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Alkyl chain structure-dependent separation of Cr(VI) from acidic solutions containing various metal ions using liquid–liquid solvent extraction by butyl-based imidazolium bromide salts

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ABSTRACT

In this study, the comparison of Cr(VI) extraction and separation from acidic solutions by solvent extraction technique in presence of Fe(III), Ni(II), Co(II), and Cu(II) was performed using four different symmetric and asymmetric imidazolium salts (IMs)-substituted butyl and isobutyl alkyl groups. The effective parameters on separation and extraction of Cr(VI) were examined in both organic and aqueous phases to identify optimum conditions. Under optimum conditions, symmetric IMs were elected as the best extractive agents and 99.45% of Cr(VI) was extracted and 99.22% of Cr(VI) was effectively stripped with higher separation factors toward the other metal ions.

Keywords: Imidazolium salts-based separation; Ionic liquids; Solvent extraction; Cr(VI) extraction; Alkyl chain structure-dependent separation

1. Introduction

Environmental pollution has became a global problem since the industrial revolution. There are many environmental organizations worldwide to alert the authorities for taking precautions against environmental pollution, especially against industrial-based heavy metal pollution. Some of the important environmental issues threatening human health have been known as water, soil, and air pollution, occurring as a result of industrial byproducts [1–3]. Heavy metal ions are well-known toxic substances for environmental sources among the hazardous substances. Every day, a huge amount of wastewater containing different heavy metal ions is released into the environment as byproducts of industrial activities. Therefore, reducing their discharge concentrations is an obligation for factories up to a limit permitted by World Health Organization and European Pollution Agency, using recovery or removal techniques on industrial effluents containing heavy metals [4,5].

Chromium is an element existing in two oxidation states, as Cr(III) or Cr(VI). Chromium compounds occur in those oxidation stages. These species have different toxicities for environmental sources and living organisms [6–8]. The toxicity of Cr(III) is not known to be as dramatic as Cr(VI). The basic adverse effect of Cr(III) on mammal organisms has been observed on liver and kidney after taking very high doses by ingestion [9–12]. In contrast to Cr(III), the toxicity of Cr(VI) has been well known for many years. The direct exposure to Cr(VI), especially in industries using Cr(VI) , such as plating or tanning industries, frequently results in an important health problem such as cancer in digestive system or

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lungs. In addition, the mutagenic effects of Cr(VI) on DNA and RNA have received considerable attention from scientists in recent years due to their oxidative properties affecting the entire life cycle. For these reasons, Cr(VI) must be removed from wastewaters before being discharged into the environment [7,13–15].

Solvent extraction (SX) has been known as the most important and widespread technique used in hydrometallurgical process. It has been used for different purposes, such as metal production, purification, recovery, or recycling. Two immiscible phases, aqueous and organic phase, are used in traditional SX processes and is also called as liquid–liquid solvent extraction (LLSX). In this process, the transfer of metal ions from the aqueous phase to the organic phase has been provided using an extracting agent (extractant). Considerable scientific efforts have been performed to replace the organic phase in SX systems by an ionic liquid (IL) over the last decade [4,16–21]. Room temperature ILs are well known as liquid ionic salts entirely consisting of organic cation and organic- or inorganic-based anion at the ambient temperature. They are non-volatile and have higher flash point because they have a negligible vapor pressure. These unique physical properties make them a safe and environmentally friendly reagent in extraction-based processes. Therefore, many scientists around the world have focused on the application of water-insoluble ILs, either as a solvent or as an extractant in SX processes [4,10,22–25].

In this work, the separation of Cr(VI) in presence of Fe(III), Co(II), Ni(II), and Cu(II) was investigated by SX process using imidazolium-based symmetric and asymmetric ILs-substituted butyl and isobutyl chains on nitrogen atoms as carriers in dichloromethane. The various parameters were studied to determine the extraction and the stripping ability and capability of imidazolium salts (IMs) as an extractant. Complex structure between IMs and Cr(VI) was explained with comparison of ATR-FTIR spectra. Complex structure of IMs-Cr(VI) was illuminated using slope analysis procedure. The best appropriate IMs for Cr(VI) extraction have been determined by evaluating the best experimental variables in examined parameters. The counter current study has been performed to determine the number of steps required to reach maximum extraction efficiency using McCabe-Thiele diagram. The separation factors of Cr(VI) on other metals have been calculated from obtained data at the optimum conditions, with respect to altering initial metal ion concentration.

2. Experimental

2.1. Reagents

The chemical reagents toluene, dichloromethane, N,N-dimethyl formamide, hexane, NH_4OH, Na_2CO_3, NaOH, HCl, HNO_3, and H_2SO_4 were purchased from Sigma–Aldrich (Seelze, Germany) and were used directly as received from the manufacturer. Imidazole, N-methyl imidazole, 1-bromo butane, and 1-bromo-2-methyl propane were purchased from VWR (Seelze, Germany) and were used for the synthesis of symmetric and asymmetric IMs without further purifications. AAS-grade standard metal solutions containing 1,000 ± 5 mg/L of Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) were purchased from Merck (Darmstadt, Germany) and directly used for the preparation of feed solutions.

2.2. IMs synthesis procedure and their characterization

Asymmetrical imidazolium salts (IM1 and IM3) were synthesized according to method in the literature [26,27]. To provide asymmetric binding of the alkyl groups to imidazolium ring, 0.5 mol of N-methyl imidazole was added and dissolved in 50-mL toluene in a 200-mL reaction flask, and 0.5 mol of alkyl bromide (butyl and isobutyl bromide) was added in portion to the solution. The reaction mixture was refluxed for 2–3 h. After heating and stirring, the reaction mixture was cooled up to room temperature, and the toluene phase was decanted. The remaining residue was exposed to washing and decanting cycles 3–4 times with 15–20-mL hexane. Afterwards, IMs were dried in vacuo for 3–4 h and were utilized directly in extraction studies.

The similar synthesis procedure was utilized in the synthesis of symmetrical imidazolium salts (IM2 and IM4), as given in the literature [28–30]. 0.5 mol of 1-H-imidazole was added and dissolved in 50-mL N-N ´-dimethyl formamide (DMF) in a 200-mL reaction flask. The mixture was stirred for 30 min at 40–50˚C and simultaneously 1.0 mol of alkyl bromide (butyl and isobutyl bromide) was added in portions. The reaction mixture was refluxed for 10–12 h. After refluxing, the reaction mixture was cooled up to room temperature. DMF phase was distilled off in vacuo. The residue was washed and decanted via 15–20-mL hexane for 3–4 times and dried in vacuo for 3–4 h. The applied reaction route is given in Fig. 1 to summarize the synthesis of symmetric and asymmetric imidazolium salts. The ^{1}H NMR values have been given below, taking into consideration the carbon

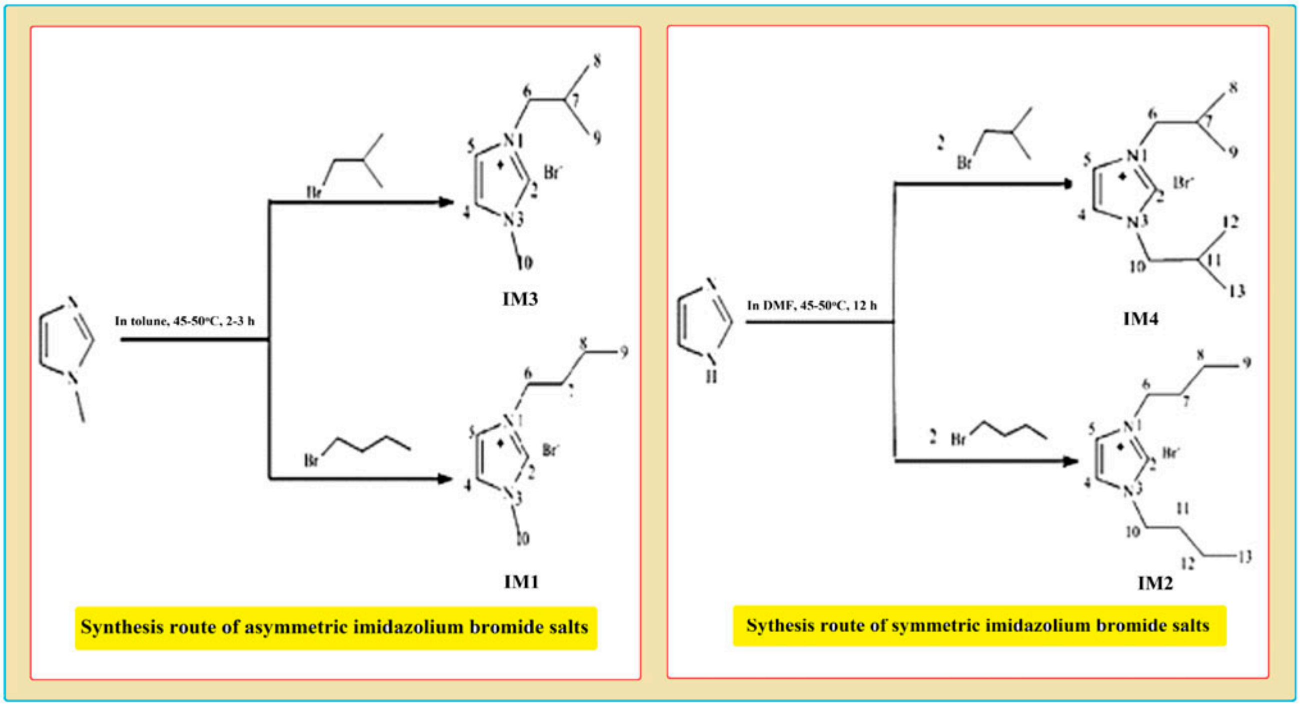

Fig. 1. Schematic representation of synthesis of symmetric and asymmetric IMs.

number demonstrated in Fig. 1. The values have been given below for each of the IMs separately. The purities of the IMs were calculated with the integration of ^{1}H NMR spectra. The results showed that average purity of IMs are 69 ± 0.1 and 75 ± 0.1%, for asymmetric and symmetric ones, respectively.

IM1; (600 mHz, CDCl3, δ, ppm) 10.31 (1H, s, C2 (acidic)), 7.41, 7.26 (2H, d, C5, C4), 4.28 (2H, m, C6) 1.87 (1H, m, C7) C10. The purity of IMs was determined as 75.0% from integration of ^{1}H NMR spectrum.

IM2; (600 mHz, CDCl3, δ, ppm) 10.02 (1H, s, C2 (acidic)), 7.47, 7.32 (2H, d, C5, C4), 4.27 (4H, m, C6, C10) 1.80 (2H, m, C7, C11). The purity of IMs was determined as 69.0% from integration of ^{1}H NMR spectrum.

IM3; (600 mHz, CDCl3, δ, ppm) 9.70 (1H, s, C2 (acidic)), 7.41, 7.29 (2H, d, C5, C4), 3.97 (2H, m, C6) 3.74 (3H, s, C10) 1.44 (2H, m, C7) 1.22(2H,m,C8) 0.58 (3H, t, C9). The purity of IMs was determined as 75.0% from integration of ^{1}H NMR spectrum.

IM4; (600 mHz, CDCl3, δ, ppm) 9.96 (1H, s, C2 (acidic)), 8.30, 7.45 (2H, d, C5, C4), 3.93, 3.72 (2H, m, C6, C10) 1.98 (4H, m, C7, C11) 1.8(4H, m, C8, C12) 0.67 (6H, t, C9, C13). The purity of IMs was determined as 68.0% from integration of ^{1}H NMR spectrum.

2.3. Preparation of aqueous solutions and extraction procedure

AAS-grade standard metal solutions were utilized in the preparation of acidic feed solution in desired metal ion concentrations. For this purpose, desired volume of standard metal solutions was taken to prepare 25-mg/L Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) containing feed solutions. Desired volume of concentrated acids (HNO_3, HCl, and H_2SO_4) was added to a volumetric flask. The acidic metal solution was diluted with deionized water (Milli-Q ultra pure water). On the other hand, stripping solutions were prepared by dissolution of bases like NH_4OH, $NaCO_3$, NaOH, and KOH by deionized water to the desired concentrations.

The experiments were carried out in a glass bottle with a screw cap, approximately having 15-mL internal volume. All the extraction and the stripping experiments were carried out batchwise at the ambient temperature (25 ± 1.0˚C). The suitable organic diluent was determined as dichloromethane to easily work with upper phase (aqueous phase) and to avoid vaporization of organic solvents. So, all the IMs were diluted to desired concentrations in organic solvents (dichloromethane). 2.0 mL of feed solution and 2.0 mL of organic phase containing IMs as carrier were agitated with a magnetic stirrer DAIHAN MS-MP8, (Seoul, South Korea) together for 3 min. Afterwards, the mixed phases were kept aside for separation of the organic and the aqueous phase for a few minutes. 100 μL of sample was taken from the acidic aqueous feed phase and metal ion concentration was determined by ICP-MS Agilent 7700x (Santa Clara, USA). The metal ion concentrations in the organic phase were calculated from the difference of the metal ion concentrations in the aqueous phase before and after extraction. So, extracted metal species were indirectly determined in the organic phase. The percentage extraction (*E%)* and the percentage stripping (*S%)* at the equilibration conditions were calculated using the following equations, respectively:

$$E\% = \frac{C_{\mathrm{i(aq)}} - C_{\mathrm{e}}}{C_{\mathrm{i(aq)}}} \times 100 \tag{1}$$

$$S\% = \frac{C_{\mathrm{e}}}{C_{\mathrm{i(org)}}} \times 100 \tag{2}$$

where $C_{\mathrm{i(aq)}}$ and $C_{\mathrm{i(org)}}$ are the initial concentration of corresponding metals in the aqueous phase and organic phase, respectively, and C_{e} is the equilibration concentration of the extracted metals. Distribution coefficient (*D*) was calculated and expressed using following equations:

$$D = \frac{C_{\mathrm{e(org)}}}{C_{\mathrm{e(aq)}}} \tag{3}$$

where $C_{\mathrm{e(org)}}$ and $C_{\mathrm{e(aq)}}$ are the total concentration of metal ions in organic and aqueous phases after equilibration.

2.4. Quantitative analysis of metal ions and physicochemical measurement of IMs

An Agilent 7700x ICP-MS (Santa Clara, USA) fitted with an octopole collision/reaction cell was used for quantitative determination of metal ions. Sample introduction system was composed of a CETAC ASX-520 model autosampler (Omaha, Nebraska, USA), a MicroMist nebulizer, and a quartz-shielded torch. After equilibration, the phases were allowed to separate and certain volume of the feed solution was taken from the aqueous phase using micropipette Brand (Wertheim, Germany), and diluted with demineralized water to a certain volume using an automatic titrator (Wertheim, Germany).

The physicochemical properties of IMs have been examined in aspects of viscosimetry, conductometry, density measurements, and the results are given in Table 1 [31]. All physicochemical measurements were performed at ambient temperature (25 ± 0.5℃) using circulating water bath without further purification. Viscosimetric and conductometric measurements of IMs have been performed by AND SV-10 (Tokyo, Japan) vibrating wire viscosimeter and Mettler Toledo SevenGo SG78—SevenGo Duo pro pH/ion/conductivity meter (Ohaio, USA), respectively. Density measurements were performed by calibrated pycnometer and the specific volume values of the IMs were calculated from density values of IMs. All measurements were performed in triplicate for the confirmation of measured parameters.

3. Results and discussions

3.1. Extraction mechanism of Cr(VI) with IMs

The metal extraction capabilities of IMs directly depend on their hydrophobic–lypophilic structures. The length, spatial shape, and the number of alkyl chains on imidazole ring are important criteria to determine their hydrophobicities [32,33]. IMs display a very good extraction capability for anionic species of metals or organic substances, like organic acids in the aqueous phase. In the acidic conditions, chromium species are generally known as anionic, like $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCrO_4^-$, and $HCr_2O_7^-$, but the speciations of the other metal ions, such as Fe(III), Co(II), Ni(II), and Cu(II), can change as anionic, cationic, or neutral depending on pH, the anion type of acid, etc. Cationic species of Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, or their anionic or neutral complexes with anion of the acids like $CoCl_3^-$, $CuCl_3^-$, $CoCl_4^{2-}$, $NiCl_2$, and $FeCl_3$ [16,34,35]. Especially, $FeCl_4^-$ complexes can be formed in higher chloride concentrations [36].

The possible extraction mechanism of Cr(VI) by IMs can be written in Eq. (4):

$$n\mathrm{IM^+Br^-_{(org)}} + \mathrm{HCrO^-_{4(aq)}} \underset{K_{\mathrm{e}}}{\Leftrightarrow} n\mathrm{IMHCrO_{4(org)}} + n\mathrm{Br^-_{(aq)}} \tag{4}$$

where the subscripts org and aq denote the organic and aqueous phases, respectively. K_{e} represents the extraction equilibrium constant and IM^+Br^- represents the IMs.

According to the Eq. (4), equilibrium constant of the extraction reaction (K_{e}) can be derived as follows:

$$K_{\mathrm{e}} = \frac{[\mathrm{IMHCrO_4}]_{\mathrm{(org)}}[\mathrm{Br^-}]^n_{\mathrm{(aq)}}}{[\mathrm{IM^+Br^-}]^n_{\mathrm{(org)}}\left[\mathrm{HCrO_4^-}\right]_{\mathrm{(aq)}}} \tag{5}$$

Table 1
Physical properties of IMs at ambient temperature (25 ± 0.5˚C)

Code	Molecular formula and weight (g/mol)	IM salt name	Conductivity (ms/cm)	Density (g/cm^3)	Specific volume (cm^3/g)	Viscosity (centipoise)
IM1	$C_8H_{15}BrN_2$ 219,122	1-butyl-3-methyl-1H-IMidazol-3-ium bromide	0.80 ± 0.02	1.23 ± 0.01	0.81 ± 0.01	363.0 ± 0.6
IM2	$C_{11}H_{21}BrN_2$ 261,202	1,3-dibütyl-1H-IMidazol-3-ium bromide	9.18 ± 0.35	1.20 ± 0.01	0.83 ± 0.01	11.1 ± 0.1
IM3	$C_8H_{15}BrN_2$ 219,122	1-isobutyl-3-methyl-1H-IMidazol-3-ium bromide	2.00 ± 0.08	1.26 ± 0.02	0.79 ± 0.02	134.0 ± 0.4
IM4	$C_{11}H_{21}BrN_2$ 261,202	1,3-diisobutyl-1H-IMidazol-3-ium bromide	4.03 ± 0.2	1.25 ± 0.01	0.80 ± 0.01	67.6 ± 0.2

$$K_e = D\frac{[\mathrm{Br}^-]^n_{(\mathrm{aq})}}{[\mathrm{IM}^+\mathrm{Br}^-]^n_{(\mathrm{org})}} \quad \rightarrow \left(D = \frac{[\mathrm{IMHCrO_4}]_{(\mathrm{org})}}{\left[\mathrm{HCrO_4^-}\right]_{(\mathrm{aq})}}\right) \tag{6}$$

$$\log K_e = \log D + n\log\frac{[\mathrm{Br}^-]_{(\mathrm{aq})}}{[\mathrm{IM}^+\mathrm{Br}^-]_{(\mathrm{org})}} \tag{7}$$

$$\log K_e = \log D + n\left(\log[\mathrm{Br}^-]_{(\mathrm{aq})} - \log[\mathrm{IM}^+\mathrm{Br}^-]_{(\mathrm{org})}\right) \tag{8}$$

$$\log D = \left(\left\{\begin{array}{c}\log K_e - n\log[\mathrm{Br}^-]_{(\mathrm{org})}\\ B\end{array}\right.\right) + n\log[\mathrm{IM}^+\mathrm{Br}^-]_{(\mathrm{org})} \tag{9}$$

$$\log D = n\log[\mathrm{IM}^+\mathrm{Br}^-]_{(\mathrm{org})} + \mathrm{B} \tag{10}$$

With the evaluation of extraction equilibrium, possible stripping mechanism of Cr(VI) can be expressed in Eq. (11) in presence of OH^- ion [37].

$$\mathrm{IMHCrO_{4(org)}} + \mathrm{OH}^- \underset{K_s}{\Leftrightarrow} \mathrm{IM}^+ + \mathrm{CrO_4^{2-}} + \mathrm{H_2O} \tag{11}$$

The relationship between extraction equilibrium constant (K_e) and distribution coefficient (D) can be explained mentioned equation above. According to Eq. (10), the graphical presentation has been performed in Fig. 2 for log D vs. log [IM^+Br^-] to determine the stochiometric rate between IMs and Cr(VI). The slope values of the straight line, which are obtained from the graph based on log D vs. log [IM^+Br^-], give us the stochiometric rate of IMs–Cr(VI) adducts. It can be observed from the graph that slope values for IM1, IM2, and IM3 were so close to 1.0 as 1.1554, 1.0008, and 0.9981 for IM1, IM2, and IM4, respectively, that they equal to 1.0. Therefore, the stochiometric coefficient (n) in Eq. (10) is accepted as equal to 1.0, which is consistent with the discussed chromium species ($HCrO_4^-$) in Eq. (4).

A new adduct between IMs and $HCrO_4^-$ has been formed in the organic phase. It can be regarded as a new kind of IMs with $HCrO_4^-$ as a counter anion [32]. So, FTIR spectra of IMs and chromate-loaded IMs were used to support anion exchange mechanism as a further proof in Fig. 3. The characteristic peaks of pure symmetric and asymmetric IMs can be clearly seen at 762, 1,166, 1,449, 2,816, 2,950, and 3,084 cm^{-1} and 747, 1,167, 1,456, 1,568, 2,861, 2,935, and 3,055 cm^{-1}, respectively. IMs show a prominent peak at 1,658 and 1,673 cm^{-1}, corresponding with aromatic C–N vibrations in FTIR. The remaining peaks in the spectra correspond to the various types of –C–H vibrations of methyl and butyl groups and dichloromethane. Khalidhasan and Rajesh [38] have reported that the $HCrO_4^-$ stretching vibrations would appear at 891 cm^{-1} and the peak intensity varies with respect to the concentration and corresponding nature of the organic extracting agent. These peaks are also seen in the spectra of chromate-loded IMs at 877 and 911 cm^{-1} for symmetric and asymmetric IMs, respectively, in the present study. In addition, water peaks at 3,367 and 3,404 cm^{-1} are seen after the SX process. The new peaks, which are observed at 877 and 911 cm^{-1}, form the presence of $HCrO_4^-$ and they provide further verification for the ion association between $HCrO_4^-$ and IMs.

3.2. *Effect of acid type and concentration on Cr(VI) extraction*

The effect of acid type and concentration in aqueous feed phase was examined on the basis of Cr(VI) extraction by LLSX using IMs as a carrier. In the first set of experiments, we focused on the role of acid type in aqueous feed solution on percentage extraction of

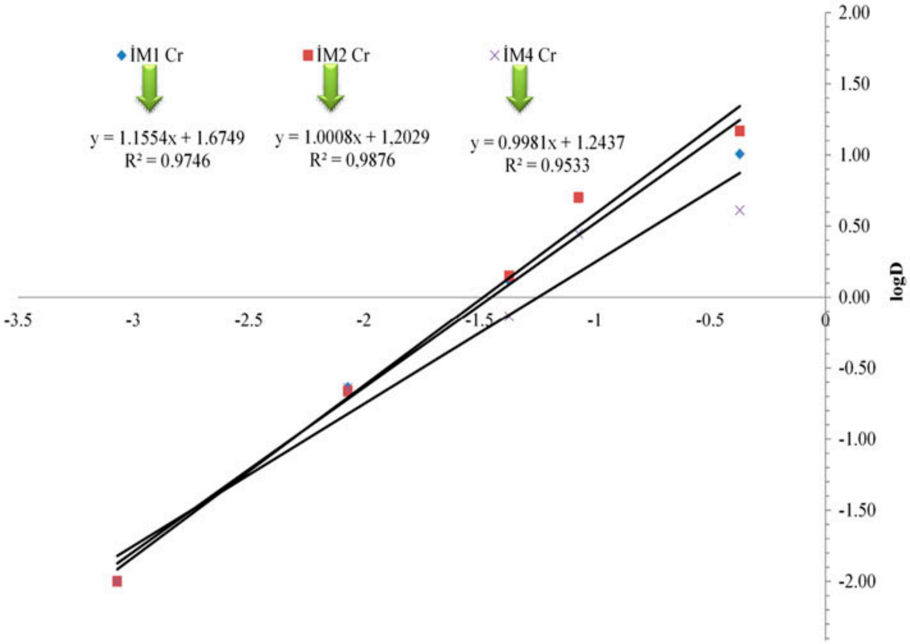

Fig. 2. Plot of Log *D* vs. Log $[IM^+Br^-]$.

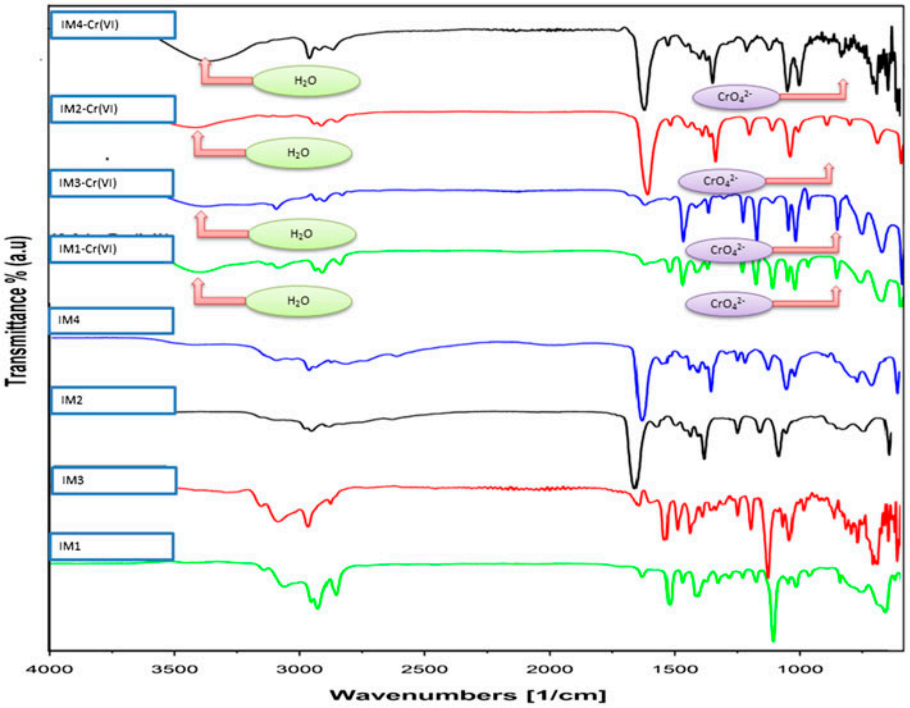

Fig. 3. ATR-FTIR spectra of pure IMs and Cr(VI)-loaded IMs.

Cr(VI) in the presence of Fe(III), Co(II), Ni(II), and Cu(II) in different acidic media (HCl, HNO_3, and H_2SO_4), when acid concentration was kept constant at 0.1 mol/L. The results are given in Fig. 4. As seen from the figure, Cr(VI) and Fe(III) extraction percentages observed were high using IM1 and IM2 compared with IM3 and IM4 for all the acid types (HNO_3, H_2SO_4, and HCl). Percentage extraction of Cr(VI) using IM1, IM2, IM3, and IM4 was obtained as 56.67, 58.59, 32.65, and 42.22%, respectively, whereas, the extraction percentages of Fe(III) were obtained as 34.51, 35.15, 35.84, and 35.28% in 0.1 mol/L H_2SO_4 medium. Percentage extraction of Co(II), Ni(II), and Cu(II) in HCl medium was moderately high for all the IMs compared with the other acid types due to the formation of anionic chloro complexes. This formation causes a decrease in the selectivity of Cr(VI) vs. Co(II), Ni(II), and Cu(II), but it causes an increase in the selectivity of Fe(III). Especially, Co(II) and Cu(II) extraction percentages in HCl medium were identified as high compared with other metal ions due to the easy formation of cobalt and copper chloride complexes. These formations can be supported by the literature, such as $CuCl_3^-$, $CuCl_4^{2-}$, $CoCl_3^-$, and $CoCl_4^{2-}$ [35]. These complexes easily react with IMs. Therefore, HCl could be identified as an impractical acid in this solution containing multiple metal ions, for the selective separation of Cr(VI). Therefore, H_2SO_4 has been selected as an appropriate acid type to obtain higher extraction efficiency for Cr(VI) and lower extraction efficiency for Fe(III), Co(II), Ni(II), and Cu(II) with the highest selectivity.

The acid concentration comprehensively affects the extraction of metal ions due to the varying ionization degrees, speciation and solubilization of metals, and charge of extractant at aqueous and organic phase interface [39,40]. Therefore, another experimental setup was established to follow-up the effect of acid concentration on percentage extraction of Cr(VI) and other metal ions. The feed solution was prepared with the constant concentrations of metals in varying concentrations of H_2SO_4 in the range of 0.001–1.0 mol/L. The phases were agitated with an equal volume of 0.05 mol/L IMs for 3 min. The results are given in Fig. 5. It can be observed from the figure that the percentage extraction of Cr(VI) increased from 47.25 to 72.66%, from 51.28 to 75.11%, from 14.72 to 45.36%, and from 32.78 to 60.20% , and the percentage extraction of Fe(III) decreased from 33.12 to 11.25%, from 29.70 to 11.47%, from 38.57 to 12.92%, and from 33.85 to 12.68% using IM1, IM2, IM3, and IM4, respectively, when the acid concentration increased from 0.001 to 0.5 mol/L. Extraction percentage of Fe(III) with each of the IMs increased with an increase in H_2SO_4 concentration up to 0.01 mol/L. Probable mechanism of the Fe(III) extraction depends on the formation of $Fe(SO_4)_2^-$ in the feed phase. At the lower acid concentrations, Fe(III) extraction rate is greater than higher acid concentrations. Increasing acid concentration makes $Fe(SO_4)_2^-$ formation impossible due to higher oxidation properties of H_2SO_4. Oxidated Fe-SO_4^{2-} species can be neutral like $FeSO_4^+$, and $FeHSO_4^+$ [41]. The extraction percentages of Cr(VI) in the range of 0.001–1.0 mol/L continuously increased. But a plateau was observed on the graph between 0.5 and 1.0 mol/L. Therefore, optimum H_2SO_4

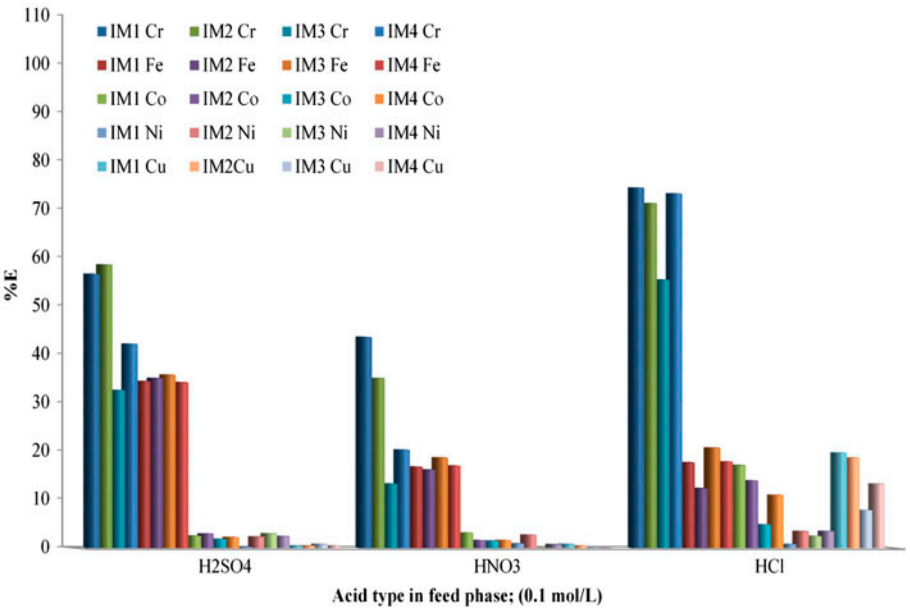

Fig. 4. Effect of acid type; organic phase: 0.05 mol/L IMs in dichloromethane, aqueous phase: 25 mg/L of Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) in 0.1 mol/L of acid, phase ratio: 1:1, phase ratio: 1:1, equilibration time; 3 min, and stirring speed; 1,000 rpm.

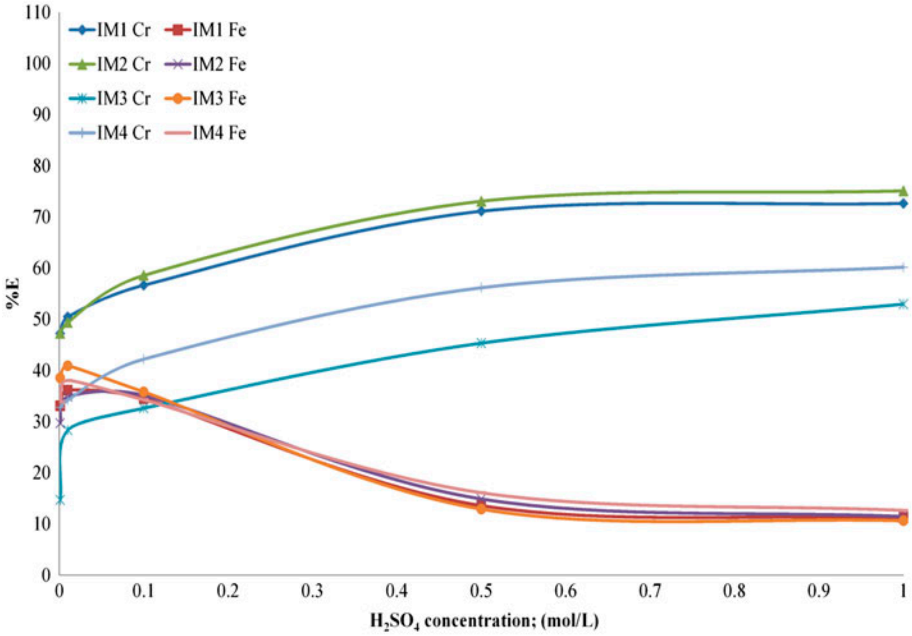

Fig. 5. Effect of acid concentration; organic phase: 0.05 mol/L IMs in dichloromethane, aqueous phase: 25 mg/L of Cr (VI), Fe(III), Co(II), Ni(II), and Cu(II) in 0.1 mol/L of H_2SO_4, phase ratio: 1:1, equilibration time; 3 min, and stirring speed; 1,000 rpm.

concentration was identified as 0.5 mol/L in the current experimental conditions due to minimum extraction percentages of Fe(III) and maximum extraction percentages of Cr(VI),whereby, the selectivity for Cr(VI) over the other metal impurities has been provided in present experimental conditions. The obtained results are coherent with previous scientific studies in the literature [42–45].

3.3. Effect of IMs concentration on Cr(VI) extraction

The extraction of metal ions in aqueous sulfate media into organic phase containing IMs as metal carriers was examined as a function of IMs concentration to evaluate the adduct formation capabilities of IMs toward Cr(VI). The concentration of imidazolium-based symmetric and asymmetric ILs substituting butyl and isobutyl groups has been accepted as an effective parameter on Cr(VI) extraction. The equilibrium constant directly depends on the extractant concentration in the first order according to the Eq. (7) mentioned above. IMs solution was prepared in the range of 0.001–0.5 mol/L when dichloromethane was used as an organic diluent. The obtained results are shown in Fig. 6. As seen in Fig. 6, Cr(VI) extraction was generally high, when we used IM1 and IM2, substituting the straight chain butyl group compared with IM3 and IM4, substituting isobutyl group. Percentage extraction of Cr(VI) using 0.5 mol/L of IM1, IM2, IM3, and IM4 was obtained as 91.05, 93.65, 62.68, and 80.36% and the percentage extraction of Fe(III) was obtained as 25.70, 27.97, 40.60, and 38.05%, respectively, in H_2SO_4 medium.

IMs already have an ionic nature. Therefore, IMs have been known as water miscible compounds. But some of the substituting long-chain alkyl groups are immiscible with water in all proportions and they form a biphasic system with water [46]. Water immiscible nature among IMs is directly related to the alkyl chain length and the number of alkyl groups on nitrogen atoms of the imidazole ring and anion structure. When the number of alkyl groups and alkyl chain length increase in the molecular structure of IMs, steric hindrance grows and water molecules cannot get near the IMs. Because of this property of hyrophobic IMs, they cannot be hydrolyzed and dissolved in water. Thus, they can be easily used in biphasic extraction processes such as LLSX, membrane-based processes, and ion exchange. Also, another factor in water solubility of IMs has been the molecular structure of the anion and interaction between the anion and IM salt. De los Rios et al. reported that there is a good consistency between the anion hydrophilicity and metal extraction capacities of IMs. Their experimental results found out the anion affect of IMs on Cd(II) and Zn(II) as $[NTf_2] < [PF_6] < [BF_4]$ [46]. The

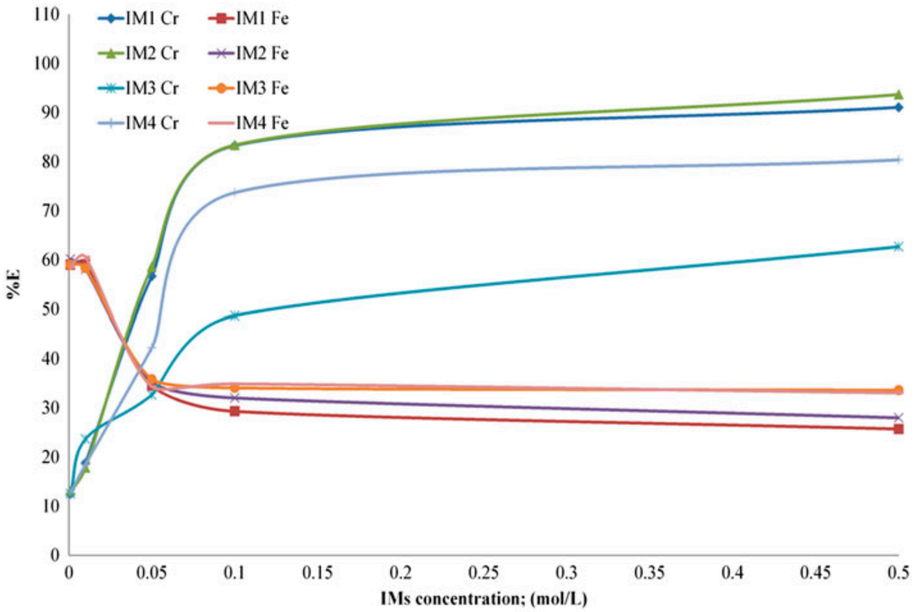

Fig. 6. Effect of IMs concentration; organic phase: 0.05 mol/L IMs in dichloromethane, aqueous phase: 25 mg/L of Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) in 0.1 mol/L of H_2SO_4, phase ratio: 1:1, equilibration time; 3 min, and stirring speed; 1,000 rpm.

chemical and physical properties of IMs directly affect the transport of the metal–IMs adducts at the aqueous–organic phase interface [47–49]. The percentage extraction of Fe(III) was approximately stable and high in the concentration range of 0.001–0.01 mol/L of IMs. Percentage extraction of Fe(III) continuously decreased with increase in molar concentration of IMs due to decreased H^+ concentration in the feed phase. This situation was confirmed with a little increase in pH value in the range from 1.0 to 1.1 in feed phase with increase in IMs concentration from 0.01 to 0.1 mol/L. After 0.1 mol/L IMs concentration, Fe(III) extraction percentage was constant. Proton exchange phenomenon probably occurred between Br^- anion of the IMs and H^+. Increasing H^+ concentration causes easy release of Br^- from the molecular structure of IMBr up to a limit of H^+ concentration. It makes the formation of IM^+ more possible and this phenomenon facilitates the reaction possibility between IM^+ and anionic metal species. Up to this concentration, Fe(III) extractions increased and after that decreased, probably due to the formation of neutral or cationic $Fe\text{-}SO_4^{2-}$ species. We can conclude that 0.01 mol/L H_2SO_4 concentration is the key concentration in Fe(III) separation from Cr(VI) for all IMs because Fe(III) extraction percentage is high and Cr(VI) extraction percentage is low in that concentration [41,45,46,50]. In contrast, the percentage extraction of Cr(VI) increased with increase in the molar concentration of IMs continuously because $HCrO_4^-$ formation is available in the working pH interval (1.0–1.1). Eq. (4) summarizes the extraction mechanism between IMs and Cr(VI). It can be inferred from the experimental results that the maximum percentage extraction of Cr(VI) over Fe(III), Co(II), Ni(II), and Cu(II) was obtained with the use of IM2 containing double *n*-butyl group on the imidazole ring at 1 and 3 positions due to their best lipophilic nature compared with the others. Therefore, 0.5 mol/L has been determined as the optimum IMs concentration.

3.4. Effect of equilibration time and stirring speed on Cr (VI) extraction

The effect of stirring speed and equilibration time in batch-type LLSX technique has been known as the controlling step of the process to make the process kinetically efficient and sustainable. So, the investigations were performed to evaluate the optimum equilibration time and stirring speed. First experimental setup was carried out on equilibration time in the range of 1–10 min. Equilibration time was not found to be more effective on extraction of Cr(VI). Percentage extraction of Cr(VI) was found to be approximately constant after first 5 min under experimental conditions. The extraction percentages of other metal impurities were also low compared with the percentage extraction of Cr(VI). Increasing equilibration time did not provide any additional contribution to extraction percentage of Cr(VI). Therefore, 5 min has been determined as the optimum equilibration time.

We know that stirring speed affects the interfacial area between aqueous phase and organic phase in liquid-based extraction techniques, such as emulsion liquid membrane [51,52] and LLSX [4]. İncreasing stirring speed causes the formation of small globules in the aqueous and the organic phase interface at the batch-type processes. Therefore, a study was performed to evaluate the effect of stirring speed on extraction percentage of Cr(VI) in the range of 300–1,200 rpm at constant equilibration time 3 min. The percentage extraction of Cr(VI) and Fe(III) was not affected significantly with the increase in stirring speed by all the IMs used as extractants up to 1,200 rpm. We have observed that the increase in stirring speed higher than 1,200 rpm has so little additional contribution on the extraction of Cr(VI) ions due to the increase in phase dispersion. Also, any negative effect with the excessive increase in stirring speed was not observed on Cr(VI) extraction. Therefore, optimum stirring speed has been accepted as 1,200 rpm during extraction and stripping experiments to make the process efficient.

3.5. Effect of phase ratio on Cr(VI) extraction

The phase ratio, which is known as the ratio of the organic phase volume to the aqueous phase volume (V_{org}/V_{aq}), is as an important parameter that it is used for the determination of the optimum volume of organic and aqueous phases. In this study, phase ratio was varied from 1:4 to 4:1, and the results are shown in Fig. 7. As seen from the figure, percentage extraction of Fe(III) was low and almost stable for all IMs with increase in phase ratio. Percentage extraction of Co(II), Ni(II), and Cu(II) was observed as low at present experimental conditions. Percentage extraction of Cr(VI) for IM1, IM2, IM3, and IM4 increased approximately 12 times with increase in phase ratio from 0.25 to 2.0 with percentage extraction value of Cr(VI) from 7.78 to 84.59% with IM1 from 8.18 to 87.36% with IM2, from 3.97 to 53.96% with IM3, and from 4.31 to 81.14% with IM4. Afterwards, the upward trend in percentage extraction of Cr(VI) was approximately stable, despite increase in phase ratio because of the stationary regimen between organic phase and aqueous phase. But, further increase in phase ratio was not investigated in this study. Using the study performed in this phase ratio range, we concluded that the organic phase can be completely filled with Cr(VI) by the way of increase in phase ratio. In brief, Cr(VI)

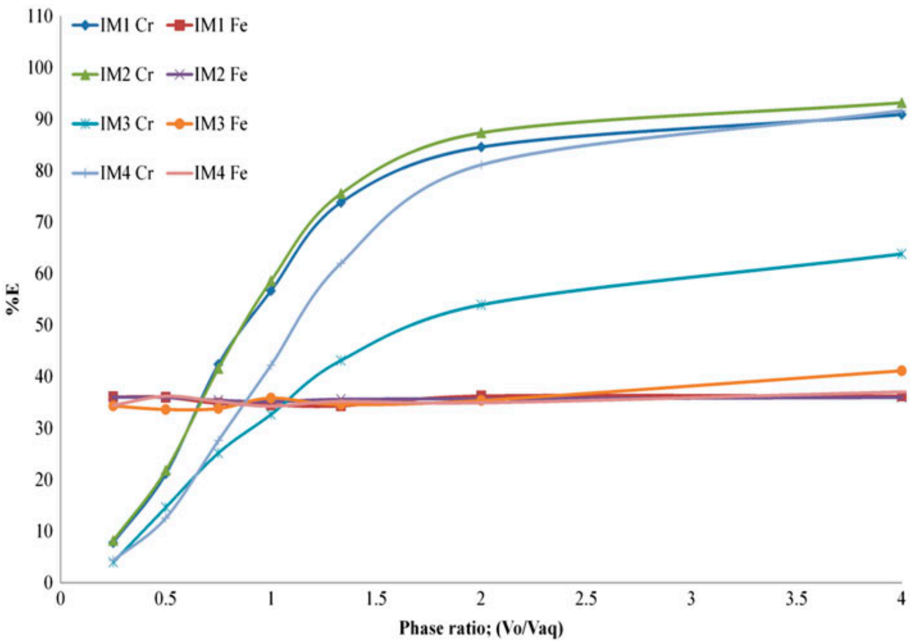

Fig. 7. Effect of IMs concentration; organic phase: 0.05 mol/L IMs in dichloromethane, aqueous phase: 25 mg/L of Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) in 0.1 mol/L of H_2SO_4, phase ratio: 1:1, equilibration time; 3 min, and stirring speed; 1,000 rpm.

Table 2
Optimum extraction conditions for the extraction of Cr(VI) in presence of Fe(III), Co(II), Ni(II), and Cu(II)

Parameter	Value
Equilibration time	5 min
Acid type and concentration in aqueous phase	0.5 mol/L H_2SO_4
Stirring speed	1,200 rpm
Extractant type and concentration	0,5 mol/L IM2
Diluent	*Dichloromethane*
Phase ratio (V_o/V_{aq})	2.0

concentration could be approximately concentrated 12 times into the organic phase when the phase ratio was 2. So, we have identified the optimum phase ratio as 2.

3.6. Determination of optimum conditions and counter current studies

The optimum extraction conditions in aqueous and organic phases for selective extraction of Cr(VI) from acidic solutions containing multiple metal ions were experimentally determined and the optimum parameter variables are shown in Table 2. Among the other investigated IMs, symmetric straight-chain butyl-substituted IM salt (IM2) has been selected as the best extractive agent for the extraction of Cr(VI) due to its different physicochemical properties, which is given in Table 1 [29]. As seen in Table 1, IM2 has different conductivity, specific, density, and viscosity values than the other IMs. Especially, lower viscosity value provides us perfect dispersion of IMs between organic and aqueous phases. A set of experiments was performed in the optimum conditions for different initial metal ion concentrations at the range of 25–500 mg/L and the results are given in Fig. 8. According to the figure, percentage extraction of Cr(VI) was observed as high for all the initial concentrations. Especially, the percentage extraction of Cr(VI) has been achieved as 99.45 and 96.02% in 25 and 500 mg/L of the initial metal ion concentrations, respectively. Also, percentage extraction of Fe(III) was relatively low and stable in that concentration range of metals as 26.79 and 30.06%, respectively. The percentage extraction of other metal ions was negligible at the same initial concentration ranges.

McCabe–Thiele graph has been used to determine how many steps of extraction circuits are required to reach the maximum extraction yields. The counter current study was performed by a set of experiments under optimum conditions when the phase ratio was 2 in Fig. 9. As seen in the figure, Cr(VI) extraction has been achieved in the first extraction circuit, with higher than 95% extraction efficiency. Extraction

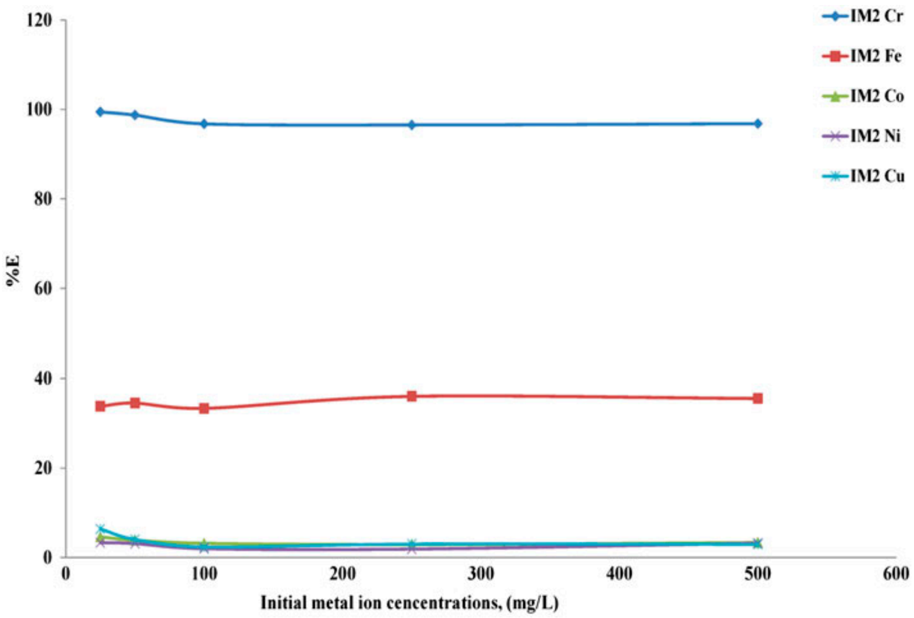

Fig. 8. Effect of initial metal ion concentration; organic phase: 0.5 mol/L IM2 in dichloromethane, aqueous phase: 25, 50, 100, 250, and 500 mg/L of Cr(VI), Fe(III), Co(II), Ni(II), and Cu(II) in 0.5 mol/L of H_2SO_4, phase ratio: 2:1, equilibration time; 5 min, and stirring speed; 1,200 rpm.

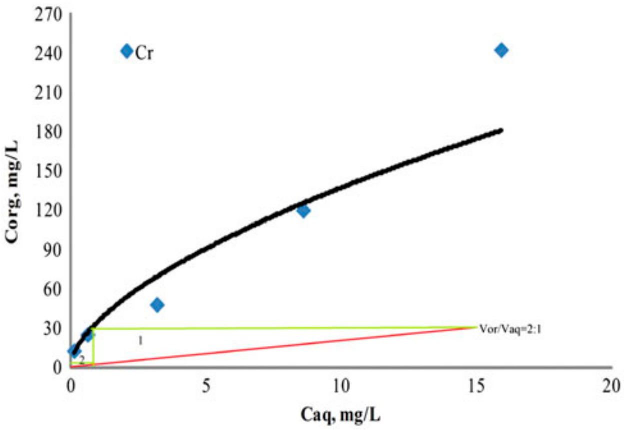

Fig. 9. McCabe–Thiele plot of Cr(VI) at optimum conditions.

capacity of the present SX process in the second extraction circuit was determined as low with respect to the first step. Total extraction percentage of Cr(VI) was determined as >99% at the end of two steps. This concludes that IM2 shows superior extraction ability toward Cr(VI) in H_2SO_4 medium and only two steps are enough to extract the whole of Cr(VI) selectively from the aqueous phase.

3.7. SX process selectivity for Cr(VI) over other metal ions

Under the optimum conditions, the separation factors of Cr(VI) over Fe(III), Co(II), Ni(II), and Cu(II) have been determined at the optimum extraction conditions in different initial metal ion concentrations. The separation factors $\beta_{\mathrm{Cr/Fe}}$, $\beta_{\mathrm{Cr/Co}}$, $\beta_{\mathrm{Cr/Ni}}$, and $\beta_{\mathrm{Cr/Cu}}$ have been calculated using Eq. (12).

$$\beta_{\mathrm{i/j}} = \frac{D_{\mathrm{i}}}{D_{\mathrm{j}}} \tag{12}$$

where D_{i} and D_{j} are the distribution coefficients of metals between organic and aqueous phases, respectively.

The results containing distribution coefficients and separation factors are given in Table 3. The table clearly indicates that the present SX system is extremely selective for Cr(VI) with respect to Co(II), Ni(II), and Cu(II) in diluted solutions within short equilibration time. Whereas, the separation factors of Cr(VI) obtained over Fe(III) were low compared with the others. It shows that the present extraction system has powerful separation capabilities than previous papers [53–55].

3.8. Effect of stripping reagent type and concentration on Cr(VI) extraction

Suitable stripping reagent and its effective concentration affect the applicability of SX process for recovery, removal, or separation of metals for industrial and environmental purposes. To investigate the appropriate stripping-phase reagent and its concentration, two individual experimental setups were performed. The metal-loaded organic phase, which is used in the stripping experiments, was prepared with a set of batch-type extraction processes conducted under optimum extraction conditions using IM2 as the extractant and acidic solution containing 250 mg/L of each of metals. Metal contents of the loaded organic phase were determined with ICP-MS measurements, performed in aqueous phase, as 241.4 mg/L Cr(VI),

Table 3
Separation factors of Cr(VI) over Fe(III), Co(II), Ni(II), and Cu(II)

	D ($C_{\mathrm{org}}/C_{\mathrm{su}}$)				
Initial concentration of metals	Cr(VI)	Fe(III)	Co(II)	Ni(II)	Cu(II)
25	180.60	0.37	0.05	0.03	0.07
50	78.48	0.36	0.04	0.03	0.04
100	30.09	0.39	0.03	0.02	0.02
250	27.85	0.42	0.02	0.02	0.03
500	30.49	0.43	0.03	0.03	0.03
	$\beta_{\mathrm{Cr/Fe}}$	$\beta_{\mathrm{Cr/Co}}$	$\beta_{\mathrm{Cr/Ni}}$	$\beta_{\mathrm{Cr/Cu}}$	
25	494	3,731	5,226	2,651	
50	219	1,946	2,415	1,859	
100	78	912	1,473	1,244	
250	66	1,615	1,432	895	
500	71	881	918	997	

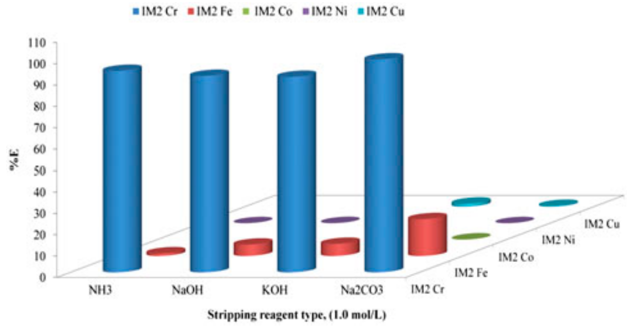

Fig. 10. Effect of stripping reagent type; organic phase; 241.4 mg/L Cr(VI), 91.1 mg/L Fe(III), 5.8 mg/L Co(II), 6,4 mg/L Ni(II), and 9.1 mg/L Cu(II) in dichloromethane, stripping phase: 1.0 mol/L, phase ratio: 2:1, equilibration time; 5 min, and stirring speed; 1,200 rpm.

91.1 mg/L Fe(III), 5.8 mg/L Co(II), 6,4 mg/L Ni(II), and 9.1 mg/L Cu(II). The prepared metal-loaded organic solution was used during stripping experiments. First experimental setup was carried out to identify the suitable stripping reagent. For this purpose, 1 mol/L of NH_3, NaOH, KOH, and Na_2CO_3 was agitated with metal-loaded organic phase and the stripping percentages are given in Fig. 10. According to the figure, the best percentage stripping of Cr(VI) was obtained as 94.34, 92.00, 91.54, and 99.00% for NH_3, NaOH, KOH, and Na_2CO_3, respectively. Although the base with the highest extraction efficiency of Cr(VI) may seem to be Na_2CO_3, however, the appropriate stripping reagent was identified as NH_3 due to selective separation of Cr(VI) on other metal ions. Especially, the percentage stripping rate between Cr(VI) and Fe(III) was determined as the key factor to improve the Cr(VI) selectivity of the present extraction system. So, NH_3 was determined as the best appropriate stripping reagent with the best percentage stripping of Cr(VI) as 94.34% and the worst percentage stripping of Fe(III) as 1.67%.

The second experimental setup was performed to determine the optimum stripping solution concentration to increase percentage stripping of Cr(VI) in the range of 0.01–2.0 mol/L. The obtained results are explained in Fig. 11. As seen from the figure, the percentage stripping of Cr(VI) increased with increase in NH_3 concentration up to 2.0 mol/L . The best stripping efficiency obtained was 99.22% with 2.0 mol/L NH_3, whereas, percentage stripping of Fe(III) generally was low with all NH_3 concentrations. In addition, the percentage stripping of Fe(III) was observed as high at lower NH_3 concentrations compared with higher NH_3 concentration. According to the result, we have concluded that Cr(VI) stripping efficiency increased with increase in hydroxide ion concentration in the stripping phase according to Eq. (11). Therefore, optimum stripping reagent and its effective concentration have been determined as 2.0 mol/L NH_3.

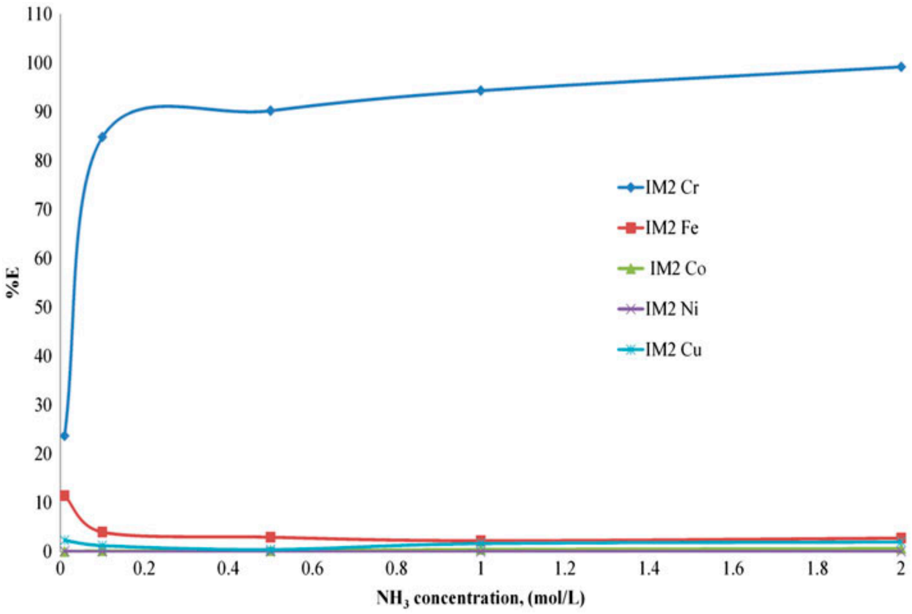

Fig. 11. Effect of NH_3 concentration; organic phase: 241.4 mg/L Cr(VI), 91.1 mg/L Fe(III), 5.8 mg/L Co(II), 6,4 mg/L Ni(II), and 9.1 mg/L Cu(II) in dichloromethane, stripping phase: 1.0 mol/L, phase ratio: 2:1, equilibration time; 5 min, and stirring speed; 1,200 rpm.

4. Conclusions

Four different room temperature ILs having different molecular structures (1-methyl-3-butyl imidazolium bromide (IM1), 1,3-dibutyl imidazolium bromide (IM2), 1-methyl-3-isobutyl imidazolium bromide (IM3), and 1,3-diisobutyl imidazolium bromide (IM4)) were synthesized as yellow viscous liquids. These reagents have been obtained and the products have been characterized with FTIR and ^{1}H NMR measurements. The characterization of the synthesized viscous yellow liquid products showed that the synthesis of ILs was successful with the purity of 75.0 ± 0.1, 69.0 ± 0.1, 75.0 ± 0.1, and 69.0 ± 0.1% for IM1, IM2, IM3, and IM4, respectively. The selective extraction of Cr(VI) in presence of Fe(III), Co(II), Ni(II), and Cu(II) has been performed with the novel improved SX process using IMs as carrier in dichloromethane. The study has showed that IMs having different alkyl chains can be used in the LLSX process as carrier. The present study has illuminated Cr(VI) extraction capacity and separation ability of IMs based on alkyl chain length and isomerism. Hydrophobic or hydrophilic character of IMs directly affects water solubility, steric hinderance, and phase dispersion. Some important results can be notated from this study:

(1) The optimum extraction conditions have been determined experimentally as stated above in Table 1.
(2) The highest extraction percentages were obtained with IM2 as extractive agent due to its higher lipophilic nature compared with the others. We have concluded that easy and efficient transfer of Cr(VI)–IMs adduct from aqueous phase to organic phase was provided by lipophilicities of IMs.
(3) The best appropriate acid and its effective concentration in aqueous feed solution containing multiple metal ions were determined as 0.5 mol/L H_2SO_4 for selective separation of Cr(VI).
(4) The best appropriate stripping agent was determined as NH_3 due to its higher stripping efficiency of Cr(VI) and lower stripping efficiency of Fe(III). The increased concentration of NH_3 in the stripping solution was terminated with the increase in Cr(VI) selectivity toward other metal ions.
(5) The stoichiometric rate between Cr(VI) and IMs was investigated based on the analysis of log D and log [IMs]. The general reaction equations have been proved for the extraction and the stripping of Cr(VI) by IMs as shown in Eqs. (4) and (11), respectively.

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