Influence of ultrasound on copper(II) transport through polymer inclusion membranes

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Abstract

Extraction of metals through polymer inclusive membranes can be used as an alternative process for solvent extraction. The harmful impact of the former process is lower than that of the latter. The PIM process also decreases the amount of solvents consumed during the process. Furthermore a smaller quantity of extractant (in the function of a carrier) is used with the PIM process. Thus the use of more expensive, higher quality extractants becomes a possibility. Triazoles derivatives are a new type of carriers in separation process of copper(II). They are used in industrial chemistry as antifungal, antimould substances, fungal grove inhibitors and as drugs in medicine. In this work 1,2,4-triazoles with the following configuration of alkyl chains: R = C_8H_{17}*;* C_9H_{19}*;* $C_{10}H_{21}$*,* $C_{11}H_{23}$*;* $C_{12}H_{25}$*;* $C_{14}H_{29}$ *and* $C_{16}H_{33}$ *were used.*

1. Introduction

In recent years wet processes, which are known in hydrometallurgy, gain more and more importance. Electronics and their waste can be a potential source of metals. Precious metals can also occur as a component of the electronic [1]. Recovery of metals in the future will not only help to dispose of waste, but will become a part of the market for recycled materials. This is a serious problem because the world's deposits of metals are getting poorer, and the wet methods can allow to obtain metals even with very poor sources. One of the metals recovery steps may be membrane methods, including presented in this study polymer inclusion membrane (PIM). In contrast to other methods such as extraction, they allow to eliminate a large amount of harmful solvents [2,3]. Polymer inclusion membranes also use small quantities of extractants in membrane in a function of the carrier [4].

1,2,4-triazoles may be a new group of previously untested modern carriers used in PIM. 1,2,4-triazole are classified to azoles. Azoles consists of one or more nitrogen atom in their cyclic structure. In triazole three nitrogen atoms occurs. They can be located in various positions known as 1,2,3-triazole and 1,2,4-triazole. Triazoles are less basis then imidazoles [5]. They are used in many branch because of their antifungal properties. They are a structure building block for wide range of antifungal compounds [6]. Their best known forms of triazole compounds are fluconazole and itraconazole. Triazoles are also used in corrosion inhibition of steel [7,8]. Their pKa is lower than pKa of imidazoles. Bacause of their properties and good thermal stability they can be used in fuel cells as a part of electrolyte [5]. In literature many studies describing complex compounds with copper(II) ions have been made [9-12]. Because triazoles create complex compounds with metal cations especially with copper(II) they can be used as potential carrier in PIM.

Ultrasounds are not new in science. This kind of sound is characterized as sound with frequency from 20 kHz up to several GHz. The frequency is above human hearing range. Ultrasounds are used in many fields. They are often used in medicine in imaging equipment (sonography) [13]. Ultrasounds are also used in testing of structures and final products. The main reason for that practice is testing without damage a product. The most practical use of ultrasounds is connected with cleaning. In chemical practice they can be used to accelerate or initiate chemical reactions and processes [14-16]. They can be also used in leaching [17]. A good influence of ultrasounds can be also used in copper(II) ions transport through PIM.

2. Experimental part

2.1. Reagents and chemicals

Copper(II) chloride used in this study was provided by Chempur (Poland); sodium chloride, POCH (Poland); Ethylenediaminetetraacetic acid, Chempur; sodium hydroxide, POCH. All reagents and chemicals are analytical grade. 1-alkyl-1,2,4-triazoles were synthesized by dr Skrzypczak.

2.2. Phases in experiments

The feeding phase consisted of 0.1 M $CuCl_2$ and of the required amount of NaCl which regulates the concentration of chloride anions (0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; and 4.5 mol/dm^3 solutions were used). The receiving phase was demineralized water.

2.3. Membrane preparation

In the structure of membrane cellulose triacetate was used as the matrix, 2-nitrophenyloctyl ether was used as the plasticizer and 1-alkyl-1,2,4-triazoles were used as carriers. All of the solutions were prepared using methylene dichloride as the solvent. To prepare membrane an appropriate volume of matrix, plasticizer and 1-decyl-1,2,4-triazole were mixed. The mixture was overflow to Petri dish and put away to special flat table where solvent is evaporated for 24 h. After that the thickness of membrane is measured and its weight is determined. In next step membranes are soaked in water for 24h and then they are ready to use in spiral channel module.

2.4. Copper(II) and chloride ions determination

The process of copper(II) ions transport was conducted in a spiral channel module (Fig.1). The concentration of copper(II) in feeding phase was measured in first four hours every 30 minutes and after that time each hour. The copper(II) concentration were determined using Spectrophotometer Shimadzu UV-2401. 0,5 ml of sample contains copper(II) ions are mixed with 2,5 ml solution to complexing copper(II) ions. The solution consists of 0,05 M EDTA with a specified amount of addition of sodium hydroxide. The pH of sample with EDTA solution has range from 5.5 to 9.5. In this range absorbance remains constant [20,21]. Chloride ions were determinate using ion chromatograph Dionex DX-100 with AS4-SC column with guard-column and ASRS-II suppressor.

2.5. Spiral channel module

In the process spiral channel module was used (Fig. 1). This kind of module has high membrane area to volume ratio. In literature the spiral channel module was used by Schlosser to transport carboxylic acids through supported liquid membranes [18,19]. The geometrics characterization of the membrane is shown in table 1. In every experiment two module channel are clamped together. Membrane is located between two modules. Every two module have antagonistic spiral because after clamped the spirals create one channel separated by membrane.

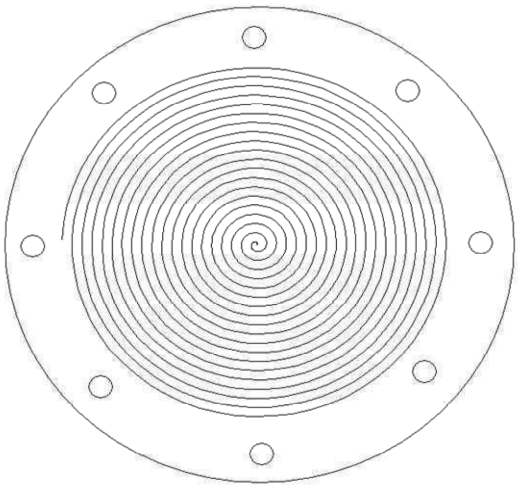

Fig.1. Spiral channel module

Table 1

Geometrical properties of spiral module

Module diameter	120 [mm]
Membrane diameter	90 [mm]
Module thickness	8 [mm]
Outer diameter of spiral	82,2 [mm]
Channel depth	0,25 [mm]
Channel width	1,42 [mm]
Channel length	2,475 [m]
Effective channel area	24,60 [cm^2]
Chennel volume	0,88 [cm^3]

In the experiment with ultrasounds an ultrasounds bath as their source was used. The generator of ultrasound has 310 W of power (Ultrasonic cleaner produced by Polsonic, Poland). This power is constant and is not changeable in the processes. The spiral module was put into ultrasound bath as shown in Fig 2. Feeding phase was pumped from reservoir through pump to channel in module and then reversed to reservoir. The receiving phase was pumped in the same sequence.

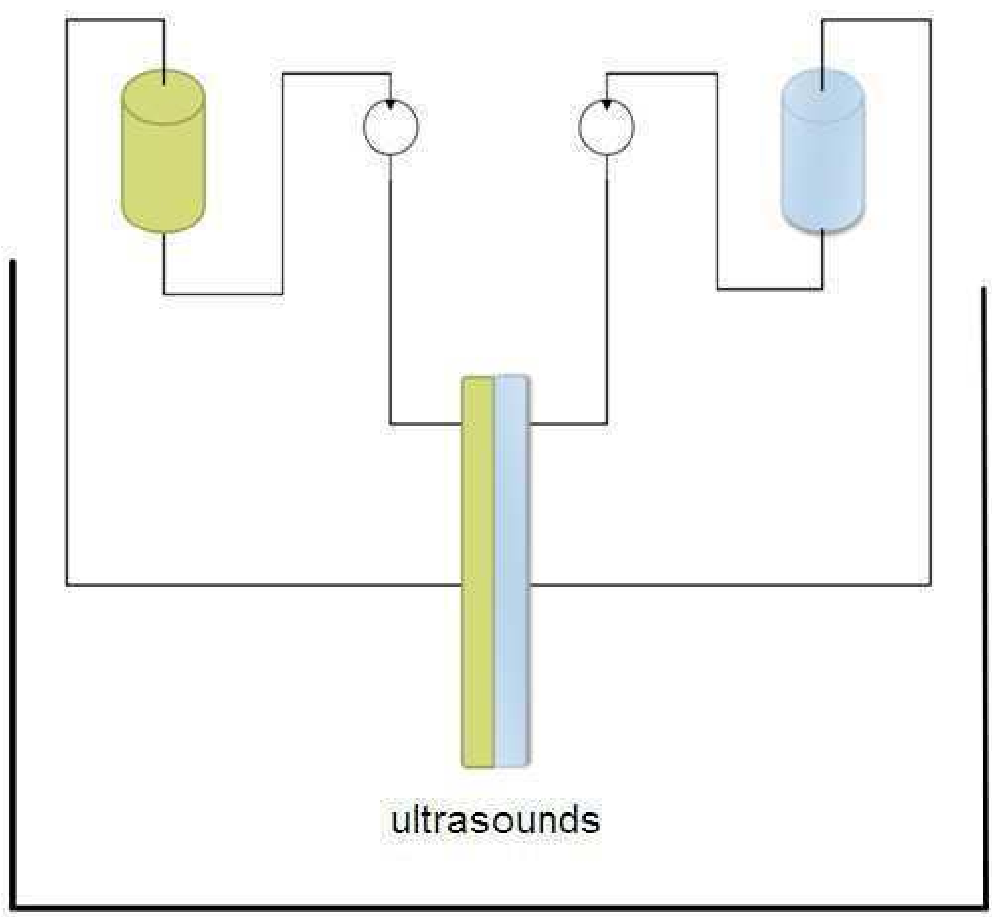

Fig.2. Scheme of equipment

3. Results and discussion

3.1. Influence of volumetric flux on copper(II) transport rate

In this experiment volumetric flux were changed. Chloride anions concentration constant equal to 2.0 mol/dm^3 in all experiments. Results show (Fig.3.) that with increasing volumetric flux to 2.0 cm^3/min. copper(II) transport rate also increases. To the higher than 2,0 cm^3/min. volumetric flux copper(II) transport rate decreases. The best results are obtained for this value. The results show that for higher volumetric flux the contact time is too short to give good results in copper(II) transport rate.

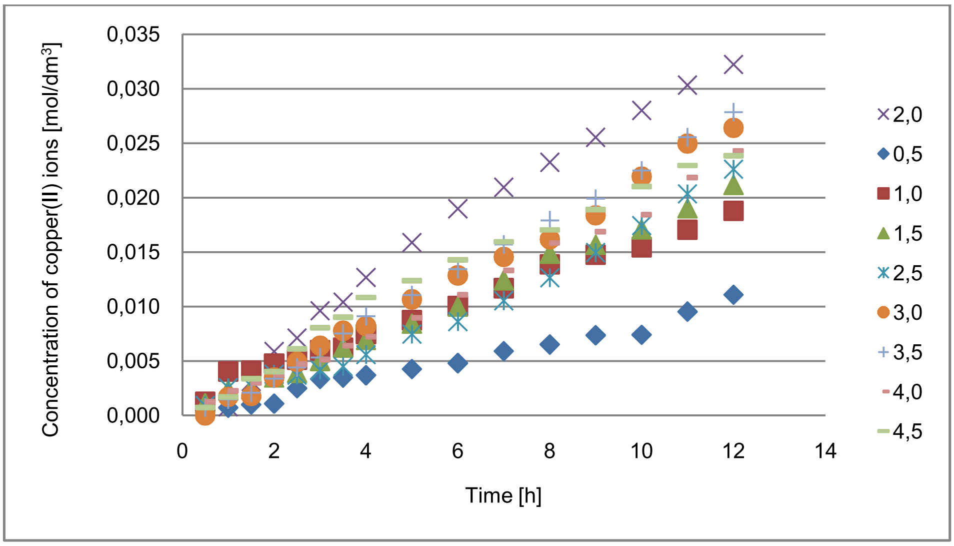

Fig.3. The influence of volumetric flux on copper(II) transport rate

3.2. Influence of chloride ions in feeding phase

In this experiment influence of chloride anions on copper(II) transport rate were measured. Chloride anions concentration were regulated with addition an appropriate amount of sodium chloride. Chloride ions concentration were regulated from 0.5 mol/dm³ to 4.5 mol/dm³ (0.5 mol/dm³ step). Volumetric flux was constant equal to 3.0 cm³/min. Results show that with increasing chloride anions concentration in feeding phase from 0.5 mol/dm³ to 1.5 mol/dm³ the copper(II) transport rate also increases (Fig.4.). With increasing chloride inions concentration above 1,5 mol/dm³ copper(II) transport rate decreases. The decreasing is shown in the Fig.5. where concentration of copper(II) ions in a function of chloride anions in receiving phase in sixth hour of process is shown. The increasing chloride anions concentration in feeding phase from 3.5 to 4.5 mol/dm³ shows that transport rate through PIM is constant.

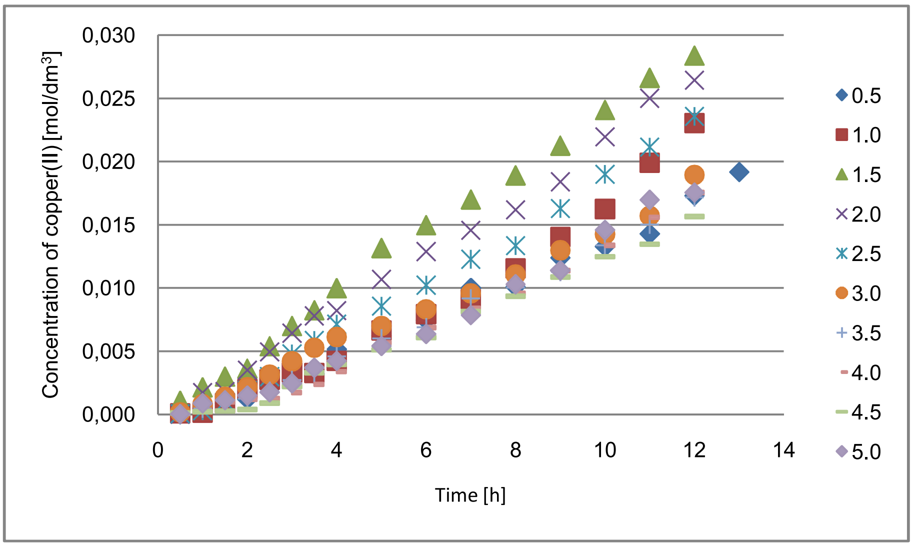

Fig.4. The influence of chloride anion concentration on copper(II) transport rate (volumetric flux constant equal to 3.0 ml/min.)

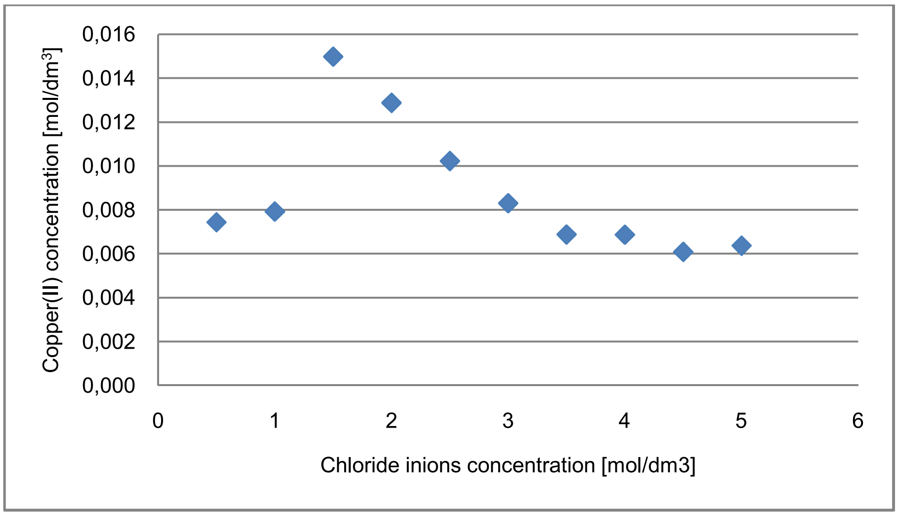

Fig.5. Copper(II) ions concentration in a function of chloride anions concentration in 6 hour of process

3.3. Influence of ultrasounds

In this part of experiment ultrasound bath was used as ultrasound source. Chloride anion concentration in feeding phase equal 2.0 mol/dm³ were used in process. Volumetric flux was changed from 0.5 to 4.5 cm³/min. The best results obtained for lowest volumetric flux. For volumetric flux equals 1.0 cm copper(II) transport rate was the highest in first 4 hours of process (Fig.6). When duration of process increases copper(II) transport rate was better for 2.0 cm³/min. of volumetric flux. For other volumetric flux copper(II) transport rate decreases but the differences were small. Comparison of process assisted with ultrasound and without ultrasound shows that with ultrasound transport rate through PIM rise up instantly. When ultrasounds were used in process membranes tends to eliminate fouling from membrane surface. Membranes after process were clean. These argument is also advantage of using ultrasound for membrane process.

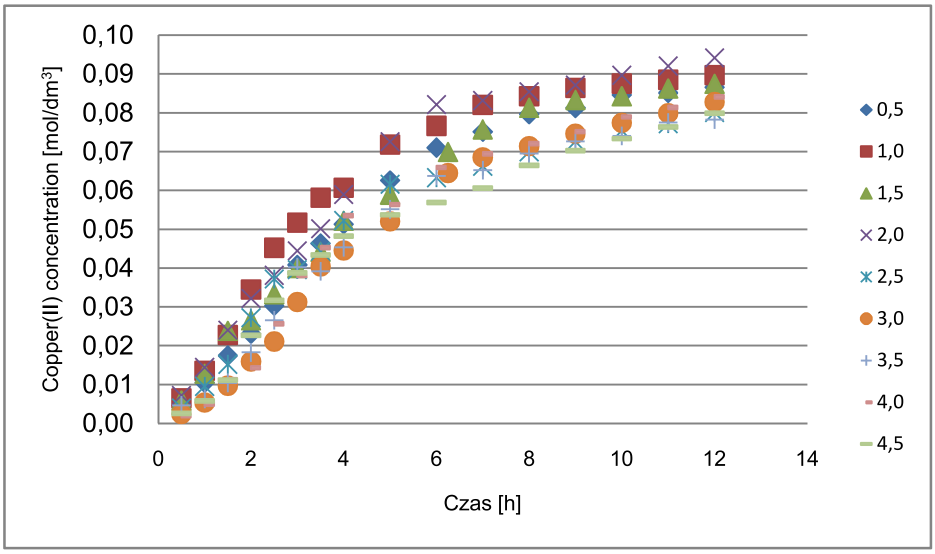

Fig.6. The influence of ultrasounds on copper(II) transport rate for different volumetric flux values (chloride anions concentration constant equal to 2.0 mol/dm³)

3.4. Influence of temperature

The influence of temperature on transport copper(II) through PIM was also measured. In this experiment constant volumetric flux equal 3.0 cm^3/min. and chloride anions concentration equal 2.0 mol/dm^3 in feeding phase were used. The temperature in process equal 20, 30, 40 and 50°C. In the Fig.7. copper(II) concentration in a function of time is shown. The results show that with increasing temperature of process, the copper(II) transport rate also increases. The best results are obtained when the highest temperatures are used. When process is assisted with ultrasounds the results obtained in this way are between results obtained for 40 and 50 Celsius degrees. The temperatures during process assisted with ultrasound are close to ~40 Celsius degree. Only in first part of process the temperature is lower, that's why the copper(II) transport rate is lower.

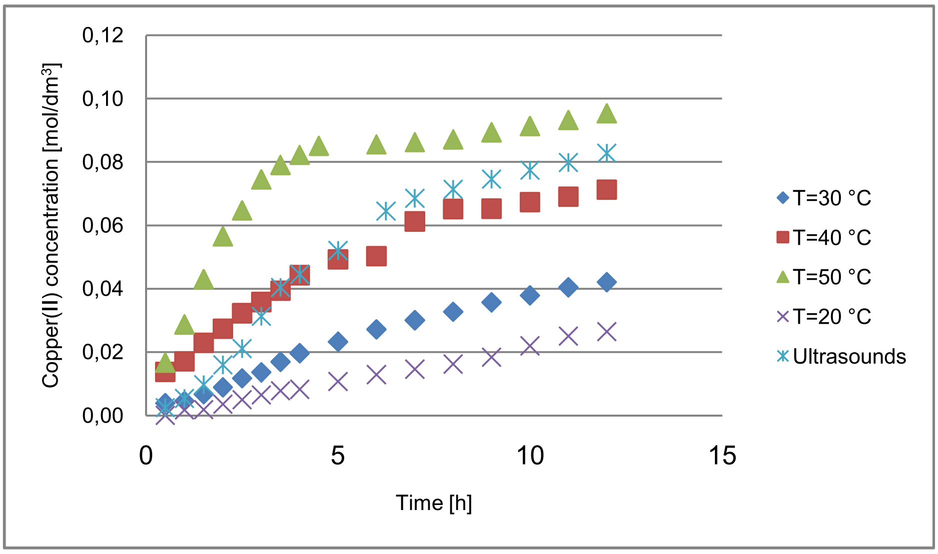

Fig.7. The influence of temperature on copper(II) transport rate (volumetric flux equal to 3.0 cm^3/min and chloride anions concentration constant equal to 2.0 mol/dm^3)

3.5. Cations and anions analyses

In all experiments copper(II) concentration and chloride anions were measured. In all experiments in this paper the chloride anions concentration in receiving phase was twice higher than copper(II) cations (Fig.8 and Fig.9). In receiving phase only pure $CuCl_2$ is presented.

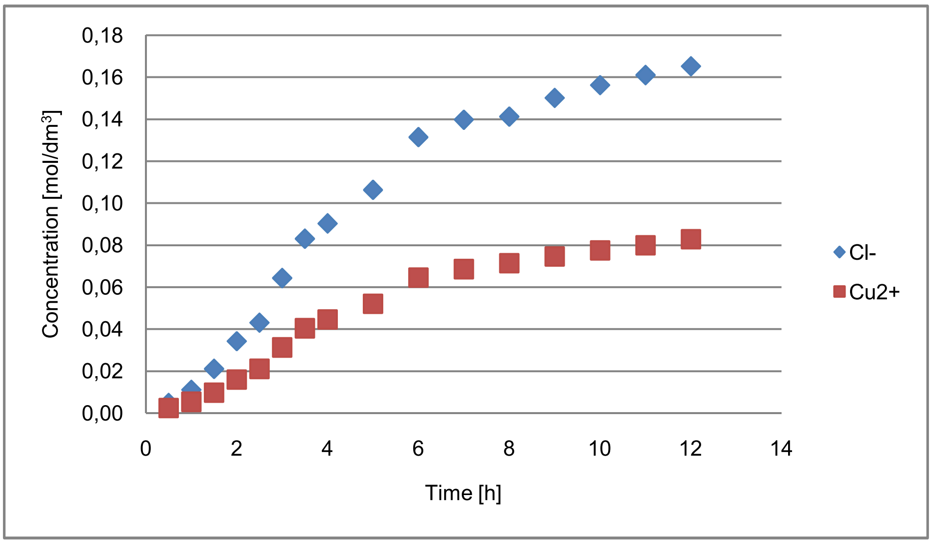

Fig.8. Copper(II) concentration and chloride anions concentration in a function of time (volumetric flux equals 3.0 ml/min., chloride anions concentration constant equal to 2.0 mol/dm^3)

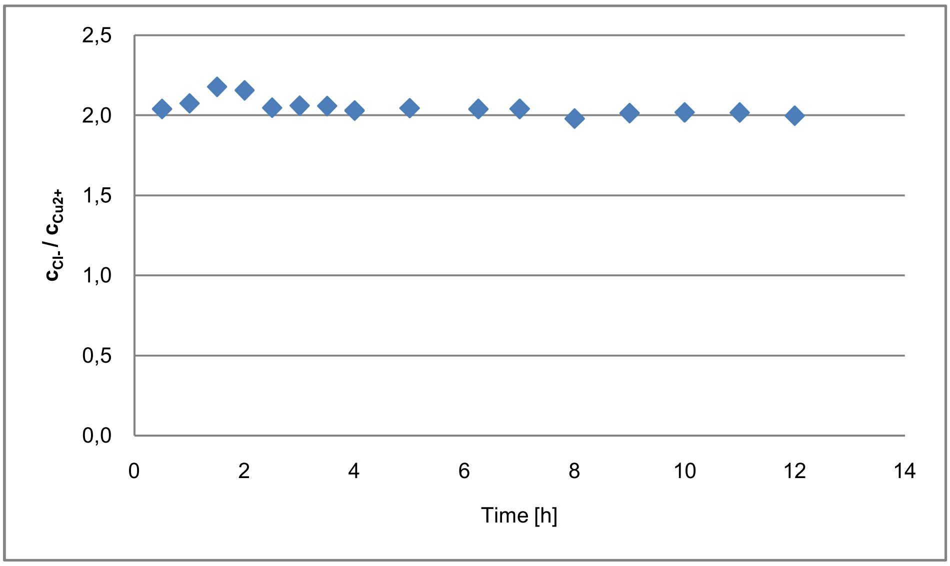

Fig.9. Ratio of chloride concentration and copper(II) ions concentration values in a function of time (volumetric flux equals 3.0 ml/min., chloride anions concentration constant equal to 2.0 mol/dm^3)

4. Conclusions

High influence of copper(II) ions transport rate on chloride anions concentration was determined. The best transport rate was obtained for Cl^- concentration of 1.5 mol/dm^3. The dependency of volumetric flux on copper(II) transport was also observed. The best results were obtained for 2.0 cm^3/min. With increasing volumetric flux to higher values no improvement of copper transport through PIM was observed. When the process is assisted with ultrasounds, the copper(II) transport rate increases compared to process without ultrasounds. The concept of using ultrasounds during membrane process can reduce fouling effect on membrane surface and in this way transport resistance can be also reduced. The temperature has also high influence for copper(II) transport. With increasing temperature copper(II) transport also increases. The optimal parameters for copper(II) ions through PIM can be determined.

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