



A new approach for cobalt (II) removal from simulated wastewater using electro membrane extraction with a flat sheet supported liquid membrane

Noor R. Kadhim^{a,*}, Hussain M. Flayeh^a, Ali H. Abbar^b

^a Environmental Engineering Department, College of Engineering, University of Baghdad, Iraq

^b Biochemical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, Iraq

ARTICLE INFO

Keywords:

Cobalt
Electro-membrane extraction
1-Octanol
Supported liquid membrane
DEHP

ABSTRACT

The aim of this work was to efficiently remove cobalt (Co) from aqueous solutions by using a novel Electromembrane Extraction (EME) technique. This novel electrochemical cell design featured two distinct glass chambers, incorporating a Supported Liquid Membrane (SLM) composed of a polypropylene flat membrane saturated with 1-octanol and a carrier substance, as well as electrodes constructed from graphite and stainless steel. The investigation covered an exploration of various effective parameters like, carrier type, voltage across the cell, donor solution pH, and the initial Co concentration, with the overarching goal of comprehending their individual effect on Co removal efficiency. Notably, two different carriers, tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) phosphate (DEHP), were systematically evaluated in combination with 1-octanol. The findings underscored the pivotal role of the cell voltage in significantly enhancing the mass transfer rate of cobalt across the membrane, thereby advancing the effectiveness of the removal process. After a comprehensive optimization process, the optimal operating conditions were established as follows: employing 1-octanol with 1.0 % v/v bis(2-ethylhexyl) phosphate as a carrier, applying a voltage of 60 V, maintaining an initial pH of 5, utilizing an initial cobalt concentration of 15 mg/L, conducting an extraction for 6 h, and employing a stirring rate of 1000 rpm. Remarkably, these conditions led to the attainment of an impressive removal efficiency of 87 %. In stark contrast, when no voltage was applied, the removal efficiency did not surpass 40 %. This underscores the pivotal role of the applied voltage in enhancing the cobalt removal process under the specified conditions.

1. Introduction

Cobalt is a transition metal that is widely used in various industrial applications such as batteries, superalloys, and catalysts. Cobalt is also an essential element in the human body, and its deficiency can lead to several health issues. However, cobalt exposure can also lead to health problems, and therefore, its detection and removal from contaminated water sources are of great importance [1–5]. Chemical precipitation, adsorption, and membrane filtration are among the diverse techniques that have been developed for the purpose of removing cobalt from water sources [6,7]. The limitations of high cost, low selectivity, and the need for extensive treatment are commonly associated with these techniques. As a result, alternative methods such as EME have been proposed to address these

* Corresponding author.

E-mail address: noor.jabbar2011d@coeng.uobaghdad.edu.iq (N.R. Kadhim).

<https://doi.org/10.1016/j.heliyon.2023.e22343>

Received 21 July 2023; Received in revised form 4 November 2023; Accepted 9 November 2023

Available online 14 November 2023

2405-8440/© 2023 Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

challenges and achieve efficient removal of cobalt from aqueous solutions [8].

In the field of environmental chemistry, Electromembrane extraction (EME) has emerged as a contemporary and effective extraction method, gaining popularity in recent times. By integrating electrophoresis and membrane-based extraction, this technique offers a selective and efficient means of extracting target analytes from complex samples. The fundamental principle of EME involves utilizing an electrical potential to propel organic or ion species from the sample matrix, passing through a porous membrane, and ultimately reaching a receiving phase. EME presents numerous advantages, including notable selectivity, high efficiency, and minimal sample preparation requirements. These factors contribute to the appeal and applicability of this method in various analytical and environmental scenarios [9,10].

Electromembrane extraction is a well-established technique for the extraction of various organic and ion species from aqueous samples in the analytical chemistry. EME uses an electric field to move analytes from the sample solution across a thin organic liquid membrane, which is supported by a porous fiber. The analytes are then trapped in the organic phase and can be subsequently analyzed by various analytical techniques [11,12]. In the EME technique, a supported liquid membrane (SLM) serves as the extraction medium. SLMs consist of thin liquid layers supported by a porous membrane. The choice of liquid phase in the SLM is crucial, as it should possess solubility and selectivity characteristics suitable for the target analytes. The porous membrane facilitates the transport of ions from the sample matrix, passing through the SLM, and ultimately reaching a receiving phase. EME stands out as a green and efficient method that has found application in the extraction of diverse metal ions, including cobalt. Its environmentally friendly nature and effectiveness make it a valuable approach in various extraction processes [13–16]. On the other hand, the sensitivity of EME could be increased since using small volume of the acceptor phase could result in large enrichment factors. Besides, if the electric potential is not applied properly, a direct bearing on specific EME characteristics could be resulted which compromise the advantages of EME [17].

Recently, a modified EME called gel electromembrane extraction (G-EME) was applied to extract target analytes from the donor phase through a biopolymer membrane towards the acceptor phase under the effect of an electric field [18,19]. In this method, various biopolymer membranes were used involving polyacrylamide, agarose, agar, tragacanth, and chitosan. In spite of considering G-EME as a very interesting method for future green analytical chemistry, many drawbacks and challenges encounter this method such as lack of aqueous-organic solvent interface, high electro-endosmosis (EEO), and low selectivity. Besides the size of two phases (donor and acceptor) undergo a change in size during extraction resulting from EEO [19]. However, the application of this method for heavy metals extraction is still at an early stage and needs further research [18,20].

One of the challenges in the EME of cobalt is the selection of a suitable organic solvent that can effectively extract cobalt from the sample solution. In recent years, the use of supported liquid membrane as an alternative to the traditional organic liquid membrane in EME has gained significant attention. The use of SLM in EME has several advantages including lower solvent consumption, improved extraction efficiency, and higher selectivity [21–24]. A progress was made by Bhatluri et al. [25] by enhancement of cadmium and lead removal in SLM via integrating with in-situ electrodeposition of heavy metals on the cathode where in their work, two electrodes were kept inside the acceptor phase only. The same author in further research applied the same procedure to remove both zinc and nickel from aqueous solutions [26]. However, applying voltage difference across SLM would give better results since by accelerating mass transfer of heavy metals due to electric field in addition to the transfer as a result of concentration difference [27].

Few studies have been conducted on the application of EME for the extraction of cobalt from aqueous samples [23,27]. Kubáň et al. [27] used porous polypropylene hollow fiber for extraction of cobalt by applying voltage from 0 to 300 V while Davarani et al. [23] used EME for extraction of cobalt from aqueous media based on flat membrane. However, further research is necessary to optimize the parameters of EME and enhance the method's efficiency and selectivity.

This paper aims to investigate the effectiveness of EME using SLM for cobalt extraction from simulated wastewater. To achieve this objective, a new configuration was used for the electrochemical cell that differs from previous studies [23,27]. The new configuration involves two interconnected glass chambers connected by a flexible holder composed of two airtight cups made from Teflon and contains four screws and nets that permits assembling and dismantling the cell with more easiness. Between these chambers, a selective membrane (SLM) was installed. Moreover, two electrodes were used in the cell, the first is a stainless-steel plate was used as a cathode while the second is a graphite plate was used as anode. These electrodes offer the advantage of cost-effectiveness with feasibility of their scale up, which had not been previously used in the previous studies for removal of heavy metals [23,27]. Stainless steel electrode has been used as a spiral ended in EME of dibutyl phthalate (DBP) where good results were obtained [28,28] and for cobalt removal using bioelectrochemical system [29]. The study comprehensively examined different parameters, including the carrier type, voltage across the cell, donor solution pH, and initial cobalt concentration, to evaluate their impact on the cobalt extraction process. By analyzing these parameters, the study aimed to enhance the understanding and effectiveness of EME using SLM for cobalt extraction from simulated wastewater.

2. Experimental

2.1. Chemicals

In all experiments, donor and acceptor solutions were prepared using deionized water. The source of cobalt ions is $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a purity of 99 % supplied from Central Thomas Baker (Mumbai, India). HCl purchased from Thomas Baker (Ambarnath, India) was used to prepare the acceptor solution at a concentration of 0.1 N. 1-octanol was used as an organic solvent in the preparation of SLM and purchased via Central Drug House (Delhi, India).

Two distinct carrier compounds were obtained from Shanghai Macklin Biochemical, located in Shanghai, China, for the specific purpose of cobalt removal via the sophisticated Electromembrane Extraction (EME) process. Two carriers were used tris(2-

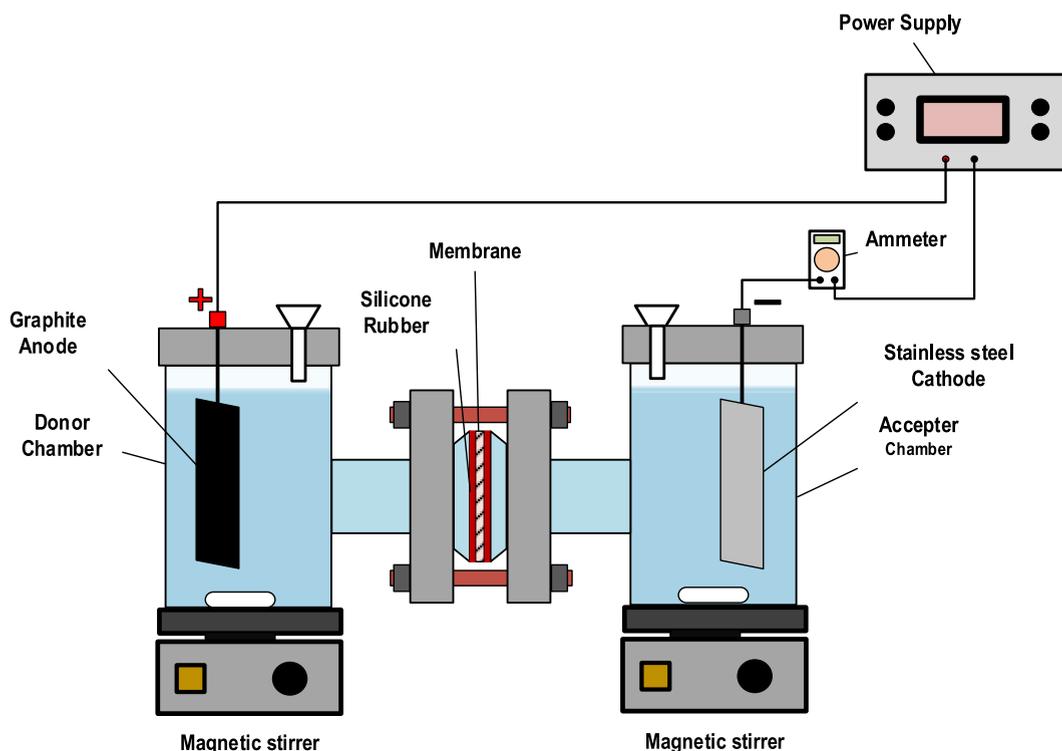


Fig. 1. EME system.

ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) phosphate (DEHP). To precisely regulate and maintain the pH levels throughout the extraction process, solutions of 0.1 M NaOH (Sodium Hydroxide) and 0.1 M HCl (Hydrochloric Acid) were skillfully employed. It is pertinent to note that the sodium hydroxide used possessed an exceptionally high purity level of 99 % and was meticulously sourced from POCH, an esteemed supplier in Poland. For the integral solid substrate component within the Supported Liquid Membrane (SLM) setup, a meticulously selected membrane sheet made from polypropylene was purchased from Jian City Qing Feng Equipment Material Co., China. This polypropylene membrane sheet has a pore size of 0.1 μm , and its thickness ranged meticulously from 0.18 to 0.22 mm, thereby serving as an essential and precise component of the SLM configuration.

2.2. Electromembrane extraction system

The cell of EME (Fig. 1) consists of two chambers, each one 137.44 mL in volume. The shape of the first chamber was cylindrical and contains 100 mL feed solution called the donor phase. Its dimensions were 7 cm in length and 5 cm in diameter. The first chamber was connected laterally with a horizontal cylindrical channel having an inside diameter of 3 mm and a length of 3 cm located above the bottom of the chamber at a distance of 2 cm. The same configuration was adopted for the second chamber. Two Teflon cups were used as covers for the chambers. Each one has a diameter of 4.8 cm and a thickness of 10 mm. Each cover has two holes: the first one for inserting the electrode while the second for feeding the solutions. A graphite plate with a length of 5 cm, thickness of 5 mm, and width of 3 cm was used as an anode. Graphite was selected as a cheap anodic material and to enhance water oxidation on its surface [29,31]. A stainless steel 316L plate was used as a cathode. It has a thickness of 2 mm with a length of 5 cm and a width of 3 cm. This marks the first instance of using these electrodes in an EME system, causing a reduction in the cost of fabrication in comparison with Pt electrodes. A polypropylene sheet with a circular shape having an active surface area of 7 cm² was used as a solid frame and then impregnated for 15 min with a solution containing 1-octanol with a suitable carrier. Subsequently, the setup was assembled by joining the two chambers together with the aid of two Teflon cups. To ensure the integrity of the assembly and prevent any potential leakage, the edges of the horizontal channels were sealed with RTV silicone rubber. Additionally, four screws and nuts were used in the assembly process for enhancing the stability of the system. These measures collectively contributed to a secure and leak-resistant configuration for the experimental setup.

The experimental setup included two magnetic bars situated within the acceptor and donor chambers to ensure consistent mixing of solutions at a constant stirring rate. A magnetic stirrer (Type/18490010, Metrohm AG, Herisau, Switzerland) equipped with variable rotation speed capabilities of up to 1000 rpm was employed for this purpose. Voltage application during EME was achieved using a power supply type UNI-T/UTP3000 made in Hong Kong with a range spanning from 20 to 60 V. To ensure precise measurement of the current applied across the cell, an ammeter with the option of measuring the current up to 0.2 A was connected in series with the power supply. Its type was UNI-T, Kowloon made in Hong Kong. All experiments of EME were performed at room temperature. Upon the

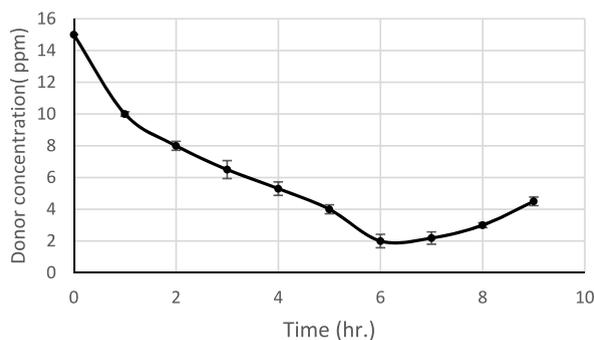


Fig. 2. Effect of extraction time. Feed solution: deionized water; initial cobalt concentration: 15 ppm; pH: 5; SLM: 1-octanol with DEHP (1 % v/v); voltage:60 V; stirring rate: 1000 rpm; acceptor solution: 0.1 M HCL.

completion of each run, each of donor and acceptor solutions were placed on 100 mL beakers separately. To ensure accurate measurement of cobalt concentration by atomic absorption spectroscopy (AAS) without potential interference from the solvent (1-octanol) employed for the Supported Liquid Membrane (SLM), the collected solutions underwent complete evaporation. Subsequently, the vials were refilled with deionized (DI) water in the same evaporated volume, followed by cobalt concentration measurement using AAS [30].

2.3. The analysis and measurements

The quantification of cobalt (Co) concentration was executed with a high degree of precision employing the state-of-the-art atomic absorption spectroscopy type-AA-7000, SHIMADZU. This advanced instrument was meticulously configured with a specialized air-acetylene flame setup, ensuring a high level of precision in the analysis process. For the accurate determination of Co^{2+} levels through Atomic Absorption Spectroscopy (AAS), a specific and well-optimized wavelength of 240.7 nm was judiciously selected, further enhancing the accuracy of the measurements. To precisely assess and monitor pH values throughout the experimental procedures, a portable pH meter of exceptional quality, procured from HANNA, a trusted source based in Romania, was deployed. This sophisticated pH meter was instrumental in delivering accurate and reliable pH measurements, an integral aspect of the meticulous experimental process. This pH meter consistently provided accurate and dependable pH measurements throughout the entirety of the experimental procedures. To calculate the efficiency of cobalt removal, Equation (1) was adopted as the standard methodology [29,31, 32]:

$$RE(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i symbolizes the initial Co concentration (ppm) in the donor phase while C_f represents the measuring Co concentration in ppm at the end of electrolysis (Δt).

3. Results and discussion

3.1. Selection the time of removal

The duration of the extraction process emerged as a pivotal factor significantly influencing the efficiency of cobalt removal. In the course of this study, the impact of time was methodically investigated, spanning a range between 1 and 9 h. Fig. 2 provides a vivid illustration of the findings. These outcomes demonstrated a progressive decline in cobalt concentration during donor phase, ultimately reaching a very low level of 2 ppm, while also producing a peak removal efficiency at an astounding rate of 87%, particularly at the 6-h mark. However, surpassing this critical 6-h threshold, a noteworthy phenomenon was observed, wherein the cobalt concentration experienced a discernible resurgence, ascending to 4.5 ppm at the 9-h mark. This intriguing observation signifies a diminishment in EME stability as the extraction duration being higher than 6h of the extraction period. Long extraction times could potentially start the dissolution and release of some SLM from its two sides into the surrounding solutions within the cell's chambers. This phenomenon could be caused a decrease in SLM thickness, which could possibly hinder the complete segregation between the donor and acceptor phases. Consequently, this could inadvertently facilitate the undesired transfer ions in a reverse direction from the acceptor to the donor phase. Similar observations and supporting evidence for this hypothesis have been previously documented by Davarani et al. [23,33]. Furthermore, Meng et al. [34] in their investigation of Cadmium (Cd) electromembrane extraction highlighted the impact of membrane thickness on mass transfer, specifically under the influence of terminal current intensity. In our own study, the current rose from 20 mA at 6 h to 100 mA at 9 h, which would cause the membrane thickness to significantly decrease after 6 h. These findings underscore the pivotal role played by membrane thickness in shaping the dynamics of the extraction process. The same phenomena was observed by Balchen et al. [35] in their work for isolation of peptides from plasma by EME where a sudden increase in current was

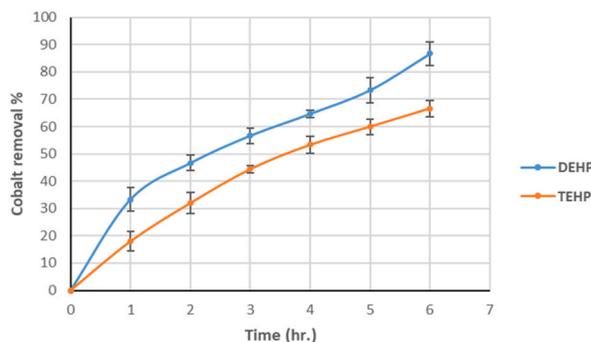


Fig. 3. Impact of carrier type on Co removal. Feed solution: deionized water; initial cobalt concentration: 15 ppm; pH: 5; voltage:60 V; stirring rate: 1000 rpm; acceptor solution: 0.1 M HCl; extraction time: 6 h.

occurred beyond 600s resulting in a bubble formation with a partial evaporation of the acceptor causing EME system being an unstable.

Based on present results, a time of extraction equal to 6 h is preferred since effective cobalt removal by EME was achieved. Hence, 6 h was fixed as an extraction time in studying the impact of other variables.

3.2. Carrier type selection

Within the process of transfer facilitated by an electric field, the using of carriers assumes a pivotal and catalytic role. These carriers are strategically to organic solvents and play a fundamental role within the intricate transfer mechanism. Notably, a prominent shared characteristic among these carriers is their inherent hydrophobic nature, which defines their modus operandi inside the solution via diffusion facilitated by the organic solvent. It is hypothesized that a proton-driven process serves as the primary basis for the effective transportation of heavy metal cations across these carriers. Analyte and proton ions are exchanged between the acceptor solution and carrier in a well planned procedure that is the basis for this transport mechanism. Then, analyte and proton ions are exchanged between the donor solution and carrier [36]. Importantly, the using of electric current serves to enhance and optimize the intricacies of this mechanism, thus elevating its efficiency and effectiveness [27]. Hence, choosing a suitable carrier is a vital step that initially should be determined in the EME process [37].

In this study, two types of compounds, namely bis(2-ethylhexyl) phosphate (DEHP) and tris(2-ethylhexyl) phosphate (TEHP), were examined after dissolving in 1-octanol to remove Co from solutions. For every carrier, a concentration of one percent (v/v) was chosen. Based on earlier studies that demonstrated 1-octanol's greater water immiscibility and effectiveness in extracting heavy metal cations, it was selected as the solvent [27,34]. This property confirms that 1-octanol stays within the pores of membrane with preventing its dissolution towards the acceptor or donor phases along stirring [38]. The effect of carrier type on CO elimination during a 6-h period is depicted in Fig. 3.

The results indicated that DEHP (bis(2-ethylhexyl) phosphate) outperformed TEHP (tris(2-ethylhexyl) phosphate) in terms of cobalt removal efficiency, achieving an impressive removal rate of 87 %, compared to the 66.67 % achieved with TEHP. This trend aligns with same observation noted during cadmium removal by EME achieved by Meng et al. [39]. Additionally, it is noteworthy that a body of prior research studies has consistently affirmed and substantiated the remarkable extraction capabilities of DEHP (bis(2-ethylhexyl) phosphate). DEHP has demonstrated its exceptional efficacy in the extraction of a diverse array of metal ions, spanning the spectrum from bivalent to trivalent ions. This empirical evidence underscores the versatility and effectiveness of DEHP as a carrier in various extraction processes, further solidifying its significance in the field of analytical chemistry and metal ion separation methodologies [40,41]. Additionally, Davarani et al. [42] found that DEHP enhanced the transport of some cations while TEHP enhanced the other so they tried different ratios of these carriers and observed that an improved result was obtained when utilizing a ratio of 1:1 for DEHP and TEHP during extraction of different heavy metals. Bhatluri et al. [25] used DEHP as a best carrier in removal of lead and cadmium from synthetic solution.

3.3. Impact of applied voltage

EME operates based on the utilization the electric field to increase transmission through SLM. The electric field strength, in turn, is determined by the applied voltage, which significantly influences the movement of ions [43]. In this study, five different voltage values ranging from 20 to 60 V were tested to assess their impact on cobalt removal using EME. The effect of applied voltage on cobalt removal is shown in Fig. 4.

The findings unequivocally show that a decrease in the final Co concentration at the donor phase, which drops from 7.2 to 2 ppm after a 6-h extraction time, is correlated with an increase in voltage values, which range from 20 to 60 V (see Fig. 4A). Furthermore, this elevation in voltage levels leads to a corresponding enhancement in the efficiency of cobalt removal, with the removal efficiency (RE%) surging from 52 % to an impressive 87 % (refer to Fig. 4B). These findings underscore the pivotal role of the applied voltage in enhancing the mass transfer of cobalt across both phases and within the DEHPA-Co(II) complex within the selective liquid membrane

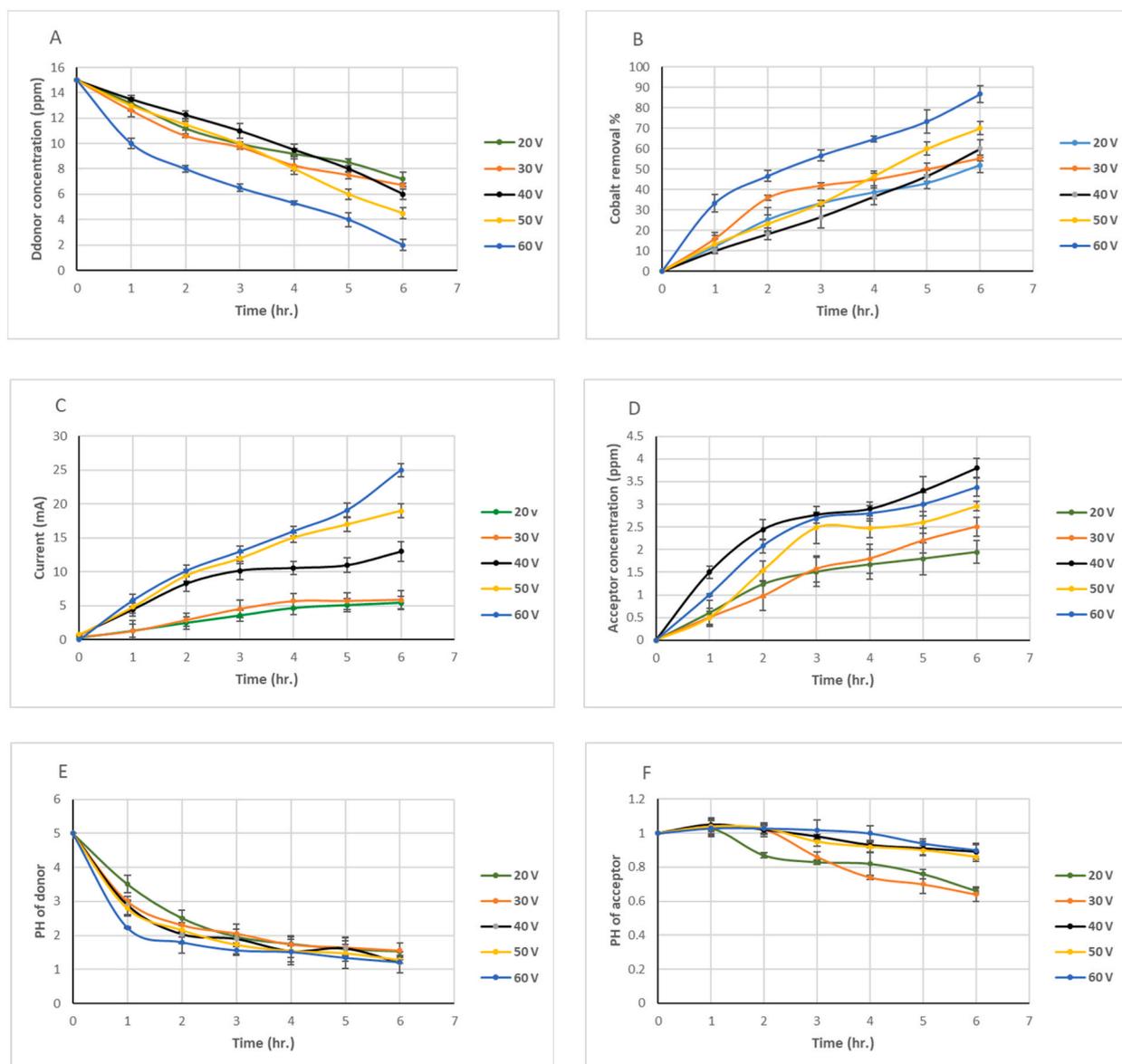


Fig. 4. The impact of voltage on parameters: A) Co concentration at the donor solution, B) Efficiency of Co removal, C) current, D) Co concentration at the acceptor, E) donor pH, and F) acceptor pH. The Feed solution: deionized water; initial cobalt concentration: 15 ppm; pH: 5; SLM: 1-octanol with DEHP (1 % v/v); acceptor solution: 0.1 M HCl; stirring rate: 1000 rpm; extraction time: 6 h.

(SLM).

A similar pattern of behavior was observed in the study conducted by Meng et al. [34] during removal of cadmium via EME, where they found that 60V is the optimal applied voltage. In their work, higher voltages were found to induce selective liquid membrane (SLM) instability. Conversely, Davarani et al. [23] found that a reduction in cadmium extraction efficiency as the voltage being higher than 60V. This decline was ascribed to membrane instability and hydrogen bubbles liberation on the cathode, as the potential of the cathode increased with higher applied voltages. Additionally, Kubáň et al. [27] discovered that the removal efficiency of cobalt exhibited a linear increase with the incremental elevation of applied voltage, up to 75V. Beyond this optimal threshold, a reduction was observed in the removal efficiency. Hence, the choice of right extraction voltage is of paramount importance in achieving efficient cobalt removal, as excessively high voltages beyond the optimum value may lead to membrane instability and a reduction in the removal efficiency.

The relationship between voltage and electric current flowing through the cell in EME is graphically depicted in Fig. 4C. Notably, there is a discernible increase in electric current with the elevation of the applied voltage. This observation provides valuable insight into selecting the most suitable voltage values for this system. A similar trend was observed by Davarani et al. [23] and Meng et al. [39].

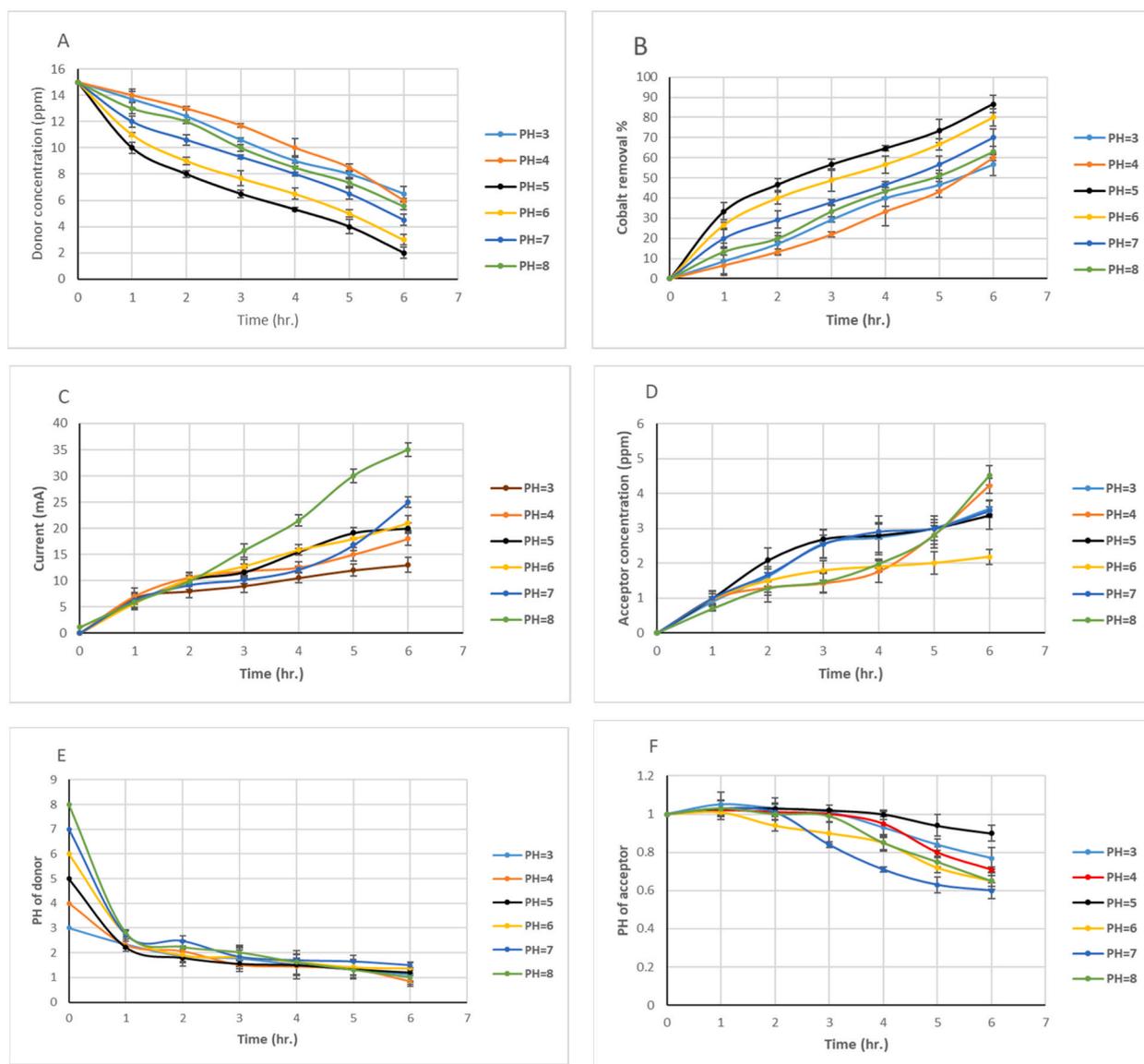


Fig. 5. Impact of initial donor pH on parameters: A) Co concentration at donor phase, B) removal efficiency of cobalt, C) current, D) Co concentration at the acceptor, E) donor pH, and F) acceptor pH. Feed solution: deionized water; initial cobalt concentration: 15 ppm; SLM: 1-octanol with DEHP (1 % v/v); voltage:60 V; stirring rate: 1000 rpm; acceptor solution: 0.1 M HCl; extraction time: 6 h.

Furthermore, the impact of applied voltage on Co concentration at the acceptor chamber is depicted in Fig. 4D. The data illustrates that at lower voltages ($\leq 40V$), the cobalt concentration in the acceptor chamber exhibits a linear increase over time. Conversely, when the voltage surpasses 40V, the cobalt concentration in the acceptor chamber reaches a level where a plateau is observed, after which the concentration continues to increase with time. These observations emphasize the pivotal role played by voltage in adjusting Co concentration inside the chamber of acceptor. Hence, voltage management can effectively be used to control the transport of Co ions and accumulating them at the acceptor phase.

During EME operation, two primary electrochemical processes occurred on the cathode and anode in the acidic solution. These reactions are as follows [44]:

At Cathode



At Anode



The accumulation of cobalt ions within the acceptor chamber is an intricately choreographed process characterized by the simultaneous interplay of multiple transfer rates, which collectively and intricately effect on Co concentration profile inside the acceptor chamber. As the fundamental mechanism, cobalt ions embark on a journey from the donor phase to the acceptor phase, traversing SLM propelled by their interfacing with DEHP [34]. Concurrently, a counterflow phenomenon unfolds, involving the migration of H^+ ions from the acceptor phase back to the donor phase. It is of paramount significance to note that the rate of cobalt ion transfer experiences a remarkable acceleration with increasing in the applied voltage. Moreover, H^+ ion generation rate undergoes augmentation, a consequence of the electrochemical process of oxidation water transpiring at the anode, as elucidated by Eq. (3). This intensified generation of H^+ ions consequently lead to a marked increasing in the levels of acidity at the donor phase, further accentuating the intricate interplay of electrochemical factors governing the cobalt ion transfer process.

inside the acceptor phase, two pivotal reactions happened namely the electrodeposition of cobalt and the generation of H_2 (as defined by Eq. (2)). The transfer rates of both cobalt and H^+ ions towards the cathode are intricately dependent on parameters like the potential of electrode, pH levels, and Co concentrations. Accordingly, cobalt accumulation rate at the acceptor phase is contingent upon the collective interplay of all these multifaceted transfer processes transpiring within acceptor phase. At low voltages, the concentration profiles shown in Fig. 4-D indicate that initially, the rate of cobalt electrodeposition is lower than cobalt transfer rate across the membrane. Nevertheless, with progressing time, Co electrodeposition rate increases and surpasses Co transfer rate through SLM. This causes a decrease in the cobalt concentration within the chamber, resulting in the observed peak in the concentration profile.

Conversely, the concentration profiles shown in Fig. 4-D at high voltages show that during the EME operation period, the co-deposition rate is consistently lower than the co-transfer rate across SLM. This can be ascribed to the influence of H_2 generating rate that competes with cobalt electrodeposition. The cobalt reduction potential ($E_0 = -0.277V$ vs. SHE [29]) is above H_2 generating potential, therefore, cobalt concentration increases over time at the acceptor chamber due to that most of current goes to hydrogen generation not for cobalt electrodeposition. This novel finding has not been previously reported in existing research.

One of new main results of this study relates to the observed pH profiles within both the donor and acceptor chambers during the EME operation, as graphically depicted in Fig. 4-E and 4-F. Notably, a substantial alteration in pH values was discerned for each phase (donor and acceptor) with the augmentation of applied voltage. As the extraction process progressed, a conspicuous increase in H^+ ion generation was observed, culminating in heightened acidity within the phase of donor, as visually evidenced in Fig. 4-E.

At the phase of acceptor, an intricate competition unfolded between the generation of H_2 and Co reduction. Results indicate that lower voltage levels induce a more alkaline solution compared to the pH at higher voltage, as demonstrated in Fig. 4-F. Hence, this phenomenon underscores that acceptor solution pH is intricately affected by the equilibrium between H_2 evolution and cobalt reduction, a balance that hinges on the applied voltage.

Based on the insights garnered from the results, it can be concluded that an applied voltage of 60 V yields the highest removal efficiency of cobalt when utilizing EME system. Accordingly, 60 V was chosen as the optimal value in further studying effects of other experimental parameters.

3.4. Impact of initial donor pH

Cobalt ions could be remained soluble in water up to pH 9 since the solubility product constant (Ksp) of cobalt hydroxide is 5.92×10^{-15} [45]. To confirm the effectiveness of the process in line with previous works [23,34], pH range for runs was chosen to be between 3 and 8, since values below 3 are not recommended.

According to Pedersen-Bjergaard et al. [46], the enhancement of ion transport and flow through SLM can be achieved by maintaining a balance. In our study, the acceptor solution was kept at a constant pH value of 1, which was achieved by using 0.1 M HCl. Choosing acceptor medium based on HCl was grounded on previous observations [23]. However, other studies utilized HNO_3 as the acceptor medium [34].

Fig. 5 clearly illustrates how the pH donor affects the extraction of cobalt and removal efficiency by showing changes in a number of critical parameters, including cobalt removal efficiency, cobalt concentration at the donor, cobalt concentration at the acceptor, pH of the donor, and pH of the acceptor, all of which change over time with respect to the initial pH of the donor. Fig. 5-A provides information about the profile of cobalt concentration in the donor solution, and Fig. 5-B illustrates how pH affects the effectiveness of cobalt removal. Results unveiled in this analysis underscore that the highest efficiency of Co removal is achieved at a pH of 5. However, it is noteworthy that this efficiency experiences a marked decline, plummeting to approximately 60 %, when the pH strays beyond 7 or decreases below 4. This implies that within the pH range of 4–7, the interaction between cobalt and DEHP is maximally efficacious. Conversely, at pH lower than 4, DEHP suffers heightened protonation, obstructing its active attachment with ions [27]. At elevated pH levels, cobalt ions (Co(II)) have the tendency of forming complex species that can notably influence their transport through the membrane.

According to these findings, pH 5 was chosen for further investigation of the influence of other factors to ensure the DEHP stability. Meng et al. [34] also found the same behavior in removal of Cd by EME, although their removal efficiency stayed unchanged above pH of 5. On the other hand, Davarani et al. [23] preferred medium with high alkalinity when using a mixture of TEHP and DEHP. Similar value of pH was taken as the best by previous works [25,26].

Fig. 5-C shows how pH affects the current flow through the cell. It is observed that deviating from pH 5 by decreasing it, leads to a reduction in the current flowing through the cell. The counter-transfer of H^+ and Co^{2+} ions play a significant role in controlling the value of current across the SLM.

The effect of initial donor pH on Co concentration at the acceptor is illustrated in Fig. 5-D. It is evident that at all pH values, the concentration of the acceptor increases initially, reaching a plateau region, and then starts to increase. This trend could be explained by

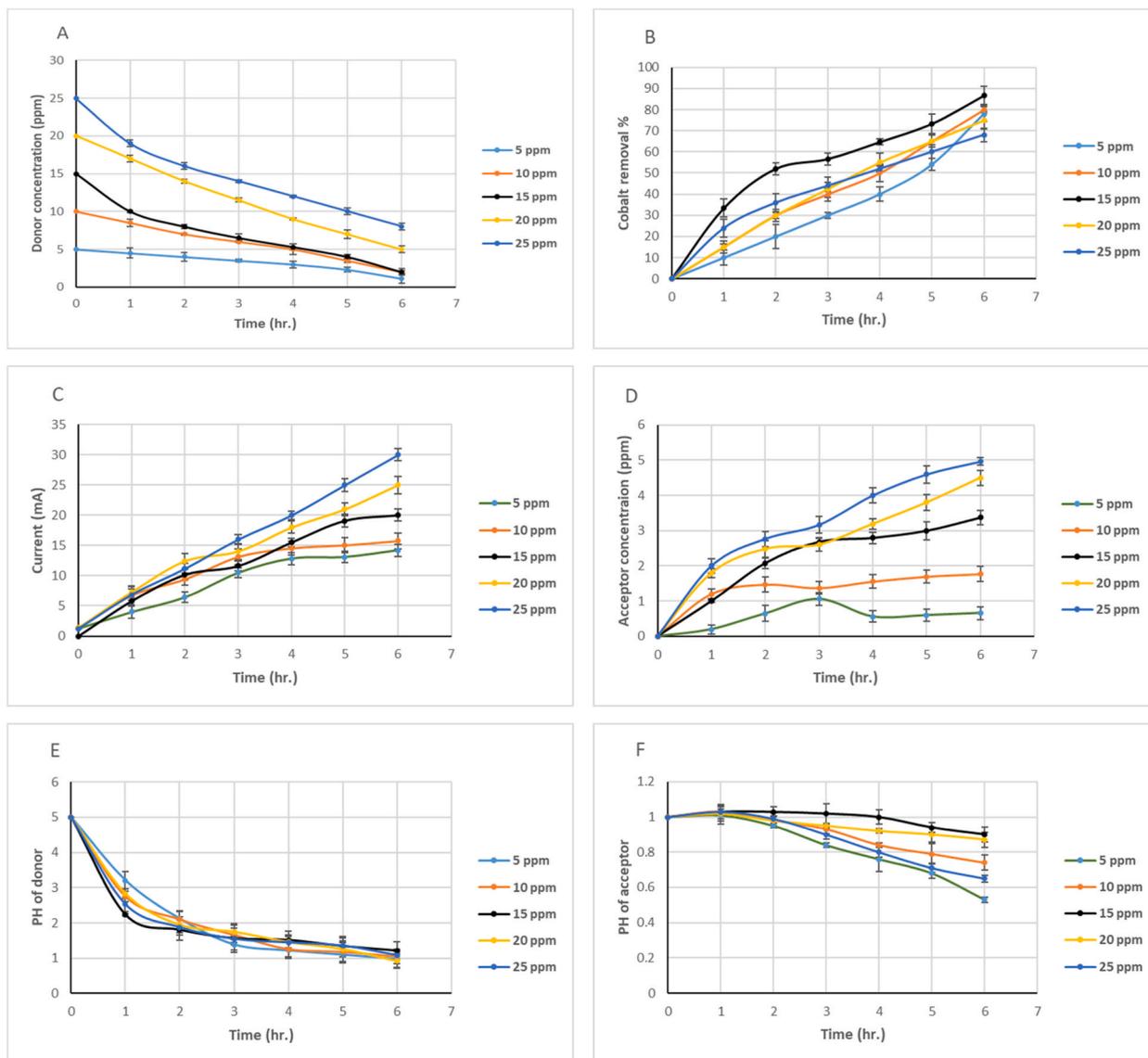


Fig. 6. Impact of initial Co concentration on parameters: A) Co concentration at the donor, B) the efficiency of cobalt removal, C) current, D) Co concentration at the acceptor, E) donor pH, and F) acceptor pH. Feed solution: deionized water; SLM: 1-octanol with DEHP (1 % v/v); voltage:60 V; stirring rate: 1000 rpm; acceptor solution: 0.1 M HCl; extraction time: 6 h.

looking for the net transfer of cobalt at the acceptor phase. At initial stage, the rate of electrodeposition is lower than the Co transfer rate across SLM. Consequently, with progress in time, Co electrodeposition rate increases and surpasses Co transport rate, resulting in a plateau region. This particular finding has not been mentioned in previous research.

As seen in Fig. 5-E, the donor pH shows a progressive decline over time, finally settling around a value near 1 at most initial donor pH levels. The fact that all donor pH values—aside from pH 3—saw a significant decline in pH within the first hour is very noteworthy.

Moreover, Fig. 5-F illustrates the impact of the donor's initial pH on the acceptor pH and shows an interesting pattern. The pH of the acceptor increases initially and then starts to fall. But it's important to note that when the initial donor pH is set at 5, the acceptor pH decreases in the last phases, albeit less dramatically.

3.5. Impact of initial Co concentration

The impact of varying the initial Co concentration on the EME system was investigated in this study, ranging from 5 to 25 ppm. Fig. 6 illustrates the results obtained from this investigation, highlighting the effect of different cobalt concentrations on the EME system. Fig. 6-A shows the profile of Cd concentration versus time at different initial Co concentration where increasing the initial Co concentration led to getting higher final concentration of Co.

Table 1

Comparison the removal of cobalt by EME with the case of removal without applied voltage.

Time(hr.)	0	1	2	3	4	5	6
EME: Co (II), ppm	15	10	8	6.5	5.3	4	2
ME: Co (II), ppm	15	14.3	13.6	12.3	11.5	10.0	9.6

Experimental results shown in Fig. 6-B, offer insights into the intricate relationship between the initial Co concentration and its removal efficiency during EME operation. The findings elucidate that as the initial concentration of Co (II) increases, there is a concurrent decrease in removal efficiency. Precisely, the efficiency of removal diminishes to 68 % at concentration of 25 ppm while it was 87 % at concentration of 15 ppm. Notably, it is important to mention that at Co concentrations lower than 15 ppm, a little decrease in the Co removal efficiency is detected when compared to cases with higher concentrations. Remarkably, these behaviors in the line with prior research findings by Swain et al., even without accounting for the current effects [47]. Furthermore, the removal rate shows a more pronounced initial phase when confronted with cobalt concentrations above 15 ppm. This is in contrast to a linear trend observed at lower concentrations. This particular behavior serves as compelling evidence of the efficient diffusion transfer of Co(II) across the membrane, which is a direct result of the judicious choosing DEHP for the EME system. Additionally, it's noteworthy that as the cobalt concentration increases, there is a proportional rise in the current flowthrough the cell, as convincingly demonstrated in Fig. 6C.

Fig. 6-D furnishes a captivating perspective into the intricate relationship between the initial Co concentration at donor with Co concentration at acceptor phase. The findings unveil distinctive behaviors contingent upon the initial concentration of cobalt. In the initial stages, the Co(II) concentration within the acceptor phase experiences a noticeable ascent, achieving a plateau after approximately 2–4 h, after which it embarks on an ascending trajectory once more. It is worth noting a particular exception in the case of an initial concentration of 5 ppm, where a unique peak is conspicuously observed at the 3-h mark. This intriguing behavior can be attributed to the nuanced interplay and competition between the rates of cobalt ion transfer from the donor chamber to the acceptor chamber via SLM. Within this complex dynamic, some of these cobalt ions undergo a process of electrodeposition on the cathode, while others persist within the acceptor phase. Consequently, this intricate competition between these two concurrent processes engenders the observed concentration dynamics, shedding light on the multifaceted nature of the cobalt ion transfer mechanism in the context of EME. At the begin of EME process, donor pH undergoes a quick decline, particularly evident in the initial stage. Following that, it shows a gradual reduction over time, as shown in Fig. 6-E. The acceptor pH profile behaves indistinguishably for all starting concentrations. As seen clearly in Fig. 6-F, the pH increases at first before starting on a downward track.

3.6. Comparison with membrane extraction without applied voltage

According to results of present work, the optimal conditions for cobalt removal by EME were an acceptor solution with pH of 5 containing cobalt ions at a concentration of 15 ppm, an acceptor solution containing 0.1 M HCl, SLM composed of DEHP (1 % v/v) dissolved in 1-octanol, a stirring rate at 1000 rpm, a voltage of 60 V, and an operation time of 6 h. Two runs were performed for evaluating the role of voltage on extraction process via SLM. Both of them at the same optimum conditions except the second without applied voltage. The results are shown in Table 1. It was observed that applying the voltage has an essential role on the mass transfer hence increasing the removal efficiency where it was raised from 51 % in case of no voltage to 87 % in case of applying 60 V. This enhancement is compatible with the Meng et al. [34] observations where they reported a rise in Cd removal from 81 % in case of no voltage to 99.9 % in case of applying 60 V after 9 h. It should be noted that Meng et al. [34] achieved a cadmium concentration of 1 ppm after 6 h. While in the present work, a minimum concentration of cobalt (2 ppm) was achieved at 6 h. Hence to reduce the concentration below this value, the SLM showed be replace with fresh one (see Fig. 1) and continuing the electrolysis for further time to the desired level of cobalt.

The electrical energy consumption (EEC) in kWh/m³ could be estimated using the following equation [48]:

$$EEC = \frac{U \times I \times t}{V} \quad (4)$$

Where (I) represents the applied current in ampere and U denotes the cell voltage in volt (V), While v is the volume of solution in liter.

It is important to mention that during the application of 60 V, the required current is very small during EME in milliampere and it was increased from 5 mA to 20 mA during 6 h resulting in of average electrical energy consumption of 45 kWh/m³ (based on Eq. (4)) which is lower than the traditional electrochemical methods [49,50].

3.7. Comparison of present work with previous studies

Table 2 shows a comparison of the present method with tradition solid liquid membrane method used for cobalt extraction. A few works were published regarding removal of cobalt by tradition SLM. It was cleared that applying electrical field give an enhancement in removal of cobalt from feed phase at lower extraction from a lower concentration of cobalt in comparison with previous works. Besides using cheap solid membrane material with available solvent and carrier has another advantage in comparison with previous works. This comparison indicates the important of EME as a valuable separation process for heavy metals.

Table 2
Comparison with traditional SLM.

Type of process	Conditions	Removal efficiency	Ref.
SLM with microporous hydrophobic PVDF film	$[Co]_{feed} = 10 \text{ mol/m}^3$, feed pH = 6.00, $[Cyanex272]_{memb.} = 750 \text{ mol/m}^3$ $[H_2SO_4]_{strip} = 100 \text{ mol/m}^3$	50 % at 7 h 99.99 % at 24 h	47
SLM with millipore Durapore GVHP4700 PVDF	Feed phase: 0.01 g/l cobalt (II) at pH 4.75. Membrane phase: (10 % v/v DP8R + 10 % v/v Acorga M5640) in Exxsol D100. $[H_2SO_4]_{strip} = 25 \text{ g/L}$	77.9 % at 4 h	[51]
SLM with Millipore Durapore GVHP 10	0.265 kg/m ³ cobalt(II) solutions in 0.2 M acetate buffer, pH 5, Membrane phase: 10 % solution of CYANEX 272 in commercial paraffin $H_2SO_4]_{strip} = 0.2 \text{ M}$	34.91 % at 2 h	[52]
EME with SLM polypropylene membrane sheet	SLM: 1-octanol with DEHP (1 % v/v), feed solution: 15 mg/l cobalt (II) in deionized water; acceptor solution: 0.1 M HCl; stirring rate: 1000 rpm; voltage: 60 V; pH: 5	87 % at 6 h	Present work

4. Conclusion

In this study, our primary objective was to harness the capabilities of Electromembrane Extraction (EME) technology to effectively eliminate cobalt from aqueous solutions. Through the strategic application of an electric field, cobalt ions were successfully transported from the donor phase, traversing SLM, and ultimately attainment the acceptor phase. The critical choice of the appropriate carrier proved instrumental in ensuring the efficient and effective transport of cobalt ions in this process. Our research outcomes unveiled a compelling insight: when employing bis(2-ethylhexyl) phosphate (DEHP) as the carrier, there was a notable 20 % increase in the removal efficiency of cobalt in comparison with the using of tris(2-ethylhexyl) phosphate (TEHP) as the carrier. This observation indicates a robust and effective complexation between cobalt and DEHP during the transfer process across the selective liquid membrane (SLM). It's imperative to underscore that even when TEHP was utilized as the carrier, it still outperformed the scenario in which no electric current was applied. This underscores the substantial impact of implementing the EME system, resulting in a remarkable increase in cobalt removal efficiency, with an approximate 50 % difference compared to scenarios where voltage was not applied. These results highlight the powerful potential of EME technology to improve cobalt removal efficiency, which represents a noteworthy development in the field of metal ion extraction from aqueous solutions.

If the system is run at a pH of 5, the voltage was shown to be the primary parameter governing cobalt mass transfer by SLM. If the pH is changed to be less than or greater than 5, no discernible improvement will be possible. The following carefully considered parameters were found to be the best for the EME process: using 1-octanol as the carrier and 1.0% v/v DEHP concentration, applying a carefully calibrated voltage of 60 V, keeping the pH at 5, using 15 mg/L of cobalt as the beginning concentration, extracting the material for 6 h, and making sure to stir continuously at 1000 rpm. Remarkably, under these highly precise and fine-tuned conditions, an exceptionally impressive removal efficiency of 87 % was remarkably achieved. Compared with traditional SLM method, the present system gives better performance. Hence using of EME offered several advantages in terms of requiring less reagents, consuming lower energy, and involving low number of steps to achieve higher Co(II) removal from low concentrations, in addition to reduce the risk of secondary contamination. Hence, this technology could be recommended on a pilot scale aimed at removing various heavy metals from diverse wastewater sources.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Noor R. Kadhim: Writing – original draft, Software, Data curation. Hussain M. Flayeh: Supervision. Ali H. Abbar: Supervision.

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.

Acknowledgment

The authors express their gratitude to the technical staff of the Environmental Engineering Department at the University of Baghdad for their valuable assistance and support throughout this study.

References

- [1] F.R. Adolfo, et al., Simultaneous determination of cobalt and nickel in vitamin B12 samples using high-resolution continuum source atomic absorption spectrometry, *Talanta* 147 (2016) 241–245.

- [2] A. Bhatnagar, A.K. Minocha, M. Sillanpää, Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent, *Biochem. Eng. J.* 48 (2) (2010) 181–186.
- [3] C. Kokkinos, A. Economou, Microfabricated chip integrating a bismuth microelectrode array for the determination of trace cobalt (II) by adsorptive cathodic stripping voltammetry, *Sens. Actuators, B* 229 (2016) 362–369.
- [4] T.S. Anirudhan, J.R. Deepa, J. Christa, Nanocellulose/nanobentonite composite anchored with multi-carboxyl functional groups as an adsorbent for the effective removal of Cobalt (II) from nuclear industry wastewater samples, *J. Colloid Interface Sci.* 467 (2016) 307–320.
- [5] M. Soyлак, L. Elci, M. Dogan, Determination of trace amounts of cobalt in natural water samples as 4-(2-thiazolylazo) resorcinol complex after adsorptive preconcentration, *Synth. React. Inorg. Met. Chem.* 30 (3) (1997) 623–631.
- [6] P. Oustadakis, S. Agatzini-Leonardou, P.E. Tsakiridis, Nickel and cobalt precipitation from sulphate leach liquor using MgO pulp as neutralizing agent, *Miner. Eng.* 19 (11) (2006) 1204–1211.
- [7] C.Y. Cheang, N. Mohamed, Removal of cobalt from ammonium chloride solutions using a batch cell through an electrogenerative process, *Sep. Purif. Technol.* 162 (2016) 154–161.
- [8] A. Parus, K. Wieszczycka, A. Olszanowski, Solvent extraction of cadmium (II) from chloride solutions by pyridyl ketoximes, *Hydrometallurgy* 105 (3–4) (2011) 284–289.
- [9] H. Tabani, S. Nojavan, M. Alexović, J. Sabo, Recent developments in green membrane-based extraction techniques for pharmaceutical and biomedical analysis, *J. Pharm. Biomed. Anal.* 160 (2018) 244–267.
- [10] W.A. Khan, et al., Hollow fiber-based liquid phase microextraction followed by analytical instrumental techniques for quantitative analysis of heavy metal ions and pharmaceuticals, *J. Pharm. Anal.* 10 (2) (2020) 109–122.
- [11] S. Pedersen-Bjergaard, C. Huang, A. Gjelstad, Electromembrane extraction—Recent trends and where to go, *J. Pharm. Anal.* 7 (3) (Jun. 2017) 141–147, <https://doi.org/10.1016/j.jpah.2017.04.002>.
- [12] C. Huang, A. Gjelstad, S. Pedersen-Bjergaard, Organic solvents in electromembrane extraction: recent insights, *Rev. Anal. Chem.* 35 (4) (2016) 169–183.
- [13] W.A. Khan, Y. Yamini, M. Baharfar, M.B. Arain, A new microfluidic-chip device for selective and simultaneous extraction of drugs with various properties, *New J. Chem.* 43 (24) (2019) 9689–9695.
- [14] N.H. Yousif, H.M. Flayeh, Process optimization study of Pb (II) removal by bulk liquid membrane (BLM), *Iraqi J. Chem. Pet. Eng.* 21 (2) (2020) 37–45.
- [15] H. Saba'A, H.M. Flayeh, Removal of dye from synthetic wastewater by liquid membrane, *J. Eng.* 28 (3) (2022) 60–72.
- [16] X. Meng, C. Wang, T. Ren, L. Wang, X. Wang, Electrodriven transport of chromium (VI) using 1-octanol/PVC in polymer inclusion membrane under low voltage, *Chem. Eng. J.* 346 (2018) 506–514.
- [17] B. Seyfinejad, M. Khoubnasabjafari, S.E. Ziaei, S.A. Ozkan, A. Jouyban, Electromembrane extraction as a new approach for determination of free concentration of phenytoin in plasma using capillary electrophoresis, *DARU J. Pharm. Sci.* 28 (2020) 615–624.
- [18] S. Yousefi, S. Makarem, W. Alahmad, F.D. Zare, H. Tabani, Evaluation of complexing agents in the gel electro-membrane extraction: an efficient approach for the quantification of zinc (II) ions in water samples, *Talanta* 238 (2022), 123031.
- [19] H. Tabani, F. Dorabadzare, S. Pedersen-Bjergaard, Gel electro-membrane extraction: an overview on recent strategies for extraction efficiency enhancement, *TrAC Trends Anal. Chem.* (2023), 116990.
- [20] H. Tabani, T. Samkumpim, W. Alahmad, F. Dorabadzare, P. Varanusupakul, In-tube gel electro-membrane combined with microfluidic paper-based device: a green and miniaturized extraction mode for the chromium speciation, *Adv. Sample Prep.* 3 (2022), 100036.
- [21] K. Maiphetho, L. Chimuka, H. Tutu, H. Richards, Technical design and optimisation of polymer inclusion membranes (PIMs) for sample pre-treatment and passive sampling—A review, *Sci. Total Environ.* 799 (2021), 149483.
- [22] R.G. Ingle, S. Zeng, H. Jiang, W.-J. Fang, Current development of bioanalytical sample preparation techniques in pharmaceuticals, *J. Pharm. Anal.* 12 (4) (2022) 517–529.
- [23] S.S.H. Davarani, N. Sheikhi, S. Nojavan, R. Ansari, S. Mansori, Electromembrane extraction of heavy metal cations from aqueous media based on flat membrane: method transfer from hollow fiber to flat membrane, *Anal. methods* 7 (6) (2015) 2680–2686.
- [24] R.E. Kannouma, M.A. Hammad, A.H. Kamal, F.R. Mansour, Miniaturization of Liquid-Liquid extraction; the barriers and the enablers, *Microchem. J.* (2022), 107863.
- [25] K.K. Bhatluri, M.S. Manna, A.K. Ghoshal, P. Saha, Separation of cadmium and lead from wastewater using supported liquid membrane integrated with in-situ electrodeposition, *Electrochim. Acta* 229 (2017) 1–7.
- [26] S.K. Mondal, M.K. Beriya, P. Saha, Separation and recovery of nickel and zinc from synthetic wastewater using supported liquid membranes with in situ electrodeposition, *Ind. Eng. Chem. Res.* 58 (23) (2019) 9970–9987.
- [27] P. Kubán, L. Strieglerová, P. Gebauer, P. Boček, Electromembrane extraction of heavy metal cations followed by capillary electrophoresis with capacitively coupled contactless conductivity detection, *Electrophoresis* 32 (9) (2011) 1025–1032, <https://doi.org/10.1002/elps.201000462>.
- [28] A. Mollahosseini, Y. Elyasi, M. Rastegari, Flat membrane-based electromembrane extraction coupled with UV-visible spectrophotometry for the determination of diethylhexyl phthalate in water samples, *Microchem. J.* 151 (2019), 104191.
- [29] D.R. Saad, Z.T. Alismael, A.H. Abbar, Removal of cadmium from simulated wastewaters using a fixed bed bio-electrochemical reactor, *J. Eng.* 26 (12) (Dec. 2020) 110–130, <https://doi.org/10.31026/j.eng.2020.12.07>.
- [30] C. Basheer, S.H. Tan, H.K. Lee, Extraction of lead ions by electromembrane isolation, *J. Chromatogr. A* 1213 (1) (Dec. 2008) 14–18, <https://doi.org/10.1016/j.chroma.2008.10.041>.
- [31] Z. Zahraa, A. kadhim, A.H. Abbar, Kinetics of electrochemical removal of nickel using bio-electrochemical reactor with packed bed rotating cylinder cathode, *Al-Khwarizmi Eng. J.* 18 (3) (Sep. 2022), <https://doi.org/10.22153/kej.2022.08.003>.
- [32] Z.A. Kadhim, A.H. Abbar, Nickel removal from simulated wastewater using a novel bio-electrochemical cell with packed bed rotating cylinder cathode, *Chem. Eng. Res. Des.* 190 (Feb. 2023) 157–173, <https://doi.org/10.1016/j.cherd.2022.12.025>.
- [33] S.S. Hosseiny Davarani, N. Sheikhi, S. Nojavan, R. Ansari, S. Mansori, Electromembrane extraction of heavy metal cations from aqueous media based on flat membrane: method transfer from hollow fiber to flat membrane, *Anal. Methods* 7 (6) (2015) 2680–2686, <https://doi.org/10.1039/C5AY00243E>.
- [34] X. Meng, J. Li, Y. Lv, Y. Feng, Y. Zhong, Electro-membrane extraction of cadmium(II) by bis(2-ethylhexyl) phosphate/kerosene/polyvinyl chloride polymer inclusion membrane, *J. Hazard Mater.* 386 (Mar. 2020), 121990, <https://doi.org/10.1016/j.jhazmat.2019.121990>.
- [35] M. Balchen, T.G. Halvorsen, L. Reubsæet, S. Pedersen-Bjergaard, Rapid isolation of angiotensin peptides from plasma by electromembrane extraction, *J. Chromatogr. A* 1216 (41) (Oct. 2009) 6900–6905, <https://doi.org/10.1016/j.chroma.2009.08.037>.
- [36] J. Peng, R. Liu, J. Liu, B. He, X. Hu, G. Jiang, Ultrasensitive determination of cadmium in seawater by hollow fiber supported liquid membrane extraction coupled with graphite furnace atomic absorption spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 62 (5) (May 2007) 499–503, <https://doi.org/10.1016/j.sab.2007.04.006>.
- [37] A. Nezhadali, R. Mohammadi, M. Mojarrah, An overview on pollutants removal from aqueous solutions via bulk liquid membranes (BLMs): parameters that influence the effectiveness, selectivity and transport kinetic, *J. Environ. Chem. Eng.* 7 (5) (Oct. 2019), 103339, <https://doi.org/10.1016/j.jece.2019.103339>.
- [38] S. Seidi, Y. Yamini, A. Heydari, M. Moradi, A. Esrafil, M. Rezazadeh, Determination of thebaine in water samples, biological fluids, poppy capsule, and narcotic drugs, using electromembrane extraction followed by high-performance liquid chromatography analysis, *Anal. Chim. Acta* 701 (2) (Sep. 2011) 181–188, <https://doi.org/10.1016/j.aca.2011.05.042>.
- [39] X. Meng, Y. Long, Y. Tian, W. Li, T. Liu, S. Huo, Electro-membrane extraction of lithium with D2EHPA/TBP compound extractant, *Hydrometallurgy* 202 (2021), 105615.
- [40] D. Wang, J. Hu, D. Liu, Q. Chen, J. Li, Selective transport and simultaneous separation of Cu(II), Zn(II) and Mg(II) using a dual polymer inclusion membrane system, *J. Memb. Sci.* 524 (Feb. 2017) 205–213, <https://doi.org/10.1016/j.memsci.2016.11.027>.
- [41] C.F. Croft, M.I.G.S. Almeida, R.W. Cattrall, S.D. Kolev, Separation of lanthanum(III), gadolinium(III) and ytterbium(III) from sulfuric acid solutions by using a polymer inclusion membrane, *J. Memb. Sci.* 545 (Jan. 2018) 259–265, <https://doi.org/10.1016/j.memsci.2017.09.085>.

- [42] S.S.H. Davarani, H.R. Moazami, A.R. Keshtkar, M.H. Banitaba, S. Nojavan, A selective electromembrane extraction of uranium (VI) prior to its fluorometric determination in water, *Anal. Chim. Acta* 783 (Jun. 2013) 74–79, <https://doi.org/10.1016/j.aca.2013.04.045>.
- [43] I.J.Ø. Kjelsen, A. Gjelstad, K.E. Rasmussen, S. Pedersen-Bjergaard, Low-voltage electromembrane extraction of basic drugs from biological samples, *J. Chromatogr. A* 1180 (1–2) (2008) 1–9.
- [44] R. Sen, et al., Electrocatalytic water oxidation: an overview with an example of translation from lab to market, *Front. Chem.* 10 (May 2022) 414, <https://doi.org/10.3389/fchem.2022.861604>.
- [45] Y.F. Orlov, R.A. Mambetova, Synthesis details and solubility product for cobalt hydroxo salt Co (OH) 1.8 ClO. 2, *Russ. J. Inorg. Chem.* 52 (7) (2007) 1002–1005.
- [46] L.E.E. Eibak, K.E. Rasmussen, E.L. Øiestad, S. Pedersen-Bjergaard, A. Gjelstad, Parallel electromembrane extraction in the 96-well format, *Anal. Chim. Acta* 828 (2014) 46–52.
- [47] B. Swain, J. Jeong, J. Lee, G.-H. Lee, Extraction of Co(II) by supported liquid membrane and solvent extraction using Cyanex 272 as an extractant: a comparison study, *J. Memb. Sci.* 288 (1–2) (Feb. 2007) 139–148, <https://doi.org/10.1016/j.memsci.2006.11.012>.
- [48] O. Larue, E. Vorobiev, C. Vu, B. Durand, Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions, *Sep. Purif. Technol.* 31 (2) (2003) 177–192.
- [49] A.J. Chaudhary, S.M. Grimes, Heavy metals in the environment. Part I: removal of cobalt from dilute effluent streams by fluidised bed electrolysis, *J. Chem. Technol. Biotechnol.* 56 (1) (1993) 15–20.
- [50] N. Tzanetakis, K. Scott, Recycling of nickel–metal hydride batteries. II: electrochemical deposition of cobalt and nickel, *J. Chem. Technol. Biotechnol. Int. Res. Process. Environ. Clean Technol.* 79 (9) (2004) 927–934.
- [51] F.J. Alguacil, M. Alonso, F.A. Lopez, A. López-Delgado, Active transport of cobalt (II) through a supported liquid membrane using the mixture DP8R and Acorga M5640 as extractant, *Desalination* 281 (2011) 221–225.
- [52] G. León, G. Martínez, M.A. Guzmán, J.I. Moreno, B. Miguel, J.A. Fernández-López, Increasing stability and transport efficiency of supported liquid membranes through a novel ultrasound-assisted preparation method. Its application to cobalt (II) removal, *Ultrason. Sonochem.* 20 (2) (2013) 650–654.