



Cite this: *New J. Chem.*, 2024, 48, 14672

Ionic polymer absorbents inspired by deep eutectic solvents to recover cobalt and nickel†

Henrique Bastos,^a Antonela Gallastegui,^b Jon López de Lacalle,^b Nicolas Schaeffer,^c Jennifer M. Pringle,^a David Mecerreyes^{*b,f} and Cristina Pozo-Gonzalo^{id *ade}

Cobalt and nickel are vital metals for the transition to a decarbonized society, currently in critical supply conditions to meet future demands. The recovery of those metals from secondary sources can mitigate this issue, as well as treating hazardous waste and increasing its economic value. In this work, ionic polymers inspired by deep eutectic solvents (DES) were studied for cobalt and nickel recovery from representative recycling solutions. These polymers were prepared by simple and fast photopolymerization process combining [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) with a series of hydroxylated compounds (e.g. alcohol and phenolic compounds). Different driving forces for metal absorption; ionic interactions, hydrogen bonding coordination, acidity of the media and polymer swelling have been investigated. The poly(METAC:1-butanol) polymer showed the highest absorption capacity ($46 \pm 5 \text{ mg g}^{-1}$ and $46 \pm 4 \text{ mg g}^{-1}$ for cobalt and nickel, respectively), competing with conventional materials. Moreover, the metal stripping and recovery step was investigated. Favourably, deionized water presented the highest desorption efficiency, in comparison with HCl, rendering this process 'greener' and highly cost-effective. Finally, the ionic polymers were successfully reused as absorbents for five absorption/desorption cycles, maintaining structural integrity. This approach can pose an alternative way of using systems inspired by DES, with application at a larger scale upon further optimizations.

Received 17th May 2024,
Accepted 30th July 2024

DOI: 10.1039/d4nj02316a

rsc.li/njc

1. Introduction

A global energetic transition is currently underway to meet the climate change goals in the coming years. Actual technologies are heavily relying on the use of critical raw materials,¹ such as cobalt and nickel which are central to energy storage devices such as lithium-ion batteries (LIBs).² Their recycling can allow the recovery of Co, Ni and other critical metals to mitigate their supply issues positively affecting the environmental footprint of energy. Moreover, the production and waste of devices containing these metals can pose significant danger to human and

environmental conditions,^{3,4} so their recycling grows in importance.

Therefore, recycling of end of life devices, applicable to spent LIBs but also other technologies, is quickly progressing from a combination of pyro- and hydrometallurgy to low cost and environmentally friendly processes.⁵ This progression is driven by the lower energy consumption and higher efficiency and selectivity when leaching and recovering most of the target metals.⁶ Hydrometallurgy still has challenges mainly regarding the use of corrosive chemicals used, such as H_2SO_4 or HNO_3 , generating hazardous wastewaters despite efforts to rendering this strategy more circular by reusing the wastewaters.⁷ Other alternative methods, such as solvometallurgy which includes non-aqueous solvents such as deep eutectic solvents (DES) and hydroxylated solvents, were proposed to solve the issues of the corrosive solvents used in hydrometallurgy.^{8,9} DESs are mixtures of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs), comprising a wide range of possible combinations that yield a solvent with a significant depression in their eutectic point. One of their values for metal recovery arises from their tunability through the component HBDs and HBAs that provide reducing capacity, metal coordination ability and acidity, which are important for an efficient end of life recycling

^a Institute for Frontier Materials, Deakin University, 221 Burwood Highway, Burwood, Victoria 3125, Australia. E-mail: cpozo@csic.es

^b POLYMAT, University of the Basque Country UPV/EHU, Avenida Tolosa 72, 20018, Donostia-San Sebastián, Spain. E-mail: david.mecerreyes@ehu.es

^c CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 – Aveiro, Portugal

^d Fundación Agencia Aragonesa para la Investigación y el Desarrollo (ARAID), Av. de Ranillas 1-D, 50018 Zaragoza, Spain

^e Instituto de Carboquímica (ICB-CSIC), C/Miguel Luesma Castán, 4, 50018, Zaragoza, Spain

^f Ikerbasque, Basque Foundation for Science, Bilbao, Spain

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4nj02316a>



processes.⁹ Additionally, DES stand out for their simple preparation and the natural, cheap, and extensive availability of their components. Hydroxylated solvents, including alcohols and phenols, showed the same abilities^{10–12} and allow optimized use of hydrometallurgical solvents for metal recovery.¹³

Although DESs have been shown to be valuable solvents for LIB recycling,⁶ their application has been mainly as alternative solvents in extraction steps of hydrometallurgical processes. Creating polymers inspired by DES, that retain their functionalities, can expand their use to recovery steps downstream of the recycling pipeline, opening new, innovative research routes. Polymers are highly beneficial in this field, as they can provide a platform for efficient metal recovery, minimising the dependence on hazardous solvents. Furthermore, the same polymer can be used in several absorption/desorption cycles. Materials such as metal–organic frameworks, zeolites, hydrogels, and membranes have been used for a more sustainable recovery of target metals such as cobalt and nickel.^{14–18} In some cases, their performance already matched the well-known ion-exchange resins,¹⁹ reaching absorption capacities for cobalt and nickel in the range of 100 mg g^{−1}. However, there are still challenges associated with their use, such as the difficulty of desorb the captured metals into another media after which they can be reintroduced into the supply chain, or reuse for several absorption/desorption cycles.

Recently, DESs monomers have been used to prepare new ionic polymers,^{20,21} where the HBA and HBD components can be chosen from a variety of chemicals including biobased ones. Interestingly, these polymeric deep eutectic systems can easily be prepared by photopolymerization,^{20,22} which is a simple and cost-efficient procedure for material preparation. In this article, a series of ionic polymers inspired by DES were synthesized and investigated to recover cobalt and nickel from solutions mimicking hydrometallurgical leachates. Inspired by our previous works,^{13,14,20} hydroxylated solvents – either alcohols such as glycerol (Gly) and ethylene glycol (EG), as well as phenolic compounds such as tannic acid (TA) – were used as HBDS for the preparation of DES-based polymers. Similarly, [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) was used as an ammonium salt HBA. From aqueous to more acidic media, the effect on metal ion speciation, ionic interactions and hydrogen bonding coordination with the HBAs or HBDS were considered to explain the performance of these absorbents. Moreover, their continuous utilization in cyclic absorption/desorption studies was investigated addressing the impact of the stripping media on the polymeric structure. Ultimately, this study aimed to provide initial proof of concept, and progress towards better understanding the use of ionic polymers for metal ion absorption.

2. Experimental

2.1. Chemicals and instrumentation

[2-(Methacryloyloxy) ethyl] trimethylammonium chloride solution (METAC, 75 wt% in water), glycerol (Gly, >99%), ethylene

glycol (EG, 99.8%), 1,3-butanediol (BdOH, >99%), 1-butanol (BuOH, 99.8%), 2-hydroxy-2-methylpropiophenone (Darocur 1173, 97%), ethylene glycol dimethacrylate (EGMA, 98%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 98%), nickel(II) chloride hexahydrate (NiCl₂·6H₂O, ReagentPlus), hydrochloric acid (HCl, 37%), pyrogallol (PGA, 97%) and tannic acid (TA, ACS reagent) were purchased from Sigma-Aldrich, and protocatechuic acid (PCA, 98%) was acquired from Alfa Aesar. Nitric acid (70%) was acquired from Ajax Finechem (Australia). All chemicals were used without further purification.

Inductively coupled plasma mass spectrometry (ICP-MS) for metal quantification analysis – absorption capacity and desorption efficiency – was carried out on a NexION 350X (PerkinElmer, USA), diluting the solutions filtered through a 0.45 µm PTFE membrane in a 2% (v/v) nitric acid aqueous solution, using external ICP grade calibration standards obtained through PerkinElmer and an internal standard solution of In and Rh used for quality control of the analysis and correction of matrix effects. Calibration standards for target metals were prepared in 2% HNO₃ as well, at concentration of 0.1, 1, 10, 100, 500 and 1000 ppb.

A UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan) was used to corroborate ICP-MS data as well as confirm Co²⁺ and Ni²⁺ speciation in the solution mixtures.

Fourier transform infrared (FTIR) spectra were recorded on a Frontier spectrometer (PerkinElmer, USA) with an attenuated total reflectance (ATR) diamond accessory (Golden Gate), using 64 scans at a resolution of 4 cm^{−1}, at room temperature with a background scan prior to measurements and correcting the resulting spectra for ATR and baseline.

Nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a Bruker Avance III instrument. The resulting solutions after the 48 h metal uptake experiments were diluted in D₂O for ¹³C-NMR assessment of polymer components leakage into the solutions.

Elemental analysis (C, H, N) was performed on the polyDES samples by using a Euro EA Elemental Analyser. 1–2 mg of each polyDES was employed for the measurements carried out in duplicates.

In all cases, at least two separate experiments in the same conditions were carried out, using the standard deviation between the obtained results as the uncertainty margin.

2.2. Polymers and metal solution preparation

Solution precursors of the polymer components were prepared by mixing METAC with two different types of hydroxylated HBDS. On one hand, METAC was mixed with alcohols (Gly, EG, BdOH, BuOH) in a 1:2 molar ratio (METAC:alcohol) with continuous stirring at 70 °C until an homogeneous solution was obtained, for up to 24 h in METAC:alcohol polymers. A second type of –OH derivatives were studied, phenolic compounds like TA, PCA and PGA. For METAC:PGA the molar ratio was 1:1, while it was 20:1 and 2:1 for TA and PCA polymers, respectively, due to the larger number of –OH in the system.

Afterwards, the ionic polymers were obtained by photopolymerization using Darocur 1173 (5 wt%) as the photoinitiator



and EGDMA as the crosslinking agent (2.5 wt% for METAC: alcohol, 5 wt% for METAC:phenolic compounds). A control polymer was also prepared under the same experimental conditions using only METAC.

These were poured into silicone moulds and UV-irradiated for 3 min in a TBK 905 UV ultraviolet curing LED Box with a lamp intensity of 200 W and a wavelength of 365 nm. The resulting polymer was peeled off the mould, dried overnight at 40 °C and stored at room temperature for application and further characterization.

Metal-containing solutions were prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, at a metal concentration of 50 mM, in either deionized water or 6 M HCl aqueous solution, of individual metals (just Co^{2+} or Ni^{2+}) or mixed in equal concentration.

2.3. Metal recovery using ionic polymers

The ionic polymers were prepared as small cylinders with 10 mm diameter to be used for metal uptake experiments. The absorption of metals was then carried out by adding 2 mL of the metal-containing solutions and allowing contact with the polymer for at least 24 h at room temperature in a closed container. The remaining solution was filtered and collected following this period and, along with the polymer, collected for further analysis. For desorption, the polymers were then washed with 3 separate fractions of 2 mL of deionized water, each for about 48 h. A desorption comparison was also carried out with HCl 37% by doing the same washing process with up to 7 separate fractions of 3 mL of acid each for about 24 h.

To assess the performance of the polymers, two parameters were used: absorption capacity and desorption efficiency. In the former, it was quantified how much metal from the metal solution was uptaken into the polymer, by the difference with metals in the remaining solution after uptake, using ICP-MS analysis. This formula takes inspiration from the established adsorption capacity calculations used for this class of materials.^{2,3} In desorption efficiency, the water fractions used for stripping the metal off the polymer were quantified by ICP-MS. The absorption capacity, q_e and the desorption efficiency, η_{DE} , were calculated as follows:

$$q_e (\text{mg metal/g polymer}) = \frac{m_{\text{initial solution}} - m_{\text{remaining solution}}}{m_{\text{dry polymer}}} \quad (1)$$

$$\eta_{\text{DE}} (\%) = \frac{m_{\text{stripping water fractions}}}{m_{\text{initial solution}} - m_{\text{remaining solution}}} \times 100 \quad (2)$$

where $m_{\text{initial solution}}$ and $m_{\text{remaining solution}}$ corresponds to the mass of metal in the initial solution which the polymer has contact with for 48 h, and the mass of metal in the remaining solution after those 48 h, respectively. The $m_{\text{dry polymer}}$ corresponds to the mass of the initial polymer, before any contact with solvent, while $m_{\text{stripping water fractions}}$ corresponds to the mass of metal in the first and second water fractions used to strip metal off the polymer after adsorption.

2.4. Polymer swelling

Swelling assays were carried out to determine maximum swelling by the polymers by immersing these in 2 mL of metal-containing solutions having deionized water or 6 M HCl aqueous solution matrices for 48 h. The resulting swelling was determined as a weight gain in percentage, as follows:

$$\text{Swelling } (\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (3)$$

where m_{wet} and m_{dry} are the mass of the polymer before and after being in contact with the respective solution mixtures for at least 24 h.

2.5. Reuse of ionic polymers for metal recovery for multiple cycles

Following the screening of various polymer compositions, the selected optimal polymers for recovery of Co^{2+} and Ni^{2+} were used in a cyclic study. In this, the same polymer was submitted to a step of absorption of metal in a mixed Co-Ni solution, followed by desorption with three water fractions, as indicated before, and reused for new absorption and desorption steps as a new cycle, until five cycles were completed. The absorption capacity and desorption efficiency were determined at each stage according to eqn (1) and (2), respectively, as well as qualitative assessments of the polymer condition before and after the five absorption/desorption cycles.

3. Results & discussion

3.1. Synthesis of ionic polymers

The ionic polymers inspired by DES investigated in this work were composed of a mixture of [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) and hydroxylated HBDs, either alcohols (glycerol – Gly, ethylene glycol – EG, 1,3-butanediol – BdOH, 1-butanol – BuOH) or phenolic compounds (tannic acid – TA, pyrogallol – PGA, protocatechuic acid – PCA) (Fig. 1), in a defined molar ratio (Table S1, ESI†). The selection of these components has been shown to promote

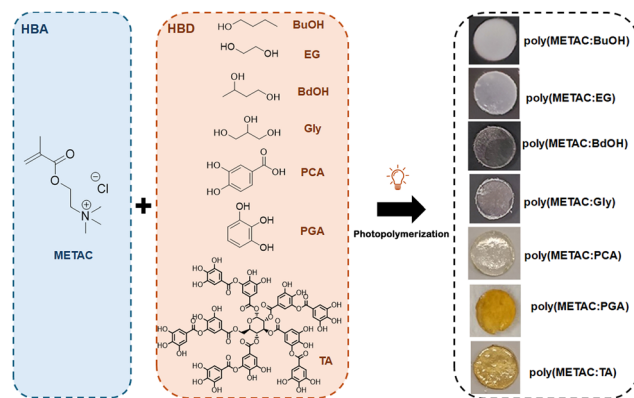


Fig. 1 Chemical structures of ionic polymer components used in this work and an initial dry polymer shown after photopolymerization of the monomer.



enhanced leaching in the case of hydroxylated solvents and DES, especially of cobalt oxides,^{13,24} while polymeric combinations of METAC and phenolic compounds showed potential to be used for metal interaction.^{14,20} The ratios of METAC:HBD were inspired by common DES compositions, such as those used in choline chloride:EG, as well as consideration of the ratio of METAC chloride moieties to the -OH groups of the HBDs. The use of both METAC and these various hydroxylated solvents allow several strategies to recover metals due to interactions between them and the metals. For example, the positively-charged ammonium of METAC could establish interactions with negatively charged metal complexes such as $[\text{CoCl}_4]^{2-}$, commonly present in hydrometallurgical leachates due to higher chloride concentrations.^{25,26} The hydroxylated solvents could also interact with these metals through the -OH moieties.^{27–30} These compositions should provide multiple contributions towards metal absorption by our polymers composed of METAC:hydroxylated HBDs solvents. Alternatively, METAC could also bond with the hydroxylated HBDs through hydrogen bonding between the chloride anion of METAC and the hydroxyl group of the other polymer component,²⁰ as reported in the formation of DES.³¹

As mentioned before, the ionic polymers were prepared from a mixture of METAC and one of the alcohols or phenolic compounds mentioned above. Photopolymerization using Darocur© 1173 as initiator occurred through a free-radical polymerization of the methacrylate moiety of the METAC monomer (Fig. S1, ESI†). The resulting polymers were labelled as polyMETAC:Gly, polyMETAC:EG, polyMETAC:BdOH, polyMETAC:BuOH, polyMETAC:TA, polyMETAC:PGA and polyMETAC:PCA depending on the chemistry of the hydroxylated HBDs. A visual inspection of each polymer after polymerization suggests differences depending on the composition. For example, all the polymers apart from polyMETAC:BuOH and polyMETAC:PCA were transparent. PolyMETAC:BuOH was white and opaque, possibly due to phase separation, while polyMETAC:PGA and polyMETAC:TA were both yellow, as previously observed in phenolic compounds prone to oxidation.³²

As reported in our previous works for this type of polymer,²⁰ the disappearance of the $\text{C}=\text{C}$ ν peak at 1637 cm^{-1} seen in all polymers suggests a high degree of polymerization (Fig. S2, ESI†). The hypsochromic shifts occurring for the $\text{C}-\text{H}$ δ group of METAC (1320 cm^{-1}) and $\text{C}-\text{O}$ ν (1165 cm^{-1}) of the alcohol HBDs support that the interaction between both components was maintained after polymerization. The polymer composition contains both units coming from METAC and the hydroxylated solvents, as a combination of both components (Fig. S3, ESI†) are present (e.g. $\text{C}-\text{H}$ ν (around 2900 cm^{-1}) and $\text{C}-\text{O}$ ν (around 1100 cm^{-1})).²⁰

3.2. Assessment of Co^{2+} or Ni^{2+} absorption by ionic polymers

The general flow of the methodology to assess the potential of ionic polymers for metal recovery is depicted in Fig. 2a. As indicated, this work focused on absorbing critical metals, such as Co^{2+} or Ni^{2+} , present in a variety of secondary waste. As will be discussed throughout the work, this absorption could

occur through multiple mechanisms, including adsorption. Generally, the ionic polymers were put in contact with solutions containing Co^{2+} or Ni^{2+} . First, the alcohol-based polymers were used in individual metal solutions. Moreover, two types of matrices of these metal solutions were considered – either aqueous deionized water (aq) or in 6 M HCl. (HCl). Although both of these matrices are aqueous in nature, their pH values are different, affecting the speciation of Co^{2+} and Ni^{2+} in the solution.^{33,34} For example, a solution of Ni^{2+} in deionized water (aq), had a pH value of 5, while in 6 M HCl this decreased to 1. In conventional hydrometallurgical processes, the leachates (metal solutions) are usually acidic,⁷ and HCl is widely used. Moreover, 6 M HCl is considered to be the concentration at which $[\text{CoCl}_4]^{2-}$ species start to emerge.³⁴ At these experimental conditions (i.e. room temperature and acid/chloride concentration), nickel species would be expected to be predominantly positively-charged,³³ thus allowing for an assessment of the metals-polymers interactions.³⁴ At these experimental conditions (i.e. room temperature and acid/chloride concentration), nickel species would be expected to be predominantly positively-charged,³³ thus allowing for an assessment of the metals-polymers interactions. Whereas, in water, both cobalt and nickel species would be positively-charged, thus allowing for comparison between metals. This comparison can be partially established by visual inspection, since most of these complexes are coloured, which is useful in a preliminary assay. Finally, the solutions in water also expands the relevance of this study to other matrices in which the recovery of metal ions is required, such as metal-contaminated water.¹⁴

Thus, solutions of 50 mM cobalt(II) chloride were prepared in either water or 6 M HCl aqueous media, showing pink and blue colour solutions respectively, and the complexes were identified in the solutions by UV-Vis (Fig. 2b and d). In water, the cobalt octahedral species $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, pink in colour, together with $[\text{CoCl}(\text{H}_2\text{O})_5]^+$ were detected (Fig. 2b). The tetrahedral $[\text{CoCl}_4]^{2-}$ complex was confirmed in acidic media (6 M HCl) by its characteristic vivid blue colour, although $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}(\text{H}_2\text{O})_5]^+$ were also present. The visual impact of the $[\text{CoCl}_4]^{2-}$ complex may be higher as a result of the higher molar absorptivity;³⁴ however it is present simultaneously with the two pink-coloured positive species. The visual impact of the $[\text{CoCl}_4]^{2-}$ complex may be higher as a result of the higher molar absorptivity;³⁴ however it is present simultaneously with the two pink-coloured positive species. The polymers containing alcohols were put in contact with the metal solutions for 48 h to assess their performance. As seen in Fig. 2c, the polymers in contact with the 6 M HCl cobalt solution changed from the transparent or white opaque colours to vivid blue colours, whereas those that were in contact with the cobalt aqueous solution had a faint pink colour (Fig. S4a, ESI†). Apart from interactions between negatively charged metal species and the positively charged trimethylammonium from METAC, other driving forces for metal uptake should be in place. This hypothesis is based on the metal uptake being observed independently of having positive or negative charged species in solution. On the other hand, the phenolic



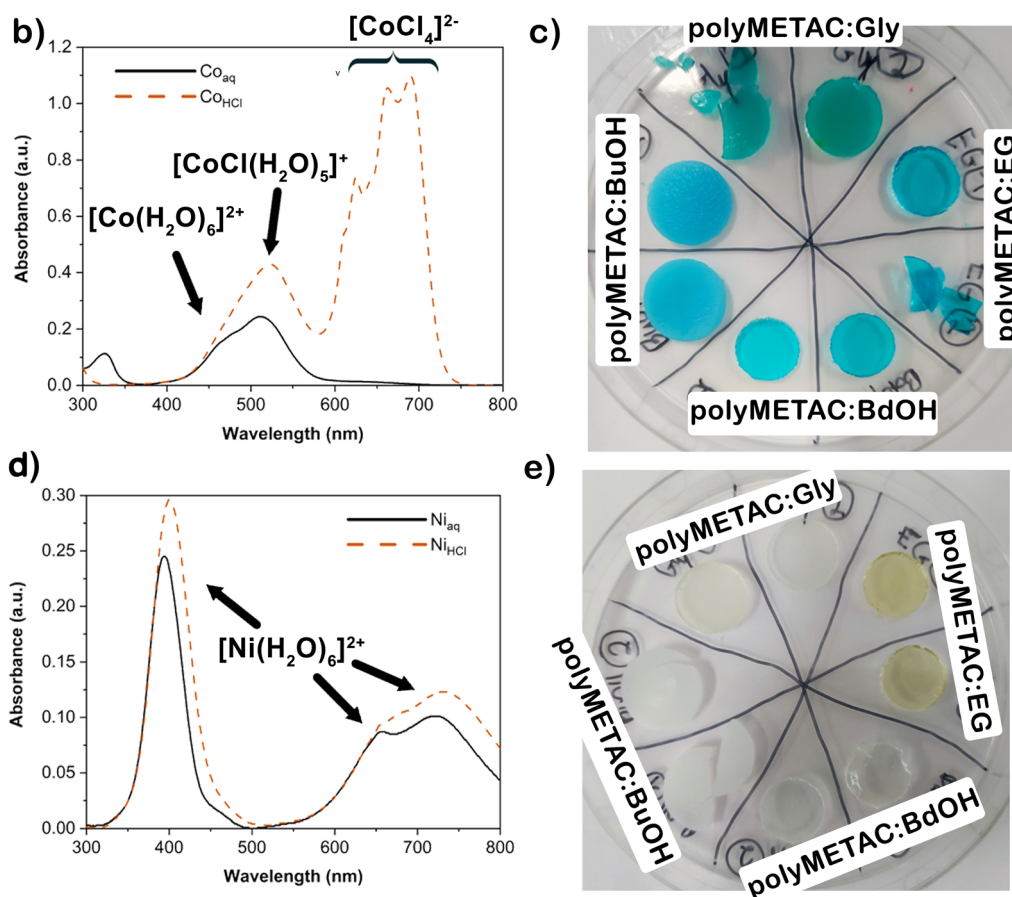
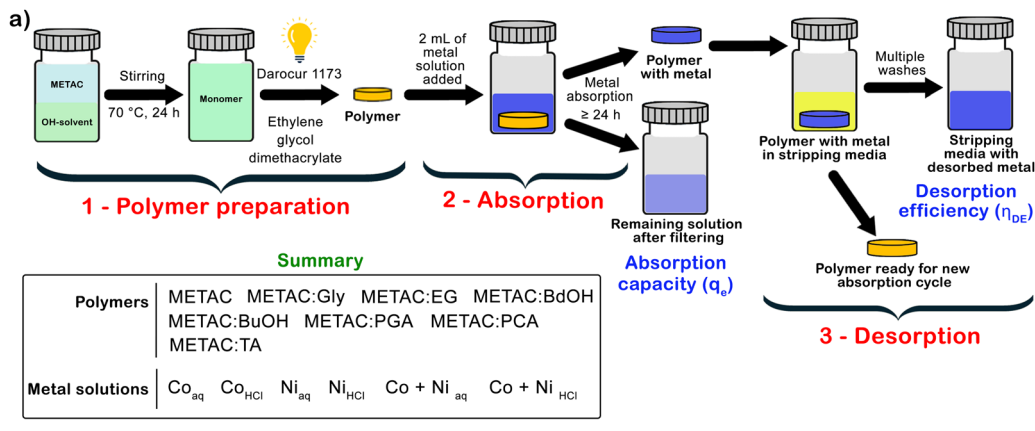


Fig. 2 (a) Schematic of the general methodology used in this work for the (1) preparation of ionic polymers, (2) absorption of metal ions from solutions using ionic polymers and (3) desorption of absorbed metal ions from the polymer into a stripping media. A summary of polymer compositions and metal ion solutions – individual or mixed metals – and in water (aq) or in 6 M HCl (HCl) is also presented. UV-Vis spectra of (b) CoCl₂·6H₂O and (d) NiCl₂·6H₂O dissolved in aq or HCl media. (c) and (e) polyMETAC:alcohol polyDES polymers after preliminary metal absorption assays – 48 h contact with either 50 mM CoCl₂·6H₂O (c) or 50 mM NiCl₂·6H₂O (e) in 6 M HCl aqueous solution. Two of each polymer were prepared for reproducibility.

compounds only showed a visible colour change when in contact with 6 M HCl Co solutions (Fig. S4, ESI[†]), whereas in the Co in water no cobalt complex uptake could be easily seen.

A similar assay was carried out for nickel, with a 50 mM nickel(II) chloride solution being prepared in water or 6 M HCl media. Both solutions were green-coloured typical of [Ni(H₂O)₆]²⁺, corroborated by UV-Vis spectra showing this

species in the 400 nm and the 600–700 nm regions (Fig. 2d).³³ However, there were not significant differences in colours between aqueous and acidic media, as seen in the cobalt solutions (Fig. 2d).³³ However, there were not significant differences in colours between the metal solution in water or 6 M HCl, as seen in the cobalt solutions (Fig. 2d), apart from the red-shift of the target regions in the UV-Vis spectra, likely due to partial



dehydration of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex, as it transitions towards $[\text{NiCl}(\text{H}_2\text{O})_5]^{+}$.^{33,35,36}

The resulting polymers after contacting the nickel chloride 6 M HCl solution are in Fig. 2e, without a generalized colour change as in the case with cobalt solutions. However, a clear bright green tone was seen in polyMETAC:EG which could be the result of specific interactions of nickel ions with the polymer components, namely EG. $[\text{Ni}(\text{EG})_3]^{2+}$ complexes have been reported before, in which the EG molecules act as bidentate ligands with Ni^{2+} through the OH moieties, forming this tris-complex, whose geometry would lead to the bright green colour.^{29,37}

Similar observations regarding the colour changes of the polymers after metal uptake was observed for the ionic polymers composed of the phenolic compounds, as seen in our previous work.²⁰ When contacted with the nickel solutions in water, the polymers did not change colour, thus nickel absorption could not be visually confirmed (Fig. S4b, ESI†).

In the preliminary assay using mixed solutions containing both cobalt and nickel, all the metal species mentioned for the individual solutions are also shown in the UV-Vis spectra of the mixed metal solution (Fig. S5a, ESI†). When the polymers got in contact with the mixed metal solution in water, the polymers remained either transparent or with a faint pink colour. With the 6 M HCl mixed metal solution, however, the polymers were all blue with a green hue, except for METAC:BuOH which was blue coloured. A visual inspection of the resulting polymers seems to indicate that there is a larger cobalt absorption compared to nickel (Fig. S5b and c, ESI†), however a more systematic study to elementally quantify the sorbed metals using ICP-MS is required.

3.3. Performance of ionic polymers as absorbents in mixed Co–Ni solutions

The focus on a more quantitative study was set on the 6 M HCl solutions containing both Co^{2+} and Ni^{2+} since it provides a more realistic situation to metal ion recovery from secondary sources recycling where acidic leachates are generated. Additionally, the presence of both metals in solution will further the

understanding of possible synergetic effects on metal uptake by a given polymer. The performance of these polymers can be measured by calculating the absorption capacity, q_e , of a given metal, with the results shown in Fig. 3a and b. First, the polymers synthesised using the series of alcohols were studied, and later expanded to the polymers with phenolic compounds. The discussion is based on polymer composition, structural integrity, and effect of the media acidity.

3.3.1. Contribution of the alcohol component of the ionic polymer on metal uptake. Generally, both cobalt and nickel were absorbed at similar levels across the different polymers, with slight changes depending on the chemical composition of the polymer (Fig. 3a). The absorption capacity of cobalt in 6 M HCl fluctuated between $24 \pm 0.3 \text{ mg g}^{-1}$ and $30 \pm 1 \text{ mg g}^{-1}$ following the trend polyMETAC:BuOH > polyMETAC:BdOH > polyMETAC:EG > polyMETAC:Gly. Therefore the polymer composition that enabled the highest absorption was polyMETAC:BuOH ($30 \pm 1 \text{ mg g}^{-1}$) and the lowest was polyMETAC:Gly ($24 \pm 0.3 \text{ mg g}^{-1}$). Regarding nickel, the same trend registered for cobalt was also seen with values ranging between $22 \pm 4 \text{ mg g}^{-1}$ (polyMETAC:Gly) and $28 \pm 1 \text{ mg g}^{-1}$ (polyMETAC:BuOH). Given by these results, there seems to be a slight influence of the chemistry of the alcohol in absorbing metals from 6 M HCl media.

As mentioned before, the UV-Vis spectra depicted only a positively charged species for Ni ($[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$) but both positively and negatively charged species ($[\text{CoCl}_4]^{2-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}(\text{H}_2\text{O})_5]^{+}$) in the case of Co. Based on the lack of major differences in metal absorption capacity, we can assume that the interactions between the negatively charged metal species (e.g. $[\text{CoCl}_4]^{2-}$) and the positively charged trimethylammonium moiety from METAC were not the only contributor. This is corroborated by the nickel complex – $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ which would have impeded its interactions with METAC due to being positively charged. An elemental analysis of the polymers was carried out for selected polymers in this work, including polyMETAC:Gly and polyMETAC:EG (Table S2, ESI†). As the percentage of nitrogen in the polymer was similar across the polymers, the variation on the ratio of absorbed metal per nitrogen could be related to the hydroxylated solvent used, but not limited.

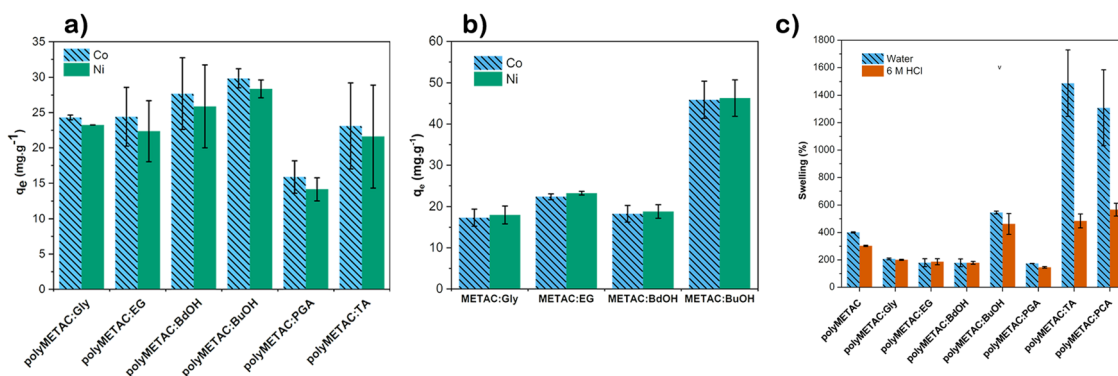


Fig. 3 Absorption capacity (a) and (b), q_e , of a range of polymers after contacting a 50 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution in 6 M HCl (a) or water (b) for at least 24 h. The absorption capacities are depicted in mg of metal – Co or Ni – per gram of initial dry polymer. (c) Swelling of polymers after contacting water or 6 M HCl solution for at least 24 h.



Thus, the absorption capacity was also measured in metal solutions in water as a control study (Fig. 3b) where Co charged species were different. In this case, there was a clearer distinction between the nature of the METAC:alcohol polymers with a wider range of absorption capacity values. While both cobalt and nickel were still absorbed at similar levels, the absorption capacity of both metal ions in the METAC:BuOH polymer were almost double as that in the 6 M HCl media, amounting to $46 \pm 5 \text{ mg g}^{-1}$ for Co^{2+} and $46 \pm 4 \text{ mg g}^{-1}$ for Ni^{2+} . For the rest of the polymers the absorption capacities followed a slightly different order than for the 6 M HCl media, such that the polyMETAC:BdOH shifted from the second best polymer to the worst in the series.

For polyMETAC:EG ($22 \pm 0.7 \text{ mg g}^{-1}$ for Co^{2+} and $23 \pm 1 \text{ mg g}^{-1}$ for Ni^{2+}), the values were comparable to the ones in 6 M HCl, although in this case, the cobalt species were only positively charged. Under those conditions, the interactions with METAC should not be present, allowing us to envision that the complexation of the alcohol with the metal could play a role. This type of chelation has also been reported for well-established silica-based materials with amine functionalization such as ethylenediaminetetraacetic acid (EDTA).³⁸

The absorption capacity in polyMETAC:Gly ($17 \pm 2 \text{ mg g}^{-1}$ for Co^{2+} and $18 \pm 2 \text{ mg g}^{-1}$ for Ni^{2+}) and polyMETAC:BdOH ($18 \pm 2 \text{ mg g}^{-1}$ for Co^{2+} and $19 \pm 2 \text{ mg g}^{-1}$ for Ni^{2+}) was lower than for the analogue experiments in 6 M HCl. The differences in the metal uptake trends using either water or 6 M HCl, combined with the performance increase of polyMETAC:BuOH in water, raises the possibility of other driving forces for the sorption of both metals in this scenario, and the role of pH on the metal uptake.

The diffusion of the metal solution into the polymer could be another possible driving force for metal uptake. Understanding the influence of the degree of swelling is important for a better understanding of the metal absorption process and also the structural stability of the polymer. The swelling of these polymers after contacting a solution of mixed cobalt and nickel in either water or 6 M HCl is depicted in Fig. 3c. METAC:BuOH showed a significantly higher swelling ($546 \pm 11\%$ in water and $463 \pm 76\%$ in 6 M HCl) compared to the other polymers in the order of 200%.

A control polymer only composed of METAC, similarly to METAC:BuOH presented a large swelling, at $401 \pm 4\%$ in water and $302 \pm 5\%$ in 6 M HCl, which could, in principle, be consistent with a higher METAC content per mass of polymer.³⁹

In turn, this could be the factor contributing to higher absorption capacity of Co^{2+} and Ni^{2+} in the higher swelling METAC:BuOH polymer in water, and not as much in the acidic one. The high water content was also seen to promote ionic mobility in porous materials, further supporting this.⁴⁰ However, this complex balance of high ionic mobility, its interactions and mechanical stability, as well as cross-linking degree⁴¹ should be considered for a consistent practical application.

3.3.2. Contribution of the phenolic component of the ionic polymer on metal uptake. A similar assessment was carried out for METAC:phenolic compound polymers, following the

potential for metal absorption given by our previous works.^{14,20} The high swelling of polyMETAC: PCA of $567 \pm 47\%$ in 6 M HCl and $1308 \pm 276\%$ in water (Fig. 3c) caused breakage of the polymer, rendering its assessment inviable. The METAC:TA polymer was considered despite the high swelling and consequent fragility ($485 \pm 51\%$ in 6 M HCl and $1488 \pm 242\%$ in water) for comparison with METAC:alcohol polymers, as it had a significantly higher number of coordinating -OH groups than any other polymer. The METAC:PGA polymer had the lowest swelling, $145 \pm 6\%$ in 6 M HCl and $174 \pm 1\%$ in water (Fig. 3c), maybe due to the lowest METAC:HBD ratio among all polymers.³⁹ The phenolic polymers were more fragile than the alcohol-based ones, but considering the lower swelling of polyMETAC:PGA and high coordination potential of polyMETAC:TA, their absorption capacity was assessed (Fig. 3a). As with the METAC:alcohol polymers, the absorption capacities were similar between cobalt and nickel, as well as between both polymers. However, the absorption capacity values were generally lower than the alcohol based polyDESS ($16 \pm 2 \text{ mg g}^{-1}$ for Co^{2+} and $14 \pm 2 \text{ mg g}^{-1}$ for Ni^{2+} for polyMETAC:PGA, and $23 \pm 6 \text{ mg g}^{-1}$ for Co^{2+} and $22 \pm 7 \text{ mg g}^{-1}$ for Ni^{2+} for polyMETAC:TA). This lower performance by the METAC:phenolic HBDs polyDES could be related to a lower ratio of -OH groups available, as there is a higher amount of METAC fraction present in these compared to the previous polymers. As mentioned, when discussing ionic polymers using alcohol components, a higher effect of the trimethylammonium moiety from METAC seems to occur for Co^{2+} when compared to Ni^{2+} , due to the chemical nature of the metal ion complexes. However, the absorption of the metal cations did not depend solely on ion exchange involving the nitrogen moiety of METAC (absorbed metal/nitrogen ratio < 1).

As general conclusions, interactions between the positively-charged ammonium of METAC and negatively-charged metal complexes, -OH coordination with the metal complexes, pH media and swelling of the membranes were explored as main driving forces for metal uptake. Interestingly, the polymer swelling seemed to be the most dominant factor in this series of ionic polymers under neutral pH conditions; however the mechanical integrity was negatively affected when swelling significantly increased.

The absorption capacities in this work were very comparable with established absorbents, such as silica and zeolites,^{18,38,42-45} ion-exchange resins,^{15,46,47} membranes,⁴⁸ as well as more novel, functionalized materials,^{49,50} including those with hydroxylated compounds.^{14,22,51-53} Values ranging from just 4 mg g^{-1} (ref. 48 and 51) to up to two orders of magnitude, such as 468 mg g^{-1} ,⁴² have been reported in the literature (Table 1).

Zeolites, for example, have a wide range of results due to the tunability of functionalizing group that can interact with the metal ions, either through chelation or electrostatic interactions. Dinu and colleagues reported a natural zeolite modified with positively charged chitosan reaching outstanding absorption capacities (468 mg g^{-1} of Co^{2+} and 247 mg g^{-1} of Ni^{2+}).⁴² More modest values were reported for the absorbents that relied only on chelation such as EDTA, with an absorption



Table 1 Examples of materials used in the uptake of cobalt and nickel ions, with comparison with our materials, based on the calculated adsorption capacities

Material	Absorption capacities	Ref.
Zeolite modified with chitosan	468 mg g ⁻¹ of Co ²⁺ 247 mg g ⁻¹ of Ni ²⁺	42
EDTA-modified silica gel	20 mg g ⁻¹ of Co ²⁺ 22 mg g ⁻¹ of Ni ²⁺	38
Diethylenetriaminepentaacetic acid-modified silica gel	16 mg g ⁻¹ of Co ²⁺ 17 mg g ⁻¹ of Ni ²⁺	38
Aliquat 336 chloride in poly(vinyl chloride)	4 mg g ⁻¹ of Co ²⁺ 0 mg g ⁻¹ of Ni ²⁺	48
Commercial resins (Dowex M4195 [®] and Ionac SR-5 [®])	29 mg g ⁻¹ of Co ²⁺ 53 mg g ⁻¹ of Ni ²⁺	47
Polyethylene glycol-silica gel	6 mg g ⁻¹ for Co ²⁺ 8 mg g ⁻¹ for Ni ²⁺	52
5,7-Dichloroquinoline-8-ol in styrene-EGDMA	11 mg g ⁻¹ for Co ²⁺ 7 mg g ⁻¹ for Ni ²⁺	53
PGA in Amberlite XAD-2	7 mg g ⁻¹ for Co ²⁺ 4 mg g ⁻¹ for Ni ²⁺	51
polyMETAC:BuOH (water)	46 mg g ⁻¹ for Co ²⁺ 46 mg g ⁻¹ for Ni ²⁺	This work
polyMETAC:BuOH (6 M HCl)	30 mg g ⁻¹ for Co ²⁺ 28 mg g ⁻¹ for Ni ²⁺	This work

capacity of 20 mg g⁻¹ of Co²⁺ and 22 mg g⁻¹ of Ni²⁺,³⁸ not changing significantly even if more carboxylic acid groups were available, as with diethylenetriaminepentaacetic acid (16 mg g⁻¹ of Co²⁺ and 17 mg g⁻¹ of Ni²⁺).³⁸ Blitz-Raith and colleagues were able to selectively recover Co²⁺ from a mixture of Co²⁺ and Ni²⁺ using immobilized Aliquat 336 chloride in poly(vinyl chloride).⁴⁸ Despite being a valuable separation technique, the absorption capacity of Co²⁺ was only about 4 mg g⁻¹. Commercial resins such as Dowex M4195[®] and Ionac SR-5[®] could achieve sorption of about 29 mg g⁻¹ of Co²⁺ and 53 mg g⁻¹ of Ni²⁺ at pH 3, decreasing to about 6 mg g⁻¹ of Co²⁺ and 29 mg g⁻¹ of Ni²⁺ at pH 1.⁴⁷

A fairer comparison with our METAC systems is the work from Pourreza and colleagues⁵² based on hydroxylated solvents, which used polyethylene glycol, attaining an absorption capacity of 6 mg g⁻¹ for Co²⁺ and 8 mg g⁻¹ for Ni²⁺, which is one order of magnitude lower than our work. Similarly, immobilized hydroxylated solvents, including components present in our polymers such as EGDMA and PGA, also resulted in similar absorption capacity values for Co²⁺ and Ni²⁺, between 4 and 11 mg g⁻¹.^{51,53}

Thus, it could be concluded that our polymers could compare well and outperform in terms of performance with some well-established materials. This initial proof of concept exhibited that these ionic polymers have easy manufacturing, tunability and variable applicability, as well as components with reduced environmental impact. Despite still facing challenges related with the understanding of its mechanisms of action and mechanical properties, this work lays a foundation for promising alternative materials in metal recovery. Additionally, there was negligible leaking of the polymer components into the metal solution during the absorption process, shown by NMR (Fig. S6 and S7, ESI[†]), supporting their stability. This is further supported by the similar FTIR spectra of polymers before and after metal uptake (for example for polyMETAC:TA,

Fig. S8, ESI[†]), which also suggest a high degree of polymerization as discussed before.

4. Optimal metal stripping and recovery using ionic polymers

The stripping of metals from the ionic polymers were also studied to aim for the reuse of the polymer. A pre-equilibration step was introduced to minimise the influence of swelling in the metal absorption capacity. A determined amount of 6 M HCl solution, based on the swelling of the METAC:alcohol polymers showed in Fig. 3c, was used. The swelling degree and trend was similar to before (METAC:BuOH > METAC:BdOH > METAC:EG > METAC:Gly) (Fig. S9, ESI[†]).

A study using concentrated HCl (37%) to strip the metal from the polymers was performed, considering the similar chemical environments in both bulk metal ion solution and inside the polymer. This was carried out by using 7 fractions of 3 mL HCl 37% to ensure the maximum release of metal while avoiding the saturation point in solution.

The recovery of metals by stripping, or desorption efficiency (%), η_{DE} , was determined based on eqn (2) (Experimental section) and shown in Fig. 4a. It can be seen that the highest desorption efficiency was for polyMETAC:BuOH (24 ± 1% for Co²⁺ and 21 ± 1% for Ni²⁺) followed by polyMETAC (20 ± 1% for Co²⁺ and 17 ± 1% for Ni²⁺) > polyMETAC:Gly (19 ± 0.3% for Co²⁺ and 15 ± 0.2% for Ni²⁺). The METAC:EG and METAC:BdOH polymers had the lowest desorption efficiency, between 12 and 14% for Co²⁺ and 9 and 10% for Ni²⁺. The larger stripping of metals from the polyDESS METAC:BuOH and only – METAC could be related to their swelling degree. Moreover, by being broken into pieces, the higher superficial area for contact with the stripping solution also increased. The lower desorption efficiency in the other METAC:alcohol polymers



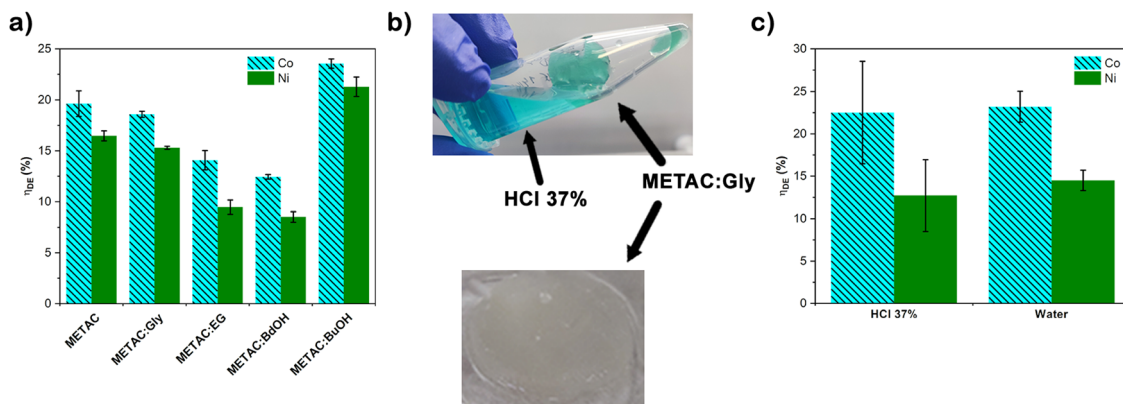


Fig. 4 (a) METAC:Gly polymer after a single wash with 3 mL of HCl 37% (top) or deionized water (bottom). (b) Desorption efficiency, η_{DE} , of a range of polymers after contacting up to 21 mL of HCl 37% in seven fractions of 3 mL to recover metal absorbed from a 50 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution in 6 M HCl. (c) Comparison of a single initial wash of 3 mL of HCl 37% or deionized water to recover metal absorbed by a METAC:Gly polymer from a 50 mM mixed cobalt and nickel solution in 6 M HCl.

could, in principle, be related to a higher metal ion complexation established with the alcohols, however this does not explain the trend observed in this study.

In all cases, η_{DE} of cobalt was higher than that of nickel, which is consistent with the chlorophillic character of this metal and the use of HCl as a stripping solution.

In order to attempt a more economical process, only one fraction of HCl and deionized water was studied, to desorb the metals from METAC:Gly polymer as a control study (Fig. 4c). It was noticeable that the desorption efficiencies using a single HCl 37% wash (3 mL) was comparable to the usage of 21 mL of HCl 37% ($23 \pm 6\%$ for Co^{2+} and $13 \pm 4\%$ for Ni^{2+}). This suggests that the maximum metal stripping with HCl 37% was reached within a single wash, and the remaining washes had negligible impact on the desorption. Interestingly, the desorption of a single deionized water wash was also similar ($23 \pm 2\%$ for Co^{2+} and $15 \pm 1\%$ for Ni^{2+}) to HCl, supporting the use of water as a cost-effective solvent. On the other hand, this promising result is another advantage over other materials such as zeolites that can, in some cases, require the more hazardous HCl solutions to achieve sufficient desorption.⁵⁴

5. Reuse of ionic polymer absorbents for multiple cycles

In a realistic application, these polymers could be expected to be reused for multiple cycles to extend their lifetime and improve the economic viability of the process. The large swelling, loss of structural integrity and breakage of some polymers, pointed to METAC:Gly and METAC:EG as the most viable (*e.g.* cost, mechanical stability and safety) polymers in the series. METAC:TA was also used for some comparisons as a representative of the best performing METAC:phenolic HBD polymer.

The absorption media was a mixed metal solution of 50 mM cobalt and 50 mM nickel in 6 M HCl, following the procedure previously mentioned (Fig. 2). After each absorption process, there was a stripping step, in which three deionized water

fractions (3 mL each) were used to strip the metals into the water. Detailed information will be reported now for poly-METAC:Gly; however similar behaviour was observed for poly-METAC:EG and polyMETAC:TA. The visual progression of the METAC:Gly polymers over the five cycles is shown in Fig. 5a. The reduction of the intensity of the blue colour of the polymers, characteristic of $[\text{CoCl}_4]^{2-}$ species, towards white/transparent suggests metal stripping from the polymer over the cycles. This was further corroborated by the pink-coloured water produced in this desorption process (Fig. 5a), which is characteristic of the Co octahedral species. This visual change of the METAC:Gly polymer occurred with a single water wash, as seen in the example in Fig. 5a. For the ionic polymers under study the metal stripping was a fast process occurring in less than five minutes. This is visually exemplified when water was added to a mixture of multiple polymers (Movie S1 in ESI†).

A quantification of the adsorption capacity and desorption efficiency was then carried out in each cycle (Fig. 5b). Unfortunately, a decrease on metal uptake was observed as a function of cycles, but the process became more favourable as the desorption efficiency, relative to the absorption, increased in each cycle.

The decrease in absorption capacity could be a consequence of changes in the polymeric structure which would be more prominent over multiple cycles. Thus, the assessment of the swelling degree of the METAC:Gly polymers over time can provide information on these fluctuations. This swelling degree at each point of absorption between cycles 1 and 5 (A1–A5) and each of the three washes in each cycle (W1–W3) is shown in Fig. 5c.

During absorption, the swelling of polyMETAC:Gly was around the 250% level, as in previous experiments. However, there is an interesting repetitive phenomenon in each cycle between absorption and desorption. After each absorption, the first water fraction used always resulted in a shrinking of the polymer. That suggests that the 6 M HCl solution that was used for pre-equilibration is exiting the polymer, or that the entrance and complexation of metals in the polymeric structure during



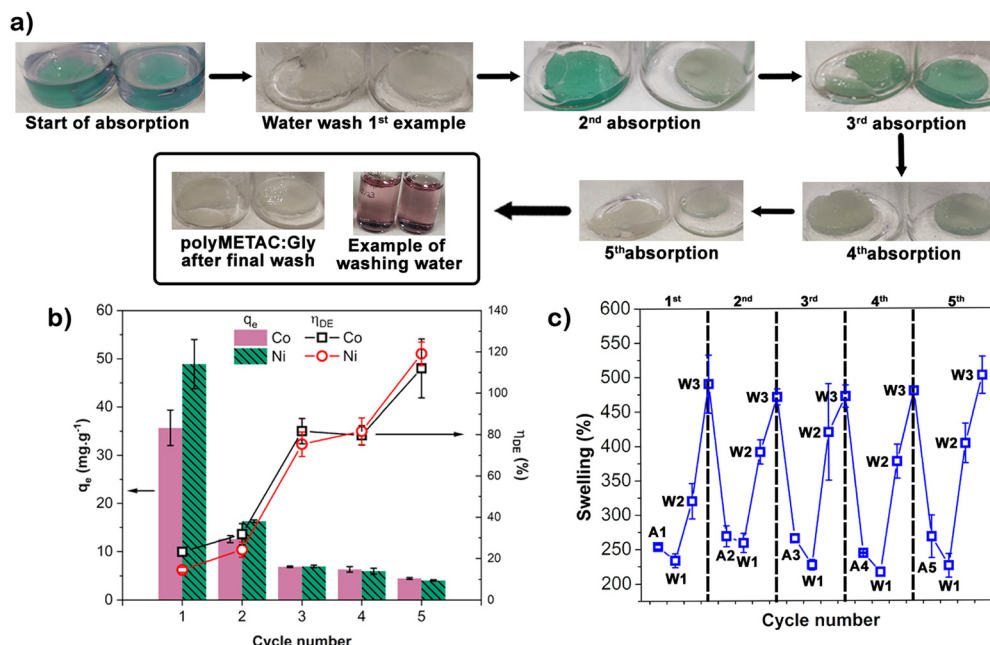


Fig. 5 (a) METAC:Gly polymer visual progression after each adsorption cycle, with the final washed polymers in the end and an example of the pink-coloured washing water obtained in each cycle. (b) Adsorption capacity (q_e , left axis) and desorption efficiency (η_{DE} , right axis) of METAC:Gly in each of the five cycles after contacting a 50 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution in 6 M HCl for absorption and using three fractions of 3 mL of deionized water in each cycle to desorb the metals. (c) Progression of the swelling degree of the METAC:Gly polymers in each cycle, either after absorption of the metals (A1–A5) or after each of the three water washes carried out in each cycle (W1–W3).

absorption causes its tightening through various interactions between the polymer and the metals. Afterwards, with the second and third water washes, the swelling of the polymer increases significantly, first to levels around 400% and in the final one around 500%. This continuous increase could be promoted by a destabilization of the polymeric structure as more water influxes the polymer. However, the swelling, but perhaps not the destabilization, was reverted as a new cycle starts with absorption of metals from a new metal solution. This swelling–shrinking cycling behaviour was already reported when polymers are in contact with aqueous media followed by submersion in an electrolyte solution.³⁹ The fast shrinking was suggested to be the result of the already ‘loosened’ polymeric structure, that would allow faster removal of water than its uptake during the metal absorption step, as the structure is more densely packed at that stage.

The same experiment was carried out for polyMETAC:EG (Fig. S10, ESI†) and polyMETAC:TA (Fig. S11, ESI†). In both cases, there is a similar profile with decrease in absorption capacity as well as the swelling–shrinking behaviour of the polymers across the five cycles. However, polyMETAC:EG has fewer swelling fluctuations, generally maintaining its swelling degree between 200% and 350%. It also had competitive absorption capacities when compared to polyMETAC:Gly. Regarding polyMETAC:TA, the absorption capacities were lower than these two, matching the comparisons established in previous sections. The swelling–shrinking character was also shown, although in Fig. S11b (ESI†) it can also be seen that this is indeed characteristic of the type of polymer and not

dependent on the metals present, as it was also verified when individual solutions of cobalt and nickel were used. Moreover, the swelling range is much higher than polyMETAC:Gly or polyMETAC:EG, reaching up to 1100% (Fig. S11b, ESI†) as seen before.

6. Conclusions

In this work, ionic polymers were designed inspired by DES based on a wide range of alcohols and phenolic compounds, which were combined with [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC). The polymers were easily obtained by photopolymerization and investigated to recover cobalt and nickel ions from water and acidic solutions.

Various driving forces were investigated to determine the metal absorption mechanism; (i) the interactions of the positive ammonium moieties from METAC with negatively charged species in solution (e.g. $[\text{CoCl}_4]^{2-}$); (ii) the coordination of metal ions with the –OH groups of alcohols or phenolic compounds, (iii) the swelling of the polymers which could also assist metal ion diffusion in solution clusters, and (iv) the media pH (more or less acidic). When screening the various polymer compositions, the METAC:BuOH polymer yielded the higher absorption capacity $46 \pm 5 \text{ mg g}^{-1}$ and $46 \pm 4 \text{ mg g}^{-1}$ for cobalt and nickel, respectively, which was in agreement with its larger swelling. However, the high degree of swelling resulted in loss of structural integrity and breakage, limiting its use for multiple cycles. The METAC:Gly and METAC:EG polymers were



the most viable (e.g. cost, mechanical stability and safety) polymers.

When comparing the absorption capacity (q_e) of the alcohol-based polymers, all of them had higher intake of cobalt and nickel than those based on phenolic compounds. The lower performance of the latter could be related lower ratio of -OH groups available, as there is a higher amount of METAC fraction present in these compared to the alcohol series.

The ability to strip absorbed metals from the polymers was studied using water and corrosive HCl, with the latter showing comparable desorption capacities with water which adds to the overall cost-effective performance. METAC:Gly and METAC:EG polymers withstood up to five cycles of absorption/desorption which was lacking in the literature for previous polymers in this type of application.

These results showed the potential for these ionic polymers, in particular, polyMETAC:Gly and polyMETAC:EG, with facile preparation to be used for cobalt and nickel absorption from mixtures. Not only were their absorption capacities competitive with some other materials, but the absorbed metal ions were also easy to desorb using small amounts of water. Thus, following optimization, these polymers could achieve higher absorptions, selectivity, performance retention and mechanical stability, posing relevant alternatives for metal ion absorption.

Data availability

The data supporting this article have been included in this article and as part of the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was partly developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, financed by national funds through the FCT/MCTES. H. Bastos acknowledges the financial support from Deakin University (DUPR Scholarship 0000038986). The authors acknowledge the Australian Research Council (ARC) Industrial transformation Training Centre for Future Energy Storage Technologies (storEnergy) (IC180100049) for funding. Financial support from EU (IONBIKE 2.0 MSCA-SE grant agreement no. 101129945), Eusko Jaurlaritza (GV-IT1525-22) and MINECO AEI (PID2020-119026GB-I00) is also acknowledged.

References

- 1 F. Maisel, C. Neef, F. Marscheider-Weidemann and N. F. Nissen, *Resour., Conserv. Recycl.*, 2023, **192**, 106920.
- 2 C. Zhang, J. Yan and F. You, *Adv. Appl. Energy*, 2023, **9**, 100116.
- 3 R. Arvidsson, M. Chordia and A. Nordelöf, *Int. J. Life Cycle Assess.*, 2022, **27**, 1106–1118.
- 4 O. Winjobi, J. C. Kelly and Q. Dai, *Sustainable Mater. Technol.*, 2022, **32**, e00415.
- 5 M. He, X. Jin, X. Zhang, X. Duan, P. Zhang, L. Teng, Q. Liu and W. Liu, *Green Chem.*, 2023, **25**, 6561–6580.
- 6 Q. Zhang, X.-W. Gao, X. Liu, Q. Gu, J. Mu and W.-B. Luo, *ACS Sustainable Chem. Eng.*, 2024, **12**(7), 2511–2530.
- 7 K. Binnemans and P. T. Jones, *J. Sustainable Metall.*, 2022, **9**, 1–25.
- 8 X. Li and K. Binnemans, *Chem. Rev.*, 2021, **121**, 4506–4530.
- 9 M. K. Tran, M. T. F. Rodrigues, K. Kato, G. Babu and P. M. Ajayan, *Nat. Energy*, 2019, **4**, 339–345.
- 10 K. Liu, S. Huang, Y. Jin, L. Ma, W.-X. Wang and J. C.-H. Lam, *J. Hazard. Mater.*, 2022, **433**, 128702.
- 11 E. Prasetyo, W. A. Muryanta, A. G. Anggraini, S. Sudibyo, M. Amin and M. Al Muttaqii, *J. Mater. Cycles Waste Manage.*, 2022, **24**, 927–938.
- 12 M. G. Rosmaninho, F. C. C. Moura, L. R. Souza, R. K. Nogueira, G. M. Gomes, J. S. Nascimento, M. C. Pereira, J. D. Fabris, J. D. Ardisson, M. S. Nazzarro, K. Sapag, M. H. Araújo and R. M. Lago, *Appl. Catal., B*, 2012, **115–116**, 45–52.
- 13 H. Bastos, N. Schaeffer, J. M. Pringle, J. A. P. Coutinho and C. Pozo-Gonzalo, *ChemSusChem*, 2023, e202300455.
- 14 A. Gallastegui, L. Porcarelli, R. E. Palacios, M. L. Gómez and D. Mecerreyes, *ACS Appl. Polym. Mater.*, 2019, **1**, 1887–1895.
- 15 Z. Liu, L. Wang, Y. Lv, X. Xu, C. Zhu, F. Liu and A. Li, *Chem. Eng. J.*, 2021, **420**, 129684.
- 16 K. S. Mason, S. Y. Huang, S. K. Emslie, Q. Zhang, S. M. Humphrey, J. L. Sessler and Z. A. Page, *J. Am. Chem. Soc.*, 2024, **146**, 4078–4086.
- 17 J. Piątek, T. M. Budnyak, S. Monti, G. Barcaro, R. Gueret, E. S. Grape, A. Jaworski, A. K. Inge, B. V. M. Rodrigues and A. Slabon, *ACS Sustainable Chem. Eng.*, 2021, **9**, 9770–9778.
- 18 L. Roshanfekr Rad and M. Anbia, *J. Environ. Chem. Eng.*, 2021, **9**, 106088.
- 19 Y. Yang, Y. Yang, C. He, Y. Wei, T. Fujita, Z. Wei, W. Yang and F. Shen, *Sep. Sci. Technol.*, 2022, **57**, 1848–1859.
- 20 J. L. De Lacalle, A. Gallastegui, J. L. Olmedo-Martínez, M. Moya, N. Lopez-Larrea, M. L. Picchio and D. Mecerreyes, *ACS Macro Lett.*, 2023, **12**, 125–132.
- 21 J. D. Mota-Morales and E. Morales-Narváez, *Matter*, 2021, **4**, 2141–2162.
- 22 A. Gallastegui, R. M. Spada, G. Cagnetta, R. A. Ponzio, S. R. Martinez, C. M. Previtali, M. L. Gomez, R. E. Palacios and C. A. Chesta, *Macromol. Rapid Commun.*, 2020, **41**, e1900601.
- 23 P. Hadi, J. Barford and G. McKay, *Chem. Eng. J.*, 2013, **228**, 140–146.
- 24 B. Lu, R. Du, G. Wang, Y. Wang, S. Dong, D. Zhou, S. Wang and C. Li, *Environ. Res.*, 2022, **212**, 113286.
- 25 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657.
- 26 V. I. Lakshmanan, M. A. Halim and S. Vijayan, *Innovative Process Development in Metallurgical Industry*, 2016, ch. 5, pp. 91–108.



- 27 V. Cool, S. Riaño, T. Van Gerven and K. Binnemans, *Sep. Purif. Technol.*, 2023, 125787.
- 28 D. Knetsch and W. L. Groeneveld, *Inorg. Chim. Acta*, 1973, 7, 81–87.
- 29 I. M. Pateli, D. Thompson, S. S. M. Alabdullah, A. P. Abbott, G. R. T. Jenkin and J. M. Hartley, *Green Chem.*, 2020, 22, 5476–5486.
- 30 M. A. Rahim, S. L. Kristufek, S. Pan, J. J. Richardson and F. Caruso, *Angew. Chem., Int. Ed.*, 2019, 58, 1904–1927.
- 31 C. Gao, R. Wang, Y. Feng, P. Chen, Y. Wang, Y. Liu and L. Sun, *Eur. Polym. J.*, 2023, 197, 112367.
- 32 S. Kobayashi and H. Higashimura, *Prog. Polym. Sci.*, 2003, 28, 1015–1048.
- 33 W. Liu, A. Migdisov and A. Williams-Jones, *Geochim. Cosmochim. Acta*, 2012, 94, 276–290.
- 34 M. Uchikoshi, *J. Solution Chem.*, 2018, 47, 2021–2038.
- 35 A. Chiboub-Fellah, J. Meullemestre, C. Spies and F. Vierling, *Transition Met. Chem.*, 1999, 24, 135–140.
- 36 N. Zhang, J. Brugger, B. Etschmann, Y. Ngothai and D. Zeng, *PLoS One*, 2015, 10, e0119805.
- 37 P. B. Lond, P. S. Salmon and D. C. Champeney, *J. Am. Chem. Soc.*, 2002, 113, 6420–6425.
- 38 E. Repo, T. A. Kurniawan, J. K. Warchol and M. E. Sillanpaa, *J. Hazard. Mater.*, 2009, 171, 1071–1080.
- 39 N. K. Goel, V. Kumar, Y. K. Bhardwaj, C. V. Chaudhari, K. A. Dubey and S. Sabharwal, *J. Biomater. Sci., Polym. Ed.*, 2009, 20, 785–805.
- 40 I. Stenina, D. Golubenko, V. Nikonenko and A. Yaroslavl'tsev, *Int. J. Mol. Sci.*, 2020, 21(15), 5517.
- 41 A. Guggliuza, *Solvent Swollen Polymer*, Springer, Berlin, Heidelberg, 2016.
- 42 M. V. Dinu and E. S. Dragan, *Chem. Eng. J.*, 2010, 160, 157–163.
- 43 N. Gupta, K. Kushwaha and A. M. C. Chattopadhyaya, *Adv. Mater. Lett.*, 2011, 2, 309–312.
- 44 F. Kriese, S. Lassen, B. Niemeyer and M. R. R. Kooh, *Adsorpt. Sci. Technol.*, 2023, 2023, 1–11.
- 45 A. Tabatabaeefar, A. R. Keshtkar, M. Talebi and H. Abolghasemi, *Chem. Eng. Technol.*, 2020, 43, 343–354.
- 46 A. B. Botelho Junior, A. D. A. Vicente, D. C. R. Espinosa and J. A. S. Tenório, *J. Mater. Res. Technol.*, 2019, 8, 4464–4469.
- 47 F. D. Mendes and A. H. Martins, *Int. J. Miner. Process.*, 2004, 74, 359–371.
- 48 A. H. Blitz-Raith, R. Paimin, R. W. Cattrall and S. D. Kolev, *Talanta*, 2007, 71, 419–423.
- 49 Z. Liu, L. Wang, Y. Jiang, Y. Lv, C. Zhu, F. Liu and A. Li, *Chem. Eng. J.*, 2022, 450, 138329.
- 50 A. Rahman, M. A. Haque, S. Ghosh, P. Shinu, M. Attimarad and G. Kobayashi, *Sustainability*, 2023, 15(3), 2431.
- 51 M. Kumar, D. P. S. Rathore and A. K. Singh, *Microchim. Acta*, 2001, 137, 127–134.
- 52 N. Pourreza, J. Zolgharnein, A. R. Kiasat and T. Dastyar, *Talanta*, 2010, 81, 773–777.
- 53 R. S. Praveen, S. Daniel and T. Prasada Rao, *Talanta*, 2005, 66, 513–520.
- 54 Y. Jin, Y. Wu, J. Cao and Y. Wu, *Desalin. Water Treat.*, 2014, 54, 511–524.

