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Selective transport of copper (II) from zinc (II), lead (II), cadmium (II), nickel (II), and cobalt (II) ions mixture through bulk liquid membrane using 5-nitro-8-quinolinol as a carrier

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ABSTRACT

The transport of Cu^{2+} ion through a chloroform ($CHCl_3$) bulk liquid membrane containing 5-nitro-8-quinolinol (NQ) as a selective carrier was studied. The NQ is an efficient carrier for the transport of Cu^{2+} from aqueous solutions containing equimolar concentration of other cations such as Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} ions. The parameters that have influence on the transport efficiency such as transport time, type, and concentration of stripping agent in acceptor phase, concentration of NQ in membrane phase, pH of donor phase, and stirring rate were examined. Under optimum conditions, the extent of Cu^{2+} transports across the liquid membrane was about 33.05% after 24 h and cation fluxes (J_M) were studied for the transport of Cu^{2+} in different membranes, and the maximum amount of J_M was 9.58×10^{-9} (mol/m^{2}s) in $CHCl_3$. The applicability of the method was examined for the separation of copper (II) ions from real liquid samples. Transport efficiency of Cu^{2+} for three replicate measurements in river liquid samples RW_1, RW_2, and RW_3 obtained 29.9 ± 2.2%, 32.0 ± 1.5%, and 30.3 ± 2.1%, respectively, after 24 h.

Keywords: Transport; Bulk liquid membrane; Copper; 5-nitro-8-quinolinol

1. Introduction

During the past years, the use of liquid membranes has gained a general interest in the treatment of effluents where solute concentrations are low and large volumes of solutions must be processed [1]. Liquid membrane is a prospective separation system that has been studied intensively by many researchers from the time it was discovered by Li [2]. Although it has not been considered significantly in industrial applications, its efficiency and economic benefits have assigned it to be as an optimal solution for a number of important problems in science and technology such as precious metal recovery [3], toxic metals [4], nonmetals [5], and organic molecule [6,7] removal from wastewater.

The use of liquid membranes containing specific metal ion carriers offers an alternative to the solvent extraction processes for selective separation and concentration of metal ions from aqueous solutions [8]. Facilitated transport by liquid membrane is a known technique for the separation of metal ions [9]. In the recent years, a remarkable increase in the application of liquid membranes in separation processes has been

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observed including bulk liquid membrane (BLM), emulsion liquid membrane, and supported liquid membrane [10,11]. Among them, the BLM represents one of the liquid membrane techniques in which a mobile carrier governs the efficiency and selectivity of the liquid membrane transport. The technique is easy to use and inexpensive to improve the efficiency of the separation process in the laboratory scale. The BLM consists of an organic phase, a donor phase, and an acceptor phase. The organic phase contains the carrier which is responsible for the transport of metal ions, having it positioned between two aqueous phases: the donor phase containing the metal ions to be transported and the acceptor phase in which metal ions will be released. Other advantages of this technique included low cost and energy consumption. The carrier plays a crucial role in order to selective extraction of the desired elements at the feed aqueous-organic interface and release them at the organic-acceptor phase interface [12].

8-Quinolinol (Hqn=C_9H_7NO) and its derivatives have been widely used as a chelating and solvent extraction agent for the spectrophotometric determination of metal ions [13–16]. NQ is a bidentate N, O donor ligand that has the ability of complex formation by some cations such as copper ions [17]. NQ is a potent anti-cancer agent whose cytotoxicity was enhanced in the presence of copper, which acts as an anti-angiogenic agent, *in vitro* and *in vivo*, and prevents the growth of tumor xenografts in mice as well [18]. In this work, NQ that is shown in Fig. 1 was used as an excellent carrier for selective transport of Cu^{2+} ions through a BLM. In the presence of hydrochloric acid (HCl) as a suitable acceptor phase, high efficient transport of Cu^{2+} ions was done across the liquid membrane at a time period of 24 h.

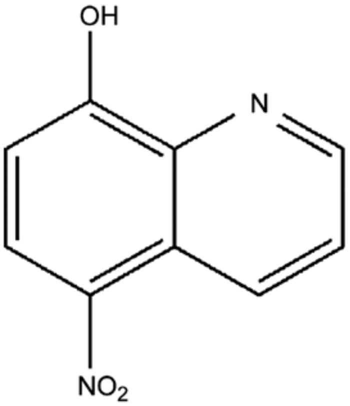

Fig. 1. Structure of NQ.

2. Experimental

2.1. Reagent

All materials and reagents used in this work such as: lead (II) nitrate, nickel (II) nitrate, cobalt (II) nitrate, zinc (II) nitrate, cadmium (II) nitrate, copper (II) nitrate, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), nitric acid (HNO_3), sodium hydroxide (NaOH), and chloroform ($CHCl_3$) were purchased from Merck (Darmstadt, Germany) without any purification. NQ was purchased from Sigma Aldrich (India).

2.2. Instrumentation

Stirring of the solutions was carried out by a Biocate STUART CB302 magnetic stirrer and a digital pH meter (827 metrohm) with a glass electrode and was used for all pH measurements. All of the concentration measurements were done by μAuto lab type (III) potentiostat with 757 VA computrace stand (Metrohm, Switzerland). The voltammograms of cations were performed by differential pulse anodic stripping voltammetry (DPASV) mode.

2.3. Procedure

All transport experiments were carried out at ambient temperature (25 ± 1°C). The experimental studies were performed by applying the U-shaped cell which is presented in Fig. 2. Source phase that contained 2.0 ml of metal ions with constant pH was adjusted by NaOH or HCl solutions. Supplied by NQ, a chloroform layer (7.0 ml) separated the two aqueous phases and bridged them together, while the receiving

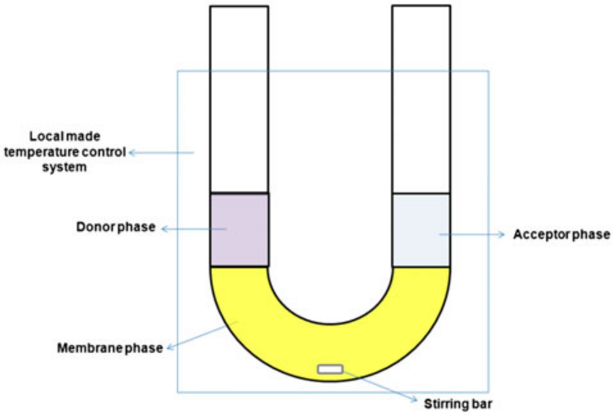

Fig. 2. The setup used for BLM transport experiments. The volumes of each chloroform, and receiving and source phases were 7, 2 and 2 ml, respectively.

phase contains 2 ml of stripping agents. Both source and reviving phases were poured on top of the organic phase that is stirred magnetically by a teflon-coated magnetic bar at speed of 200 rpm. The internal diameter of U-tube is 10 mm, and the copper (II) ion concentration in both source and receiving phases was determined by DPASV method in optimum conditions as portrayed in Table 1.

The blank experiments were carried out in the same way without any NQ and the cation flux (J_M) values were calculated through the relation below [19]:

$$J_M = (C_{(\text{receiving})} \times V)/(A \times t) \tag{1}$$

where $C_{(\text{receiving})}$ is the concentration (M) of cations in the receiving phase, V is the volume (dm^3) of receiving phase, A is the effective area (m^2) of membrane, and t (s) is the time.

3. Results and discussion

3.1. Effect of donor phase pH

The effect of the donor phase pH on the efficiency of Cu^{2+} ions transport was studied (Fig. 3). It is quite clear that the transport of Cu^{2+} ions is influenced by the pH of feed phase. The results revealed that the copper ions transport occurs at a range of pH from 3 to 6. At lower pH values, there was a decrease in the percentage of transport of copper probably due to protonation of NQ resulting in the increase of solubility of NQ in aqueous phase leading to membrane bleeding [20]. The efficiency of transport decreases at higher pH values due to competition between hydroxide ions and NQ for complexation with copper ions, and then copper ions can be formed to copper hydroxide as participation in donor phase. Since the concentration of Cu^{2+} ions in donor phase is 1×10^{-4} M and the K_{sp} of Cu $(OH)_2$ is 2.6×10^{-19}, we weren't able to increase the pH higher than 6.7. The optimum value in the present study appears in pH 6, in which a high degree of copper ions transport is achievable.

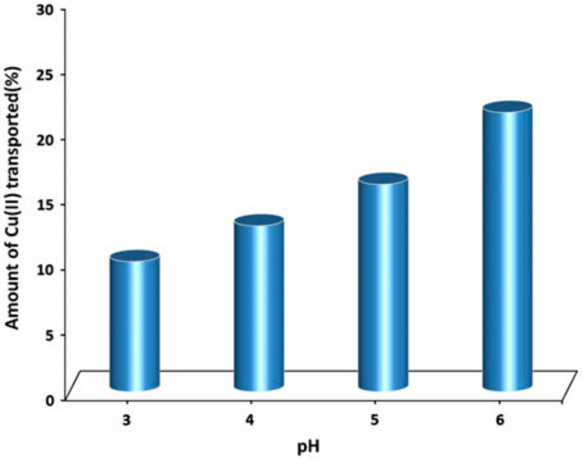

Fig. 3. Effect of donor phase pH on transport % of Cu^{2+} ions. Feed phase: 1×10^{-4} M solution of six cation mixture at different pH, membrane phase: 1×10^{-4} M of NQ in chloroform, receiving phase: 0.1 M HCl, transport time: 24 h, and stirring rate: 150 rpm.

Table 1
Optimum operating conditions of DPASV measurements

Parameter	Amount
Cell volume (mL)	11.6
Initial purge time (s)	100
Deposition potential (v)	−1.15
Deposition time (s)	10
Equilibration time (s)	10
Start potential (v)	−1.15
End potential (v)	0.1
Pulse time(s)	0.04
Pulse amplitude (v)	0.05
Voltage step (v)	0.1
Sweep rate (v/s)	0.0595

3.2. Concentration effect of NQ

The concentration of carrier is an important factor that affects the transport efficiency. In order to investigate the influence of NQ concentration on the transport efficiency, different concentrations of carrier (1×10^{-5}, 5×10^{-5}, 1×10^{-4}, and 5×10^{-4} M) were examined. The maximum transport occurs at a concentration of 1×10^{-4} M, as demonstrated in Fig. 4. By increasing the concentration of NQ greater than 1×10^{-4} M, a decrease in the transport efficiency was observed. At high concentrations because of hydrogen bonding between NQ molecules, dimerization and accumulation may be done. Excessive amounts of carrier can result in carrier aggregation in some cases [21,22].

In addition, a blank experiment was performed in which the membrane did not contain any carrier and no detectable movement of Cu^{2+} was found through the liquid membrane; therefore, the concentration was fixed at 1×10^{-4} M.

3.3. Effect of stirring rate

The stirring rates influence on the membrane phase was studied to obtain uniform mixing and to

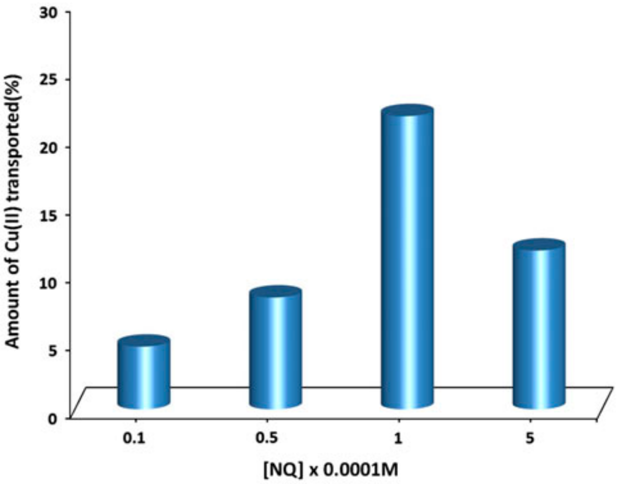

Fig. 4. Effect of NQ concentration on transport % of Cu^{2+} ions. Feed phase: 1 × 10^{-4} M solution of six cation mixture with pH 6, membrane phase: NQ in chloroform, receiving phase: 0.1 M HCl, time = 24 h, and stirring rate: 150 rpm.

minimize the thickness of aqueous boundary layer in the donor and acceptor phase for an effective permeation [23]. Four stirring rates were used, allowing the liquid membrane stability at 25°C, while the NQ concentration in membrane phase was 1×10^{-4} M. At stirring rates higher than 200 rpm, mixing of source and receiving phase occurs. As shown in Fig. 5, it can be concluded that the percentage of Cu^{2+} ions transport went higher as the stirring rate increased, proving that the stirring of the membrane phase has effect on the transport of Cu^{2+} ions. Accordingly, at low stirring rates, the transport efficiency was decreased.

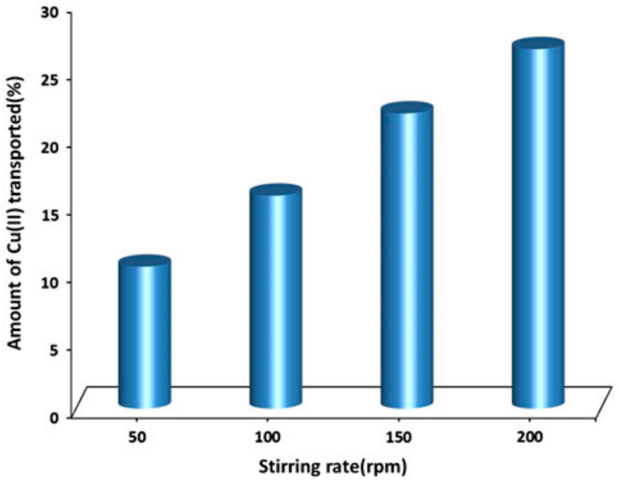

Fig. 5. Effect of stirring rate on transport % of Cu^{2+} ions. Feed phase: 1 × 10^{-4} M solution of six cation mixture at pH 6, membrane phase: 1 × 10^{-4} M of NQ in chloroform, receiving phase: 0.1 M HCl, and transport time: 24 h.

3.4. Effect of stripping agent as the acceptor phase

One of the important parameters influencing the transport efficiency is the type of the stripping agent used in the acceptor phase. Therefore, the stripping ability of various inorganic acids such as HCl, HNO_3, H_2SO_4, and CH_3COOH was tested and its concentrations were optimized. As shown in Fig. 6, it was observed that the transported amounts of copper ions increased in the order $HCl > HNO_3 > H_2SO_4 > CH_3COOH$ (0.1 M each). Because CH_3COOH is a weak acid, it could not establish required pH difference between acceptor and donor phase, as well as three other strong acids for releasing the Cu^{2+} ions according to suggested mechanism. Also, acetate ions obtained of acid dissociation to form complexes with copper ions is much less than the chloride ions in the same condition. Moreover, it may be due to relatively high permeability and flux of strong mineral acids which leads to high recovery factor [24–27]. It was observed that the maximum transport was obtained when the concentration of hydrochloric acid was maintained at 0.1 M.

3.5. Effect of time

The variation of copper concentration with time was measured in both donor and acceptor phases. Fig. 7 illustrates that an increase in time increases the amount of metal ions extracted from donor phase into the acceptor phase and decreases the amount of metal

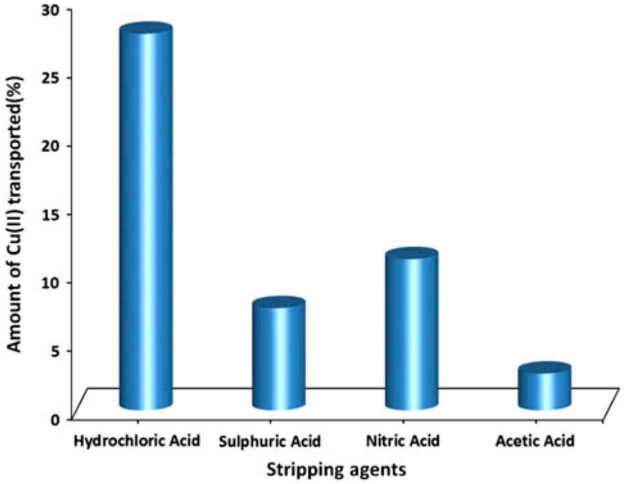

Fig. 6. Effect of stripping agents on transport % of Cu^{2+} ions. Feed phase: 1 × 10^{-4} M solution of six cation mixture at pH 6, membrane phase: 1 × 10^{-4} M of NQ in chloroform, receiving phase: 0.1 M solution of HCl, HNO_3, H_2SO_4, and CH_3COOH, transport time: 24 h, and stirring rate: 200 rpm.

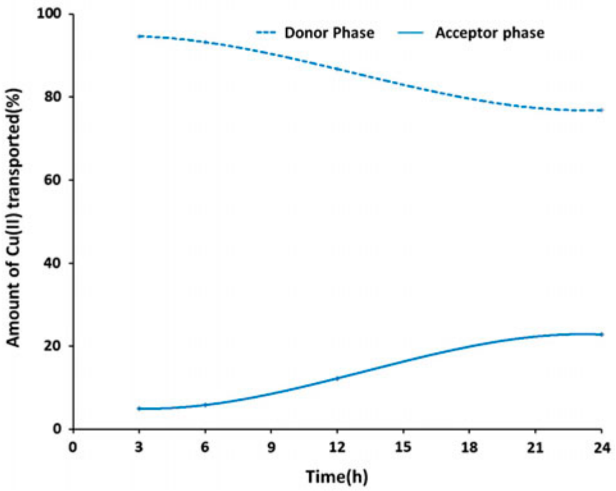

Fig. 7. Effect of time on transport % of Cu^{2+} ions. Feed phase: 1 × 10^{-4} M solution of six cation mixture with pH 6, membrane phase: 1 × 10^{-4} M of NQ in chloroform, receiving phase: 0.1 M HCl, and stirring rate: 200 rpm.

ions remaining in donor phase. Therefore, further experiments were carried out during 24 h [28].

3.6. *Proposed mechanism for transport*

On the basis of the obtained results, the mechanism for the copper ions transport across the liquid membrane is proposed as shown in Fig. 8. At the donor phase, Cu $(NQ)_2$ complex which has been formed at the donor phase/membrane interface dissolves in the membrane phase and gets distributed throughout the organic membrane. At the interface in between the membrane and acceptor phase, the stripping agent HCl releases the Cu^{2+} ions. The carrier anion receives proton from the acidic acceptor phase and diffuses back into the organic membrane as a neutral carrier. The released carrier becomes available at the membrane/donor phase interface for maintaining the continuity of the copper transport till its concentration is too low to form a complex with the carrier. This mechanism is the same as Cu^{2+} selective transport by 8-hydoxyquinoline as the carrier [20].

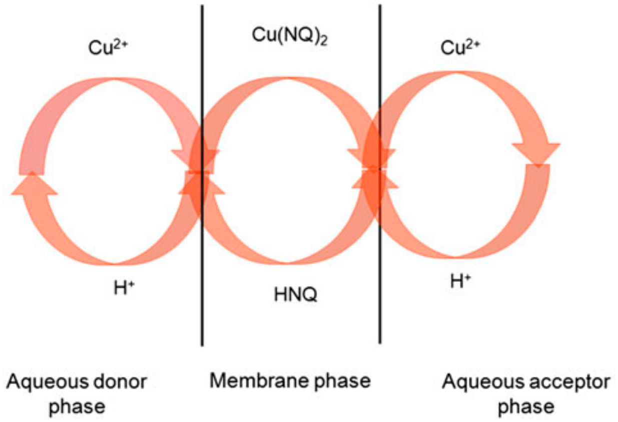

Fig. 8. Schematic representation of the copper ions transport mechanism.

3.7. *Selectivity and reproducibility of BLM technique*

In order to investigate the selectivity of the presented method to transport the Cu^{2+} ions, equimolar mixtures of the Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} ions were placed in the donor phase. The transport of these mixtures was investigated and the cation flux (J_M) values were calculated and reported. Comparison of the results shown in Table 2 depicts that the transport of Cu^{2+} ions is selective and thus, it is concluded that copper ions can be separated from another present cation by this method, and no other cations will interfere in this system. NQ could form a complex with Cd^{2+} and Zn^{2+} [29] and rare-earth ions [30] in special condition. The reproducibility of this system under the optimum conditions was studied by

Table 2
Selective transport of Cu^{2+} ions in presence of equimolar mixture of Zn^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, and Ni^{2+} fixed at pH 6, membrane phase: 1 × 10^{-4} M of NQ in chloroform, receiving phase: 0.1 M HCl, transport time: 24 h, and stirring rate: 200 rpm

Cation	Remained in donor phase (%)	Transported to receiving phase (%)	$J_{max}\times 10^{-9}$ (mol/m^2)/S
Cu^{2+}	66.3	33.05	9.58
Pb^{2+}	100	0	0
Cd^{2+}	100	0	0
Zn^{2+}	100	0	0
Co^{2+}	100	0	0
Ni^{2+}	100	0	0

Table 3
Validation of proposed methodology for Cu^{2+} determination in spiked river water samples ($n = 3$) [Feed phase: 1×10^{-4} M solution of Cu^{2+} spiked in river water adjusts at pH 6, membrane phase: 1×10^{-4} M of NQ in chloroform, receiving phase: 0.1 M HCl, transport time: 24 h, and stirring rate: 200 rpm.]

Sample	Remained in donor phase Cu^{2+} (%) ± RSD%	Transported to receiving phase Cu^{2+} (%) ± RSD%
[a]RW 1	66.3 ± 1.3	29.9 ± 2.2
RW 2	65.8 ± 1.9	32.0 ± 1.5
RW 3	69.1 ± 1.6	30.3 ± 2.1

[a]RW = River water.

performing five replicate transport experiments. The percent of metal ion transport after 24 h was 33.05 ± 3.39%.

3.8. Applications

In order to access the applicability of the present method, it was applied for the recovery of copper ions from river water samples. Three real water samples including river water were provided from Daroungar River in Dargaz, Iran. The results indicated that the concentration of Cu^{2+} cations in all three samples was under the detection limit. Thus, separate samples were spiked with the target compound and as the results in Table 3 depict, Cu^{2+} ions are selectively transported using this new separation system.

4. Conclusion

There is little research for copper ions transport using quinolines as the carrier. The carrier activity of 8-hydroxy quinoline (oxine) toward the facilitated transport of copper ions through chloroform BLM has been studied [20]. Transport efficiency of copper ions by oxine as carrier was reported to be 99.5%, while there is not any interfering ion. We have studied the relative transport of copper ions through a chloroform–NQ BLM. The possible mechanism of transport was investigated and the optimum conditions were found as the following: 1×10^{-4} M solution of Cu^{2+} in donor phase, 1×10^{-4} M of NQ in chloroform as membrane, pH of the donor phase maintained at 6, HCl (0.1 M) was used as a stripping solution in the acceptor phase, and transport time was 24 h and had stirring rate fixed at 200 rpm. The simplicity, low cost, and high degree of selectivity obtained by the membrane system represent its potential applicability for selective removal and concentration or purification of copper (II) from its mixtures in the presence of Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, and Co^{2+} ions from real water samples.

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