THE REMOVAL OF HEAVY METALS USING THE BULK LIQUID MEMBRANE TECHNIQUE

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ABSTRACT

In recent years, heavy metal pollution has become a worldwide problem due to their high toxic potential and tendency to accumulate in the body. In the present paper was studied the possibility of removing heavy metals using the bulk liquid membrane technique, which proved to be a useful tool in many applications of this type. The transport of a mixture of three metal cations (Mn (II), Fe (II) and Fe (III)) through the bulk liquid membrane was tested. The transport studies were carried out in the membrane system consisting of: the source phase - solution of Mn (II), Fe (II) and Fe (III) in hydrochloric acid medium, the membrane - solution of trioctylmethylammonium chloride (Aliquat 336) in chloroform, the receiving phase – solution of dilute hydrochloric acid. In optimal transport conditions, efficiencies of less than 10% for the removal of Mn (II), of less than 30% for Fe (II) and of about 90% for Fe (III) were obtained.

Keywords: *heavy metals, iron, manganese, liquid membrane, bulk liquid membrane.*

1. INTRODUCTION

Heavy metals are known as highly toxic pollutants that can cause adverse effects on the environment and human health (Varma. V et al., 2013), adverse effects such as cancer, neurological disorders, functional blocking of the essential enzymes, hormonal imbalances, nutritional deficiencies and autoimmune disorders. These may affect the liver and bones (Rahman M. M. et al., 2014; Dastgheib S. A., Rockstraw D. A., 2001).

Heavy metals can be removed using several separation processes, such as: membrane techniques, ion exchange, organic solvent extraction, electrochemical processes, reverse osmosis, adsorption processes, precipitation processes, biosorption, biological processes, evaporation (Fu F., Wang, Q., 2011; Srinath, T. et al., 2002).

The precipitation process is carried out by means of substances such as: hydroxide, carbonate and sulphides (Fu F., Wang Q., 2011; Huisman J. L. et al., 2006; Alvarez M. T. et al., 2007; Matlock M. M. et al., 2002c).

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There have been various studies regarding the removal of heavy metals by ion exchange on resins and liquid ion exchange. Resins can be of several types: synthetic organic resins and inorganic gels (Alyüz, B., Veli, S., 2009).

In the adsorption process, there are used various adsorbent materials: aluminum silicates (natural zeolite, natural mineral silicate) and silicates (Kanem ($Na_2Si_4O_9*5H_2O$), magadiite ($Na_2Si_{14}O_{29}*9H_2O$), kenyaite ($Na_2Si_{22}O_{45}*10H_2O$)) (Erdem E. et al., 2004; Guerra D. L. et al., 2009), activated sludge, ash , sludge (Varma. V et al., 2013), acid activated carbons derived from oil palm and coconut shells (Rahman M. M. et al., 2014), chemically (N_2S) treated granular activated carbon (Meena A. K. et al., 2010), chitosan (Saifuddin M., & Kumaran P., 2005) and carbon nanotubes (Wang H. J. et al., 2007a).

Removal of heavy metals may be performed by biological treatment. Regarding this process, there were performed experiments in which there was used activated sludge (Mittal A., 2011).

J. N. Kumar (Kumar J. N., & Oommen C., 2012) studied the removal of heavy metals (Cd, Hg, Pb, As and Co) from aqueous solutions by biosorption using freshwater alga Spirogyra hyalina. Other materials with features biosorbante are: microbial biomass (fungi, bacteria and yeast), non-living biomass (crab shells, lignin), algal biomass and non-biological materials (sawdust, eggshells, potato peels, coffee husks, citrus peel and gels from sugar beet) (Fu F., Wang, Q., 2011).

Tomas Bakalár et al. (Bakalár T. et al., 2009) studied the removal of heavy metals (Cu, Ni and Zn) using reverse osmosis process. In the experiments performed it was found that high concentrations of heavy metals in the process are done in optimum conditions at high pressures.

One of the processes used to remove heavy metals is solvent extraction. Over time, there have been used many kinds of solvents, namely: tributylphosphate (TBP) diluted in various organic solvents (chloroform, kerosene, n-hexane, n-heptane, isododecan, dichloromethane, n-dodecane, n-decanol), D2EHPA, Cyanex 921, Cyanex 272, Lix 84 and mixtures of organic solvent in kerosene (1-(4'-dodecyl)phenyl-3-tert-butyl-1,3-propanedione,1-phenyl-3-heptyl-1,3-propanedione, 1-phenyl-4-ethyl-1,3-octanedione). In recent studies vegetable oils have been used as an alternative to petroleum-based organic solvents (Teng T. T. et al., 2012).

The electrochemical processes present several advantages, such as: they can be easily controlled, low operating cost, heavy metals and organic pollutants can be removed simultaneously and without further additions of reagents and are very effective. Processes that are part of this category are: electro-coagulation, electro-flotation, electro-dialysis, electro-chemical reduction and anodic oxidation (Fu F., Wang, Q., 2011; Chen G. H., 2004).

Membrane technique is an alternative to traditional techniques, and one of the most popular techniques is the liquid membrane technique. Liquid membrane are divided into three categories, namely: bulk liquid membrane, supported liquid membrane and emulsion liquid membrane. Studies have demonstrated that they can be successfully used in removing heavy metals (López-López J. A. et al., 2010).

In this paper the removal of heavy metals, Fe (II), Fe (III) and Mn (II), using the bulk liquid membrane was studied.

2. EXPERIMENTAL

Materials, apparatus and methods

All the reagents used were of analytical grade.

Chloroform, Aliquat 336 (trioctylmethylammonium chloride) and hydrochloric acid were purchased from Merck and manganese (II) chloride tetrahydrate, ammonium iron (II) sulfate hexahydrate and ferric chloride were purchased from Fluka.

The transport experiments were carried out in a wall in wall type of cell presented in a previous paper (Diaconu I. et al., 2010).

The transport experiments were carried out at room temperature, (t=21±1°C), with a stirring speed of 180 rpm and the transport time of 18 hours (Diaconu I. et al., 2010).

The membrane system was composed of: a source phase (SP), a membrane (M) and a receiving phase (RP). The source phase (SP) was formed from an ammonium iron (II) sulfate hexahydrate solution, a ferric chloride solution and manganese chloride tetrahydrate solution of concentration $5*10^{-4}$ mol/L (for each solution) in the presence of HCl 2.5 mol/L. The volume of source phase was 20 cm^3. The membrane (M) was formed from an Aliquat 336 solution of concentration 10^{-2} mol/L in chloroform. The volume of membrane was 50 cm^3. The receiving phase (RF) was formed from a HCl solution of concentration 10^{-3} mol/L. The volume of receiving phase volume was 7 cm^3.

The content of Fe (II), Fe (III) and Mn (II) in the source phase and the receiving phase was determined with a spectrophotometer LAMDA UV-VIS-NIR (Perkin Elmer Life and Analytical Sciences), while the content of Fe (II), Fe (III) and Mn (II) in the membrane was determined from the mass balance.

3. RESULTS AND DISCUSSIONS

The transport mechanism was correlated with the formation of chemical species (Wu H. et al., 2015) such as: $FeCl_z^{2-z}$ (z = 1-3), $FeCl_y^{3-y}$ (y = 1-4) and $MnCl_x^{2-x}$ (x = 1-6), formed by the three cations in the presence of HCl, according to the equilibrium:

For Fe (II):

$$Fe^{2+} + Cl^- \rightleftharpoons FeCl^+$$

$$Fe^{2+} + 2Cl^- \rightleftharpoons FeCl_2$$

$$Fe^{2+} + 3Cl^- \rightleftharpoons FeCl_3^-$$

For Fe (III):

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$$

$$Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+$$

$$Fe^{3+} + 3Cl^- \rightleftharpoons FeCl_3$$

$$Fe^{3+} + 4Cl^- \rightleftharpoons FeCl^-_4$$

For Mn (II):

$$Mn^{2+} + Cl^- \rightleftharpoons MnCl^+$$

$$Mn^{2+} + 2Cl^- \rightleftharpoons MnCl_2$$

$$Mn^{2+} + 3Cl^- \rightleftharpoons MnCl_3^-$$

$$Mn^{2+} + 4Cl^- \rightleftharpoons MnCl_4^{2-}$$

$$Mn^{2+} + 5Cl^- \rightleftharpoons MnCl_5^{3-}$$

$$Mn^{2+} + 6Cl^- \rightleftharpoons MnCl_6^{4-}$$

These chemical species form a complex with the carrier at the interface feed phase|membrane, crosses through the chloroform membrane that contains the carrier and decomposes at the interface membrane|stripping phase.

The carrier used in the separation process, Aliquat 336, is specific for anionic species thus the equilibrum can occur at the interface source phase – membrane (Mishra R. K. et al., 2011):

$$(MCl_x^{n-x})_{SP} + ([R_3NCH_3]Cl)_M \rightleftharpoons (R_3NCH_3MCl_x^{n-x})_M + (Cl^-)_{SP}$$

where: SP – source phase, M – membrane

The transport of the three metal cations through the chloroform liquid membrane was performed by a coupled transport mechanism with the Cl^- anion co-transporter (figure 1).

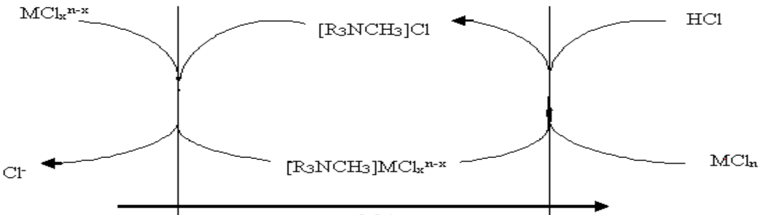

Figure 1. The scheme of the transport mechanism of the studied heavy metals in the presence of Aliquat 336 as carrier

The efficiency of the transport was determined using molar percentage composition. The equation used to calculate the molar percentage composition of the membrane system phases:

$$\%mol = \frac{C_{Faq} \times V_{Faq}}{C_{FS_0} \times V_{FS_0}} \times 100$$

where: % mol = molar percentage of the membrane system;
C_{Faq} = aqueous phase concentration, mol/L;
V_{Faq} = aqueous phase volume, L;
C_{FS0} = initial source phase concentration, mol/L;
V_{FS0} = initial source phase volume, L.

The molar percentage composition of the membrane was determined by the mass balance of the membrane system phases.

The formation of complex anions (anions able to complex with the carrier in the petraction process of the liquid membrane) is dependent on the concentration of hydrochloric acid in the source phase. Therefore, the concentration of hydrochloric acid in the source phase was the main experimental parameter studied. The concentration of HCl in the source phase was varied between 1-2.5 mol/L. The concentration of Aliquat 336 was 10^{-2} mol/L in all experiments, and the concentration of HCl in the receiving phase was 10^{-3} mol/L, so as not to precipite the iron ions in the solution of receiving phase (undesirable phenomenon in the transport process). The concentration of metal cation was $5*10^{-4}$ mol/L (the usual concentration in experiments of this kind)

The best results were obtained in the Fe (III) transport.

In Figures 2-4 is presented the time efficiency of the transport of Fe (III) at various concentrations of HCl in the source phase.

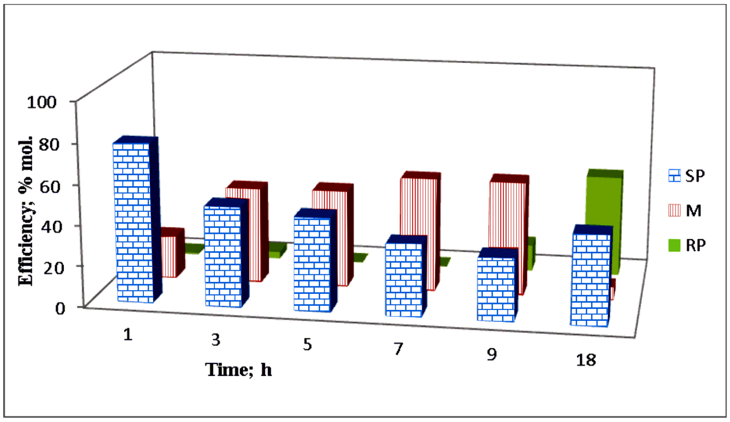

Figure 2. The time efficiency of the transport of Fe (III) cation at the concentrations of HCl in the source phase 1 mol/L

Working conditions: Source phase: $5*10^{-4}$ mol/L ferric chloride (Fe (III)) solution, 1 mol/L HCl solution; Membrane: 10^{-2} mol/L Aliquat 336 in chloroform; Receiving phase: 10^{-3} mol/L HCl solution; transport time: 18 hours; the stirring speed of the phase: 180 rpm.

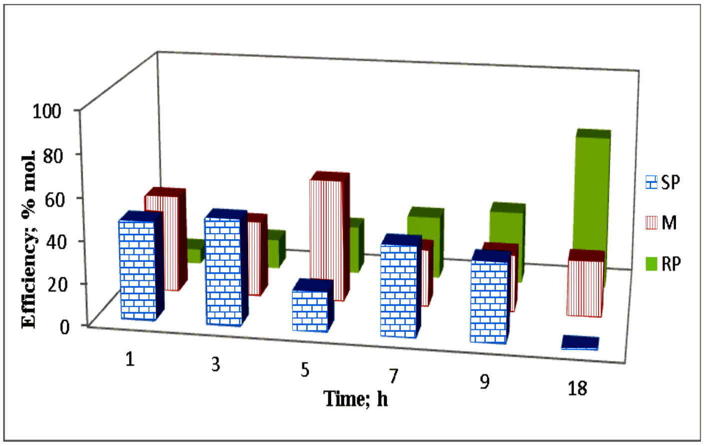

Figure 3. The time efficiency of the transport of Fe (III) cation at the concentrations of HCl in the source phase 2 mol/L

*Working conditions: Source phase: 5*10^{-4} mol/L ferric chloride (Fe (III)) solution, 2 mol/L HCl solution; Membrane: 10^{-2} mol/L Aliquat 336 in chloroform; Receiving phase: 10^{-3} mol/L HCl solution; transport time: 18 hours; the stirring speed of the phase: 180 rpm.*

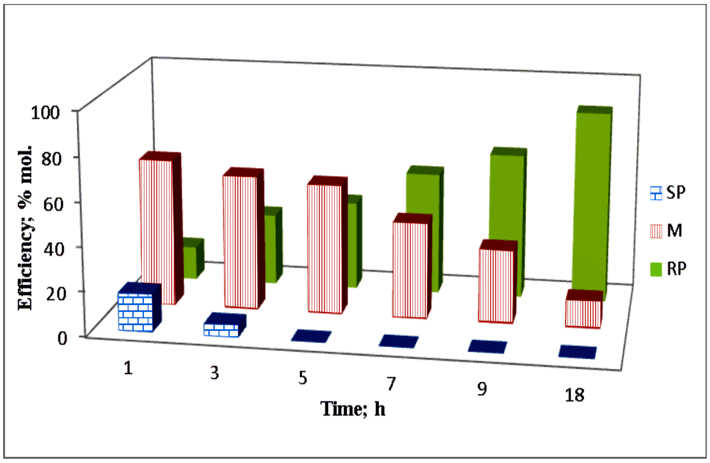

Figure 4. The time efficiency of the transport of Fe (III) cation at the concentrations of HCl in the source phase 2.5 mol/L

*Working conditions: Source phase: 5*10^{-4} mol/L ferric chloride (Fe (III)) solution, 2.5 mol/L HCl solution; Membrane: 10^{-2} mol/L Aliquat 336 in chloroform; Receiving phase: 10^{-3} mol/L HCl solution; transport time: 18 hours; the stirring speed of the phase: 180 rpm.*

The experimental data demonstrated that iron removal was influenced by the duration of the process and concentration of HCl in the source phase. Thus, an efficiently iron removal was done in time and increases with the increasing concentration of HCl in the source phase. A maximum efficiency was obtained for the time transport of 18 hours and the concentration of HCl 2.5 mol/L in the source phase.

Similar studies were carried out for the other cations, but the results were unsatisfactory. The results obtained for the competitive transport of the three cations are shown in Figure 5.

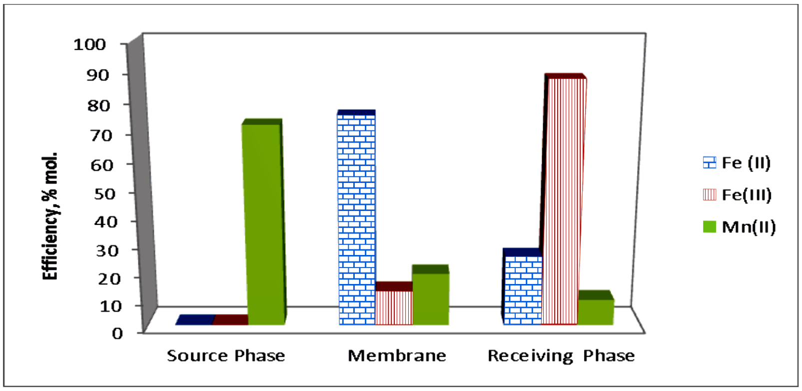

Figure 5. The competitive transport of Fe (II), Fe (III) and Mn (II) cations

Working conditions: Source phase: $5*10^{-4}$ *mol/L ammonium iron (II) sulphate hexahydrate (Fe (II)) solution,* $5*10^{-4}$ *mol/L ferric chloride (Fe (III)) solution and* $5*10^{-4}$ *mol/L mangansese (II) chloride tetrahydrate (Mn (II)) solution, 2.5 mol/L HCl solution; Membrane:* 10^{-2} *mol/L Aliquat 336 in chloroform; Receiving phase:* 10^{-3} *mol/L HCl solution; transport time: 18 hours; the stirring speed of the phase: 180 rpm*

The competitive transport of the three cations was performed for the optimal transport conditions of removing each of them: source phase: $5*10^{-4}$ mol/L ammonium iron (II) sulphate hexahydrate (Fe (II)) solution, $5*10^{-4}$ mol/L ferric chloride (Fe (III)) solution and $5*10^{-4}$ mol/L mangansese (II) chloride tetrahydrate (Mn (II)) solution, 2.5 mol/L HCl solution; membrane: 10^{-2} mol/L Aliquat 336 in chloroform; receiving phase: 10^{-3} mol/L HCl solution; transport time: 18 hours; the stirring speed of the phase: 180 rpm

In the experiments carried out it has been found that Fe (III) has the highest efficiency of transport and recorded a yield of about 90% compared with Fe (II) which recorded a lower yield of 30% and Mn (II) whose yield did not exceed 10%.

The results lead also to the possibility of separation of Fe (III), Mn (II) and Fe (II) cations using the bulk liquid membrane technique (Figure 5).

4. CONCLUSIONS

In this article, the behavior of the transport through the bulk liquid membrane of Fe (II), Fe (III) and Mn (II) cations in the presence of Aliquat 336 as carrier was studied.

The experimental data showed that the three cations may be removed using the bulk liquid membranes with different yields, the best results being obtained for the Fe (III) cations.

Because of the distribution of the cations in the membrane system (Mn (II) mainly in the source phase, Fe (II) in the membrane and Fe (III) in the receiving phase), the three cations may, also, be separated.

In optimal transport conditions, efficiencies less than 10% for the removal of Mn (II), of less than 30% for Fe (II) and of about 90% for Fe (III) were obtained.

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