Separation of Nickel and Cobalt Through Speciation in an Ion Exchange-Deep Eutectic Solvent System

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1. Introduction

Heavy metal contamination presents a serious risk to both ecosystems and human health, highlighting the urgent need for innovative and sustainable remediation technologies. A recently developed Deep Eutectic Solvent-Ion Exchange (DES-IX) system offers an effective approach for recovering heavy metals. By harnessing the distinctive properties of DESs, this system provides a targeted and environmentally responsible alternative to conventional recovery techniques. Previous studies have explored the use of DESs in separating cobalt and nickel, demonstrating the coordination behaviour of Ni^{2+} and Co^{2+} in choline chloride, carboxylic acid DESs (such as malonic, succinic, glutaric, glycolic, and lactic acid), which supports their potential for selective metal separation. [1]

The sustainable nature of DESs plays a crucial role in improving the overall environmental impact of heavy metal recovery processes. Composed of naturally derived and biodegradable components, DESs align with green chemistry principles, helping to minimise ecological harm. [2] This eco-friendly characteristic makes DES-IX an attractive option for responsible metal recovery applications. Furthermore, the DES-IX system is adaptable to a wide range of heavy metal ions, including lead, cadmium, copper, cobalt, and nickel. This flexibility enhances its potential for use across various industrial sectors. The selective ion exchange process, enabled by the unique chemical structure of DESs, improves the efficiency of heavy metal recovery while reducing the generation of secondary waste, an issue commonly associated with traditional methods. [3] The ability to separate cobalt and nickel is particularly valuable for decontamination, where recovering these metals from waste materials and water is essential. [4]

In this study, we have developed an efficient, cost-effective, and environmentally sustainable technology for cobalt and nickel separation and recovery. Using choline chloride-ethylene glycol (ChCl:EG) DES, we achieved the complete dissolution of both cobalt and nickel. By adjusting the water content in the DES, we facilitated the separation of Co^{2+} and Ni^{2+} species. Introducing ion exchange media, in both cationic and anionic forms, into the hydrated DES further enabled effective separation and selective removal of these metal species. Additionally, by optimising the DES composition and water content, this approach has the potential to extend to the recovery of other heavy metals. This system presents a viable solution for addressing challenges in waste treatment and resource management, particularly with corrosion products related to nuclear systems. Gaining insights into the interactions between DESs, metal ions, and ion exchange media will be instrumental in advancing the development of DES-IX systems for sustainable resource recovery and decommissioning.

2. Methodology

2.1 Synthesis of DES

ChCl-pTSA DES was prepared by mixing pTSA and ChCl (2:1 molar ratio), heating to 60°C, and stirring at 400 rpm for 2 hours until fully dissolved. ChCl-EG DES was synthesised similarly but with a 1:2 molar ratio. Both DES mixtures were prepared in open-air conditions to mimic real applications and cooled to room temperature before use.

2.2 Hydration of DES

Water was added to DES to reduce viscosity and improve IX resin incorporation. Hydration levels were set at 0, 20, 40, 60, and 80 wt % after metal oxide dissolution, as 100 wt % (pure water) showed minimal dissolution. The hydrated DES was then contacted with IX resins.

2.3 Metal Dissolution and Separation

NiO and CoO (0.1 g) were added to 5 mL of DES and stirred for 48 hours until fully dissolved. Then, 0.1 g of IX resin (Purolite™ NRW150, NRW160, PFA445, A555) was introduced, and the solution was shaken for 48 hours at room temperature. Resins were separated via syringe filtration, and experiments were repeated three times. The supernatant was stored in 3 wt % nitric acid for ICP-OES analysis.

3. Results and Discussion

The formation of ChCl:pTSA (2:1) and ChCl:EG (1:2) DESs was confirmed through FTIR analysis, which provided evidence of key molecular interactions. Spectral shifts associated with hydrogen bonding and ionic interactions indicated successful complexation between components.

For ChCl:pTSA, modifications in the hydroxyl and sulfonyl stretching regions suggested hydrogen bonding and interactions with chloride ions. Similarly, in ChCl:EG, broadening of the hydroxyl stretch confirmed strong hydrogen bonding, while shifts in the C-O and C-N stretching regions highlighted structural stabilisation. These spectral changes distinguish the DESs from their individual components, reinforcing their unique physicochemical properties.

3.1 Ni and Co Speciation

The speciation of Ni and Co is highly influenced by the solvation environment, leading to distinct coordination behaviours in water and DESs. In aqueous systems, these metals primarily exist as hydrated cations, whereas in DESs, they tend to form anionic chloride complexes. This transformation affects their electronic transitions, which can be monitored using UV-Vis spectroscopy.

3.2 Speciation in Pure Water

In pure water, Ni^{2+} and Co^{2+} predominantly form octahedral hexaaqua complexes, $[Ni(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$, due to strong ion-dipole interactions with surrounding water molecules. Under neutral to mildly acidic conditions, these hexaaqua species remain stable. However, at higher pH, partial deprotonation can lead to the formation of hydroxide species such as $[Ni(OH)]^+$ or $[Co(OH)]^+$.

3.3 Speciation in Pure DES

In chloride-rich DES environments, Ni^{2+} and Co^{2+} form anionic chloride complexes such as $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$, adopting tetrahedral coordination. Depending on water content, mixed species like $[CoCl_4(H_4O)_4]^{2-}$ may form. Ni^{2+}, due to its smaller radius and higher charge density, can also stabilise higher coordination states such as $[NiCl_6]^{4-}$ under certain conditions.

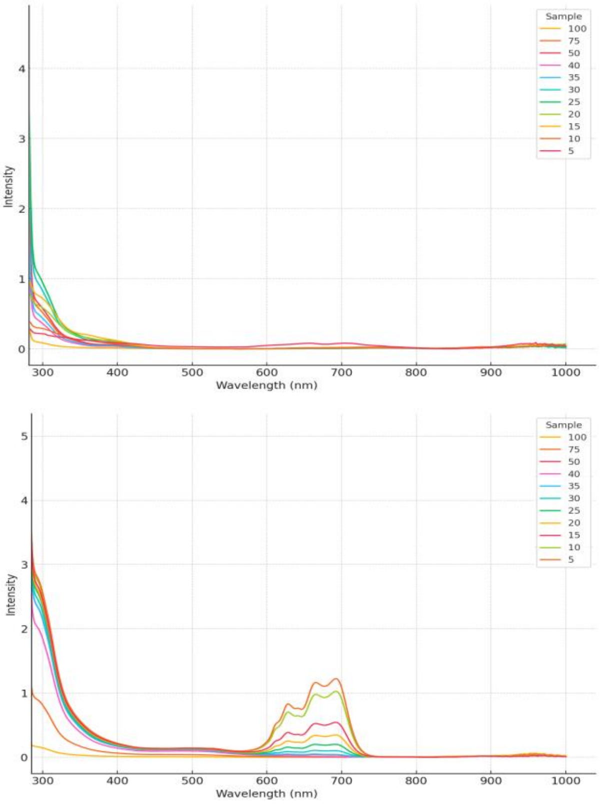

Figure 2. UV-vis analysis of Ni and Co in hydrated a) ChCl:pTSA - Ni, b) ChCl:pTSA – Co showing speciation transitions.

3.4 UV-Vis Analysis of Metal Coordination

The electronic transitions of Ni and Co reflect their different coordination geometries in water and DES.

In water, Ni^{2+} exhibits d-d transitions at 390-430 nm and 600-700 nm, while Co^{2+} has a weak absorption at 510-530 nm due to the ${}^4T_1g(F) \rightarrow {}^4T_1g(P)$ transition.

In DES, ligand-to-metal charge transfer (LMCT) and d-d transitions dominate and therefore $[NiCl_4]^{2-}$ shifts its absorption to 500-600 nm and 700-800 nm, resulting in a yellow-green colour. In constrast, $[CoCl_4]^{2-}$ absorbs strongly in the 600-700 nm range, giving its characteristic intense blue colour.

3.5 Effect of Hydration on Speciation

As water content increases, metal coordination gradually transitions from chloride-dominant to hydrated species. In EG-based DES, this occurs at ~30 % hydration for Co, while in pTSA-based DES, it shifts at ~40 % hydration, suggesting the HBD component affects chloride complex stability. Ni follows a similar trend, but with less pronounced changes, particularly in pTSA-DES.

3.6 Potential for Ni-Co Separation via Ion Exchange (IX)

The differences in Ni and Co speciation across hydration levels open avenues for selective separation using IX resins. Ni forms more stable chloride complexes than Co, which could allow tailored resins to selectively bind one species over the other. The hydration-dependent shifts in coordination chemistry offer a potential route for separation based on their affinity for chloride versus water ligands. The UV-vis analysis showing the metal ion speciation change with increasing hydration % can be seen in Figure 2.

3.7 Single-Metal Uptake via Ion Exchange (IX)

Batch IX experiments were conducted using the selected cationic and anionic resins to assess the removal of Ni and Co from DES solutions with varying hydration levels. Resins were contacted with metal-containing DES solutions for 48 hours, with experiments performed in triplicate.

For cation exchange resins, removal was minimal in non-hydrated DES due to the predominance of anionic metal chloride complexes ($[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$). However, as hydration increased, cationic species (Ni^{2+}, Co^{2+}) formed, significantly improving metal uptake. The efficiency was slightly higher in ChCl:EG than in ChCl:pTSA, likely due to differences in viscosity.

Conversely, anion exchange resins effectively removed anionic metal species in non-hydrated DES, but removal efficiency declined with increasing hydration as the stability of metal-chloride complexes decreased due to solvation of the DES. Despite this, complete removal was not achieved even at low hydration levels, potentially due to mass transfer limitations associated with viscosity. The theoretical ion exchange capacities of the resins further supported the impact of viscosity on ion exchange performance.

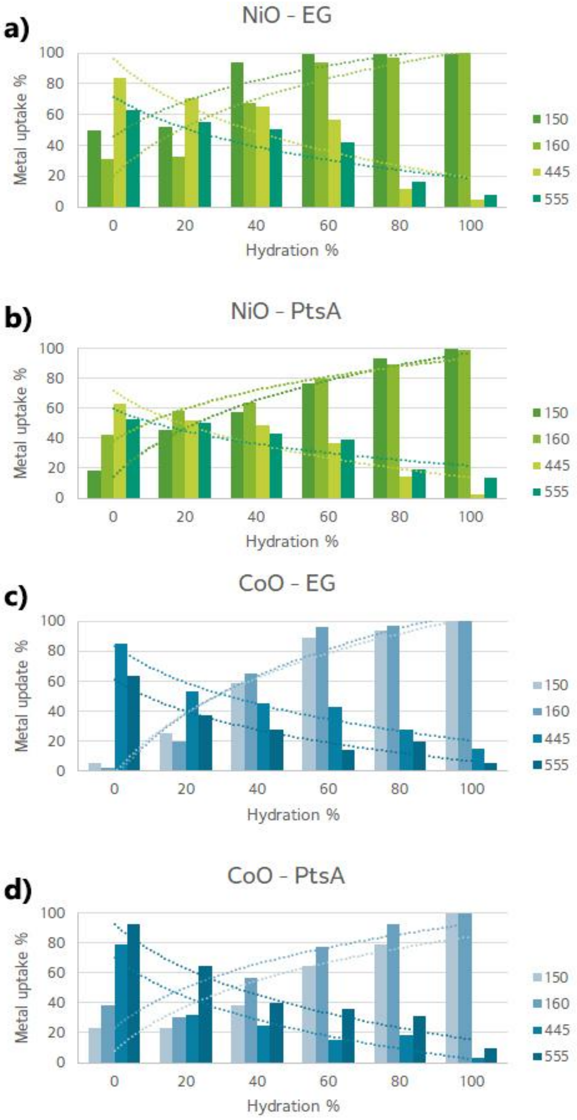

Figure 3. Single metal removal of Ni and Co from hydrated ChCl:pTSA and ChCl:EG DESs a) NRW150, b) NRW160, c) PFA445, and d) A555.

3.8 Multi-Metal Uptake via Ion Exchange (IX)

The selective separation and recovery of Ni and Co are essential for applications in nuclear waste management, spent lithium-ion battery recycling, and mining. Batch IX experiments were conducted using Ni-Co DES solutions to evaluate metal uptake behaviour under varying hydration conditions.

3.8.1 Cation Exchange Resin Uptake of Ni^{2+} and Co^{2+}

At low hydration levels (0-30 %), high DES viscosity and strong metal-ligand interactions restricted ion mobility, limiting uptake. Co, forming weaker complexes than Ni, was preferentially removed at this stage. As hydration increased (30-60 %), viscosity decreased, and metal complexes dissociated, improving Ni^{2+} and Co^{2+} availability. Due to its higher charge density, Ni^{2+} showed stronger binding at higher hydration, leading to similar uptake levels for both metals. At 60-80 % hydration, Ni^{2+} uptake surpassed Co^{2+} due to its greater affinity for resin active sites, with near-complete removal achieved at 80-100 % hydration.

3.8.2 Anion Exchange Resin Uptake via Anionic Complexes

At low hydration (0-30 %), Ni and Co predominantly existed as stable anionic chloride complexes ($[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$), enabling effective removal by anion resins. Ni formed more stable complexes than Co, resulting in a slightly higher uptake. As hydration increased (30-60 %), solvation weakened chloride complex stability, reducing the selectivity difference between Ni and Co. At high hydration (60-80 %), complex dissociation led to minimal uptake, as stable anionic species were no longer present.

In summary, cation resins were most effective at high hydration, while anion resins performed best at low hydration, allowing selective separation based on hydration-dependent speciation. Metal removal efficiency was confirmed via ICP-OES analysis.

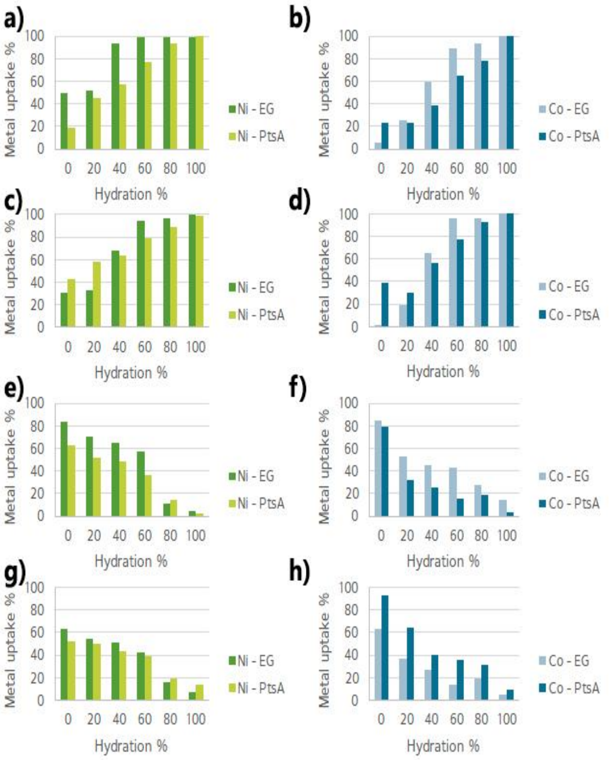

Figure 4. Species separation of Ni and Co in DES solutions, ChCl:pTSA and ChCl:EG with varying hydration and subsequent removal with IX resins a – b) NRW150, c-d) NRW160, e-f) PFA445 and g-h) A555.

4. Conclusion

This study demonstrated the dissolution, selective separation, and recovery of Ni and Co using DES across different hydration levels. Dissolution efficiency was highest at around 20 % hydration, with near-complete dissolution (~75-80 %) for both metals, while full dissolution occurred in pure DES. Hydration played a key role in metal speciation, shifting from anionic chloride complexes ($[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$) in non-hydrated DES to hydrated cations ($[Ni(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$) in water, enabling controlled separation through ion exchange.

Cation exchange resins effectively removed Ni^{2+} and Co^{2+} at higher hydration levels, while anion resins were most efficient at low hydration, capturing anionic species. However, as hydration increased, complex stability decreased, reducing anion resin performance. Optimising ion exchange conditions based on solvation environments enhances metal recovery, supporting sustainable recycling efforts. The DES-IX system provides environmental advantages, including reduced solvent volatility, lower energy requirements, and minimal bioaccumulation risks, positioning it as a promising approach for efficient and eco-friendly metal recovery.

REFERENCES

[1] Amphlett JTM, Ogden MD, Wang W, Choi S, Probing Ni2+ and Co2+ speciation in carboxylic acid based deep eutectic solvents using UV/Vis and FT-IR spectroscopy, J. Mol. Liq. 318: 114217 (2020)

[2] Smith EL, Abbott AP and Ryder KS, Deep Eutectic Solvents (DESs) and Their Applications, Chem. Rev. 114: 11060-11082 (2014).

[3] Amphlett JTM and Choi S, The effect of increasing water content on transition metal speciation in deep eutectic solvents, J. Mol. Liq. 332: 115845 (2021).

[4] Nayoung Kim, Wonseok Yang, James Amphlett, Dokyu Kang, Yunu Lee, Jae Joon Kim, Ho Jin Ryu, Sungyeol Choi, Surface decontamination of protective duplex oxide layers on stainless steel waste using deep eutectic solvents, J Hazard Mater. 425: 128000 (2022).