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Parametric studies on the removal of nickel using emulsion liquid membrane

N. Rajamohan[a,*], M. Rajasimman[b], Fatma Al Qasmi[a]

[a]*Chemical Engineering section, Faculty of Engineering, Sohar University, Oman, email: rnatarajan@soharuni.edu.om (N. Rajamohan), fqasmi@soharuni.edu.om (F. Al Qasmi)*
[b]*Department of Chemical Engineering, Annamalai University, India, email: simms@rediffmail.com (M. Rajasimman)*

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ABSTRACT

Removal of Nickel(II) ions from aqueous solution was investigated in this study using emulsion liquid membrane under a wide range of operating conditions. ELM solution was prepared in an emulsification reactor at a high emulsification rotating speed of 3000 rpm by mixing toluene (organic solvent), D2EHPA (carrier/extractant), span 80 (surfactant) and sulfuric acid (stripping phase). Effects of operating parameters, namely pH of the internal phase, external phase, initial concentration of nickel, surfactant concentration,carrier concentration and type of organic solvent on metal removal efficiency were studied. A maximum removal efficiency of 98% was obtained for 10 ppm of initial concentration of nickel(II) in the external feed phase. The removal efficiency decreased with increase in metal concentration. The optimal pH of the stripping and external phases were determined as 1 and 11 respectively with the maximum removal efficiency achieved greater than 95%. The optimal carrier concentration was found to be 2% (v/v), while the 6% (v/v) surfactant concentration yielded optimal results. Among the various solvents tested, toluene was found to be the suitable one.

Keywords: Metal; Liquid membrane; Extraction; Surfactant

1. Introduction

Wastewater generated from most industrial activities containing significant levels of heavy metals are reported to cause a serious effect on both environment and public health. According to the World Health Organization report, the most toxic metals are identified as aluminium, chromium, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead [1]. Heavy metals are used in many industrial applications such as mining activities, metal electroplating, pigment manufacturing and petroleum refining [2]. Due to their predominant use, a large volume of wastewater generated from these industries contain high level of toxic metals. Heavy metals cannot broken down naturally by using microorganisms because of their chemical inertness, non–biodegradable nature and can only accumulate in living organisms causing serious problems and environmental disorders. Nickel is considered as one of these hazardous metals existing in wastewater. It is widely used in different types of industrial processes [3]. Nickel, existing in the air, water and soil at low levels , is released into troposphere layer from power plants, volcanos and forest fires. Nickel is known as the 24th most abundant element existing in the Earth’s crust forming about 3% of the composition of the earth [4] and widely distributed in an environment due to both natural sources and industrial activities. In addition, human exposure to nickel–polluted dusts and fumes at low or at high levels may cause a serious diseases such as lung fibrosis, kidney diseases and cancer [5,6]. Hence, a clean-up and a reduction of the nickel pollution into environment has become an integral part in nickel waste management. Different types of physico-chemical methods have been suggested to remove nickel industrial effluents especially wastewater such as chemical precipitation, electrochemical treatment, filtration, ion exchange, and adsorption [3]. Some of these processes may be expensive, especially when the concentration of nickel metal ions in the wastewater are high and some of them have operational problems or may require a higher energy consumption [8,9]. In general, both chemical and physical processes which

*Corresponding author.

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are totally associated with principles of mass and heat transfer can be used to extract heavy metals from wastewater [8]. Physical processes such as reverse osmosis depends on using of pure solvent which give a high efficiency with expensive cost. Since most of the traditional processes suffer from some disadvantages represented in the amount of energy consumption, quality of the used materials and type of conditions the processes work on, hence a looking for alternative technologies has become a concern for many engineers and industrialists [9]. Emulsion liquid membrane (ELM) is proposed as an alternative purification technique used for the removal of metals and a higher efficiency separation process enhanced by combination of stripping and extraction in the same system [1]. Removal metals like cadmium [10], lead [11], cobalt [12] and copper [13] have been successfully investigated. The objectives of this study are to synthesize an emulsion liquid membrane and study the effect of operating parameters on the Nickel extraction performance in emulsion liquid membrane reactor and the choice of extraction agents and the concentration of nickel studied added to the novelty of this study.

2. Materials and methods

2.1. Chemicals

The chemicals used in formation of ELM solution are di-2-ethyl hexyl phosphoric acid (D2EHPA) and sorbitan monooleate (Span 80) and toluene [Merck, Germany]. In addition, Sulfuric acid is used as a stripping phase (internal phase) to enhance the stability of prepared ELM solution. 0.1 M of HCl and 0.1 M of NaOH are used as the buffering agents to maintain the pH of stripping phase and pH of external feed phase. The external feed phase consists of Nickel sulphate ($NiSO_4$) as a source of nickel(II) ions.

2.2. Optimization experiments

Table 1 describes the operating parameters used for removal of nickel(II) with their ranges.

Table 1
Operating parameters for nickel(II) removal

Parameter	Range
Surfactant concentration	[2–6][a]
Carrier concentration	[2–6][b]
pH of stripping phase	1–2
pH of feed phase solution (external phase)	3–11
Initial concentration of Nickel(II) in feed solution	10–200 ppm
Type of solvent	Toluene/Xylene/ Ethyl acetate/ Tetrachloroethylene

a = Volume of surfactant with respect to the total volume of membrane phase (v/v) %, b = Volume of carrier with respect to the total volume of membrane phase (v/v) %.

2.3. ELM preparation

ELM solution was prepared in a batch emulsification reactor at a high emulsification rotating speed of 3000 rpm by mixing 240 ml of toluene (organic solvent), 5 ml of D2EHPA (carrier/extractant) and 5 ml of span 80 (surfactant). Then, 250 ml of H_2SO_4 acid (internal/stripping phase) was added drop wise to stirred solution in order to enhance ELM solution stability and metal transport through the liquid membrane phase. The solution was stirred for a time duration of 12 min in order to obtain a very white viscose ELM solution.

2.4. ELM experiments for nickel(II) removal

The aqueous synthetic feed solution was prepared by dissolving nickel sulphate $NiSO_4$ in a distilled water. 200 ppm of nickel sulphate solution was prepared as stock solution and different concentrations were prepared by serial dilution.

Liquid-liquid extraction of nickel(II) is carried out by adding 100 ml of prepared ELM solution (organic phase and internal phase) with 1000 ml of aqueous feed solution (external feed phase) into a second reactor provided with temperature and pH sensors .

The product existing from ELM reactor was separated by filtration. Nickel(II) ions will represent a raffinate section which is collected in volumetric flask. A sample from treated feed solution was analysed for residual metal concentration. The experimental set-up is shown in Fig. 1.

2.5. Estimation of nickel(II) in the samples

The performance of ELM reactor was evaluated by measuring the inlet and outlet concentration of nickel(II) ions in feed solution for each experiment at fixed intervals. The raffinate separated by filtration was analysed for residual nickel concentration using UV–spectrofotometer (Biochrom,UK) at an optimal wavelength of 420 nm .

The performance of the ELM extraction technique was evaluated by the removal efficiency:

$$RE\ \% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where C_o and C_e are the initial and final concentration (mg/L) of the nickel ions in aqueous feed solution, respectively.

3. Results and discussion

3.1. Performance of ELM process

The performance of ELM process which is dependent on its capacity to remove the nickel(II) ions from prepared synthetic solution was investigated by varying the operating parameters such as pH_i of stripping (internal) phase, pH_0 of external feed phase, initial concentration of nickel in external feed phase, surfactant concentration, carrier concentration and type of organic solvent

The removal of nickel(II) ions by using ELM process is governed by the hydrometallurgy field which can be explained by the following equations [7]:

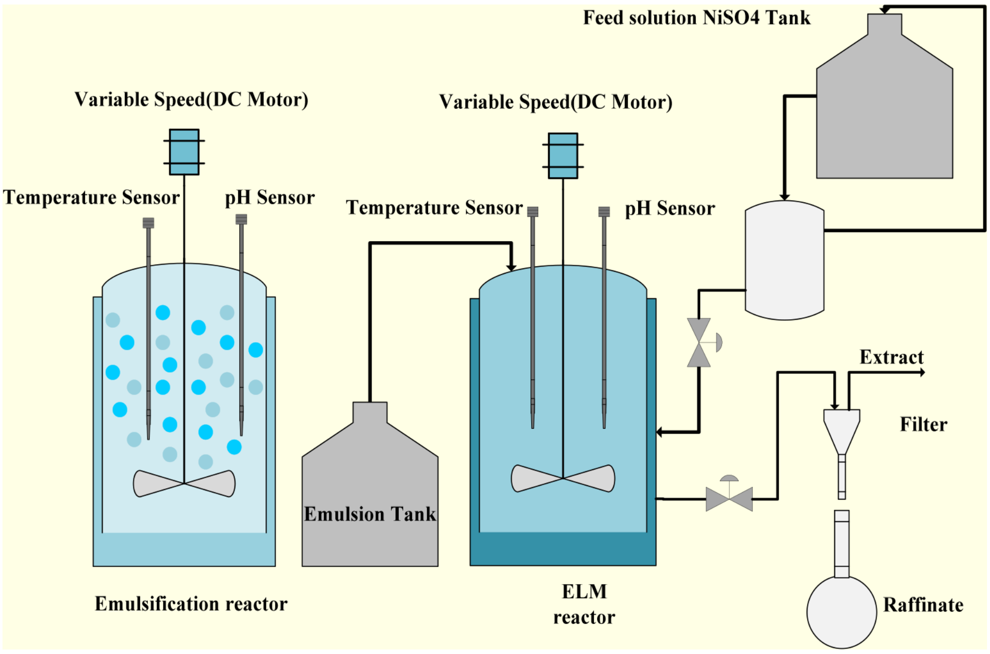

Fig 1. Schematic diagram of the ELM process.

$$Ni^{+2}_{aq} + 2H_2R_{2org} \rightarrow NiR_2 \cdot 2HR_{org} + 2H^+_{aq} \quad (2)$$

$$NiR_2 \cdot 2HR_{org} + 2H^+_{int} \rightarrow Ni^{+2}_{int} + 2H_2R_{2org} \quad (3)$$

Eq. (2) represents the extraction reaction where the D2EHPA dimmer (H_2R_{2org}) extracts the Nickel(II) ion Ni^{+2}_{aq} from external feed phase to form a complex compound $NiR_2{\cdot}2HR_{org}$ and releases H^+_{aq} ion into external feed phase. Eq. (3) represents the stripping reaction occurring in ELM process where the complex compound $NiR_2{\cdot}2HR_{org}$ reacts with H^+_{int} available in stripping (internal) phase. The facilitated transport behaviour of nickel(II) metal ions through ELM which was flowing from the external feed phase into the stripping phase consists of four steps. The first step is diffusion of nickel(II) ions through the external feed phase boundary film. The second step is distribution of nickel(II) ions between the external feed phase and liquid membrane phase. The third step is diffusion of nickel(II) ions through the liquid membrane phase and the fourth step is stripping of nickel(II) ions into the stripping (internal) phase [14]. The optimum values of operating parameters used in formation of emulsion liquid membrane are emulsification time = 5 min, emulsification rotating speed= 3000 rpm and $C_{stripping\ agent}$ = 1 M. These parameters were constant in all prepared emulsion liquid membrane solutions . All experiments on performance of ELM process were perfomed for a time duration of 30 min.

3.2. Effect of pH_i of stripping (internal) phase

Fig. 2 shows the effect of pH of stripping phase on nickel(II) ion removal. The experimental conditions used for this purpose are C_0 = 50 ppm, $C_{surfactant}$ = 2 v/v%, $C_{carrier}$ = 6 v/v% at agitation speed of 200 rpm in ELM reactor for a time duration of 30 min. The removal efficiency of nickel(II) ions decreased with increase in the pH_i of stripping phase. When pH_i of stripping phase is 1.0, the removal efficiency of nickel(II) was about 97% while it decreased to 85% at pH 2.0. The lower value of pH could have influenced the solubility of the nickel ions. Similar trends were reported [13] which showed that the extraction of Copper ions was decreasing with increasing the pH_i of stripping phase (H_2SO_4) from 0.5 to 5.0.

3.3. Effect of pH_0 of external feed phase

pH of the external feed phase plays an important role in the capability of the extraction process for removal of

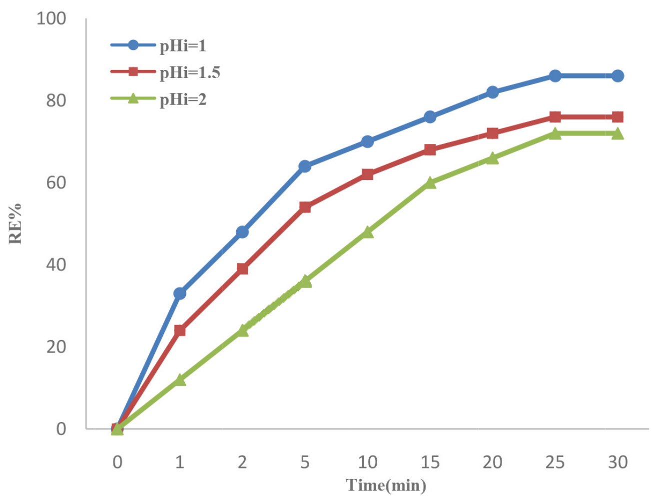

Fig. 2. Effect of pHi of stripping phase [C_0 = 50 ppm, $C_{surfactant}$ = 6 v/v%, $C_{carrier}$ = 2 v/v%, agitation speed = 200 rpm].

nickel(II) ions. The equilibrium constant of the reaction occurring between the metal ions and the carrier at interface of the external and the membrane phase is reported to be influenced by the pH_0 of external feed phase, which needs to be controlled. The effect of pH_0 of external feed phase was studied within the range of 3 to 11. The buffering agents were used to maintain the pH_0 of external feed phase under the experimental conditions of $pH_i = 1$, $C_0 = 50$ ppm, $C_{surfac tant}$ = 6 v/v%, $C_{carrier}$ = 2 v/v% at agitation speed of 200 rpm in ELM reactor. The effects pH_0 of external feed phase were shown in Fig. 3. The relation between pH_0 of external feed phase and the removal efficiency of Nickel(II) ions was found to be directly proportional. Results from related studies [12] found that pH_0 of external feed phase should be maintain at 13.6 in order to obtain high removal efficiency of cadmium ions through ELM system. Alaguraj et al. [13] reported that an increase in removal of Copper was associated with a decrease in the acidity of external feed phase and pH_0 of external feed phase should be maintain in the basic range of 8–10. Based on the experimental results, the optimal pH_0 of external feed phase was chosen to be 11 which produced 95% of removal efficiency of nickel(II) ions by ELM process.

3.4. Effect of initial concentration of nickel(II) in external feed phase (C_0)

The effect of initial concentration of nickel(II) in external feed phase was studied in the range of 10–200 ppm under the experimental conditions of $pH_i = 1$, $pH_0 = 11$, $C_{surfactant}$ = 6 v/v%, $C_{carrier}$ = 2 v/v% at agitation speed of 200 rpm in ELM reactor. The effect of nickel(II) concentration is shown in Fig. 4. The removal efficiency of nickel(II) ions was high when there was a reduction in metal ions concentration in external feed phase. High concentration of nickel(II) ions may decrease significantly the rate of mass transfer due to reduction of internal phase capacity to strip the extracted nickel(II) ions from external feed phase. In other words, the region of interface between external feed phase and liquid membrane phase becomes saturated rapidly with nickel(II) ions. Therefore, the Nickel complex compounds permeate very slowly through the membrane phase and this happens because of mass transfer resistance created by high nickel(II) ion concentration. A maximum removal efficiency of nickel(II) ion of 98% was obtained for 10 ppm of initial concentration of nickel(II) in the external feed phase while a minimum removal efficiency of 55% obtained was obtained for 200 ppm of initial concentration of nickel(II) in the external feed. Study on recovery of copper (II) from wastewater reported similar observations [13]. When the initial concentration of copper ions was very high, the surface of emulsion droplets became saturated very fast with copper ions and the metal-carrier complex compounds found difficulty to diffuse through the membrane phase to release the copper ions into the stripping phase due to mass transfer resistance created by high concentration of copper ions.

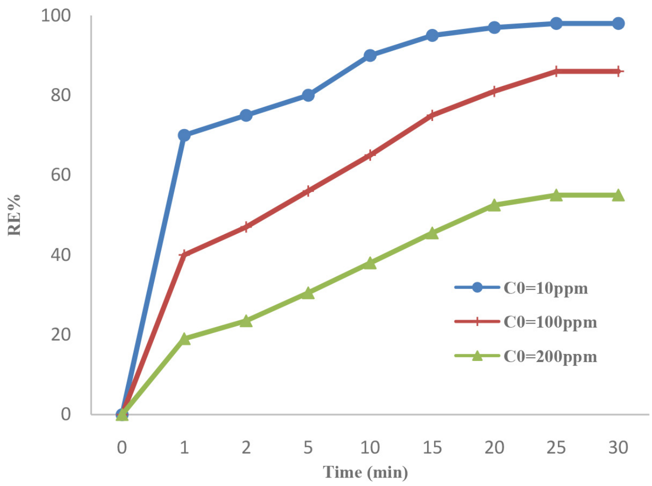

Fig. 4. Effect of initial concentration of Nickel(II) in external feed phase [pHi = 1, $pH_0 = 11$, $C_{surfactant}$ = 6 v/v%, $C_{carrier}$ = 2 v/v%, agitation speed in ELM reactor = 200 rpm].

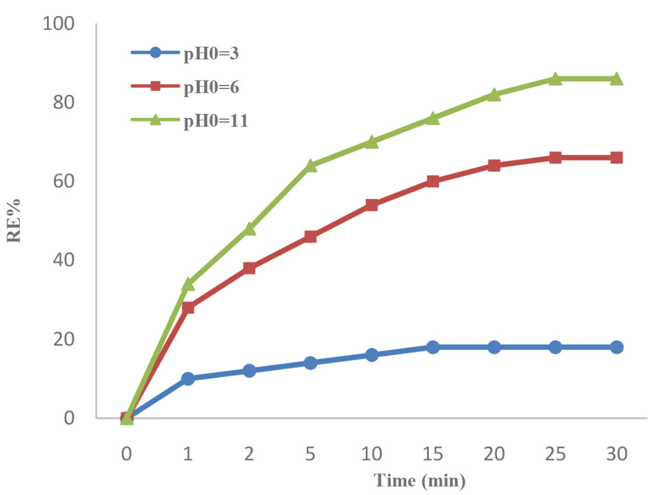

Fig. 3. Effect of pH_0 of external feed phase [pHi = 1, C_0 = 100 ppm, $C_{surfactant}$ = 6 v/v%, $C_{carrier}$ = 2 v/v%, agitation speed in ELM reactor = 200 rpm].

3.5. Effect of surfactant concentration

The most important component in formation of emulsion liquid membrane solution is the surfactant. The critical influence of surfactant (Span 80) concentration of 2 v/v%, 3 v/v% and 6 v/v% on removal efficiency of nickel(II) ions and water solubility in ELM process was examined under the experimental conditions of pHi = 1, $pH_0 = 11$, C_0 = 100 ppm, $C_{carrier}$ = 2 v/v% at agitation speed of 200 rpm in ELM reactor. As shown in Fig. 5, the removal efficiency of nickel(II) increased gradually from 0 to 30 min for three different surfactant concentrations. In addition, it can be clearly seen that the high values of removal efficiency can be obtained by using of low values of surfactant concentrations. The surfactant is concentrating on liquid membrane and external feed interface and reduce surface tension of emulsion droplets and by doing this small droplets size will be obtained and a large area will be available to increase the mass of nickel(II) ions. The minimum removal efficiency of nickel(II) ions that can be obtained in ELM process is 85% when surfactant concentration is 6 v/v%. The increase in surfactant concentration increases the membrane thickness which in turn lead to decrease the diffusion rate of nickel(II)

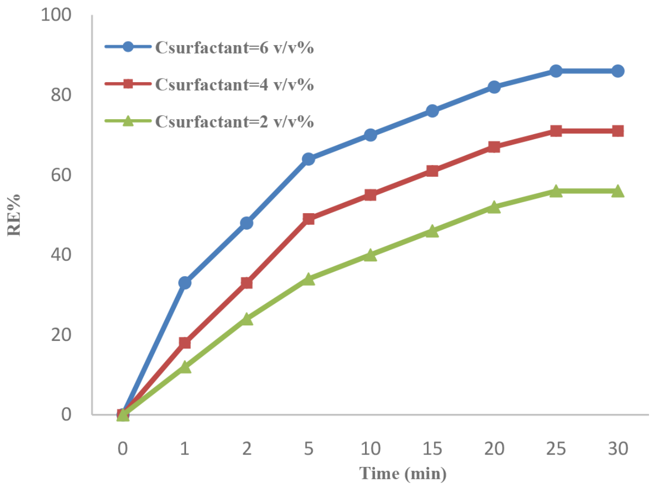

Fig. 5. Effect of surfactant concentration [pHi = 1, pH_0 = 11, C_0 = 100 ppm, $C_{carrier}$ = 2 v/v%, agitation speed in ELM reactor = 200 rpm].

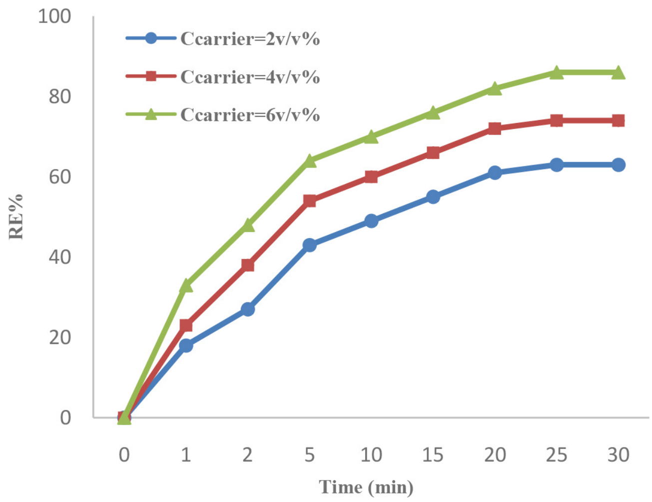

Fig. 6. Effect of carrier concentration [pHi = 1, pH_0 = 11, C_0 = 100 ppm, $C_{surfactant}$ = 2 v/v%, agitation speed in ELM reactor = 200 rpm].

ions in ELM process. Lesser quantities of surfactant will result in membrane weakness while excess surfactant result in higher resistance to diffusion. As a result, the removal efficiency of nickel(II) ions decreases due to lower transport of nickel(II) ions into the membrane phase. That is why the concentration of surfactant should be optimized in ELM process to be at lowest value which is 2 v/v%. 2 v/v% of surfactant concentration give the maximum removal efficiency of 98% of nickel(II) ions. Sabry et al. [11] proved that the increase in surfactant concentration reduces the removal efficiency of lead ions due to mass transfer resistance caused by surfactant film. Moreover, Mortaheb et al. [10] reported that surfactant concentration which was about 3 wt% of the membrane phase was considered as the desired value in separation of cadmium ions by ELM system.

3.6. Effect of carrier concentration

The effectiveness of extraction process is associated to diffusion rate of extracted metal ions through the membrane phase which can be improved by adding carrier into membrane solution. Consequently, the influence of carrier (D2EHPA) concentration of 2 v/v%, 3 v/v% and 6 v/v% on removal efficiency of nickel(II) ions was studied under the experimental conditions of pH_i = 1, pH_0 = 11, C_0 = 100 ppm, $C_{surfactant}$ = 2 v/v at agitation speed of 200 rpm in ELM reactor. It was observed that the removal efficiency of nickel(II) ions is increasing with the time as described in Fig. 6 in all three carrier concentrations. However, a reduction of removal efficiency is associated with an increase in carrier concentration. For example, the minimum removal efficiency of nickel(II) ions obtained in ELM process is 85% when carrier concentration is 6 v/v%. The carrier D2EHPA reacts with nickel(II) ions at the interface of the external feed phase and the membrane phase in order to form carrier-metal complex compounds which can diffuse easily through the membrane. Following that, the metal ions are released into the internal phase of membrane while carriers come back to external feed phase across the membrane phase. Higher quantities of carrier used in membrane formation will lead to increase the membrane thickness which cause a decrease in extraction rate of metal ions. Studies on removal of chromium using sunflower oil as a solvent in ELM process explained the effect of carrier [15]. Also, it was illustrated by Sabry et al. [11] and Chiha et al. [14] that increasing the concentration of carrier promotes the permeation swelling, which in turn lead to dilute the aqueous stripping phase and decreases the efficiency of the process.

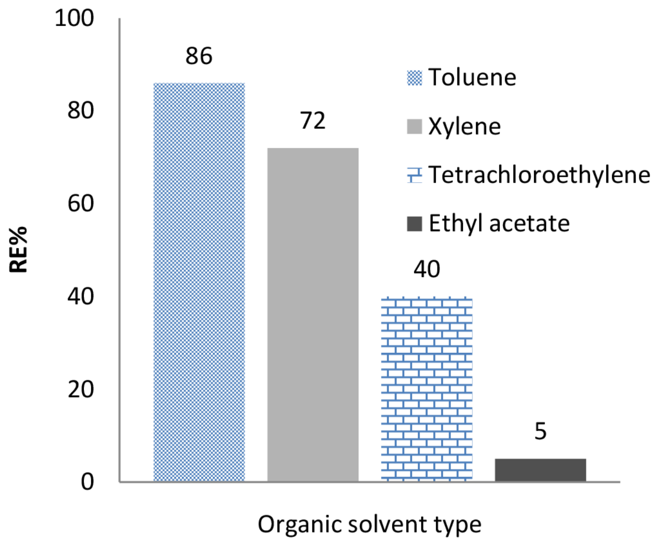

Fig. 7. Effect of type of organic solvent [pHi = 1, pH_0 = 11, C_0 = 100 ppm, $C_{surfactant}$ = 2 v/v%, $C_{carrier}$ = 2 v/v%, agitation speed in ELM reactor = 200 rpm].

3.7. Effect of type of organic solvent

The selection of suitable organic solvent is based on its characteristic including specific gravity, viscosity, flash point, high boiling point and according to their polar nature. The effect of type of organic solvent on removal efficiency was investigated under the experimental conditions of pHi = 1, pH_0 = 11, C_0 = 100 ppm, $C_{surfactant}$ = 2 v/v%, $C_{carrier}$ = 2 v/v% at agitation speed of 200 rpm in ELM reactor. The emulsion solution was prepared by using various types of organic solvents including toluene, xylene, ethyl acetate and tetrachloroethylene. The results in Fig. 7 shows that when toluene was used in preparation of emulsion liquid membrane solution the removal efficiency of nickel(II) ions was 90%. When xylene was used in preparation of emulsion liquid membrane solution the removal efficiency of nickel(II) ions was 73%, while the removal efficiency of nickel(II) ions was about 40% when tetrachloroethylene was used. Ethyl acetate have not be used in preparation of emulsion liquid membrane solution because the removal efficiency of nickel(II) ions was 5%. The organic solvent is observed to influence the interaction patterns in the solution.

4. Conclusion

In this research investigation, application of emulsion liquid membrane to extract the Nickel(II) ions from synthetic solution was studied. The experiments were conducted to obtain the optimum values of operating parameters which gave the best conditions for maximum removal of Nickel(II) ions. pHi of 1 was selected to be the best value which gave 97% of Nickel(II) removal while pH_0 of 11 was selected to be the best value which gave 95% of Nickel(II) removal. 2 v/v% of carrier (D2EHPA) concentration, 2 v/v% of surfactant (SPAN80) and Toluene as the organic solvent are found as optimal choices for better removal of nickel(II).This research has proved the potential of emulsion liquid membrane as a suitable alternative for the removal of nickel.

References

[1] C. Ye ,Y. Sun, X. Pei, J. Sun, Y. Wu, Mass transfer and equilibrium characteristics of defluorination from groundwater by emulsion liquid membrane, J. Chem. Tech. Biotechnol., 92 (2017) 76–82.
[2] N. Othman, R.N.R. Sulaiman, H.A. Rahman, N.F.M. Noah, N. Jusoh, M. Idroas, Simultaneous extraction and enrichment of reactive dye using green emulsion liquid membrane system, Environ. Technol., (2018) 1–9, article online.
[3] I. Aloma, M.A. Martin–Lara, I.L. Rodriguez, G. Blazquez, M. Calero, Removal of Nickel(II) ions from aqueous solutions by biosorption on sugarcane bagasse, J. Taiwan Inst. Chem. E., 43 (2012) 275–281.
[4] M. Cempel, G. Nikel, Nickel: A review of its sources and environmental toxicology, J. Environ. Stud., 15 (2006) 375–382.
[5] N. Rajamohan, Parametric experiments and kinetic studies on the removal of nickel using strong acid cation exchange resin 001 x7, Desal. Water Treat., 56 (2015) 2477–2484.
[6] B. Alyuz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater., 167 (2009) 482–488.
[7] T.T. Teng, M. Soniya, G. Muthu Raman, A. Talebi, Role of emulsion liquid membrane in separation processes. Wastewater Engineering: Advanced Wastewater Treatment Systems, 2014.
[8] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters, J. Environ. Manage., 92 (2011) 407–418.
[9] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents, Bioresour. Technol., 99 (2008) 3935–3948.
[10] H.R. Mortaheb, H. Kosuge, B. Mokhtarani, M.H. Amini, H.R. Banihashemi, Study on removal of cadmium from wastewater by emulsion liquid membrane, J. Hazard. Mater., 165 (2009) 630–636.
[11] R. Sabry, A. Hafez, MaalyKhedr, A. El–Hassanin, Removal of lead by an emulsion liquid membrane, Part I, Desalination, 212 (2007) 165–175.
[12] Y.T. Mohamed, L.M.S. Hussin, H.M.H. Gad, A.A.M. Daifullah, S.A. Abo–El–Enein, Membrane stability and removal of cobalt from waste solution using liquid emulsion membrane, J. Membr. Separ. Technol., 2 (2013) 102–108.
[13] M. Alaguraj, K. Palanivelu, M. Velan, Removal of Cu (II) using emulsion liquid membrane, Int. J. Chem. Tech. Res., 1 (2009) 722–726.
[14] M. Chiha, O. Hamdaoui, A. Fatiha, C. Pétrier, Study on ultrasonically assisted emulsification and recovery of copper (II) from wastewater using an emulsion liquid membrane process, Ultrason. Sonochem., 17 (2010) 318–325.
[15] P. Davoodi–Nasab, A. Rahbar–Kelishami, M. Raji–Asadabadi, Fast and efficient chromium(VI) pertraction with Aliquat 336 in emulsion liquid membrane using sunflower oil as a high potential solvent, Desal. Water Treat., 80 (2017) 234–246.