IOP Conference Series: Materials Science and Engineering

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To cite this article: Muhammad Cholid Djunaidi *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **205** 012010

IOP Conf. Series: Materials Science and Engineering **205** (2017) 012010 doi:10.1088/1757-899X/205/1/012010

Recovery Of Chromium Metal (VI) Using Supported Liquid Membrane (SLM) Method, A study of Influence of NaCl and pH in Receiving Phase on Transport

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Abstract. Chromium metal(VI) is a valuable metal but in contrary has high toxicity, so the separation and recovery from waste are very important. One method that can be used for the separation and recovery of chromium (VI) is a Supported Liquid Membrane (SLM). SLM system contains of three main components: a supporting membrane, organic solvents and carrier compounds. The supported Membrane used in this research is Polytetrafluoroethylene (PTFE), organic solvent is kerosene, and the carrier compound used is aliquat 336. The supported liquid membrane is placed between two phases, namely, feed phase as the source of analyte (Cr(VI)) and the receiving phase as the result of separation. Feed phase is the electroplating waste which contains of chromium metal with pH variation about 4, 6 and 9. Whereas the receiving phase are the solution of HCl, NaOH, HCl-NaCl and NaOH-NaCl with pH variation about 1, 3, 5 and 7. The efficiency separation is determined by measurement of chromium in the feed and the receiving phase using AAS (Atomic Absorption Spectrophotometry). The experiment results show that transport of Chrom (VI) by Supported Liquid membrane (SLM) is influenced by pH solution in feed phase and receiving phase as well as NaCl in receiving phase. The highest chromium metal is transported from feed phase about 97,78%, whereas in receiving phase shows about 58,09%. The highest chromium metal transport happens on pH 6 in feed phase, pH 7 in receiving phase with the mixture of NaOH and NaCl using carrier compound aliquat 336.

1. Introduction

Chemical and metallurgical industries are the main producers of metal-bearing liquid effluents. Due to the toxic character of several metals contained in the metal-bearing wastewater, it needs to be treated before final discharge to the environment. Thus, industries are increasingly being forced either by the administration, regulatory, cost pressures and social pressures to reduce the amount and environmental sensitivity of the liquid waste they produce [1].

Chromium has fairly high toxicity value and potentially as harmful pollutant when waste industries is not processed first and directly discharged into the environment. The concentration of chromium (III) and (VI) in electroplating liquid waste or metal coating industry is generally higher than the threshold values allowed. The maximum amount allowable of total chromium present in healthy water is 0.05 mg L^{-1}. However, chromium metal is also useful for people in daily activities as well as in industrial processes, such as for electroplating [2].

Toxic but valuable of this metals in another hand, causes the separation and recovery of waste containing chromium are essential. Recycling and re-use is an important aspect in the development of the industry in the future.

IOP Conf. Series: Materials Science and Engineering **205** (2017) 012010 doi:10.1088/1757-899X/205/1/012010

One of the methods for separating metal ions is liquid separation membrane [3]. In the liquid membrane technique, carrier compounds play an important function. Carrier compound as a facilitator is determinant in the separation performance from the feed phase. A carrier compound should has high ability of extraction via stable complex formation within the membrane, high selective separation towards certain species, good solubility as well as diffusion coefficient in the suitable organic solvent (membrane) and can be used in relatively small amounts [4]. In addition, the selectivity of carrier compound towards certain metal ions is determined by the active groups present on the carrier compound.
There are several methods that can be used for the separation and recovery of metals using Liquid Membrane including Supported Liquid Membrane (SLM), Emulsion Liquid Membrane or ELM and Bulk Liquid Membrane or BLM. BLM is used for separation of Cr(III), Cu(II) and Cd(II) with carrier compound that has active atom N and S so that the transport efficiency was Cd(II)>Cu(II)>Cr(III) based on HSAB (Hard Soft Acid Base) theory [5].
SLM is a separation technique consisting of two homogen phases that are feed phase and receiving phase separated by semipermeable membrane. The advantages of SLM are a little amount of carrier compound required, simple and inexpensive operation [6]. SLM system contains three main components: a supporting membrane, organic solvents and carrier compounds. The separation with SLM is largely determined by the selectivity and effectivity of the compounds (carrier). Type of carrier compound determines how much ionic metal can be transported to the receiving phase.
Solangi, et al (2013) [7] in his research reported that SLM is efficient in transport Cr(VI) using calixarene carrier and NaOH receiving solution. Whereas Khasanah (2001) [8] used SLM to subtract the Cl anion from sea water desalination with the supported membrane PTFE impregnated with the carrier compound aliquat 336 with the desalination percentage of about 96,69% for aliquat compound 336 and 100% for aliquat compound 336-TBP on pH 6 in receiving phase.
Based on the information above, this research uses method of SLM with the supported PTFE membrane and aliquat carrier compound 336 in karosen. The pH variation on feed phase are about 4, 6, 9 and 1, 3, 5, 7 on receiving phase. The solution used on receiving phase are HCl, NaOH, HCl-NaCl and NaOH-NaCl. Those variation aim to make Cr(VI) ion in electroplating liquid waste can be separated and to produce purer metal and separated from its matrics.

2. Experiment Setup

2.1 . Studying the Effect of pH receiving phase
To study the effect of pH in the receiving phase, we make various pH, namely, 1, 3, 5 and 7. Whereas feed phase uses the electroplating liquid waste with pH 4. The carrier compound used is aliquat 336 1M.

2.2. Studying the Effect of pH Feed phase
To study the effect of pH in the feed phase, the variation of pH is made i.e. 4, 6, and 9, while the receiving phase uses solution consisting of NaOH-NaCl 1M at pH 7. The carrier compounds used is Aliquat 336 1M.

2.3. Studying the Effect of NaCl consentration in receiving phase.
To study the effect of NaCl in the receiving phase, the variation of NaCl concentration are made, i.e. 0M, 0.5M, 1M and 1.5M in pH 7. Meanwhile, feed phase uses the electroplating waste with pH 6. The carrier compounds used is aliquat 336 1M.

2.4. Studying the Effect of pH in receiving phase with NaCl addition
To study the effect of NaCl addition in receiving phase with the variation of pH, the solution in receiving phase is made from HCl-NaCl mixture 1 M for pH 1, 3, 5; and NaOH-NaCl mixture 1 M for

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pH 7. In the meantime, the feed phase uses the electroplating waste with pH 4 and the carrier compound used is aliquat 336.

3. Result and Discussion

The initial step is measurement of the levels of Cr (VI) in wastewater with AAS. The result shows that the wastewater contains 1055 mg/L of Cr (VI).

3.1. The effect of pH of receiving phase

To study the effect of pH of the receiving phase, a series of pH variation is made from HCl and NaOH mixture in different level: 1, 3, 5, and 7; meanwhile, the pH of feed phase is constant coming from the electroplating waste at pH 4. Furthermore, the aliquat 336 is used as a carrier compound in membrane phase. The result can be seen in table 1.

Table 1. The effect of pH of Receiving phase on Cr(VI) transport using aliquat 336 as carrier compound

pH receiving phase	% transport From Feed to Membrane Phase	% transport In Receiving Phase (From Membrane Phase)
1	61.86	6.61
3	57.65.	1.51
5	67.63	0.99
7	71.62	1.46

As seen in table 1, when the pH of receiving phase increases the transport of Cr(VI) from feed phase is also high; however, unfortunately low concentration can be transported into the receiving phase since Cr(VI) is trapped in the membrane phase. However, transport of Cr(VI) into receiving phase is low with the increasing pH of receiving phase and slightly becoming high when the pH is acid. In order to make alkaline (bases) condition in the receiving phase we use NaOH while use HCl is for making acid condition. This condition resulting in low transport of Cr(VI) into the receiving phase when the pH is high because OH- ion has smaller affinity than Cl-, consequently, Cl ions are more easily exchange with $HCrO_4^-$ ions which will be released into the receiving phase.

3.2. The influence of pH of Feed phase

In feed phase, the pH is varied by 4, 6 and 9 meanwhile in the receiving phase pH is constant at pH 7 by adding NaCl 1M as seen in table 2.

In the transport process, $HCrO_4^-$ ion that has already been bound in the membrane phase will be released into the receiving phase, while the anions in the receiving phase will be bound by the membrane. The addition of Cl^- in the receiving phase aims to replace $HCrO_4^-$ so that $HCrO_4^-$ will be released easily into receiving phase. The high concentration of $HCrO_4^-$ ions is found in receiving phase because the Cl^- has higher affinity to the aliquat 336 than to the OH^- ion [12].

Table 2. The relationship between % transport of Cr(VI) with variation of pH of feed phase in receiving phase (pH constant at 7 and NaCl 1M).

pH feed phase	% transport From Feed to Membrane Phase	% transport In Receiving Phase (From Membrane Phase)
4	50.36	22.59
6	97.78	46.56
9	91.29	40.35

3.3. The effect of NaCl concentration addition in receiving phase

To determine the effect of NaCl concentration added to receiving phase, the NaCl concentration is varied from 0M, 0.5M, 1M to 1.5M. The Effect of NaCl on transport in the receiving phase can be seen in table 3. It can be seen in table 3 that the higher the NaCl concentration, the higher Cr(VI) can be transported. Nevertheless, at NaCl 1.5M transport of Cr(VI) decreases due to the high osmotic pressure so that the carrier compound aliquat 336 is relased easily from membrane phase. The highest transport of Cr(VI) occurs at concentration of NaCl 1M with the percentage of Cr(VI) transport of about 97.78% in feed phase and 58.09% in receiving phase.

Table 3. The effect of NaCl concentration in receiving phase on transport of Cr(VI)

Concentration of NaCl (xM)	% transport From Feed to Membrane Phase	% transport In Receiving Phase (From Membrane Phase)
0	37.91	2.48
0.5	83.79	46.56
1	97.78	58.09
1.5	85.52	55.88

3.4. The Effect of pH of receiving phase with NaCl addition.

To compare the effect of pH and $C1^-$ ion on Cr(VI) transport, further study is conducted. The impact of pH variation of receiving phase with NaOH-NaCl 1M liquid can be seen at table 4. Table 4 shows that the addition of NaCl 1M in receiving phase affects the chromium metal transport. In comparison to the table 1 by using the same pH variation, chromium metal transport is high if NaCl solution is used in receiving phase. The highest transport of metal still occurs at pH 7 transporting metal from feed phase. On the one hand, it can be seen from table 1 that the higest transport of metal to receiving phase happens at pH 1. It may occur since at pH 7 there is no $C1^-$ ion resulting in the chromium metal is hard to release in receiving phase. Whereas, at pH 1 as shown it table 4 the concentration of NaCl is more than 1M with the result that the high osmotic pressure causes the aliquat 336 carrier compound aparts from the membrane, so that it leads to low metal transport.

Table 4. The effect of pH variation of receiving phase towards Cr(VI) transport with aliquat 336 as carrier compound and NaOH-NaCl as liquid receiving.

pH receiving phase	% transport from feed Phase to Membrane phase	% transport in Receiving phase
1	87.23	7.38
3	94.35	24.61
5	97.51	20.84
7	97.78	58.09

According to data from table 3 and 4, it can be concluded that metal chromium that can be transported using aliquat 336 as carrier compound in SLM is high because the concentration of anion ($C1^-$) in the receiving phase increases chromium metal transport significantly.

4. Conclusion

This study shows that transport of Chrom (VI) by Supported Liquid membrane (SLM) is influenced by pH solution in feed phase and receiving phase. Furthermore, the NaCl addition in receiving phase increases the number of Cr (VI) in receiving phase.

1. The higest percentage of chromium metal is 97.78 % in feed phase and 58.09 % in receiving phase with aliquat 336 carrier compound.
2. The greatest chromium metal transport occur at pH 6 in feed phase and pH 7 on receiving phase with the mixture of NaOH and NaCl 1M.

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