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Solvent extraction of chromium(VI) from hydrochloric acid solution with trialkylamine/kerosene

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ABSTRACT

The extraction equilibrium of Cr(VI) with trialkylamine (N235, R_3N, $R = C_8$–C_{10}) using kerosene as the diluent was investigated. The influence of various analytical parameters such as pH, equilibrium time, temperature, extractants, and diluents was systematically evaluated. The structure of organic solution was identified by Fourier transform infrared spectroscopy (FTIR). The results indicated that 99.99% Cr(VI) was extracted by N235 in kerosene under the optimum separation conditions. Results also observed that the relative affinities of different anions to N235 were in the order of $NO_3^- < PO_4^{3-} < SO_4^{2-} < Cl^-$. Thermodynamic functions revealed that the extraction process was exothermic in nature, and the enthalpy (ΔH) associated with the extraction process was calculated to be −35.95 kJ mol^{-1} at 298 K. Slope method analysis showed that the log D vs. log [N235] plots were straight lines with slope nearly 3.0 with kerosene, n-heptane, and n-dodecane as the diluents, but mole method analysis indicated that the molar ratio between N235 and hexavalent chromium ion in the extracted complex was identified to be 1. The loaded organic solvent was regenerated with NaOH, $NaNO_3$, $NaHCO_3$, and $N_2H_4 \cdot H_2SO_4$. The regenerated solvent could be reused in succeeding extraction of chromium(VI). FTIR confirmed that the structure of the loading organic solution can be destroyed in light.

Keywords: Solvent extraction; Hexavalent chromium; Trialkylamine; Photolysis

1. Introduction

Solvent extraction is widely used in a variety of industries for both the upgrading and purification of a range of elements and chemicals. Chromium(VI) is a toxic element for living organisms because of its carcinogenicity and mutagenicity and its control generates a hazardous and costly waste [1]. The extensive use of chromium in the leather tanning, electroplating, metallurgy, and dyeing industries has resulted in environmental pollution [2]. Thus, its elimination from effluents is a primary target before discharge to the environment.

Different processes such as solvent extraction, chemical precipitation, ion exchange, adsorption, and membrane separation have been investigated for the removal of chromium(VI). It is noteworthy that solvent extraction is one of the most effective techniques for the recovery of chromium which is widely used in separation science [3]. With this technique, the amine extractants such as tertiary amines

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(Alamine 336 and trioctylamine [TOA]) and quaternary ammonium salts (Aliquat 336) have attracted great interest from researchers due to their superiority to selectively extract metal ions such as Zn [4], Cr(III) [5], Pd [6] noble metals [7], and rare earth metals [8]. In addition, a number of researches related to the solvent extraction of chromium(VI) with amine extractant are available in the literature [9–15].

The extraction mechanism is complicated with different extractants. Sengupta et al. studied the extraction of Cr(VI) by tri-n-octylamine (TOA) from different inorganic acids solutions. The extracted species is $HCrO_4^-$ from HCl solution and $Cr_2O_7^{2-}$ or $HCr_2O_7^-$ from sulfuric acid solution [16,17]. Lo and Shiue [12] investigated the extraction of chromium(VI) from aqueous solutions of 0.1 M ionic strength by Aliquat 336 in a mixture of kerosene and xylene. The hydrogen chromate ion ($HCrO_4^-$) is the major extractable species of Cr(VI) at pH 3.53–3.75. Venkateswaran et al. [18] investigated the extraction of hexavalent chromium with tetrabutyl ammonium bromide (TBAB) in dichloromethane at pH 1 ± 0.1, a 1:1 TBAB: $HCrO_4^-$ complex was proven by slope method. Kalidhasan and Rajesh [19,20] evaluated the ability of tetrabutylammoniumiodide, tribenzylamine on the extraction of chromium(VI) in acidic medium, molar ratio of the extracted complex was identified to be 1:1 at acidic solution.

N235 is a straight chain trialkylamine with excellent chemical stability and has been studied as extractant for separation. However, little research has been done to investigate the role of tertiary amine N235 on the extraction equilibrium of Cr(VI). The mechanism of the complex reaction of chromium(VI) with tertiary amine is complicated. Thus, it is necessary to evaluate the extraction mechanism in detail. In addition, the foundation of recycling is the stability of the loading organic solution. A literature survey has revealed that little is known about the stability of solvent in the separation process. Therefore, we also focus on the stability of organic solution in the extraction reaction.

The objective of this work was to evaluate the effect of tertiary amine N235 on the extraction of Cr(VI). Thus, we here investigated the detoxification of chromium(VI) from wastewater using N235 as the extractant and kerosene as diluent. In order to design and optimize the solvent extraction reaction, we also analyzed the influence of different experimental parameters. Besides, the regeneration of the organic solution was studied to realize the reuse of extractant.

2. Materials and methods

2.1. Reagents and chemicals

Trialkylamine (N235), a kind of C_8–C_{10} saturated straight-chain tertiary amine mixture, was obtained from Shaoyang Institute of Chemical Industry (Hunan, China). Its average molecular weight was 387 g mol^{-1} and its density was 0.816 kg dm^{-3} (25℃). The diluents of kerosene, ethyl acetate, dimethylbenzene, n-hexane, n-octanol, isooctane, n-heptane, and n-dodecane were of AR grade (Tianjin Hengxing Chemical Preparation Co., Ltd). Both reagents were used without further purification.

A stock solution of Cr(VI) was prepared with K_2CrO_7 of AR grade (Tianjin Yongda Chemical Reagent Co., Ltd). To obtain different pH values, the initial pH of the aqueous solution was adjusted with dilute hydrochloric acid solution unless otherwise stated. The extracting solvent was prepared by dissolving appropriate volume of N235 in diluent to obtain organic solutions of different concentrations. All other reagents in this study were of AR grade. Milli-Q water was used in the preparation of solutions.

2.2. Experimental procedure

In the extraction equilibrium test, the organic solution and the simulated wastewater (100 mg L^{-1}) were mixed in a glass-stoppered conical flask and shaken mechanically at 145 rpm for 15 min in a thermostatically controlled water bath at a fixed temperature of 298 K at pH 1.0 ± 0.1 with the organic/aqueous (O/A) ratio being 1:1. After phase separation, UV–vis spectrophotometer (722, Shanghai) was used to measure the concentration of hexavalent chromium in the aqueous phase at a wavelength of 540 nm based on the complex formation between 1,5-diphenylcarbazide and Cr(VI). A PHS-3C pH meter was used for the pH measurements. Infrared spectra of the organic solutions were collected on a Fourier transform infrared spectrometer (SPECTRUM ONE B, Perkin–Elmer). The Cr(VI) concentration in the organic phase was calculated on the basis of mass balance.

The distribution ratio of chromium, *D*, was calculated using Eq. (1)

$$D = [\overline{\mathrm{Cr}}]_T/[\mathrm{Cr}]_T \quad (1)$$

where the overbar and the subscript “*T*” denote the organic phase and the total concentration, respectively.

The metal loaded solvent was stripped with NaOH, $NaNO_3$, $NaHCO_3$, or $N_2H_4 \cdot H_2SO_4$ to recover the extracted Cr(VI). All the experiment runs were carried out in duplicate and the analysis was conducted in triplicate for each run. Confidence limit of 96% was used for reliable results.

2.3. Separation of Cr(VI) from acidic solution by N235

The structure and IR spectra of tertiary amine N235 are displayed in Figs. 1 and 2. Fourier transform infrared spectroscopy (FTIR) spectra indicated that the strong absorption peak of methylene appear at 2,855 and 2,926 cm^{-1}, assigned to the symmetric and asymmetric stretching vibration of CH_2 stretches in trialkylamine, respectively. The peak at 1,466 cm^{-1} indicated the presence of CH_2, and the absorption peak at 721 cm^{-1} assigned to the rocking vibration of CH_2. The strong peak near 1,377 cm^{-1} could be due to the symmetric flexural vibration of CH_3. The characteristic absorption peak of tertiary amine N235 appears at 1,098 cm^{-1}. The absorption peak at 1,098 cm^{-1} seems to be the location of complex reaction [21].

Extraction mechanism of tertiary amine is that the basic nitrogen atom can react with variety of inorganic and organic acids to form amine salts and then amine salts react with metallic anion by anion exchange and achieve the goal of separation. The general reactions can be described in Eqs. (2) and (3) [22].

Protonation:

$$(R_3N)_{org} + H^+ + A^- \Leftrightarrow (R_3NH^+A^-)_{org} \qquad (2)$$

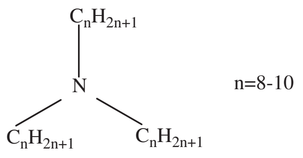

Fig. 1. Structure of N235.

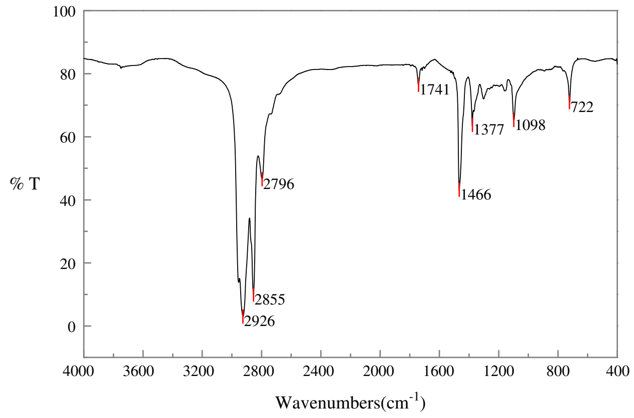

Fig. 2. FTIR spectra of N235.

Exchange:

$$n(R_3NH^+A^-)_{org} + B^{n-}_{aq} \Leftrightarrow [(R_3NH^+)_nB^{n-}]_{org} + nA^-_{aq} \qquad (3)$$

The Cr(VI) ions exist in acidic solution in different forms, such as dichromate($Cr_2O_7^{2-}$), hydrogen chromate($HCrO_4^-$). The fraction of any particular Cr(VI) species is dependent on the Cr(VI) concentration and pH (Fig. 3) [23,24]. Thus, the amine salt extracted the anionic species by an anion exchange mechanism with $HCrO_4^-$ or $Cr_2O_7^{2-}$ at the acidic pH. Therefore, the ion-pair formation at pH 1.0 can be described as follows:

$$R_3NH^+Cl^-_{(org)} + HCrO^-_{4(aq)} \Leftrightarrow [(R_3NH^+)HCrO_4^-]_{(org)} + Cl^-_{(aq)} \qquad (4)$$

$$2R_3NH^+Cl^-_{(org)} + Cr_2O^{2-}_{7(aq)} \Leftrightarrow [(R_3NH^+)_2Cr_2O_7^{2-}]_{(org)} + 2Cl^-_{(aq)} \qquad (5)$$

3. Results and discussion

3.1. Effect of inorganic acid

Different types of inorganic acids, HCl, H_2SO_4, H_3PO_4, and HNO_3 were used to adjust the pH value of simulation wastewater, respectively. The operation conditions were 100 mg L^{-1} of Cr(VI) in acid media and 0.0032 mol L^{-1} N235 diluted in kerosene as organic solution. Fig. 4 suggested that the distribution coefficient D depended strongly on the nature of the type of acid due to the different complex ability of anions (Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^-) with tertiary amine. The distribution coefficient was improved in the following sequence: $HNO_3 < H_3PO_4 < H_2SO_4 < HCl$. Similar observation has been found with tri-n-butyl phosphate (TBP) as the extractant [25]. Thus, HCl was selected for the pH adjustment of simulation wastewater in the following experiments.

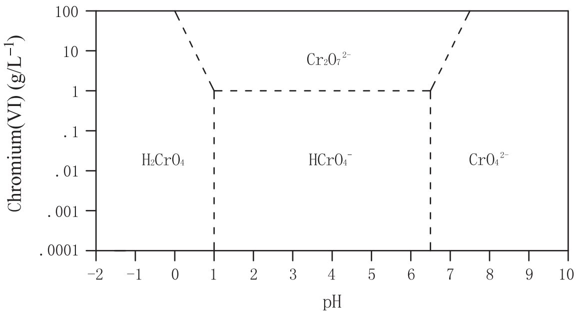

Fig. 3. Speciation diagram of Cr(VI) [14,21].

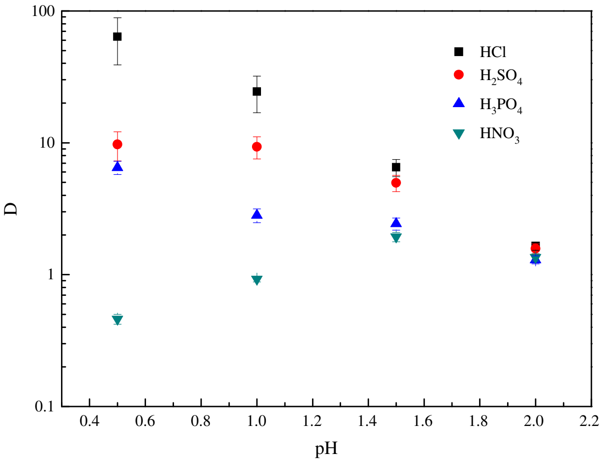

Fig. 4. Effect of inorganic acids on the extraction of Cr(VI).

3.2. Effect of pH value and the N235 concentration

Fig. 5 shows the D values at 298 K as a function of the equilibrium pH at different concentrations of N235. It is illustrated that a decrease in hydrogen ion concentration causes a decrease in the rate of association of Cr(VI) with the N235. This is due to the decrease in H^+ that occurs with increasing pH. The pH of the solution is critical for Cr(VI) extraction and acidic pH at 0.5 ± 0.1 is essential for maximum extraction. The results also indicated that the relationship between log D and pH was a straight line, and the distribution coefficient increased with increasing N235 concentration due to the availability of more reactive sites for chromium(VI). It is agreed with the trend using TBP in kerosene as extractant solvent [25].

3.3. Effect of equilibration time

The influence of equilibration time on the separation of chromium(VI) using N235 was investigated. The extraction results in Fig. 6 implied that 15 min was sufficient for the separation and concentration of hexavalent chromium from its HCl solutions with 0.0032 mol L^{-1} N235 diluted in kerosene. The reaction rate was relatively fast. El-Hussaini [26] also observed that the extraction of Cr(VI) with tertiary amine was slightly improved by increasing the shaking time and achieved to extraction equilibrium after 15 min.

3.4. Effect of the extractant

The extraction abilities of hexavalent chromium with basic extractants (tertiary amine N235 and quaternary amine salt Aliquat336), acidic extractant DEHPA, and neutral extractant TBP were investigated, respectively. Fig. 7 shows the extraction behavior of chromium(VI) with different extractants as a function of pH. Increasing order of the distribution coefficient followed the sequence of TBP < DEHPA < Aliquat336 < N235 < N235 + TBP. The reason is that the mechanism of acidic extractant for metal ion extraction is a cation exchange reaction, and for neutral extractants is a complexation reaction with neutral molecules. However, basic extractants consist of alkyl ammonium species can react with metallic anion ($HCrO_4^-$ or $Cr_2O_7^{2-}$) to form the extracted complex. In addition, it also indicated that the extraction ability of N235 was obviously stronger than Aliquat 336. However, the opposite conclusions had been discovered by El-Hefny and Senol et al. due to the structural differences of Alamine and N235 [13,15]. Ten percent TBP added into the organic solution (N235 diluent in kerosene)

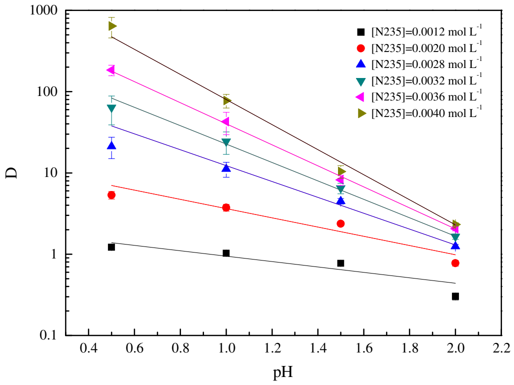

Fig. 5. Effect of pH value and [N235] on the extraction of Cr(VI).

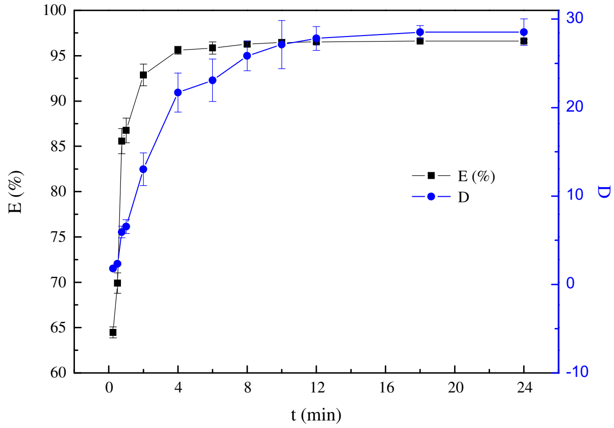

Fig. 6. Effect of equilibration time.

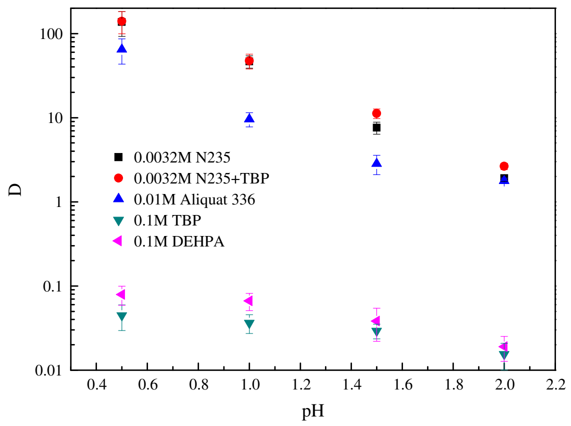

Fig. 7. Effect of extractants.

had little effect on the extraction of the metal. Thus, tertiary amine N235 was selected as the extractant in the following experiment.

3.5. Effect of temperature

The linear relation between log D and $1/T$ with 0.0032 mol L^{-1} as the extractant is described in Fig. 8. As can be observed that, pH value has influence on the enthalpy change under the experimental conditions. The plot of log D vs. $1/T$ for the extraction of the metal gave a straight line, and the slopes of the straight line was 1.88 (pH = 1.0). The enthalpy change of −35.95 kJ mol^{-1} was calculated using the Van't Hoff equation, indicating that the extraction of Cr(VI) from hydrochloric acid medium using N235 as the extractant is an exothermic process. This is in accordance with the findings of Someda et al. [14].

Based on the ΔH value, the free energy ΔG and entropy ΔS were calculated using Eqs. 7 and 8, respectively. The free energy change (ΔG) and entropy change (ΔS) were found to be equal to −7.58 kJ mol^{-1} and −95.18 J mol^{-1} K^{-1} at 298 K, respectively. The values of thermodynamic functions indicate that the extraction of Cr(VI) in this system at 298 K was a spontaneous exothermic reaction.

$$\frac{\Delta \log D_{\mathrm{Cr}}}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{6}$$

$$\Delta G = -2.303RT \log D_{\mathrm{Cr}} \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

3.6. Extraction isotherm of chromium(VI) by trialkylamine

In order to evaluate the loading capacity of trialkylamine for Cr(VI), the extraction distribution isotherm was obtained by contacting 100 mg L^{-1} hexavalent chromium solution with 0.0032 mol L^{-1} N235 at different A:O ratios from 1 to 6 and O:A ratios from 5 to 1 at equilibrium pH 1.0. Fig. 9 illustrated that the calculations of the optimal load of organic solution could be based on mass balance, and the maximum loading was 206.95 mg L^{-1}.

3.7. Effect of the diluent

Commercial diluents were mainly selected in view of industrial application. The behavior of 0.0032 mol L^{-1} N235 mixed with different diluents viz. kerosene, ethyl acetate, dimethyl benzene, n-hexane, n-octanol, isooctane, n-heptane, and n-dodecane at the pre-equilibrated pH of 0.5–2.0 had been evaluated for the extraction of Cr(VI). The results are displayed in Fig. 10(a). Results showed that aromatic diluents such as xylene, and commercial diluents like kerosene,

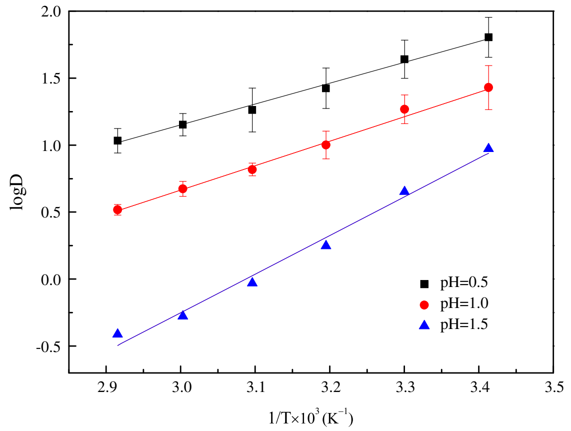

Fig. 8. Effect of temperature.

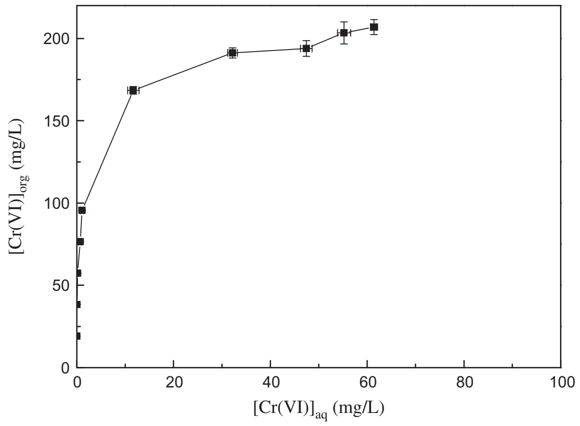

Fig. 9. Extraction equilibrium isotherm for Cr(VI).

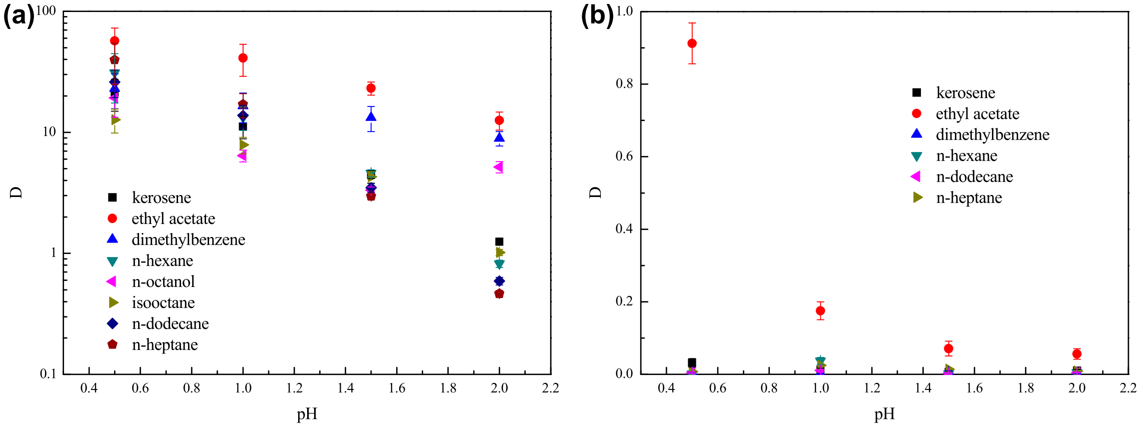

Fig. 10. Effect of diluents with extractant (a) or no extractant (b).

n-hexane, n-heptane, and n-dodecane were efficient for chromium(VI) extraction with N235. Similar observations were made by Agrawal et al. [27].

The effects of diluents on the metal extraction can be related to the dipolarity/polarizability and hydrogen-bond-donating/accepting abilities of organic solvents. The dielectric constant of n-octanol is 10.34, and the viscosity is 10.64, resulting in decrease of free electric charge. It is easy for extracted complexes with hydration layer to be dissolved in the organic solution because of the strong polarity of ethyl acetate, and hence the extraction ability of Cr(VI) from acidic solution by trialkylamine (N235, R_3N, $R = C_8–C_{10}$) using ethyl acetate as the diluent was excellent. In addition, the extraction properties with no extractant added in the kerosene, xylene, and ethyl acetate solution were also evaluated (Fig. 10(b)). It is indicated that extraction behavior can be observed with ethyl acetate as the organic solution. Furthermore, taking into account the toxicity of xylene and n-hexane, kerosene, n-heptane, and n-dodecane were considered to be used for commercial purposes without affecting the extraction of chromium(VI).

3.8. Stoichiometry of extracted species

The stoichiometry of the extracted species was determined by measuring the distribution ratio of Cr(VI) at varying extractant concentrations. The relationship between the distribution ratio and the N235 concentration is shown in Fig. 11(a) on a log–log scale. The plot of log D vs. log N235 give a straight line of slope of 3, indicating that the extraction reaction is complicated and extracted complex is $Cr_2O_7^{2-} \cdots + 2NHR_3$ or $HCrO_4^- \cdots + NHR_3$.

The relationship of the mole ratio between the loading chromium(VI) concentration and the N235 concentration is displayed in Fig. 10(b). The result showed that complexation reaction between chromium and N235 in organic solution occurred. On the basis of the equimolar series method analysis, the molar ratio between N235 and hexavalent chromium ion in the extracted complex was identified to be 1 at pH 1.0, and mole ratio between chromium(VI) and N235 was 1.0. Similar observations are found for tertiary amine TOA in kerosene by Kumbasar et al. and Hostarex A327 (tertiary amine) in cumene by Alguacil et al. [28,29]. On the basis of slope method and equimolar series method analysis, the extracted complex ratio was different. Based on the analysis of the anionic species in Fig. 3 and literature material, the extracted complex seems to be $HCrO_4^- \cdots + NHR_3$ with 100 mg L^{-1} simulated wastewater at pH 1.0.

3.9. Stability of organic solution before stripping

The stability of the loading organic solution is the foundation of reuse. Thus, in order to investigate its stability in the separation process, the loading organic solution was deposited in different environmental conditions to observe the change of the solution. The result was shown in Fig. 12. The "a" and "b" represent the environment conditions of in the dark and in the light, respectively. It is illustrated that the colors of solutions fade obviously in light and the solution structure changed owning to photolysis. The precipitation of photolysis was dried in 1 h at 80℃ after filtration. The infrared spectrum of the precipitate is displayed in Fig. 13. It has been illustrated that the peaks at about 3,362 cm^{-1} is the typical symmetric or asymmetrical stretching vibration peaks of NH_2, the

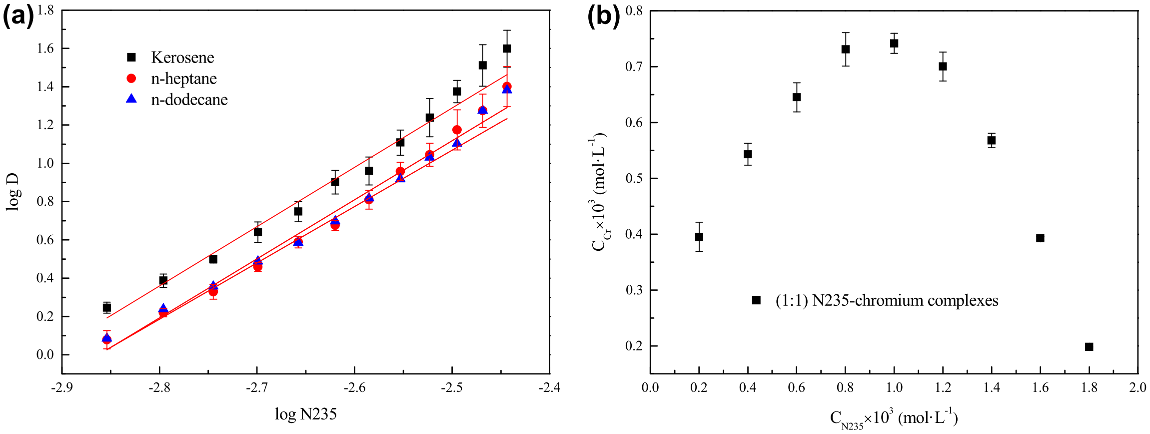

Fig. 11. Stoichiometry of the extracted ion pair by the slope method (a) and by equimolar series method (b).

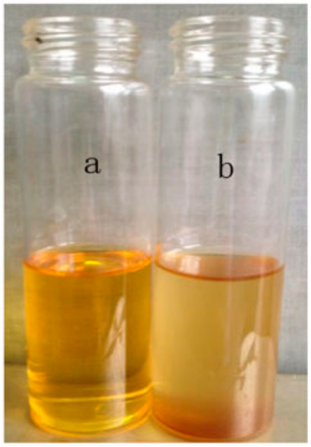

Fig. 12. The loading organic solution deposit in different environment conditions.

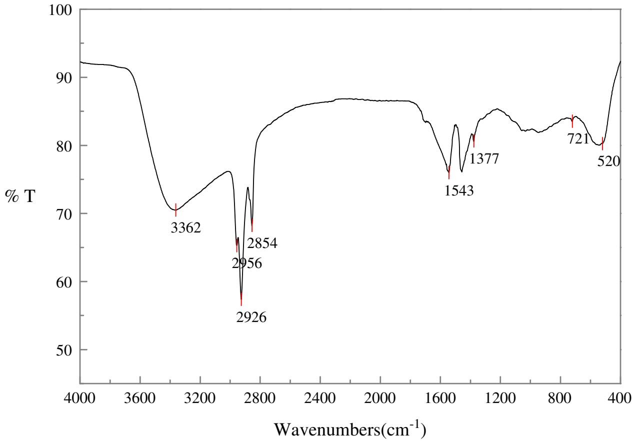

Fig. 13. FTIR spectra of the precipitate.

peaks at about 1,542 and 1,457 cm^{-1} are the variable-angle vibration of NH_3^+ and NH_4^+, respectively. The reason seems to be that the N atom can combined with H^+ ions with the stimulation of light.

3.10. Stripping of loaded organic and reuse of the extractant

Stripping of the metal from the loaded organic solution can be achieved by breaking down of the anionic metal complex. For any commercial operation, it is necessary to reuse the organic solution without significant loss of extraction ability. The aqueous phase was equilibrated with the organic phase at a 1:1 phase ratio. Sodium hydroxide, sodium nitrate, sodium bicarbonate, and hydrazine sulfate was used as the stripping reagent. The results are displayed in Table 1. It is illustrated that NaOH, $NaNO_3$, and $NaHCO_3$ can realize the recovery of chromium(VI) and the reuse of the extractant. In addition, 10 g L^{-1} hydrazine sulfate is an effective reducing agent and can reduce the carcinogenic chromium(VI) to the less toxic chromium(III) species. The influence of NaOH concentration on the recovery of Cr(VI) is shown in Table 2. The results indicated that the concentration of NaOH stripping solution has no significant effect on the recovery of chromium(VI). The stripping reagent such as NaCl, NaOH, Na_2SO_4, NH_4Cl, NH_4OH, HCl, and HNO_3 were used for evaluating the recovery of chromium(VI) by Agrawal and NaOH was also to be selected for the regeneration of the extractant [27].

For assessment of the recycling behavior of N235, successive extraction and stripping cycles of Cr(VI) were carried out. The raffinate was separated, and the loaded organic phase was stripped with 0.1 mol L^{-1} of NaOH solution. After separation of the strip solution,

Table 1
Effect of different stripping agent on the recovery of Cr(VI)

	Kerosene (%)	n-Heptane (%)	n-Dodecane (%)
0.1 mol L^{-1} NaOH	98.9 ± 0.7	96.8 ± 1.7	94.4 ± 1.5
1 mol L^{-1} $NaNO_3$	94.2 ± 1.2	92.1 ± 1.0	92.3 ± 1.6
0.5 mol L^{-1} $NaHCO_3$	96.3 ± 0.8	95.2 ± 1.2	94.2 ± 1.4

Table 2
Effect of NaOH concentration on stripping of Cr(VI) from loaded organic at 298 K

NaOH (mol L^{-1})	$Cr(VI)_{f,ini}$ (mg L^{-1})	$Cr(VI)_{s,eq}$ (mgL^{-1})	R (%)
0.001	98.88	45.30	45.8 ± 1.4
0.01	98.88	95.10	96.2 ± 1.1
0.05	98.88	95.46	96.5 ± 2.0
0.1	98.88	97.80	98.9 ± 0.7

the regenerated extractant was used for further cycles of extraction and stripping tests. No appreciable decrease in the extraction efficiency (%E) was observed during six regeneration steps. The reaction mechanism was summarized as follows.

$$[(R_3NH)\cdot HCrO_4]_{(org)} + 22NaOH_{(aq)} \Leftrightarrow R_3N_{(org)} + Na_2CrO_{4(aq)} + 2H_2O \qquad (9)$$

4. Conclusions

The extraction method demonstrates the utility of N235 using kerosene as the diluent for the separation of chromium(VI) from hydrochloric acid solutions. The optimized conditions for extraction of Cr(VI) were investigated. The results demonstrated that the optimum extraction condition was N235 as the extractant diluted in kerosene at the pre-equilibrated pH of 1.0. The thermodynamic functions (enthalpy change ΔH, free energy change ΔG, and entropy change ΔS) for the extraction of Cr(VI) have been calculated, and the ΔH, ΔG, and ΔS at 298 K were −35.95, −7.58, and −95.18 J mol^{-1} K^{-1}, respectively, indicating that the extraction reaction was a spontaneous exothermic process. Furthermore, the light can influence the stability of the loading organic solution and the structure of the solution can be destroyed by photolysis. NaOH concentration had no significant effect on the percentage of extraction and 98.91% of the Cr(VI) could be recovered with 0.1 mol L^{-1} of NaOH solution. The regenerated metal extractant could be used for six extraction and stripping cycles with good precision and reproducibility.

Acknowledgments

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