

Electro-enhanced Ion Transport through Bulk-Liquid Membrane

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DC potential-reinforced bulk-liquid membrane transport (PR-BLMT) was studied using Fe (II)-1,10-phenanthroline complex (Fe-Phen) as a model, for the first time. Indeed, this electro-enhanced ion transport study was performed by combination of the electro-membrane extraction (EME) and bulk-liquid membrane transport (BLMT). Iron (II) ions were transported from 3 mL aqueous solution (pH=4.3) into 1.5 mL of 1.0 M HNO₃ solution through 12 mL dichloromethane containing 5×10⁻³ M 1,10-phenanthroline. Ion transport was significantly improved by applying a DC voltage within the transport process. To maximize the transport, the important experimental variables including pH and volumes of donor and acceptor phases, ionic strength, type and volume of BLM, extraction time, DC potential, and type of electrode were studied. The results showed that exhaustive transport of Fe (II) ions through organic membrane was possible in the range of 0.2-27 μg mL⁻¹ (R²=0.998) with a relative standard deviation (RSD) of 3.5% (n=8). The applicability of the proposed PR-BLMT method to interfering matrices was evaluated by successful transport of Fe (II) ions in different real water samples.

Keywords: Electro-enhanced ion transport; Bulk-liquid membrane; Fe (II) ion; UV-Vis spectrophotometry.

1. INTRODUCTION

Iron, as a ubiquitous element in the universe, seems to be the most important metal in forming earth and affecting biological systems [1]. Widespread applications of iron cause environment and drinking water to be polluted by its ions. Thus, its extraction, transport, purification and sensitive determination methods have been of continuing interest, in recent years. Atomic absorption spectrometry (AAS) [2, 3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4,5], X-ray fluorescence (XRF) spectrometry [6], arc/spark optical emission spectrometry (A/S-OES) [7], cathodic stripping voltammetry (CSV) [8] and polarography [9], as well as spectrophotometric are

the most commonly used techniques for determination of iron [10]. However, spectrophotometric methods have some advantages over other mentioned techniques such as simplicity, availability, low-cost and reasonable selectivity and sensitivity.

Liquid membrane (LM) separation has been the subject of extensive investigations due to its advantages over solid membrane (SM) methods and liquid-liquid extraction (LLE) techniques, since its introduction in the 1960s [11]. LM is generally an organic solvent separates two miscible aqueous phases from each other, which are called donor (DP) and acceptor phases (AP). In suitable thermodynamic conditions at the interface of DP and LM, some components are transported from DP to LM. The reverse transport from LM to AP is also simultaneously occurred. Membrane separation is one of the important approaches used in analytical and industrial separations and specific transport of metal ions through liquid membranes is well known as the building block for many biological activities [12, 13]. Accordingly, expanding and development of effective methodologies to achieve selective transport of metal ions through liquid membranes have become significantly advantageous. Simplicity, high separation efficiencies, ambient temperature operation and modular construction of membrane transport technique have made it a desirable approach in various technologies such as simulation and modification of biochemical processes, removal of pollutants from water and wastewater, precious metal recovery, recovery of heavy metals from aqueous solutions and purification of chemicals [14]. Other significant benefits of membrane separation over the traditional procedures include high selectivity, low solvent and energy consumption, low capital and operating costs, high enrichment factor and high flux. Membrane separation combines extraction and stripping into a single step. It operates in non-equilibrium mass-transfer conditions and therefore its function is not limited to the equilibrium features [15].

Despite the widespread application of membrane separation techniques, they suffer from some serious limitations such as inefficiency and low speed. Especially, selective transport of metal ions across LMs is too slow in particular (sometimes more than 24 hours) and inefficient in general [16]. DC potential-reinforced membrane separation or electro-membrane extraction (EME) is a simple, efficient, and cost-effective promising alternative to membrane transport. It has minimum environmental impact and its acceptor solutions are compatible with many of general analytical instruments [17]. The basics of this method rely on the electrically induced transfer of charged species from one aqueous solution (donor) into another aqueous solution (acceptor), across a thin layer of a water immiscible solvent (membrane). Two working electrodes are placed into the donor and acceptor solutions. Application of DC electric potential in EME significantly increases the extraction speed of ionic species. Compared to other extraction methods, additional extraction selectivity is achieved in EME, since only charged species can be transferred.

Several reports have been published in describing possible theoretical models for EME as well as numerous reports reviewed its latest instrumental developments and applications [18, 19]. Despite the technological advances in presenting more efficient techniques of liquid membrane transport, troubleshooting and eliminating drawbacks of the existing techniques would be the matter of extensive investigations. In this respect, the main objective of the present work is study of DC potential-reinforced bulk-liquid membrane transport (PR-BLMT) of iron ions using Fe (II)-1,10-phenanthroline complex (Fe-Phen), as a known simple model, and to enhance the efficiency and reduce transport time.

2. EXPERIMENTAL

2.1. Chemicals and instruments

All inorganic acids, bases and salts were of analytical-reagent grade and provided by Merck (Darmstadt, Germany). Hydroxylamine hydrochloride, 1,10-phenanthroline, carbon tetrachloride (CCl_4), chloroform (CHCl_3), dichloromethane (CH_2Cl_2), and dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), were purchased from Aldrich. A stock solution of iron (5×10^{-3} M) was prepared by dissolving appropriate amounts of Mohr's salt (ferrous ammonium sulfate) in double distillate water. A buffer solution was prepared using hydroxylamine hydrochloride and sodium acetate to adjust pH of the donor phase.

UV-Vis spectrophotometric measurements were performed using a T70-UV-Vis spectrophotometer (PG Instrument, UK). A programmable handmade DC power supply, capable to covert 220 V AC to 1-1000 V DC, was carried out to perform PR-BLMT experiments. Double distilled water was prepared using a SHIN SAENG (Korea) glass distiller and used through the experiments.

2.2. PR-BLMT setup and procedure

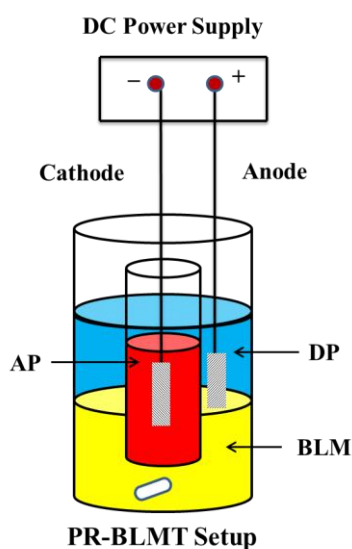


Figure 1. Schematic representation of the DC potential-reinforced bulk-liquid membrane transport (PR-BLMT) setup (AP: acceptor phase, DP: donor phase, BLM: bulk-liquid membrane).

A glass beaker (I.D.: 30 mm), holding a glass tube (I.D.: 10 mm) in its center, was used for the PR-BLMT experiments (Figure 1). It separated donor (DP, 3 mL, pH=4.3) and acceptor (AP, 1.5 mL, HNO_3 1.0 M) phases using a 12 mL liquid membrane (LM, CH_2Cl_2 containing 5×10^{-3} M Phen). LM was located at the bottom of the glass beaker, lying below DP and AP for bridging them. The organic membrane layer was magnetically stirred (200 rpm) using a proper Teflon-coated stir bar to create maximum contact between the membrane and aqueous phases. The PR-BLMT cell was covered by aluminum foil to minimize the evaporation and light exposure. All PR-BLMT experiments were carried out at room temperature. To reinforce the transport using DC voltage two aluminum electrodes

(50 mm length, 10 mm width, 0.01 mm thickness) were immersed into DP (as the anode) and AP (as the cathode). The anode and cathode were safely connected to the positive and negative terminals of a DC power supply. To acquire the transport results after each PR-BLMT experiment, both DP and AP were analyzed for iron content using UV-Vis spectrophotometry. After completion of the extraction (60 min) the power supply was turned off and AP and DP collected. Then, each solution was transferred to a 5 mL volumetric flask, containing appropriate volumes of 1,10-phenanthroline and acetate buffer solutions, and diluted to the volume with water. Finally, the absorbance of solution was recorded at 510 nm and its iron content determined against a suitable external calibration curve ($R^2 > 0.99$).

3. RESULTS AND DISCUSSION

The complex resulted from the interaction of Fe (II) and Phen is Ferriin ($[\text{Fe}(\text{phen})_3]^{3+}$) which generally is used as an indicator for titrimetric determination of iron in aqueous solutions [20, 21]. The intermediate active chromophore is $[\text{Fe}(\text{phen})_3]^{2+}$ ion which can be oxidized to the ferric derivative $[\text{Fe}(\text{phen})_3]^{3+}$, with a redox potential of +1.06 V in acidic solution. Intense color of the ferrous complex arises from a charge-transfer transition which occurs unusually from metal-to-ligand. In this study, Fe-Phen complex was carried out to evaluate the enhancement effect of DC potential on the transport of Fe (II) ions, as a known and simple model.

3.1. Effect of donor phase pH

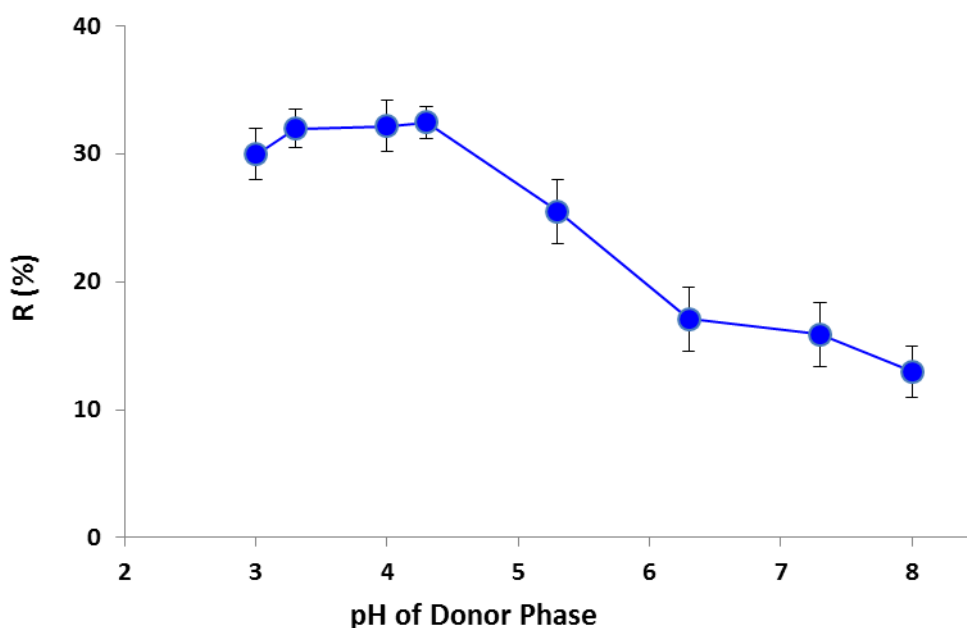


Figure 2. Effect of donor phase pH on the transport efficiency of iron ions using the PR-BLMT method (condition: donor: 4 mL aqueous solution; acceptor: 3 mL 2.0 M HNO_3 ; membrane: 14 mL 5×10^{-3} M Phen in CH_2Cl_2 ; DC voltage: 160 V; transport time: 50 min).

One of the most important variables in PR-BLMT procedures is pH of the DP and AP. It should be adjusted to ensure of remaining analyte species in their ionic forms and also to prevent interfering effects of hydronium and hydroxyl ions during the transport process [22]. Therefore, the effect of donor's pH on the transport efficiency was investigated. The results showed that the maximum transport efficiency is achieved in the pH range of 3.3-4.3 (Figure 2). Thus, 4.3 was selected as the optimal pH value of DP for subsequent studies. For accurate control of pH sodium acetate buffer was used. To ensure complex formation between all iron ions and Phen, hydroxylamine hydrochloride (0.001 M) was added to DP to preserve all irons in +2 oxidation states.

3.2. Acid concentration in acceptor phase

Another critical variable in RP-BLMT is characteristic of AP, due to its effect on the stripping of transported metal ions from LM. AP should contain an optimized concentration of a stripping reagent (e.g., mineral acid) for complete depletion of membrane [23]. For this purpose, solutions of different mineral acid were investigated. The results revealed that nitric acid is quite appropriate. Additionally, the concentration of nitric acid in AP was optimized over the range of 0.05-3.0 M (Figure 3). The maximum transported amounts of Fe (II) ions were obtained at 1.0 M nitric acid.

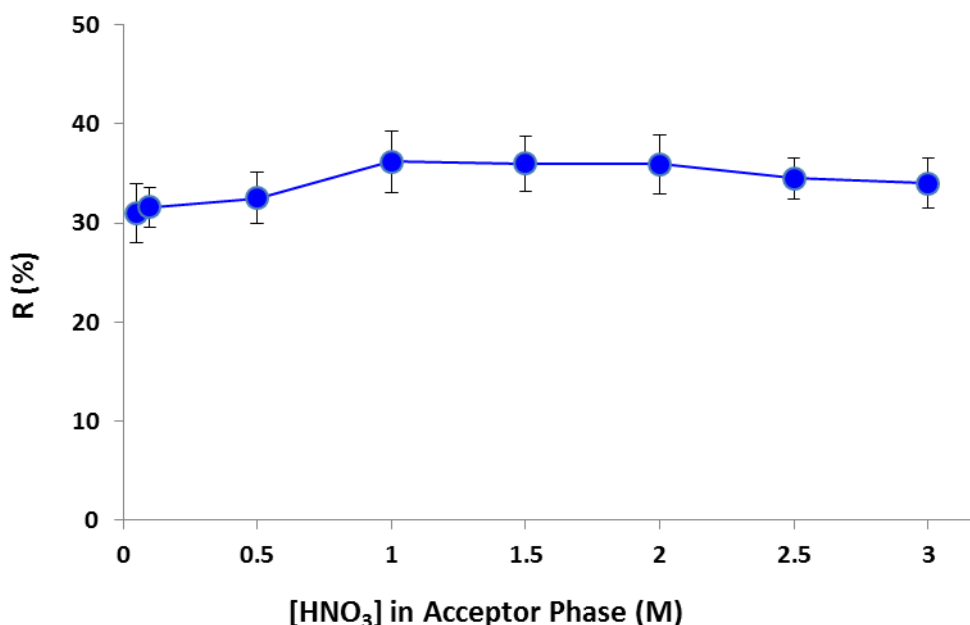


Figure 3. Effect of HNO₃ concentration in acceptor phase on the PR-BLMT efficiency (condition: donor: 4 mL aqueous solution with pH=4.3; acceptor: 3 mL HNO₃ solution; membrane: 14 mL 5×10⁻³ M Phen in CH₂Cl₂; DC voltage: 160 V; transport time: 50 min).

3.3. Effect of ionic strength in DP and AP

The effect of ionic strength on the PR-BLMT efficiency was investigated by varying the concentration of sodium nitrate (NaNO₃) in DP in the range of 0-4% (w/v). As indicated in Figure 4,

the transport of Fe (II) ions was increased with increasing NaNO_3 contents and reaches to a maximum at 3% (w/v). Further increasing of NaNO_3 concentration revealed no considerable effect on the transport efficiency. Therefore, 3% (w/v) was selected as NaNO_3 concentration in DP for further experiments. Similar experiments showed that addition of NaNO_3 to AP had a decreasing effect on the transport efficiency (Figure 4). Thus, further studies were conducted without adding salt to AP.

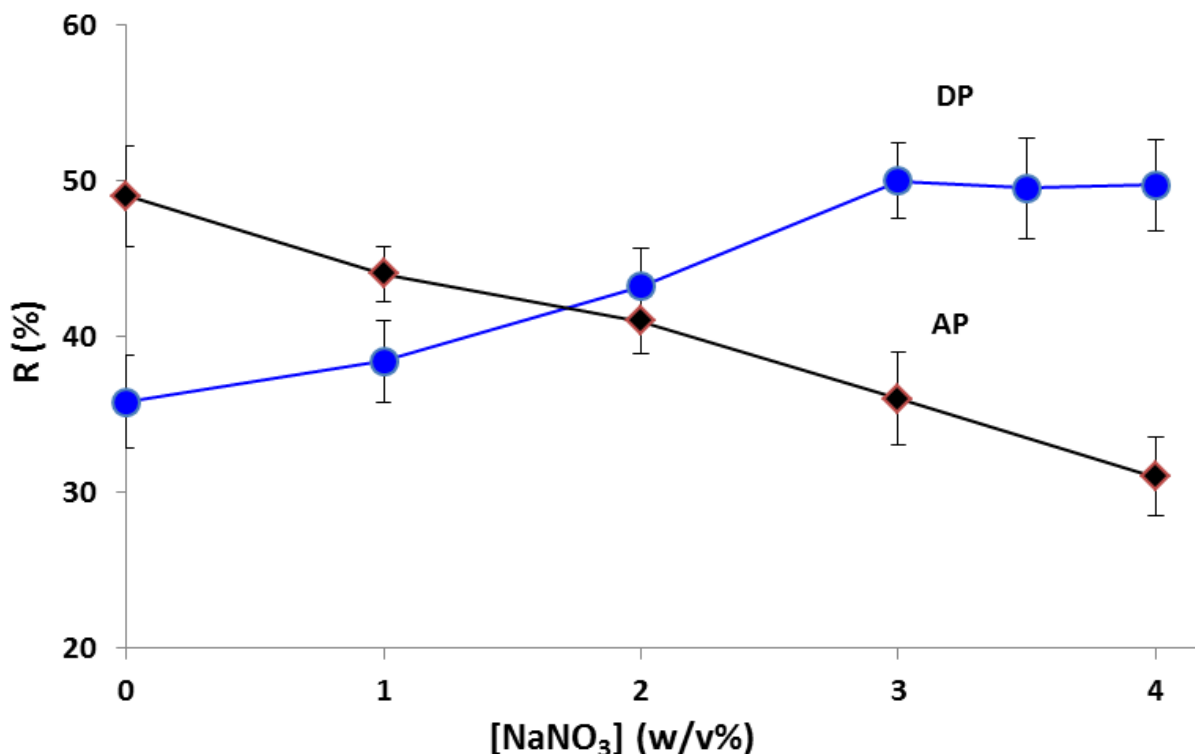


Figure 4. Effect of donor and acceptor ionic strength on the transport efficiency (condition: donor: 4 mL aqueous solution with pH=4.3; acceptor: 3 mL 1.0 M HNO_3 solution; membrane: 14 mL 5×10^{-3} M Phen in CH_2Cl_2 ; DC voltage: 160 V; transport time: 50 min).

3.4. Nature of the organic liquid membrane

Appropriate choice of the organic solvent, as the diluent and membrane, is a key factor in PR-BLMT to achieve the highest transport efficiency. The function of an extractant-carrier based transport strategy is strongly correlated to the physical parameters of diluents such as polarity, viscosity and permittivity [24]. LM must have very low solubility in water to avoid dissolution in DP and AP. Additionally, it must have low electrical conductivity to prevent the passage of electricity and consequently the evaporation and bubble formation, resulting from the electrolysis [25]. The effect of LM's type on the transport efficiency was evaluated by applying CCl_4 , CHCl_3 , CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$. The results revealed that under the constant experimental conditions the percentage of Fe (II) transported was in the order of $\text{CCl}_4 < \text{CHCl}_3 < \text{C}_2\text{H}_4\text{Cl}_2 < \text{CH}_2\text{Cl}_2$. Accordingly, CH_2Cl_2 was selected as the best choice of LM for further studies.

3.5. Transport time

To assess the effect of transport time, variations of the transport efficiency were studied as a function of time. As shown in Figure 5, the transported amount was increased with time up to 60 min and then remains constant at longer times. Thus, 60 min was selected as the optimal transport time. It should be noted that, this time is much longer in similar reported methods, without applying DC voltage [23, 26].

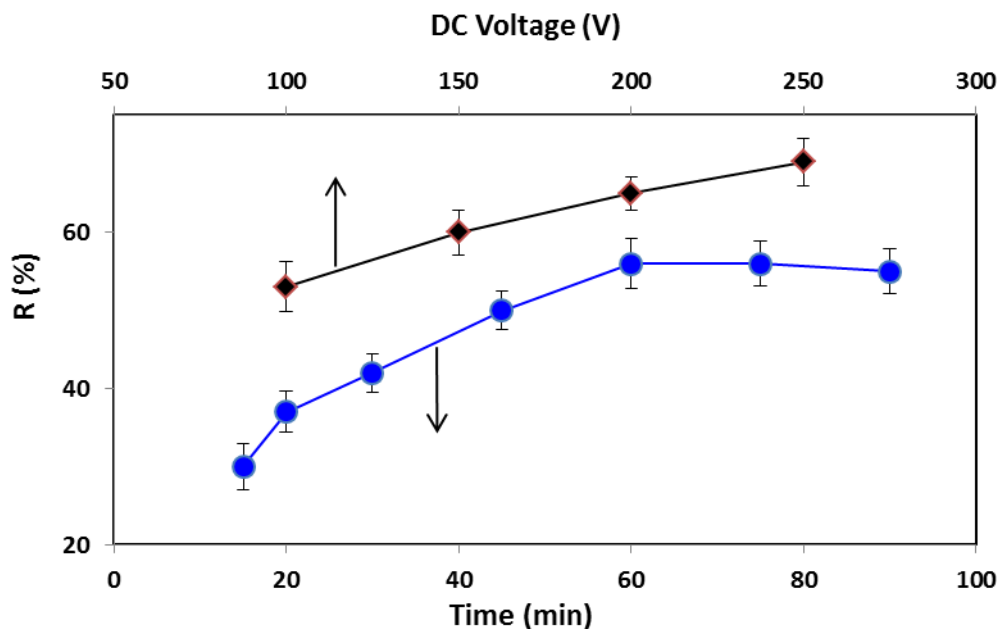


Figure 5. The transport efficiency vs. time and DC voltage (condition: donor: 4 mL aqueous solution with pH=4.3; acceptor: 3 mL 1.0 M HNO₃ solution; membrane: 14 mL 5×10⁻³ M Phen in CH₂Cl₂).

3.6. Effect of applied DC potential

The applied DC potential across BLM is the main driving force in PR-BLMT and consequently a crucial variable for an efficient transport. To optimize this parameter, the PR-BLMT procedure was conducted with different voltages in the range of 100-250 V (Figure 5). The results show that DC potential has a semi-linear increasing effect on the transport efficiency. However, the voltages higher than 250 V were not tested, due to avoid possible bubble formation and sparking. Finally, 250 V was selected as the optimal value for subsequent studies.

3.7. Effects of AP, DP and LM volumes

In PR-BLMT, volumes of the three involved phases are among the most important factors which influence the transport efficiency. Thus, volumes of DP, AP and LM were studied over the ranges of 1-5, 1-3 and 8-22 mL, respectively. The results (Figure 6) showed that the optimum volumes

for DP, AP and LM were 3, 1.5 and 12 mL, respectively. To achieve the highest efficiency and reliability in the PR-BLMT method, materials of the electrodes were also examined. Conducting the PR-BLMT experiments by applying copper, tin, stainless steel and aluminum electrodes showed that aluminum was the best choice for preparation of anode and cathode electrodes in PR-BLMT.

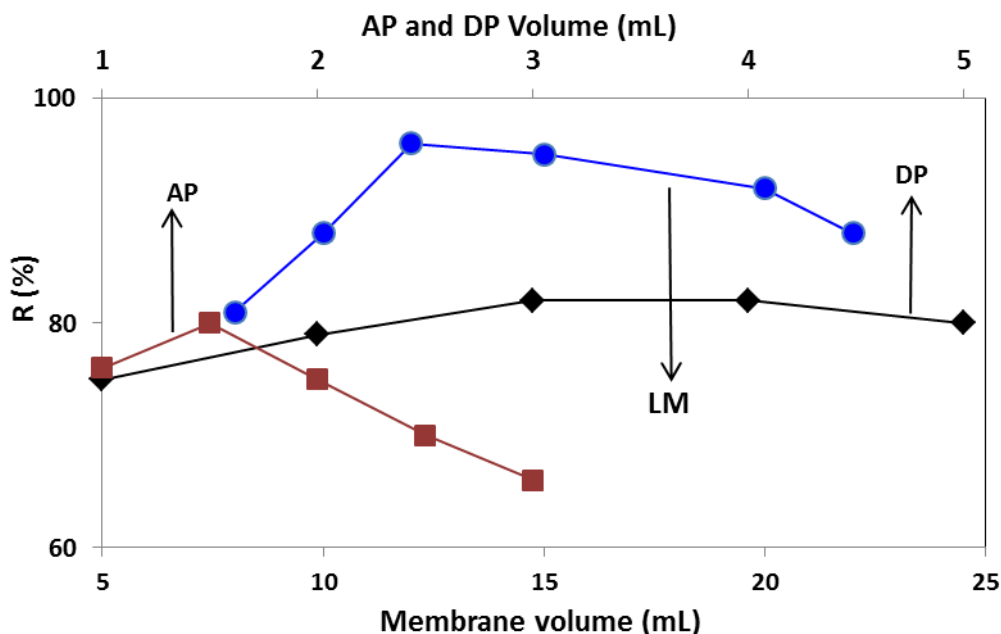


Figure 6. Effect of DP, AP and LM volumes on the transport efficiency (condition: donor: aqueous solution with pH=4.3; acceptor: 1.0 M HNO₃ solution; membrane: 5×10⁻³ M Phen in CH₂Cl₂; DC voltage: 250 V; transport time: 60 min).

3.8. Analytical performances

To investigate the reproducibility of the PR-BLMT system, the percentages of the transported Fe (II) ions were determined by performing ten replicated experiments under the optimal conditions. The relative standard deviation (RSD) for ten replicated transport was found to be 3.5%. The results showed that exhaustive transport of Fe (II) ions through organic membrane was possible in the range of 0.2-27 μg mL⁻¹. The proposed PR-BLMT procedure was also compared with traditional BLMT, under the optimized conditions. The transport efficiency of traditional BLMT was 8% after 540 min, while it was found to be ≥94% for PR-BLMT after 60 min. The developed PR-BLMT method was finally applied for the transport and analysis of iron ions in four real samples including river water, urban wastewater and three industrial wastewater samples from steel industries. The results (Table 1) demonstrated that the presence of coexisting species in natural sample matrices cannot create meaningful differences in the results of the method. The results obtained by the proposed PR-BLMT method were compared with those obtained by an approved LLE-FAAS method [27]. Performing of the proper statistical t-tests showed that the results of the two methods had no significant (meaningful) difference. However, LLE is a non-environmentally-friendly classical extraction method which needs

large volumes of organic solvent and longer times. Therefore, the developed PR-BLMT procedure can be successfully carried out for transport of Fe (II) ions in real samples with different interfering species.

Table 1. Transport and determination of Fe (II) ions in real samples by the proposed PR-BLMT method and comparison of the results with a validated LLE-FAAS procedure.

Sample	Fe(II) transported and determined ($\mu\text{g mL}^{-1}$)	
	PR-BLMT-UV-Vis	LLE-FAAS
Industrial wastewater 1 ^a	4590 (2.2) ^b	4568 (3.0) ^b
Industrial wastewater 2	0.34 (3.4)	0.36 (4.5)
Industrial wastewater 3	0.22 (3.3)	0.25 (4.9)
Urban wastewater	1.3 (1.5)	1.6 (2.8)
River water	0.20 (4.2)	0.22 (4.5)

^a The sample was diluted to match with the linear dynamic range of the method.

^b RSD of three replicate experiments.

4. CONCLUSIONS

The results of this study demonstrated the usefulness of the newly developed RP-BLMT technique, which combined the extraction and stripping processes in a single step. It significantly reduced the time and expenses of the transport and solvent inventory requirements. It was also found that applying DC voltage across BLM significantly increases the efficiency of uphill transport of Fe (II) ions against its concentration gradient. In conclusion, it was revealed that the most dramatic advantage of PR-BLMT exists at the extremes of transport time compared to that of the traditional BLMT techniques. The developed RP-BLMT method was successfully applied for the transport of iron ions in real water samples with different coexisting species.

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