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Separation and concentration of rare earth elements from wastewater using electrodialysis technology

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ABSTRACT

Rare earth elements (REEs) including Scandium (Sc) are critical raw materials which are greatly needed in the advancement of many modern technologies. Due to the problems associated with the primary extraction of mining ores, the procurement of Sc and REEs from the secondary resources are currently explored adopting the principle of sustainability and circular economy. Herein, for the first time, the Electrodialysis (ED) technology based on electrochemical membrane separation process is successfully applied to separate and concentrate REEs from the diluted aqueous system. The overall performance of ED process in the recovery of Sc^{3+} ions from the wastewater was assessed by applied current, voltage, feed concentration, feed pH, co-ion competition and the overall energy consumption of the process. The REE recovery using the ED process was subjected to systematic investigations using both chronopotentiometric and chronoamperometric analyses. The results showed that ED process could be very promising in the recovery of Sc^{3+} ions (~99.52% removal) from the diluted wastewater, consuming the energy of only 0.26 kWh/m^3 when operated at constant voltage mode (Sc^{3+} concentration of 20 ppm, pH 4, 1 h).

1. Introduction

Rare earth elements (REEs) include a set of elements, consisting of 15 lanthanides along with 2 pseudo lanthanides (scandium, Sc and yttrium, Y). Although the term dictates "rare", the occurrence of REEs is abundant in Earth's crust. The similar physicochemical properties of REEs hinder their efficient separation process from each other as well as from the ore minerals as a mixture. According to the European Commission report published in 2017, REEs along with Sc are added to the list of 27 new critical raw materials [1]. Owing to their rare and unique physicochemical, magnetic and optical properties, the demand of these critical elements is escalating with its utilization in the advancements of many modern technologies such as electric vehicles, electronic devices, and high-performance magnets. Especially, Sc is highly sought-after for the development of aeronautical, space and defense technologies [2]. However, there is a restricted supply of REEs

because of the difficulty in their exploitation processes. Hence, there is a huge gap between the demand and supply resulting in volatile market prices of REEs. This serves as the main initiative to recover or recycle them from secondary resources such as mining effluents and industrial wastewaters. Furthermore, the concept of the circular economy supporting sustainable development by converting waste to resources provides an added incentive to procuring REEs from secondary sources.

In order to recover or recycle REEs from secondary resources, several techniques, including ion exchange (IX), bio-sorption, adsorption, solvent extraction, and precipitation [2–4], have been commonly applied for recovering REEs from aqueous systems. Among these techniques, solvent extraction is found effective in the treatment of concentrated streams while the adsorption process is quite advantageous for treating the diluted REE streams. A fundamental limitation of the adsorption process is that the removal and recovery of target elements are carried out in two stages i.e. adsorption and desorption. Further, the

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regeneration of the exhausted adsorbents requires chemicals (i.e. concentrated acidic or basic solutions), thus, causing secondary wastes and additional operation cost [5]. Recently, the application of electrochemical membrane technology has grasped enormous research interests in the field of the target ion extraction owing to its lower energy consumption and environmental-friendly in nature [6–8] . In this aspect, electrodialysis (ED) technology is gaining significance for the separation and concentration of ionic species in aqueous systems with the removal and recovery process occurring simultaneously [9]. This membrane-based separation process initially intended for water desalination, has been extended for its use in the wastewater treatment in terms of selective removal of target ions and other charged molecules while also producing clean water [10–12]. Using ED process, the target ions can be extracted by means of electrically charged membranes under the influence of an electrical potential difference acting as a driving force. Up to now, the ED process has been investigated for the separation and concentration of ionic species such as chromium [13,14], copper [13], zinc, nickel [15], silver [16], cobalt [17], ammonium [14], phosphorus [18], nitrate and hardness ions [19,20]. Studies on the utilization of ED technology for the separation and concentration of REEs is very limited or scarce in the literature. Besides, in terms of REE (such as Sc) separation and concentration, ED process can offer several advantages over other state-of-the-art processes such as precipitation, solvent extraction and sorption. Some of the limitations observed with sorption and precipitation processes were the need for a higher solution pH and the generation of secondary wastes such as spent adsorbents and sludge. The solution pH plays a major role in the REE extraction process because REEs tend to precipitate as hydroxides at higher pHs (> 6) [21–24]. Therefore, ED technology can serve as a promising candidate to extract REEs at acidic pHs over the other technologies such as sorption and precipitation. Further, it has to be noted that lower Sc concentration (< 10–15 ppm) is typically found in the industrial waste streams [25,26]. In such diluted systems of larger volumes, ED process could be advantageous over solvent extraction process in terms of selective separation and concentration of REEs.

Hence, in this work, we aim to explore the potential of the ED process to separate and concentrate Sc^{3+} ions effectively from the diluted streams. We also present the separation and concentration of Sc^{3+} ions from synthetic mono-component and multicomponent feed solutions (Fe^{3+}, Al^{3+} and other REEs) using the ED process. The main objectives of this work are listed below: a) to optimize the operating parameters such as the feed concentration and applied current/voltage for an efficient ED removal and recovery process; b) to investigate the current–voltage relationship with regards to constant-current (CC) mode and constant-voltage (CV) mode for the ED operation; c) to determine the interference of other REEs and competing ions present in the aqueous system; d) to estimate the energy consumption of the process for the separation and concentration of Sc^{3+} ions.

2. Experimental section

In this work, the construction of ED cell (See Fig. 1) involves three compartments i.e. dilute, concentrate and rinse compartments, separated by a series of anion exchange membranes (AEM) and cation exchange membranes (CEM) between the electrodes (AEM-CEM-AEM). The AEM used in this study is obtained from PCCell (PC SA – strongly alkaline with polyester reinforcement) comprising of ammonium functional groups, an electrical resistance of 1.8 Ω cm^2, a thickness of 100–110 μm and water content of 14 wt%. Similarly, the CEM used in this study is also procured from PCCell (PC SK – strongly acidic with sulfonic acid functional groups) with an electrical resistance of 2.5 Ω cm^2, a thickness of 100–120 μm, water content of 9 wt% and polyester reinforcement. The electrodes used for this lab-scale ED cell are titanium with Pt/Ir coating as the anode and stainless steel as the cathode. The dilute and concentrate compartments are formed by interposed polymeric spacers of 0.45 mm thickness for water flow
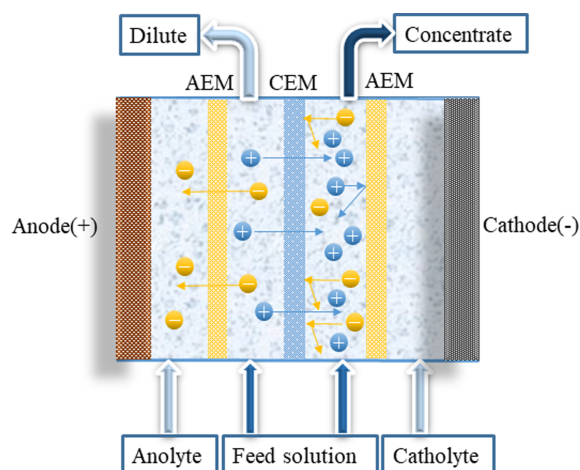

Fig. 1. Schematic illustration of ED cell configuration used in this study.

between ion exchange membranes with an active membrane area of 64 cm^2. The sulfuric acid, 0.1 M H_2SO_4, was used as the anolyte as well as catholyte solution for rinsing the electrodes. The desired concentration of Sc (5–80 ppm) was prepared from scandium chloride hexahydrate salt (VWR International; 99.9% metal basis) and was used as the feed solution in this study. The synthetic Sc^{3+} feed solutions of 200 mL (of same concentration; initial feed pH 4) were circulated into dilute and concentrate compartments while 250 mL volume of 0.1 M H_2SO_4 anolyte and catholyte was pumped through the rinse compartments. The flow rate was maintained constant at 40 mL min^{-1} for all the compartments.

The desired concentrations of REEs and of interfering ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}) in the aqueous samples were prepared from the ICP standard stock solutions of 1000 ppm (in 5% nitric acid). The initial and final concentrations of the target ions before and after the ED treatment were determined by induced coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110). All electrochemical experiments were performed using a potentiostat (OctoStat5000, Ivium) with software for monitoring and data acquisition. Additionally, pH and conductivity values were monitored and measured using multi-parameter meter (inoLab® Multi 9620 IDS, WTW).

3. Results and discussion

In ED system, applying constant current or voltage results in ion transport across CEM and AEM yielding clean water in the dilute compartment and extracted REEs (as "concentrates") in the concentrate compartment [27]. Hence, the applied electrical field plays a key role in driving the ions to migrate across the membranes. The current (I) and voltage (V) relationship were firstly studied by recording polarization curves using the same ED operating conditions of this study (i.e. same cell configuration, solution volume, pH, flow rate) to determine the optimum current for the ED process [5,28,29]. The linear voltage sweep was performed from 0 V to 4 V at a scan rate of 5 mV s^{-1} to obtain the I-V curves. Fig. 2 shows the polarization curves displaying the change in current for the feed concentrations of 20, 80 and 160 ppm. When the cell voltage was below 0.5 V, the corresponding current was almost zero indicating the applied energy was too low at this point. As the applied voltage was scanned from 0.5 V to 1.75 V, the current increased slowly to ~58 mA in the region dominated by constant and ohmic resistance. Following this, the resistance increases upon the concentration depletion at the membrane interface, evident by the formation of a plateau. The limiting current I_{lim} was estimated from this region as shown in Fig. 2, based on the calculation from other reported works in the past [29]. At this stage, the applied energy was used for
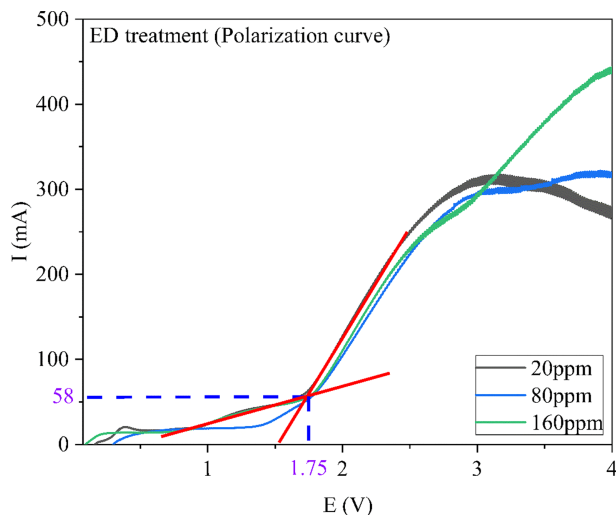
Fig. 2. The limiting current determination of ED cell using different concentrations of Sc^{3+} solutions (20 ppm, 40 ppm, 160 ppm,) at a flowrate of 40 mL min^{-1} and voltage scanning from 0 V to 4 V with a scanning rate of 5 mV s^{-1}.

transporting ions from the bulk solution to the membrane/solution interface. When the voltage was over 1.75 V, a significant increase of current was observed and this could be attributed to the water-splitting occurring at the membrane/solutions interface [29]. This phenomenon is common when operating the system at over-limiting current conditions. Based on these observations, we studied the ED performance in the current range of 50–100 mA and voltage range of 1–3 V.

In order to determine the Sc removal/recovery performance by ED process, initially, the tests were conducted with mono-component Sc^{3+} system by varying the operating conditions to assess the influence of applied current/voltage and Sc^{3+} feed concentration on ED performance. There are two electrochemical characterization methods for monitoring the efficacy of ED process i.e. chronopotentiometry (constant current "CC" mode) and chronoamperometry (constant voltage "CV" mode). Based on previous works in the literature [30,31], CC mode is more widely used compared to CV mode for the ED process. In CC mode, a constant current is applied to the ED cell under study, and the time-dependent voltage profile is measured [32]. On the other hand, the literature states that the faster current–voltage equilibrium time of the ED process could be achieved when operating at CV mode [33]. Hence, in this study, a comparative analysis of ED performance on Sc removal and recovery was conducted when operating at CC as well as CV mode.

Each experiment was conducted in batch mode by recirculating the ScCl$_3$ solution of the same concentration through the dilute and concentrate compartments. With the electric potential difference acting as a driving force, the Sc^{3+}ion strips away from the dilute compartment and migrates across the CEM to the concentrate compartment. On the other hand, Cl$^-$ ion passes through AEM easily to move towards the rinse compartment. So, firstly, in order to investigate the effect of applied current on the ED process, the chronopotentiometric analysis was conducted by applying the constant current of 50, 75 and 100 mA for the treatment period of 60 min for the Sc^{3+} feed concentration of 20 ppm.

The removal efficiency (in %) i.e. the Sc/REE removal from the dilute compartment was estimated by using Eq. (1).

$$removal~~\% = \frac{C_{D,i} - C_{D,f}}{C_{D,i}} \times 100 \tag{1}$$

where C_i and C_f represent initial and final REE concentration (ppm i.e. mg/L) in the dilute compartment, respectively.

Similarly, the recovery efficiency (in %) i.e. the Sc/REE recovery in
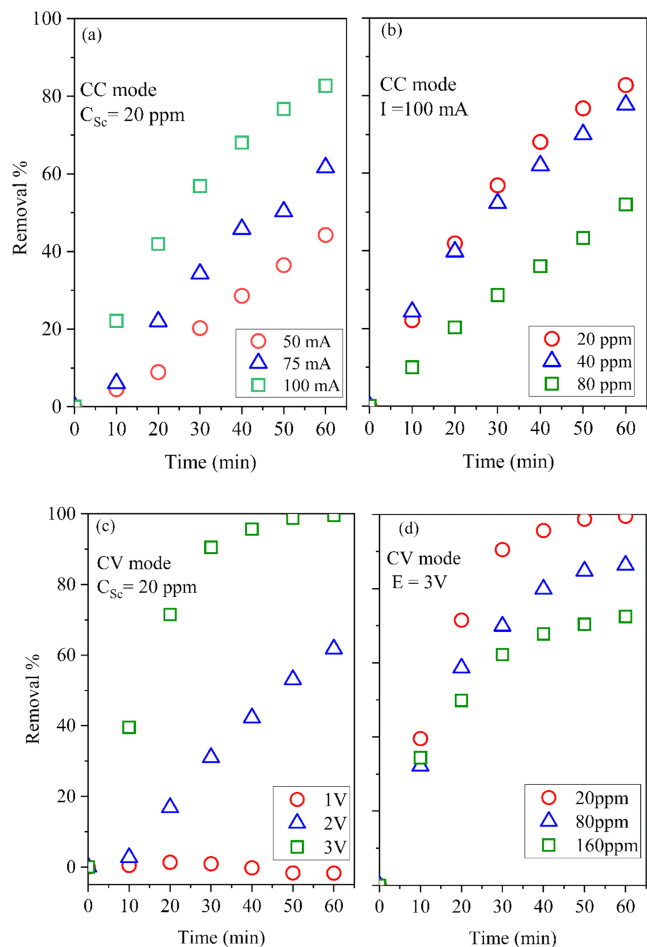
Fig. 3. Plots of batch ED tests at constant current (CC) mode: a) Sc^{3+} removal % vs. time at different constant currents (50, 75, 100 mA) applied to 20 ppm Sc^{3+} feed solution; b) Sc^{3+} removal % vs. time at different concentrations of feed solution (20, 40, 80 ppm) with constant current of 100 mA; and constant voltage (CV) mode: c) Sc^{3+} removal % vs. time at different constant voltages (1, 2, 3 V) applied to 20 ppm Sc^{3+} feed solution; d) Sc^{3+} removal % vs. time at different concentrations of feed solution (20, 40, 160 ppm) with constant current of 3 V.

the concentrate compartment was estimated by using Eq. (2).

$$recovery~~\% = \frac{C_{C,f} - C_{C,i}}{C_{C,i}} \times 100 \tag{2}$$

where C_i and C_f represent initial and final REE concentration (ppm i.e. mg/L) in the concentrate compartment, respectively.

Fig. 3a) shows the Sc^{3+} removal of 44.24%, 61.67%, and 82.70% in the dilute compartment for the constant current of 50, 75 and 100 mA. The results show that the ion flux across the membrane (effective membrane area of 64 cm^2) increases with the increase in current density [34]. At this condition of constant 100 mA, the maximum Sc^{3+} ion depletion occurs from the initial concentration of around 18 ppm to 3 ppm while the Sc^{3+} concentrate of ~32 ppm (recovery of 75%) was attained on the neighboring concentrate compartment. Further, the effect of the Sc^{3+} feed concentration on the removal and recovery of Sc^{3+} ions was studied by applying a constant current of 100 mA with varied concentrations of Sc^{3+} feed solution (20 ppm, 40 ppm, and 80 ppm). Fig. 3b) shows that the Sc^{3+} removal efficiency decreases with increase in feed concentration, recording around 82.70%, 77.64%, and 51.95% for the initial Sc^{3+} concentration of 20, 40 and 80 ppm, respectively when operated at the constant current of 100 mA. The reduced ion transport number with the increase in ionic strength could
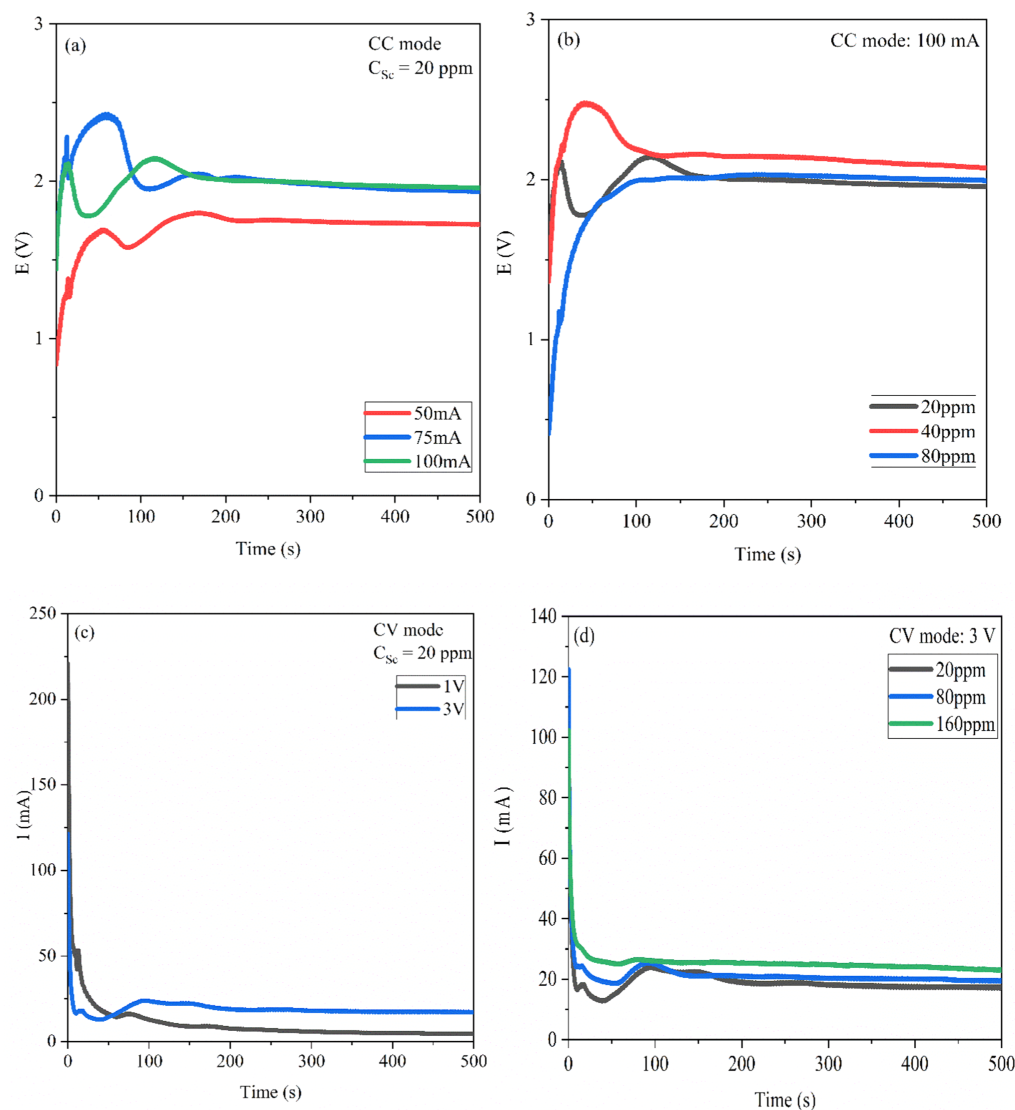
Fig. 4. a) Cell voltage vs. time – one-hour ED treatment of 20 ppm Sc^{3+} solution with different applied constant current (CC mode: 50 mA, 75 mA, 100 mA) and a flow rate at 40 mL min^{-1}; b) Cell voltage vs. time – one-hour ED treatment of different concentrations of Sc^{3+} solution (20, 40, 80 ppm) with applied constant current 100 mA (CC mode) and a flow rate at 40 mL min^{-1}; c) Cell voltage vs. time – one-hour ED treatment of 20 ppm Sc^{3+} solution with different applied constant voltage (CV mode: 1 V and 3 V) and a flow rate at 40 mL min^{-1}; d) Cell voltage vs. time – one-hour ED treatment of different concentrations of Sc^{3+} solution (20, 80, 160 ppm) with applied constant voltage 3 V (CV mode) and a flow rate at 40 mL min^{-1}.

be a consequence of reduced Donnan exclusion effect [35].

The chronoamperometric measurements (CV mode) revealed the influence of applied voltage on the ion removal efficiency (Fig. 3c). With an increase in the applied voltage, the substantial increase in Sc^{3+} removal % was observed. The applied voltage of 1 V was too low to induce any ion migration showing a negligible Sc^{3+} removal of ~1%. A significant rise in removal efficiency (~61.75%) was witnessed on applying a constant voltage of 2 V. With the further increase to 3 V, the maximum Sc^{3+} removal efficiency of ~99.52% was recorded. The other studies also reported the significant influence of the applied potential on the ion removal efficiency [36,37]. A similar observation of a decrease in ion removal efficiency was detected with the increase in feed concentration when operating at constant voltage mode as well (Fig. 3d).

Fig. 4 illustrates the voltage difference required to induce constant current (CC mode) and the current measured at a fixed potential difference (CV mode) as a function of treatment time. From the chronopotentiometric response (Fig. 4a and b), it can be seen that when the current of 50 mA (i.e. $< I_{lim}$) is applied, the increase in resistance occurs very gradually over the time owing to the concentration polarization. It means that the increased resistance is observed at the depleted side of the membrane while the resistance is low on the other side of the membrane (i.e. enriched side). So, until a new steady state is

attained, figures, the voltage keeps increasing to maintain the constant current. When the constant current of 75 and 100 mA ($> I_{lim}$) is applied, the depletion of membrane interface occurs causing the resistance to rise sharply. This phenomenon can be observed in the figures from the sharp voltage peaks at the over-limiting current density and lower ionic strength as a result of quick ion depletion and rise in resistance. At higher ionic strength and lower applied current density, a gradual bump can be observed. Similar observations were made from the chronoamperometric response profiles.

Further, the energy consumption (EC, kWh/m^3) of the ED process was calculated using the following Eq. (3) [38].

$$EC = \frac{UIt}{V}$$ (3)

where U is the voltage of ED; I is the current (A); t is the duration time of the ED process (h), and V is the volume of treated solution (L).

The evaluation of these two modes of ED operations was made based on the energy consumption of the process. The estimated energy consumption values showed the competitive edge of chronoamperometric measurements (CV mode: 0.26–0.35 kWh/m^3 for the removal% of 57.68–99.52) over chronopotentiometric (CC mode: 0.43–1.06 kWh/m^3 for the removal% of 44.24–82.70). Besides, the obtained values were found comparable to the data found in literature for low energy
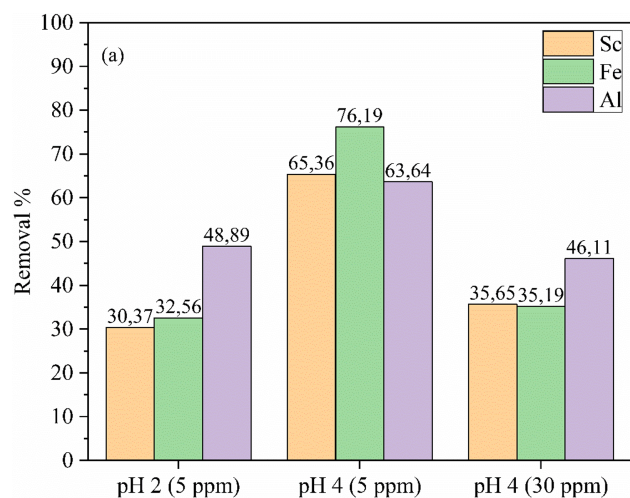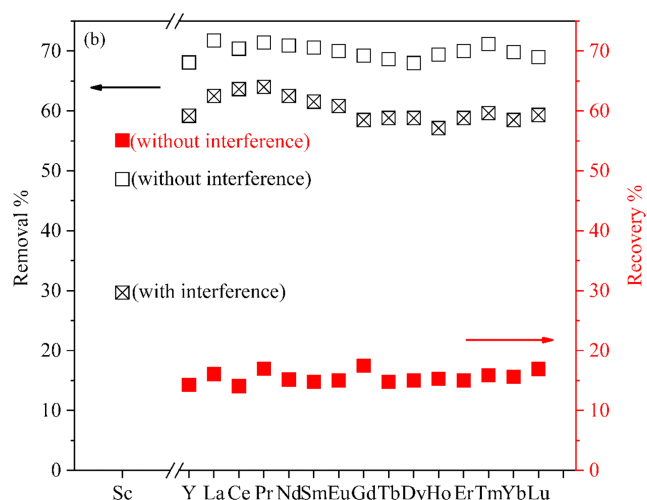
Fig. 5a. Removal % of synthetic solutions containing Sc^{3+}, Fe^{3+}, and Al^{3+} of 5 ppm -30 ppm with adjusted pH of 2 and 4 under ED process (applied constant current of 100 mA and a flow rate at 40 mL min^{-1} and 60-min treatment time).

Fig. 5b. Removal % and recovery % of synthetic solutions containing all REEs of 5 ppm with and without competing cations as interferences with adjusted pH of 4 under ED process (applied constant current of 100 mA and a flow rate at 40 mL min^{-1} and 60-min treatment time).

consuming ED systems (ranging from 0.2 to 4 kWh/m^3) for the separation of metal ions from wastewater. Some notable examples of reported values from recent studies are Cr^{6+} (1.21 kWh/m^3 [39], 2–4 kWh/m^3 [37]) Ag^+ (3.96 kWh/m^3) [40], Ni^{2+} (0.208 kWh/m^3 [41], 0.64 kWh/m^3 [42,43], 2.8 kWh/m^3 [15]), Cu^{2+} (2 kWh/m^3 [44]) and Pb^{2+} (0.16–0.36 kWh/m^3 [45,46]) removal.

Finally, to understand the applicability of using ED system for the separation and concentration of Sc and REEs for the real wastewater, further investigations were conducted in the direction of the process selectivity of extracting Sc^{3+} in the presence of other common pollutants and contaminants existing in the industrial wastewater. The interference studies (Fig. 5a) were designed for a system containing uniform concentrations of Sc^{3+}, Al^{3+}, and Fe^{3+} ions. The choice of the ionic mixture is to simulate the condition closer to the red mud/bauxite residue liquor where Sc^{3+} ions co-exist with Fe and Al impurities of higher concentrations. Since acid leaching is the most commonly used technique for the extraction of elements from the process residues, the liquor obtained is generally acidic. Hence, the tests were conducted in this study at pH 2–4 to study the effect of pH on the Sc^{3+} removal and recovery process. It must be noted that the REE hydrolysis occurs from pH 6 whereas Sc^{3+} ions can hydrolyze from pH 5. So, the pH of the feed solution was not opted above 4 throughout this study. As expected, the overall total ion removal efficiencies improved with the increase in feed pH. At acidic pH 2, the presence of augmented H^+ ions can affect the Sc^{3+} removal process. With the increase in solution pH to 4, the rise in Sc^{3+} removal was observed from 30.37% to 65.36%, similarly observed in the case of Fe^{3+} (32.56 to 76.19%) and Al^{3+} (48.89 to 63.64%) ions. The interesting observation made here is that the removal of Al^{3+} ions was predominant at pH 2 in comparison to Sc^{3+} and Fe^{3+} ions. With the rise in pH, the trend shifted towards Sc^{3+} and Fe^{3+} ions recording further increase in removal efficiencies of 34.99% and 43.63%, respectively, in comparison to Al^{3+} ions (14.75%). On further increasing the co-ion competition by increasing the feed concentration to 30 ppm (each), the decline in removal efficiencies was noted. Also, to determine the selective separation efficiency between Sc^{3+} and other competing ions, the selective separation efficiency parameter (S(t)) was calculated using Eq. (4) [6] as,

$$S(t) = \frac{(C_{A,t}/C_{A,0}) - (C_{B,t}/C_{B,0})}{(1 - (C_{A,t}/C_{A,0})) + (1 - (C_{B,t}/C_{B,0}))} * 100\% \qquad (4)$$

where $C_{A,0}$ and $C_{B,0}$ are the initial concentrations of component A and B at time 0, respectively; $C_{A,t}$ and $C_{B,t}$ are the concentrations of A and B at

time t, respectively.

Based on this calculation, the selective separation efficiency parameters of Sc^{3+} (t-30 min) were estimated as -3.48% (Fe^{3+}/Sc^{3+} at pH 2 and $C_0 = 5$ ppm), -7.65% (Fe^{3+}/Sc^{3+} at pH 4 and $C_0 = 5$ ppm) and 0.65% (Fe^{3+}/Sc^{3+} at pH 4 and $C_0 = 30$ ppm). These results show that the selective separation of Sc^{3+} over Fe^{3+} increases with an increase in solution pH and feed concentration. Similar observations were also found in case of Al^{3+}/Sc^{3+}, indicating selective separation efficiency parameters of -23.37% and 1.33% at pH 2 and pH 4, respectively, for an initial concentration of 5 ppm. The similar properties of Sc^{3+}, Al^{3+} and Fe^{3+} ions in terms of ionic size and chemical behavior makes the selective recovery of Sc^{3+} over Al^{3+} and Fe^{3+} ions a complicated process at this stage [47].

Furthermore, the intraseries behavior of REE was also investigated to comprehend the separation behavior among the REEs because most of the REEs are present together in ores or processing residues. The findings (Fig. 5b) showed about 70% removal of all other REEs and 50% removal of Sc^{3+} ions with the applied current of 100 mA when tested using a mixed system containing 5 ppm of each REE. The presence of interference in the form of common monovalent, divalent and trivalent cations (uniform concentration of Na^+, Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, and Fe^{3+} ions) hindered the removal of trivalent REEs, showing a slight drop in efficiency fro m 70% to 60% for other REEs. However, a significant decline in Sc^{3+} removal from 55 to 30% was observed. Further, in comparison to the single component system (only Sc^{3+} of 80 ppm – Fig. 2), the overall REE removal efficiency was higher. The discrepancies in removal efficiencies in single-component and mixed solutions could arise from the Sc^{3+} saturated membranes. The mechanism behind this separation phenomena of Sc^{3+} and other REEs are not clearly known at this point. Further investigations are certainly required to understand the transport of REEs across the membranes, concentration polarization associated with the membranes and limiting/over-limiting current and voltage profiles. Besides, the selectivity of the Sc^{3+} and REE removal process must be enhanced with the development of selective ion-exchange membranes or electrodes.

4. Conclusion

The effect of operating parameters (i.e. applied current/voltage, feed concentration, and pH) on the removal and recovery efficiency of the ED process were investigated. The voltage and current relationship were investigated using both chronopotentiometric and

chronoamperometric measurements. The results showed that the ED operation using CV mode (0.255 kWh/m^3) results in lower energy consumption in comparison to the operation using CC mode (0.975 kWh/m^3). These estimated values are coherent with the reported lower energy consuming ED systems (0.2–4 kWh/m^3) for metal recovery. Moreover, the findings also suggested that the selectivity separation efficiency parameters for Sc^{3+} over the competing ions increased with an increase in solution pH and feed concentration. To further enhance the selective separation of Sc^{3+} over competing ions using ED system, the development of new selective electrodes or membranes focusing on higher ion selectivity, lower costs, lower resistance etc., can be a promising direction. In addition, future research works must aim at gaining more insights into the usage of real effluents focusing on long-term sustainability, system scale-ups, optimization of system design and process, economic viability and integrated methodologies for better performance.

CRediT authorship contribution statement

Changbai Li: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Data curation. **Deepika L. Ramasamy:** Conceptualization, Methodology, Investigation, Writing - original draft, Data curation, Writing - review & editing, Validation, Visualization, Supervision. **Mika Sillanpää:** Conceptualization, Writing - review & editing, Resources, Project administration. **Eveliina Repo:** Conceptualization, Methodology, Writing - review & editing, Resources, Project administration, Funding acquisition.

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.

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