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ORIGINAL SCIENTIFIC PAPER – ORIGINALAN NAUČNI RAD

EFFICIENCY OF SODIUM DODECYL BENZEN SULFONATE IN REMOVAL OF PB(II) IONS TROUGH BULK LIQUID MEMBRANE SYSTEMS

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ABSTRACT

In this paper, the influence of the anionic surfactant, sodium dodecyl benzene sulfonate (SDBS) on the efficiency of Pb(II) ions removal through a bulk liquid membrane system, were investigated. Different organic solvents were used as liquid membranes: dichloromethane and chloroform. Macrocyclic ligands: 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, and benzo-18-crown-6 dissolved in organic solvents were used as carriers for Pb(II) ions. Metal ions concentration in aqueous phases was monitored by flame atomic absorption spectrophotometry, after 3 hours of membrane transport. The results showed that the presence of the anionic surfactant SDBS in the receiving phase reduces the content of Pb(II) ions in the source phase and increases the transport rate removed Pb(II) ions to the receiving phase. Among the applied solvents, the highest efficiency in the role of liquid membrane showed dichloromethane, for all applied macrocyclic ligands. From the aspect of the used macrocycle, the addition of an anionic surfactant in the receiving phase with dichloromethane reflected in an increased amount of removed Pb(II) ions from the source phase, following the order: 18C6>B18C6>DCH18C6>DB18C6. Chloroform as a liquid membrane reflected also in an increased amount of removed Pb(II) ions from the source phase, following the order: 18C6>DB18C6>DCH18C6>B18C6. 18-crown-6 (18C6) compared to other ligands proved to be a selective and efficient carrier for the transport of Pb(II) ions via BLM, removing 71% of transported Pb (II) ions from the source phase through dichloromethane while chloroform slightly lower transport rate (63.4%) was achieved for the same used macrocycle.

Keywords: sodium dodecyl benzene sulfonate, Pb(II) removal, bulk liquid membrane.

INTRODUCTION

Heavy metals have been widely investigated by many researchers due to their significant hazardous impact on human health and the environment, and they are considered as major sources of environmental contamination due to their toxic nature and their ability to accumulate (Maitra, 2016). Lead is a well-known highly toxic metal considered as a priority pollutant (Mondal, 2009). It is an industrial pollutant, which enters the ecosystem through the soil, air, and water. Generally speaking, lead pollution, spreading over earth and groundwater, comes from natural sources and industrial effluents (Hu et al., 2011). The application of different systems in transport experiments used for the selective removal of toxic metal ions from natural resources is very interesting in recent years (Shokrollahil, 2009). One of the most efficient applications of these systems is based on the implementation of the "bulk liquid membrane" (BLM) system, which includes a combination of three processes: extraction, diffusion, and re-extraction of an analyte (Nipamanjari et al., 2010). The use of liquid membranes containing ion carriers offers an alternative to solvent extraction in selective removal of metal ions from the source aqueous phase and their concentration. Surfactant

systems have been recognized as very useful alternatives for improving analytical methodologies and the development of new concepts in analytical chemistry. The coexistence of hydrophilic and lipophilic part in the same surfactant molecule (polar ″head″ and non-polar ″tail″) enables their aggregation in formations known as micelles (Flores et al., 2011). At concentrations higher than ″critical micellar concentration″ (CMC), surfactants can provide a certain level of solubilization for hydrophobic organic compounds. Among different types of surfactants, anionic ones (AZPC) whose share in global production and sale revenues is the highest, deserve special attention. They dissociate in aqueous solutions to form an active anion. The anionic group of surfactants is connected to the hydrophobic chain directly or indirectly via covalent bonds, and its acidic nature results in the ready formation of salts, and the associated dissolution of the anionic surfactant in water. Sodium dodecylbenzene sulfonate (DBS) is a very useful and widely used anionic surfactant. It is used as the active ingredient of laundry detergent and as an anti-caking agent in many domestic and industrial materials, including chemical fertilizers.

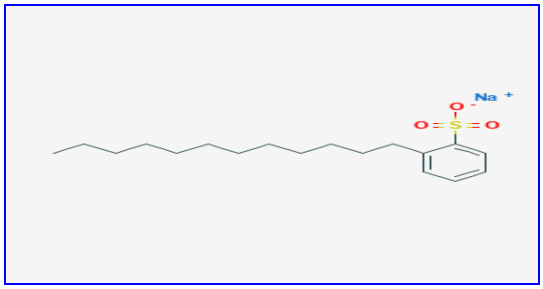

Figure 1. Chemical structure of SDBS

The adsorption of anionic surfactants in a wide concentration range is investigated to understand the application of anionic surfactants to remediation of contaminated soil and groundwater (Ko et al., 1998). In this paper, we examined the effect of an anionic surfactant SDBS in the receiving phase on the efficiency of removing Pb(II) ions, through a bulk liquid membrane system. It has been shown that, in the course of the carrier-mediated transport of a metal ion, the use of an anionic surfactant laying at the MP/RP interface can successfully catalyze the exchange process of the metal ion and measurably facilitate its transport (Rouhollahi et al., 2007). The addition of these surfactants to the receiving phase leads to better transport efficiency. In earlier investigations, authors (Malihe et al., 2010) assumed that the most influencing process during transport experiments was metal ions release from complex in membrane phase to receiving aqueous phase through contact surface between two phases. Based on this assumption, the mechanism for metal ion transport was proposed in Figure 2.

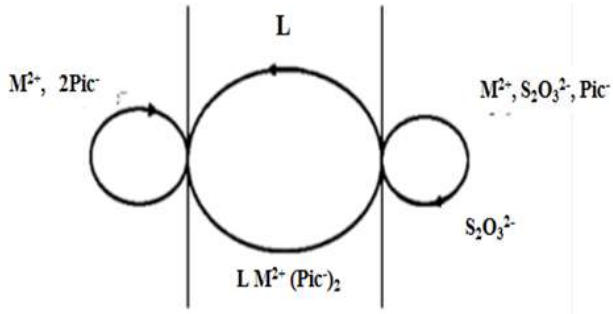

Figure 2. Proposed mechanism of metal ion transport through an organic liquid membrane containing dissolved ligand (L), from SP (contains: M^{2+} cations and counter ions picrate Pic^-) to RP (contains stripping thiosulphate ions)

After the complexation of the carrier with Pb(II)ion on the left side of the membrane (CE-Pb^{2+}), $(Pic^{-})_2$ ion-pair is formed at the SP-MP interface and diffuses down its concentration gradient within the organic phase. On the right side of the membrane, at the MP-RP interface, the metal ion would be released into the receiving phase. At this stage, the free carrier diffuses back across the liquid membrane and the Pb (II) transport cycle starts again.

MATERIALS AND METHODS OF WORK

For every transport experiment, two aqueous solutions and one non-aqueous organic solution (membrane), were prepared, as follows.

Source Phase solutions were prepared using the AAS standard metal ion solutions (Pb^{2+}) from Merck, and picric acid (99%, Kemika) and adjusted to pH = 5, using the acetic buffer solution. Membrane Phase solutions were prepared by dissolving different macrocyclic ligands: 18-crown-6, 18C6; benzo-18-crown-6, B18C6; dibenzo-18-crown-6, DB18C6; dicyclohexano-18-crown-6, DCH18C6 (99%, ACROS ORGANICS) in different organic solvents: dichloromethane (DCM), chloroform (CH), (p.a. Kemika).

Receiving Phase solutions were prepared also in acetic buffer medium (pH = 5), by dissolving sodium thiosulphate (p.a. Sigma-Aldrich) in it and adding anionic surfactant: sodium dodecyl benzene sulphonate (SDBS) p.a. (Sigma-Aldrich).

Procedure

Transport experiments involved the application of a cylindrical glass vessel, "transport cell" (Figure 3.), with an inner diameter of 5 cm, containing a glass tube (2 cm in diameter) in a central position. The central tube represents a physical barrier between the two aqueous phases. The source phase (SP) contained 10 mL of a mixture of tested metal ion ($1 \cdot 10^{-3}$mol/L) and the counter ion, picrate ($1 \cdot 10^{-3}$ mol/L). The receiving phase (RP), which is outside the central tube, contained a stripping agent (sodium thiosulphate) and anionic surfactant SDBS. The membrane phase (MP) contained 50 mL of a suitable ligand ($1 \cdot 10^{-3}$ mol/L) dissolved in an organic solvent; the membrane layer lies beneath the aqueous phases and connects them. The membrane phase is mixed with a magnetic stirrer so that under these conditions the contact surfaces between the aqueous phases are straight and precisely defined.

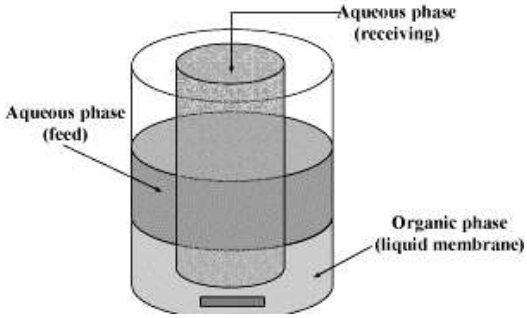

Figure 3. "Transport cell" used for the experiment: SP-source phase; RP-receiving phase; MP-membrane phase; A-magnetic stirrer (Fahmideh-Rad et al., 2010)

Instruments

pH measurements of aqueous solutions were performed using the pH meter (GLP31 Crison Instruments). Quantification of metal ions removed during the transport experiments was obtained by Flame Atomic Absorption Spectrometry technique, using the instrument Perkin Elmer AAnalyst 200.

RESULTS AND DISCUSSION

The liquid membrane used in this study is schematically shown in Figure 3. The Pb (II) ions are transported from the source phase (SP) to the receiving phase (RP) via the dichloromethane and chloroform membrane phase (MP). The movement of charged species (carrier-metal complex) through the hydrophobic liquid membrane is accomplished by the presence of a large lipophilic anion, such as picrate, in the source phase. Since in our previous investigations of BLM systems (Suljkanović et al., 2017), significant interactions between metal cations and nonionic surfactants lead to certain removal of cations (up to 62% of Pb(II) with Brij 58 in chloroform) from the source phase into the membrane, enabling possible application of some nonionic surfactants as carriers for cations. In this paper, transport experiments followed by Pb(II) complexation with different macrocyclic ligands (18C6; DB18C6; B18C6 and DCH18C6) within dichloromethane and chloroform as a liquid membrane, including anionic surfactant; sodium dodecylbenzene sulfonate (SDBS), in receiving phase was investigated. Previous research has shown, that the addition of anionic surfactants to the final phase of the transport system increases the transport efficiency of metal cations according to the principle of electrostatic attraction of positive cations and negative molecules of anionic surfactants (Rouhollahi et al., 2007). The presence of the anionic surfactant SDBS in the receiving phase reduces the content of Pb(II) ions in the source phase and increases the transport rate removed Pb(II) ions to the receiving phase. The results showed that SDBS displayed, better efficiency in the removal of Pb(II) ions measured in the final phase with dichloromethane comparing with chloroform, used as a liquid membrane. SDBS added to the receiving phase, probably according to the principle of electrostatic attraction, may sob Pb^{2+} via ion exchange, whereby dissociating sodium dodecyl sulfate (SDS) in aqueous solution, the formed Na (I) ions may replace some exchangeable Pb^{2+} cation located on the water-organic phase surface. At the same time, dodecyl sulfate anions (DS^-) have a negative hydrophilic head that attracts Pb (II) cations to the final phase and thus increases the efficiency of transport. Regarding the efficiency of macrocycles as a ligand in the membrane, in these systems with an anionic surfactant, all 18C6 derivatives are very close to each other, which indicates a positive effect in complexation with Pb(II) ions.

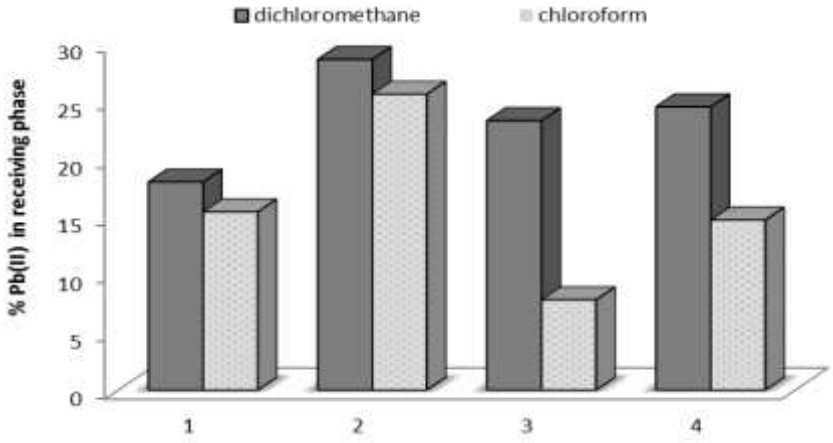

Figure 3. Influence of the anionic surfactant SDBS on the efficiency transported Pb(II) ions into receiving phase
1-18C6; 2-DB18C6; 3-B18C6; 4-DCH18C6

In Table 1. sodium dodecylbenzene sulfonate (SDBS) was used as an additional anionic surfactant. From the aspect of the used macrocycle, the addition of an anionic surfactant in the receiving phase with dichloromethane reflected in an increased amount of removed Pb(II) ions from the source phase, following the order: 18C6>B18C6>DCH18C6>DB18C6. Chloroform as a liquid membrane reflected also in an increased amount of removed Pb(II) ions from the source phase, following the order: 18C6>DB18C6>DCH18C6>B18C6.

18-crown-6 (18C6) compared to other ligands proved to be a selective and efficient carrier for the transport of Pb(II) ions via BLM, removing 71% of transported Pb (II) ions from the source phase through dichloromethane while chloroform slightly lower transport rate (63.4%) was achieved for the same used macrocycle.

Table 1. Measured content of Pb(II) ions in aqueous phases of BLM system after 3h of transport for different crown ethers and anionic surfactant (SDBS) in receiving phase

Type of macrocycle in DCM membrane	**% Pb(II)**			
	SP	**MP**	**RP**	**REMOVAL**
18C6	**28,5**	**53.5**	**18**	**71.5**
DB18C6	**39.7**	**31.7**	**28.6**	**60.3**
B18C6	**29.7**	**47**	**23.3**	**70.3**
DCH18C6	**34.3**	**41.2**	**24.5**	**65.7**
Type of macrocycle in CH membrane	**% Pb(II)**			
	SP	**MP**	**RP**	**REMOVAL**
18C6	**37.6**	**48**	**15.4**	**63.4**
DB18C6	**44.7**	**29.7**	**25.6**	**55.3**
B18C6	**59.3**	**33**	**7.7**	**40.7**
DCH18C6	**50.3**	**35**	**14.7**	**49.7**

CONCLUSIONS

According to the principle of electrostatic attraction, dissociating sodium dodecyl sulfate (SDBS) in aqueous solution, the formed Na (I) ions may replace some exchangeable Pb(II) ions located on the water-organic phase surface and increases transport efficiency. Introducing SDBS in the receiving phase to a systems with different macrocycle crown ethers, showed increased transport efficiency for all used ligands 18-crown-6 due to its very lipophilic character and its corresponding cavity size for selective complexation with Pb(II) ion, compared to other ligands proved to be a selective and efficient carrier, removing 71.5 % transported Pb(II) ions from source phase through dichloromethan as a liquid membrane after 3 hours of transport experiment. Among the applied solvents, the highest efficiency in the role of liquid membrane showed dichloromethane, for all applied macrocyclic ligands

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ULOGA NATRIJUM-DODECIL BENZEN SULFONATA PRI UKLANJANJU Pb(II) IONA SISTEMOM TEČNE MEMBRANE

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APSTRAKT

U ovom radu istražen je uticaj anionskog surfaktanta, natrijum dodecil benzen sulfonata (SDBS) na efikasnost uklanjanja Pb (II) jona kroz sistem tečnih membrana. Kao tečne membrane korišteni su različiti organski rastvarači: dihlormetan i hloroform. Makrociklični ligandi: 18-kruna-6, dibenzo-18-kruna-6, dicikloheksano-18-kruna-6 i benzo-18-kruna-6 rastvoreni u organskim rastvaračima korišteni su kao nosači Pb (II) metalnih iona. Koncentracija metalnih iona u vodenim fazama praćena je atomskom apsorpcionom spektrofotometrijom, nakon 3 sata transporta kroz membranu. Rezultati su pokazali, da prisustvo anionskog surfaktanta SDBS u krajnjoj vodenoj fazi rezultuje smanjenju sadržaja Pb (II) iona u izvornoj fazi i povećava brzinu transporta uklonjenih Pb (II) iona u krajnjoj fazi. Među korištenim rastvaračima, najveću efikasnost u ulozi tečne membrane pokazao je dihlormetan za sve primenjene makrociklične ligande. S aspekta korištenog makrocikla, dodavanje anionskog surfaktanta u krajnju fazu s dihlormetanom kao tečnom membranom je rezultiralo povećanom količinom uklonjenih Pb (II) iona iz izvorne faze slijedećim redoslijedom: 18C6> B18C6> DCH18C6> DB18C6. Izmjereni sadržaj uklonjenih Pb(II) iona u hloroformu kao tečnoj membrani je također bio povećan a efikasnost makrocikličnih liganada je prikazana slijedećim redoslijedom: 18C6> DB18C6> DCH18C6> B18C6. 18-kruna-6 (18C6) u poređenju sa drugim ligandima se pokazao selektivnim i efikasnim nosačem za transport Pb(II) iona preko BLM-a, uklanjajući 71% transportovanih iona iz izvorne faze kroz dihlorometan dok je uz hloroform postignuta nešto niža stopa transporta (63,4%) za isti korišteni makrociklični ligand.