Synergistic extraction of Cr(VI) from Ni(II) and Co(II) by flat sheet supported liquid membranes using TIOA and TBP as carriers

Volkan Eyupoglu[1*], Ahmet Surucu[2], Ahmet Kunduracioglu[3]

[1]*Cankiri Karatekin University, Department of Chemistry, Faculty of Science, 18100 Cankırı, Turkey*
[2]*Pamukkale University, Department of Chemistry, Faculty of Education, 20017, Denizli-Turkey*
[3]*Pamukkale University, Deparment of organic agriculture, Tavas Vacational High School, 20017, Denizli-Turkey*
[*]*Corresponding author: e-mail: volkan@karatekin.edu.tr*

In present study, the synergistic separation of Cr(VI) has been investigated from synthetic acidic solution containing Cr(VI), Co(II) and Ni(II) by flat sheet supported liquid membrane (FSSLM) technique using triisooctylamine (TIOA) and tri-n-butyl phosphate (TBP) as carriers. The main goal of the study was based in the exploring of the synergistic effect of TBP on selective extraction of Cr(VI) in presence of Co(II) and Ni(II) ions. The various parameters related with membrane and aqueous solution properties were studied to identify the optimum extraction and stripping conditions of the Cr(VI) through FSSLM. In the optimum conditions, initial mass flux (J_0) and separation factors ($\beta_{Cr/Co}$ and $\beta_{Cr/Ni}$) were obtained as 1.49 x 10^{-05} (kg/m^{2}s), 382.2 and 725.3 respectively from aqueous H$_2$SO$_4$ media through Celgard 2500 (Celgard Inc., USA) polymer support. As a result, the considerable synergistic influence on selective transport of Cr(VI) through FSSLM using TIOA and TBP as carriers has been identified.

Keywords: flat sheet supported liquid membrane, selective extraction of Cr(VI), TIOA, TBP, synergistic extraction, facilitated mass transfer.

INTRODUCTION

The removal of heavy metals from industrial wastewaters and the other effluents have been accepted as an important issue by scientists due to increasing heavy metal-based industries and environmental sensitivities at last two decades. Discharging of industrial wastewaters to the surface or underground water sources directly affects the environment and public health[1]. Chromium compounds have been widely used in electroplating, metal finishing, leather tanning, photography, dyes, textile industries and in so many different industries. The toxic chromium effluents is discharged as a by-product of these industries containing high concentration of Cr(VI). Chromium is generally found in two oxidation states as trivalent and hexavalent in aqueous solutions. Cr(VI) is generally known as more toxic species of the chromium compared with Cr(III) species. Cr(III) is an essential chromium species for the mammals in glucose, fat or protein metabolism[2–4]. On the other hand, some scientific studies noted that at higher concentration of Cr(III) may adversely effect the habitats[5–6].

Anionic Cr (VI) species, which are HCrO$_4^-$, CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, are known as bioaccumulative and mutagenic due to their high mobility across cell membrane and their oxidizing potential on the biological molecules and structures[7]. Therefore, especially Cr(VI) must be eliminated from environmental sources to prevent its harmful effects on ecosystem. The improvement of fast, economic and effective techniques for removal of Cr(VI) should be applied to the industries that use high amounts of chromium, because of the increase in industrial-based environmental problems around the World[8–10].

Cr (VI), Ni (II), Zn (II), Cu (II), Hg(II), Pb(II), As(VI) and Cd (II) are known as main heavy metal contaminants encountered in industrial wastewater. Because liquid effluents are converted to the sludge before discharging to the environment, industrial based solid heavy metal waste discharging is generally higher than liquid one. Therefore, hazardous heavy metal contents of liquid effluents should be removed or reduced as much as possible to decrease hazardous effect of the wastes before precipitation of the heavy metal content. On the other hand, precious metals such as Au, Pt, Ag, Ni, Co and etc. should be selectively recovered from the main wastewater streams to restore them to economy [11–12]. Chromium, nickel and cobalt are frequently used with together in many different industry branches like as electroplating, metal finishing, dyes and etc. Cobalt and nickel are known as more precious metal compared with chromium. So, removal of chromium from industrial wastewater containing cobalt and nickel seems to be more crucial step before separation of cobalt and nickel from eachother[13].

Many studies in scientific literature have been mentioned that different extractant types have been employed for Cr(VI) extraction from different sources up to day. The amine derivatives such as trioctylamine(TOA), tri--n-isooctylamine (TIOA) and tribenzylamine (TBA) and etc. which have long or short chain aliphatic or aromatic amines containg a basic nitrogen atom, that they have capable of forming amine salts with anionic species in the source phase, have been used for this purposes[14–16]. The other category of extractants for Cr(VI) extraction has been well known as neutral or solvating extractants like as tributyl phosphate (TBP) and triocytlphosphine oxide (TOPO), which have capable of the extraction of neutral species in the source phase[6, 17–18]. Synergistic extraction processes have been gained an importance against to single extractant based processes due to their higher extraction efficiencies and fast extraction and stripping kinetic. Therefore, the combination of TIOA and TBP has been investigated to selectively extract Cr(VI) from acidic solution. Identifying of the exact rate of extractants are well known as important step in synergistic extraction process to make the process more efficient and more economic. Therefore, the scientists have spent a lot of effort to investigate effective synergistic extractant couples and their effective rate in separation processes[19].

The several methods to recover heavy metals from aqueous solutions have been already reported in the scientific literature. Solvent extraction (SX) has been widely used as effective technique which is characterized by higher metal selectivity and high purity products[20]. But more organic solvent consumption, higher set-up cost, two step operation (extraction and stripping) and toxic substance discharging properties of SX processes have been directed the scientists to find more economic and ecologic process. MBPs combine the extraction and stripping process in one step operation. These processes don't need to so much chemical, organic solvent and energy. Liquid membrane (LM)'s processes were explored by Li et al.[21] at the end of nineteenth century as an alternative process for selective extraction of metals among membrane-based processes (MBPs)[22–23]. Supported liquid membrane (SLM) technique has been known as flexible liquid membrane technique that many different shapes of supports and support materials can be used in this process among the MBPs. Some advantages of SLMs over traditional separation techniques are the lower requirement of the organic phase, capital and operating costs, energy consumption and higher mass transfer coefficients in one step operation and etc.[24–25]

In the present study, the selective synergistic extraction of Cr(VI) from acidic aqueous solutions containing Co(II) and Ni(II) was carried out by FSSLMs using TIOA and TBP as carriers. The effect of various experimental parameters on the Cr(VI) extraction such as pH, diluent type, stripping phase reagent type and concentration, mixing speed, extractant and synergistic extractant concentrations etc. have been studied and the optimum extraction and stripping conditions have been determined. Membrane permeabilities and initial mass flux values were calculated by monitoring extracted Cr(VI), Ni(II) and Co(II) concentrations on the basis of mg/L using FAAS (Shimadzu AA-6701GF spectrophotometer) in the feed and stripping phase as a function of time. Permeation coefficient (P) and initial mass fluxes (J_0) were calculated from obtained experimental data using Eq. 1 and Eq.2 respectively.

EXPERIMENTAL

Chemicals

$K_2Cr_2O_7$, $CoCl_2 6H_2O$, $NiCl_2 6H_2O$, NaOH, and H_2SO_4 were purchased from Reidel-De Haen (Seelze, Germany) and all of the reagents was analytical grade. TIOA and TBP were purchased from MERCK (Darmstadt, Germany) and they were used directly without applying any purificaton process. Diluents; chloroform, carbon tetrachloride, n-decanol, toluen were purchased from various chemical reagent suppliers like as Reidel-De Haen and Fluka (Seelze, Germany and St., Louis, USA respectively). Commercially available polypyroplene flat sheet membranes were used in the transport experment of Cr(VI) and were provided free of charge from Celgard Inc. (Celgard Inc., USA). All aqueous metal solutions were prapared by dissolving their salts with ultra pure deioised water (MilliQ ultra pure water).

Analytical methods

Membrane permeability were determined by monitoring Cr(VI), Ni(II) and Co(II) concentration by FAAS (Shimadzu AA-6701GF spectrophotometer) in the feed and stripping phase as a function of time. Three squential measurements were performed to determine Cr(VI) Co(II) and Ni(II) concentrations. Resuls were found to be reproducible within ±3% confidence interval.

Flat-sheet supported liquid membrane preparation and measurements

Competitive transport of Cr(VI), Ni(II) and Co(II) ions were studied using a two-compartment permeation cell,which is made from glass. Each compartments were separated with FSSLM, which has 19.63 cm² surface area (A), as schematically shown both permeation test cell and transport mechanism on Figure 1. The liquid membranes containing TIOA and TBP in organic diluent were allowed to impregnate into the pores of polymer supports, microporous hydrophobic polypropylene Celgard 2500 (25 μm thick, 0.209 x 0.054 μm pore size and 55% porosity), in all of the experiments for 12 h. After that, the polymer support whose pores filled with liquid membrane, was removed from liquid membrane solution and was placed into the permiation cell.
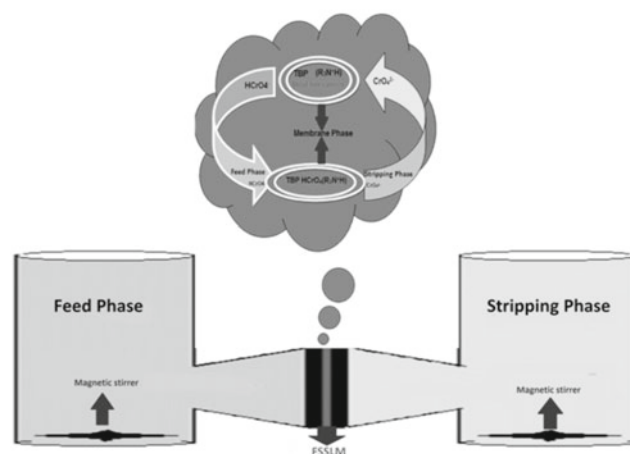

Figure 1. The graphical illustration of permeation cell and transport mechanism of Cr(VI) throughout FSSLM

Acidic feed solutions containing Cr(VI), Ni(II) and Co(II) ions were prepared by dissolution of metal salts. Acid concentration of feed solution was adjusted by adding desired volume of the concentrated acid. NaOH solution was used as stripping phase and was prepared by dilution of solid NaOH pellets in ultra pure water. The feed and stripping phases were mixed by a magnetic stirrer at the desired mixing speeds at the ambient temperature to avoid concentration polarisation conditions at the membrane interfaces and in the bulk of the solutions. 1.0 mL of samples were periodically taken from both feed and stripping phases during the transport experiments. Flame atomic absorption spectroscopy (FAAS) (Shimadzu 6701GF, Japan) were used for determination of trace amount of Cr(VI), Ni(II) and Co(II) after dilution of samples with ultra pure water. pH measurements were performed with a Schott model CG840 pH meter (Germany). Membrane permeabilities and initial mass fluxes for each of experiments were determined by monitoring Cr(VI), Ni(II) and Co(II) concentrations in

the feed phase as a function of time. The permeation coefficient (P) and initial mass flux (J_0) was calculated with using Eq. 1 and Eq. 2 respectively;

$$ln \frac{c_f}{c_0} = P \frac{A\varepsilon}{V_f} t \tag{1}$$

$$J_0 = \frac{dc_f}{dt} \frac{V_f}{A\varepsilon} \tag{2}$$

where: A is the membrane area (cm^2), V_f is the volume of the feed phase (cm^3), ε is porosity of the polymer membranes, C_f and C_0 are the concentrations of chromium in the feed phase at elapsed time and time zero, respectively (mg/L) and t elapsed time (h).
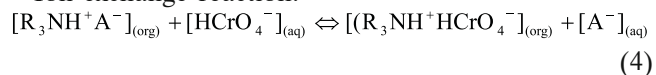
Permeation model of Cr(VI) in FSSLM

The main anionic species of Cr(VI) in the aqueous solutions have been known as $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, $Cr_2O_7^{2-}$. The total amount of Cr(VI) and the pH dictating particular chromium species will predominate in the aqueous phase. When pH is lower than 0.5, chromic acid ($H_2Cr_2O_7$) is predominant. On the other hand, in the moderate acidic pH, $Cr_2O_7^{2-}$ anions are converted into $HCrO_4^-$ anions in acidic aqueous solution, while the total Cr(VI) concentration is lower than $(1.26 - 1.74) \times 10^{-2}$ mol/L [14]. In addition that, the total Cr(VI) concentration is higher than this critical concentration values, Cr(VI) is generally found as CrO_4^{2-} anions in slightly acidic solution while $Cr_2O_7^{2-}$ anions are dominate in the same solution. In this studies, Cr(VI) was extracted using TBP and TIOA in the form of $HCrO_4^-$ [1, 26].

TIOA is known as a water insoluble extractant containing long chain alkyl group. It can easily extract the anionic species forming oil-soluble adducts at acidic pH. Nitrogen atom in TIOA are more stable in terms of charge disturbution due to long chain alkyl groups. Therefore basicity of TIOA makes it more stable compared with the other ammonia analaoques. The general extraction reactions of Cr(VI) with TIOA (R_3N) can be given in two steps that first step is protonation and second step is ion exchange [26].

Protonation reaction:

$$[R_3N]_{(org)} + [HA]_{(aq)} \Leftrightarrow [R_3NH^+A^-]_{(org)} \tag{3}$$

Ion exchange reaction:

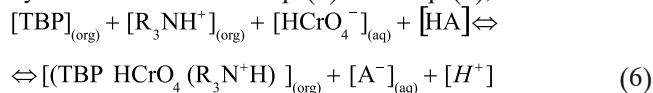$$[R_3NH^+A^-]_{(org)} + [HCrO_4^-]_{(aq)} \Leftrightarrow [(R_3NH^+HCrO_4^-]_{(org)} + [A^-]_{(aq)} \tag{4}$$

Where: R_3N is TIOA, A is anion of the mineral acid. According to Eq. 4, protonated $HCrO_4^-$ exchanges with A^- located in $R_3NH^+A^-$. This reaction can be carried out as a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase. According to reactions above, Cr(VI) in the feed solution should be kept in mild acidic region, whereas the stripping phase should be kept in strong basic region to fastly neutralize the protonised TIOA (R_3NH^+) [26].

On the other hand, TBP is a solvating extractant and its main role was determined as replacing the coordinated water molecules around the adduct of $R_3NH^+HCrO_4^-$ in present extraction process, Thus, transport affinity and equilibrium constant of Nerst between organic membrane phase and aqueous feed phase will be increased with using TBP due to increasing organic character of $R_3NH^+HCrO_4^-$. According to Nerst distribution law, it

can be estimated that the extraction of anionic chromium species should be increased by using TBP in the membrane phase. The possible extraction reaction between TBP and $HCrO_4^-$ can be written in following equation [14].
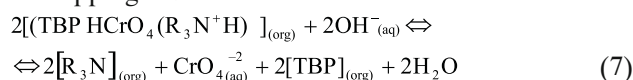
$$[TBP]_{(org)} + [HCrO_4^-]_{(aq)} + [HA] \Leftrightarrow [(TBPH_2CrO_4]_{(org)} + [A^-]_{(aq)} \tag{5}$$

The synergistic extraction of Cr(VI) using TBP and TIOA with together can be written as Eq. (6) below by a combination of Eq. (4) and Eq. (5);

$$[TBP]_{(org)} + [R_3NH^+]_{(org)} + [HCrO_4^-]_{(aq)} + [HA] \Leftrightarrow$$
$$\Leftrightarrow [(TBP \; HCrO_4 \; (R_3N^+H)]_{(org)} + [A^-]_{(aq)} + [H^+] \tag{6}$$

The adduct $[TBP \; HCrO_4(R_3N^+H)]_{org}$ giving above diffuses through FSSLM up to it reaches to membrane and striping phase interfaces. The following reaction can be written to summarize the decomposition of $[(TBP \; HCrO_4 \; (R_3N^+H)]_{(org)}$ complex in membrane-stripping phase interface in presence of OH^-.

Stripping side reaction:

$$2[(TBP \; HCrO_4(R_3N^+H)]_{(org)} + 2OH^-_{(aq)} \Leftrightarrow$$
$$\Leftrightarrow 2[R_3N]_{(org)} + CrO_4^{-2}_{(aq)} + 2[TBP]_{(org)} + 2H_2O \tag{7}$$

RESULTS AND DISCUSSIONS

Effect of diluent

In this studies, various diluents such as xylene, toluene, chloroform, dichloromethane were investigated the maximum initial mass flux of Cr(VI) and using TIOA-TBP synergistic extraction system through FSSLM. Initial mass flux of Cr(VI), Ni(II) and Co(II) are shown in Figure 2. The diluents and their physicochemical properties directly effects the ion transport, because the membrane performance and the stability in LM process is as same as conventional solvent extraction process [28–30]. It can be seen from the Figure 2, the best initial mass flux of Cr(VI) was obtained as $2.48 \cdot 10^{-6}$ when chloroform and dichloromethane were used. It has been suggested that the polarity of diluents are the most decisive factor to determine effective diluent while preparing LM composition. On the other hand, membrane stability and rapid transport is the major factor to be made in choosing a diluents [31]. Some physicochemical properties of the diluents were given in Table 1. It clearly appears from Table 1 that approximately same initial mass flux values were obtained in Cr(VI) transport using organic diluents having similar molecular structure and similar physicochemical properties like as viscosity, dielectric constant and density. In addition, chloroform and dichloromethane exhibits some chemical interaction with polypropylene. But they do not solve the polypropylene at ambient temperature. This interactions leads to the expansion of the pores. So, TIOA-TBP-Cr(VI) adducts can be easily move into the pores of polymer membrane support.

According to obtained results that the best Cr(VI) initial mass flux was obtained with chloroform within 8 h for TIOA-TBP synergistic extraction system due to its lower viscosity and dielectic constant and well consistency between polypropylene and chloroform. Whereas, slightly lower transport values were observed for Cr(VI) with using the other diluents compared with chloroform.

Table 1. Dielectric constants, viscosities and densities of diluents at 20°C [32]

| Diluent	Dielectric constant [–]	Viscosity [mPa.s]	Density [kg/m³]	Aromatics [%]
Toluene	2.38	0.560	865	100
Xylene	2.36	0.650	860	100
Dichloromethane	8.93	0.413	1325	–
Chloroform	4.81	0.117	1492	–
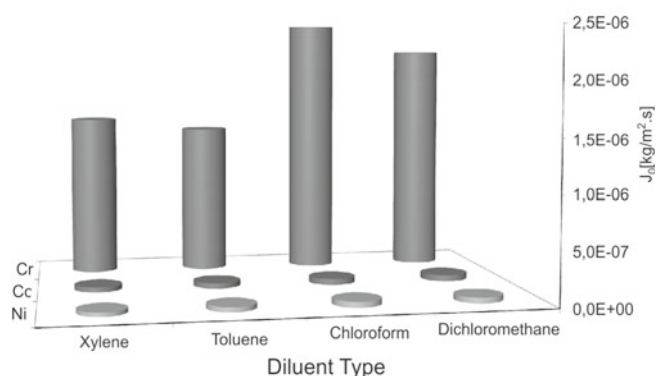
Figure 2. Effect of diluent on initial mass flux of Cr(VI): Extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type and concentration: 0.5 mol/L H_2SO_4; feed phase metal concentration for Cr(VI)/Co(II)/Ni(II); 200 mg/L; mixing speed: 1200 rpm; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

Figure 3. Effect of mixing speed on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type and concentration: 0.5 mol/L H_2SO_4; feed phase metal concentration for Cr(VI)/Co(II)/Ni(II): 200 mg/L; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

Effect of mixing speed in feed and stripping phases

The effect of mixing speed in the feed and stripping phases were studied in the range of 600–1500 rpm to find optimal mixing speed that allows effective permeation of Cr(VI) through the FSSLM. The effect of mixing speed on initial mass flux throughout the supported liquid membrane for Cr(VI), Ni(II) and Co(II) were studied experimentally and the results were shown in Figure 3. The effect of mixing speed in feed and stripping phase on initial mass flux of Cr(VI) were determined that they resemble each other. Therefore, mixing speed in both sides was tested with together experimentally throughout the studies. Initial mass flux was increased with increasing mixing speed from 600 rpm to 1200 rpm. Further increasing of mixing speed from 1200 rpm, declining of initial mass flux was observed. This observation indicated that the aqueous boundary layer thickness betwen membrane phase and aqueous phases is diminished continuously with increasing mixing speed and the boundary layer thickness was determined as optimum in 1200 rpm. It can be concluded that stable membrane and feed and stripping phase matching are provided in optimal boundary layer thickness[33]. The decrease in initial mass flux with further increase in mixing speed above 1200 rpm can be explained with high turbulence formation in the interfaces. It causes displacement of carrier from the membrane pores. Therefore, 1200 rpm was determined as optimum mixing speed, which has reached higher initial mass flux value as 2.48×10^{-6} within 8 h to provide both stable and sustainable membrane system in our experimental conditions.

Effect of acid type and concentration in the feed phase

Acid concentration has been accepted as a base parameter for the selective separation of metals in SX processes and MBPs. In present work, acid concentration of feed solution was studied in two steps, which are the
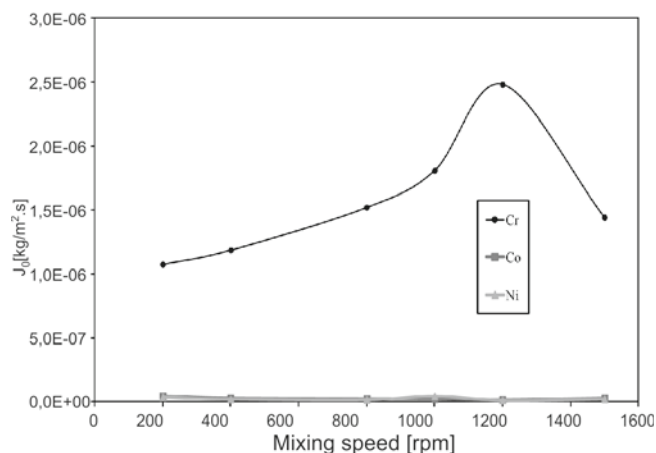
acid type and acid concentration, to provide selective and synergic extraction of Cr(VI) from Co(II) and Ni(II) using TIOA and TBP as carriers using FSSLM. The acid concentration of the feed solution was adjusted by adding desired volume of concentrated H_2SO_4. The selection of mineral acid type in feed solution was tested with using HCl, HNO_3 and H_2SO_4. In present studies, we were used basic and neutral extractants with together. Therefore, the same acidic conditions in the feed phase should be suitable for the working of the extractants[14]. All results were showed in Figure 4 and Figure 5. As an initial study to determine the suitable acid type, same concentration of the acids (0.5 mol/L) were investigated to obtain the optimum initial mass flux of Cr(VI) in our experimental conditions. The higher initial mass flux for Cr(VI) were obtained for H_2SO_4 with higher selectivity. Initial mass flux values of Cr(VI) for HCl and H_2SO_4 are approximately close to eachother. But HNO_3 is so lower than they. This result can be explained with the formation of anionic and neutral complexes of metals in chloride and sluphate media that these metal complexes occurs the adduct with TIOA and TBP in the FSSLM and feed phase interphase. Some anionic or neutral Co(II) species like as $CoCl_4^{2-}$, $CoCl_3^{-}$, $CoCl_2$ can be occurs in HCl media, at feed phase and they can be extracted by both TIOA and TBP from feed phase. This extraction adversly effects the selectivity of Cr(VI) over Co(II) through FSSLM process. In addition, HNO_3 is more oxidative than the others. This properties of HNO_3 causes the formation of more oxidative and low extractable species like as $H_2Cr_2O_7$. So, the extraction percentage of Cr(VI) when we used different acids can be ordered as $H_2SO_4 > HCl > HNO_3$.

On the other hand, effect of acid concentration was conducted using H_2SO_4 at the range of 0.1–1.0 mol/L.
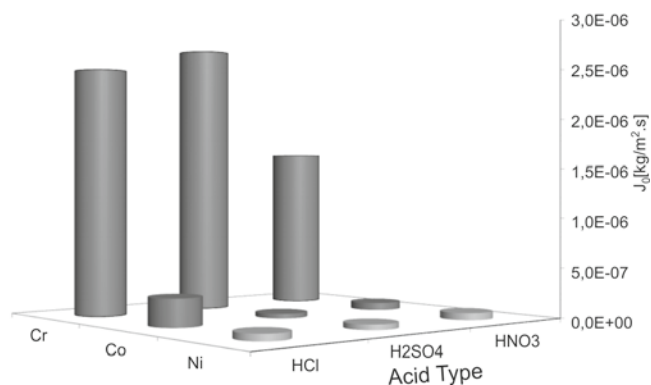
Figure 4. Effect of acid type in feed solution on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid concentration: 0.5 mol/L; metal concentration of feed phase for Cr(VI)/Co(II)/Ni(II): 200 mg/L; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

The acid concentration on initial mass flux of Cr(VI) were shown in Figure 5. According to the results, the feed solution containing 0.5 mol/L H_2SO_4 has higher initial mass flux value. The Figure 5. indicates that initial mass flux of Cr(VI) moderately increased with increase in acid concentration in the range of 0.1–0.5 mol/L. Cr(VI) transport was moderately decreased at the higher acid concentrations in the range of 0.5–1.0 mol/L. Actually the inital mass flux of Cr(VI) increases with the increase in proton concentration up to a limit of 0.5 mol/L. Many scientific studies about Cr(VI) extraction were mentioned that extraction percentage is directly related to the fractions of $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the donor phase with increasing or decreasing of pH. Similar results were obtained by other scientists[1, 10, 14–15, 19, 26]. These species may not ionise completely at higher acid concentration to form an adduct with TIOA and TBP. The extraction percentage and initial mass flux values was obtained as high within 8 h using 0.5 mol/L H_2SO_4 and it was determined as an optimum acid type and concentration.

Effect of stripping reagent type and concentration

Combining the extraction and the stripping operations is well-known as crucial properties of the liquid membranes. In scope of this properties, selection of appropriate stripping reagent and its concentration plays effective role in transport studies in all of MBPs. The effect of stripping reagent type for synergistic extraction of Cr(VI) using TIOA and TBP system were tested for 0.5 mol/L of Na_2CO_3, KOH and NaOH. The results were shown in Figure 6. The stripping mechanism of Cr(VI) depends on Eq. 7. According to Eq. 7, $[(TBP\ HCrO_4(R_3N^+)H]_{(org)}$ complexes were decomposed in the stripping phase and the membrane phase interface by intervention of basic aqueous solutions. For this purposes, basic stripping reagents were investigated as aqueous stripping phase[34]. NaOH was determined as the best stripping reagent compared with Na_2CO_3, KOH. Same concentration of the other stripping reagents were not found as effective as NaOH because of their low activities in lower concentrations. According to Figure 6 NaOH was determined as best initial stripping reagent in lower
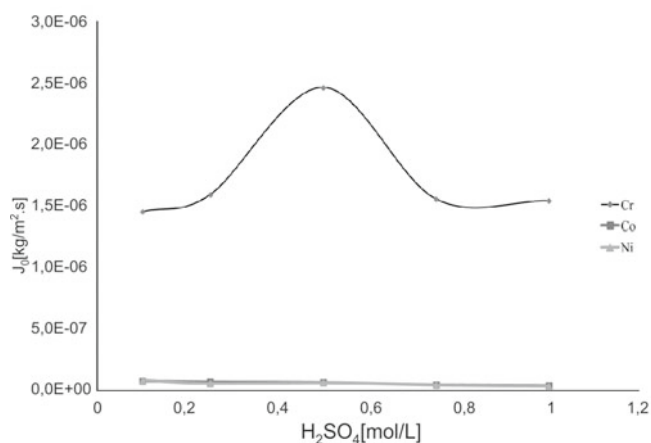

Figure 5. Effect of acid concentration in feed solution on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type: H_2SO_4; metal concentration of feed phase for Cr(VI)/Co(II)/Ni(II): 200 mg/L; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500
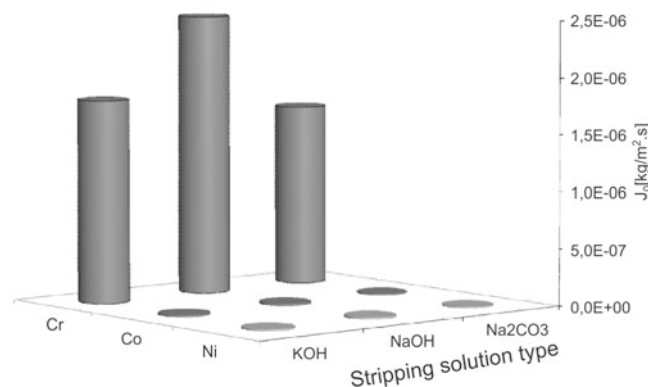

Figure 6. Effect of stripping agent type on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type: 0.5 mol/L H_2SO_4; metal concentration of feed phase for Cr(VI)/Co(II)/Ni(II): 200 mg/L; stripping solution concentration: 1.0 mol/L; membrane support: Celgard 2500

lower concentration and its initial mass flux value was obtained as 2.36 x 10^{-06}.

The another experimental set-up was conducted to determine the effective concentration of NaOH in stripping phase. Fort his purpose, different concentrations of NaOH was prepared in the range of 0.5–4.0 mol/L to experimentally investigate suitable stripping reagent concentration. All results were shown in Figure 7. According to the results 1.0 mol/L NaOH was determined as the best stripping reagent concentration. In this concentration, initial mass flux value was obtained as 2.48 x 10^{-06} within 8 h. On the other hand, the figure clearly indicates that with increase in molar concentration of NaOH, initial mass flux value increases and it tends to reach a maximum at 1.0 mol/L concentration of NaOH. The saturation of the driving force for diffusion throughout the FSSLM causes to increase the adduct of $[(TBP\ HCrO_4(R_3N^+)H]_{(org)}$ in stripping phase-FSSLM interface. On the other hand, increase in stripping solution viscosity with increasing NaOH concentration leads to decrease in inital mass flux
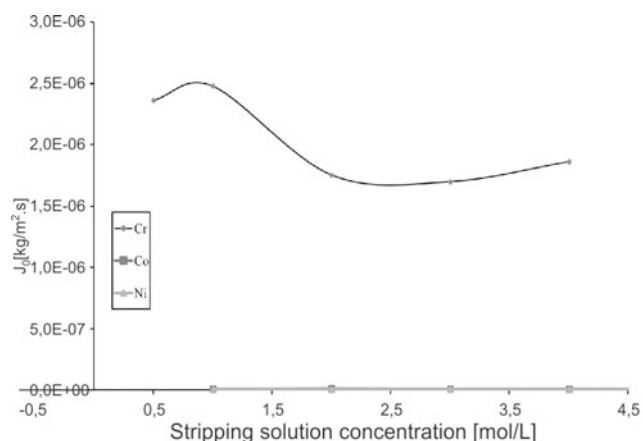
Figure 7. Effect of stripping agent concentration on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type: 0.5 mol/L H$_2$SO$_4$; metal concentration of feed phase for Cr(VI)/Co(II)/Ni(II): 200 mg/L; stripping solution type: NaOH; membrane support: Celgard 2500
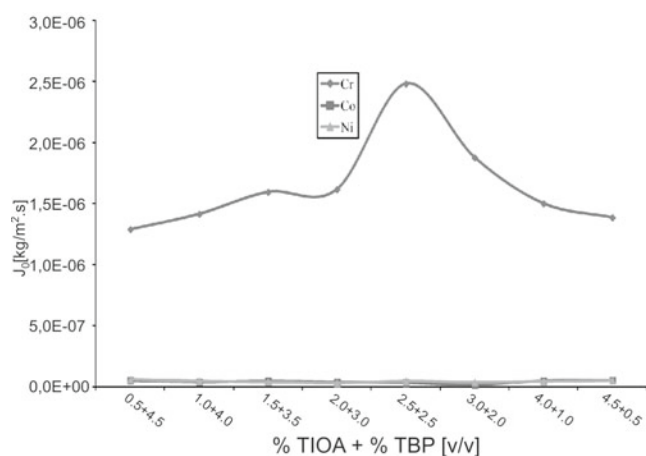

Figure 8. Effect of TIOA and TBP concentration in FSSLM on initial mass flux of Cr(VI): Diluent (Chloroform): 95% v/v; feed phase acid type and concentration: 0.5 mol/L H$_2$SO$_4$; feed phase metal concentration for Cr(VI)/Co(II)/Ni(II); 200 mg/L; mixing speed: 1200 rpm; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

of Cr(VI) due to inefficient interacts of OH$^-$ ions with adduct on the membrane surface[35].

Effect of TIOA and TBP concentration in FSSLM

The effect of TIOA and TBP in the membrane phase on initial mass flux of Cr(VI) were studied in different volume ratio of TIOA and TBP. Liquid membrane phase consisted of 9.5 mL organic solvent and 0.5 mL extractant mixture. When volume percentage of TIOA was decreased, volume percentage of TBP was increased. Thus, we tried to obtain a research opportunities to investigate all volume percentages of TIOA and TBP on the Cr(VI) extraction. The results were shown in Figure 8. According to the results, it was observed that initial mass fluxes of Cr(VI) were increased from 1.29 x 10^{-06} to 2.48 x 10^{-06} kg/m^2 · s within 8 h when used (4.5% TIOA + 0.5% TBP) and (2.5% TIOA + 2.5% TBP) of extractant mixtures respectively. Initial mass flux of Cr(VI) was decreased up to 1.38 x 10^{-06} kg/m^2 within 8 h, when used (0.5% TIOA + 4.5% TBP) as extractant mixture. These results clearly indicate that Cr(VI) extraction abilities of TBP is higher than TIOA but they almost close eachother in present experimental conditions. Same results were reported in the other scientific studies[36–37]. Optimum TIOA and TBP concentration for Cr(VI) extraction was determined in 2.5% v/v TIOA and 2.5% v/v TBP. However, decreasing initial mass flux of Cr(VI) throughout FSSLM in higher TIOA percentage can be explained in terms of the increase in carrier viscosity in the membrane phase due to increasing membrane resistance at higher TIOA percentages[38].

We have used tributyl phosphate (TBP) as a synergist to reach maximum inital mass flux in this study. Therefore, it could be understood that the extraction efficiency was increased up to a limit of a volüme percentage balance between TIOA and TBP. In addition, TBP behaves as both a synergist and a modifier in membrane phase that it prevents third phase formation in FSSLM. Further decrease in TBP percentage from optimum percentage of TIAO and TBP, initial mass flux of Cr(VI) was decreased again due to precipitation of [(TBP HCrO$_4$(R$_3$N$^+$)H]$_{(org)}$

on surface of FSSLM that it can be observed with naked eye. There are many synergistic extraction studies in scientific literature to improve effective process for metal separation, recovery or removal using amine and solvating extractants together[6, 37–40]. According to these studies, adduct formation between the TIOA and TBP was represented in Eq. 6 that this reaction could be also formed in the FSSLM. According to Marcus and Kertes[41], the nature of the extracted adduct in presence of combined extractant can be expected to be [(TBP HCrO$_4$(R$_3$N$^+$)H]$_{(org)}$. On the other hand, TBP acts as a Lewis base and replaces with the coordinated water molecules of the adduct [(TBP HCrO$_4$(R$_3$N$^+$)H]$_{(org)}$ in highly acidic medium. The replacement of TBP with coordinated water molecules and TBP is responsible for the enhanced extraction into the organic phase because of enhancing organic phase affinity and organic character[39].

Optimum conditions

The optimum conditions were obtained with testing of the parameters. The effective variables were determined as a results of the experiments. The optimum conditions for selective extraction of Cr(VI) from aqueous solutions containing Co(II) and Ni(II) and they were shown in Table 2.

The effect of metal concentration in the feed solution was investigated at the optimum conditions and the results were presented in Figure 9. As seen Cr (VI) concentration in the feed solution was studied at the range of 100–1500 mg/L. The selective extraction of Cr(VI) in the acidic feed solution was achieved for 100 mg/L

Table 2. Optimum Conditions for selective extraction of Cr(VI)

Parameter	Value
Diluent	Chloroform
Acid type and concentration of feed solution	0.5 mol/L H$_2$SO$_4$
Stripping reaget type and concentration	1.0 mol/L NaOH
Mixing speed	1200 rpm
TIOA and TBP concentration	2.5% v/v and 2.5 v/v
Polymer support	Celgard 2500(ε = 0.55; Φ = 0.29 x 0.054 µm; δ = 25 µm)

of Cr(VI) solution as >99.9% within 6 h, for 200 mg/L of Cr(VI) solution as >99.9% within 7 h, for 500 mg/L of Cr(VI) solution as 98.2% within 8 h, for 750 mg/L of Cr(VI) solution as 95.0% within 8 h, for 1000 mg/L of Cr(VI) solution as 93.4% within 8 h, for 1500 mg/L of Cr(VI) solution as 89.2% within 8 h respectively. It can be inferred from the results that higher percentage extraction values were obtained in the optimum conditions even concentrated acidic metal solutions due to optimized driving force throughout the membrane. In addition to these discussions, it can be inferred that the improved optimum conditions for Cr(VI) transport can be use to removal of Cr(VI) from industrial and the municipal effluents, containing concentrated and diluted Cr(VI) species.
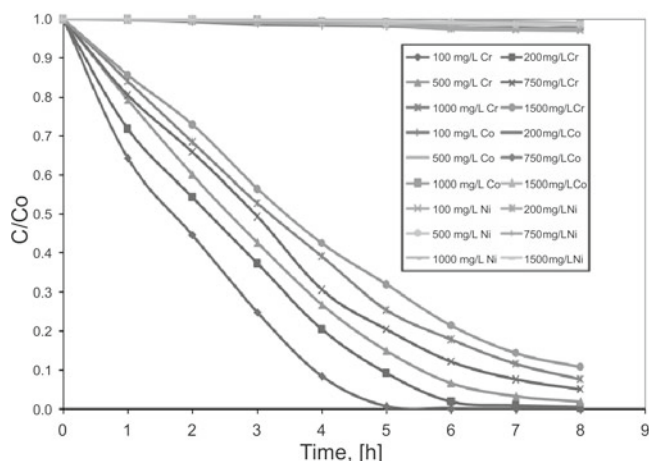

Figure 9. Effect of optimum conditions on percent extraction of Cr(VI): Diluent (Chloroform): 95% w/w; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type and concentration: 0.5 mol/L H₂SO₄; mixing speed: 1200 rpm; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

The stability and reusability test of present process for selective extraction of Cr(VI) was additionaly performed with a set of experiment and the obtained results were given in Figure 10. The experiment was conducted in optimum conditions using 2000 mg/L of Cr(VI), Co(II) and Ni(II) feed solution by taking samples at predetermined time intervals for 96 h. As seen from the figure that the stability of FSSLM was protected for 72 h. After that time, a little degradations were observed in membrane stability, because the balance of chemical potential between feed and stripping phases were broken due to the termination of Cr(VI) transport. It can be inferred from the results that accumulation of adduct [(TBP HCrO₄(R₃N⁺)H]₍ₒᵣg₎ in the FSSLM may be back-extracted into the feed phase. This phenomenon was verified by increase in Cr(VI) concentrations in the feed phase. In addition to stability test, reusability was investigated with used membrane, which was used in long term operation, to identify the membrane stability. The result of this examination was shown in Figure 10. According to the results, a little changes were identified in Cr(VI) extraction and stripping efficiencies when used membrane was re-used. Especially sixty hours later, a significant decrease have been observed in the extraction and the stripping efficiencies compared with the extraction and stripping efficiencies of first used membrane. Therefore,

reusability of FSSLM has been revealed as possible with small disadvantage encountered in stripping prosess at the end of work cycle during eight days.
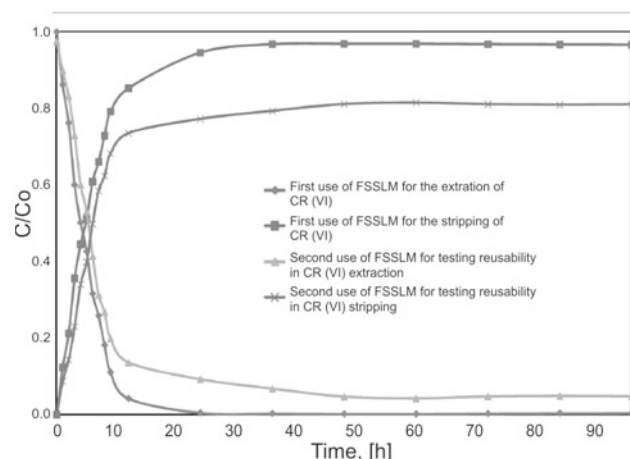

Figure 10. The stability test of FSSLM in the optimum conditions; Cr(VI)/Co(II)/Ni(II): 2000 mg/L, Diluent (Chloroform): 95% w/w; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type and concentration: 0.5 mol/L H₂SO₄; mixing speed: 1200 rpm; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

Membrane selectivity

The separation factors of Cr(VI) over Ni(II) and Co(II), $\beta_{Cr/Co}$, $\beta_{Cr/Ni}$ are given respectively according to Eq. (8), based on initial feed concentration and stripped concentration in the optimum conditions. All of the separation factors were tabulated in Table 3. According to Table 3, the higher separation factors was obtained for Cr(VI) over Co(II) and Ni(II) ($\beta_{Cr/Co}$ and $\beta_{Cr/Ni}$) as 382.2 and 725.3 reespectively.

$$\beta_{Cr/Co} = \frac{(C_{Cr}/C_{Ni})_{Strip}}{(C_{Cr}/C_{Ni})_{Feed,0}} \qquad (8)$$

CONCLUSIONS

FSSLM process using TIOA and TBP to selectively separate Cr(VI) from the acidic aqueous solutions containing Co(II) and Ni(II) was investigated in present study. Following conclusions can be drawn respectively.

1) The optimum conditions for selective separation of Cr(VI) using FSSLM process were developed experimentally as stated in Table 2. The best initial mass flux of Cr(VI) was obtained with 0.5 mol/L H₂SO₄ solution as 1.49×10^{-05} kg/m²·s in the feed phase. The extraction rate and inital mass flux values were decreased and FFSLM was unstable above or below this concentration. The other acidic mediums for selective separation of Cr(VI) were not found as effective in present study. Especially in HCl media, some anionic or neutral Co(II) species like as $CoCl_4^{2-}$, $CoCl_3^{-}$, $CoCl_2$ can be formed in the feed phase. The formation adversly affects the selectivity of FSSLM process in terms of Cr(VI) over Co(II) and Ni(II), since these species can be extracted with both TIOA and TBP as well.

2) The best initial mass flux of Cr(VI) was obtained with membrane phase composition of 2.5% v/v TIOA and 2.5% v/v TBP as 2.48×10^{-06} kg/m²·s. The nature of organometalic complex in the presence of TIOA and TBP was confirmed as [(TBP HCrO₄(R₃N⁺)H]₍ₒᵣg₎.

Table 3. Separation factors for equimolar feed mixtures: Diluent (Chloroform): 95% w/w; extractant (TIOA) 2.5% v/v synergist (TBP) 2.5% v/v; feed phase acid type and concentration: 0.5 mol/L H_2SO_4; mixing speed: 1200 rpm; stripping solution type and concentration: 1.0 mol/L NaOH; membrane support: Celgard 2500

	100 ppm					200 ppm					500 ppm				
Time	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$
Feed 0	102.6	104.7	102.6			207.7	208.6	203.1			519.2	521.4	506.8		
Strip 1	0.1	0.1	36.7	382.2	725.3	0.2	0.2	57.3	289.8	290.7	0.5	0.5	104.2	211.2	211.9
Strip 2	0.4	0.3	56.7	157.6	224.3	1.1	1.0	92.5	85.1	93.9	0.7	0.5	202.0	290.6	459.2
Strip 3	0.7	0.5	77.1	114.7	169.3	2.1	1.8	127.2	61.3	71.8	2.2	1.4	290.8	134.2	206.4
Strip 4	0.9	0.6	94.1	108.8	154.9	2.8	2.4	161.5	58.4	68.3	5.0	4.0	371.0	75.7	95.3
Strip 5	1.0	0.8	102.0	106.3	134.5	3.3	3.0	184.4	57.4	63.5	6.2	5.4	430.9	71.6	82.1
Strip 6	1.2	1.3	102.6	82.2	77.9	4.4	4.2	199.4	46.7	48.4	2.8	4.5	473.2	174.2	109.3
Strip 7	1.3	1.5	102.6	79.1	71.7	4.6	5.3	201.4	45.1	38.8	3.3	7.2	490.9	153.1	70.0
Strip 8	1.1	1.5	102.6	97.7	69.1	5.2	5.4	202.4	39.5	38.3	5.0	7.5	497.8	102.3	68.5
	750 ppm					1000 ppm					1500 ppm				
Time	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$	Co	Ni	Cr	$\beta_{Cr/Co}$	$\beta_{Cr/Ni}$
Feed 0	758.1	761.2	759.9			1007.3	1011.5	1012.9			1526.5	1532.9	1512.9		
Strip 1	0.7	0.7	148.3	200.6	201.2	1.0	1.0	160.0	162.4	162.9	1.5	1.5	215.9	146.7	147.2
Strip 2	4.1	3.7	259.5	63.8	70.4	1.3	0.8	319.0	252.2	422.8	4.0	3.3	408.9	102.2	126.3
Strip 3	5.7	4.6	385.1	67.5	84.3	2.1	0.6	477.8	230.0	854.5	5.3	3.0	658.6	125.0	219.4
Strip 4	8.3	6.8	527.9	63.6	77.8	5.5	3.5	616.8	111.0	174.7	6.4	3.4	869.8	136.1	258.5
Strip 5	5.9	4.7	604.0	103.0	128.2	7.7	6.2	754.3	96.8	120.6	9.8	7.5	1030.3	105.8	138.5
Strip 6	5.8	9.3	667.4	115.4	71.7	11.0	10.3	832.1	75.2	80.5	13.8	12.7	1187.6	86.9	94.5
Strip 7	6.5	9.3	703.0	107.9	75.9	9.9	13.6	896.0	89.6	65.6	13.2	18.8	1296.6	98.9	69.8
Strip 8	9.0	9.7	721.9	80.2	74.9	11.2	12.1	935.9	83.0	77.2	18.2	19.6	1349.4	74.7	69.8

The main effect of TBP was described in aspect of the replacement of the water molecules within organometallic complex $(R_3NH^+HCrO_4^-xH_2)_{(org)}$). In addition, it is inferred from the results that TBP causes the replacement in the adduct structure. This novel adduct formation facilitates the transport of Cr(VI) from feed phase to membrane phase due to enhanced organic character of organometallic adduct forming in feed and membrane phase interface [TBP HCrO$_4^-$ (R$_3$N$^+$H)].

3) The higher selective extraction of Cr(VI) on Co(II) and Ni(II), n the optimum conditions was achieved in the the range of 100–1500 mg/L. Extraction efficiencies of Cr(VI) were obtained as 99.9 and 89.2% at the end of 8 hours with the aqueous feed solution mixtures of 100 mg/L of Cr(VI), Co(II), Ni(II) and 1500 mg/L of Cr(VI), Co(II), Ni(II). On the other hand, separation factors of $\beta_{Cr/Co}$ and $\beta_{Cr/Ni}$ was calculated as 382.2 and 725.3 respectively for aqueous solution containing 100 mg/L Cr(VI), Co(II), Ni(II) in the optimum conditions.

As a result of present work, synergistic separation and removal of Cr(VI) from acidic aqueous solutions containing Co(II) and Ni(II) using TIOA and TBP as carriers has been performed with higher Cr(VI) initial mass flux values. In addition, the study presents suitable application route how to use it industrial or municipal purposes like as tannery or Cr-Ni plating industries or polluted lakes, river and etc. to separate and remove Cr(VI) species from acidic media

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