no. 3397 https://www.scopus.com/inward/record.uri?eid=2-s2.0-85084638536&doi=10.3390%2fSU12083397&partnerID=40&md5=dd198408703e5d3aaaa59dcac6af89f9, DOI: 10.3390/SU12083397

Aravossis, K.G., Kapsalis, V.C., Kyriakopoulos, G.L., Xouleis, T.G., Development of a holistic assessment framework for industrial organizations, (2019) Sustainability (Switzerland), 11 (14), https://www.scopus.com/inward/record.uri?eid=2-s2.0-85071345908&doi=10.3390%2fsu11143946&partnerID=40&md5=3501b754c240eb4e508e2d93c2fbbee7, DOI: 10.3390/su11143946

Kapsalis, V.C., Kyriakopoulos, G.L., Aravossis, K.G., Investigation of ecosystem services and circular economy interactions under an inter-organizational framework, (2019) Energies, 12 (9), art. no. 1734, . https://www.scopus.com/inward/record.uri?eid=2-s2.0-85066053518&doi=10.3390%2fen12091734&partnerID=40&md5=bf3293e829108db164ed6dfea9c31a6d, DOI: 10.3390/en12091734

Yun, T., Chung, J.W., Kwak, S.-Y., Recovery of sulfuric acid aqueous solution from copper-refining sulfuric acid wastewater using nanofiltration membrane process, (2018) Journal of Environmental Management, 223, pp. 652-657. https://www.scopus.com/inward/record.uri?eid=2-s2.0-85049337324&doi=10.1016%2fj.jenvman.2018.05.069&partnerID=40&md5=ffe3f282aa4f41b4eac5f106c9edbdab, DOI: 10.1016/j.jenvman.2018.05.069

Chakrabarty, T., Pérez-Manríquez, L., Neelakanda, P., Peinemann, K.-V., Bioinspired tannic acid-copper complexes as selective coating for nanofiltration membranes, (2017) Separation and Purification Technology, 184, pp. 188- https://www.scopus.com/inward/record.uri?eid=2-s2.0-85018768627&doi=10.1016%2fj.seppur.2017.04.043&partnerID=40&md5=26bc89bdf4d4347a1553836bf4484a19, DOI: 10.1016/j.seppur.2017.04.043

Sun, J., Zhang, L., Xie, B., Fan, L., Yu, S., Separation efficiency and stability of thin-film composite nanofiltration membranes in long-term filtration of copper sulphate and sulphuric acid mixture, (2015) Desalination and Water Treatment, 53 (7), pp. 1822-1833. https://www.scopus.com/inward/record.uri?eid=2-s2.0-

84922413693&doi=10.1080%2f19443994.2013.860629&partnerID=40&md5=655fa143d1ec9a2d4444946682413c29, DOI: 10.1080/19443994.2013.860629
Ahmad, A.L., Ooi, B.S., A study on acid reclamation and copper recovery using low pressure nanofiltration membrane, (2010) Chemical Engineering Journal, 156 (2), pp. 257-263.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-73249143862&doi=10.1016%2fj.cej.2009.10.014&partnerID=40&md5=205b88117d944e589ca8a6cacbc33d93, DOI: 10.1016/j.cej.2009.10.014

Reviewer #5:
This manuscript evaluated the performance of a commercial acid-resistant membrane for valorizing hydrometallurgical copper acidic effluents. The authors conducted comprehensive experimental studies as well as mathematical modeling to determine the membrane permanence to different species in synthetic wastewater effluents. The results were clearly presented. The data supported the conclusion reasonably well. This study is relevant for resource recovery from industrial wastewater and would be of interest to the readers of CEJ. It may be accepted after the comments below accepted.
We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.
1. Highlights should be rewritten to reflect the major finding of this work.
As indicated by the reviewer, the highlights were modified accordingly to reflect the major findings of the work completed.
2. In the Introduction, the authors mentioned that stability of NF membrane is a big issue to treat acidic wastewater effluent. They investigated the performance of Duracid NF membrane in this work. However, it is not clear why the authors showed special interest on this membrane. More background information on Duracid NF membrane would help justify the advantage of this membrane over others.
As suggested by the reviewer, more information was provided in the manuscript. To our knowledge, there were two potential membranes suitable for treating this kind of effluents: Duracid (Suez), Hydracore 70pHT (Hydranautics) and MPF-34 (Koch). At the same acidity levels, the Hydracore 70pHT and MPF-34 show lower metal rejections than Duracid (see the references below). Therefore we selected Duracid membrane. From our previous experience, we discarded the ceramic membranes since at that pH we have observed rejections below 10%.
A. Manis, K. Soldenhoff, E. Jusuf, F. Lucien, Separation of copper from sulfuric acid by nanofiltration, in: Fifth Int. Membr. Sci. Technol. Conf., 2003.
T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, J. Memb. Sci. 480 (2015) 74–82. doi:10.1016/j.memsci.2015.01.013.
Although the membrane active layer chemistry of the acid resistant NF membranes has not been evaluated in an extensive way as conventional membranes, the Duracid active layer (sulphonamide) is totally different than the ones from Koch and Hydranautics, as well as the new membranes from Dupont and Laxess, all of them based on polyethersulphonated layers. The initial performance indicators (e.g. rejections and flux), which were found in a scarce number of publications, made this membrane of interest for this application.
3. For 2.1 Experimental set-up, I would suggest adding a schematic diagram to better illustrate the experimental processes.
As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.
4. Lines 27-30, page 14, the author claimed that the positive charged membrane surface was due to partial and fully protonation of amine and sulfonic groups. I don't think it is correct for sulfonic groups because they are generally strong acids and partially deprotonated even under very acidic pH. So, sulfonic groups are negatively charged rather positively charged.
According to Sata (2004) and Tanaka (2015), the acidity constants of sulphonic groups in a polymeric matrix (i.e. ion-exchange membranes) might be below 1. Therefore at the operating conditions, it can be expected the sulphonic groups to be partially protonated.
Sata, T., 2004. Ion exchange membranes: preparation, characterization, modification and application. Royal Society of Chemistry.
Tanaka, Y., 2015. Ion exchange membranes: fundamentals and applications, 2nd ed.
5. How stable was the Duracid NF membrane over long-term operation? A stability test

would be helpful to demonstrate the application potential of this membrane.
The membrane was replaced for each experiment. Therefore, it was no possible to evaluate the membrane stability at long-term exposition. After each experiment, we performed cleanings with water, in order to compare the hydraulic membrane permeability with the one from a virgin membrane. Marginal changes were observed (<2%), which suggested the membrane did not change. In addition, membranes were analysed by SEM, and no changes were observed at the surface. It should be added that the membrane stability was not one of the research questions identified in the experimental plan as the working conditions were far away from the claimed stability of such membrane (20% H_2SO_4). In any case, it will be necessary to run accelerated studies in strong acidic solutions (up to 2-5 M H_2SO_4) or long operation cycles with spiral-wound modules to identify any aging mechanism. Results from the long operation cycles using commercial sperial-wound are expected to be finnished along 2021, which will include any membrane auptosy if possible.
6. Chemical equilibrium model used to establish the speciation diagrams of different species in synthetic wastewater effluent should be provided.
Speciation diagrams were built with the Hydra/Medusa software. As indicated by the reviewer, this was pointed out in the manuscript. The Hydra database was used for performing the calculations, and only some new data were introduced for describing the potential scailing events along the concentration stage. These values have been collected in table 2.

Reviewer #6:
Overview and general recommendation:
Following circular economy principles, it is of great significance to recover valuable metals from acidic waste stream produced in copper hydrometallurgy industry by using high acidity resistance nanofiltration (NF) membranes. Besides, It is a good design to adjust the experimental results to the Solution-Electro-Diffusion-Film (SEDF) model to determine the membrane permeances to species. Combining theory with experiment, the prediction capability of the SEDF model, together with the developed empirical equations for the permeances, was proposed as a tool for designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry. Because of this, current research is about the relevance of a topic and general interest to magazine readers.
On the one hand, I found the paper to be overall well written and much of it to be well described. I believe that the authors have undergone a lot of research and conducted a scientific and reasonable design. The combination of theory and experiment makes this data set seem quite useful for this purpose. On the other hand, There are still some problems in this paper. Therefore, I recommend publication of this paper after the revisions. I explain my concerns in more detail below.
We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.
1. Section4.1, I have noticed the characterization of the extreme acid-resistant Duracid NF membrane, but I am also interested in whether the structure and performance of the extreme acid-resistant Duracid NF membrane have changed after it has been treated with different acid waste liquor from hydrometallurgical copper industry. Therefore, please supplement the relevant characterization.
We have only used one membrane for each experiment, and no characterisation of the membrane structure was performed. With the membrane cleaning with water, we have determined the hydraulic membrane permeability and was compared with the one from a virgin membrane. Marginal changes were observed between both values (<2%). It should be added that the membrane stability was not one of the research questions identified in the experimental plan as the working conditions were far away from the claimed stability of such membrane (20% H_2SO_4). In any case, it will be necessary to run accelerated studies in strong acidic solutions (up to 2-5 M H_2SO_4) or long operation cycles with spiral-wound modules to identify any aging mechanism. Results from the long operation cycles using commercial sperial-wound are expected to be finnished along 2021, which will include any membrane auptosy if possible.
2.Whether the extreme acid-resistant Duracid NF membrane has been polluted in the treatment of different acidic waste liquids in the hydrometallurgical copper industry, and how stable is the extremely acid-resistant stearic acid film?
The experimental plan of this study was fully based on the use of flat sheet modules. After performing the experiments, the membrane surface was analysed by SEM, to

	monitor the potential formation of scaling or potential chemical damage. As filtration test had only two hour of operation neither morphological changes nor the formtation of precipitates on the membrane surface were observed. However, as indicated by the reviewer, concerns on such issues, specially formation if mineral phases on the surface of the membrane are expected with solutions from hydrometallurgical industries. The main elements of concern are Fe(III) and Al(III), as they precipitate in the form of hydroxisulphates even at acidic pH values. For this reason, one of the efforts of the modelling tool was devoted to have a prediction of the potential scaling at the membrane surface. Additionally to this fouling mechanism, the membrane resistance at even medium acidity levels (pH 1) needs to be addressed. This stage will be evaluated from laboratory to pilot scale in a copper hydrometallurgical site. 3. In this paper, two experiments were designed to evaluation of species rejection at different TMP and evaluation of species rejection at varying concentrations. However, there is no evaluation experiment for species rejection at varying the cross-flow velocity (cfv), so you can consider whether the cross-flow velocity (cfv) has an impact on the rejection rate of different species in the feed solution. As indicated by the reviewer, the cross-flow velocity has a large impact on species rejections. At low cfv, the effect of concentration polarisation becomes quite significant, thus making the concentration of solution species at the interface solution-membrane large. This causes a decrease in rejections. However, the membrane performance and the transport of species across are not affected, in terms of intrinsic rejections. Therefore, experiments were not conducted at different cfv.

Departament d'Enginyeria Química
UNIVERSITAT POLITÈCNICA DE CATALUNYA

Dr. Professor Tejraj M Aminabhavi
Editor on Chemical Engineering Journal,

Barcelona, 15/08/2020

Dear Mr,

Please find enclosed the revised version of our manuscript: "*Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents" by: Julio López, Oriol Gibert and José Luis Cortina* (**Reference CEJ-D-20-09918**).

We have considered all the comments and suggestions made by the reviewers and we hope that the manuscript will now be suitable for publication in **Chemical Engineering Journal.**

A listed response to the reviewer's comments and a marked original copy is provided on separate sheets.

I look forward to hearing from you.

Yours faithfully,

Dr. Julio López (corresponding author)
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Ref: CEJ-D-20-09918

Title: *Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents*

Journal: Chemical Engineering Journal

Dear Proff. Tejraj M Aminabhavi,

Thank you for your invitation to resubmit our manuscript after addressing all reviewer comments. We have completed the review of your manuscript, and a summary of the raised comments and the comments and changes made could be found in the next pages below. We have considered all issues mentioned in the reviewers' comments, and we have outlined every change made point by point, and provide suitable rebuttals for any comments not addressed. The revised manuscript is now submitted for your consideration with all the corrections made.

I look forward to receiving your comments.

Kind regards,

Julio Lopez

Reviewers' comments:

Reviewer #1:

The manuscript with the title "Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents" is about the characterization of the commercial nano filter (NF) membrane's (Duracid) ability to filter unwanted elements from highly acidic aqueous solutions. The manuscript also attempts to generate an empirical expression that can predict the amount of unwanted elements filtered by the membrane to the concentration of the unwanted elements in the aqueous solutions.

To be clear, the investigation of the Duracid ability to filter ions and other organic compounds from aqueous solutions is not novel and has been performed by various research works, thus lowering the value of this manuscript eventhough the manuscript target a different set of elements filtered. However, the inclusion of an empirical expression that can predict the amount of elements filtered is a novel and important idea that can aid the understanding of the dynamics of nano filtration process and enhance the knowledge in the area.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

For the manuscript to be accepted, a few issues needs to be improved.

(1) Typical in a lot of manuscript is the lack of clarity of the problem. While the manuscript does include sufficient background to the subject matter, the problem in the currently available technology or the knowledge gap is not clearly described. Please include the analysis on the available knowledge in predicting the amount of unwanted elements that will be

filtered by nano filters and how this is still in sufficient such that a new empirical expression needs to be developed.

As indicated by the reviewer, the clarity of the problem has been defined at the end of the introduction. The main concern about NF membranes is to predict its behaviour properly as there are many parameters, such as solution composition, active layer properties and operation conditions, that influence their performance. In this work, we have been able to predict the performance of NF membranes properly by studying first the behaviour of an acid resistance membrane as the Duracid and then by developing analytical expressions that correlate that effect on membrane permeances.

(2) One of the stated goals of the research is to characterized the Duracid NF for the collections of copper and its derivative compounds from waste stream. In addition, the manuscript contains a lot of information about copper and its derivative compounds in the Introduction section. However, the solutions used for the filtration experiments contain only one copper containing solutions. Something is missing in between the discussion in the manuscript or in the experimental design.

As suggested by the reviewer, more information was provided in the introduction. Copper sulphides, such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S) and covellite (CuS), are used as raw materials in the copper hydrometallurgical industry. Mineral leaching is usually performed with sulphuric acid, accompanied by an oxidation (oxygen). The effluent will contain H_2SO_4, Cu^{2+} and other impurities, such as Fe and As, among others. Therefore, experiments were conducted only with Cu(II) as major component.

(3) The experimental setup is hard to be understood without a diagram. Please include a diagram to help with the description of the experimental setup as presented in section 2.1.

As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.

(4) On page 10, the description of the equations (1) and (2) should be proper; equation (1) describe the relation between flow and membrane permeance under virtual/transient/uncorrected concentrations, whereas equation (2) describe the relation between flow and membrane permeance at real/laboratory concentrations. Please fix the description of the equations. In addition, the whole mathematical moddeling is not sufficiently described. For example, why is the relation between flow and and memberane permeance at virtual/transient/uncorrected concentrations are needed? Why cannot the membrance permeance at real concentrations be measured/calculated directly from the experimental data?

As suggested by the reviewer, the section related to mathematical modelling was modified.

Equation 1 describes the transport of species in the concentration polarization layer. This concentration polarization layer is formed at the membrane boundary layer during the filtration process and implies an accumulation of solutes which causes higher osmotic pressures (i.e. low permeate flux) and a decrease in the rejections.

Instead, equation 2 shows the description of species transport across the membrane. This one uses virtual concentrations, which are those in thermodynamic equilibrium with a sub-given point at the membrane. The use of virtual concentrations makes no necessary to provide more data about the membrane rather than membrane permeances. If virtual concentrations were not used, it would be necessary to characterise the membrane exhaustively to determine pore size, membrane charge, diffusion coefficient inside the membrane and distribution coefficients, among others. These experiments are carried out with single salts, and conditions can vary when treating a mixture of electrolytes, as in the present work.

Additionally, membrane permeances cannot be determined directly. The presence of concentration polarisation can make that the concentration of species at the boundary layer to be from 2 to 6 times higher than the bulk solution. Besides, the differences of transport of species generate an electric field inside the active membrane layer, which is hard to measure experimentally.

(5) On the results and discussion of the XPS results on page 13, the thickness of the active layer is claimed to be 250 nm. However, there is not enough evidence neither in the Figure 2 nor in other figures/tables/supplementary information to show that value. Please clarify how this value is obtained.

The active layer thickness was measured from the SEM images at x10000. Figure 2 was modified in order to show the active layer properly. As the literature is very scarce about Duracid membrane, specially from a characterization point of view, we were not able to provide results from others researchers.

(6) In section 4.4, the empirical expression is developed based on the amount of copper sulfate filtered. In an environment where other copper compounds are present, will the empirical expression still be valid? Please include some discussion on the validity fo the empirical expression when other copper species are present in the waste effluents.

The empirical expressions are only valid for Cu(II) and taking into account the composition of the treated solution in terms of total sulphate concentration. In any diiferent environment with other complexing ions (e.g. inorganic or organic), their rejection will be defined according to their nature and the membrane main tranport mechanisms. For each scenario, an empirical expression could be defined using the procedure developed in this work. As indicated by the reviewer, a discussion was added to the manuscript.

(7) In the conclusion section, the first paragraph, line 3 "...which revealed that the membrane was made of polysulphonamide..." should be changed to "...which suggested that the membrane was made of polysulphonamide...".

As indicated by the reviewer, the phrase was modified accordingly.

Reviewer #2:

Authors have present the Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents. i recommend the acceptance of this paper after the authors have carefully addressed my following comments.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

Abstract:

1. Page 2, Line 39: "Rmpirical" mathematical equations … what is the "Rmpirical" refer to?

As indicated by the reviewer, the typo was corrected to "Empirical".

Introduction

2. Please has literature review on alternative methods for Cu recovery from high acidic effluent and What made you to choice nanomembrane methods compare to other methods such as adsorption by activated carbon? Some recommendation: Valorisation of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions, Microwave steam activation, an innovative pyrolysis approach to convert waste palm shell into highly microporous activated carbon.

As indicated by the reviewer, a section related to alternative methods for Cu recovery was added. The works suggested by the reviewer have been carefully revised and cited. We have selected nanofiltration membranes as they provide two streams: one containing a purified acid, and another one containing a high concentration of metals without the need for a regeneration step as with activated carbon. The research under development indicates that NF should be seen as a way just to reduce the amount of efluents (in terms of volume or flow) to be treated. A final stage using any sorption, ion-exchange or selective precipitation stage will be needed as indicated by the reviewer.

3. Highlight the novel of your methods compares to other researchers of using nano-membrane as well.

As indicated by the reviewer, the novelty has been highlighted. The main concern about NF membranes is to predict its behaviour properly as there are many parameters, such as solution composition, active layer and operation conditions, that influences their performance. In this work, we have been able to predict the performance of NF membranes properly by studying first the behaviour of Duracid membrane and then by developing analytical expressions that correlate that effect on membrane permeances.

4. Why has Duracid NF membrane been selected? What is your main contribution to the model study?

Most of the commercial nanofiltration membranes are made of polyamide, which made the susceptible of suffernig hydrolysis at pH lower than 2. To overcome that issue, most of the main membrane producers (Hydranautics, Koch, GE) have developed membranes to cover the extreme acidic ranges(e.g. 5-20 wt. %) in the last decades. From the described providers, Duracid membrane can achieve higher concentration factors (rejections higher than 90%). In previous works, we have determined the performance of Hydranautics, Koch an even ceramic membranes (TiO_2). However, they did not provided the requeriments needed to treat acidic waters (i.e. metal rejection, permeate purity). It should be also mentioned that there is scarce information on the description of mass transport processes with such type of membranes. Thus, a second important objective was the effort to increase the knowledge in this field.

Experimental setup

5. Please provide schematics diagram for better understanding

As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.

6. Please explain in detail "Three synthetic solutions (I, II and III)".

As indicated by the reviewer, the phrase was modified accordingly. The solutions correspond at the effluent from the solvent extraction stage at three different periods in a copper hydrometallurgical plant.

7. Please explain the experiment design/how do you experiment with detail.

As indicated by the reviewer, data about the experimental design was provided in the manuscript. The three solutions were treated with the Duracid membrane to evaluate the species rejection at different TMP, and therefore to determine the membrane permeances to species. After that, solutions I and III were treated at a constant TMP to evaluate the metal concentration factors, and therefore the prediction capabilities of the mathematical model. The experimental design was developed taking into account the experience of the research group in this field on the last decade and references have been provided.

Membrane characterisation

8. Please analyse and relate the membrane characterisation results to its applications.

As indicated by the reviewer, the results from membrane characterisation were related to its applications and the text has been modified appropriately.

9. Point the uniqueness of nano membrane compare to others membrane.

As indicated by the reviewer, the uniqueness of the membrane was compared to other commercial membranes. The discussion has been centred on their properties for having resistance in strongly acidic media.

Influence of solution composition

10. Page 14, line 14-17: the paragraphs is too short.

As indicated by the reviewer, the extension of the paragraph was enlarged.

Reviewer #4:

The manuscript deals with an interesting topic, being organized in alignment with a plethora of advanced analytical techniques. Besides, the outcomes unveil novel knowledge in the field of nanofiltration membrane technologies for the valorisation of copper acidic effluents. In this respect, the manuscript can be accepted for publication at the "Chemical Engineering Journal" after the consideration of the review comments suggested.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

1) At the Abstract section, the "Rmpirical" can be changed to "Empirical".

As indicated by the reviewer, the typo was corrected.

2) Regarding the research objective of "designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry", authors reported the co-presentation of Cu, Fe, Zn, and As. Therefore, authors are recommended to develop distinct subsections in which the following issues can be succinctly discussed:

a) Effect of ionic strength, referring to the competitive sorption of the other metals towards the main Cu recovery.

b) Effect of pH, involving the chemical bonds' development and their affection to the main Cu sorption mechanism and recovery.

c) Prospects of metals' recovery from the effluents, including a short discussion for each one from the aforementioned elements to be treated. Otherwise, authors could discuss whether the disposal of the waste stream containing these low amounts of impurities "as is" could be environmentally sustainable and ecologically safe.

Two or more extra subsections within the main section 4 are recommended.

As indicated by the reviewer, a paragraph regarding the recovery of Cu, Fe, Zn and As was added in Section 4.4. The influence of the described parameters have been taing into account on the modeling formulation stages.

The effect of ionic strength and pH is already discussed in section 4.2.1.

The pH can affect:

i) The membrane charge, making it more positive because of the higher protonation degree of amine groups. This implies that cations will be better rejected.

ii) The equilibrium bisulphate (HSO_4^-)/sulphate (SO_4^{2-}). Low pH values shift the equilibrium towards the formation of HSO_4^-, which is less rejected than SO_4^{2-} in agreement with dielectric exclusion.

The effect of ionic strength influences the equilibrium reactions in terms of activity coefficients.

3) The highlighted points can be enriched with numerical data and quantitative information, in order to strengthen the novelty of the analysis conducted.

As indicated by the reviewer, the highlights were modified accordingly. The main performamce indicators of Duracid membrane with hydrometallurgical acidic solutions have been stressed. Results of the modelling stage were directed to provide an exercise of predicting a filtration stage of a hydrometallurgical acidic solution.

4) The context of the circular economy involvement (and its key-worded inclusion) at the Cu recovery is intuitive and, in this respect, the theoretical background has to be solidified at the first paragraph of the Introduction section. Therefore, I recommend authors to consider indicative papers that I listed at the end of my review comments, which authors can consider and cite at the revised version of their study.

As indicated by the reviewer, the first paragraph has been solidified and the indicative papers has been considered and cited.

5) The underlined subheading-formats has to be removed and these subsections' can be numbered in alignment with the main headings. Similarly, the bold-typed Tables, Annex, Equations has to be changed to plain/normal typing.

As indicated by the reviewer, the underlined subheading formats, as well as the bold-type format, has been removed.

6) The section of mathematical modeling is poorly developed, thus, in depth explanation of the process and variables' functionality, it is needed. Particularly, the citing information has to be utilized in a more descriptive manner:

a) All variables can be accompanied by one explanatory sentence of functionality, values-range taken, and units' measured, where applicable.

b) All input and output of the Solution Electro-Diffusion Film (SEDF) model can be denoted in the form of a Table.

As requested by the reviewer, a depth explanation of the mathematical model and variables' functionality was provided.

7) There is a large portion of subheadings that are extended to more than two lines, thus, rephrasing and shortening them is needed. The narrative following can offer a fairly well description of the relevant issues/aspects studied.

As indicated by the reviewer, subheadings have been rephrased and shortened to avoid its extension to be more than two lines.

8) The narrative flow is structured mainly on membrane characterization and modeling presentation, being narrowed in discussing only Tables and Figures, whereas a synthesis and coherent discussion of the outcomes is actually missing. Therefore, authors are recommended to upgrade their analysis and verify/prove its significance by noting those shortcomings, limitations, and future developmental challenges of their analysis towards similar settings of

environmental and interfacial/surface chemistry interest. Two or three cross-cited and descriptive argumentation are adequate and, to this end, literature refresh and update with the indicative list of published papers given below, it can considered and cited.

As proposed by the reviewer, an up-grade of the analysis in the results and discussion section has been introduced. Intially, the cross-cited option to compare the performance with data published for Duracid membrane was not possible due to the scarce data found at the scientific level. Therefore, the performance of Duracid membrane was compared to other acid resistant membranes (MPF-34 and Hydracore 70pHT). It must be highlighted that there are not so much information about these two, specially in the modelling part as the membrane properties are so different to standard NF membranes (polyamide-based). Therefore, additionally references to cover this information have been provided.

9) The Conclusions section is out of scope since it is not a place to summarize the methodology adopted and the outcomes yielded but, based on them, authors are recommended to succinctly reiterate the drivers and the barriers concluded by the analysis. The current text content of the Conclusions section could be selectively retrieved and relocated to the aforementioned new paragraphs (review comment 7).

As indicated by the reviewer, the Conclussions section has been modified. The information has been relocated in Results and Discussion section. Accordingly, the conclusions section is devoted to the drivers and and barriers identified in this study.

10) The extensive notation of Tables' data in italics (where applicable) has to be revised in plain-normal typing, while the boxes of Figure 8 do not make sense, since their naming is missing.

As indicated by the reviewer, the notation of tables has been modified to plain-normal typing. Regarding Figure 8, each box represents one membrane module. A phrase was added to the caption to clarify it.

11) At citations of the References section other page-ranged are mentioned with the "pp." while others not. Check and revision is suggested in alignment with the journal's guidelines.

As indicated by the reviewer, the Journal’s Guidelines has been consulted. Accordingly, references from a chapter in a book include the term “pp”.

Zamparas, M., Kyriakopoulos, G.L., Drosos, M., Kapsalis, V.C., Kalavrouziotis, I.K., Novel composite materials for lake restoration: A new approach impacting on ecology and circular economy, (2020) Sustainability (Switzerland), 12 (8), art. no. 3397

https://www.scopus.com/inward/record.uri?eid=2-s2.0-85084638536&doi=10.3390%2fSU12083397&partnerID=40&md5=dd198408703e5d3aaaa59dcac6af89f9, DOI: 10.3390/SU12083397

Aravossis, K.G., Kapsalis, V.C., Kyriakopoulos, G.L., Xouleis, T.G., Development of a holistic assessment framework for industrial organizations, (2019) Sustainability (Switzerland), 11 (14), https://www.scopus.com/inward/record.uri?eid=2-s2.0-85071345908&doi=10.3390%2fsu11143946&partnerID=40&md5=3501b754c240eb4e508e2d93c2fbbee7, DOI: 10.3390/su11143946

Kapsalis, V.C., Kyriakopoulos, G.L., Aravossis, K.G., Investigation of ecosystem services and circular economy interactions under an inter-organizational framework, (2019) Energies, 12 (9), art. no. 1734, .

https://www.scopus.com/inward/record.uri?eid=2-s2.0-85066053518&doi=10.3390%2fen12091734&partnerID=40&md5=bf3293e829108db164ed6dfea9c31a6d, DOI: 10.3390/en12091734

Yun, T., Chung, J.W., Kwak, S.-Y., Recovery of sulfuric acid aqueous solution from copper-refining sulfuric acid wastewater using nanofiltration membrane process, (2018) Journal of Environmental Management, 223, pp. 652-657.

https://www.scopus.com/inward/record.uri?eid=2-s2.0-85049337324&doi=10.1016%2fj.jenvman.2018.05.069&partnerID=40&md5=ffe3f282aa4f41b4eac5f106c9edbdab, DOI: 10.1016/j.jenvman.2018.05.069

Chakrabarty, T., Pérez-Manríquez, L., Neelakanda, P., Peinemann, K.-V., Bioinspired tannic acid-copper complexes as selective coating for nanofiltration membranes, (2017) Separation and Purification Technology, 184, pp. 188-

https://www.scopus.com/inward/record.uri?eid=2-s2.0-85018768627&doi=10.1016%2fj.seppur.2017.04.043&partnerID=40&md5=26bc89bdf4d4347a1553836bf4484a19, DOI: 10.1016/j.seppur.2017.04.043

Sun, J., Zhang, L., Xie, B., Fan, L., Yu, S., Separation efficiency and stability of thin-film composite nanofiltration membranes in long-term filtration of copper sulphate and sulphuric acid mixture, (2015) Desalination and Water Treatment, 53 (7), pp. 1822-1833.

https://www.scopus.com/inward/record.uri?eid=2-s2.0-84922413693&doi=10.1080%2f19443994.2013.860629&partnerID=40&md5=655fa143d1ec9a2d4444946682413c29, DOI: 10.1080/19443994.2013.860629

Ahmad, A.L., Ooi, B.S., A study on acid reclamation and copper recovery using low pressure nanofiltration membrane, (2010) Chemical Engineering Journal, 156 (2), pp. 257-263.

https://www.scopus.com/inward/record.uri?eid=2-s2.0-73249143862&doi=10.1016%2fj.cej.2009.10.014&partnerID=40&md5=205b88117d944e589ca8a6cacbc33d93, DOI: 10.1016/j.cej.2009.10.014

Reviewer #5:

This manuscript evaluated the performance of a commercial acid-resistant membrane for valorizing hydrometallurgical copper acidic effluents. The authors conducted comprehensive experimental studies as well as mathematical modeling to determine the membrane permanence to different species in synthetic wastewater effluents. The results were clearly presented. The data supported the conclusion reasonably well. This study is relevant for resource recovery from industrial wastewater and would be of interest to the readers of CEJ. It may be accepted after the comments below accepted.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

1. Highlights should be rewritten to reflect the major finding of this work.

As indicated by the reviewer, the highlights were modified accordingly to reflect the major findings of the work completed.

2. In the Introduction, the authors mentioned that stability of NF membrane is a big issue to treat acidic wastewater effluent. They investigated the performance of Duracid NF membrane in this work. However, it is not clear why the authors showed special interest on this membrane. More background information on Duracid NF membrane would help justify the advantage of this membrane over others.

As suggested by the reviewer, more information was provided in the manuscript. To our knowledge, there were two potential membranes suitable for treating this kind of effluents: Duracid (Suez), Hydracore 70pHT (Hydranautics) and MPF-34 (Koch). At the same acidity levels, the Hydracore 70pHT and MPF-34 show lower metal rejections than Duracid (see the references below). Therefore we selected Duracid membrane. From our previous experience, we discarded the ceramic membranes since at that pH we have observed rejections below 10%.

> *A. Manis, K. Soldenhoff, E. Jusuf, F. Lucien, Separation of copper from sulfuric acid by nanofiltration, in: Fifth Int. Membr. Sci. Technol. Conf., 2003.*
>
> *T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, J. Memb. Sci. 480 (2015) 74–82. doi:10.1016/j.memsci.2015.01.013.*

Although the membrane active layer chemistry of the acid resistant NF membranes has not been evaluated in an extensive way as conventional membranes, the Duracid active layer (sulphonamide) is totally different than the ones from Koch and Hydranautics, as well as the new membranes from Dupont and Laxess, all of them based on polyethersulphonated layers. The initial performance indicators (e.g. rejections and flux), which were found in a scarce number of publications, made this membrane of interest for this application.

3. For 2.1 Experimental set-up, I would suggest adding a schematic diagram to better illustrate the experimental processes.

As indicated by the reviewer, a diagram for the experimental set-up was provided in section 2.1.

4. Lines 27-30, page 14, the author claimed that the positive charged membrane surface was due to partial and fully protonation of amine and sulfonic groups. I don't think it is correct for sulfonic groups because they are generally strong acids and partially deprotonated even under very acidic pH. So, sulfonic groups are negatively charged rather positively charged.

According to Sata (2004) and Tanaka (2015), the acidity constants of sulphonic groups in a polymeric matrix (i.e. ion-exchange membranes) might be below 1. Therefore at the operating conditions, it can be expected the sulphonic groups to be partially protonated.

> *Sata, T., 2004. Ion exchange membranes : preparation, characterization, modification and application. Royal Society of Chemistry.*
>
> *Tanaka, Y., 2015. Ion exchange membranes : fundamentals and applications, 2nd ed.*

5. How stable was the Duracid NF membrane over long-term operation? A stability test would be helpful to demonstrate the application potential of this membrane.

The membrane was replaced for each experiment. Therefore, it was no possible to evaluate the membrane stability at long-term exposition. After each experiment, we performed cleanings with water, in order to compare the hydraulic membrane permeability with the one from a virgin membrane. Marginal changes were observed (<2%), which suggested the membrane did not change. In addition, membranes were analysed by SEM, and no changes were observed at the surface. It should be added that the membrane stability was not one of the research questions identified in the experimental plan as the working conditions were far away from the claimed stability of such membrane (20% H_2SO_4). In any case, it will be necessary to run accelerated studies in strong acidic solutions (up to 2-5 M H_2SO_4) or long operation cycles with spiral-wound modules to identify any aging mechanism. Results from the long operation cycles using commercial sperial-wound are expected to be finnished along 2021, which will include any membrane auptosy if possible.

6. Chemical equilibrium model used to establish the speciation diagrams of different species in synthetic wastewater effluent should be provided.

Speciation diagrams were built with the Hydra/Medusa software. As indicated by the reviewer, this was pointed out in the manuscript. The Hydra database was used for performing the calculations, and only some new data were introduced for describing the potential scailing events along the concentration stage. These values have been collected in table 2.

Reviewer #6:

Overview and general recommendation:

Following circular economy principles, it is of great significance to recover valuable metals from acidic waste stream produced in copper hydrometallurgy industry by using high acidity resistance nanofiltration (NF) membranes. Besides, It is a good design to adjust the experimental results to the Solution-Electro-Diffusion-Film (SEDF) model to determine the membrane permeances to species. Combining theory with experiment, the prediction capability of the SEDF model, together with the developed empirical equations for the permeances, was proposed as a tool for designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry. Because of this, current research is about the relevance of a topic and general interest to magazine readers.

On the one hand, I found the paper to be overall well written and much of it to be well described. I believe that the authors have undergone a lot of research and conducted a scientific and reasonable design. The combination of theory and experiment makes this data set seem quite useful for this purpose. On the other hand, There are still some problems in this paper. Therefore, I recommend publication of this paper after the revisions. I explain my concerns in more detail below.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

1. Section4.1, I have noticed the characterization of the extreme acid-resistant Duracid NF membrane, but I am also interested in whether the structure and performance of the extreme acid-resistant Duracid NF membrane have changed after it has been treated with different acid waste liquor from hydrometallurgical copper industry. Therefore, please supplement the relevant characterization.

We have only used one membrane for each experiment, and no characterisation of the membrane structure was performed. With the membrane cleaning with water, we have determined the hydraulic membrane permeability and was compared with the one from a virgin membrane. Marginal changes were observed between both values (<2%). It should be added that the membrane stability was not one of the research questions identified in the experimental plan as the working conditions were far away from the claimed stability of such membrane (20% H_2SO_4). In any case, it will be necessary to run accelerated studies in strong acidic solutions (up to 2-5 M H_2SO_4) or long operation cycles with spiral-wound modules to identify any aging mechanism. Results from the long operation cycles using commercial sperial-wound are expected to be finnished along 2021, which will include any membrane auptosy if possible.

2.Whether the extreme acid-resistant Duracid NF membrane has been polluted in the treatment of different acidic waste liquids in the hydrometallurgical copper industry, and how stable is the extremely acid-resistant stearic acid film?

The experimental plan of this study was fully based on the use of flat sheet modules. After performing the experiments, the membrane surface was analysed by SEM, to monitor the potential formation of scaling or potential chemical damage. As filtration test had only two hour of operation neither morphological changes nor the formtation of precipitates on the membrane surface were observed. However, as indicated by the reviewer, concerns on such issues, specially formation if mineral phases on the surface of the membrane are expected with solutions from hydrometallurgical industries. The main elements of concern are Fe(III) and Al(III), as they precipitate in the form of hydroxisulphates even at acidic pH values. For this reason, one of the efforts of the modelling tool was devoted to have a prediction of the potential scaling at the membrane surface. Additionally to this fouling mechanism, the membrane resistance at even medium acidity levels (pH 1) needs to be addressed. This stage will be evaluated from laboratory to pilot scale in a copper hydrometallurgical site.

3. In this paper, two experiments were designed to evaluation of species rejection at different TMP and evaluation of species rejection at varying concentrations. However, there is no evaluation experiment for species rejection at varying the cross-flow velocity (cfv), so you can consider whether the cross-flow velocity (cfv) has an impact on the rejection rate of different species in the feed solution.

As indicated by the reviewer, the cross-flow velocity has a large impact on species rejections. At low cfv, the effect of concentration polarisation becomes quite significant, thus making the concentration of solution species at the interface solution-membrane large. This causes a decrease in rejections. However, the membrane performance and the transport of species across are not affected, in terms of intrinsic rejections. Therefore, experiments were not conducted at different cfv.

Highlights

- Valorisation of acidic waters using nanofiltration (NF) in the Cu industry
- Characterisation of Duracid membrane as polysulphonamide
- High metal rejections (>85%) and acid recovery (rejection below 40%) with Duracid
- Precipitation of calcium and iron sulphates during the process
- Use of SEDF model as a designing tool for scaling-up

Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents

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Abstract

The exhaustion of Cu reserves minable and processable with the available technology is forcing the hydrometallurgical copper industry to seek alternative sources of Cu. Following circular economy principles, researchers' attention has focused on the recovery of valuable metals from the acidic waste streams generated. Nowadays, membrane technologies are being selected as the first alternative for the treatment and valorisation of such acidic waste streams. Among them, a new generation of high acidity resistance nanofiltration (NF) membranes offer the alternative for acid recovery while providing a metal-enriched stream. In this work, the extreme-acid resistant Duracid membrane was evaluated for the valorisation of different synthetic acidic waste streams from the hydrometallurgical Cu industry. These waters were characterised by a high acidity (pH 0.5–1.5) and the presence of Fe (11–14 g/L), Zn (0.7 – 1.4 g/L) and As (0.5–0.7 g/L), among others. Initially, the membrane was characterised by different techniques (SEM, FTIR-ATR, XPS). Experiments were performed under constant and varying permeate flux and feed water composition. Metals were effectively rejected (>90%), whereas H^+ easily permeated through the membrane. The experimental results were adjusted to the Solution-Electro-Diffusion-Film (SEDF) model to determine the membrane permeances to species. Empirical mathematical equations were developed and validated to express the dependence of permeances on solution composition. Finally, the prediction capability of the SEDF model, together with the developed empirical equations for the permeances, was proposed as a tool for designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry. The model predicted gypsum scaling onto the membrane and therefore anticipated the need of applying antiscalants.

Keywords: sulphuric acid effluents; scaling-up; Duracid; modelling acid transport; circular economy

1. Introduction

Although copper resources are estimated to exceed 5000 million tonnes worldwide taking into account the already discovered, undiscovered and potentially profitable deposits, the Cu reserves minable and processable with the available technology may be limited to 830 million tonnes. These reserves are expected to be exhausted within the next 40 years [1]. In views of the growing scarcity of naturals resources such as minable minerals, the European Union (EU) proposed in 2015 an action plan to move towards a circular economy to improve resource efficiency and promote sustainable growth. Circular economy systems maintain the added value in products for as long as possible, while the generation of wastes is avoided or reduced. Under this scheme, once a product has reached the end of its life, it must be used to create further value. It is required a transformation of both production and consumption systems into marketable products to implement circular economy schemes, where the design and engineering are factors of immense importance [2]. It is estimated that the implementation of circular economy schemes can reduce the need for input materials by 17-24%, which can bring an economic saving of 630 billion € in the industries of the EU [3–5]. Nowadays, circular economy examples can be found, such as the recovery of P to restore eutrophic waters [6] and the recovery of rare earth elements from phosphogypsum waste [7], among others. Additionally, circular economy schemes promote sustainability in terms of energy consumption, environmental protection and the longevity of raw materials [8].

Conventional extraction of Cu from high-purity Cu-minerals in sulphide form (chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S; and covellite, CuS) is done through a pyrometallurgical process after milling and leaching the Cu-mineral with sulphuric acid, accompanied with oxidation with air, yielding a final leachate characterised by an acidic pH ($0.5<pH<2.0$) and Cu(II) content up to 6 g/L Cu (II) [9]. However, the exhaustion of high-purity copper ores has made necessary to exploit lower quality Cu-minerals often in oxidised form (brochantite, $CuSO_4$; azurite,

$2CuCO_3 \cdot Cu(OH)_3$; cuprite, Cu_2O) and containing impurities such as Fe, Zn and As. The relatively low content of Cu and the presence of impurities in the mined minerals requires the application of new processes such as the two-stage solvent extraction and electrowinning (SX/EW) process, which produces a Cu-enriched solution (with Cu concentration higher than 35 g/L and low amounts of impurities) that is reduced using an electrolytic procedure (electrowinning) to produce pure Cu. The process generates an overall waste stream that contains high concentrations of sulphuric acid and metals (Zn, Cu, Sb, Bi, As…) [10,11]. This waste stream is usually treated by the addition of quicklime (CaO(s)) to neutralise the acidity and remove metals as hydroxides [11,12] prior to discharge into the natural water receiving bodies. The high value of the compounds present in the waste stream has centred the attention of researchers, who following circular economy principles aim at their recovery from the acidic waste streams.

Over the past years, research has focused in the valorisation of acidic waters, and different technologies have been proposed, such as activated carbon [13,14], ion-exchange resins [15,16] and solvent extraction [17,18], among others. Although these technologies can be useful for acid or metal recovery, two drawbacks are associated with them: i) an additional treatment unit to purify the acid or metal, and ii) the need of a regeneration step for the activated carbon, ion-exchange resins or organic phase in solvent extraction, which can increase the costs of the process.

In order to overcome the disadvantages of the methods mentioned above, membrane technologies have gained importance in the industry. They nowadays are widely applied in many fields, since they allow to recover valuable compounds with the permeate or remove an undesirable compound from the feed stream. The advantages of membrane processes comprise low energy consumption, ability to be combined and integrated with other separation processes, the possibility of working at mild conditions and no need for additives [19]. Among the different membrane technologies, nanofiltration (NF) membranes are drawing increasing attention because of their high rejection of multivalent species (e.g. metal cations), while allowing the transport of monovalent ones (e.g. acids) [20–23]. For example, Nÿstrom et al. [20] purified nitrate and sulphate acidic solutions, achieving high rejections of metals (>98%) with the NF-45 membrane. Erikson et al. [21] studied how to purify 33% H_2SO_4 containing metals such as Fe, Zn, Cd and Cu. Metal rejections were higher than 99%, while 50% of the acid was recovered. González et al. [22] reported similar findings when purifying H_3PO_4 solutions with NF and reverse osmosis (RO) membranes (>95% for Fe, Mg and Al, among others), concluding that NF allowed higher acid recovery (80%) and permeate fluxes (4 times higher than RO membranes). López et al. [23] studied the performance of a polyamide-based membrane (NF270) in treating an effluent characterised by the presence of strong (HCl/H_2SO_4) and weak (H_3AsO_4) acids (pH<1), and metals (e.g. Fe, Cu, Zn). Metals were rejected by 80%, whereas the acid permeated easily across the membrane. However, As was not rejected (<40%) because of its presence as a non-charged species ($H_3AsO_4(aq)$).

Undoubtedly, one of the most challenging issues of the NF membranes for the treatment of acidic effluent wastes is to resist the low pH values typically found in these waters, which can be as extreme as pH<1. In fact, due to the high acidity of the solutions, most of the commercial NF membranes (usually polyamide-based) are not suitable because of the possibility of suffering hydrolysis in such acidic media. The large potential economic market associated to the mining activities has promoted the development of new families of ceramic [24,25] and polymeric active layers [26–28] to deal with this challenge, but much effort is still needed with regards to their performance of these new family of membranes in terms of rejection and solvent flux, membrane lifetime and description of solute transport processes. Although a significant new generation of membranes is under development, some commercial membranes can be found, such as the Duracid (Suez) and the MPF-34 (Koch). Duracid membrane has found to provide high metal rejections at pH 0.5 (almost 100%) [29], whereas the MPF-34 showed lower rejections (80%) at these acidity levels [30].

Another issue that needs to be addressed with NF is the lack of numeric tools for scale-up and process design. Unlike RO membranes, where the performance depends only on the operation parameters (e.g. pressure and recovery ratio), the performance NF membranes also depends on the feed solution composition, the properties of the active layer and the interactions between both. Such dependence makes that a species can behave very differently, from passing easily across the membrane (displaying even negative rejections) to being completely removed (rejections higher than 90%) [31–33]. This varying behaviour has posed difficulties in developing successful mathematical tools for predicting the performance of NF membranes at large scale.

Among the developed ones, phenomenological models are of considerable value. They treat the membrane as a “black box”, which avoids an extensive membrane characterisation, and describe the separation of components in terms of solute passage and water flux [34]. Among them, the Solution-Diffusion (SD) model has been widely applied, and not only for NF but also for RO membranes [28,31–33]. It assumes that the transport is due to differences in diffusion coefficients across a dense membrane (i.e. the membrane is considered not to have fixed pores). This model has later been expanded to incorporate electric migration effects due to the different rates of species transport, giving rise to the so-called Solution-Electro-Diffusion (SED) model. Finally, the integration of the film theory into the SED model has proved to provide an even more accurate description of the membrane performance in terms of rejections and a more reliable estimation of possible scaling events. This model, referred to as Solution Electro-Diffusion Film (SEDF) model [32,33,35], has been applied for electrolytes mixtures of one dominant salt and trace salts. All these models have in common that the transport of species is defined by a phenomenological coefficient termed permeance (P_i), which expresses the easiness of the species i to permeate through the membrane.

To sum up, NF membranes can be useful for the valorisation of acidic effluents, as they allow to recover a free acidic stream in the permeate, which can be re-used internally and thus promoting circular economy schemes instead of traditional methods based on neutralisation/precipitation. However, the dependence of the performance of NF membranes on solution composition, active layer and operation parameters, has made that there is still a lack of numerical tools to predict its performance properly and also for scaling-up. The main objective of this work was to characterise using Scanning Electron Microscopy (SEM), Fourier-transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) mode and X-ray photoelectron spectroscopy (XPS) techniques and evaluate the suitableness of the extreme acid-resistant Duracid NF membrane (Suez) for the valorisation of synthetic solution mimicking a waste stream from a hydrometallurgical copper industry. Experiments were performed under constant and varying permeate flux and feed water composition, and experimental data were adjusted with the SEDF model to determine the membrane permeances to species. Since these coefficients were found to depend on the solution composition, empirical mathematical equations were developed to express such dependence. Then, these equations were validated in further experiments. Finally, the mathematical model was used to design a pilot plant for treating 1 m^3/h of this effluent.

2. Experimental

2.1. Experimental set-up

Figure 1 shows the experimental set-up. Experiments were performed with flat-sheet membranes placed in a cross-flow test cell (GE SEPA™ CF II, 0.014 m^2) with a spacer in the feed channel. The feed solution was kept in a thermostatic tank (30 L) at constant temperature (22±2°C) and pumped to the cross-flow cell with a high-pressure diaphragm pump (Hydra-Cell, USA). The trans-membrane pressure (TMP) and the cross-flow velocity (cfv) were controlled by a by-pass (in the feed line) and needle valve (in the concentrate line). Moreover, two manometers were allocated before and after the membrane test cell to monitor the TMP. Just before the discharge of the concentrate in the feed tank, a flow-meter and a pre-filter cartridge were placed. The latter one was made of polypropylene (100 µm), whose function is to avoid that any erosion product reached the pump. A three-way valve in the permeate line allowed to collect samples.

Two sets of experiments were performed according to their objective:

- Evaluation of species rejection at different TMP. The effect of TMP on the rejections of the different species present in feed solution was studied by varying it from the osmotic pressure to 32 bar at cfv of 0.7 m/s. Feed water composition was maintained constant by recirculating both membrane outputs (permeate and concentrate streams) back to the feed tank. Experimental data were fitted by the SEDF model and membrane permeances (P_i) were determined.
- Evaluation of species rejection at constant TMP and varying concentrations. Unlike the previous set, the membrane was operated at a fixed TMP and cfv of 0.7 m/s, and concentrations in the feed tank were varied by recirculation the concentrated stream but not the permeate stream, which was withdrawn out of the system. Concentration factor and rejection of metals by the NF membrane were calculated during the experiments. Empirical mathematical expressions of the dependence of P_i on water composition developed from the previous sets were also validated.

For the performance of each experiment, a 140 cm^2 piece of the membrane was cut and placed in Milli-Q water overnight. Then, the membrane was placed in the test cell and compacted with deionised water for 2 h at 32 bar and 1 m/s and with the solution to be treated at the same conditions. Then, the experiments were performed. After completion of the experiment, the set-up was cleaned with a diluted sulphuric acid solution (0.1 M) and with deionised water to remove any impurity than may be left inside.

2.2. Membrane and solutions

Three synthetic solutions (named I, II and III as shown in Table 1) mimicking waste effluents from the solvent extraction stage of a SX/WE process at three different periods in a hydrometallurgical industry located in the South of Spain were prepared. These waste effluents were extensively monitored under the H2020 research project OREOPTIM. As can be seen, they were characterised by an acid pH ($0.6<pH<1.6$) and the presence of metals, mainly iron, which was present either as Fe(II) or Fe(III). Other metals such as zinc, copper and calcium, among others were present at lower concentrations. Annex A collects the speciation diagrams (built with the Hydra/Medusa software [36]) for the elements in solution. The three solutions were treated with the Duracid membrane to evaluate the species rejection at different TMP. Additionally, solutions I and III were treated at a constant TMP to evaluate the metal concentration factors.

In order to prepare the synthetic solutions, the following chemicals were used: H_2SO_4 (96 wt%, Sigma-Aldrich); $FeSO_4·7H_2O$ (99%, Sigma-Aldrich); $Fe_2(SO_4)_3·5H_2O$ (98%, Sigma-Aldrich); $ZnSO_4·7H_2O$ (100%, Panreac); Na_2SO_4 (>99%, Sigma-Aldrich); $Na_2HAsO_4·7H_2O$ (98%, Sigma-Aldrich); $CaSO_4·2H_2O$ (100%, Scharlau); $CuSO_4$ (100%, Panreac); $NiSO_4·6H_2O$ (98%, Sigma-Aldrich) and $MnSO_4·xH_2O$ (99%, Sigma-Aldrich).

Table 2 collects the most likely mineral phases to precipitate on the membrane. Scaling may occur by the precipitation of Fe(III) as hydroxide ($Fe(OH)_3(s)$), oxyhydroxide ($FeOOH(s)$) or as jarosite ($AFe_3(SO_4)_2(OH)_6(s)$, where A=Na or H_3O). Besides, gypsum ($CaSO_4·2H_2O$) can be formed at the membrane surface.

The membrane tested in this study was the acid-resistant Duracid NF membrane (developed by Suez), whose properties are shown in Table 3.

2.3. Analytical techniques

2.3.1. Aqueous samples

Several techniques were used to determine the composition of the liquid samples.

Inductively Coupled Plasma Mass (7800 ICP-MS from Agilent Technologies) and Optical Emission Spectrometer (5100 ICP-OES from Agilent Technologies) were used to determine the concentration of the elements in solution.

Since the solution contained a mixture of Fe(II) and Fe(III), redox titrations were carried out to measure the concentration of Fe(II) with an automatic titrator (Mettler Toledo T70) using a Pt electrode and potassium dichromate (K_2Cr2O_7) as titrant solution. Acid-base titrations to measure the concentration of H^+ were not performed because of the presence of metals. The increase in pH along the titration would lead to the precipitation of metals, thus providing an inaccurate measurement of the H^+ concentration. Then, it was determined by using a pH-glass electrode (GLP 22, Crison). From the speciation analysis, and taken into account the ionic strength, the activity coefficients were determined and used to calculate the concentration of H^+. However, the error associated with measures below pH 1, could be up to 0.2 pH units.

2.3.2. Solid samples: membranes and precipitates generated along with the filtration experiments

Before analysis of any solid sample, it was dried in an oven at 40°C for more than 72 h.

The morphology of both samples (membrane and precipitate), which were previously metallised with an alloy of Pt/Pd, was obtained by Scanning Electron Microscopy (JEOL JSM-7001F) at an acceleration voltage of 20.0 keV for secondary-electron imaging (SEI).

The FTIR-ATR mode (JASCO FT/IR-4100) spectrum of the active layer of the Duracid membrane was recorded between 4000 and 600 cm^{-1} with 64 scanning times, providing a resolution of 4 cm^{-1}. The active layer was also analysed by XPS (SPECS system) to determine its elementary composition. The equipment used an Al anode XR50 source operating at 150 W and a Phoibos MCD-9 detector at vacuum lower than 10^{-8} mbar. The area of analysis was 0.8 mm^2 with a binding energy accuracy of 0.1 eV.

The mineral phases were identified with X-ray Diffraction (XRD) after grinding the sample into powder. A D8 Advance diffractometer (Bruker) was used with a Bragg-Brentano configuration θ-2θ and a vertical goniometer. The equipment has a Cu X-ray tube, which allows to work up to 40 kV and 40 mA. The spectrum was recorded from 15° to 60° with steps of 0.020°. The identification of mineral phases was performed with EVA software (Bruker).

3. Mathematical modelling

The fitting of experimental data in this study was obtained according to the SEDF phenomenological model [34].

The model considers the concentration polarization layer (Eq. 1), where the transport of species is due to a combination of a diffusion gradient, electromigration and convective flux [32].

Concentration polarization layer

$$j_i = -P_i^{\delta} \cdot \left(\frac{dc_i'}{dx'} + z_i \cdot c_i' \cdot \frac{d\varphi'}{dx'} \right) + J_v \cdot c_i' \qquad (1)$$

Where j_i is the flow of component i (mol/L·µm/s), x' is the dimensionless position (-), P_i^{δ} is the concentration polarization layer permeance to species i (µm/s), c_i' is the concentration of component i (mol/L), z_i is the valence charge of component i (-), φ' is the dimensionless virtual electrostatic potential (-) and J_v is the trans-membrane flow of solvent through the membrane (µm/s).

The concentration polarization layer permeances relate the diffusion coefficient of component i (D_i^δ, µm²/s) [41] with the mean thickness of the concentration polarization layer (δ, µm) by $\delta = {D_i^\delta}/{P_i^\delta}$. Since the value of δ is unknown, it will be one of the parameters to determine.

The transport of species across the membrane results from a combination of diffusion and electromigration (Eq. 2). The model uses "virtual concentrations", which are defined as those in thermodynamic equilibrium with a given point inside the membrane. The use of virtual concentrations makes no necessary to introduce other membrane properties, rather than membrane permeances. These are the parameters of interest and characterise the transport of species across the membrane. These ones depend on the membrane and species properties, as well as the interactions between both. Moreover, the partition coefficients (ratio between virtual and real concentrations) are included within the permeances [34]. The membrane permeances to species can range from values close to zero (related to the less permeable species) to values higher than 100 µm/s (high permeable species).

Membrane

$$j_i = -P_i \cdot \left(\frac{dc_i}{dx} + z_i \cdot c_i \cdot \frac{d\varphi}{dx}\right) \tag{2}$$

Where x is the dimensionless position in the membrane (-), P_i is the membrane permeance to species i (µm/s), c_i is the concentration of component i (mol/L) and φ is the dimensionless virtual electrostatic potential (-).

Additionally, the transport equations in the concentration polarization layer and membrane must be subjected to [32]:

- Electroneutrality condition:

$$\sum z_i \cdot c_i = 0 \tag{3}$$

- Zero-current flow:

$$\sum z_i \cdot j_i = 0 \tag{4}$$

- Flux conservation:

$$-P_i^{\delta} \cdot \left(\frac{dc_i'}{dx'} + z_i \cdot c_i \cdot \frac{d\varphi}{dx'}\right) + J_v \cdot c_i' = -P_i \cdot \left(\frac{dc_i}{dx} + z_i \cdot c_i \cdot \frac{d\varphi}{dx}\right) \tag{5}$$

The solvent flux across the membrane (J_v) was described as follows (Eq. 6) [42].

$$J_v = k_w \cdot (TMP - \Delta\pi) \tag{6}$$

Where k_w is the hydraulic permeability of the membrane (µm/(s·bar)) and $\Delta\pi$ is the differences of osmotic pressure between feed-solution membrane interface and permeate (bar), which was calculated according to the van't Hoff equation.

Saturation indexes (SI, -) were calculated according to Eq. 7 to determine the potential scaling events at the membrane surface [42].

$$SI = \log\left(\frac{IAP}{K_{so}}\right) \tag{7}$$

Where IAP is the ionic activity product of a given mineral and K_{so} is the solubility constant (given in Table 2).

To sum up, Table 4 collects the model inputs, outputs and fitting parameters. The system of differential equations was solved in Matlab (function ode23s, based on Runge-Kutta method), and in order to fit the experimental data properly, the membrane permeances and concentration polarisation layer were varied.

4. Results and discussion

4.1. Membrane characterisation

The Duracid membrane was analysed by FTIR-ATR (Figure 2, Table S1 Supplementary Information) and XPS (Table 5, Figure S1 Supplementary Information) to determine its functional groups and its elementary composition.

The resultant FTIR-ATR spectrum resulted in a superposition of the active layer and the intermediate layer (polysulphone), due to the higher radiation penetration depth than the active layer thickness. The FTIR-ATR spectrum revealed the presence of NH_2 in primary amides (1584 cm^{-1}, NH_2 deformation); C=C in benzene ring in aromatic compounds (1486 cm^{-1}, ring stretch); SOH_3 in sulphonic groups (1241 cm^{-1}, S=O stretch); SO_2NH_2 in sulphonamides (1151 cm^{-1}, SO_2 sym. stretch) and C-NH_2 in primary aliphatic amines (1105 cm^{-1}, C-N stretch). Moreover, some peaks related to the SO_2 groups in the polysulphone were observed at 1321, 1292 and 1167 cm^{-1} [43].

Contrarily, the XPS allowed to analyse only the active layer because of its lower penetration depth (<20 nm). From the elementary analysis with XPS, it was observed that the membrane was composed by C (76.0%), O (14.3%), N (4.8%) and S (4.9%). Hydrogen was not included due to the unsuitability of XPS for its analysis. The analysed peaks were centred in 167 eV for S(2p), 284.9 eV for C(1s), 399 for N(1s) and 531 eV for O(1s). As can be seen, the ratio S/N approached 1, which suggested that most of the N atoms of the active layer were bounded to S atoms. Additional information about the membrane structure can be obtained by deconvoluting the main element peaks (Table 5, Figure S1 in Supplementary information).

For the Duracid membrane, three different peaks were identified for C(1s): at 284.7 eV, which was assigned to C-C, C-H and C=C chemical bonds; at 285.3 eV related to C-N and C-S group; and C-O bond at 288.4 eV. For oxygen, only one peak was identified, which was related to C-

SO_2-C and C-SO_3H groups. For nitrogen, two peaks were identified: at 399.6 eV, which was related to –C-NR_2 (R=C, H) and SO_2-NH_2 groups; and at 401.6 eV, associated with –NH_3^+ groups. Finally, for sulphur, two chemical bonds were identified: at 167.7 eV for C-SO_2-C and 169.1 eV for -NH_2-SO_3H [44–46].

From both analyses (FTIR-ATR and XPS), it was revealed that Duracid membrane had an active layer made of polysulphonamide, in agreement with Weinman [40]. Accordingly, the membrane had ionisable amine (R-NH) and sulphonic (R-SO_3H) groups, which were responsible for the membrane charge.

The chemistry of the active layer is a parameter of huge importance, especially related to the membrane stability when treating acidic waters. The fact that most of the available commercial membranes have a polyamide-based active layer makes them susceptible of suffering an acid attack at long term operation [47,48]. However, the presence of sulphonic groups can make the membrane stable in acidic media. For example, Hoseinpour et al. [49] compared the stability of polyamide, polysulfonamide and poly(amide-sulfonamide) membranes after soaking the membranes in 10% wt. H_2SO_4 at 55 °C, and concluded that the polysulphonamide membranes presented the highest stability, whereas the one made of polyamide has the lowest one.

The morphology of the Duracid membrane is shown in Figure 3. The three membrane layers are clearly distinguishable: i) the polyester layer, where the membrane is supported; ii) the polysulphone layer and; iii) the active layer (sulphonamide). From the SEM image at x10000 amplifications, it was possible to see at the top a dense layer, which corresponded to the active layer. Additionally, it was possible to measure its thickness, which was to be of 250 nm.

4.2. Dependence of membrane rejection of solution composition and trans-membrane pressure

4.2.1. Influence of solution composition

Figure 4 collects the rejection of the different elements as a function of trans-membrane flux for the solutions I (Fig 4.a), II (Fig 4.b) and III (Fig 4.c).

Figure 4.a shows the rejection curves for the elements in solution I. As can be seen, Fe(III) showed the highest rejections with values between 91 and 97%, followed by the bivalent metals and As, whose rejections ranged between 85 and 94%. SO_4 presented lower rejections, with values within the range 80-90%. The highest rejection values for multivalent metals, As and SO_4 contrasted with the rejections of monovalent metals. For example, Na rejections varied between 52 to 72%, while H^+ ones ranged from -5 to 26%.

The selectivity of the membrane can be explained with the main exclusion mechanisms: the Donnan and dielectric exclusion. Additionally, the solution speciation is an important parameter, since the different species from one element can be affected in one way or another by the above-mentioned exclusion mechanisms.

Donnan exclusion postulates that the membrane carries fixed charges, which exclude the co-ions in solution (same charge as the membrane). In contrast, ions with an opposite charge (counter-ions) are transported across the membrane [50,51]. The Duracid membrane, at pH below 4.3, presents a positive charge because of the partial and fully protonation of amine ($R\text{-}NH_2^+$) and sulphonic ($R\text{-}SO_3H$) groups, respectively. This positive charge repels the cations (e.g. Fe^{3+}, Fe^{2+}) which are highly rejected by the membrane. Conversely, the transport of anions was favoured across the membrane (e.g. HSO_4^-) because of the electrostatic attractions between them and the positively charged membrane surface. Nevertheless, the electroneutrality conditions must be fulfilled on the permeate side. Then a stoichiometric number of cations such as Na^+ and H^+ permeate because of their higher diffusivity, smaller size and absolute charge among the metal cations [52].

The dielectric exclusion is caused by the interaction between ions and bound electric charges induced in the membrane at the interface solution/membrane with different dielectric constants, such as the polymeric matrix and the bulk solution. The effect of dielectric exclusion is more pronounced than Donnan exclusion, because the ion-exclusion free energy is proportional to the square of the ion charge, whereas in the Donnan exclusion such dependence is linear [53,54]. This phenomenon explained why the transport of multivalent was more impeded, following then the sequence: Fe(III)>M(II)>Na>H^+.

The increase in the concentration of all the elements (solution II) resulted in a different behaviour of the membrane, as shown in Figure 4.b. Multivalent metal rejections barely varied (88-95%) but significant changes were observed for the other elements in solution. SO_4 and As rejections were lower than the ones for metals (from 60 to 77% as permeate flux increased). This variation can be related to changes in the speciation due to the decrease in pH (see Annex A). At pH 1.53 of solution I, the main anion in solution was SO_4^{2-} (37% of total sulphate), but as acidity increased, its percentage decreased to 17% while HSO_4^- percentage increased from 17 to 42%. The prevalence of HSO_4^- over SO_4^{2-} promoted the transport of SO_4 across the membrane in agreement with Donnan and dielectric exclusions. The fact that a higher amount of SO_4 was transported across the membrane enhanced the transport of monovalent species, such as Na^+ (33-65%) and H^+ (12-40%) Regarding the As, at pH of 0.86 of solution II it became fully protonated as H_3AsO_4 (95%), while $H_2AsO_4^-$ accounted for only 5% of the total As. The fact that As was mainly present as a neutral species suggested that its transport was not favoured nor impeded by the membrane.

Some differences in the membrane behaviour can be observed after a further decrease of pH to 0.65 in solution III (Figure 4.c). The low pH favoured the predominance of H_3AsO_4 and HSO_4^-, which for the same reasons discussed above resulted in even lower rejections than in the previous (60-77%). In this case, SO_4 rejections varied from 52% to 69%, whereas As rejections ranged from 35% to 53%. As a result, lower cation rejections were observed. For example, lower rejections were achieved for multivalent metals (80-90%), Na (18-45%) and H^+ (-6 to 19%).

Table 6 collects data about NF performance with acidic waters. Only one work was found in the literature reporting the performance of the Duracid membrane at acid pH (<1.5). Schütte et al. [29] treated the leaching of a sewage sludge with the Duracid membrane for phosphorous recovery. The residual stream was composed by H_2SO_4 (pH 0.5), Fe (1.3 g/L), P (0.8 g/L) and Ca (0.6 g/L), among others. Metals were effectively rejected (>95%), whereas SO_4 (rejections between 25-40%) and PO_4 (30-55%) were transported across the membrane. The lower rejections of SO_4 reported may be explained by the even lower pH in comparison with the present study. Other studies were performed at similar acidity levels as the one present in this work. Tanninen et al. [55] evaluated the performance of another acid-resistant membrane (MPF-34) for the treatment of acidic copper concentrated solutions (0.22 mol/L H_2SO_4 and 0.47 M $CuSO_4$). $CuSO_4$ was rejected by 78%, while H_2SO_4 was transported easily across the membrane (rejection of 10%). Guastalli et al. [56] mimicked an effluent from industrial rising water (pH 1.2, 39.2 g/L H_3PO_4, 2.7 g/L Al) and evaluated the H_3PO_4 recovery with the MPF-34 membrane. The membrane rejected Al completely (100%), whereas 56% of H_3PO_4 was transported across the membrane. López et al. [23] observed also similar As rejections when treating a copper smelter effluent (pH 0.64, 18 g/L SO_4^{2-}, 0.3 g/L As(V), 0.1 g/L Fe) with the NF270 membrane. Metals were rejected by more than 80%, whereas SO_4 was transported across the membrane (20-40%). The low rejections of As (10-30%) were related to its presence as a neutral species (H_3AsO_4).

Results from Table 6 show the suitability of Duracid membrane for treating this kind of waters. Figure 5.a shows a comparison at 20 bar between Duracid (solution II) and commercial acid-resistant membranes (HydraCoRe 70pHT and MPF-34) filtering acidic mine waters at pH 1 [57,58]. Among them, Duracid membrane shows the highest rejections for both double and triple-charged metals. Additionally, it showed a relatively good acid transport, with values between the ones from HydraCoRe 70pHT and MPF-34. The differences in the behaviour can be related to the properties of the active layer (Figure 5.b). On one side, HydraCoRe 70pHT is a sulphonated polyethersulphone membrane with ionisable sulphonic groups. According to Sata [59] and Tanaka [59], the acidity constants of these groups in a polymeric matrix (i.e. ion-exchange membranes) might be below 1. Therefore, under the negative membrane charge of HydraCoRe 70pHT, sulphate (e.g. HSO_4^-) would be rejected, thus leading to high rejection of the counter-ions (e.g. H^+ and metals). On the other one, the positive charge of the MPF-34, which is given by ionisable amine and carboxylic groups, suggests that its performance would be similar to the Duracid one. However, data from literature showed that MPF-34 presents relatively lower rejections, which can be due to a more open structure.

4.2.2. Determination of membrane permeances to species

The SED model was able to fit properly the data shown in Figure 4 (solid lines), and membrane permeances to species (collected in Figure 6) were determined.

The lowest values were obtained for the multivalent metals (from 0.15 to 0.41 µm/s), in agreement with the Donnan and dielectric exclusion, and barely varied with the solution composition and pH. Because of their presence as multivalent cations (e.g. Fe^{2+}, Fe^{3+}, Zn^{2+}), they were expected to be repelled by the positively charged membrane, showing then the lowest membrane permeances. These values contrasted with the ones for monovalent cations (e.g. H^+ and Na^+), with values one order of magnitude larger (7.87–10.27 µm/s and 1.85–5.14 µm/s for H^+ and Na^+, respectively) in agreement with the dielectric exclusion.

The effect of chemical speciation can also be seen if membrane permeances to SO_4^{2-} and AsO_4^{3-} are compared. As explained previously, the decrease in pH favoured the formation of

HSO_4^- and H_3AsO_4, which were less rejected by the membrane. For example, permeance to SO_4^{2-} increased from 1.32 µm/s to 18.68 µm/s when pH was lowered, whereas the ones to AsO_4^{3-} augmented from 0.35 µm/s to 5.00 µm/s. Instead, metals were all as free-ions (e.g. Fe^{2+}, Fe^{3+}, Ca^{2+}) and no significant changes in speciation happened within the pH range evaluated.

No studies are found in literature concerning the characterisation of species transport using membrane permeances to species for the Duracid membrane. In a similar scenario, López et al. [23] determined membrane permeances for NF270 (polyamide-based) for an acidic effluent from a copper smelter. The membrane exhibited a positively charged surface (pH 0.64 < IEP) because of the ionisation of its amine and carboxylic groups. The lowest membrane permeances values were for multivalent metals (0.0001 – 0.7 µm/s) because of Donann and dielectric exclusion. On the opposite side, the highest values were obtained for H^+ (>100 µm/s), H_3AsO_4 (60 µm/s) and HSO_4^- (30 µm/s).

4.3. Evaluation of the acid recovery and metal concentration

The dependence of the calculated membrane permeances to species on solution composition was observed. Bason et al. [60] and Yaroschuck [61] proposed that such dependence on concentration can be approximated by the function described as follows:

$$P_i = a_o + a_1 \cdot C^{a_2} \tag{8}$$

where a_0, a_1 and a_2 are fitting parameters, and C is the concentration of the electrolyte.

This mathematical expression was used to describe the dependence of membrane permeances as a function of the total composition of the solution. Since all the salts were added as sulphates, the equation was referred to the concentration of SO_4 in solution (i.e. SO_4). The fitting and such equations are collected in Figure 7. As can be seen, the mathematical equations (lines) reproduce the obtained membrane permeances accurately.

These empirical expressions are only valid for each element taking into account the total sulphate concentration in the solution. In any different environment with other species, their rejection would be defined according to their nature (e.g. anion or cation, free or complexed in solution) and the membrane exclusion mechanisms. Therefore, another empirical expression should be defined using the same procedure.

The prediction capabilities of the model using the functions defined above for the calculation of P_i were validated by two further filtration experiments at 32 bar where permeate was continuously withdrawn from the system, and only the rejection stream was recirculated, therefore modifying the feed composition as the experiments proceeded. Because of the elements in solution get concentrated, experiments were carried out with solutions I (at pH 1.53) and III (at pH 0.65) to have one in the range and another one outside of the membrane permeance fitting (from 27.1 to 56.1 g/L SO_4).

The experimental data and their fitting with the model are shown in Figure 8 in terms of rejection and concentration factor for each element in the solution versus %permeate recovery. The %permeate recovery was defined as the volume of permeate withdrawn regarding the initial volume of the feed tank solution. For the solution I (at pH 1.53) (Figure 8.a), multivalent metal and As rejections were higher than 90% over the whole range of permeate recoveries. SO_4 rejections were slightly lower, with values between 90 and 88%. These values strongly contrasted with the rejections for Na and H^+, which decreased from 65% to 45%and from 30% to 19%, respectively, as permeate recovery increased. Regarding the concentration factors (Figure 8.c), the metals exhibited the highest values because of their high rejections, followed by SO_4, Na and H^+.

As in the previous section, the performance of the membrane varied at higher concentrations. For the solution at pH 0.65, metal rejections (Figure 8.b) were lower than in the previous case, from 88 to 84% in the range 0-50% of permeate recovery. However, in this case, the As exhibited lower rejections because of its non-protonated form (i.e. H_3AsO_4), varying from 58% to 51%. As in the previous cases, the higher acidity increased the transport of SO_4; with rejections around 67% for the same permeate recovery range. In addition, Na and H^+ showed lower rejections, with values 44-21% and 20-5%, respectively. In terms of concentration factors (Figure 8.d), the metal exhibited the highest ones, followed by SO_4, Na and H^+.

For both cases, the expressions of the dependence of membrane permeances to species on solution composition given in Figure 7 were able to properly predict the separation performance in terms of rejections and concentration factors (with the exception of As, for which the mathematical model tended to underestimate its rejection). Therefore, the mathematical model can be used for scaling-up, as it can provide an accurate description of the transport of species across the membranes with membrane permeances. Additionally, the fact that considering the film-theory allow to know the concentration of the elements in the membrane itself, and therefore to determine the potential scaling events.

During the experiments, precipitates were formed in the feed tank of the acidic solution. These samples were collected, dried at 40°C for 72 h and analysed by FSEM-EDAX. Figure 9a-c shows the morphology of the precipitates formed along with the experiment. The chemical analysis revealed that it was mainly formed by O (55.4±5.0%), S (20.4±1.5%), Fe (13.1±3.0%) and Ca (4.7±2.2%). Accordingly, the precipitate formed was attributed to a mixture of gypsum (Figure 8.b, rod-type minerals) and iron sulphates. Additionally, the presence of iron hydroxy-sulphates could not be discarded, but most of them are typically formed at pH higher than 1.8. Additionally, other elements were found at lower concentrations, such as Na (2.9±1.9%), Cu (1.2±0.9%), Zn (1.2±1.0%) and As (1.1±1.1%). The low presence of these minerals could be due to a co-precipitation or adsorption with the above-described minerals. Figure 9.d shows hexagonal crystals mainly made of As, Fe and O that could be attributed to scorodite ($FeAsO_4 \cdot 2H_2O(s)$). Its formation takes place at high Fe(III) and $H_2AsO_4^-$ concentrations, and occurs at pH above 1. It was not possible to find studies evaluating the scaling in such acidities and only studies regarding the formation of Fe, As, Ca and SO_4 mineral phases in copper tank electrolytes have been described in natural media (acidic mine drainage), as the case of the Iron Mountains (California, USA), where sulphuric acid concentration reached values up to 10 M [62]. Additionally, the mineral databases and solubility constants should be reviewed to extend the performance of the scaling events when treating strong acidic streams by NF. Due to the fact that permeate was withdrawn from the solution, the concentration of the metals in solution increased (Figure 8.c-d); thus the solubility was exceeded, and mineral phases were formed in the feed tank solution.

The sample analysis of the sample by XRD (Figure S2, Supplementary Information) revealed the precipitate was formed by calcium sulphate ($CaSO_4$(s)), iron-hydroxy oxide (FeOOH(s)) and iron sulphate ($FeSO_4$(s)).

4.4. Design projection of the Duracid membranes for acid recovery and metal concentration

Using the expressions for membrane permeances to species as a function of total SO_4 concentration (Figure 7), a design projection for a NF unit for the treatment of 1 m^3/h of an effluent from a hydrometallurgical copper plant comprising the SX/EW process was developed. The composition of feed water is given in the one of solution II (Table 1). The NF unit was designed to include 7 spiral-wound Duracid NF2540F30 modules (1.4 m^2, max. cfv of 1.6 m^3/h [37]) arranged in a “Christmas-tree” configuration (Figure 9) with 3 stages working at a flow rate of 0.56 m^3/h each spiral-wound module and a TMP of 50 bar, with a conversion of 60%. In order to minimise CAPEX costs, the concentrate stream was partially recirculated with a ratio between the concentrate and the recirculate flows of 1 (the flow-rate of streams 7 and 10 is the same).

Table 7 collects the predicted flow-rate and composition of each stream (identified with circles in Figure 10). As can be seen, with the proposed configuration, 60% of the initial solution was recovered as permeate. This was mainly composed of H_2SO_4 (0.16 mol/L H^+) with a low content of metals (total concentration <1.73 g/L, mainly Na). The concentration of As in the permeate was estimated to be 0.43 g/L, although it must be bear in mind that the model overestimates As concentration as shown previously.

Table 8 shows the predicted rejections and the concentration factors obtained in each stage. The highest concentration factors were estimated for the divalent and trivalent metals (2.26-2.30), followed by the SO_4 (1.98), Na and As (1.68-1.67) and H^+ (1.47). The fact that it is possible to obtain a metal-rich stream can make feasible the recovery of valuable metals (Zn, Cu) from waste.

This enriched-metal stream can be used for the recovery of valuable metals. Selective precipitation with Na_2S for Cu and Zn can be performed by controlling the pH and the pS (pS = -log(S_2^-)) [63]. However, As can co-precipitate as As_2S or As_2S_5, which can affect the final quality of the product. Therefore, it must be necessary to remove As before Cu and Zn recovery. Reig et al. [64] proposed the use of selectrodialysis for As removal in waters containing H_2SO_4, Cu and Zn. They were able to recover the 80% of Cu(II) and 87% of Zn(II) with a low amount of As (0.02 %). Once removed, solvent extraction [10,11], selective precipitation with Na_2S [63] or even the use of selective ion-exchange resins can be used to recover Cu and Zn [15]. Once that Cu and Zn have been recovered, precipitation with an alkali after oxidising Fe(II) to Fe(III) can be performed for Fe recovery [65,66].

From the data obtained with the mathematical model, it was possible to determine the scaling potential at the membrane surface in each stage. The saturation indexes are collected in Table 9 from the concentrations at the membrane surface predicted by the model.

Saturation indexes above zero were obtained for gypsum at stages 2 and 3, which indicated that gypsum scaling might occur at the membrane surface in stage 2 and 3.

Figure 11 shows the speciation diagram made the Hydra-Medusa code for the Ca-Fe-As(V)-SO_4 system where the percentage of Ca and Fe species were calculated from the concentrations at the membrane surface. According to the speciation diagram, the formation of gypsum was expected at pH values above 0.3, which was in agreement with the precipitate detected in the experiments described previously. However, the formation of Fe(III) minerals was not expected to occur at pH values below 1.8, in disagreement with the precipitates made up by Fe, Ca, SO_4. Despite these discrepancies between the predicted and the experimentally detected nature of precipitates, the model satisfactorily anticipates scaling and thus the use of antiscalants should be considered if NF membranes are operated under the conditions of the study.

5. Conclusions

Duracid membrane was characterised by SEM, FTIR-ATR and XPS analysis, which suggested that the membrane was made of polysulphonamide with ionisable amine (R-NH) and sulphonic (R-SO_3H) groups, which are responsible for the membrane charge.

The results showed that Duracid membrane is suitable for the treatment of acidic effluents because it was able to reject dissolved metals (>85%), whereas H^+ was transported (<40%). The effect of pH in the equilibrium HSO_4^-/SO_4^{2-} and $H_3AsO_4/H_2AsO_4^-$ was observed, where at low pH the transport of HSO_4^- and H_3AsO_4 was favoured. Additionally, it was possible to reach concentration factors near to 2 for a permeate recovery of 50%, with almost near-zero rejections for the acid. It must be highlighted the presence of calcium and iron sulphates precipitates with traces of Cu, Zn and As. Moreover, the SEDF model was able to fit the rejection curves properly for all elements and both sets of experiments, and membrane permeances (P_i) to the different species were determined. Mathematical expressions as a function of total sulphate concentration were developed and validated experimentally to take into account the dependence of P_i on solution composition. Discrepancies were found for As, whose concentration in the permeate was overestimated by the model.

Regarding the operation of Duracid membrane, the effect of cfv and membrane stability should be studied. The cfv affects the fluid hydrodynamics (i.e. mass transfer from the feed solution to the membrane) directly and therefore, the rejections. Accordingly, a correlation which relates concentration polarization thickness and cfv would allow to consider this effect. Membrane stability will define if the process is sustainable at long-term operation. However, there are no works devoted to studying the stability of Duracid membrane. Despite of SEDF model being able to predicting the behaviour of Duracid membrane, there are some issues to be solved. One of them is related to the coprecipitation or adsorption of traces, such as Na, Cu, Zn and As, onto Ca or Fe minerals, as the results from speciation equilibrium did not showed any precipitation of traces. Therefore, an exhaustive characterisation of mechanisms of adsorption or coprecipitation of traces should be performed in order to be included in the model. Additionally, if any antiscalant is added to the solution, it will be necessary to study how it retards the precipitation of minerals in order to consider this effect in the model.

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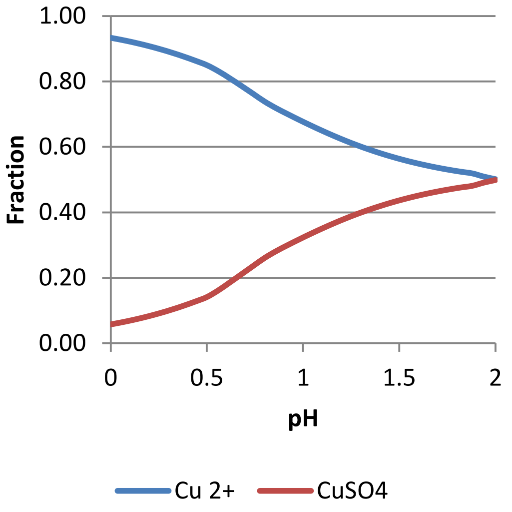
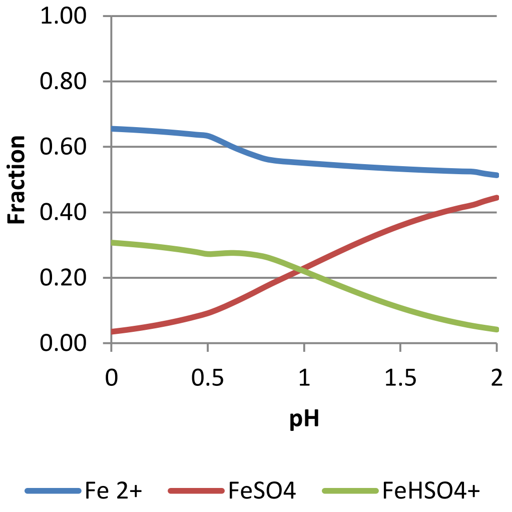
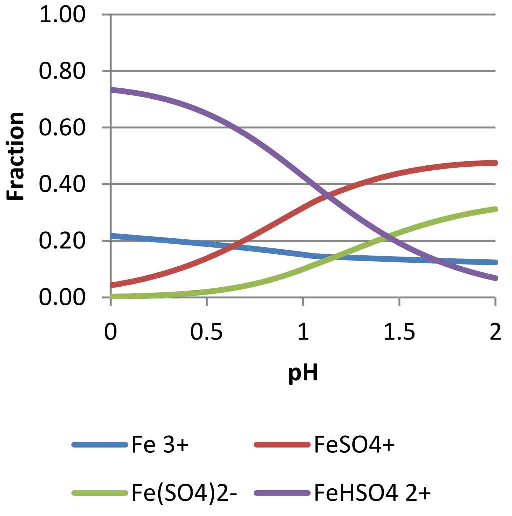
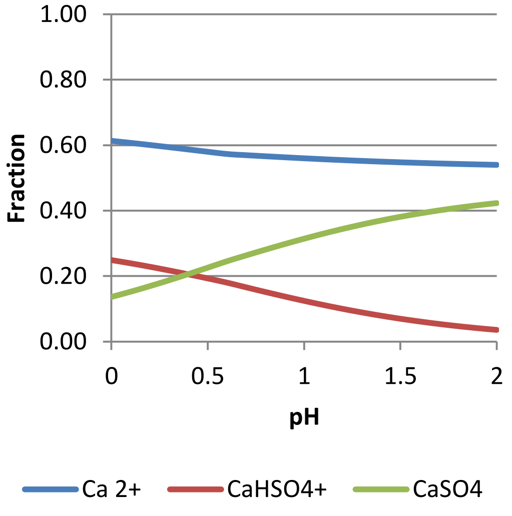
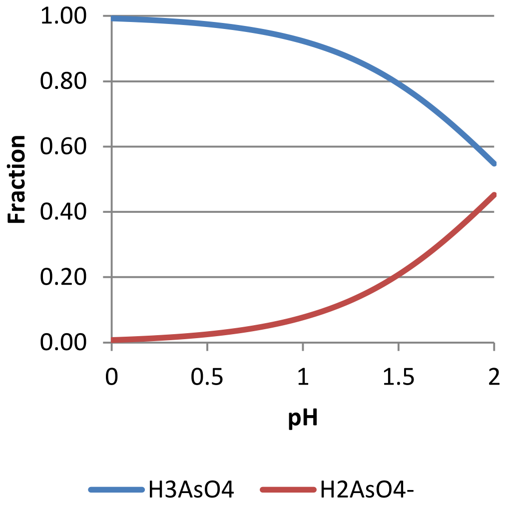
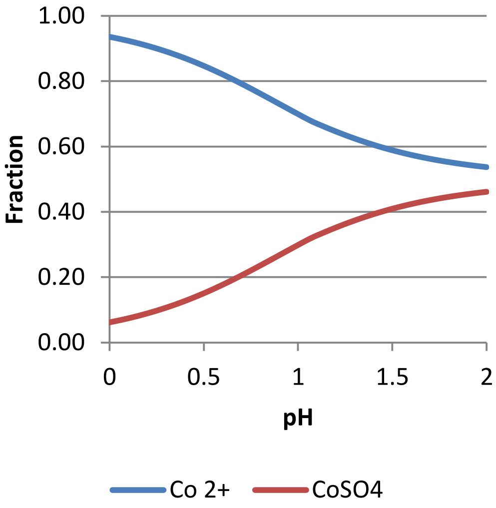
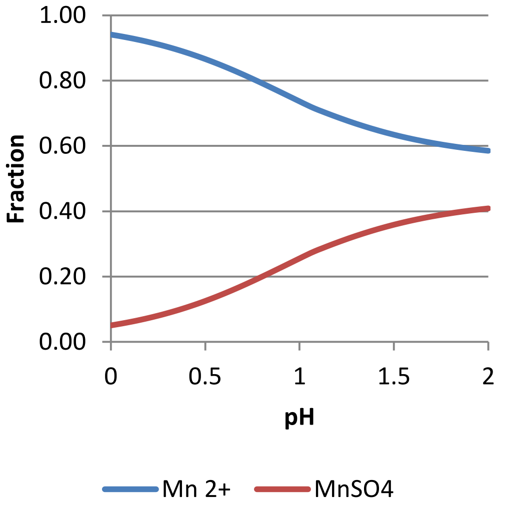
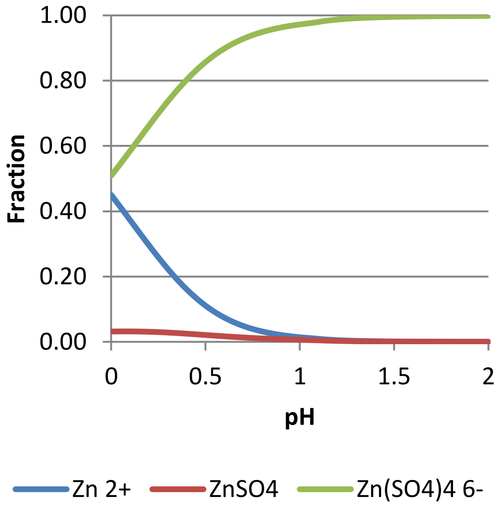
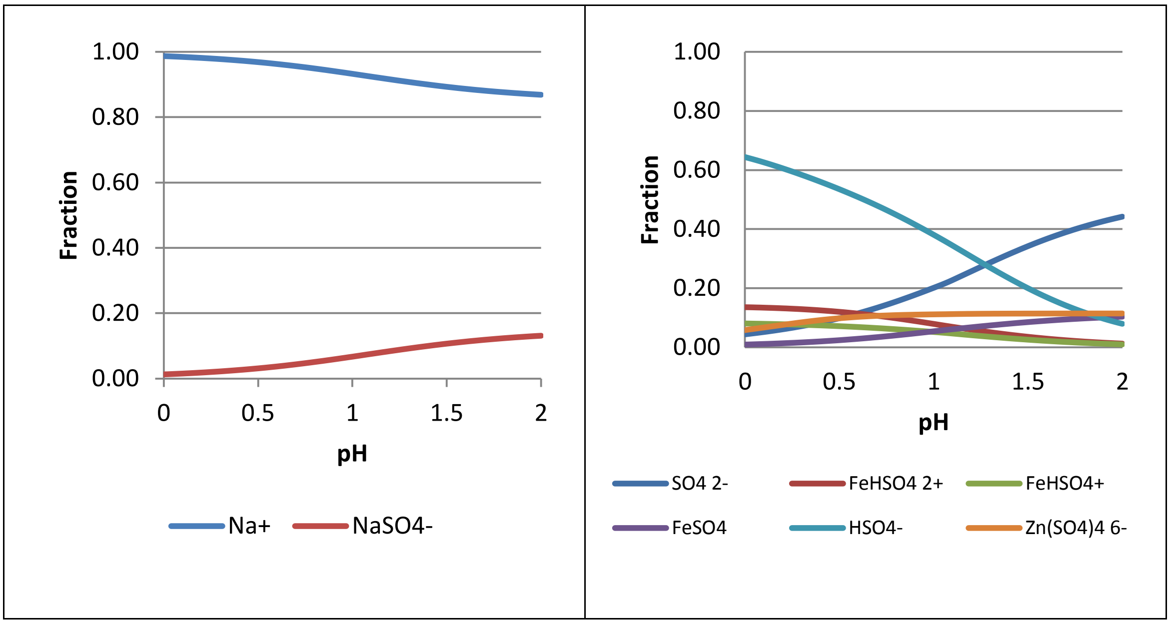
Annex A. Speciation diagrams

Cu(II)	Fe(II)
	
Fe(III)	Ca(II)
	
As(V)	Ni(II)

	
Mn(II)	Zn(II)
	
Na(I)	SO_4



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Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents

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Abstract

The exhaustion of Cu reserves minable and processable with the available technology is forcing the hydrometallurgical copper industry to seek alternative sources of Cu. Following circular economy principles, researchers' attention has focused on the recovery of valuable metals from the acidic waste streams generated. Nowadays, membrane technologies are being selected as the first alternative for the treatment and valorisation of such acidic waste streams. Among them, a new generation of high acidity resistance nanofiltration (NF) membranes offer the alternative for acid recovery while providing a metal-enriched stream. In this work, the extreme-acid resistant Duracid membrane was evaluated for the valorisation of different synthetic acidic waste streams from the hydrometallurgical Cu industry. These waters were characterised by a high acidity (pH 0.5–1.5) and the presence of Fe (11–14 g/L), Zn (0.7 – 1.4 g/L) and As (0.5–0.7 g/L), among others. Initially, the membrane was characterised by different techniques (SEM, FTIR-ATR, XPS). Experiments were performed under constant and varying permeate flux and feed water composition. Metals were effectively rejected (>90%), whereas H^+ easily permeated through the membrane. The experimental results were adjusted to the Solution-Electro-Diffusion-Film (SEDF) model to determine the membrane permeances to species. Empirical mathematical equations were developed and validated to express the dependence of permeances on solution composition. Finally, the prediction capability of the SEDF model, together with the developed empirical equations for the permeances, was proposed as a tool for designing a NF unit to valorise acidic streams from the hydrometallurgical Cu industry. The model predicted gypsum scaling onto the membrane and therefore anticipated the need of applying antiscalants.

Keywords: sulphuric acid effluents; scaling-up; Duracid; modelling acid transport; circular economy

1. Introduction

Although copper resources are estimated to exceed 5000 million tonnes worldwide taking into account the already discovered, undiscovered and potentially profitable deposits, the Cu reserves minable and processable with the available technology may be limited to 830 million tonnes. These reserves are expected to be exhausted within the next 40 years [1]. In views of the growing scarcity of naturals resources such as minable minerals, the European Union (EU) proposed in 2015 an action plan to move towards a circular economy to improve resource efficiency and promote sustainable growth. Circular economy systems maintain the added value in products for as long as possible, while the generation of wastes is avoided or reduced. Under this scheme, once a product has reached the end of its life, it must be used to create further value. It is required a transformation of both production and consumption systems into marketable products to implement circular economy schemes, where the design and engineering are factors of immense importance [2]. It is estimated that the implementation of circular economy schemes can reduce the need for input materials by 17-24%, which can bring an economic saving of 630 billion € in the industries of the EU [3–5]. Nowadays, circular economy examples can be found, such as the recovery of P to restore eutrophic waters [6] and the recovery of rare earth elements from phosphogypsum waste [7], among others. Additionally, circular economy schemes promote sustainability in terms of energy consumption, environmental protection and the longevity of raw materials [8].

Conventional extraction of Cu from high-purity Cu-minerals in sulphide form (chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S; and covellite, CuS) is done through a pyrometallurgical process after milling and leaching the Cu-mineral with sulphuric acid, accompanied with oxidation with air, yielding a final leachate characterised by an acidic pH ($0.5<pH<2.0$) and Cu(II) content up to 6 g/L Cu (II) [9]. However, the exhaustion of high-purity copper ores has made necessary to exploit lower quality Cu-minerals often in oxidised form (brochantite, $CuSO_4$; azurite,

$2CuCO_3 \cdot Cu(OH)_3$; cuprite, Cu_2O) and containing impurities such as Fe, Zn and As. The relatively low content of Cu and the presence of impurities in the mined minerals requires the application of new processes such as the two-stage solvent extraction and electrowinning (SX/EW) process, which produces a Cu-enriched solution (with Cu concentration higher than 35 g/L and low amounts of impurities) that is reduced using an electrolytic procedure (electrowinning) to produce pure Cu. The process generates an overall waste stream that contains high concentrations of sulphuric acid and metals (Zn, Cu, Sb, Bi, As…) [10,11]. This waste stream is usually treated by the addition of quicklime (CaO(s)) to neutralise the acidity and remove metals as hydroxides [11,12] prior to discharge into the natural water receiving bodies. The high value of the compounds present in the waste stream has centred the attention of researchers, who following circular economy principles aim at their recovery from the acidic waste streams.

Over the past years, research has focused in the valorisation of acidic waters, and different technologies have been proposed, such as activated carbon [13,14], ion-exchange resins [15,16] and solvent extraction [17,18], among others. Although these technologies can be useful for acid or metal recovery, two drawbacks are associated with them: i) an additional treatment unit to purify the acid or metal, and ii) the need of a regeneration step for the activated carbon, ion-exchange resins or organic phase in solvent extraction, which can increase the costs of the process.

In order to overcome the disadvantages of the methods mentioned above, membrane technologies have gained importance in the industry. They nowadays are widely applied in many fields, since they allow to recover valuable compounds with the permeate or remove an undesirable compound from the feed stream. The advantages of membrane processes comprise low energy consumption, ability to be combined and integrated with other separation processes, the possibility of working at mild conditions and no need for additives [19]. Among the different membrane technologies, nanofiltration (NF) membranes are drawing increasing attention because of their high rejection of multivalent species (e.g. metal cations), while allowing the transport of monovalent ones (e.g. acids) [20–23]. For example, Nÿstrom et al. [20] purified nitrate and sulphate acidic solutions, achieving high rejections of metals (>98%) with the NF-45 membrane. Erikson et al. [21] studied how to purify 33% H_2SO_4 containing metals such as Fe, Zn, Cd and Cu. Metal rejections were higher than 99%, while 50% of the acid was recovered. González et al. [22] reported similar findings when purifying H_3PO_4 solutions with NF and reverse osmosis (RO) membranes (>95% for Fe, Mg and Al, among others), concluding that NF allowed higher acid recovery (80%) and permeate fluxes (4 times higher than RO membranes). López et al. [23] studied the performance of a polyamide-based membrane (NF270) in treating an effluent characterised by the presence of strong (HCl/H_2SO_4) and weak (H_3AsO_4) acids (pH<1), and metals (e.g. Fe, Cu, Zn). Metals were rejected by 80%, whereas the acid permeated easily across the membrane. However, As was not rejected (<40%) because of its presence as a non-charged species (H_3AsO_4(aq)).

Undoubtedly, one of the most challenging issues of the NF membranes for the treatment of acidic effluent wastes is to resist the low pH values typically found in these waters, which can be as extreme as pH<1. In fact, due to the high acidity of the solutions, most of the commercial NF membranes (usually polyamide-based) are not suitable because of the possibility of suffering hydrolysis in such acidic media. The large potential economic market associated to the mining activities has promoted the development of new families of ceramic [24,25] and polymeric active layers [26–28] to deal with this challenge, but much effort is still needed with regards to their performance of these new family of membranes in terms of rejection and solvent flux, membrane lifetime and description of solute transport processes. Although a significant new generation of membranes is under development, some commercial membranes can be found, such as the Duracid (Suez) and the MPF-34 (Koch). Duracid membrane has found to provide high metal rejections at pH 0.5 (almost 100%) [29], whereas the MPF-34 showed lower rejections (80%) at these acidity levels [30].

Another issue that needs to be addressed with NF is the lack of numeric tools for scale-up and process design. Unlike RO membranes, where the performance depends only on the operation parameters (e.g. pressure and recovery ratio), the performance NF membranes also depends on the feed solution composition, the properties of the active layer and the interactions between both. Such dependence makes that a species can behave very differently, from passing easily across the membrane (displaying even negative rejections) to being completely removed (rejections higher than 90%) [31–33]. This varying behaviour has posed difficulties in developing successful mathematical tools for predicting the performance of NF membranes at large scale.

Among the developed ones, phenomenological models are of considerable value. They treat the membrane as a "black box", which avoids an extensive membrane characterisation, and describe the separation of components in terms of solute passage and water flux [34]. Among them, the Solution-Diffusion (SD) model has been widely applied, and not only for NF but also for RO membranes [28,31–33]. It assumes that the transport is due to differences in diffusion coefficients across a dense membrane (i.e. the membrane is considered not to have fixed pores). This model has later been expanded to incorporate electric migration effects due to the different rates of species transport, giving rise to the so-called Solution-Electro-Diffusion (SED) model. Finally, the integration of the film theory into the SED model has proved to provide an even more accurate description of the membrane performance in terms of rejections and a more reliable estimation of possible scaling events. This model, referred to as Solution Electro-Diffusion Film (SEDF) model [32,33,35], has been applied for electrolytes mixtures of one dominant salt and trace salts. All these models have in common that the transport of species is defined by a phenomenological coefficient termed permeance (P_i), which expresses the easiness of the species i to permeate through the membrane.

To sum up, NF membranes can be useful for the valorisation of acidic effluents, as they allow to recover a free acidic stream in the permeate, which can be re-used internally and thus promoting circular economy schemes instead of traditional methods based on neutralisation/precipitation. However, the dependence of the performance of NF membranes on solution composition, active layer and operation parameters, has made that there is still a lack of numerical tools to predict its performance properly and also for scaling-up. The main objective of this work was to characterise using Scanning Electron Microscopy (SEM), Fourier-transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) mode and X-ray photoelectron spectroscopy (XPS) techniques and evaluate the suitableness of the extreme acid-resistant Duracid NF membrane (Suez) for the valorisation of synthetic solution mimicking a waste stream from a hydrometallurgical copper industry. Experiments were performed under constant and varying permeate flux and feed water composition, and experimental data were adjusted with the SEDF model to determine the membrane permeances to species. Since these coefficients were found to depend on the solution composition, empirical mathematical equations were developed to express such dependence. Then, these equations were validated in further experiments. Finally, the mathematical model was used to design a pilot plant for treating 1 m^3/h of this effluent.

2. Experimental

2.1. Experimental set-up

Figure 1 shows the experimental set-up. Experiments were performed with flat-sheet membranes placed in a cross-flow test cell (GE SEPA™ CF II, 0.014 m^2) with a spacer in the feed channel. The feed solution was kept in a thermostatic tank (30 L) at constant temperature (22±2°C) and pumped to the cross-flow cell with a high-pressure diaphragm pump (Hydra-Cell, USA). The trans-membrane pressure (TMP) and the cross-flow velocity (cfv) were controlled by a by-pass (in the feed line) and needle valve (in the concentrate line). Moreover, two manometers were allocated before and after the membrane test cell to monitor the TMP. Just before the discharge of the concentrate in the feed tank, a flow-meter and a pre-filter cartridge were placed. The latter one was made of polypropylene (100 μm), whose function is to avoid that any erosion product reached the pump. A three-way valve in the permeate line allowed to collect samples.

Two sets of experiments were performed according to their objective:

- Evaluation of species rejection at different TMP. The effect of TMP on the rejections of the different species present in feed solution was studied by varying it from the osmotic pressure to 32 bar at cfv of 0.7 m/s. Feed water composition was maintained constant by recirculating both membrane outputs (permeate and concentrate streams) back to the feed tank. Experimental data were fitted by the SEDF model and membrane permeances (P_i) were determined.
- Evaluation of species rejection at constant TMP and varying concentrations. Unlike the previous set, the membrane was operated at a fixed TMP and cfv of 0.7 m/s, and concentrations in the feed tank were varied by recirculation the concentrated stream but not the permeate stream, which was withdrawn out of the system. Concentration factor and rejection of metals by the NF membrane were calculated during the experiments. Empirical mathematical expressions of the dependence of P_i on water composition developed from the previous sets were also validated.

For the performance of each experiment, a 140 cm^2 piece of the membrane was cut and placed in Milli-Q water overnight. Then, the membrane was placed in the test cell and compacted with deionised water for 2 h at 32 bar and 1 m/s and with the solution to be treated at the same conditions. Then, the experiments were performed. After completion of the experiment, the set-up was cleaned with a diluted sulphuric acid solution (0.1 M) and with deionised water to remove any impurity than may be left inside.

2.2. Membrane and solutions

Three synthetic solutions (named I, II and III as shown in Table 1) mimicking waste effluents from the solvent extraction stage of a SX/WE process at three different periods in a hydrometallurgical industry located in the South of Spain were prepared. These waste effluents were extensively monitored under the H2020 research project OREOPTIM. As can be seen, they were characterised by an acid pH ($0.6<pH<1.6$) and the presence of metals, mainly iron, which was present either as Fe(II) or Fe(III). Other metals such as zinc, copper and calcium, among others were present at lower concentrations. Annex A collects the speciation diagrams (built with the Hydra/Medusa software [36]) for the elements in solution. The three solutions were treated with the Duracid membrane to evaluate the species rejection at different TMP. Additionally, solutions I and III were treated at a constant TMP to evaluate the metal concentration factors.

In order to prepare the synthetic solutions, the following chemicals were used: H_2SO_4 (96 wt%, Sigma-Aldrich); $FeSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich); $Fe_2(SO_4)_3 \cdot 5H_2O$ (98%, Sigma-Aldrich); $ZnSO_4 \cdot 7H_2O$ (100%, Panreac); Na_2SO_4 (>99%, Sigma-Aldrich); $Na_2HAsO_4 \cdot 7H_2O$ (98%, Sigma-Aldrich); $CaSO_4 \cdot 2H_2O$ (100%, Scharlau); $CuSO_4$ (100%, Panreac); $NiSO_4 \cdot 6H_2O$ (98%, Sigma-Aldrich) and $MnSO_4 \cdot xH_2O$ (99%, Sigma-Aldrich).

Table 2 collects the most likely mineral phases to precipitate on the membrane. Scaling may occur by the precipitation of Fe(III) as hydroxide ($Fe(OH)_3(s)$), oxyhydroxide ($FeOOH(s)$) or as jarosite ($AFe_3(SO_4)_2(OH)_6(s)$, where A=Na or H_3O). Besides, gypsum ($CaSO_4 \cdot 2H_2O$) can be formed at the membrane surface.

The membrane tested in this study was the acid-resistant Duracid NF membrane (developed by Suez), whose properties are shown in Table 3.

2.3. Analytical techniques

2.3.1. Aqueous samples

Several techniques were used to determine the composition of the liquid samples.

Inductively Coupled Plasma Mass (7800 ICP-MS from Agilent Technologies) and Optical Emission Spectrometer (5100 ICP-OES from Agilent Technologies) were used to determine the concentration of the elements in solution.

Since the solution contained a mixture of Fe(II) and Fe(III), redox titrations were carried out to measure the concentration of Fe(II) with an automatic titrator (Mettler Toledo T70) using a Pt electrode and potassium dichromate (K_2Cr2O_7) as titrant solution. Acid-base titrations to measure the concentration of H^+ were not performed because of the presence of metals. The increase in pH along the titration would lead to the precipitation of metals, thus providing an inaccurate measurement of the H^+ concentration. Then, it was determined by using a pH-glass electrode (GLP 22, Crison). From the speciation analysis, and taken into account the ionic strength, the activity coefficients were determined and used to calculate the concentration of H^+. However, the error associated with measures below pH 1, could be up to 0.2 pH units.

2.3.2. Solid samples: membranes and precipitates generated along with the filtration experiments

Before analysis of any solid sample, it was dried in an oven at 40°C for more than 72 h.

The morphology of both samples (membrane and precipitate), which were previously metallised with an alloy of Pt/Pd, was obtained by Scanning Electron Microscopy (JEOL JSM-7001F) at an acceleration voltage of 20.0 keV for secondary-electron imaging (SEI).

The FTIR-ATR mode (JASCO FT/IR-4100) spectrum of the active layer of the Duracid membrane was recorded between 4000 and 600 cm^{-1} with 64 scanning times, providing a resolution of 4 cm^{-1}. The active layer was also analysed by XPS (SPECS system) to determine its elementary composition. The equipment used an Al anode XR50 source operating at 150 W and a Phoibos MCD-9 detector at vacuum lower than 10^{-8} mbar. The area of analysis was 0.8 mm^2 with a binding energy accuracy of 0.1 eV.

The mineral phases were identified with X-ray Diffraction (XRD) after grinding the sample into powder. A D8 Advance diffractometer (Bruker) was used with a Bragg-Brentano configuration θ-2θ and a vertical goniometer. The equipment has a Cu X-ray tube, which allows to work up to 40 kV and 40 mA. The spectrum was recorded from 15° to 60° with steps of 0.020°. The identification of mineral phases was performed with EVA software (Bruker).

3. Mathematical modelling

The fitting of experimental data in this study was obtained according to the SEDF phenomenological model [34].

The model considers the concentration polarization layer (Eq. 1), where the transport of species is due to a combination of a diffusion gradient, electromigration and convective flux [32].

Concentration polarization layer

$$j_i = -P_i^{\delta} \cdot \left(\frac{dc_i'}{dx'} + z_i \cdot c_i' \cdot \frac{d\varphi'}{dx'}\right) + J_v \cdot c_i' \qquad (1)$$

Where j_i is the flow of component i (mol/L·µm/s), x' is the dimensionless position (-), P_i^{δ} is the concentration polarization layer permeance to species i (µm/s), c_i' is the concentration of component i (mol/L), z_i is the valence charge of component i (-), φ' is the dimensionless virtual electrostatic potential (-) and J_v is the trans-membrane flow of solvent through the membrane (µm/s).

The concentration polarization layer permeances relate the diffusion coefficient of component i (D_i^{δ}, µm²/s) [41] with the mean thickness of the concentration polarization layer (δ, µm) by $\delta = {D_i^{\delta}}/{P_i^{\delta}}$. Since the value of δ is unknown, it will be one of the parameters to determine.

The transport of species across the membrane results from a combination of diffusion and electromigration (Eq. 2). The model uses "virtual concentrations", which are defined as those in thermodynamic equilibrium with a given point inside the membrane. The use of virtual concentrations makes no necessary to introduce other membrane properties, rather than membrane permeances. These are the parameters of interest and characterise the transport of species across the membrane. These ones depend on the membrane and species properties, as well as the interactions between both. Moreover, the partition coefficients (ratio between virtual and real concentrations) are included within the permeances [34]. The membrane permeances to species can range from values close to zero (related to the less permeable species) to values higher than 100 µm/s (high permeable species).

Membrane
$$j_i = -P_i \cdot \left(\frac{dc_i}{dx} + z_i \cdot c_i \cdot \frac{d\varphi}{dx}\right) \qquad (2)$$

Where x is the dimensionless position in the membrane (-), P_i is the membrane permeance to species i (µm/s), c_i is the concentration of component i (mol/L) and φ is the dimensionless virtual electrostatic potential (-).

Additionally, the transport equations in the concentration polarization layer and membrane must be subjected to [32]:

- Electroneutrality condition:

$$\sum z_i \cdot c_i = 0 \qquad (3)$$

- Zero-current flow:

$$\sum z_i \cdot j_i = 0 \tag{4}$$

- Flux conservation:

$$-P_i^{\delta} \cdot \left(\frac{dc_i'}{dx'} + z_i \cdot c_i \cdot \frac{d\varphi}{dx'}\right) + J_v \cdot c_i' = -P_i \cdot \left(\frac{dc_i}{dx} + z_i \cdot c_i \cdot \frac{d\varphi}{dx}\right) \tag{5}$$

The solvent flux across the membrane (J_v) was described as follows (Eq. 6) [42].

$$J_v = k_w \cdot (TMP - \Delta\pi) \tag{6}$$

Where k_w is the hydraulic permeability of the membrane (µm/(s·bar)) and $\Delta\pi$ is the differences of osmotic pressure between feed-solution membrane interface and permeate (bar), which was calculated according to the van't Hoff equation.

Saturation indexes (SI, -) were calculated according to Eq. 7 to determine the potential scaling events at the membrane surface [42].

$$SI = \log\left(\frac{IAP}{K_{so}}\right) \tag{7}$$

Where IAP is the ionic activity product of a given mineral and K_{so} is the solubility constant (given in Table 2).

To sum up, Table 4 collects the model inputs, outputs and fitting parameters. The system of differential equations was solved in Matlab (function ode23s, based on Runge-Kutta method), and in order to fit the experimental data properly, the membrane permeances and concentration polarisation layer were varied.

4. Results and discussion

4.1. Membrane characterisation

The Duracid membrane was analysed by FTIR-ATR (Figure 2, Table S1 Supplementary Information) and XPS (Table 5, Figure S1 Supplementary Information) to determine its functional groups and its elementary composition.

The resultant FTIR-ATR spectrum resulted in a superposition of the active layer and the intermediate layer (polysulphone), due to the higher radiation penetration depth than the active layer thickness. The FTIR-ATR spectrum revealed the presence of NH_2 in primary amides (1584 cm^{-1}, NH_2 deformation); C=C in benzene ring in aromatic compounds (1486 cm^{-1}, ring stretch); SOH_3 in sulphonic groups (1241 cm^{-1}, S=O stretch); SO_2NH_2 in sulphonamides (1151 cm^{-1}, SO_2 sym. stretch) and C-NH_2 in primary aliphatic amines (1105 cm^{-1}, C-N stretch). Moreover, some peaks related to the SO_2 groups in the polysulphone were observed at 1321, 1292 and 1167 cm^{-1} [43].

Contrarily, the XPS allowed to analyse only the active layer because of its lower penetration depth (<20 nm). From the elementary analysis with XPS, it was observed that the membrane was composed by C (76.0%), O (14.3%), N (4.8%) and S (4.9%). Hydrogen was not included due to the unsuitability of XPS for its analysis. The analysed peaks were centred in 167 eV for S(2p), 284.9 eV for C(1s), 399 for N(1s) and 531 eV for O(1s). As can be seen, the ratio S/N approached 1, which suggested that most of the N atoms of the active layer were bounded to S atoms. Additional information about the membrane structure can be obtained by deconvoluting the main element peaks (Table 5, Figure S1 in Supplementary information).

For the Duracid membrane, three different peaks were identified for C(1s): at 284.7 eV, which was assigned to C-C, C-H and C=C chemical bonds; at 285.3 eV related to C-N and C-S group; and C-O bond at 288.4 eV. For oxygen, only one peak was identified, which was related to C-

SO_2-C and C-SO_3H groups. For nitrogen, two peaks were identified: at 399.6 eV, which was related to –C-NR_2 (R=C, H) and SO_2-NH_2 groups; and at 401.6 eV, associated with –NH_3^+ groups. Finally, for sulphur, two chemical bonds were identified: at 167.7 eV for C-SO_2-C and 169.1 eV for -NH_2-SO_3H [44–46].

From both analyses (FTIR-ATR and XPS), it was revealed that Duracid membrane had an active layer made of polysulphonamide, in agreement with Weinman [40]. Accordingly, the membrane had ionisable amine (R-NH) and sulphonic (R-SO_3H) groups, which were responsible for the membrane charge.

The chemistry of the active layer is a parameter of huge importance, especially related to the membrane stability when treating acidic waters. The fact that most of the available commercial membranes have a polyamide-based active layer makes them susceptible of suffering an acid attack at long term operation [47,48]. However, the presence of sulphonic groups can make the membrane stable in acidic media. For example, Hoseinpour et al. [49] compared the stability of polyamide, polysulfonamide and poly(amide-sulfonamide) membranes after soaking the membranes in 10% wt. H_2SO_4 at 55 °C, and concluded that the polysulphonamide membranes presented the highest stability, whereas the one made of polyamide has the lowest one.

The morphology of the Duracid membrane is shown in Figure 3. The three membrane layers are clearly distinguishable: i) the polyester layer, where the membrane is supported; ii) the polysulphone layer and; iii) the active layer (sulphonamide). From the SEM image at x10000 amplifications, it was possible to see at the top a dense layer, which corresponded to the active layer. Additionally, it was possible to measure its thickness, which was to be of 250 nm.

4.2. Dependence of membrane rejection of solution composition and trans-membrane pressure

4.2.1. Influence of solution composition

Figure 4 collects the rejection of the different elements as a function of trans-membrane flux for the solutions I (Fig 4.a), II (Fig 4.b) and III (Fig 4.c).

Figure 4.a shows the rejection curves for the elements in solution I. As can be seen, Fe(III) showed the highest rejections with values between 91 and 97%, followed by the bivalent metals and As, whose rejections ranged between 85 and 94%. SO_4 presented lower rejections, with values within the range 80-90%. The highest rejection values for multivalent metals, As and SO_4 contrasted with the rejections of monovalent metals. For example, Na rejections varied between 52 to 72%, while H^+ ones ranged from -5 to 26%.

The selectivity of the membrane can be explained with the main exclusion mechanisms: the Donnan and dielectric exclusion. Additionally, the solution speciation is an important parameter, since the different species from one element can be affected in one way or another by the above-mentioned exclusion mechanisms.

Donnan exclusion postulates that the membrane carries fixed charges, which exclude the co-ions in solution (same charge as the membrane). In contrast, ions with an opposite charge (counter-ions) are transported across the membrane [50,51]. The Duracid membrane, at pH below 4.3, presents a positive charge because of the partial and fully protonation of amine ($R-NH_2^+$) and sulphonic ($R-SO_3H$) groups, respectively. This positive charge repels the cations (e.g. Fe^{3+}, Fe^{2+}) which are highly rejected by the membrane. Conversely, the transport of anions was favoured across the membrane (e.g. HSO_4^-) because of the electrostatic attractions between them and the positively charged membrane surface. Nevertheless, the electroneutrality conditions must be fulfilled on the permeate side. Then a stoichiometric number of cations such as Na^+ and H^+ permeate because of their higher diffusivity, smaller size and absolute charge among the metal cations [52].

The dielectric exclusion is caused by the interaction between ions and bound electric charges induced in the membrane at the interface solution/membrane with different dielectric constants, such as the polymeric matrix and the bulk solution. The effect of dielectric exclusion is more pronounced than Donnan exclusion, because the ion-exclusion free energy is proportional to the square of the ion charge, whereas in the Donnan exclusion such dependence is linear [53,54]. This phenomenon explained why the transport of multivalent was more impeded, following then the sequence: Fe(III)>M(II)>Na>H^+.

The increase in the concentration of all the elements (solution II) resulted in a different behaviour of the membrane, as shown in Figure 4.b. Multivalent metal rejections barely varied (88-95%) but significant changes were observed for the other elements in solution. SO_4 and As rejections were lower than the ones for metals (from 60 to 77% as permeate flux increased). This variation can be related to changes in the speciation due to the decrease in pH (see Annex A). At pH 1.53 of solution I, the main anion in solution was SO_4^{2-} (37% of total sulphate), but as acidity increased, its percentage decreased to 17% while HSO_4^- percentage increased from 17 to 42%. The prevalence of HSO_4^- over SO_4^{2-} promoted the transport of SO_4 across the membrane in agreement with Donnan and dielectric exclusions. The fact that a higher amount of SO_4 was transported across the membrane enhanced the transport of monovalent species, such as Na^+ (33-65%) and H^+ (12-40%) Regarding the As, at pH of 0.86 of solution II it became fully protonated as H_3AsO_4 (95%), while $H_2AsO_4^-$ accounted for only 5% of the total As. The fact that As was mainly present as a neutral species suggested that its transport was not favoured nor impeded by the membrane.

Some differences in the membrane behaviour can be observed after a further decrease of pH to 0.65 in solution III (Figure 4.c). The low pH favoured the predominance of H_3AsO_4 and HSO_4^-, which for the same reasons discussed above resulted in even lower rejections than in the previous (60-77%). In this case, SO_4 rejections varied from 52% to 69%, whereas As rejections ranged from 35% to 53%. As a result, lower cation rejections were observed. For example, lower rejections were achieved for multivalent metals (80-90%), Na (18-45%) and H^+ (-6 to 19%).

Table 6 collects data about NF performance with acidic waters. Only one work was found in the literature reporting the performance of the Duracid membrane at acid pH (<1.5). Schütte et al. [29] treated the leaching of a sewage sludge with the Duracid membrane for phosphorous recovery. The residual stream was composed by H_2SO_4 (pH 0.5), Fe (1.3 g/L), P (0.8 g/L) and Ca (0.6 g/L), among others. Metals were effectively rejected (>95%), whereas SO_4 (rejections between 25-40%) and PO_4 (30-55%) were transported across the membrane. The lower rejections of SO_4 reported may be explained by the even lower pH in comparison with the present study. Other studies were performed at similar acidity levels as the one present in this work. Tanninen et al. [55] evaluated the performance of another acid-resistant membrane (MPF-34) for the treatment of acidic copper concentrated solutions (0.22 mol/L H_2SO_4 and 0.47 M $CuSO_4$). $CuSO_4$ was rejected by 78%, while H_2SO_4 was transported easily across the membrane (rejection of 10%). Guastalli et al. [56] mimicked an effluent from industrial rising water (pH 1.2, 39.2 g/L H_3PO_4, 2.7 g/L Al) and evaluated the H_3PO_4 recovery with the MPF-34 membrane. The membrane rejected Al completely (100%), whereas 56% of H_3PO_4 was transported across the membrane. López et al. [23] observed also similar As rejections when treating a copper smelter effluent (pH 0.64, 18 g/L SO_4^{2-}, 0.3 g/L As(V), 0.1 g/L Fe) with the NF270 membrane. Metals were rejected by more than 80%, whereas SO_4 was transported across the membrane (20-40%). The low rejections of As (10-30%) were related to its presence as a neutral species (H_3AsO_4).

Results from Table 6 show the suitability of Duracid membrane for treating this kind of waters. Figure 5.a shows a comparison at 20 bar between Duracid (solution II) and commercial acid-resistant membranes (HydraCoRe 70pHT and MPF-34) filtering acidic mine waters at pH 1 [57,58]. Among them, Duracid membrane shows the highest rejections for both double and triple-charged metals. Additionally, it showed a relatively good acid transport, with values between the ones from HydraCoRe 70pHT and MPF-34. The differences in the behaviour can be related to the properties of the active layer (Figure 5.b). On one side, HydraCoRe 70pHT is a sulphonated polyethersulphone membrane with ionisable sulphonic groups. According to Sata [59] and Tanaka [59], the acidity constants of these groups in a polymeric matrix (i.e. ion-exchange membranes) might be below 1. Therefore, under the negative membrane charge of HydraCoRe 70pHT, sulphate (e.g. HSO_4^-) would be rejected, thus leading to high rejection of the counter-ions (e.g. H^+ and metals). On the other one, the positive charge of the MPF-34, which is given by ionisable amine and carboxylic groups, suggests that its performance would be similar to the Duracid one. However, data from literature showed that MPF-34 presents relatively lower rejections, which can be due to a more open structure.

4.2.2. Determination of membrane permeances to species

The SED model was able to fit properly the data shown in Figure 4 (solid lines), and membrane permeances to species (collected in Figure 6) were determined.

The lowest values were obtained for the multivalent metals (from 0.15 to 0.41 µm/s), in agreement with the Donnan and dielectric exclusion, and barely varied with the solution composition and pH. Because of their presence as multivalent cations (e.g. Fe^{2+}, Fe^{3+}, Zn^{2+}), they were expected to be repelled by the positively charged membrane, showing then the lowest membrane permeances. These values contrasted with the ones for monovalent cations (e.g. H^+ and Na^+), with values one order of magnitude larger (7.87–10.27 µm/s and 1.85–5.14 µm/s for H^+ and Na^+, respectively) in agreement with the dielectric exclusion.

The effect of chemical speciation can also be seen if membrane permeances to SO_4^{2-} and AsO_4^{3-} are compared. As explained previously, the decrease in pH favoured the formation of

HSO_4^- and H_3AsO_4, which were less rejected by the membrane. For example, permeance to SO_4^{2-} increased from 1.32 µm/s to 18.68 µm/s when pH was lowered, whereas the ones to AsO_4^{3-} augmented from 0.35 µm/s to 5.00 µm/s. Instead, metals were all as free-ions (e.g. Fe^{2+}, Fe^{3+}, Ca^{2+}) and no significant changes in speciation happened within the pH range evaluated.

No studies are found in literature concerning the characterisation of species transport using membrane permeances to species for the Duracid membrane. In a similar scenario, López et al. [23] determined membrane permeances for NF270 (polyamide-based) for an acidic effluent from a copper smelter. The membrane exhibited a positively charged surface (pH 0.64 < IEP) because of the ionisation of its amine and carboxylic groups. The lowest membrane permeances values were for multivalent metals (0.0001 – 0.7 µm/s) because of Donann and dielectric exclusion. On the opposite side, the highest values were obtained for H^+ (>100 µm/s), H_3AsO_4 (60 µm/s) and HSO_4^- (30 µm/s).

4.3. Evaluation of the acid recovery and metal concentration

The dependence of the calculated membrane permeances to species on solution composition was observed. Bason et al. [60] and Yaroschuck [61] proposed that such dependence on concentration can be approximated by the function described as follows:

$$P_i = a_o + a_1 \cdot C^{a_2} \tag{8}$$

where a_0, a_1 and a_2 are fitting parameters, and C is the concentration of the electrolyte.

This mathematical expression was used to describe the dependence of membrane permeances as a function of the total composition of the solution. Since all the salts were added as sulphates, the equation was referred to the concentration of SO_4 in solution (i.e. SO_4). The fitting and such equations are collected in Figure 7. As can be seen, the mathematical equations (lines) reproduce the obtained membrane permeances accurately.

These empirical expressions are only valid for each element taking into account the total sulphate concentration in the solution. In any different environment with other species, their rejection would be defined according to their nature (e.g. anion or cation, free or complexed in solution) and the membrane exclusion mechanisms. Therefore, another empirical expression should be defined using the same procedure.

The prediction capabilities of the model using the functions defined above for the calculation of P_i were validated by two further filtration experiments at 32 bar where permeate was continuously withdrawn from the system, and only the rejection stream was recirculated, therefore modifying the feed composition as the experiments proceeded. Because of the elements in solution get concentrated, experiments were carried out with solutions I (at pH 1.53) and III (at pH 0.65) to have one in the range and another one outside of the membrane permeance fitting (from 27.1 to 56.1 g/L SO_4).

The experimental data and their fitting with the model are shown in Figure 8 in terms of rejection and concentration factor for each element in the solution versus %permeate recovery. The %permeate recovery was defined as the volume of permeate withdrawn regarding the initial volume of the feed tank solution. For the solution I (at pH 1.53) (Figure 8.a), multivalent metal and As rejections were higher than 90% over the whole range of permeate recoveries. SO_4 rejections were slightly lower, with values between 90 and 88%. These values strongly contrasted with the rejections for Na and H^+, which decreased from 65% to 45%and from 30% to 19%, respectively, as permeate recovery increased. Regarding the concentration factors (Figure 8.c), the metals exhibited the highest values because of their high rejections, followed by SO_4, Na and H^+.

As in the previous section, the performance of the membrane varied at higher concentrations. For the solution at pH 0.65, metal rejections (Figure 8.b) were lower than in the previous case, from 88 to 84% in the range 0-50% of permeate recovery. However, in this case, the As exhibited lower rejections because of its non-protonated form (i.e. H_3AsO_4), varying from 58% to 51%. As in the previous cases, the higher acidity increased the transport of SO_4; with rejections around 67% for the same permeate recovery range. In addition, Na and H^+ showed lower rejections, with values 44-21% and 20-5%, respectively. In terms of concentration factors (Figure 8.d), the metal exhibited the highest ones, followed by SO_4, Na and H^+.

For both cases, the expressions of the dependence of membrane permeances to species on solution composition given in Figure 7 were able to properly predict the separation performance in terms of rejections and concentration factors (with the exception of As, for which the mathematical model tended to underestimate its rejection). Therefore, the mathematical model can be used for scaling-up, as it can provide an accurate description of the transport of species across the membranes with membrane permeances. Additionally, the fact that considering the film-theory allow to know the concentration of the elements in the membrane itself, and therefore to determine the potential scaling events.

During the experiments, precipitates were formed in the feed tank of the acidic solution. These samples were collected, dried at 40°C for 72 h and analysed by FSEM-EDAX. Figure 9a-c shows the morphology of the precipitates formed along with the experiment. The chemical analysis revealed that it was mainly formed by O (55.4±5.0%), S (20.4±1.5%), Fe (13.1±3.0%) and Ca (4.7±2.2%). Accordingly, the precipitate formed was attributed to a mixture of gypsum (Figure 8.b, rod-type minerals) and iron sulphates. Additionally, the presence of iron hydroxy-sulphates could not be discarded, but most of them are typically formed at pH higher than 1.8. Additionally, other elements were found at lower concentrations, such as Na (2.9±1.9%), Cu (1.2±0.9%), Zn (1.2±1.0%) and As (1.1±1.1%). The low presence of these minerals could be due to a co-precipitation or adsorption with the above-described minerals. Figure 9.d shows hexagonal crystals mainly made of As, Fe and O that could be attributed to scorodite ($FeAsO_4{\cdot}2H_2O(s)$). Its formation takes place at high Fe(III) and $H_2AsO_4^-$ concentrations, and occurs at pH above 1. It was not possible to find studies evaluating the scaling in such acidities and only studies regarding the formation of Fe, As, Ca and SO_4 mineral phases in copper tank electrolytes have been described in natural media (acidic mine drainage), as the case of the Iron Mountains (California, USA), where sulphuric acid concentration reached values up to 10 M [62]. Additionally, the mineral databases and solubility constants should be reviewed to extend the performance of the scaling events when treating strong acidic streams by NF. Due to the fact that permeate was withdrawn from the solution, the concentration of the metals in solution increased (Figure 8.c-d); thus the solubility was exceeded, and mineral phases were formed in the feed tank solution.

The sample analysis of the sample by XRD (Figure S2, Supplementary Information) revealed the precipitate was formed by calcium sulphate ($CaSO_4$(s)), iron-hydroxy oxide (FeOOH(s)) and iron sulphate ($FeSO_4$(s)).

4.4. Design projection of the Duracid membranes for acid recovery and metal concentration

Using the expressions for membrane permeances to species as a function of total SO_4 concentration (Figure 7), a design projection for a NF unit for the treatment of 1 m^3/h of an effluent from a hydrometallurgical copper plant comprising the SX/EW process was developed. The composition of feed water is given in the one of solution II (Table 1). The NF unit was designed to include 7 spiral-wound Duracid NF2540F30 modules (1.4 m^2, max. cfv of 1.6 m^3/h [37]) arranged in a "Christmas-tree" configuration (Figure 9) with 3 stages working at a flow rate of 0.56 m^3/h each spiral-wound module and a TMP of 50 bar, with a conversion of 60%. In order to minimise CAPEX costs, the concentrate stream was partially recirculated with a ratio between the concentrate and the recirculate flows of 1 (the flow-rate of streams 7 and 10 is the same).

Table 7 collects the predicted flow-rate and composition of each stream (identified with circles in Figure 10). As can be seen, with the proposed configuration, 60% of the initial solution was recovered as permeate. This was mainly composed of H_2SO_4 (0.16 mol/L H^+) with a low content of metals (total concentration <1.73 g/L, mainly Na). The concentration of As in the permeate was estimated to be 0.43 g/L, although it must be bear in mind that the model overestimates As concentration as shown previously.

Table 8 shows the predicted rejections and the concentration factors obtained in each stage. The highest concentration factors were estimated for the divalent and trivalent metals (2.26-2.30), followed by the SO_4 (1.98), Na and As (1.68-1.67) and H^+ (1.47). The fact that it is possible to obtain a metal-rich stream can make feasible the recovery of valuable metals (Zn, Cu) from waste.

This enriched-metal stream can be used for the recovery of valuable metals. Selective precipitation with Na_2S for Cu and Zn can be performed by controlling the pH and the pS (pS = -log(S_2^-)) [63]. However, As can co-precipitate as As_2S or As_2S_5, which can affect the final quality of the product. Therefore, it must be necessary to remove As before Cu and Zn recovery. Reig et al. [64] proposed the use of selectrodialysis for As removal in waters containing H_2SO_4, Cu and Zn. They were able to recover the 80% of Cu(II) and 87% of Zn(II) with a low amount of As (0.02 %). Once removed, solvent extraction [10,11], selective precipitation with Na_2S [63] or even the use of selective ion-exchange resins can be used to recover Cu and Zn [15]. Once that Cu and Zn have been recovered, precipitation with an alkali after oxidising Fe(II) to Fe(III) can be performed for Fe recovery [65,66].

From the data obtained with the mathematical model, it was possible to determine the scaling potential at the membrane surface in each stage. The saturation indexes are collected in Table 9 from the concentrations at the membrane surface predicted by the model.

Saturation indexes above zero were obtained for gypsum at stages 2 and 3, which indicated that gypsum scaling might occur at the membrane surface in stage 2 and 3.

Figure 11 shows the speciation diagram made the Hydra-Medusa code for the Ca-Fe-As(V)-SO_4 system where the percentage of Ca and Fe species were calculated from the concentrations at the membrane surface. According to the speciation diagram, the formation of gypsum was expected at pH values above 0.3, which was in agreement with the precipitate detected in the experiments described previously. However, the formation of Fe(III) minerals was not expected to occur at pH values below 1.8, in disagreement with the precipitates made up by Fe, Ca, SO_4. Despite these discrepancies between the predicted and the experimentally detected nature of precipitates, the model satisfactorily anticipates scaling and thus the use of antiscalants should be considered if NF membranes are operated under the conditions of the study.

5. Conclusions

Duracid membrane was characterised by SEM, FTIR-ATR and XPS analysis, which suggested that the membrane was made of polysulphonamide with ionisable amine (R-NH) and sulphonic (R-SO_3H) groups, which are responsible for the membrane charge.

The results showed that Duracid membrane is suitable for the treatment of acidic effluents because it was able to reject dissolved metals (>85%), whereas H^+ was transported (<40%). The effect of pH in the equilibrium HSO_4^-/SO_4^{2-} and $H_3AsO_4/H_2AsO_4^-$ was observed, where at low pH the transport of HSO_4^- and H_3AsO_4 was favoured. Additionally, it was possible to reach concentration factors near to 2 for a permeate recovery of 50%, with almost near-zero rejections for the acid. It must be highlighted the presence of calcium and iron sulphates precipitates with traces of Cu, Zn and As. Moreover, the SEDF model was able to fit the rejection curves properly for all elements and both sets of experiments, and membrane permeances (P_i) to the different species were determined. Mathematical expressions as a function of total sulphate concentration were developed and validated experimentally to take into account the dependence of P_i on solution composition. Discrepancies were found for As, whose concentration in the permeate was overestimated by the model.

Regarding the operation of Duracid membrane, the effect of cfv and membrane stability should be studied. The cfv affects the fluid hydrodynamics (i.e. mass transfer from the feed solution to the membrane) directly and therefore, the rejections. Accordingly, a correlation which relates concentration polarization thickness and cfv would allow to consider this effect. Membrane stability will define if the process is sustainable at long-term operation. However, there are no works devoted to studying the stability of Duracid membrane. Despite of SEDF model being able to predicting the behaviour of Duracid membrane, there are some issues to be solved. One of them is related to the coprecipitation or adsorption of traces, such as Na, Cu, Zn and As, onto Ca or Fe minerals, as the results from speciation equilibrium did not showed any precipitation of traces. Therefore, an exhaustive characterisation of mechanisms of adsorption or coprecipitation of traces should be performed in order to be included in the model. Additionally, if any antiscalant is added to the solution, it will be necessary to study how it retards the precipitation of minerals in order to consider this effect in the model.

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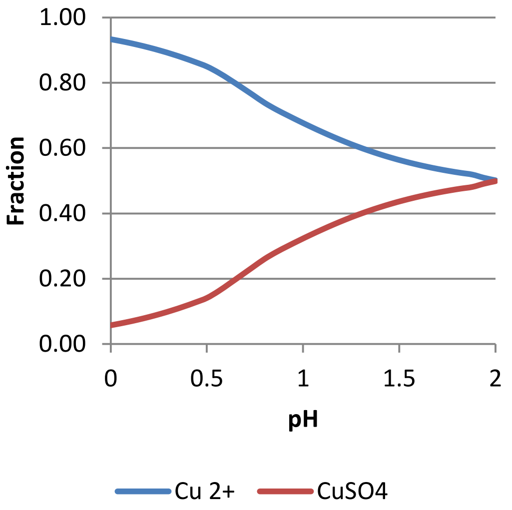
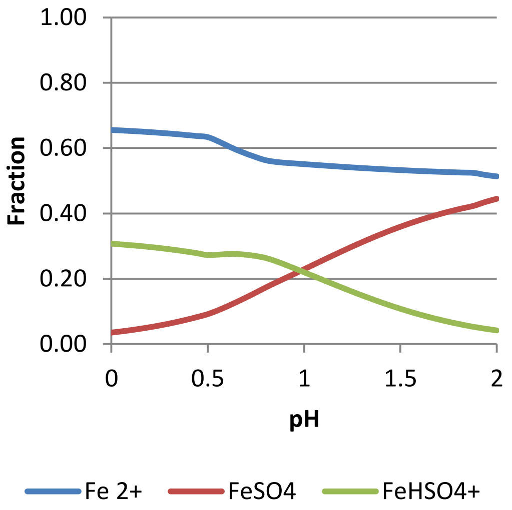
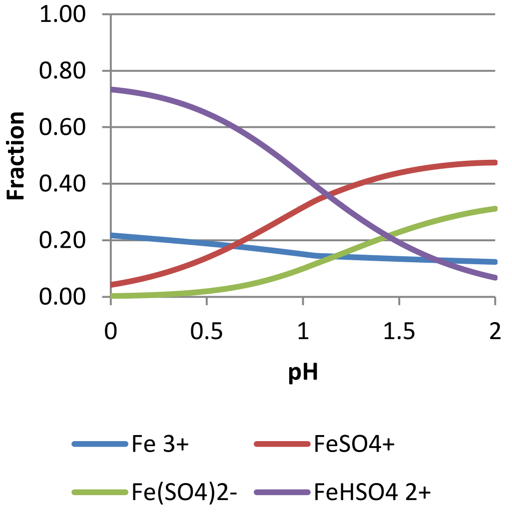
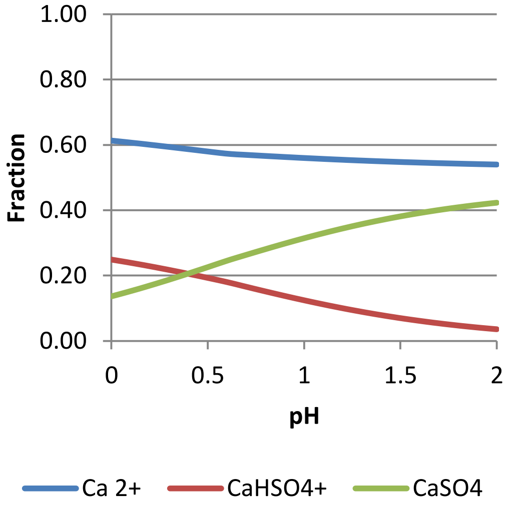
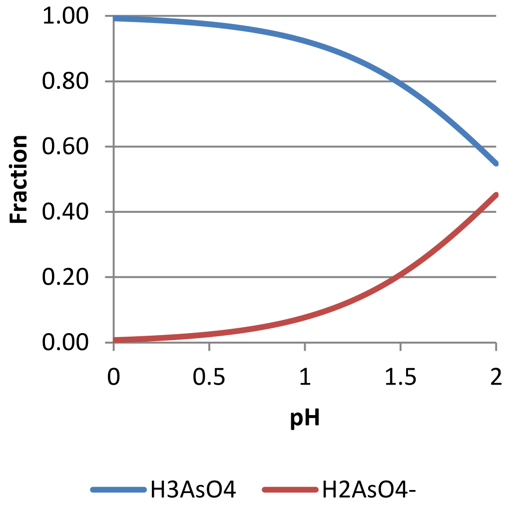
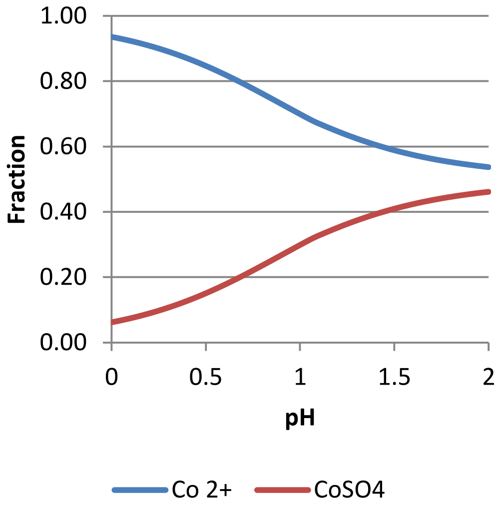
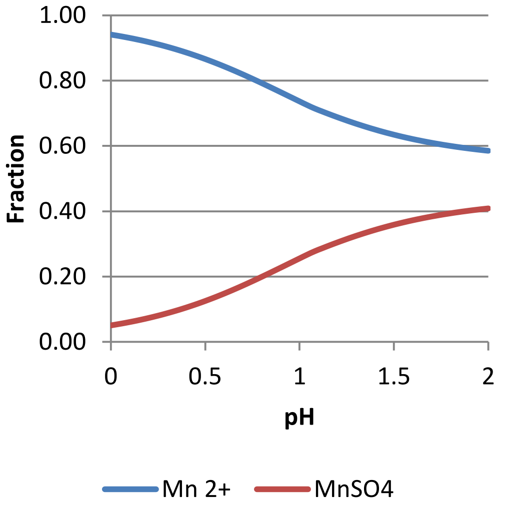
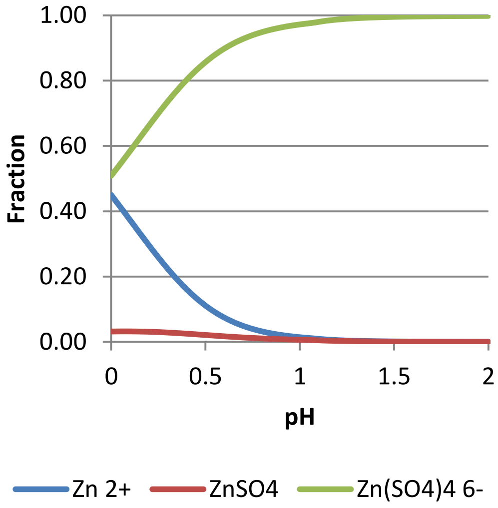
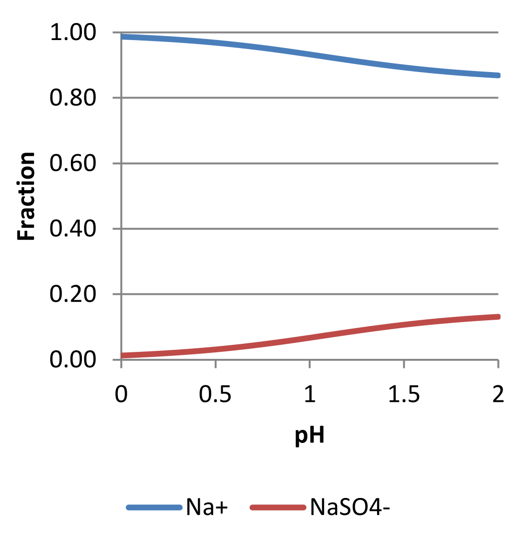
Annex A. Speciation diagrams

Cu(II)	Fe(II)
	
Fe(III)	Ca(II)
	
As(V)	Ni(II)

	
Mn(II)	Zn(II)
	
Na(I)	SO_4



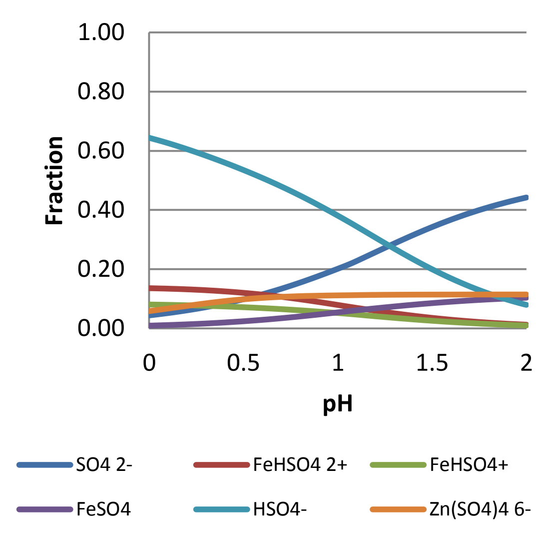


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Table 1. Composition (mg/L) of the synthetic solutions mimicking the acidic waters generated in a hydrometallurgical copper plant. Values refer to total concentrations.

	Solution I	Solution II	Solution III
pH	1.53	0.83	0.65
SO_4*	27085	36086	56185
Fe(II)	6390	4161	9516
Fe(III)	4566	3923	5318
Zn	772	1090	1434
Na	649	1331	962
As	508	774	672
Ca	500	588	600
Cu	230	647	1054
Ni	98	150	196
Mn	60	102	160

[*] SO_4 refers for simplicity in the text to SO_4^{2-}

Table 2. Most likely mineral phases to be formed at the membrane surface [36]

Precipitation reactions	-log K
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\ (s) + 3H^+$	-4.9
$Fe^{3+} + 2H_2O \rightarrow FeOOH(s) + 3H^+$	-1
$3Fe^{3+} + 2SO_4^{2-} + 7H_2O \rightarrow H_3OFe_3(SO_4)_2(OH)_6(s) + 5\ H^+$	5.4
$3Fe^{3+} + Na^+ + 2SO_4^{2-} + 6H_2O \rightarrow NaFe_3(SO_4)_2(OH)_6(s) + 6H^+$	5.3
$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$	4.6
$8Fe^{3+} + 12.5\ H_2O + 1.75\ SO_4^{2-} \rightarrow Fe_8O_8(OH)_{4.5}(SO_4)1.75 + 20.5\ H^+$	-18.0

Table 3. Properties of the Duracid membrane [29,37–40]

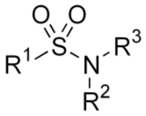
Active layer	Sulfonamide based	
Support	Polysulfone	
Pore size (nm)	0.47	
Contact angle (°)	62.2 ± 4.2	
Iso-electric point (IEP)	4.3	
Molecular weight cut-off (Da)	150 – 300	
Water permeability at TMP = 7 bar (L/m^2 h)	8	

Table 4. Model inputs, outputs and fitting parameters

Inputs	Fitting parameters	Outputs
Concentration of species at bulk solution (mol/L)	Concentration polarization layer thickness, δ (µm/s)	Transmembrane flux, Jv (µm/s)
Diffusion coefficients at bulk solution, D_i^{δ} (µm^2/s)	Membrane permeances to species, P_i (µm/s)	Concentration of species at the permeate (mol/L)
Valence charge of species, z_i (-)		Saturation indexes, SI (-)
Solubility constants, K_{so}		
Transmembrane pressure, TMP (bar)		
Hydraulic permeability, Kw (µm/(s·bar))		

Table 5. Elementary composition of Duracid membrane and peak assignment [44–46]

	%	Binding energy (eV)	Bond	%
C(1s)	76.0	284.7	C-C, C-H C=C	38.4
		285.3	C-N / C-S	58.2
		288.4	C-O	3.4
O(1s)	14.3	531.6	C-SO_2-C C-SO_3H	100
N(1s)	4.8	399.6	-C-NR_2 (R=C,H) SO_2-NH_2	88.6
		401.6	-NH_3^+	11.4
S(2p)	4.9	167.7	C-SO_2-C	89.1
		169.1	-NH_2-SO_3H	10.9

Table 6. NF performance in acidic waters

Membrane	Feed solution	Operation conditions	Rejections	Reference
Duracid (polysulphonamide)	pH: 0.65 SO_4: 18.7 g/L Fe: 14.8 g/L Zn: 1.4 g/L Cu: 1g/L Na: 0.9 g/L As: 0.6 g/L	10.6 µm/s 32 bar	Metals: 88-95% SO_4: 65% As: 55% Na: 49% H^+: 19%	This work
Duracid (polysulphonamide)	pH: 0.5 Fe: 1.3 g/L Al: 0.1 g/L K: 0.15 g/L S: 4.5 g/L P: 0.8 g/L	10 L/m^2h 15 bar	Fe: >97% Al: >97% K: 40% S: 40% P: 55%	[29]
MPF-34 (proprietary)	H_2SO_4: 19.6 g/L $CuSO_4$: 75 g/L	20 L/m^2h 20 bar	H_2SO_4: 10% $CuSO_4$: 78%	[55]
MPF-34 (proprietary)	pH: 1.2 H_3PO_4: 39.2 g/L Al: 2.7 g/L	4.74 L/m^2h 10 bar	Al: 100% H_3PO_4: 44%	[56]
MPF-34 (proprietary)	pH 1.0 Al: 0.6 g/L Fe: 2.2 g/L Cu, Zn: 0.04 g/L	5.6 µm/s 20 bar	H^+: -11% Al, Fe,REEs: 80% Cu, Zn: 79% SO_4: 50%	[57]
HydraCoRe 70pHT (sulphonated polyethersulphone)	REEs: 0.06 g/L SO_4: 9.5 g/L	15.4 µm/s 20 bar	H^+: 30% Al, Fe,REEs: 90% Cu, Zn: 76% SO_4: 89%	[58]
NF270 (Polyamide)	pH: 0.64 SO_4^{2-}: 18 g/L Cl^-: 3.9 g/L As: 0.3 g/L Na: 0.1 g/L Fe: 0.1 g/L Zn: 0.07 g/L	42 µm/s 20 bar	Metals: >80% SO_4: 45% As: 30% H^+: 25% Cl^-: 0%	[23]

Table 7. Predicted flow-rate and composition of each stream in the pilot-plant design. Stream numbers are identified with circles in Figure 10 (feed composition corresponds to stream 1).

Stream	Q (m^3/h)	H$^+$ (mol/L)	Composition (g/L)									
			SO_4^{2-}	Fe^{3+}	Fe^{2+}	Na^+	Zn^{2+}	Ca^{2+}	As	Cu^{2+}	Ni^{2+}	Mn^{2+}
1	1.00	0.24	36.1	3.90	4.13	1.33	1.09	0.59	0.77	0.65	0.15	0.10
2	1.40	0.27	45.9	5.29	5.65	1.59	1.48	0.80	0.93	0.88	0.20	0.14
3	1.14	0.31	54.7	6.48	6.90	1.84	1.80	0.97	1.08	1.07	0.25	0.17
4	0.26	0.12	8.1	0.20	0.26	0.50	0.08	0.04	0.28	0.05	0.01	0.01
5	0.97	0.33	62.1	7.53	8.02	2.03	2.09	1.12	1.18	1.24	0.29	0.20
6	0.17	0.17	12.1	0.38	0.40	0.77	0.14	0.07	0.47	0.08	0.02	0.01
7	0.40	0.36	71.3	8.91	9.51	2.24	2.46	1.33	1.29	1.46	0.34	0.23
8	0.16	0.21	15.3	0.57	0.51	0.98	0.19	0.10	0.63	0.11	0.02	0.02
9	0.60	0.16	11.2	0.35	0.37	0.71	0.12	0.07	0.43	0.08	0.02	0.01
10	0.40	0.356	71.3	8.91	9.51	2.24	2.46	1.33	1.29	1.46	0.34	0.23

Table 8. Predicted rejections at each stage and total concentration factor for the NF scheme proposed in Figure 10 (feed composition corresponds to stream 1).

	H^+	SO_4^{2-}	Fe^{3+}	Fe^{2+}	Na^+	Zn^{2+}	Ca^{2+}	AsO_4^{3-}	Cu^{2+}	Ni^{2+}	Mn^{2+}
	Rejection (%)										
Stage 1	56.1	82.4	96.2	95.4	68.5	94.6	94.4	69.4	94.3	95.2	94.6
Stage 2	43.8	77.8	94.2	94.2	58.1	92.5	92.4	56.8	92.2	93.5	92.5
Stage 3	36.2	75.3	92.5	93.7	51.5	91.1	91.1	47.0	90.8	92.5	91.2
	Concentration factor										
Global	1.47	1.98	2.29	2.30	1.68	2.26	2.26	1.67	2.26	2.28	2.26

Table 9. Saturation index of the most likely mineral phases to be formed at the membrane surface

	$Fe(OH)_3\,(s)$	$FeOOH(s)$	$H_3OFe_3(SO_4)_2(OH)_6\,(s)$	$NaFe_3(SO_4)_2(OH)_6\,(s)$	$CaSO_4{\cdot}2H_2O(s)$	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}(s)$
Stage 1	-8.5	-4.6	-13.2	-13.5	-0.2	-75.5
Stage 2	-2.7	-2.7	-15.6	-15.8	0.1	-68.0
Stage 3	-1.9	-1.9	-12.0	-12.3	0.4	-58.9

Figures

Figure 1. Experimental set-up for the evaluation of species rejection

Figure 2. Duracid membrane FTIR-ATR spectrum

Figure 3. SEM images from the Duracid active and support layers (x500 amplifications at 2.00 kV), and the cross-section at x100, x2500 and x10000 amplifications at 2.00 kV

Figure 4. Rejection curves for the elements in solution as a function of permeate flux with the solution (a) I, (b) II and (c) III. Symbols: experimental data; continuous lines: model

Figure 5. (a) Rejection of the elements in solution and (b) schematic representation of exclusion mechanisms for Duracid, HydraCoRe 70pHT and MPF-34 membranes

Figure 6. Calculated membrane permeances to species for the experiments performed

Figure 7. Membrane permeances as a function of total sulphate concentration (mol/L) in the feed solution. Symbols: calculated membrane permeances; continuous lines: fitting

Figure 8. (a,b) Rejection curves and (c,d) concentration factor as a function of permeate recovery at 32 bar for the solution I and III. Symbols: experimental data; continuous lines: model

Figure 9. SEM images (at 2.00 kV) from the precipitates formed in the feed tank at: a) x50, b) x1500, c) x1500 magnifications and d) details mineral structure in 7c at x5000 magnification

Figure 10. Design scheme of NF the pilot plant for treating Cu(II)-rich streams generated in a Cu(II) hydrometallurgical plant (each box represents one membrane module)

Figure 11. Speciation diagrams (built with Hydra/Medusa software [36]) for (a) Fe(III) and (b) Ca(II) for the Ca-Fe-As(V)-SO_4 system with the composition at the membrane surface in stage 3

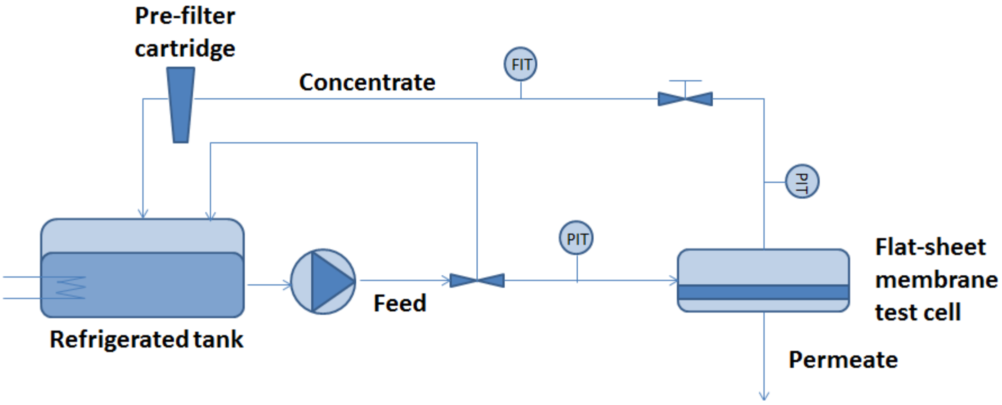

Pre-filter cartridge
Concentrate
FIT
PIT
PIT
Flat-sheet membrane test cell
Refrigerated tank
Feed
Permeate

Figure 1

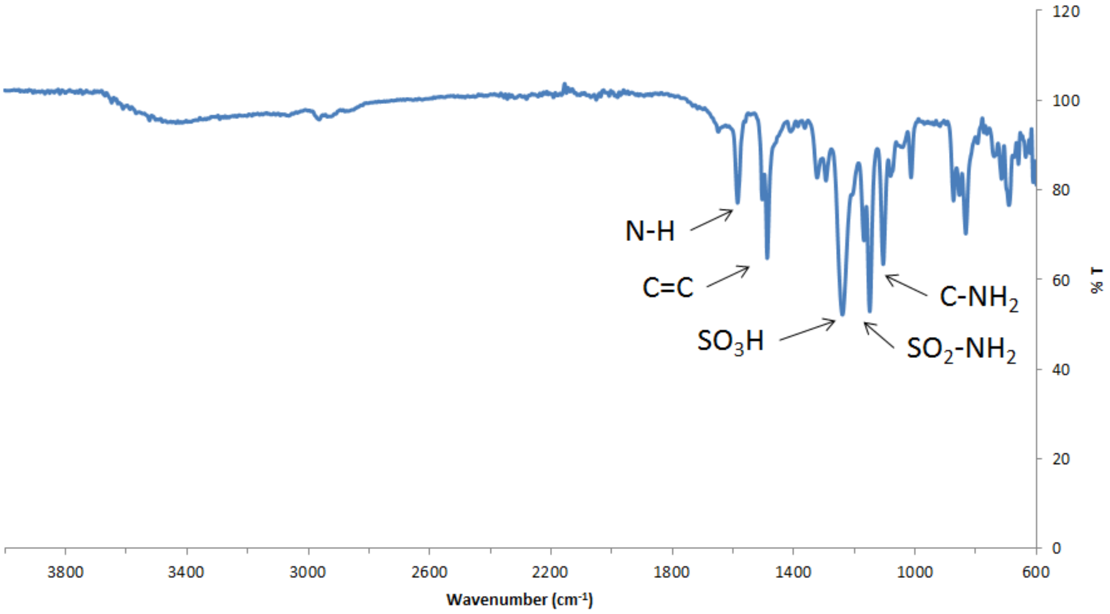

120
100
80
60
40
20
0
% T
N-H
C=C
SO_3H
SO_2-NH_2
C-NH_2
3800
3400
3000
2600
2200
1800
1400
1000
600
Wavenumber (cm^{-1})

Figure 2

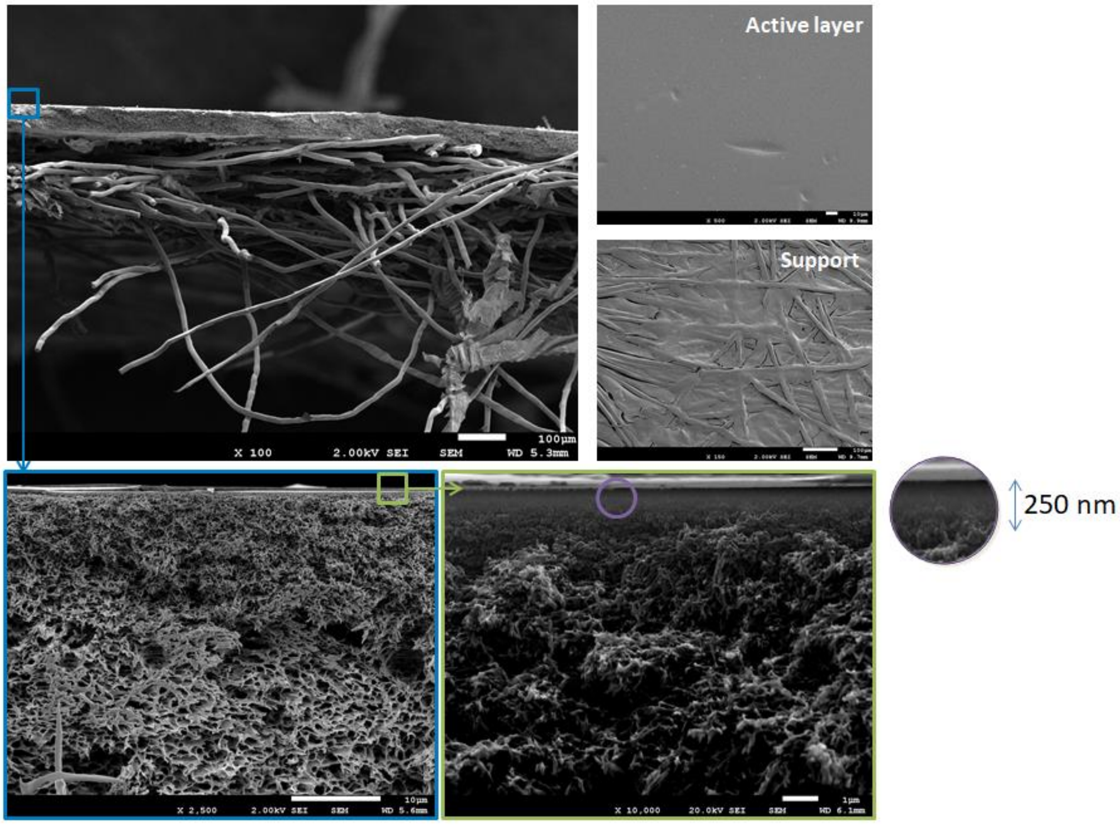

Active layer
Support
100µm
X 100 2.00kV SEI SEM WD 5.3mm
10µm
X 2,500 2.00kV SEI SEM WD 5.6mm
1µm
X 10,000 20.0kV SEI SEM WD 6.1mm
250 nm

Figure 3

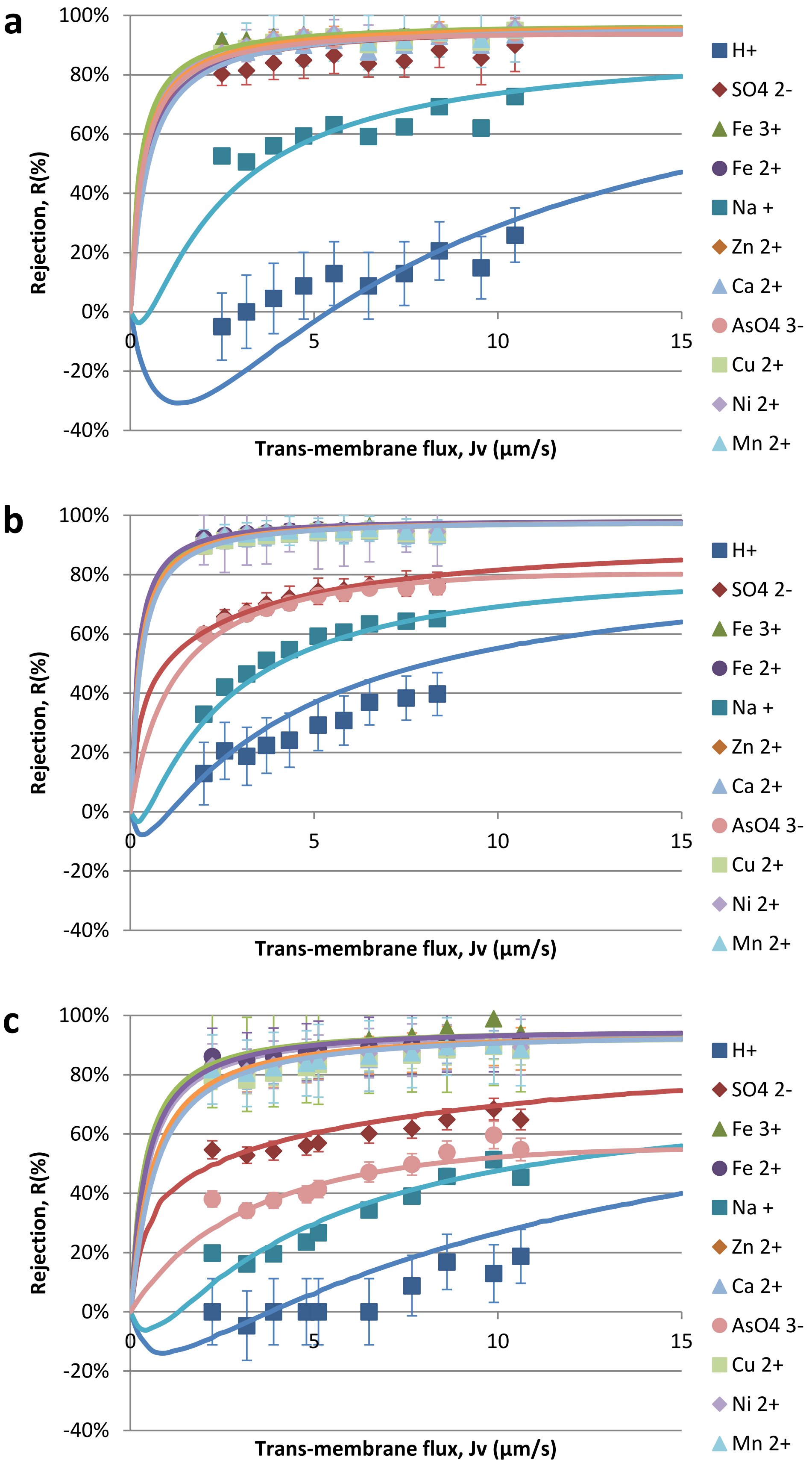

a
b
c
100%
80%
60%
40%
20%
0%
-20%
-40%
Rejection, R(%)
0
5
10
15
Trans-membrane flux, Jv (µm/s)
H+
SO4 2-
Fe 3+
Fe 2+
Na +
Zn 2+
Ca 2+
AsO4 3-
Cu 2+
Ni 2+
Mn 2+

Figure 4

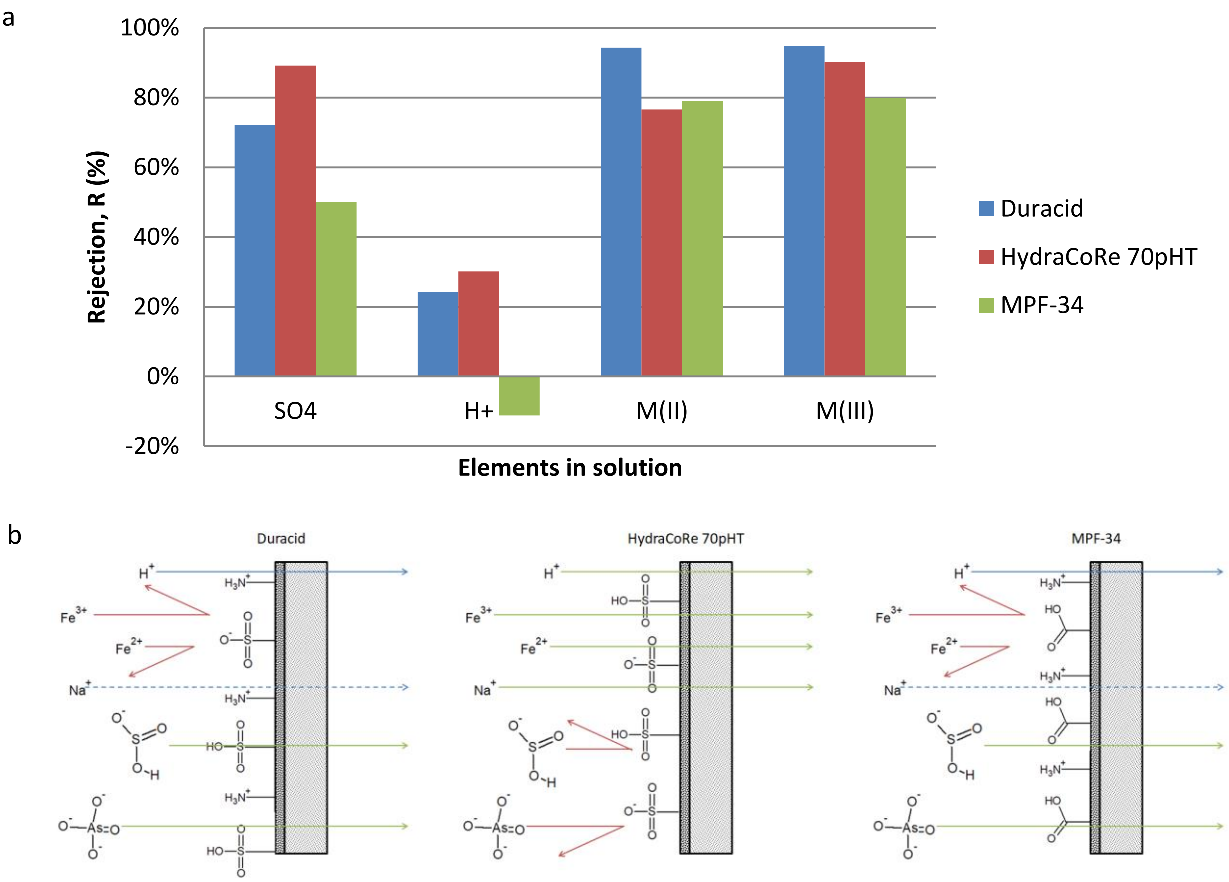

a
Rejection, R (%)
100%
80%
60%
40%
20%
0%
-20%
SO4
H+
M(II)
M(III)
Elements in solution
Duracid
HydraCoRe 70pHT
MPF-34
b
Duracid
HydraCoRe 70pHT
MPF-34
H+
Fe3+
Fe2+
Na+
H3N+
HO
O-
S
O
H
As

Figure 5

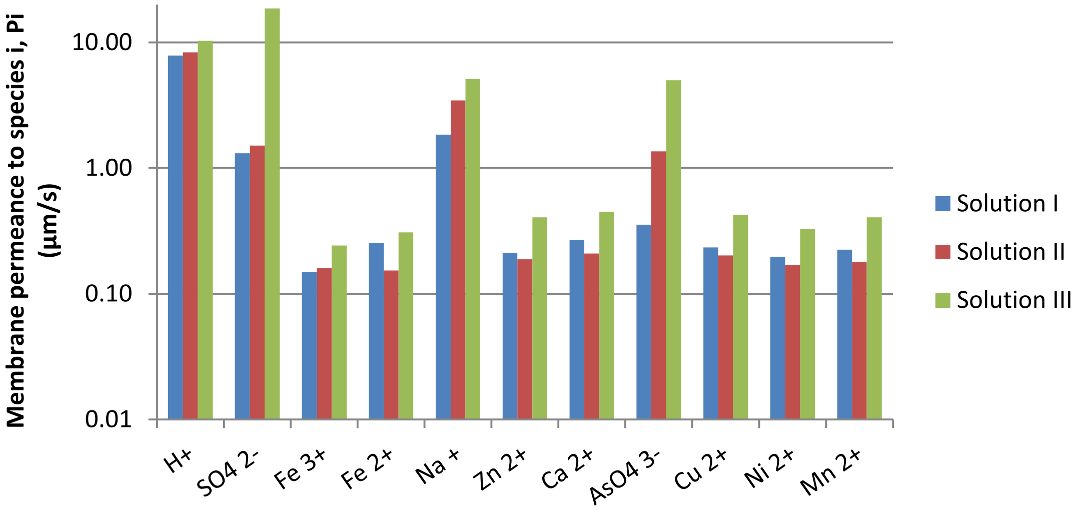
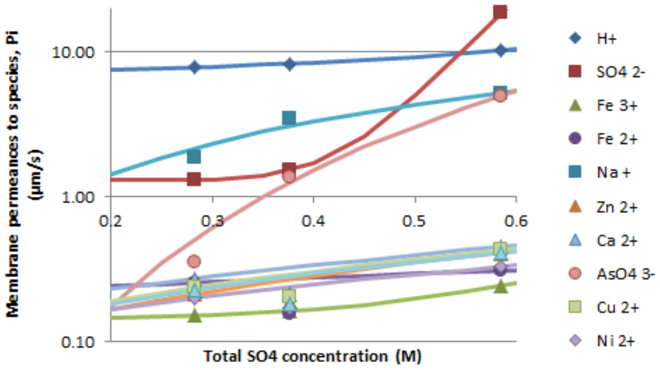

Membrane permeance to species i, Pi (µm/s)
10.00
1.00
0.10
0.01
H+
SO4 2-
Fe 3+
Fe 2+
Na +
Zn 2+
Ca 2+
AsO4 3-
Cu 2+
Ni 2+
Mn 2+
Solution I
Solution II
Solution III

Figure 6



$$P_{H^+} = 7.46+11.53\cdot[SO_4^{2-}]^{2.64}$$

$$P_{SO_4^{2-}} = 1.29+3275.95\cdot[SO_4^{2-}]^{9.77}$$

$$P_{Fe^{3+}} = 0.144+0.857\cdot[SO_4^{2-}]^{4.07}$$

$$P_{Fe^{2+}} = 0.206+0.180\cdot[SO_4^{2-}]^{1.05}$$

$$P_{Na^+} = 9.94\cdot[SO_4^{2-}]^{1.20}$$

$$P_{Zn^{2+}} = 0.077+0.634\cdot[SO_4^{2-}]^{1.22}$$

$$P_{Ca^{2+}} = 0.163+0.588\cdot[SO_4^{2-}]^{1.35}$$

$$P_{AsO_4^{3-}} = 26.8\cdot[SO_4^{2-}]^{3.13}$$

$$P_{Cu^{2+}} = 0.109+0.628\cdot[SO_4^{2-}]^{1.27}$$

$$P_{Ni^{2+}} = 0.095+0.422\cdot[SO_4^{2-}]^{1.12}$$

$$P_{Mn^{2+}} = 0.098+0.593\cdot[SO_4^{2-}]^{1.22}$$

Figure 7

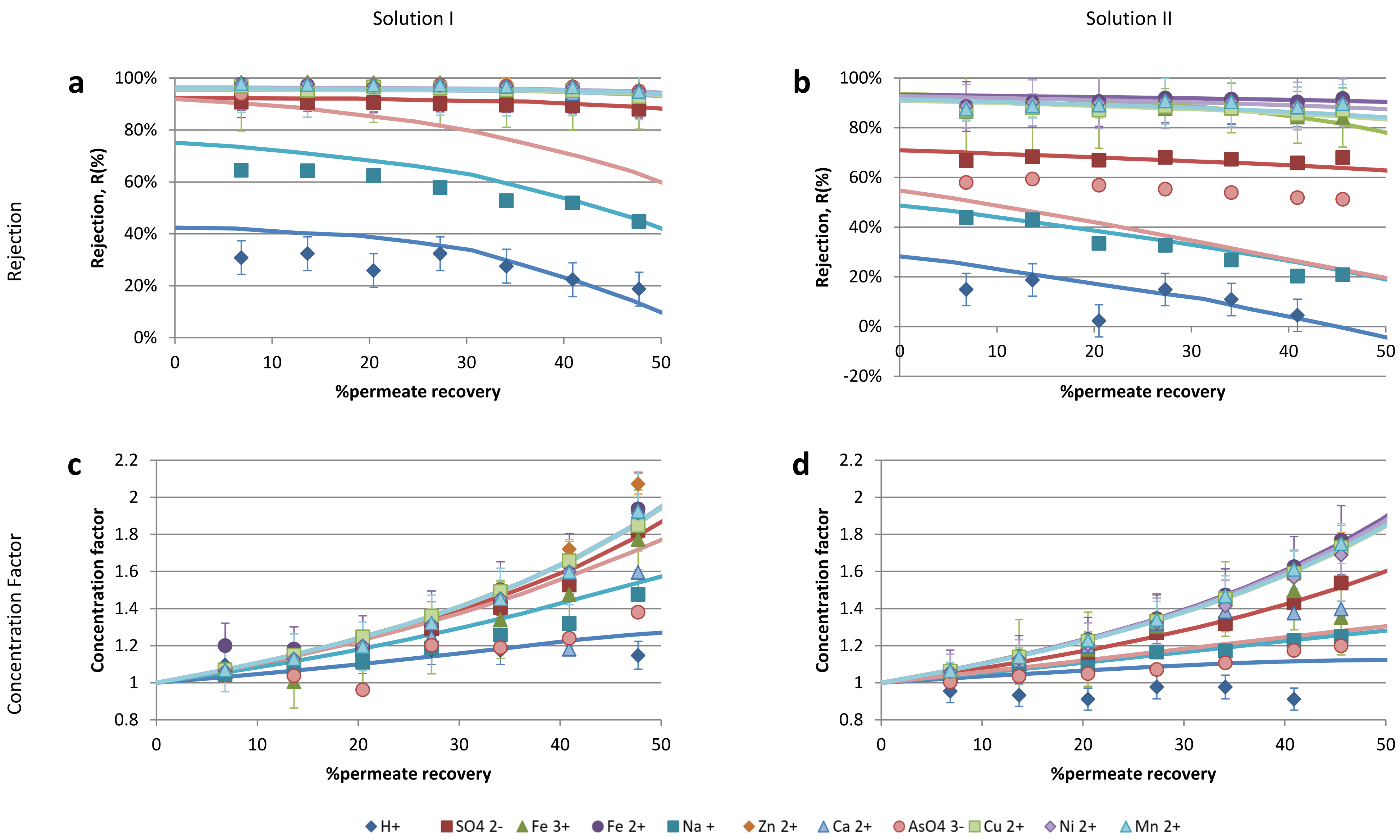

Solution I
Solution II
Rejection
Concentration Factor
a
b
c
d
Rejection, R(%)
100%
80%
60%
40%
20%
0%
-20%
Concentration factor
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0
10
20
30
40
50
%permeate recovery
H+
SO4 2-
Fe 3+
Fe 2+
Na +
Zn 2+
Ca 2+
AsO4 3-
Cu 2+
Ni 2+
Mn 2+

Figure 8

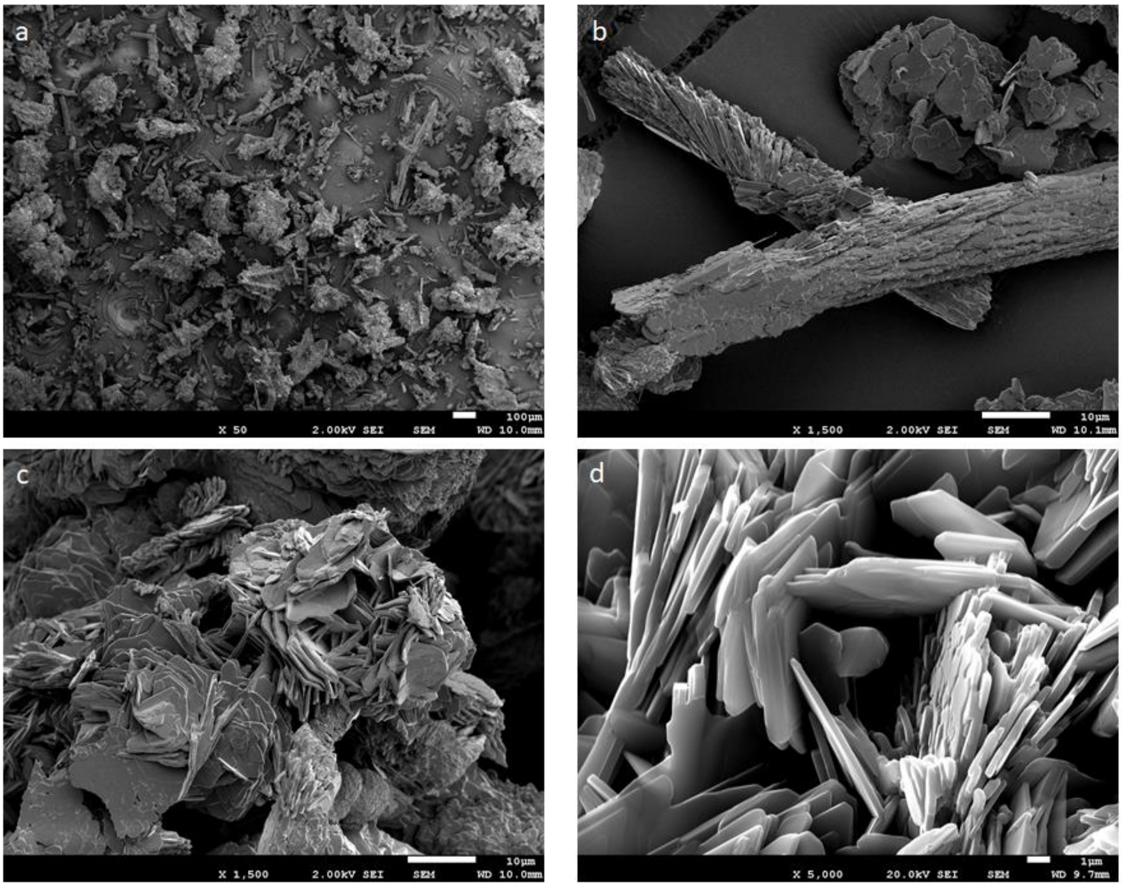

a
100µm
X 50 2.00kV SEI SEM WD 10.0mm
b
10µm
X 1,500 2.00kV SEI SEM WD 10.1mm
c
10µm
X 1,500 2.00kV SEI SEM WD 10.0mm
d
1µm
X 5,000 20.0kV SEI SEM WD 9.7mm

Figure 9

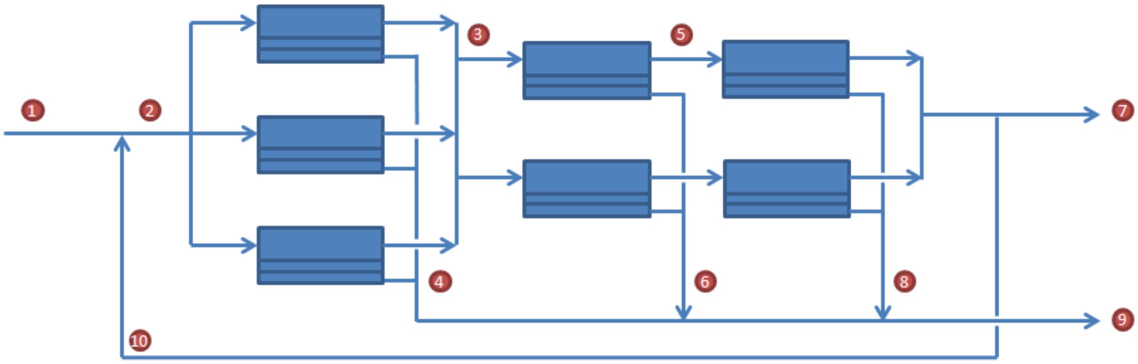


Figure 10

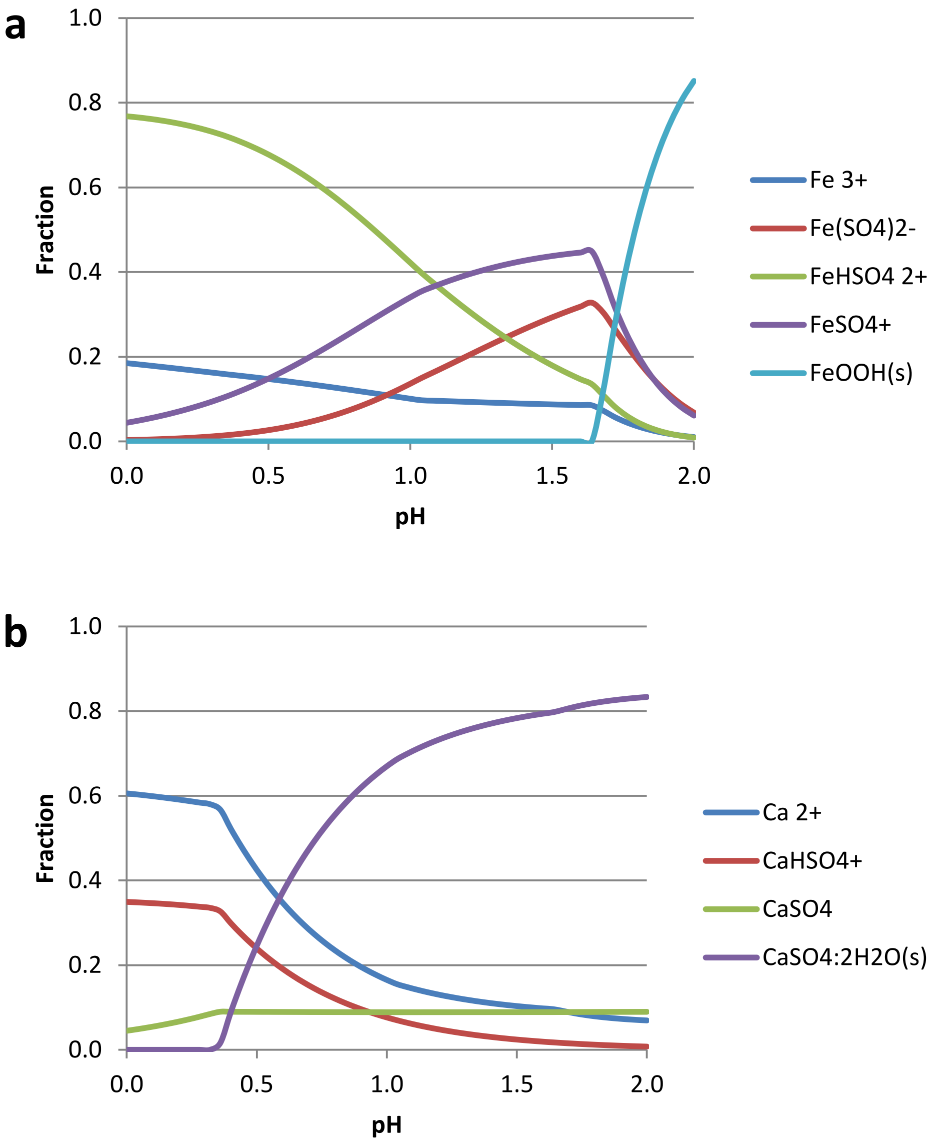

a
1.0
0.8
0.6
0.4
0.2
0.0
Fraction
0.0
0.5
1.0
1.5
2.0
pH
Fe 3+
Fe(SO4)2-
FeHSO4 2+
FeSO4+
FeOOH(s)
b
1.0
0.8
0.6
0.4
0.2
0.0
Fraction
0.0
0.5
1.0
1.5
2.0
pH
Ca 2+
CaHSO4+
CaSO4
CaSO4:2H2O(s)

Figure 11

Supplementary Material

Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: