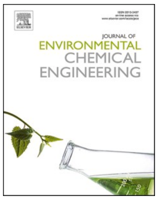
Journal of Environmental Chemical Engineering 12 (2024) 114070

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Sorption strategies for recovering critical raw materials: Extracting trace elements from saltworks brines

V. Vallès [a,b,*], M. Fernández de Labastida [a,b], O. Gibert [a,b], A. Leskinen [c], R.T. Koivula [d], J. López [a,b], J.L. Cortina [a,b,e]

[a] *Chemical Engineering Department, Escola d'Enginyeria de Barcelona Est (EEBE), Universitat Politècnica de Catalunya (UPC)-BarcelonaTECH, C/ Eduard Maristany 16, Campus Diagonal-Besòs, Barcelona 08019, Spain*
[b] *Barcelona Research Center for Multiscale Science and Engineering, C/ Eduard Maristany 16, Campus Diagonal-Besòs, Barcelona 08019, Spain*
[c] *Nuclear Safety, VTT Technical Research Centre of Finland Ltd., P.O. Box 1000, Espoo FI-02150, Finland*
[d] *Department of Chemistry-Radiochemistry, University of Helsinki, P.O. Box 55, Helsinki FI-00014, Finland*
[e] *CETaqua, Carretera d'Esplugues, 75, Cornellà de Llobregat 08940, Spain*

ARTICLE INFO

Keywords:
Aminophosphonic
Bis-(2,4,4-trimethylpentil-) phosphinic
Sodium titanium oxide hydrate
Zirconium oxide
Copper (II) hexacyanoferrate
Critical raw materials
Chelating sorbents

ABSTRACT

Rising population, industrialisation, and resource demand intensify resource limitations, particularly critical for European Union (EU) industries dependent on raw materials. Based on economic importance and supply risk, 32 Critical Raw Materials (CRMs) and two strategic raw materials were identified in 2023. With most CRMs sourced outside the EU, sea mining emerges as a promising secondary resource for CRMs extraction from seawater, although the harvest of Trace Elements (TEs) will require energy-intensive processes. Several EU-funded projects explore circular economy and resource recovery, considering sorption methods' potential to extract TEs from brines. Commercial polymeric (IRC747, S940, MTX8010) and inorganic (SbTreat, SrTreat) sorbents, plus another synthesised inorganic one (CuHCF), were assessed for recovering TEs (cobalt, gallium, germanium, rubidium, strontium, caesium) from saltworks brines (bitterns). Polymeric sorbents, containing chelating functional groups, effectively targeted cobalt, gallium, and strontium, commercial inorganic sorbents favoured cobalt, gallium, germanium and strontium, and CuHCF targeted rubidium and caesium. Kinetic batch experiments demonstrated rapid element retention ($\leq$30 min) by most sorbents. In dynamic column experiments, high sorption capacities were observed for cobalt and gallium with the polymeric sorbents, particularly for aminophosphonic sorbents (IRC747 and S940) ($\geq$2.1 mg/g). SrTreat exhibited also a high sorption capacity of 7 mg/g for strontium, SbTreat achieved 20 mg/g for gallium and germanium and CuHCF retained rubidium (10 mg/g) and caesium (70 mg/g). Acidic desorption effectively recovered (>70 %) most of the elements from the sorbents, achieving concentration factors up to 708 for cobalt with IRC747 and S940, highlighting the potential valorisation of saltworks bitterns.

1. Introduction

The increasing population, industrialisation and demand for raw materials extremely raise the current resources constraint [1]. These facts highlight a growing concern since, without the proper resources, industries in the European Union (EU) and around the world will not be able to restock their raw materials, which are crucial to move forward on their production and, therefore, for their economy. Considering the economic importance of these raw materials and their supply risk, 14 Critical Raw Materials (CRMs) for the EU were initially identified and listed in 2011. Since then, the list has been reviewed several times and in its last update (in 2023), it was enlarged to 32 CRMs and two additional Strategic Raw Materials (SRMs) (some CRMs had been also considered SRMs) [2].

Since most of the CRMs/SRMs are mainly supplied by countries outside the EU, diversification of supply, recycling, reuse and resource efficiency are driving the EU's attention to develop domestic production and processing capacities [3]. In fact, the EU is launching initiatives, such as the European Green Deal [4] and the European Critical Raw Materials Act [5] aiming to enhance resource efficiency and promote the recovery of raw materials from secondary sources. For instance, several research projects focused on circular economy and resource recovery are

---

[*] Corresponding author at: Chemical Engineering Department, Escola d'Enginyeria de Barcelona Est (EEBE), Universitat Politècnica de Catalunya (UPC)-BarcelonaTECH, C/ Eduard Maristany 16, Campus Diagonal-Besòs, Barcelona 08019, Spain.
E-mail address: victor.valles.nebot@upc.edu (V. Vallès).

https://doi.org/10.1016/j.jece.2024.114070
Received 8 May 2024; Received in revised form 30 August 2024; Accepted 4 September 2024

being funded by the EU [6,7], some of them promoting the sea mining concept to recover raw materials (critical or not) from seawater brines [8,9]. Seawater has been considered a promising secondary source for extracting CRMs and SRMs as it encompasses nearly every element found in the periodic table [10], despite the fact that most of them are often at concentrations below the mg/L range and, in certain instances, at μg/L levels [11]. In this case, they are often referred to as Trace Elements (TEs). Some minerals have been extracted from seawater since ancient times [12,13]. However, TEs recovery is not economically feasible due to the energy-intensive process needed to recover them [14–16].

Brines are often preferred over seawater since they are more concentrated and therefore mineral and raw materials extraction is easier [17]. Nowadays, the attention is focused on *bitterns*, which are produced as a consequence of solar and wind evaporation of seawater in saltworks [18]. The bittern, which represents the residual brine produced after reaching NaCl crystallisation, is a Ca-free solution up to 40 times higher concentrated than seawater [19]. Despite this fact, most of the TEs are still at μg/L levels. For this reason, sorption methods (i.e. adsorption, ion exchange, solid-phase extraction) should be considered for the recovery of these elements from seawater and/or brines, due to their low-cost operation, sorbents' high variety and selectivity, and long lifetime, since sorbents can be reused many times [20–23].

Sorbents' potential to recover valuable elements has been proven over the years, although the research on TEs sorption extraction from brines is still very scarce (from bitterns almost inexistent [24]). CsTreat, a highly selective commercial hexacyanoferrate compound ($K_2CoFe(CN)_6$) for Cs removal, was evaluated by Gibert et al. [25] in column mode targeting Cs and Rb. Sorption capacities of 44 and 238 mg/g for Cs and Rb, respectively, were achieved with a Cs and Rb spiked (20 mg/L) Seawater Reverse Osmosis (SWRO) brine (i.e. 70 g/L NaCl, 6.4 g/L SO_4^{2-}, 2.5 g/L Mg^{2+}). Furthermore, Peterková et al. [26] doped this brine up to 5–80 mg/L of both Cs and Rb to perform batch equilibrium sorption tests. In this case, 32 and 47 mg/g Langmuir maximum sorption capacities (Q_{max}) were reported for Cs and Rb, respectively. In batch mode, Naidu et al. [27] demonstrated that KCuFC presented a higher Langmuir maximum sorption capacity towards Rb (Q_{max}=144 mg/g) after testing several different synthesised hexacyanoferrate compounds (KCuFC, KNiFC, KCoFC and KFeFC). Additionally, a new sorbent (KCuFC-PAN) was also prepared after encapsulating the compound with better performance (KCuFC) in polyacrylonitrile (PAN). This new sorbent presented a Q_{max} of 105 mg/g for Rb. When testing it against a simulated SWRO brine ($6\cdot10^{-5}$ M Rb, 0.2–2.5 M NaCl) with a 0.2 $g_{sorbent}/L_{brine}$ dose, its sorption capacity was reduced by 12–30 %. However, when K was also present in the SRWO brine (0.5 M), the Rb uptake capacity of the sorbent decreased by 65–70 %. When KCuFC-PAN was evaluated in column mode, the authors reported an 86 mg/g Rb sorption capacity and a 95 % recovery after desorbing it with 0.2 M KCl. The sorption capacity towards Rb was only reduced by 16 % after applying a new sorption-desorption cycle. Several commercial sorbents (CsTreat, Ammonium Molybdophosphate (AMP), a natural zeolite and Amberlite FPC 3500) and a Resorcinol Formaldehyde (RF) synthesised sorbent were compared by Nur et al. [28] in terms of Sr removal. Among them, the highest uptake (>95 %) was achieved by the Na-form of RF when ≥1 $g_{sorbent}/L_{solution}$ doses for all sorbents were used against 10 mg/L Sr mono-component solutions. Since Ca and Mg are the main competitors for Sr, its sorption was reduced to 40–60 % (depending on the dose) when synthetic seawater (20 g/L Na, 2 g/L Mg, 1 g/L Ca, 0.85 g/L K and 0.01 g/L Sr) was evaluated. Desorption experiments were also performed with 1 and 2 M NaCl and NaOH. However, only NaCl was effective at desorbing >90 % of Sr when 0.1 g of saturated RF was tested with 100 mL of solution. In addition, RF column mode experiments were also conducted using Sr (10 mg/L) mono-component solution, the synthetic seawater previously described, and the synthetic seawater without Ca and Mg. Sorption Sr capacities of 22, 6 and 11 mg/g were reported, respectively, which demonstrated the influence of potential competitors on Sr sorption. In a study conducted by Arroyo et al. [29], Li recovery from brines was evaluated by applying commercial polymeric sorbents containing sulphonic (K2629) and iminodiacetic (TP207 and TP208) functional groups. The researchers found that, with a 1 $g_{sorbent}/50\ mL_{solution}$, only 20 min were required to remove >95 % of Li from 10 mg/L mono-component solutions. After sorbents saturation, an elution was performed with 50 mL of HCl, desorbing 74–87 % of Li with 3 M HCl and 80–90 % with 4 M HCl. The sorbents were subsequently reused after converting them to H- and Na-form. Whereas 98 % Li was removed by all sorbents in their Na-form, the H-form of TP207 and TP208 presented lower removals of 52 % and 40 %, respectively. Although Li removal was successfully demonstrated with synthetic solutions, testing the sorbents against real SWRO brines (15.3 g/L Na^+, 28.7 g/L Cl^-, 4.60 g/L SO_4^{2-} and 0.60 mg/L Li^+) showed only 30–80 % of Li retention, depending on the functional group of the sorbent and the dose used (0.2 or 0.4 $g_{sorbent}/mL_{solution}$). These studies collectively demonstrate the potential for recovering low-concentrated valuable elements from seawater brines. Considering the current state-of-the-art, there is a huge research scarcity devoted to extract elements in the order of μg/L in high salinity media, as the case of seawater saltworks bitterns. Furthermore, the current policies are pushing research to develop alternative routes for mineral extraction from secondary wastes, as the bitterns. In fact, Randazzo et al. [17] recently estimated that the valuable minerals that could be extracted from each cubic meter of bittern produced in the Mediterranean region would lead to a gain of 190 €. For example, considering an average composition of the bitterns, the authors reported that up to 1116, 0.28 and 0.70 tons/year of Li, Ga and Ge would be respectively produced from bitterns only in the Mediterranean basin, which represent 0.3 %, 0.1 % and 0.5 % of the global corresponding element production. Therefore, the present work aims to fill the gap by evaluating different polymeric and inorganic sorbents to selectively extract Co, Ga, Ge, Rb, Sr and Cs from saltworks bitterns. More in detail, this work investigates the performance of polymeric sorbents containing aminophosphonic functional groups (IRC747 and S940), impregnated organo-phosphinic functional groups (MTX8010) and inorganic sorbents (SbTreat (sodium titanium oxide hydrate), SrTreat (zirconium oxide) and CuHCF (copper (II) hexacyanoferrate)) to recover TEs (Co, Ga, Ge, Rb, Sr, Cs) from saltworks bitterns. The sorbents selected were identified in a previous work [24], where different sorbents were evaluated in batch mode with synthetic bitterns to evaluate the extraction and elution performance. In this work, the sorption kinetics were firstly evaluated in batch tests. Then, dynamic column experiments were conducted under different conditions to assess the effect of competing ions on the sorbent capacity of each TE. Finally, elution was evaluated to determine the concentration factor and recovery percentage for each TE.

2. Materials and methods

2.1. Chemicals

Synthetic solutions were used in all the experiments performed. The following analytical grade chemicals were used to prepare those solutions: LiCl (Sigma-Aldrich and Merck), H_3BO_3 (Sigma-Aldrich and VWR), $CoCl_2\cdot6H_2O$ (Alfa Aesar and Merck), Rb_2CO_3 (Sigma-Aldrich), RbCl (Merck), $SrCl_2\cdot6H_2O$ (Alfa Aesar and J.T. Baker), CsCl (Glentham LIFE SCIENCES and Merck), NaCl (Glentham LIFE SCIENCES and Merck), KCl (Sigma-Aldrich and Merck), $MgCl_2\cdot6H_2O$ (Sigma-Aldrich and Merck), $CaCl_2\cdot2H_2O$ (Sigma-Aldrich and Merck), NaBr (Sigma-Aldrich and VWR), Na_2SO_4 anhydrous (Glentham LIFE SCIENCES and Supelco), NaOH (Glentham LIFE SCIENCES and J.T. Baker), 37 % HCl (Sigma-Aldrich), 95–97 % H_2SO_4 (Merck), 10,000 mg/L Ge ICP Standard (Alfa Aesar), 1005 mg/mL Ge AAS standard (Sigma-Aldrich) and 10,000 mg/L Ga ICP Standard (Alfa Aesar and J.T. Baker).

2.2. Sorbents

Up to six different sorbents were evaluated in the present study, including three polymeric and three inorganic ones. Their main properties are collected in Table S1. Among the polymeric ones, MTX8010 is an impregnated sorbent containing the bis-(2,4,4-trimethylpentil-) phosphinic acid, while the others (IRC747 and S940) are microporous chelating sorbents with aminophosphonic functional groups. Among the three inorganic sorbents, CuHCF is a Cu-hexacyanoferrate compound synthesised for the present study, while the others (SrTreat and SbTreat) are commercial Nures® sorbents. CuHCF was synthesised by adopting a recipe from Harjula et al. [30] using $CuSO_4$ as a source, to facilitate easier elution of Cs and Rb, compared to CsTreat, from sorbents tested in a previous study [24]. SrTreat has a sodium titanium oxide hydrate structure, whereas SbTreat has a zirconium oxide structure.

The polymeric sorbents were conditioned before using them. The conditioning procedure consisted of agitating for 1 h the sorbents with 1 M NaOH under magnetic stirring, keeping a solid/liquid ratio of 20 $g_{sorbent}/L_{solution}$. Then, to displace the NaOH excess, several washes with deionised water were applied to the sorbents until a neutral pH was achieved. MTX8010 was only washed with deionised water, as exposure to NaOH causes the removal of the active extractant impregnated on the sorbent. The inorganic sorbents were not conditioned before the experiments.

2.3. Model solution composition

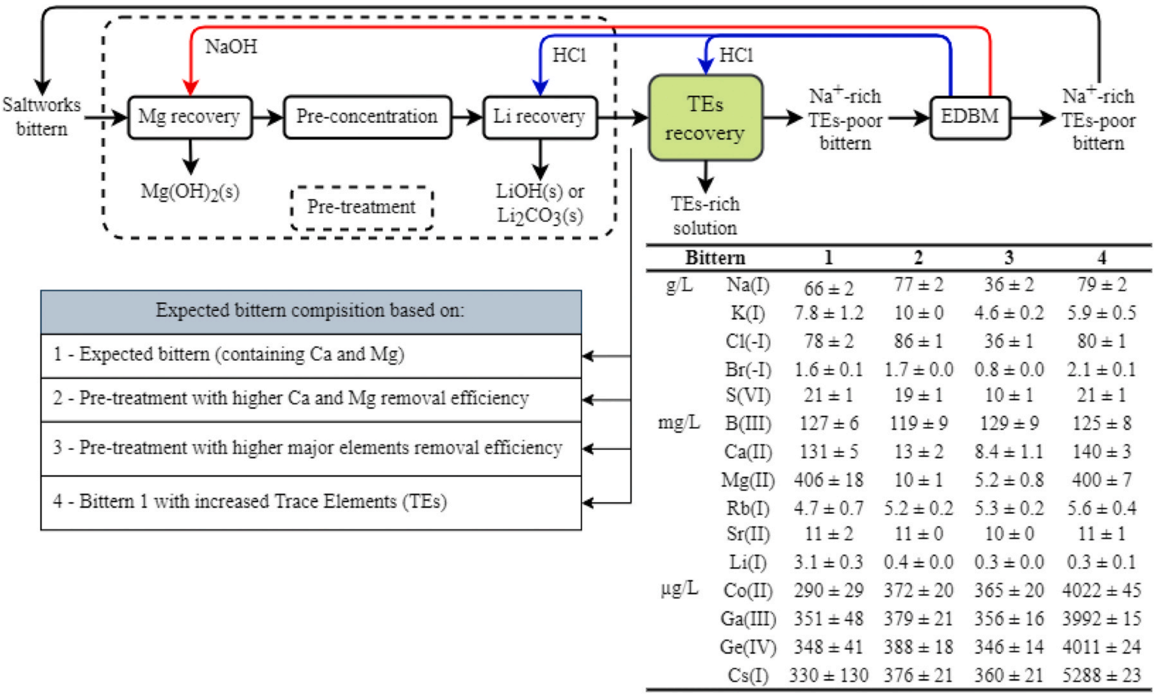
Model solutions were prepared to simulate different bittern compositions typically found after the pre-treatment of the bittern valorisation cycle developed in the SEArcularMINE project. This project is one of the EU-funded projects that aims to recover CRMs and SRMs specifically from the solar saltworks bitterns, targeting selectively Mg, Li, B and other TEs (Sr, Cs, Rb, Co, Ga, Ge) [9]. The valorisation cycle comprises a first stage aimed at the recovery of Mg via precipitation as $Mg(OH)_2(s)$ with NaOH [31,32]. Then, the clarified bittern goes to a pre-concentration step, after which Li and subsequently other TEs are recovered [24,33–35]. Electrodialysis with bipolar membranes (EDBM) constitutes the last step of the process which guarantees the circularity of the process, as both NaOH and HCl are produced from the exhausted bittern by applying an external electric field [36,37]. A scheme of the circular approach is represented in Fig. 1, where those elements in g/L are considered major elements, and those in mg/L or µg/L are considered minor elements or TEs.

Considering that different efficiency removals could be achieved along the stages included in the pre-treatment section represented in Fig. 1, four synthetic bitterns (adjusted to pH≈7 considering the expected bicarbonate values in the bitterns) were prepared for the purpose of the present study:

- Bittern 1: bittern expected to be received at the TEs-recovery unit (see Fig. 1) after the pre-treatment stages as a most conservative scenario, considering Ca and Mg low removal in the pre-treatment.
- Bittern 2: bittern expected to be received at the TEs-recovery unit after the pre-treatment stages, but with low content of Ca and Mg (<0.02 g/L). According to the results reported by Battaglia et al. [32], higher Ca and Mg removals have been considered in the pre-treatment compared to bittern 1.
- Bittern 3: bittern expected to be received at the TEs-recovery unit after the pre-treatment stages, but with low content of Ca and Mg (<0.02 g/L) and lower concentration of major elements. It is assumed that a lower concentration factor would be achieved in the pre-concentration step.
- Bittern 4: bittern 1 after increasing the TEs' (Co, Ga, Ge, Cs) concentration up to 5 mg/L to achieve the inorganic sorbents' saturation on these elements.

2.4. Sorbents' kinetic performance in metal extraction batch experiments

The kinetic performance of each sorbent was determined by evaluating the extraction of the elements in solution after spending several hours in contact under magnetic stirring (polymeric sorbents) in a beaker or axial rotation in a vial (inorganic sorbents) with bittern 1, therefore evaluating the sorbents with the most conservative scenario. A solid/liquid ratio of 30 $g_{sorbent}/L_{bittern}$ (or batch factor (BF) of 33 mL/g) was used. The pH and composition of the bittern were monitored at 10, 20 and 30 minutes and after each hour. A maximum contact time of 7 h



	Bittern	1	2	3	4
g/L	Na(I)	66 ± 2	77 ± 2	36 ± 2	79 ± 2
	K(I)	7.8 ± 1.2	10 ± 0	4.6 ± 0.2	5.9 ± 0.5
	Cl(-I)	78 ± 2	86 ± 1	36 ± 1	80 ± 1
	Br(-I)	1.6 ± 0.1	1.7 ± 0.0	0.8 ± 0.0	2.1 ± 0.1
	S(VI)	21 ± 1	19 ± 1	10 ± 1	21 ± 1
mg/L	B(III)	127 ± 6	119 ± 9	129 ± 9	125 ± 8
	Ca(II)	131 ± 5	13 ± 2	8.4 ± 1.1	140 ± 3
	Mg(II)	406 ± 18	10 ± 1	5.2 ± 0.8	400 ± 7
	Rb(I)	4.7 ± 0.7	5.2 ± 0.2	5.3 ± 0.2	5.6 ± 0.4
	Sr(II)	11 ± 2	11 ± 0	10 ± 0	11 ± 1
	Li(I)	3.1 ± 0.3	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.1
µg/L	Co(II)	290 ± 29	372 ± 20	365 ± 20	4022 ± 45
	Ga(III)	351 ± 48	379 ± 21	356 ± 16	3992 ± 15
	Ge(IV)	348 ± 41	388 ± 18	346 ± 14	4011 ± 24
	Cs(I)	330 ± 130	376 ± 21	360 ± 21	5288 ± 23

Fig. 1. Scheme of SEArcularMINE process outline for saltworks bittern and composition of the synthetic bitterns. Adapted from Vallès et al. [38].

was considered for inorganic sorbents due to their high selectivity nature [24], whereas for polymeric ones, the test was prolonged to 24 h. The sorption or extraction efficiency (%) of a certain element was determined by Eq. (1).

$$Sorption = 100\%\cdot\frac{C_0 - C_t}{C_0} \tag{1}$$

Where C_0 and C_t are the measured concentration (mg/L or μg/L) of an element in the bittern before starting the experiment and at time t, respectively.

2.5. Dynamic metal extraction column performance

The column mode tests with polymeric sorbents were performed by filling transparent polyvinyl chloride (PVC) columns (13 mm inner diameter, 100 mm length and 67 mm maximum bed length) with the selected sorbent (2.7 ± 0.3 g). A peristaltic pump (Gilson Minipuls 3) was used to pump the inlet solution upwards through the columns. Samples were collected from the outlet of the columns with a fraction collector (Gilson Fraction Collector FC 204). To compare results from different experiments, the volume treated was converted to Bed Volumes (BV), a dimensionless parameter, following Eq. (2).

$$BV = \frac{V_t}{V_{sor}} \tag{2}$$

Where V_t is the volume (L) of solution treated by the columns at time t and V_{sor} is the volume (L) of the packed-bed of sorbent.

Column mode experiments consisted of two stages (sorption and desorption). In the first stage, bitterns were pumped through the column at 1.90 ± 0.14 BV/h (0.20 mL/min). For these tests (see Table 1), bitterns 2 and 3 were used as more realistic scenarios than the conservative bittern 1, which did not consider high Ca and Mg removal in the pretreatment. After achieving the saturation of the sorbents, 1 M HCl was inlet to the column at 0.50 ± 0.03 BV/h (0.05 mL/min) to elute the sorbed elements.

Regarding the inorganic sorbents, the column experiments were performed by filling 1 mL glass columns (Econo®, 5 mm inner diameter and 50 mm length) with SbTreat (0.6 g), SrTreat (0.8 g) and CuHCF (0.3 g). The fillings were aided with 10 mM $NaNO_3$ solution to avoid air bubbles and the consequent channelling of the column. A peristaltic pump (Gilson Minipuls 3, Watson Marlow 2058, or Ismatec IPS) was used to pump the bittern in a downward direction. Samples were collected from the outlet of the columns with a fraction collector (Pharmacia LKB-RediFrac). As the inorganic sorbents are highly selective sorption materials, the length of a column experiment until saturation can last multiple times longer than those with less selective sorption materials. Therefore, SbTreat and SrTreat columns were studied with bittern 1 and 3, respectively, with increasing flow rates of 6, 12 and 18 BV/h (0.10, 0.20 and 0.30 mL/min) to select an effective flow rate with reasonable experiment time for the subsequent set of tests. Since SrTreat was expected to target Sr, bittern 3 was initially selected for this sorbent, as the main competitors Ca and Mg were excluded. However, SrTreat was also studied with bittern 1 at 12 BV/h (0.20 mL/min) for comparison with SbTreat. The second set of column experiments was designed to simulate a pH-swing, and the experimental conditions were designed based on the experience with the sorption capacities and behaviour in column mode. Consequently, the concentration of the target TEs (Co, Ga, Ge, Cs) was increased from 500 μg/L to 5 mg/L, resulting in bittern 4. Feeding of bittern 4 at 18 BV/h (0.30 mL/min) through the columns was continued until the target elements' saturation was achieved. The subsequent desorption was performed (18 BV/h, 0.30 mL/min) with selected acid and base, namely 0.1 M NaOH and 0.1 M H_2SO_4 [24]. A new synthesised inorganic sorbent (CuHCF) targeting mainly Cs was included in this pH-swing study, as previous research by Vallès et al. [24] demonstrated that polymeric sorbents did not have high affinity towards it, and that Cs could not be recovered from the only inorganic sorbent able to capture it (i.e. CsTreat). Along the pH-swing with sorption-desorption cycles, the sorbents' integrity was studied by analysing Zr, Ti and Cu in SbTreat, SrTreat and CuHCF samples, respectively, as these elements were crucial components in the sorbents' structure. The pH-swing was repeated three times and washings (20 mL of 10 mM $NaNO_3$) were carried out between each solution change. A summary of the dynamic column experimental campaign is presented in Table 1.

Table 1
Dynamic column experimental campaign with the four bitterns.

Sorbent	Bittern			
	1	2	3	4
IRC747	-	✓	✓	-
S940	-	✓	✓	-
MTX8010	-	✓	✓	-
SbTreat	✓	-	-	✓
SrTreat	✓	-	✓	✓
CuHCF	-	-	-	✓

From the column experiments, three parameters were derived: (i) sorption capacity (q_s, mg/$g_{sorbent}$), assessing the sorbents' element uptake; (ii) the dimensionless Concentration Factor (CF, -) for each element, quantifying the degree of concentration in the eluate compared to the initial feed solution; and (iii) the Recovery ratio (R, %), evaluating the sorbents' efficacy in recovering elements during the elution/desorption step. These parameters are calculated according to Eqs. (3), (4) and (5) [38].

$$q_s = \frac{m_s}{m_{sor}} = \frac{C_0\int_0^{V_b}\left(1-\frac{C}{C_0}\right)dV}{m_{sor}} \tag{3}$$

$$CF = \frac{\frac{1}{V_d}m_d}{C_0} = \frac{\frac{1}{V_d}\int_0^{V_d} CdV}{C_0} \tag{4}$$

$$R = 100\%\cdot\frac{m_d}{m_s} = 100\%\cdot\frac{\int_0^{V_d} CdV}{C_0\int_0^{V_b}\left(1-\frac{C}{C_0}\right)dV} \tag{5}$$

Where the sorbed and desorbed mass (mg) of an element are represented by m_s and m_d; the element's concentration (mg/L) at the outlet of the column and in the feed solution are depicted as C and C_0, respectively; the volume (L) of bittern and desorption solution used in sorption and desorption stages are represented by V_b and V_d; and m_{sor} is the mass (g) of sorbent used.

It must be noticed that the flow rates used during the current research may seem low and not suitable for large-scale applications. However, converting them to BV/h units, the 0.20 mL/min used for polymeric sorbents would represent about 1.90 BV/h, whereas the 0.10 mL/min for inorganic ones would represent 6 BV/h. Therefore, considering a large pilot in which a column may contain, as example, 50 L of sorbent, those flow rates would become 95 and 300 L/h for polymeric and inorganic sorbents, respectively, which may fit with the expected ones for the upscaled scenario.

2.6. Analytical techniques

When working with polymeric sorbents, pH monitoring was performed using a glass electrode pH-meter (GLP 22, CRISON). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Mass Spectroscopy (ICP-MS) with a 5100 ICP-OES and 7800 ICP-MS (Agilent Technologies), respectively, were employed to determine the elemental composition of the samples. 2 % HNO_3 was used to dilute the samples, which were later filtered through 0.22 μm before their analysis. For the bitterns' characterisation, Cl^- and Br^- were analysed by ion chromatography (Dionex ICS-1100, Agilent Technologies). The IONPAC® AS23 anion-exchange column was used with an eluent solution consisting of a mobile phase of a mixture of 4.5 mmol/L Na_2CO_3 and 0.8 mmol/L $NaHCO_3$.

When working with the inorganic sorbents, the pH measurements were performed using a glass electrode pH-meter (Thermo Scientific Orion VersaStar) and the elemental analyses in the samples were carried out using Agilent SVDV ICP-OES and Thermo Element2 HR-ICP-MS. The samples were diluted in 1 % HNO_3 before the measurements.

3. Results and discussion

3.1. Metal extraction kinetic performance of the sorbents

The kinetic results for the polymeric sorbents are represented in Fig. S1.a-c, where only those elements that were extracted at percentages above 20 % are plotted. For IRC747 (Fig. S1.a), it can be observed that Co and Ga reached >90 % sorption in less than 10 min, in concordance with the findings of Lebron et al. [39], where the same sorbent required 20–30 min to get saturated with Co in front of a Direct Contact Membrane Distillation concentrate solution containing 49 mg/L of Co. However, Ca and Mg, which are known as competitors, also attained >90 % in that period of time, in agreement with Abusultan et al. [40]. In addition, within the first 20 min of the experiment, only 80 % of Sr was sorbed. At equilibrium (after 24 h), that value only increased to 86 %. According to the sorbents structure and the speciation of the sorbed components in solution, ion exchange is expected to be the main sorption mechanism of IRC747, in which its functional group $(–CH_2–NH–CH_2–PO_3^{2-}2Na^+)$ would have replaced the two Na^+ for the bivalent cations or the Ga-oxoacid, as represented in Fig. S2 [24,41].

Regarding S940 kinetics (Fig. S1.b), sorption of Co and Ga reached values of 86 % and 87 %, respectively, after 1 h of experiment, whilst between one and two hours were needed to achieve >90 % sorption of Co. After 24 h, 95 % Co sorption was attained, but Ga remained approximately at the same value as at the beginning of the experiment, around 85 %. Although S940 is expected to behave similarly to IRC747, neither Sr nor Ca sorption were observed at all (<15 % at equilibrium). In that case, only 50 % Mg was sorbed. The distinct performance between both sorbents may be related to the form in which they were used (Na- or H-form) as, according to the pH profile, it seems that S940 still remained in the H-form when the test was performed. Therefore, as S940 and IRC747 have the same functional group, the same sorption mechanism is expected but with its H-form $(–CH_2–NH–CH_2–PO_3^{2-}2H^+)$.

MTX8010 sorbent behaviour against bittern 1 was also tested and represented in Fig. S1.c. In that case, the sorbent was able to sorb Ga, for which an extraction of >90 % was achieved in less than 20 min. In addition, complete sorption (>99 %) was attained at equilibrium and, even after 24 h, all other elements were sorbed by less than 10 %, except for around 20 % Co. The extraction process was associated with a decrease of the bittern's pH from 7 to below 4 as the sorbent was applied in its H-form, since conditioning this sorbent with the NaOH would have caused its extractant release. According to Vaughan et al. [42] findings, the performance of the sorbent in terms of sorption capacity for Co could be improved by slightly increasing the pH during the test. According to the sorbent structure, the sorption mechanism for both Co and Ga is expected to occur as ion exchange involving two bis-(2,4,4-trimethylpentil-) phosphinic acids per each Co and three per each Ga retained, as represented in Fig. S3 [24,42].

The kinetic performance for the inorganic sorbents is represented in Fig. S1.d-f, where only those elements with extractions higher than 20 % were plotted. The SbTreat results (Fig. S1.d) show that Ga and Ge were completely removed from the solution within the first 15 min. Co sorption reached approximately 30 % in 7 h, whereas for all the other measured elements the removal percentage remained low (<10 %), demonstrating the material's excellent selectivity towards Ga and Ge. That was already expected, due to the zirconia-based material's anionic exchange character, which would fit with the oxoacid speciation of both elements, apart from the possibility of operating with inner sphere complexation [24,43]. The pH remained around 5.5 throughout the experiment. The SrTreat kinetics (Fig. S1.e) show that complete sorption was achieved within 15 min only for Ge. The target element Co achieved >99 % sorption in 1 h, whereas maximum sorption of approximately 90 % was achieved for Sr in 7 h. Ga achieved approximately 40 % sorption in 7 h whereas Li complete sorption was achieved within 2 h. The sorption percentages for Rb and Cs remained approximately at 10 % during the experiment. The pH remained just below 9 throughout the test. Due to the sodium titanium oxide hydrate structure of SrTreat, ion exchange would be the main sorption mechanism, although the Ge fast sorption might be explained by the possibility of hydrogen bonds formation between its neutral oxoacid species and the sorbent's structure [44]. The CuHCF results (Fig. S1.f) show that Cs and Ge complete sorption was achieved within 15 min, whereas 1 h contact time was needed for Rb. Relatively fast sorption was also seen for Co, which was almost totally sorbed in 3 h. Sr reached approximately 30 % sorption and Ga around 80 % in 7 h. While the most accepted mechanism for Cs sorption is its ion exchange with the K^+ (or other alkali metals) present in hexacyanoferrate compounds [45,46], the neutral Ge-oxoacid would probably be sorbed via formation of hydrogen bonds with the cyanide group of CuHCF structure.

3.2. Column operation performance of the sorbents in the metal extraction processes from model bitterns

3.2.1. Metal extraction performance with polymeric sorbents

Fig. 2 represents the breakthrough and elution curves obtained as a function of the volume treated expressed as BV when testing the polymeric sorbents with bittern 2 presenting low Ca and Mg content. Both aminophosphonic sorbents (IRC747 and S940) were tested until 2600 BV (Fig. S4), but to better visualize their behaviour the graphs were plotted until 100 BV.

The major elements are represented in Supplementary Information (Fig. S5), as most of them were not retained by the sorbents and, therefore, the concentrations at the inlet and outlet were the same ($C/C_0=1$) in just 1–2 BV. A similar behaviour was observed for some of the TEs (Li, Rb, Cs), especially when testing S940. When using IRC747, around 18 BV and 32 BV were needed to get the sorbent saturated with Sr and Ge, respectively, while only 2 BV for Cs and 5 BV for Li and Rb were required. When using S940, Sr also required 18 BV, but Li, Ge, Rb and Cs were not retained. Both sorbents had an extreme affinity towards Co and Ga and, although a slight increase in C/C_0 (0.2–0.3 along the first 100 BV) was observed, after 2600 BV they did not even reach a C/C_0 of 0.1. In addition, it can also be regarded that IRC747 got completely saturated with Ca and Mg (Fig. S5) after treating 80 BV and 188 BV, respectively, while 24 BV and 80 BV were needed with S940 for both Ca and Mg. As already mentioned in Section 3.1, the main sorption mechanisms explaining the affinity of both IRC747 and S940 towards the retained TEs would be ion exchange phenomena, as represented in Fig. S2 [24,41].

Regarding their desorption, both sorbents presented practically the same behaviour, where 7 BV of 1 M HCl were needed to completely elute the sorbed elements from them. Regarding the IRC747, peaks of maximum concentration were around 120 mg/L of Sr and 546 mg/L Co. However, peaks of 1.4 g/L Mg and 460 mg/L Ca were also achieved. No peak of Ga was observed at all (<1 mg/L), even though it was retained in the sorbent. Concerning the S940, the same behaviour was observed. In this case, the peaks for Sr and Co reached values of 108 and 545 mg/L. Nevertheless, 1.4 g/L and 440 mg/L of Mg and Ca, respectively, were also present in the eluate. Although it was only tested for a $LiHCO_3$ brine (1.4 M) containing Ca and Mg (≈35 mg/L), Yi et al. [47] reported that 1 M HCl, the same solution used in the present study, successfully eluted the sorbed elements in IRC747. Similar to IRC747, Ga was not present in the eluate either (<1 mg/L).

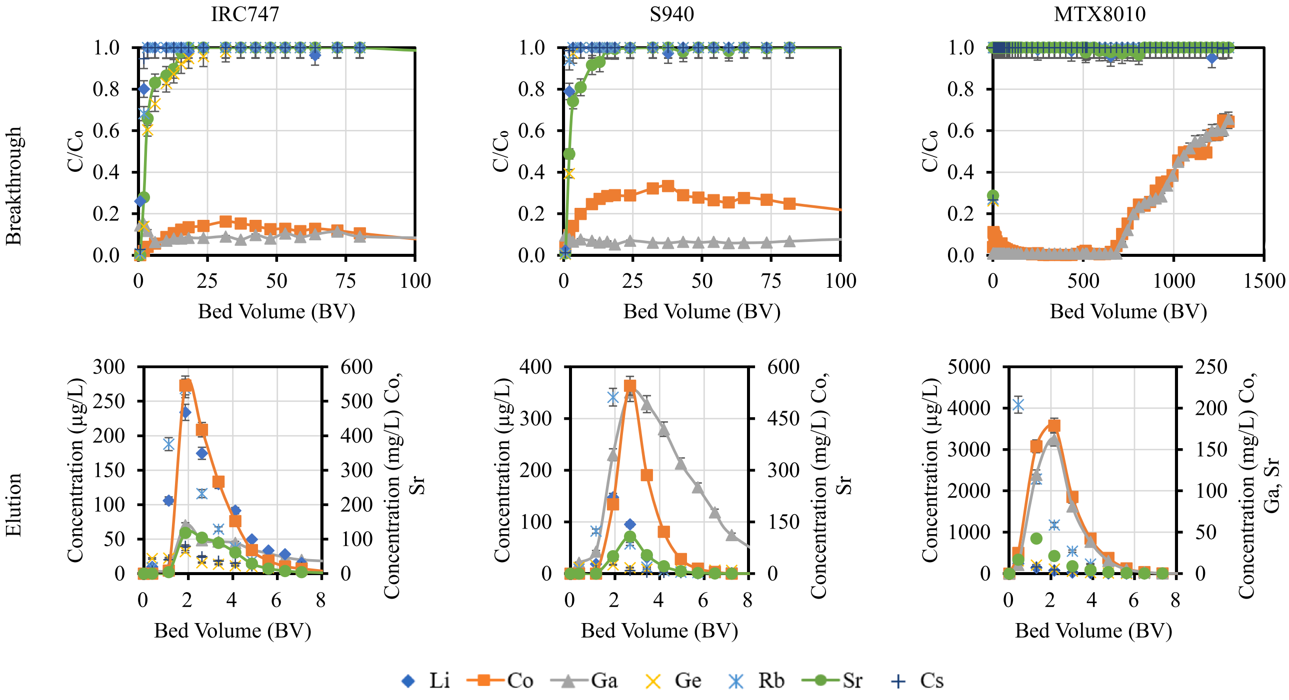


Fig. 2. Breakthrough and elution curves of TEs as a function of the BV for the IRC747, S940 and MTX8010 sorbents using the bittern 2. Sorption: 1.90 ± 0.14 BV/h. Elution: 0.50 ± 0.03 BV/h using 1 M HCl.

In the case of the impregnated sorbent MTX8010, despite being able to retain Ca and Mg for 124 BV and 186 BV, the elements for which this sorbent exhibited the highest affinity were Co and Ga, as their breakthrough started once 650 BV were treated. Although around 1300 BV were treated until the experiment was finished, the sorbents did not get completely saturated with these two elements, as the last and highest C/C_0 value obtained was around 0.7. The rest of TEs were not sorbed by MTX8010. This impregnated sorbent is expected to sorb these elements for which it presented affinity by an ion exchange process in which the retained element would have displaced the proton of two bis-(2,4,4-trimethylpentil-) phosphinic acids in the case of bivalent cations (Co^{2+}, Ca^{2+} and Mg^{2+}) and three in the case of Ga ($H_4GaO_4^-$), as represented in Fig. S3 [24,42].

For this sorbent, 7 BV of 1 M HCl were also needed to finish the elution of the sorbed elements. In that case, the Ca and Mg maximum concentrations achieved were around 86 and 137 mg/L. Regarding the

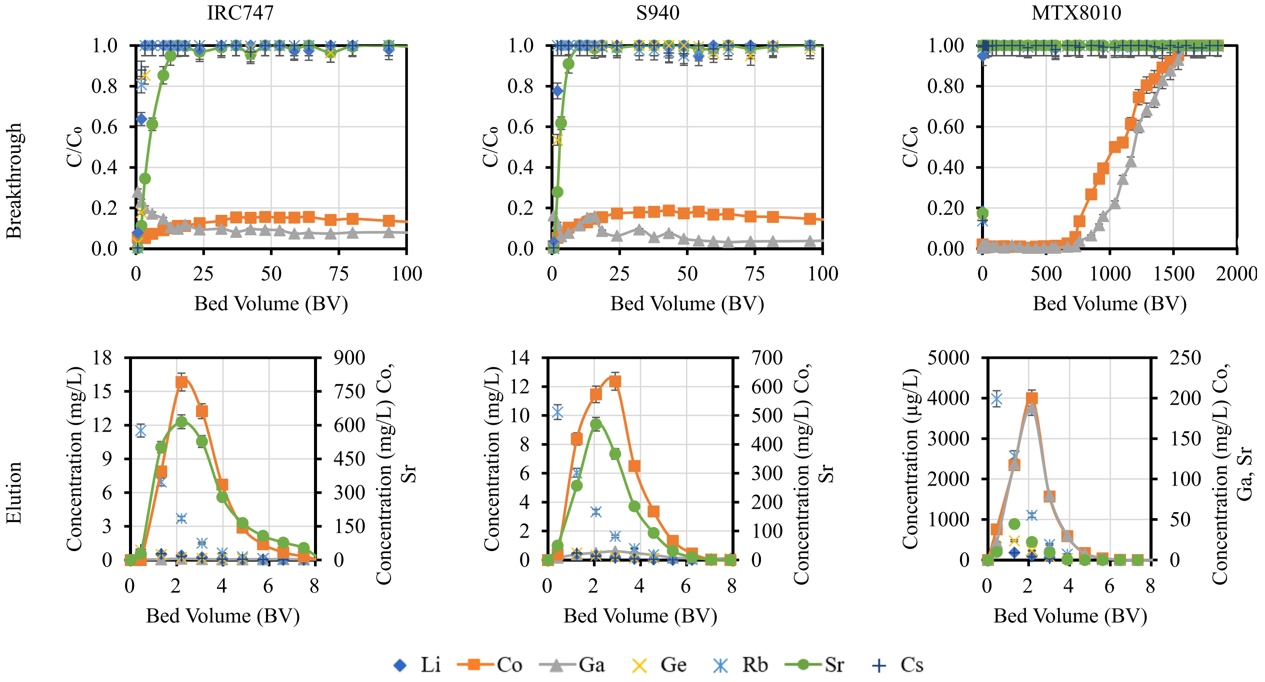


Fig. 3. Breakthrough and elution curves of TEs as a function of the BV for the IRC747, S940 and MTX8010 sorbents using the bittern 3. Sorption: 1.90 ± 0.14 BV/h. Elution: 0.50 ± 0.03 BV/h using 1 M HCl.

only two sorbed TEs, the elution peak was attained after 2 BV, and their maximum concentration was around 180 mg/L for Co and 160 mg/L for Ga.

The breakthrough and elution profiles of the polymeric sorbents when evaluating the bittern 3 (with lower concentration of major elements and low content of Ca and Mg) are provided in Fig. 3. As with the previous bittern, aminophosphonic tests were run until 2600 BV (Fig. S6), but, for simplicity, the graphs were plotted until 100 BV. Similar to the previous case, as most of the major elements were not retained by the sorbents, they are represented in the Supplementary Information (Fig. S7).

Similar profiles were obtained to the ones shown in Fig. 2, but it took around 16 BV and 10 BV for IRC747 and S940, respectively, to get saturated with Sr. In addition, as lower content of major elements was present in the solution, the profiles of Ca and Mg were slightly displaced to a higher BV, especially for S940, whose breakthroughs started at 19 BV and 13 BV, respectively. Furthermore, 311 BV and 204 BV were treated before IRC747 was saturated with Ca and Mg, whereas 208 BV and 123 BV were respectively needed to do it with the S940. It must be highlighted that, when changing from bittern 2–3, the order of Ca and Mg profiles was inverted since the first breakthrough observed with bittern 2 was for Ca, while it was for Mg when evaluating bittern 3. This phenomenon of inverting affinities' order was already observed by Vallès et al. [38] and Louati et al. [48], who attributed it to the difference in the ionic strength of the solutions used.

In this case, the most undesirable element during the elution was Ca, whose maximum concentration reached 1.6 g/L and 1.2 g/L for IRC747 and S940, respectively. This was related to the displacement of the breakthrough point of Ca towards higher values. Additionally, the concentrations of Mg were slightly lower than in the previous case, reaching values of 947 mg/L and 775 mg/L for IRC747 and S940, respectively. Moreover, the concentration for the TEs reached higher values than in the previous case. For instance, the concentration of Sr reached 615 mg/L and 470 mg/L for IRC747 and S940, respectively, while the ones for Co were 792 mg/L and 618 mg/L. However, as it was shown in the previous experiment, no Ga could be recovered.

In the case of treating bittern 3 with MTX8010 (Fig. 3), a complete breakthrough was observed for both Co and Ga after 1600 BV, although its beginning was slightly displaced until 730 BV in this case. In addition, Ca and Mg breakthrough curves started from the first BV, and no more sorption of these elements was observed after treating 100 BV of bittern.

In this desorption stage, just 4 BV were enough to recover the elements retained by MTX8010, and maximum peaks were obtained within the 2.2 BV. In this case, maximum concentrations of Co and Ga in the elution reached 200 and 188 mg/L, respectively. However, Ca and Mg maximum concentration achieved 50 and 64 mg/L in contrast to the ones obtained with the other bittern (86 and 137 mg/L), which, in fact, was more convenient as these two bivalent cations are known as competitor elements of most of the processes along the SEArcularMINE project.

The sorption capacities, concentration factors (CFs) and recovery ratios were determined as performance parameters according to Eqs. (3)-(5), respectively, to compare the sorbents' performance after evaluating both bitterns. The recovery ratios are represented in the Supplementary Information (Fig. S8).

The polymeric sorbents presented similar TE sorption capacity values for bitterns 2 and 3 (Table 2). IRC747 showed values >2.1 mg/g for both Co and Ga, while S940 got higher values (>2.7 mg/g) for these elements. These sorption capacities for both sorbents, as shown with the ">" sign, are expected to be higher than those reported since their saturation was not achieved in this study. In the case of MTX8010, the impregnated sorbent with bis-(2,4,4-trimethylpentil-) phosphinic acid, a sorption capacity of around 0.9 mg/g was reached for both elements, although when testing bittern 2, the sorbent was not completely saturated and, therefore, the capacity could be slightly higher. Among the other TEs present in the bitterns, the only one that showed some affinity for the sorbents (0.1 mg/g) was Sr, but only for IRC747 and S940. The only major elements that were slightly retained by the sorbents were Ca and Mg. Their sorption capacities, detailed in Table 2, ranged from 0.2 to 1.5 mg/g depending on the sorbent and bittern evaluated. Regarding these two elements, it must be highlighted that all sorbents were first saturated with Ca and then on Mg, except for both aminophosphonic sorbents when evaluating bittern 3.

Table 2
Sorption capacities (in mg/g) for those elements that presented affinity for the polymeric sorbents. ">" sign refers to the fact that complete saturation was not achieved, being expected higher values than the ones reported.

Sorbent	Bittern	Co	Ga	Sr	Ca	Mg
IRC747	2	>2.2	>2.1	0.1	0.4	1.1
	3	>2.1	>2.1	0.1	1.5	0.5
S940	2	>2.7	>2.7	0.1	0.2	0.5
	3	>2.7	>2.7	0.1	1.1	0.4
MTX8010	2	>0.9	>0.9	n.r.	0.4	0.7
	3	0.8	0.9	n.r.	0.3	0.3

n.r.: not retained.

When comparing the CFs (Fig. 4), both aminophosphonic sorbents got similar values, being the highest ones those attained for Co (around 408 for bittern 2, with low content of Ca and Mg, and around 708 for bittern 3, the one with low content of major elements). Comparing the ones obtained for Sr, a similar trend was observed, with values that ranged between 3 and 4 for bittern 2 and between 17 and 25 for bittern 3. No concentration was achieved for Ga, as the highest CF obtained was 1. Finally, Ca and Mg got CFs around 9–15 and 40–60, respectively, for the bittern without Ca and Mg; while for the other one the CFs was slightly higher (60–80 for Ca and 62–73 for Mg). These results confirm the need to achieve the highest removal ratio of both Ca and Mg in the pre-treatment stages of the SEArcularMINE process to maximise the concentration of the TEs. In the case of MTX8010, reducing the concentration of the major elements did not strongly affect the CFs achieved for TEs, since they were 157–160 for Co and 133–154 for Ga. It did not affect either the values obtained for Ca (1.8–2.1) and Mg (3.4–4.5). No CF was determined for Sr, as this element was not retained by MTX8010.

As shown in Fig. S8, all elements that were retained by the polymeric sorbents were fully extracted during the desorption step with 1 M HCl, except Ga from both aminophosphonic sorbents, likely due to the strong chelate ring that could be formed [24]. However, according to the suppliers' recommendations [49,50], regenerating the sorbent with NaOH after the acid elution also aids in eluting the elements still retained in the sorbents while preparing them for reuse.

The results obtained were in concordance with the scarce literature on TEs uptake from brines. Lebron et al. [39], for example, reported a maximum theoretical exchange capacity for Co on IRC747 of 6.5 mg/g, which is in the same order of magnitude as the sorption capacities obtained (>2.1 mg/g) for both aminophosphonic sorbents in this study (IRC747 and S940), considering that they did not achieve complete saturation.

The high CFs achieved for these sorbents in the effluent of the columns allowed to obtain a TEs-rich stream. Therefore, this could be considered an alternative source to obtain these TEs by precipitation methods. For example, Ga and Co could be recovered as hydroxides by NaOH reactive precipitation after raising the pH to 5 and 10, respectively, and the subsequent addition of $Na_2SO_4(s)$ can cause $SrSO_4(s)$ precipitation. Ge can be precipitated with tannic acid or sulphide/hydrogen sulphide solutions in the form of $GeO_2(s)$ or $GeS(s)$, respectively [35]. Nevertheless, to successfully obtain these TEs precipitates, the presence of their main competitors Ca and Mg should be minimised to avoid $Ca(OH)_2(s)$, $Mg(OH)_2(s)$ and/or $CaSO_4{\cdot}2\,H_2O(s)$ precipitation.

3.2.2. *Metal extraction performance with inorganic sorbents*

Among the first set of inorganic column experiments, the same trend was observed for the selected sorbents despite evaluating different flow

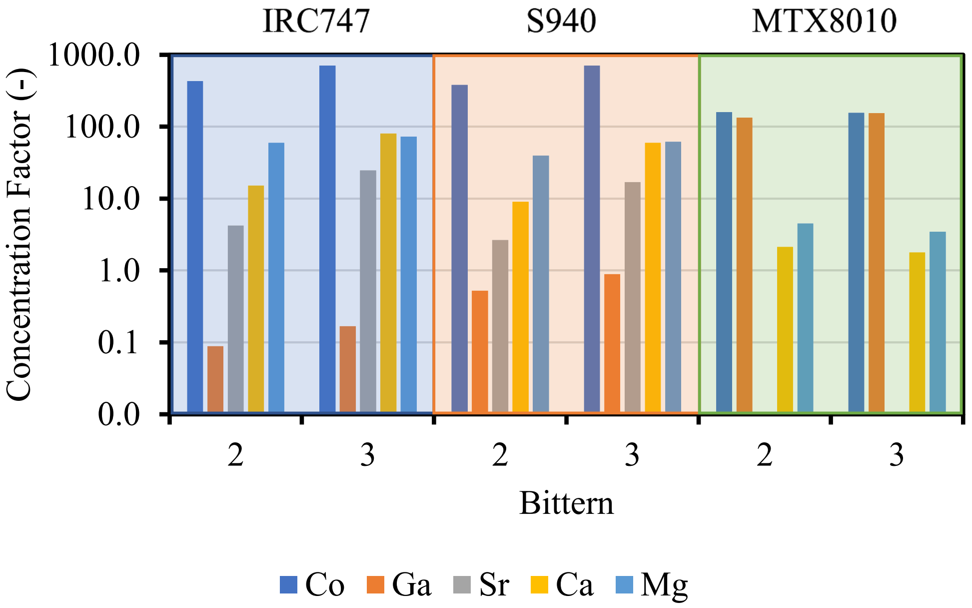


Fig. 4. Comparison of the concentration factors achieved depending on the bittern treated and on the polymeric sorbent used.

rates (6, 12, 18 BV/h). The tests performed at 12 BV/h are shown in Fig. 5, whereas those performed at 6 and 18 BV/h can be found in Fig. S9 (SbTreat, bittern 1) and Fig. S10 (SrTreat, bittern 3). For the 12 BV/h SbTreat test with bittern 1 (Fig. 5.a), Ga and Ge were fully retained up to 175 BV, whereas all other elements presented similar breakthrough curves among themselves (Li, Co, Rb, Sr, Cs – Fig. 5.a; B, Ca and Mg (i.e. major elements) – Fig. S11.a). SrTreat results with bittern 3 (with low content of Ca, Mg and major elements) at 12 BV/h (Fig. 5.b) demonstrated that the Co target element was fully retained up to 220 BV. Efficient retentions were also observed for Ga and Ge, apart from a slight delayed breakthrough for Li compared to other non-targeted elements. A slow breakthrough of Sr was observed at 120 BV, reaching a C/C_0 value of only 0.5 by the end of the experiment. When testing SrTreat also with bittern 1 (Fig. 5.c for TEs and Fig. S11.b for major elements) an early breakthrough was observed for Sr, although it did not reach complete saturation either at the end of the experiment (C/C_0=0.9 at 220 BV). This highlighted the fact that Sr sorption was affected by the presence of competing ions, especially bivalent ones such as Ca and Mg.

The sorption capacities of the inorganic sorbents SbTreat and SrTreat treating bitterns 1 and 3, respectively, with increasing flow rates are shown in Table 3. SbTreat showed a relatively constant sorption capacity for B (≈4.5 mg/g), Ca (≈1.6 mg/g), Rb (≈0.1 mg/g) and Sr (≈0.3 mg/g) for all flow rates, whereas there was no uptake for Co, Li and Cs (sorption capacity <0.05 mg/g). The total sorption capacities of target elements Ga and Ge were not reached, as already seen in Fig. 5.a. SrTreat results show that the total sorption capacities for Co, Ga, Ge and Sr were not reached either, while the one for Rb remained at 0.1 mg/g for all flow rates. Therefore, as the sorption of target elements Co and Sr from bittern 3 was efficient, the column experiment with SrTreat was repeated with bittern 1 at 12 BV/h (Fig. 5.c). Saturation of Ga, Ge and Co was not reached either, while C/C_0 of 0.9 was reached for Sr by the end of the experiment. These results show that the absence of the main competing elements, Ca and Mg, did not affect Co sorption whereas Sr sorption was lowered.

As demonstrated by the first set of SbTreat and SrTreat column results (Table 3), maximum sorption capacities for the targeted elements of SbTreat (Ga and Ge) and SrTreat (Co and Sr) were not achieved. Therefore, their maximum capacities were experimentally determined at 18 BV/h increasing the TEs' content up to 5 mg/L (bittern 4) to achieve saturation within reasonable experimental time. Since neither the inorganic nor the polymeric sorbents targeted Rb or Cs, and Vallès et al. [24] reported that another inorganic sorbent (i.e. CsTreat) was able to capture but not elute them, the CuHCF was included in this study after synthesising it following the recipe from Harjula et al. [30]. However, the small amount obtained forced to limit its application to evaluate only bittern 4 at 18 BV/h aiming to achieve its saturation. In addition, polymeric sorbents, which allowed to recover completely most of the sorbed elements, have better mechanical and chemical stability in acidic media, and sorbed elements cannot be eluted from some inorganic sorbents [51]. Thus, it was decided to study the cyclability of the three inorganic sorbents (SbTreat, SrTreat and CuHCF), during the feeding of bittern 4, along three sorption-desorption pH-swing cycles. The sorbents' integrity studies showed effectively no release of Zr and Ti from SbTreat and SrTreat, respectively. For instance, the Zr releases from SbTreat during the three pH-swings decreased in each cycle, being 0.13, 0.07 and 0.06 % (w/w), whereas Ti releases from the SrTreat were constantly about 0.28 % (w/w). However, the pH-swing treatment for the CuHCF caused a complete collapse of the material's structure (maximum of 6.0 % (w/w)) and, consequently, only one pH-swing cycle was performed.

The breakthrough curves for the target elements of SbTreat, SrTreat and CuHCF treated with the first cycle of bittern 4 are shown in Fig. 6. The second and third cycles of SbTreat and SrTreat are presented in Fig. S12 and Fig. S13, respectively. The results showed that 6000 and 7000 BV of bittern 4 were required to almost saturate SbTreat in Ga and Ge, respectively. Around 1400 BV were needed for SrTreat to saturate with Co, whereas Sr saturation was reached approximately after 400–450 BV. Lastly, CuHCF required approximately 1100 BV to become saturated with Rb, whereas Cs breakthrough needed 8000 BV to reach saturation.

According to the literature, SbTreat could operate by inner sphere complexation. Nevertheless, the performance observed for Ga and Ge, both as oxoacids species, may be better explained by the anionic exchange character related to zirconia-based materials [24,43]. In the case of SrTreat, Co and Sr would have replaced the Na^+ attached to the hydroxyl group of its sodium titanium oxide hydrate structure [44]. Although some surface sorption/precipitation is sometimes discussed within the hexacyanoferrate compounds as CuHCF, pure ion exchange with the K^+ contained in their crystal structure is the sorption mechanism typically most accepted for alkali metals such as Cs or Rb [45,46].

The desorption of inorganic sorbents, shown in Fig. 6, was carried out with 30–50 mL of 0.1 M H_2SO_4 and 0.1 M NaOH. The columns were

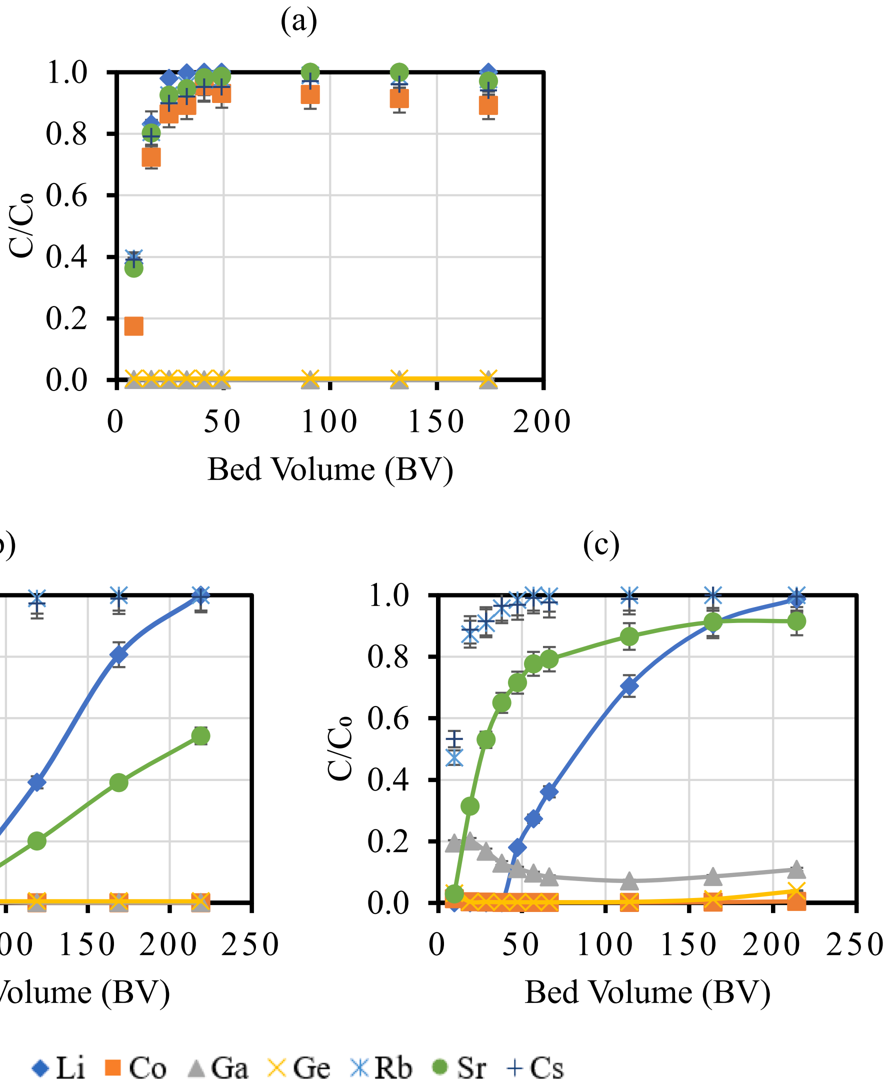


Fig. 5. Breakthrough curves of TEs as a function of the BV for the (a) SbTreat using the bittern 1 and for the (b) SrTreat using the bittern 3 and (c) the bittern 1. Sorption: 12 BV/h.

Table 3
Sorption capacities (in mg/g) of SbTreat and SrTreat in column experiments with bittern 1 and 3 and increasing flow rates.

Element	SbTreat, bittern 1			SrTreat, bittern 3			SrTreat, bittern 1
	6 BV/h	12 BV/h	18 BV/h	6 BV/h	12 BV/h	18 BV/h	12 BV/h
Li	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Co	<0.05	<0.05	<0.05	>0.1	>0.1	>0.3	>0.2
Ga	>0.1	>0.2	>0.4	>0.1	>0.1	>0.3	>0.1
Ge	>0.1	>0.2	>0.4	>0.1	>0.1	>0.3	>0.2
Rb	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sr	0.3	0.3	0.3	>2.4	>3.3	>4.0	>1.0
Cs	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B	4.7	4.4	4.5	n.a.	n.a.	n.a.	1.3
Ca	1.7	1.5	1.7	n.a.	n.a.	n.a.	6.2
Mg	6.2	5.8	5.5	n.a.	n.a.	n.a.	4.6

n.a.: not analysed.

washed with 20–30 mL of 10 mM $NaNO_3$ when changing between different solutions. The SbTreat elution results in Fig. 6 show that Ge was mainly eluted only with acid, whereas Ga was recovered with both acid and base during the first recovery cycle. However, both elements were able to be totally recovered (Fig. S14). In the subsequent pH-swing cycles, lower recoveries were achieved for Ga (70–75 %) whereas Ge recovery remained at >99 %. The Ga and Ge CFs (Fig. 7) were approximately 30–60 with 0.1 M H_2SO_4, whereas CFs with 0.1 M NaOH were 5–7 for Ge and 4–14 for Ga. The SrTreat results show that both Co and Sr were recovered only with acid, whereas Co recovery was higher (75 %) than Sr (15 %). In the subsequent pH-swing cycles Co recovery increased to >99 % whereas Sr recovery lowered to 10 %. The CFs obtained for Co were 11–15 with 0.1 M H_2SO_4 whereas the maximum CF for Sr was 2. The only recovery cycle of CuHCF showed immediate release of Cs and Rb. However, the Cs and Rb recoveries were significantly smaller (<5 %) compared to the Ga and Ge from SbTreat or the Co and Sr from SrTreat. Throughout the elution studies, optimisation of neither the contact time (i.e. lowering of the flow rate) nor the elution volume were carried out. The optimisation would have most likely increased CFs.

The sorption capacities for the three sorption-desorption cycles performed are summarised in Table 4. It was observed that the Ga sorption capacities of SbTreat were relatively constant between 22 and 23 mg/g, whereas the ones for Ge decreased mainly between the first and second cycle (17, 10 and 9 mg/g). The same trend was observed in SrTreat regarding Co sorption capacity, which lowered from 2 to 1 mg/g. However, the Sr sorption capacities were constant at 7 mg/g. In the

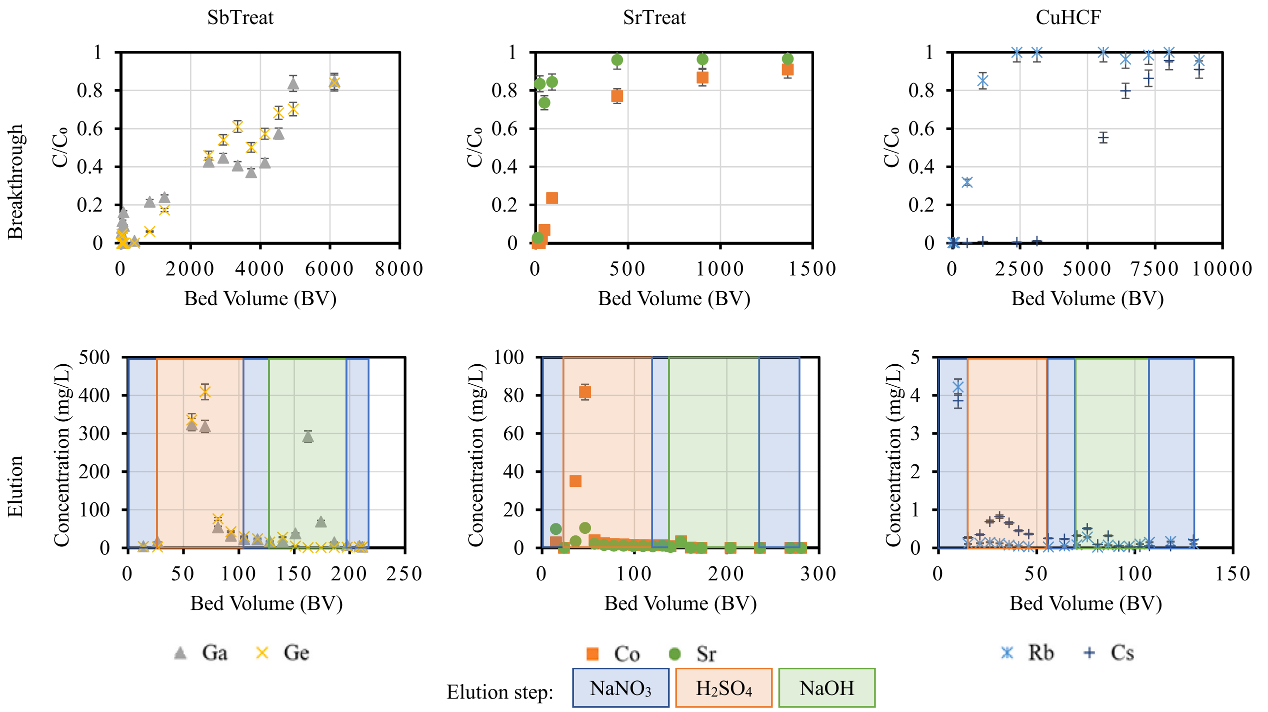


Fig. 6. Breakthrough and elution curves of target TEs as a function of the BV for the first pH-swing cycle for the SbTreat (Ga, Ge), SrTreat (Co, Sr) and CuHCF (Rb, Cs) columns using the bittern 4. Sorption and elution: 18 BV/h.

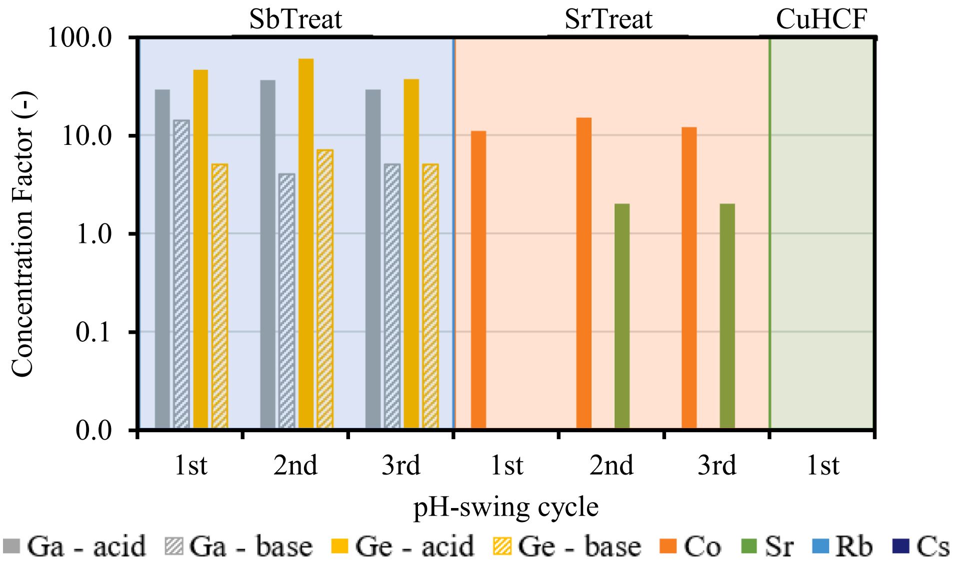


Fig. 7. Comparison of the concentration factors achieved depending on the inorganic sorbent used and the pH-swing cycle performed when using bittern 4.

Table 4
Sorption capacities (in mg/g) of targeted elements by inorganic sorbents along the sorption-desorption pH-swing cycles with bittern 4.

Sorbent	Cycle	Ga	Ge	Co	Sr	Rb	Cs
SbTreat	1	23	17	-	-	-	-
	2	23	10	-	-	-	-
	3	22	9	-	-	-	-
SrTreat	1	-	-	2	7	-	-
	2	-	-	1	7	-	-
	3	-	-	1	7	-	-
CuHCF	1	-	-	-	-	10	70

case of CuHCF, up to 10 and 70 mg/g were retained for Rb and Cs, respectively. Values in concordance with the literature were achieved in this study, since Rae et al. [52] reported a maximum Langmuir sorption capacity of 9.6 mg/g for Sr when using SrTreat whereas 1.9 mg/g was reported in their dynamic study (feed concentration of 1.5 mg/L Sr). In addition, Bok-Badura et al. [53] recently reported a Cs maximum sorption capacity of 148 mg/g for a sorbent based on CuHCF immobilized in pectin. However, when they tested the sorbent with a seawater media, this capacity decreased to 105 mg/g, which is in the range of this current study's achievements, considering that bitterns are even more concentrated than seawater.

4. Conclusions

This study evaluated several sorbents for recovering CRMs/SRMs from saltworks bitterns. Commercial polymeric sorbents (IRC747, S940, MTX8010) effectively targeted Co, Ga, and Sr, though MTX8010 showed no affinity for Sr. Among inorganic commercial sorbents, SbTreat targeted mainly Ga and Ge, while SrTreat targeted Co and Sr. CuHCF was synthesised to recover Rb and Cs.

Kinetic batch experiments demonstrated that most sorbents retained their target elements within 30 minutes, although pH fluctuations affected the performance of S940 and MTX8010.

Dynamic column experiments revealed Co and Ga sorption capacities near 1 mg/g for MTX8010 and up to 2.7 mg/g for IRC747 and S940, with potential for higher capacities since saturation was not reached for the latter two. Acidic (1 M HCl) desorption yielded high CFs, with both Co and Ga reaching 160 for MTX8010 and with Co reaching 708 for IRC747 and S940 after treating bittern 3. Nearly all elements were fully recovered during acidic desorption, although Ga desorption from IRC747 and S940 could be enhanced using NaOH. Complete saturation of the targeted elements was not achieved with the inorganic sorbents treating bitterns 1 or 3. Therefore, increasing the concentration of TEs in bittern 4 enabled SbTreat to achieve Ga and Ge sorption capacities of 20 mg/g, although Ge capacity dropped to 10 mg/g after one sorption-desorption cycle. SrTreat maintained a stable Sr capacity of 7 mg/g, but Co capacity decreased from 2 to 1 mg/g after one cycle. CuHCF, designed for Rb and Cs recovery, achieved capacities of 10 and 70 mg/g, respectively, but degraded after desorption, limiting CuHCF for a single use. pH-swing desorption fully eluted Ga and Ge from SbTreat, though Ga recovery dropped to 70–75 %, with CFs around 40. SrTreat achieved a maximum Sr recovery of 15 % and Co recovery of >99 % after the first cycle, resulting in a CF of about 10.

Overall, the current study demonstrates the potential of using sorbents for recovering CRMs/SRMs from saltworks bitterns, which have historically been considered a waste stream, constituting a promising and environmentally friendly approach.

Declaration of Competing Interest

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.

Data availability

Data will be available in Zenodo

Acknowledgements

This work was supported by the EU within SEArcularMINE (Circular Processing of Seawater Brines from Saltworks for Recovery of Valuable Raw Materials) project – Horizon 2020 programme, Grant Agreement No. 869467. This output reflects only the authors' view. The European Health and Digital Executive Agency (HaDEA) and the European Commission cannot be held responsible for any use that may be made of the information contained therein. V. Vallès research was developed under an FPI-UPC fellowship from Universitat Politècnica de Catalunya (UPC) and funded by the Banco Santander. J. López research was developed under the Margarita Salas postdoctoral fellowship from Ministerio de Universidades (MIU) and funded by the European Union-NextGeneration EU. Support for the research of J.L. Cortina was also received through the "ICREA Academia" recognition for excellence in research funded by the Generalitat de Catalunya. Finally, the Integration of waste processing technologies to ensure a safe, circular and sustainable battery value chain by promoting urban and industrial mining (MET4LIBS) project (TED2021–131583B-I00) financed by the Spanish Ministry of Science and Innovation and by the Catalan Government (ref. 2021-SGR-596) are also acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.114070.

References

[1] European Commission, Study on the EU's list of Critical Raw Materials (2020) Final Report, Publications Office of the European Union, 2020. https://doi.org/10.2873/11619.

[2] European Commission, Study on the critical raw materials for the EU 2023 – Final report, Publications Office of the European Union, 2023. https://doi.org/10.2873/725585.

[3] S. Carrara, S. Bobba, D. Blagoeva, P.Alves Dias, A. Cavalli, K. Georgitzikis, M. Grohol, A. Itul, T. Kuzov, C. Latunussa, L. Lyons, G. Malano, T. Maury, Á. Prior Arce, J. Somers, T. Telsnig, C. Veeh, D. Wittmer, C. Black, D. Pennington, M. Christou, Supply chain analysis and material demand forecast in strategic technologies and sectors in the EU – A foresight study, Luxembourg (2023), https://doi.org/10.2760/386650.

[4] European Commission, The European Green Deal, (2019). ⟨https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en⟩ (Accessed 14 February 2024).

[5] European Commission, European Critical Raw Materials Act, (2023). ⟨https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/green-deal-industrial-plan/european-critical-raw-materials-act_en⟩ (Accessed 14 February 2024).

[6] REECOVERY, Circular economy to produce critical raw materials from mining wastewater - REECOVERY, (2022). ⟨https://www.reecovery.eu/⟩ (Accessed 1 February 2024).

[7] METALLICO, Demonstration of battery metals recovery from primary and secondary resources through a sustainable processing methodology - METALLICO, (2023). ⟨https://metallico-project.eu/⟩ (Accessed 1 February 2024).

[8] SEA4VALUE, Development of radical innovations to recover minerals and metals from seawater desalination brines - SEA4VALUE, (2020). ⟨https://sea4value.eu/⟩ (accessed 15 March 2024).

[9] SEArcularMINE, Circular Processing of Seawater Brines from Saltworks for Recovery of Valuable Raw Materials - SEArcularMINE, (2020). ⟨https://searcularmine.eu/⟩ (accessed 15 March 2024).

[10] C.A. Quist-Jensen, F. Macedonio, E. Drioli, Membrane crystallization for salts recovery from brine—an experimental and theoretical analysis, Desalin. Water Treat. 57 (2016) 7593–7603, https://doi.org/10.1080/19443994.2015.1030110.

[11] P. Loganathan, G. Naidu, S. Vigneswaran, Mining valuable minerals from seawater: a critical review, Environ. Sci.: Water Res. Technol. 3 (2017) 37–53, https://doi.org/10.1039/c6ew00268d.

[12] M.O. Mavukkandy, C.M. Chabib, I. Mustafa, A. Al Ghaferi, F. AlMarzooqi, Brine management in desalination industry: from waste to resources generation, Desalination 472 (2019) 114187, https://doi.org/10.1016/j.desal.2019.114187.

[13] I. Ihsanullah, J. Mustafa, A.M. Zafar, M. Obaid, M.A. Atieh, N. Ghaffour, Waste to wealth: a critical analysis of resource recovery from desalination brine, Desalination 543 (2022) 116093, https://doi.org/10.1016/j.desal.2022.116093.

[14] T. Jeppesen, L. Shu, G. Keir, V. Jegatheesan, Metal recovery from reverse osmosis concentrate, J. Clean. Prod. 17 (2009) 703–707, https://doi.org/10.1016/j.jclepro.2008.11.013.

[15] U. Bardi, Extracting minerals from seawater: an energy analysis, Sustainability 2 (2010) 980–992, https://doi.org/10.3390/su2040980.

[16] B.K. Pramanik, L.D. Nghiem, F.I. Hai, Extraction of strategically important elements from brines: constraints and opportunities, Water Res. 168 (2020) 115149, https://doi.org/10.1016/j.watres.2019.115149.

[17] S. Randazzo, F. Vicari, J. López, M. Salem, R. Lo Brutto, S. Azzouz, S. Chamam, S. Cataldo, N. Muratore, M. Fernández de Labastida, V. Vallès, A. Pettignano, G. D. Staiti, S. Pawlowski, A. Hannachi, J.L. Cortina, A. Cipollina, Unlocking hidden mineral resources: characterization and potential of bitterns as alternative sources of critical raw materials, J. Clean. Prod. 436 (2024) 140412, https://doi.org/10.1016/j.jclepro.2023.140412.

[18] S. Gorjian, F.J. Jamshidian, B. Hosseinqolilou, Feasible solar applications for brines disposal in desalination plants, in: A. Kumar, O. Prakash (Eds.), Solar Desalination Technology, Springer, Singapore, 2019, pp. 25–48, https://doi.org/10.1007/978-981-13-6887-5.

[19] CORDIS, Circular Processing of Seawater Brines from Saltworks for Recovery of Valuable Raw Materials | SEArcularMINE Project, (2021). https://doi.org/10.3030/869467.

[20] A. Kumar, G. Naidu, H. Fukuda, F. Du, S. Vigneswaran, E. Drioli, J.H. Lienhard, Metals recovery from seawater desalination brines: technologies, opportunities, and challenges, ACS Sustain. Chem. Eng. 9 (2021) 7704–7712, https://doi.org/10.1021/acssuschemeng.1c00785.

[21] S.E. Can Sener, V.M. Thomas, D.E. Hogan, R.M. Maier, M. Carbajales-Dale, M. D. Barton, T. Karanfil, J.C. Crittenden, G.L. Amy, Recovery of critical metals from aqueous sources, ACS Sustain. Chem. Eng. 9 (2021) 11616–11634, https://doi.org/10.1021/acssuschemeng.1c03005.

[22] X. Zhang, W. Zhao, Y. Zhang, V. Jegatheesan, A review of resource recovery from seawater desalination brine, Rev. Environ. Sci. Biotechnol. 20 (2021) 333–361, https://doi.org/10.1007/s11157-021-09570-4.

[23] A. Brewer, J. Florek, F. Kleitz, A perspective on developing solid-phase extraction technologies for industrial-scale critical materials recovery, Green Chem. 24 (2022) 2752–2765, https://doi.org/10.1039/d2gc00347c.

[24] V. Vallès, J. López, M. Fernández de Labastida, O. Gibert, A. Leskinen, R. T. Koivula, J.L. Cortina, Polymeric and inorganic sorbents as a green option to recover critical raw materials at trace levels from sea saltwork bitterns, Green Chem. 25 (2023) 700–719, https://doi.org/10.1039/d2gc02338e.

[25] O. Gibert, C. Valderrama, M. Peterkóva, J.L. Cortina, Evaluation of selective sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis rejected brine, Solvent Extr. Ion.-. Exch. 28 (2010) 543–562, https://doi.org/10.1080/07366299.2010.480931.

[26] M. Petersková, C. Valderrama, O. Gibert, J.L. Cortina, Extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis concentrate using selective sorbents, Desalination 286 (2012) 316–323, https://doi.org/10.1016/j.desal.2011.11.042.

[27] G. Naidu, P. Loganathan, S. Jeong, M.A.H. Johir, V.H.P. To, J. Kandasamy, S. Vigneswaran, Rubidium extraction using an organic polymer encapsulated potassium copper hexacyanoferrate sorbent, Chem. Eng. J. 306 (2016) 31–42, https://doi.org/10.1016/j.cej.2016.07.038.

[28] T. Nur, P. Loganathan, J. Kandasamy, S. Vigneswaran, Removal of strontium from aqueous solutions and synthetic seawater using resorcinol formaldehyde polycondensate resin, Desalination 420 (2017) 283–291, https://doi.org/10.1016/j.desal.2017.08.003.

[29] F. Arroyo, J. Morillo, J. Usero, D. Rosado, H. El Bakouri, Lithium recovery from desalination brines using specific ion-exchange resins, Desalination 468 (2019) 114073, https://doi.org/10.1016/j.desal.2019.114073.

[30] R. Harjula, J. Lehto, Method for cesium removal from radioactive waste liquids and method for producing hexacyanoferrates, WO9750092A1 (1997).

[31] S. Romano, S. Trespi, R. Achermann, G. Battaglia, A. Raponi, D. Marchisio, M. Mazzotti, G. Micale, A. Cipollina, The role of operating conditions in the precipitation of magnesium hydroxide hexagonal platelets using NaOH solutions, Cryst. Growth Des. 23 (2023) 6491–6505, https://doi.org/10.1021/acs.cgd.3c00462.

[32] G. Battaglia, M.A. Domina, R. Lo Brutto, J. Lopez Rodriguez, M. Fernandez de Labastida, J.L. Cortina, A. Pettignano, A. Cipollina, A. Tamburini, G. Micale, Evaluation of the purity of magnesium hydroxide recovered from saltwork bitterns, Water 15 (2023) 29, https://doi.org/10.3390/w15010029.

[33] H.M. Saif, R.M. Huertas, S. Pawlowski, J.G. Crespo, S. Velizarov, Development of highly selective composite polymeric membranes for Li+/Mg2+ separation, J. Membr. Sci. 620 (2021) 118891, https://doi.org/10.1016/j.memsci.2020.118891.

[34] H.M. Saif, J.G. Crespo, S. Pawlowski, Lithium recovery from brines by lithium membrane flow capacitive deionization (Li-MFCDI) – a proof of concept, J. Membr. Sci. Lett. 3 (2023) 100059, https://doi.org/10.1016/j.memlet.2023.100059.

[35] V. Vallès, M. Fernández de Labastida, J. López, G. Battaglia, D. Winter, S. Randazzo, A. Cipollina, J.L. Cortina, Sustainable recovery of critical elements from seawater saltworks bitterns by integration of high selective sorbents and reactive precipitation and crystallisation: Developing the probe of concept with on-site produced chemicals and energy, Sep. Purif. Technol. 306 (2023) 122622, https://doi.org/10.1016/j.seppur.2022.122622.

[36] T. León, S. Abdullah Shah, J. López, A. Culcasi, L. Jofre, A. Cipollina, J.L. Cortina, A. Tamburini, G. Micale, Electrodialysis with bipolar membranes for the generation of NaOH and HCl solutions from brines: an inter-laboratory evaluation of thin and ultrathin non-woven cloth-based ion-exchange membranes, Membranes 12 (2022) 1204, https://doi.org/10.3390/membranes12121204.

[37] A. Filingeri, J. Lopez, A. Culcasi, T. Leon, A. Tamburini, J. Luis Cortina, G. Micale, A. Cipollina, In-depth insights on multi-ionic transport in Electrodialysis with bipolar membrane systems, Chem. Eng. J. 468 (2023) 143673, https://doi.org/10.1016/j.cej.2023.143673.

[38] V. Vallès, M. Fernández de Labastida, J. López, J.L. Cortina, Selective recovery of boron, cobalt, gallium and germanium from seawater solar saltworks brines using N-methylglucamine sorbents: column operation performance, Sci. Total Environ. 923 (2024) 171438, https://doi.org/10.1016/j.scitotenv.2024.171438.

[39] Y.A.R. Lebron, V.R. Moreira, L.V. de S. Santos, M.C.S. Amaral, Membrane distillation and ion exchange combined process for mining wastewater treatment, water reuse, and byproducts recovery, Chem. Eng. J. 466 (2023), https://doi.org/10.1016/j.cej.2023.143181.

[40] A.A.M. Abusultan, J.A. Wood, T. Sainio, A.J.B. Kemperman, W.G.J. van der Meer, A hybrid process combining ion exchange resin and bipolar membrane electrodialysis for reverse osmosis remineralization, Desalination 573 (2024), https://doi.org/10.1016/j.desal.2023.117209.

[41] Z. Hubicki, D. Kołodyńska, Chapter 8 - selective removal of heavy metal ions from waters and waste waters using ion exchange methods, Ion. Exch. Technol. (2012) 193–240, https://doi.org/10.5772/51040.

[42] J. Vaughan, C. Dieters, W. Fu, K. Byrne, Properties of Lewatit® TP272, a commercial solvent impregnated cation exchange resin for cobalt recovery, Miner. Eng. 88 (2016) 2–8, https://doi.org/10.1016/j.mineng.2015.07.005.

[43] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, K. Ooi, T. Hirotsu, Selective adsorption of phosphate from seawater and wastewater by amorphous zirconium hydroxide, J. Colloid Interface Sci. 297 (2006) 426–433, https://doi.org/10.1016/j.jcis.2005.11.011.

[44] J. Lehto, R. Koivula, H. Leinonen, E. Tusa, R. Harjula, Removal of Radionuclides from Fukushima Daiichi Waste Effluents, Sep. Purif. Rev. 48 (2019) 122–142, https://doi.org/10.1080/15422119.2018.1549567.

[45] C. Loos-Neskovic, S. Ayrault, V. Badillo, B. Jimenez, E. Garnier, M. Fedoroff, D. J. Jones, B. Merinov, Structure of copper-potassium hexacyanoferrate (II) and sorption mechanisms of cesium, J. Solid State Chem. 177 (2004) 1817–1828, https://doi.org/10.1016/j.jssc.2004.01.018.

[46] T. Vincent, C. Vincent, E. Guibal, Immobilization of metal hexacyanoferrate ion-exchangers for the synthesis of metal ion sorbents - a mini-review, Molecules 20 (2015) 20582–20613, https://doi.org/10.3390/molecules201119718.

[47] W. tao Yi, C. yan Yan, P. hua Ma, Removal of calcium and magnesium from LiHCO3 solutions for preparation of high-purity Li2CO3 by ion-exchange resin, Desalination 249 (2009) 729–735, https://doi.org/10.1016/j.desal.2009.01.034.

[48] I. Louati, F. Guesmi, A. Chaabouni, C. Hannachi, B. Hamrouni, Effect of ionic strength on the ion exchange equilibrium between AMX membrane and electrolyte solutions, Water Qual. Res. J. Can. 51 (2016) 60–68, https://doi.org/10.2166/wqrjc.2015.006.

[49] Dupont, AmberSep IRC747 UPS Product Data Sheet, IRC747 Prod. Data Sheet (2020).

[50] Purolite, Purolite S940 Product Data Sheet, S940 Product Data Sheet. (2022).

[51] A.A. Zagorodni, Chapter 2 - Ion exchangers, their structure and major properties, in: Ion Exchange Materials: Properties and Applications, Elsevier, Oxford, 2007, pp. 9–54, https://doi.org/10.1016/B978-008044552-6/50003-4.

[52] I.B. Rae, S. Pap, D. Svobodova, S.W. Gibb, Comparison of sustainable biosorbents and ion-exchange resins to remove Sr2+ from simulant nuclear wastewater: batch, dynamic and mechanism studies, Sci. Total Environ. 650 (2019) 2411–2422, https://doi.org/10.1016/j.scitotenv.2018.09.396.

[53] J. Bok-Badura, A. Kazek-Kęsik, K. Karon, A. Jakóbik-Kolon, Highly efficient copper hexacyanoferrate-embedded pectin sorbent for radioactive cesium ions removal, Water Resour. Ind. 28 (2022) 100190, https://doi.org/10.1016/j.wri.2022.100190.