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Original scientific paper

Zinc (II) removal from simulated wastewater by electro-membrane extraction approach: adopting an electrolysis cell with a flat sheet supported liquid membrane

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Abstract

The aim of this study is to utilize the electromembrane extraction (EME) system as a manner for effective removal of zinc from aqueous solutions. A novel and distinctive electrochemical cell design was adopted consisting of two glass chambers, a supported liquid membrane (SLM) housing a polypropylene flat membrane infused with 1-octanol and a carrier. Two electrodes were used, a graphite as anode and a stainless steel as cathode. A comprehensive examination of several influential factors including the choice of carrier, the applied voltage magnitude, the initial pH of the donor solution, and the initial concentration of zinc was performed, all in a concerted effort to ascertain their respective impacts on the efficiency of zinc elimination. Two distinct carriers, namely tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) phosphate (DEHP) were evaluated, in a tandem with utilization of 1-octanol. The results revealed essential role played by the applied voltage in augmenting the rate of mass transfer of zinc across the membrane. The best operating conditions were utilized for 1-octanol enriched with 1.0 vol.% bis(2-ethylhexyl) phosphate as a carrier, applied voltage of 60 V, initial pH of 5, initial zinc concentration of 15 mg L^{-1}, extraction duration of 6 hours, and stirring rate of 1000 rpm. Surprisingly, operating under these meticulously devised conditions culminated in the outstanding removal efficiency of 87.3 %. In comparison with no applied voltage, a substantial enhancement in removal efficiency was observed, transcending from a meager 36.67 % to an impressive 87.3 % at 60 V, suggesting thus a tremendous potential of EME as an efficacious technique for the elimination of heavy metals.

Keywords
Heavy metal removal; ion transport; electrochemical treatment; membrane selectivity; organic solvent; membrane carriers

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Introduction

The presence of non-biodegradable heavy metals in water and wastewater poses a serious threat to our water resources. With the growing population, clean drinking water is crucial for all living beings. Industries like electrical appliances, electroplating, atomic energy, power plants, and refineries often release contaminated waste into water bodies during their processes. This disrupts the ecological balance and harms the flora and fauna. Heavy metals, being non-biodegradable, can accumulate in organisms when consumed through water. While trace amounts of heavy metals are needed for biochemical processes in the human body, excessive levels in drinking water can lead to health issues such as nausea, indigestion, diarrhea, skin allergies, tooth fluorosis, and even cancer [1]. According to the World Health Organization, zinc-containing liquids are considered hazardous because of their acute toxicity, which should be discharged at concentrations lower than 5 mg L^{-1}. Furthermore, zinc may accumulate in the water body leading to inhibit biological treatment processes, and therefore its treatment is mandatory [2-4].

In recent years, there has been a significant progress in the development of various separation and extraction techniques. These techniques can be categorized into three primary groups: solid-based, liquid-based, and membrane-based methods [5-9]. Among these methods, membrane-based techniques are distinguished for their exceptional effectiveness in purifying samples and removing various interferences. One particularly exciting variation within membrane-based extractions is known as electromembrane extraction (EME), which offers enhanced efficiency and selectivity. EME operates on the principle of electrokinetic migration, whereby ionized species move under the influence of an electric field across a membrane that is impregnated with an organic solvent. What makes EME particularly appealing is the ability to achieve selectivity by controlling the direction and strength of the electric field, as well as by manipulating the composition of the immobilized organic solvent. Furthermore, the extraction time is significantly reduced in this method due to the enhanced mass transport of analytes facilitated by electrical forces [10].

The primary objective of this study is to investigate the application of electromembrane extraction (EME) in the removal of zinc (II) ions from a simulated wastewater, highlighting the pressing need for effective treatment methods. The simulated wastewater in question contains zinc, which is categorized as waste material, thereby highlighting the importance of developing suitable strategies for its elimination and recovery. In order to tackle this challenge, an electrochemical cell provided with a specific supported liquid membrane was thoroughly examined. The study aims to comprehensively analyze various variables such as applied voltage, pH and concentration of zinc ions and their impact on the extraction process, with the ultimate goal of establishing an efficient and environmentally sustainable approach for treating solutions that contain zinc.

Experimental

Chemicals

Throughout all the experiments, deionized water was employed as the solvent for preparation of both donor and acceptor solutions. The cation of interest, zinc(II), was derived from a nitrate salt ($ZnNO_3$) acquired as a stock solution from Central Thomas Baker (Mumbai, India). The acceptor solution, on the other hand, was prepared using hydrochloric acid (HCl) obtained from Thomas Baker (Ambernath, India). In the supported liquid membrane (SLM) procedure, 1-octanol, sourced from Central Drug House (Delhi, India), was utilized as the chosen organic solvent.

For the purpose of zinc removal using electromembrane extraction (EME), two distinct carriers, specifically tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) phosphate (DEHP), were procured from Shanghai Macklin Biochemical (Shanghai, China). To regulate the pH value, sodium hydroxide (NaOH) obtained from POCH (Poland) was utilized. The solid material employed in the liquid membrane was a polypropylene membrane sheet sourced from Jian City Qing Feng Equipment Material Co. China. This particular sheet had a thickness ranging from 0.18 to 0.22 mm, accompanied by an average pore size of 0.1 microns.

Electromembrane extraction system

The electromembrane extraction cell, illustrated in Figure 1, comprises a pair of chambers, each boasting a volumetric capacity of 137.44 cm^3. The first chamber exhibits a cylindrical morphology and serves as the reservoir for the donor phase, accommodating 100 ml. It possesses a diameter of 5 cm and a length of 7 cm. A cylindrical horizontal channel, measuring 3 cm in diameter and 3 cm in length, is positioned on the lateral side of this chamber, situated 2 cm above its base. The second chamber adheres to an identical design as the first one and houses the acceptor phase, also occupying a volume of 100 ml. Both chambers are equipped with Teflon covers, measuring 4.8 cm in diameter and 10 mm in thickness. These covers are furnished with a pair of holes: one serving for the electrode fixation and the other for the introduction of solutions. To function as the anode, an electrode composed of graphite is employed, featuring dimensions of 5 cm in length, 3 cm in width, and 5 mm in thickness. The choice of graphite as an anodic material is based on its high oxygen overvoltage (1.7 V *vs*. standard hydrogen electrode (SHE)) in comparison with platinum who has the ability to accelerate the anodic oxidation of water due to its low oxygen overvoltage (1.3 V *vs*. SHE). The use of graphite would provide favorable electrochemical conditions for EME [11,12]. The cathode employed in the system comprised a stainless steel 316L plate, characterized by dimensions measuring 5 cm in length, 3 cm in width, and 2 mm in thickness. Notably, this represents the first usage of such electrodes within an electromembrane extraction (EME) system, resulting in reduced production expenses when compared to platinum electrodes.

A circular polypropylene membrane sheet, possessing an active surface area of 7 cm^2, underwent impregnation with 1-octanol and a suitable carrier for a duration of 15 minutes. Subsequently, it was carefully positioned between the channels of the two chambers, ensuring precise alignment, and then securely affixed by employing two hermetically sealed cups, encompassing each respective channel. To enhance structural stability, four screws and nets were employed. Prior to the assembly of the membrane with the channels, the edges of each channel were thoughtfully enveloped with RTV silicone rubber, thereby guaranteeing a leak-proof arrangement.

In order to ensure continuous agitation and proper homogenization of the solution, two magnetic bars were positioned in both the acceptor and donor chambers. To achieve this, a magnetic stirrer boasting a variable rotational speed spanning from 0 to 1000 rpm (Metrohm AG Herisau, Type 18490010, Switzerland) was employed. The electromembrane extraction (EME) system was operated across a range of voltages, specifically within the interval of 20 to 60 V, which was supplied by a UNI-T power source (Type: UTP3000, Hong Kong). To accurately gauge the electrical current flowing through the EME system, an ammeter equipped with a maximum current capacity of 0.2 A (UNI-T, Kowloon, Hong Kong) was employed and connected in series. All EME experiments were conducted under ambient temperature conditions. To mitigate any potential interference stemming from the solvent used for selective laser melting (SLM) and absorption of zinc ions during atomic absorption measurements, the acceptor and donor solutions were precisely collected in separate glass vials at the end of each run. Subsequently, the collected solutions underwent heating until complete evaporation of all aqueous constituents took place [13]. Subsequent to the afore-mentioned process, the vials were emptied, and replenished with deionized (DI) water. Afterwards, samples were retrieved from these vials for the purpose of identifying the presence of zinc through the utilization of atomic absorption spectroscopy (AAS).

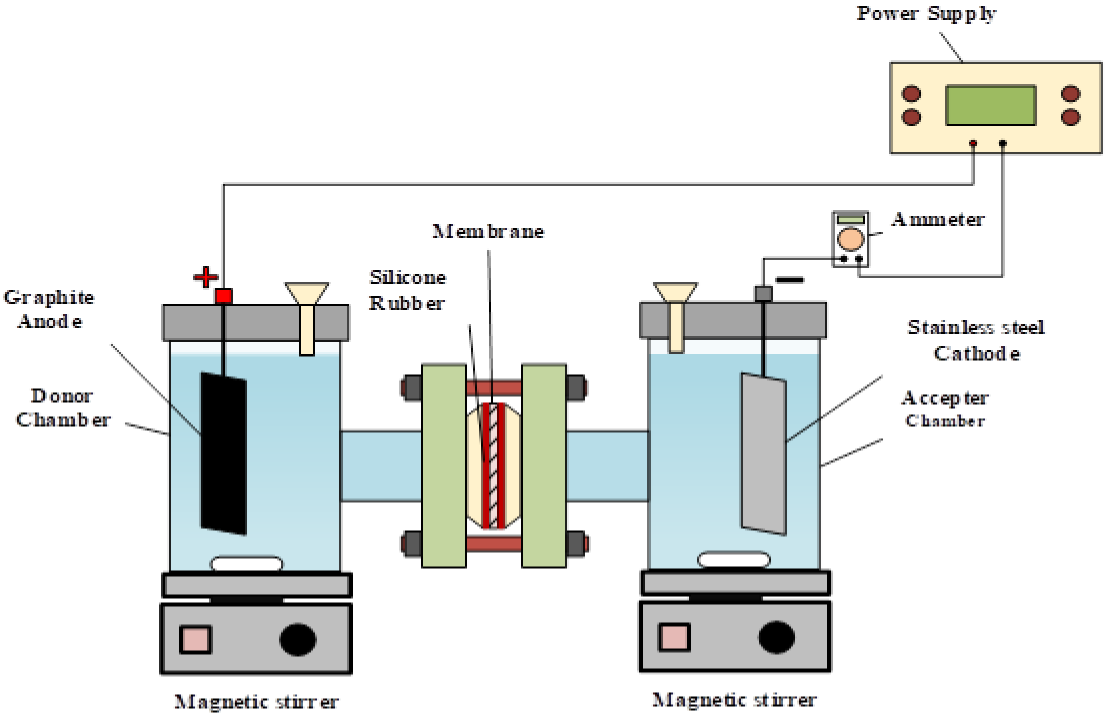

Figure 1. *EME system*

Analysis and measurements

For the analysis of the samples, a cutting-edge AA-7000 atomic absorption spectroscopy instrument manufactured by SHIMADZU (Japan) was utilized, employing an air-acetylene flame configuration. The distinctive wavelength employed for the detection and quantification of zinc cations within the realm of atomic absorption spectroscopy was 213.9 nm. To ascertain pH levels of the samples, a portable pH meter sourced from HANNA (Romania) was employed.

The efficiency of zinc removal was calculated by Equation (1) [14,15]:

$$\mathrm{RE} = \frac{C_\mathrm{i}-C_\mathrm{f}}{C_\mathrm{i}}100 \tag{1}$$

where C_f / ppm is the final Zn(II) concentration at the end of electrolysis, while C_i / ppm represents the initial Zn(II) concentration.

Results and discussion

Selection of the extraction time

The duration of the extraction process plays a key role in ensuring optimal efficiency for zinc removal. Within the scope of this investigation, the extraction time was thoroughly explored over a range from 1 to 9 hours, as visually depicted in Figure 2. The outcomes revealed a gradual reduction in zinc concentration within the donor phase, ultimately attaining a peak removal efficiency of 87 % after 6 hours. Nevertheless, exceptional the 6-hour mark, the zinc concentration exhibited an upward trend once again, closing to 4.8 ppm after 9 hours. This discernible pattern serves to emphasize that the stability of the electromembrane extraction (EME) system becomes compromised when the extraction time exceeds the 6-hour threshold.

One can posit the hypothesis that an extended duration of the extraction process causes the dissolution and subsequent expulsion of a fraction of the selective liquid membrane (SLM) into the aqueous solutions present on both sides of the cell. Consequently, this gives rise to a reduction in the thickness of the liquid membrane, potentially impeding the thorough segregation of the two aqueous phases across the membrane. Analogous observations were previously reported by Davarani *et al.* [13], corroborating thus the current findings. Additionally, Meng *et al.* [16] revealed that the thickness of the membrane, which is influenced by the terminal current intensity, exerts a notable influence on mass transfer. In our own experimental endeavors, a noteworthy escalation in current intensity was observed, increasing from 20 mA at the 6 hour mark to 220 mA at the 9 hour mark, thereby signifying a substantial reduction in the thickness of the membrane after the 6 hour period. Drawing upon these insights, an extraction time of 6 hours was deemed as the optimal duration, as it yielded effective zinc removal through the utilization of the EME system. Consequently, this specific time frame was chosen for subsequent investigations in order to examine the impacts of other variables.

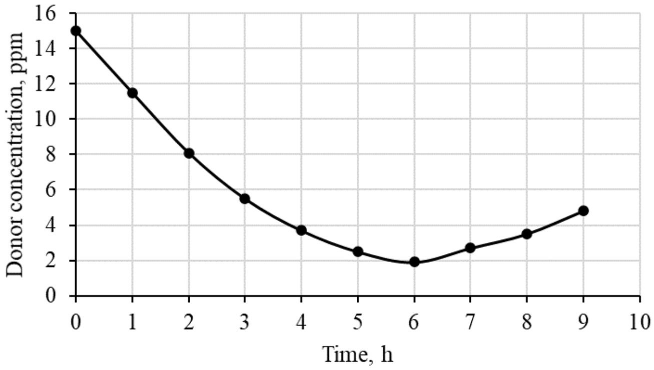

Figure 2. *Effect of extraction time on the removal efficiency. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; stirring rate: 1000 rpm; pH 5; voltae: 60 V*

Selection of the carrier

Despite optimization of the electromembrane extraction (EME) system in terms of the organic solvent selection, as well as donor and acceptor solutions, recent studies have highlighted the potential benefits of incorporating various carriers as additives to the organic solvents in the context of diffusive hollow fiber liquid-phase microextraction (HF-LPME) of heavy metal cations. These carriers have been shown to enhance the overall transport of analytes through a selective solid liquid membrane (SLM) and into an acceptor solution. The prevailing transport mechanism for divalent heavy metal cations is believed to rely on proton-driven processes, which involve the exchange of proton/analyte ions between the carrier and the donor solution, followed by the exchange of analyte ion/proton within the carrier/analyte complex and the acceptor solution. This mechanistic process has been observed to be further potentiated through the application of an electric field. Consequently, a range of additives, including dithizone, DEHP, 8-hydroxyquinoline, and α-hydroxyisobutyric acid, were systematically evaluated in combination with 1-octanol for their effectiveness in facilitating the EME of heavy metal cation [17,18]. Therefore, selecting an appropriate carrier is a crucial initial step in the EME process [19].

In the present investigation, a comprehensive exploration was conducted involving two distinct classes of compounds, specifically bis(2-ethylhexyl) phosphate (DEHP) and tris(2-ethylhexyl) phosphate (TEHP), as potential carriers in conjunction with 1-octanol for the purpose of zinc removal from solution. The carriers were employed at a concentration of 1 vol.%. The selection of 1-octanol as the solvent was predicated upon prior scientific inquiries that underscored its remarkable efficacy in extracting heavy metal cations, as well as its notable immiscibility with water. This unique attribute ensures the confinement of 1-octanol solely within the membrane pores, thereby preventing any undesired dissolution into the donor or acceptor phases during the agitation process [20]. The outcomes of the experimental endeavors illustrated in Figure 3, strongly illuminate the discernible impact of the carrier type on the time-dependent zinc removal performance during a duration of six hours.

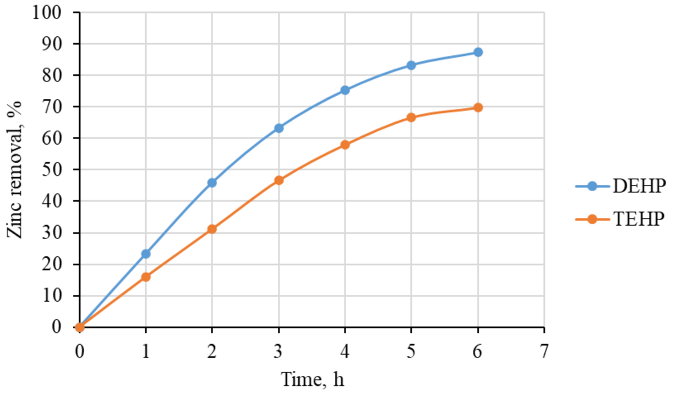

Figure 3. *Effect of carrier type on the removal efficiency. Initial zinc concentration: 15 ppm; feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; pH 5*

The empirical observations showed a noticeable disparity in the zinc removal efficiency between DEHP and TEHP, with DEHP manifesting a remarkable superiority by attaining an impressive removal rate of 87.3 %, while TEHP yielded a comparatively lower rate of 69.78 %. A parallel discernment was reported by Meng *et al.* [16] concerning cadmium(II) ions, thereby corroborating the consistency of the aforementioned trend. Davarani *et al.* [13] observed improved results when using a 1:1 ratio of DEHP and TEHP carriers. Furthermore, precursor investigations have substantiated DEHP-commendable aptitude for extracting diverse metal ions encompassing both bivalent and trivalent species, further accentuating its efficacy as a proficient extraction agent [21,22].

In general, transport of metal ions *via* SLM relies on one of three possible mechanisms: proton drive, anion drive, and counter-gradient drive of metal ions [17]. According to Meng *et al.* [16] and Kubáň *et al.* [18], when pH of the acceptor phase is highly acidic, the most likely transport mechanism for divalent heavy metal ions *via* SLM is proton drive. Hence the mechanism of zinc transport could be interpreted as follows: at the sample/membrane interface, the proton of DEHP or TEHP was exchanged by Zn(II) ions to form a Zn-DEHP or Zn-TEHP complexes in the liquid membrane and release H^+ into the donor, then Zn- DEHP or Zn-TEHP complexes are diffused to the membrane/stripping solution interface where DEHP or TEHP is protonated and Zn(II) is released into the acceptor solution. The experimental observations showed that the pH of acceptor is slightly increased then declined to be near 1. Hence, the efficiency of extraction of Zn in both careers is high during the operation. However, the extraction of zinc by DEHP is high due to the complexation degree with zinc ions in comparison with TEHP.

Many research works have affirmed DEHP as a good career for extraction of various heavy metals due to its stable chemical composition, low solubility in aqueous solution, good loading and stripping characteristics, and commercial availability [23].

Effect of the applied voltage.

Electromembrane extraction (EME) is predicated upon harnessing an electric field to facilitate the transport across a liquid membrane. The magnitude of this electric field, inextricably linked to the applied voltage, exerts a substantial influence on the ion migration dynamics [24]. In this research, a comprehensive evaluation was undertaken to scrutinize the ramifications of five discrete voltage values at the range of 20 to 60 V upon the efficacious removal of zinc *via* the EME system. The discernible consequences of the extraction voltage on zinc elimination are presented in Figure 4.

The experimental findings unequivocally elucidate that a progressive elevation of voltage values from 20 to 60 V prompts appropriate reduction in the ultimate zinc concentration within the donor phase, with a final concentration of zinc from 4.9 to 1.9 ppm following a six-hour timeframe (Figure 4A). Concurrently, this voltage augmentation yields a corresponding enhancement in the efficacy of zinc elimination, exemplified by increasing the removal efficiency (RE) from 67 to 87.3 % (Figure 4B). Such findings manifestly underscore the essential role of applied voltage in augmenting the transference of zinc mass across the dual phases and throughout the Zn(II)-DEEHPA complex embedded within the selective solid liquid membrane (SLM). Analogous outcomes were observed in the study of Meng *et al*. on the EME of cadmium [16], where optimal applied voltage of 60 V was discerned. Unfortunately, their research revealed that those higher voltages engendered SLM instability. Conversely, Davarani *et al.* [25] reported a decrement in cadmium extraction efficiency beyond 60 V, attributing this diminution to the generation of bubbles and concomitant membrane instability. Therefore, the careful choice of the right extraction voltage becomes crucial in achieving effective zinc removal. Using a voltage higher than the optimal threshold can lead to membrane instability and result in reduced extraction efficiency.

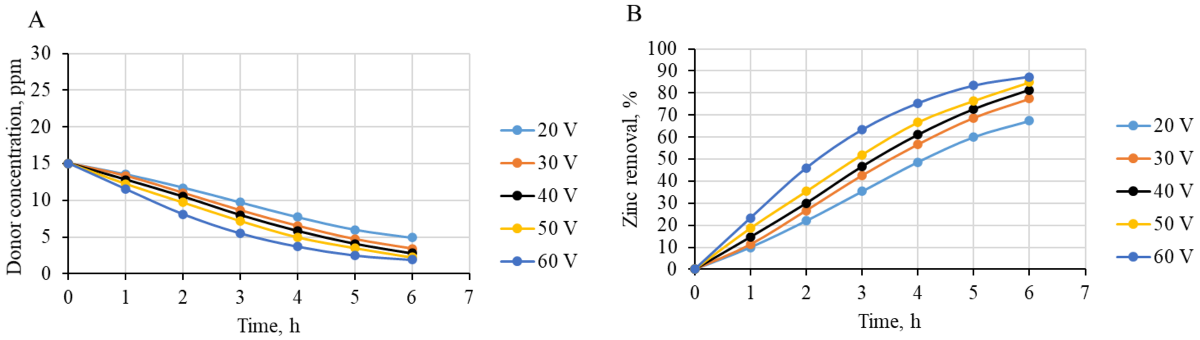

Figure 4. *Effect of applied voltage on: A) concentration of zinc in the donor solution, B) zinc removal efficiency: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; pH 5*

The interplay between the applied voltage and the electric current traversing the membrane within the EME system is graphically presented in Figure 5A. It is worth noting that an increase in the applied voltage leads to the proportional rise in the electric current, and that relation seems to be linear. This can be interpreted as the applied voltage increases more zinc ions will be transferred across SLM, leading to increasing the current pass through the SLM. This empirical observation furnishes invaluable discernment in the judicious selection of optimal voltage values for the specific system under analysis. Remarkably similar findings were reported by Davarani *et al.* [13] reinforcing the coherence and reliability of this observed trend.

Moreover, the influence of the applied voltage on the zinc concentration within the acceptor chamber is intensely elucidated in Figure 5B. The collected data manifest a noteworthy pattern wherein at all voltages, the zinc concentration initially exhibits an ascending trajectory, reaching a peak value. However, after this initial increase, a slight decline in concentration is observed before the concentration starts to rise again.

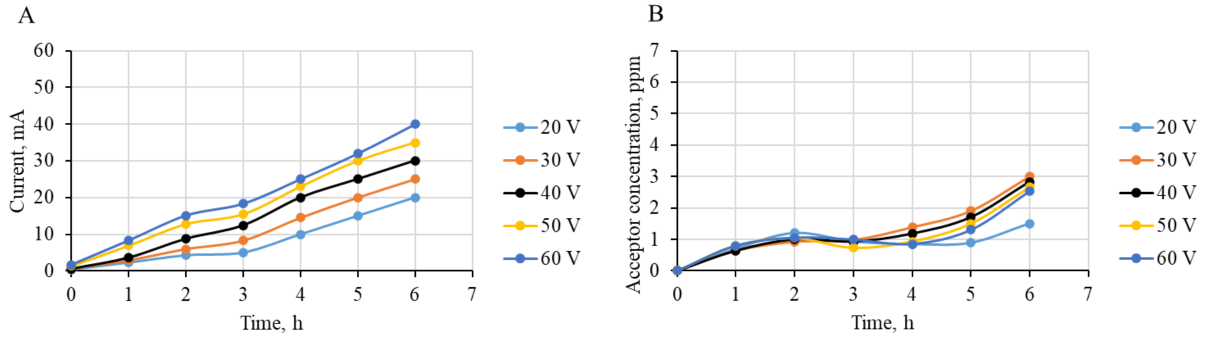

Figure 5. *Effect of applied voltage on: A) current, B) concentration of zinc in the acceptor. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; pH 5*

These intriguing findings highlight the intricate relationship between the applied voltage and the dynamics of zinc concentration within the acceptor chamber. They emphasize that different voltage levels can cause distinct concentration profiles, showcasing the complex interplay between voltage manipulation and the transport and accumulation processes of zinc ions in the acceptor phase.

For EME, the main electrochemical reactions at the cathode and anode in the acidic solution are presented by Equations (2) and (3) [26],

at cathode: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ (E_0 = +0.0V *vs*. SHE) (2)

at anode: $H_2O \rightarrow 1/2O_{2(g)} + 2H^+_{(aq)} + 2e^-$ (E_0 = +1.23V *vs*. SHE) (3)

The accumulation of zinc ions within the receiving chamber is an intricately intertwined phenomenon involving many simultaneous transport rates that collectively constitute the temporal profile of zinc concentration. At its core, this process entails the complex transport of zinc ions from the donor chamber to the acceptor chamber, facilitated by their intricate interplay with DEHP. Simultaneously, there is a concomitant counter-transport of H^+ ions from the acceptor chamber back to the donor chamber. These parallel and interconnected transport phenomena compose the intricate dynamics of zinc accumulation within the acceptor chamber over time [16]. As the applied voltage is augmented, the velocity of zinc transfer experiences a corresponding augmentation. Furthermore, the rate at which H^+ ions are generated from water oxidation at the anode (as expressed by equation 4) also intensifies, inducing a rise in the acidity levels within the donor phase. Within the acceptor phase, two distinct reactions are manifested, *i.e.,* production of hydrogen gas (as depicted by equation 3) and electrodeposition of zinc. The rate at which each reaction proceeds, thereby dictating the transfer rate towards the cathode, depends upon factors such as the electrode potential, ion concentration, and pH. Consequently, the rate at which zinc accumulates within the acceptor chamber is a cumulative outcome arising from the intricate interplay of these various transfer processes transpiring within the chamber.

For all voltage conditions, the concentration profiles depicted in Figure 5B illustrate an initial scenario where the rate of zinc electrodeposition lags behind the rate of zinc transfer *via* the membrane. However, as time elapses, the rate of zinc electrodeposition escalates and surmounts the rate of zinc transfer across the membrane. Consequently, the zinc concentration within the chamber diminishes, thereby giving rise to the noticeable peak observed in the concentration profile.

At longer time, under high voltage conditions, the concentration profiles presented in Figure 5B elucidate a distinct pattern whereby the rate of zinc deposition consistently trails behind the rate of zinc transfer across the membrane throughout the entire duration. This notable observation can be attributed to the influential presence of hydrogen evolution, which competes with zinc electrodeposition within the acceptor chamber. Since the reduction potential of zinc (E_0 = -0.76 V *vs.* SHE) exceeds that of hydrogen, a consequential outcome arises wherein the zinc concentration progressively increases over time within the acceptor chamber [12].

One of the noteworthy discoveries in this investigation pertains to the pH profiles observed in the donor and acceptor phases throughout the course of the extraction process, as visually presented in Figures 6A and 6B. A striking observation emerged, indicating that the pH values of both the donor and acceptor solutions experienced a substantial impact as the applied voltage increased. As the extraction process advanced, an augmented generation of H^+ ions became evident, consequently leading to sharp acidity levels within the donor phase, as depicted in Figure 6A. Within the acceptor phase, a fascinating dynamic unfolded, where the occurrence of hydrogen evolution competed for dominance with the reduction of zinc. Notably, under high voltage conditions, the rate of hydrogen reduction initially exceeded that of zinc reduction, resulting in a discernible increase in alkalinity within the acceptor solution. This intriguing observation is exemplified by the pH profiles presented in Figure 6B. Evidently, the pH of the acceptor solution stands as a tangible manifestation of the delicate equilibrium between hydrogen evolution and zinc reduction, a balance intricately influenced by the applied voltage.

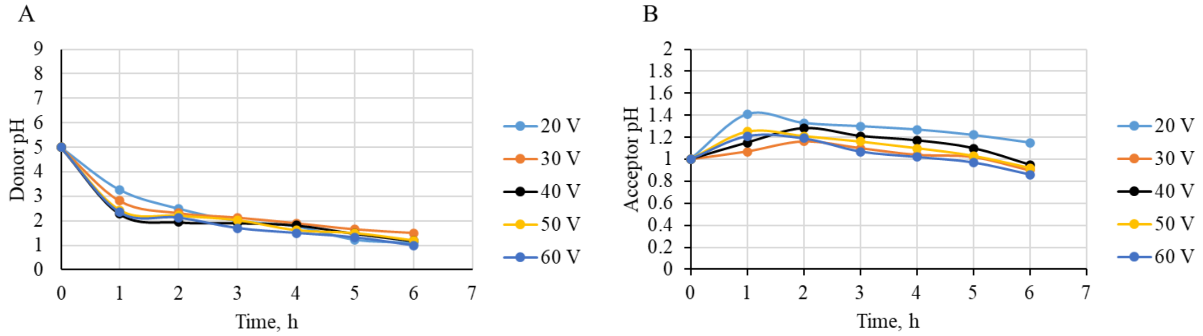

Figure 6. *Effect of applied voltage on: A) pH of the donor, and B) pH of the acceptor. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; pH 5*

The findings derived from this study substantiate that the applied voltage of 60 V engenders the utmost efficacy in zinc removal through the utilization of the EME system. Consequently, this voltage magnitude was elected as the optimal selection for subsequent investigations into the diverse impacts of additional variables.

Effect of the initial pH of donor

The solubility product constant (K_{sp}) of zinc hydroxide ($Zn(OH)_2$) is 3.00×10^{-16}, signifying that zinc ions have the capacity to remain in a soluble state until pH reaches a value as high as 9. This suggests that under alkaline conditions, zinc ions can maintain their solubility without undergoing precipitation as zinc hydroxide [14,27]. In order to ascertain the efficacy of the procedure, taking into account prior investigations and scholarly research, it is imperative to ensure the robustness and efficiency of the process [13,16]. To establish optimal experimental conditions, a pH range from 3 to 8 was selected, as values below 3 are deemed unfavorable and not recommended based on previous scientific discourse and expert advice [16].

As highlighted by Pedersen-Bjergaard *et al.* [15], attainment of an optimal balance is essential for enhancing ion transport and fluid dynamics within the liquid membrane. In the present work, initial pH of 1 in the acceptor solution was used *via* employing 0.1 M hydrochloric acid (HCl) solution. The choice of HCl as the acceptor medium was based on previous empirical findings [25], while alternative research endeavors have utilized nitric acid (HNO_3) as the acceptor medium [16].

Figure 7 elucidates the influence of donor pH on the extraction and removal efficiency of zinc, offering a comprehensive depiction of various parameters, encompassing removal efficiency, donor concentration, acceptor concentration, donor pH, and acceptor pH, as they evolve over time in relation to the initial pH of the donor solution. Figure 7A depicts the concentration profile of zinc in the donor phase, while Figure 7B displays the impact of pH on the removal efficiency.

The findings emphasized that the utmost removal efficiency is attained at pH 5, exhibiting a substantial decline to 75 and 63 % when the pH surpasses 7 or descends below 4, respectively. This signifies that the bonding between zinc and DEHP reaches its optimal effectiveness within the pH range of 4 to 7. Below pH 4, DEHP experiences heightened protonation, impeding its efficacious bonding with ions [16]. At elevated pH levels, Zn(II) ions can form complicated species that impinge upon their translocation through the membrane. In light of these significant observations, pH 5 was selected as the focal point for subsequent explorations concerning the influence of additional parameters to ascertain the steadfastness of DEHP. Notably, Meng *et al.* [16] corroborated this pattern in their investigations, although with a constant removal efficiency beyond pH 5. In contrast, Davarani *et al*. [25] favored an alkaline media, employing a blend of DEHP and TEHP.

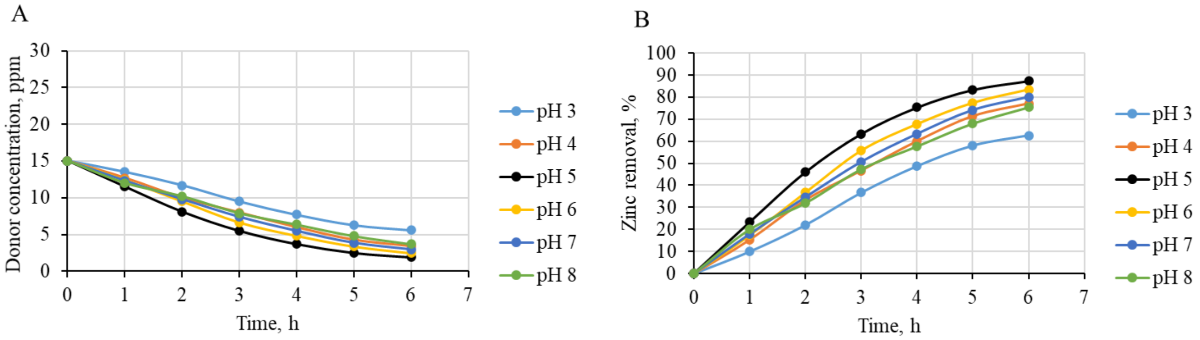

Figure 7. *Effect of initial pH of the donor on: A) concentration of zinc in the donor solution, B) zinc removal efficiency. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V*

The interplay between pH and the electrical current traversing the cell is visually presented in Figure 8A. Notably, any deviation from pH 5, through an upward shift, manifests as a decrement in the magnitude of the current coursing through the cell. This phenomenon can be attributed to the consequential counter-transfer of H^+ and Zn^{2+} ions, which assumes an essential role in dictating the amplitude of the electrical current traversing the membrane.

The impact of the initial pH of the donor solution on the concentration of zinc within the acceptor chamber is visually presented in Figure 8B. A noteworthy observation is that as the pH value increases, the time required to reach the maximum concentration of zinc in the acceptor solution decreases except for pH 6. Subsequently, the concentration begins to decrease and then exhibits a subsequent increase. This intriguing behavior can be elucidated by considering the overall net transfer of zinc occurring within the acceptor chamber. When the initial pH of the donor solution is lower than 5, the rate of zinc electrodeposition initially lags behind the rate of zinc transfer across the membrane. However, as time progresses, the rate of zinc electrodeposition intensifies and surpasses the rate of zinc transport, resulting in a peak of concentration within the acceptor solution. Importantly, this specific finding has not been documented in prior research, adding a novelty to our understanding of zinc extraction dynamics.

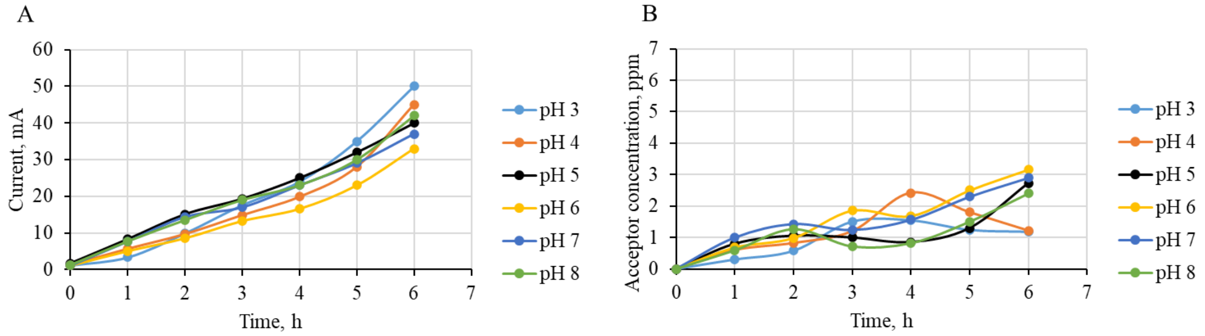

Figure 8. *Effect of initial pH of the donor on: A) current, B) concentration of zinc in the acceptor. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V*

The pH dynamics of the donor solution over time and its convergence towards a value close to 1 are graphically represented in Figure 9A. It is evident that a significant decline in pH occurs within the initial hour for all initial pH of the donor solution larger than 4. Furthermore, the influence of the initial donor pH on the pH of the acceptor solution is illustrated in Figure 9B. Notably, a novel finding emerges, whereby the pH of the acceptor solution exhibits an initial increase followed by a decrease with time. These intriguing observations shed new light on the intricate pH dynamics within the EME system, unveiling previously unexplored phenomena related to the interplay between donor and acceptor pH levels.

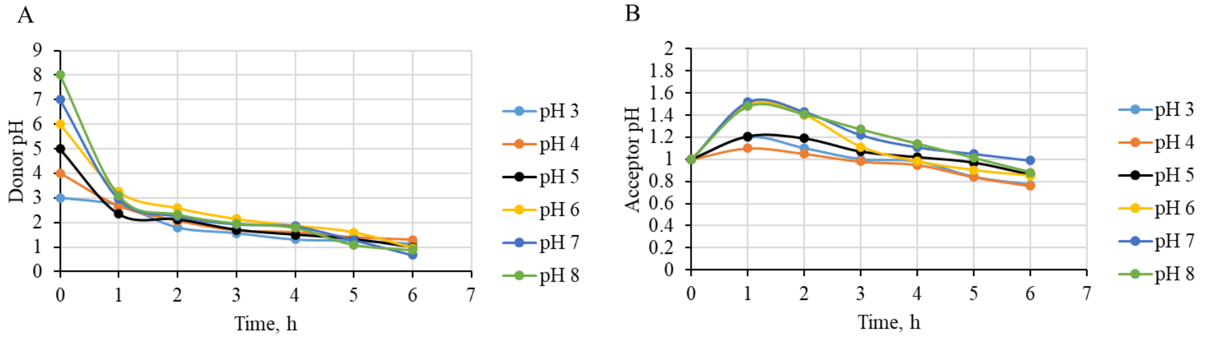

Figure 9. *Effect of initial pH of the donor on: A) pH of the donor, and B) pH of the acceptor. Initial zinc concentration: 15 ppm; carrier: DEHP (1 vol.%); feed solution: DI water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V*

Effect of the initial concentration of zinc

In order to explore the influence of the initial zinc concentration on the electro-membrane extraction (EME) process, a comprehensive investigation was conducted in this study, encompassing a range of concentrations from 5 to 25 ppm. The outcomes of this investigation are visually presented in Figure 10, wherein the impact of diverse zinc concentrations on the EME process is prominently showcased.

The empirical findings, as illustrated in Figure 10, elucidate the correlation between the initial concentration of Zn(II) and the efficiency of its elimination through the electromembrane extraction (EME) process. The results manifest a discernible inverse relationship, whereby an increase in the initial concentration of Zn(II) ions engenders a concomitant diminishment in the removal efficiency.

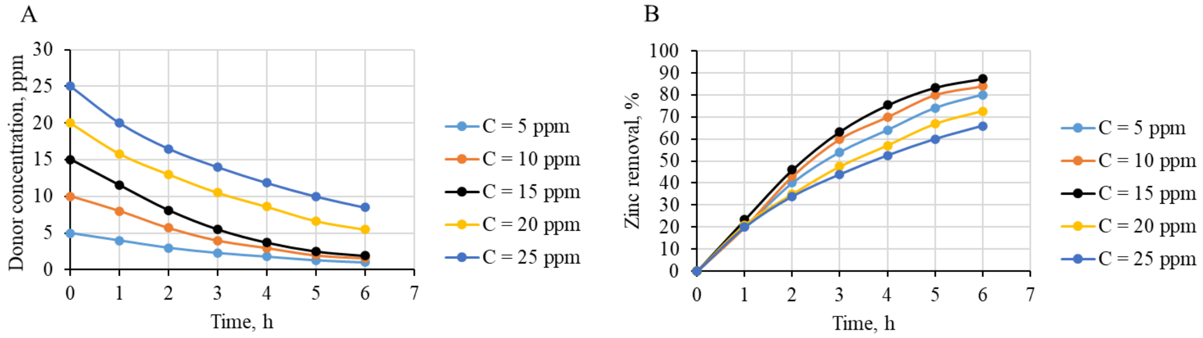

Figure 10. *Effect of initial concentration of zinc on: A) concentration of zinc in the donor solution, B) zinc removal efficiency. Carrier: DEHP (1 vol.%); feed solution: deionized water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V; pH 5*

Specifically, the removal efficiency undergoes a notable decline from 87 % at 15 ppm to 66 % at 25 ppm. It is noteworthy to highlight that concentrations below 15 ppm exhibit a marginal reduction in removal efficiency. These observations are consistent with previous research by Swain *et al*. even without shedding current [28]. Moreover, the removal rate demonstrates a distinct pattern depending on the initial concentration of Zn(II). For concentrations above 15 ppm, the removal rate exhibits a higher initial stage, indicative of efficient diffusion and transfer of zinc ions facilitated by the chosen carrier (DEHP), thereby affirming the appropriateness of this carrier for the EME process. Conversely, for lower concentrations, the removal rate displays a linear trend, suggesting a consistent and steady transfer of zinc ions across the membrane.

An intriguing observation is made regarding the relationship between the concentration of zinc and the current passing through the system. As the concentration of zinc increases, the magnitude of the current also increases, as evidenced in Figure 11A. It can be seen that the current is increased linearly with time as well as with increasing the initial concentration of zinc ions. This can be interpreted as the increasing of zinc ions concentration, the complexation of DEHP with zinc ions increases leading to increase the current transfer across the SLM. Similar observation was noted by Meng *et al.* [16]. In Figure 11B, the influence of the initial concentration of Zn (II) ions on their concentration in the acceptor phase is presented. The results reveal a distinct behavior dependent on the initial concentration. At all initial concentrations, the concentration of Zn (II) in the acceptor phase initially rises, reaching a maximum value after approximately 2 to 4 hours, followed by a subsequent decline during the fourth hour. However, following this decline, the concentration of Zn (II) starts to rise again with the passage of time for concentration ≤ 15 ppm. Notably, the decrease in acceptor concentration commences after approximately 4 hours.

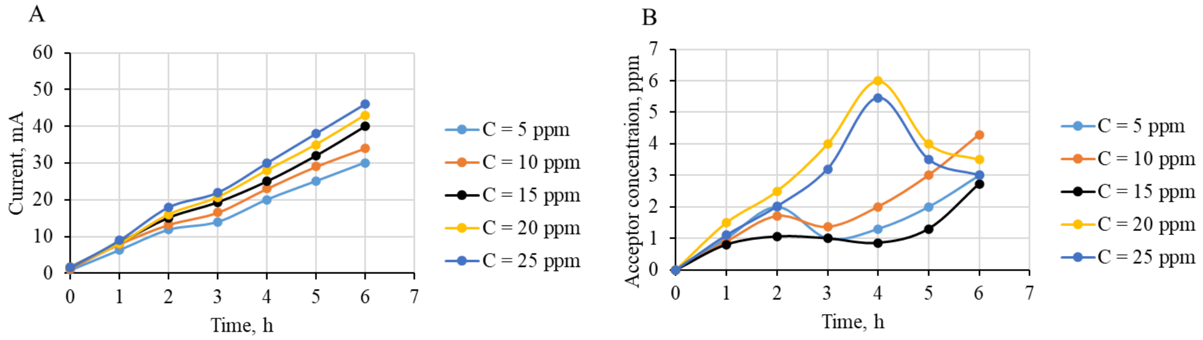

Figure 11. *Effect of initial concentration of zinc on: A) current, B) concentration of zinc in the acceptor. Carrier: DEHP (1 vol.%); feed solution: deionized water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V; pH 5*

This behavior can be attributed to the transfer of zinc ions from the donor phase to the acceptor phase *via* the liquid membrane. While some of these ions remain in the acceptor phase, others undergo electrodeposition on the cathode. Consequently, a competition arises between these two processes, leading to the observed peak in concentration at the initial stage, which eventually diminishes.

During the early stages of the EME process, the pH of the donor phase experiences a rapid decrease in the initial stage of the experiments, followed by a gradual decline over time, as illustrated in Figure 12A. In contrast, the pH profile of the acceptor phase irrespective of the initial concentration, exhibits a similar trend. Initially, the pH undergoes an increase but subsequently starts to decline, as depicted in Figure 12B.

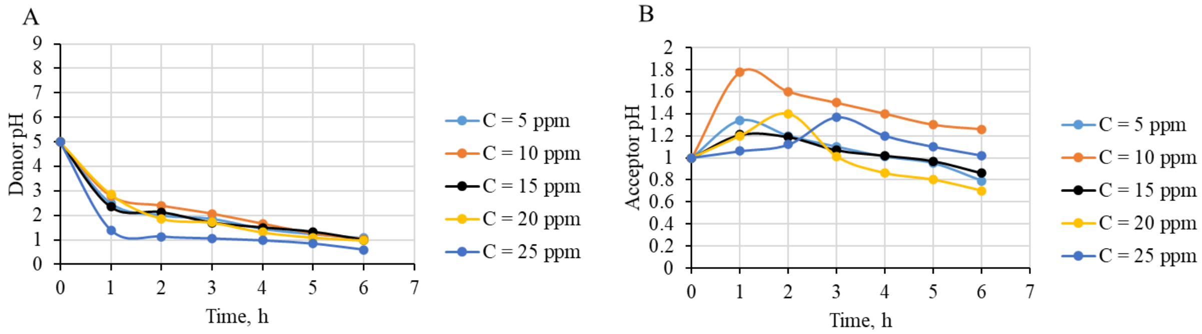

Figure 12. *Effect of initial concentration of zinc on: A) pH of the donor, and B) pH of the acceptor. Carrier: DEHP (1 vol.%); feed solution: deionized water; acceptor solution: 0.1 M HCl; SLM: 1-octanol; extraction time: 6 h; stirring rate: 1000 rpm; voltage: 60 V; pH 5*

Comparison with membrane extraction without applied voltage

Based on the comprehensive findings obtained from this study, the optimal operating conditions for the membrane extraction process were determined as follows: utilization of the supported liquid membrane (SLM) with 1-octanol serving as the solvent, DEHP (1 vol.%) as the carrier agent, a feed solution comprising deionized water containing 15 ppm of zinc, 0.1 M HCl as the acceptor solution, and conduction of the extraction process for a duration of 6 hours, maintaining a stirring rate of 1000 rpm, applying a voltage of 60 V, and setting the pH at 5. To assess the influence of the applied voltage on the membrane extraction process, two separate runs were performed: the first run about the optimal conditions with an applied voltage, and the second run involving identical conditions but without applying any voltage. The results obtained from these runs are presented in Table 1. Evidently, the application of voltage yielded a significant enhancement in the removal efficiency, with an increase from 36.67 % without voltage to 87.3 % when an applied voltage of 60 V was utilized. This improvement aligns with the observations reported by Meng *et al.* [16], who observed an escalation in cadmium removal efficiency from 81 % without voltage to 99.9 % when an applied voltage of 60 V was employed for a duration of 9 hours.

Table 1. *Comparison between zinc removal by EME with membrane extraction without voltage*

Time, h	0	1	2	3	4	5	6
Zn (II) removal by EME, ppm	15	10	8	6.5	5.3	4	1.9
Zn (II) removal by membrane extraction, ppm	15	14	13.5	12.45	11.3	10.1	9.5

Conclusion

The aim of the present work was to conduct EME technique for effective eliminating zinc from aqueous solutions. By subjecting the system to an applied electric field, the transfer of zinc ions was successfully performed from the donor solution, through a supported liquid membrane (SLM), and finally reaching the acceptor aqueous solution. The results revealed the superiority of bis(2-ethylhexyl) phosphate (DEHP) as a carrier, showing a significant removal efficiency of 87.3 % compared to 69.78 % for tris(2-ethylhexyl) phosphate (TEHP).

The applied voltage emerged as the first dominant parameter dictating the mass transfer of zinc across the SLM. By implementing the EME system, a significant and impressive increase of over 50 % in zinc removal efficiency was achieved in comparison with the case of no voltage supplied. To achieve optimal conditions for the EME process, it was necessary to use 1-octanol imbued with 1.0 vol.% DEHP as the carrier, voltage of 60 V, and initial zinc concentration of 15 mg L^{-1} with maintained initial pH 5. The extraction should be performed for 6 hours, keeping the stirring rate at 1000 rpm. Under these conditions, a remarkable removal efficiency of 87.3 % was achieved, which is evidence of the effectiveness of the proposed approach.

Using EME has several inherent advantages in comparison with traditional methodologies such as adsorption and precipitation. This technique requires fewer reagents, consumes significantly less energy, and has a simplified procedure with fewer steps. Furthermore, EME could be adopted for large-scale applications targeting the elimination of diverse heavy metals from a range of wastewater sources.

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