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Compressed Air-Assisted Solvent Extraction (CASX) for Chromate Removal: Regeneration and Recovery

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Abstract: Compressed air-assisted solvent extraction (CASX), was employed to remove Cr(VI) from synthetic wastewater and electroplating wastewater with the effects of pH, extractant/diluent ratio, solvent dosage, and competing anion concentration on Cr(VI) removal efficiency explored. The dosages required for Cr(VI) removal are dependent upon the speciation of Cr(VI) with molar ratio between Aliquat 336 and Cr(VI) of 1:1 and 2.8:1 for HCrO_4^- and CrO_4^{2-} , respectively. Efficiency of Cr(VI) regeneration is influenced by pH and chloride ion concentrations. Based on the affinity order of $\text{HCrO}_4^- > \text{Cl}^- > \text{CrO}_4^{2-} > \text{OH}^-$ to Aliquat 336 concluded from this study, alternation of Cr(VI) species to CrO_4^{2-} by raising solution pH up to 8 and addition of chloride (50 times more of Aliquat 336 dosage applied) can satisfy the Cr(VI) regeneration from the spent solvent phase.

Keywords: Aliquat 336, Cr(VI), recovery, solvent extraction

INTRODUCTION

Chromate-containing wastewater is extremely toxic and has to be properly treated before being discharged. Chromium removal by extraction related

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processes have been extensively investigated recently, including liquid-liquid extraction (1), supported liquid membranes (SLM) (2–5), and bulk liquid membrane (4,6). These processes come with various degrees of success and shortfalls. For example, long extraction time and high solvent dosage, i.e., low aqueous/solvent ratio (A/S ratio), are required to achieve high contaminant removal efficiency for traditional liquid-liquid extraction (7).

In our previous studies (8,9), a novel process, compressed air-assisted solvent extraction (CASX), was proposed and studied for metal removal. The proposed process incorporates an air-pressured solvent tank to provide air-oversaturated solvent and a glass reactor to house metal-containing samples to be treated. Through pressurization of the solvent, i.e., a mixture of extractant and diluent (to avoid confusion term “solvent” should refer only to the mixture of extractant + diluent), with compressed air, CASX generate micro-sized solvent-coated air bubbles (MSAB) instantaneously, making the extraction process extremely fast even with very high A/S ratio. Applied for Cr(VI) removal from acidic electroplating wastewater (initial Cr(VI) of 645 mg l^{-1} and pH of 1.96), CASX achieved completely removal of Cr(VI) with A/S ratio of 115 and extraction time of less than 10 sec. In the case of removing Cd(II) (50 mg l^{-1}) from synthetic wastewater (8), a remarkable removing efficiency was seen in high A/S ratios of 714 and 1190 with the solvent having the extractant/diluent weight ratio of 1:1 and 5:1, respectively (8). Meanwhile, MSAB have very different physical properties, such as size and density, compared to the emulsified solvent droplets, making the separation and the recovery of the solvent from treated effluent very easy.

In this study, the removal of Cr(VI) by CASX under various experimental conditions and regeneration/recovery of Cr(VI) from spent solvent were studied. The specific objectives of this study are to investigate

1. Cr(VI) removal by CASX, exploring the effects of operation conditions such as pH, extractant/diluent ratio, solvent dosage, and competing anion concentration on Cr(VI) removal efficiency, and
2. the recovery of Cr(VI) from the spent solvent, investigating the effects of regenerant compositions on Cr(VI) recovery efficiency.

EXPERIMENTAL

All chemicals were of reagent grade. Synthetic wastewaters containing Cr(VI) were prepared from potassium chromate (Riedel-de Haën) diluted with deionized water. Trioctylmethylammonium chloride (Aliquat 336),

a quaternary ammonium salt, obtained from ACROS was employed as the metal carrier (5,10,11). Kerosene (CPC Corporation, Taiwan) purchased from a local gas station was chosen as the organic diluent. Various weight ratios of Aliquat 336/kerosene mixtures, i.e., the solvent, were prepared before experiments. Electroplating wastewater was collected from a local electroplating facility in northern Taiwan during 2004/10-2005/7, and the pH of wastewater is quite acidic with Cr(VI) concentration in the ranges of 400–887 mg l⁻¹ (12,13).

The schematic setup of the proposed process has been described in our previous papers (8,9). It consists of a solvent tank made of stainless steel with a solvent compartment (I.D. of 10 cm; height of 10 cm) connecting to air compartment (I.D. of 10 cm; height of 5 cm) through a narrow passage (I.D. of 1 cm; length of 5 cm) and a glass column reactor (I.D. of 6 cm; height of 50 cm) housing 500 ml of Cr(VI)-containing aqueous solution (pre-equilibrated in a 25°C water bath). After generating solvent-coated air bubbles, the aqueous phase was allowed to react with solvent-coated air bubbles for 5 min under gentle aeration (0.61 min⁻¹). In order to determine the dosage of the solvent, the solvent was refilled to the pressurized vessel to the liquid level marked previously, and therefore the amount of the solvent added was determined.

Samples taken from the reactor were filtered immediately under vacuum through a 1.2 µm GF/C glass microfiber filter paper (Whatman, Middlesex, UK). As indicated previously (8), the membrane filtration is quite effective for separating the solvent from the aqueous solution, with more than 99.97% of chemical Oxygen Demand (COD) were removed by a 1.2 µm filter paper. Cr(VI) was analyzed colorimetrically according to the standard method 3500B, and COD was analyzed followed the standard method 5520C (14).

After Cr(VI) was extracted to the solvent phase and separation of Cr(VI)-loaded solvent from treated water was achieved (15), Cr(VI) can be stripped from the solvent phase with suitable regenerant added. In the current study, to prevent the loss of the solvent phase during the solvent recovery process imparting complication on the interpretation of regeneration result, a regenerant was applied immediately to the samples collected right after CASX treatment accompanying with residual Cr(VI) concentration (C_r) detection. After the regenerant was added, samples were mixed for at least an hour and filtered. According to the preliminary data, the equilibrium can be attained within one hour. Cr(VI) concentration in the filtrate was analyzed (C_t) and regeneration efficiency was calculated using the following equation.

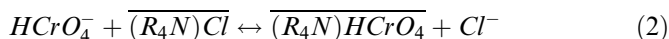
$$\text{Regeneration}(\%) = \frac{C_r - C_t}{C_i - C_t} \times 100\% \quad (1)$$

where C_i , C_t , and C_r are the concentration of Cr(VI) in the initial solution, after CASX treatment, and after regeneration process, respectively.

RESULTS AND DISCUSSION

Effect of Aliquat 336/Kerosene Ratio

The effects of different Aliquat 336/kerosene ratios, 1:1 and 5:1, on Cr(VI) removal by the CASX process were investigated using the mixtures of wastewaters collected from a local electroplating facility in northern Taiwan. Initial pH and Cr(VI) concentration of the wastewater tested are 2.0~2.2 and 645 mg l⁻¹, respectively. As indicated in Fig. 1, the Cr(VI) removal efficiency is independent of Aliquat 336/kerosene ratios while it is dependent on the amount of Aliquat 336 applied. At the pH and concentration studied, Cr(VI) presents mainly as hydrogen chromate ion in the system (12), and the removal of Cr(VI) by Aliquat 336 can be described under the assumption of stoichiometric of 1:1 molar ratio between Cr(VI) and Aliquat 336 shown in reaction (2) (5,11,16).



With the assumption of 1:1 molar ratio between HCrO_4^- and Aliquat 336, a straight line for Cr(VI) removal efficiency as a function of Aliquat

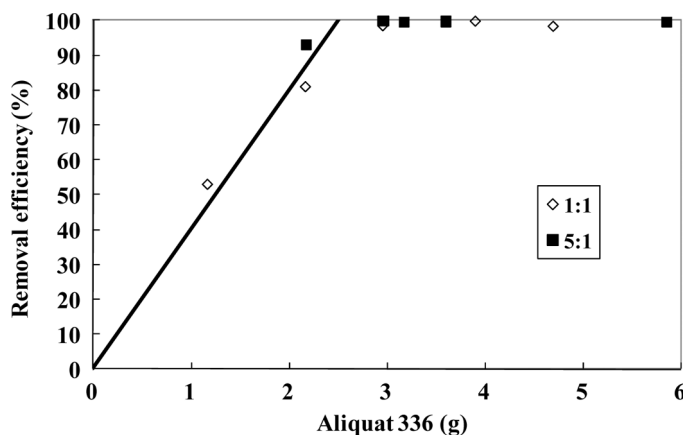


Figure 1. Cr(VI) removal efficiency as function of Aliquat 336 dosages for Aliquat 336/kerosene ratios of 1:1 and 5:1, respectively. Initial Cr(VI) concentration = 645 mg l⁻¹. Initial pH = 2.0~2.2. Volume treated = 500 ml.

336 dosage was drawn, fitting the experimental data quite well (see Fig. 1). Thus, complete removal of Cr(VI) from a 500-ml of the wastewater with initial concentration of 645 mg l^{-1} , i.e., 0.0062 mol of Cr(VI) in the solution, will need 2.5 g of Aliquat 336 ($\text{MW} = 404.15$). At this dosage, concentration of Cr(VI) in the solvent phase for the system treated with Aliquat 336/kerosene ratio of 1:1 is around 45.7 g l^{-1} while that with Aliquat 336/kerosene ratio of 5:1 is around 76.1 g l^{-1} , making the recovery and the reuse of Cr(VI) economically possible.

Effects of pH

The effect of initial pH on Cr(VI) removal by CASX was studied in the pH ranges of $1 \sim 9$ with synthetic wastewater containing Cr(VI) of 100 mg l^{-1} . Under the pH range and Cr(VI) concentration studied, the dominated Cr(VI) species is HCrO_4^- for pH ranging from 1 to 6 and is CrO_4^{2-} for pH from 7 to 9, based upon the modeling by the chemical equilibrium software, Mineql+ (pK_{a1} and pK_{a2} are 0.86 and 6.51, respectively) (17). Several studies have reported firmly of pH dependence of Cr(VI) removal, showing that the removal efficiency decreased with increasing pH (4,18–20). For example, Venkateswaran and Palanivelu studying the Cr(VI) removal by SLM using tri-*n*-butyl phosphate (TBP) as carrier reported that the Cr(VI) removal efficiency decreased with increasing pH from 1.0 to 5.0, and no Cr(VI) removal at pH 5 was observed within an extraction duration up to 8 hrs (18).

As indicated in Fig. 2, the relationships of the Cr(VI) removal efficiency vs. Aliquat 336 dosage can be grouped into two distinguishable groups. One group is represented by filled symbols and is for initial pHs ranging from 1 to 6. The other is represented by open symbols and is for initial pHs of 7 to 9. Since Aliquat 336 is a quaternary ammonium salt and solution pH would not affect the speciation of Aliquat 336 in the solvent phase, the effect of the initial pH on the Cr removal is mainly related to the dominant species of Cr(VI) in the aqueous phase.

The differences of Cr(VI) removal phenomena reported by others (4,18–20) to the present one are mainly due to variable metal carriers employed. Aliquat 336 used in this study contains a positively charged quaternary ammonium functional group which might be less susceptible to pH influence at the pH range been investigated. On the other hand, TBP or carriers containing tertiary amine functional groups have to form cationic species through protonation in order to interact with the anionic Cr(VI) and are highly pH dependent (4,15,16).

As the dominant species changes from HCrO_4^- to CrO_4^{2-} for $\text{pH} > 6$ conditions, the dosage of Aliquat 336 required for removing CrO_4^{2-} should

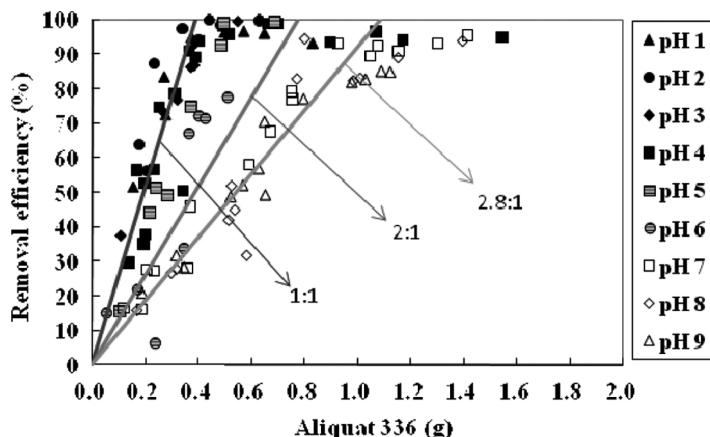
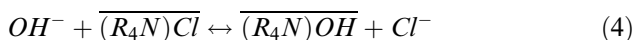
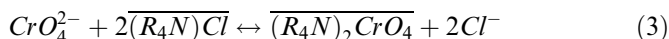


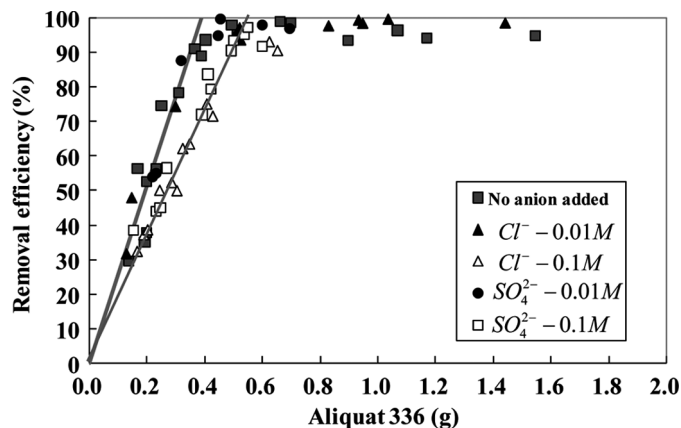
Figure 2. Cr(VI) removal efficiency as function of Aliquat 336 added for various initial pHs. Aliquat 336/kerosene ratio = 1:10. Initial Cr(VI) concentration = 100 mg l^{-1} . Volume treated = 500 ml.

be twice the amount for removing the same percentages of HCrO_4^- according to the exchange reaction between chloride and CrO_4^{2-} described in Eq. (3) by others (5,11). However, the theoretic line based on 2:1 stoichiometric molar ratio between Aliquat 336 and CrO_4^{2-} does not fit well to the experimental data (see Fig. 2). Instead, the best Aliquat 336 and CrO_4^{2-} ratio to fit the experimental data is 2.8, indicating that the competition of hydroxide ions for Aliquat 336 as indicated in Eqs. (4) (16) has taken place and/or the distribution coefficient between CrO_4^{2-} and Aliquat 336 is much weaker than that between HCrO_4^- and Aliquat 336 (16,21).

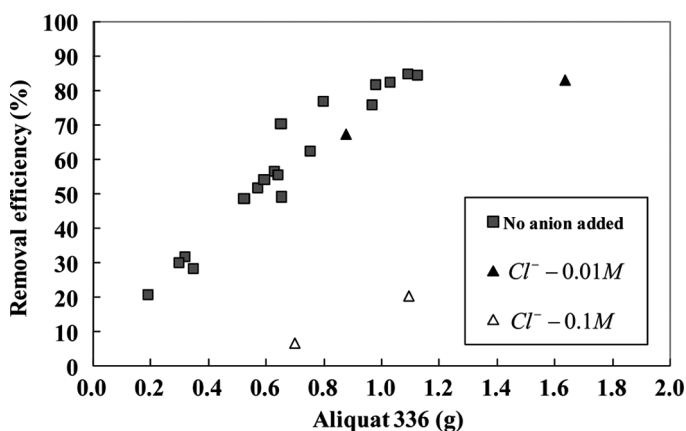


Effects of Anion Concentration

Equations (2)–(4) shown above reveal that the Cr(VI) removal might be affected by the presence of competing anions such as chloride and sulfate. According to Galan et al. (5), the presence of these anions has been shown to affect the Cr(VI) removal efficiency. In this study, the effect of anions were first tested at fixed pH of 4.0 initially with anion concentrations of ranging from 0 to 0.1 M and Cr(VI) concentration of 100 mg l^{-1} .



(a)



(b)

Figure 3. Cr(VI) removal efficiency as function of Aliquat 336 added for various anion concentrations at (a) fixed pH of 4.0 and (b) 9.0, respectively. Initial Cr(VI) concentration = 100 mg l^{-1} . Aliquat 336/kerosene ratio = 1:10.

As indicated in Fig. 3a, both chloride and sulfate concentrations of up to 0.01 M did not show any impact on the removal of Cr(VI), and anion concentrations of as high as 0.1 M for both anions show slight impact on the removal efficiency.

As indicated previously, the dominated Cr(VI) species is HCrO_4^- at the acidic pH range, which has much stronger affinity to Aliquat 336 than that of CrO_4^{2-} (16,21). Therefore, the effect of chloride on Cr(VI) removal efficiency was further investigated at pH of 9.0 to explore the change of Cr(VI) species from HCrO_4^- to CrO_4^{2-} . As indicated in Fig. 3b, the chloride

concentration of 0.01 M has no impact but that of 0.1 M has a much more severe impact than that observed at pH 4.0 condition. The presence of chloride ions at the concentration of 0.1 M has decreased the removal efficiency from 50 and 80% to 7 and 20%, respectively, for the two Aliquat 336 dosages that have been introduced. Based on these results, one can conclude that the affinity of these anions for Aliquat 336 is in the order of $\text{HCrO}_4^- > \text{Cl}^- > \text{CrO}_4^{2-}$.

Cr(VI) Regeneration

Based on the results shown above, the pH and anions which have a impact on the removal efficiency of Cr(VI), would also affect the regeneration of Cr(VI) from the spent solvent. Several regeneration conditions were investigated and applied to samples taken from CASX system. After CASX treatment, residual Cr(VI) concentration (C_r) in both the aqueous phase and the dose of Aliquat 336 applied were determined. The amount of Cr(VI) removed by CASX, i.e., the amount of Cr(VI) in the solvent phase, could then be calculated. Various NaOH concentrations and chloride-to-Aliquat 336 molar ratios (1:1, 10:1, 50:1, and 100:1 and denoted as 1X, 10X, 50X, and 100X, respectively) were applied by adding NaCl as a regenerant for extracting chromium ion. After the regenerant was added, samples were mixed for at least one hour and then filtered. Cr(VI) concentration and pH in the filtrate were analyzed for calculating the regeneration efficiency.

Figure 4 indicates that both the pH and the chloride ion concentration have great impact on the regeneration efficiency of Cr(VI). At pHs lower than 7, the dominated Cr(VI) species is HCrO_4^- which has high affinity to Aliquat 336 (16,21) with a regeneration efficiency less than 20% even though the applied chloride-to-Aliquat 336 molar ratio was up to 100. On the other hand, the regeneration efficiency increases with increasing pH of above 7. There are two possible explanations for the observation. One is the change of Cr(VI) speciation from HCrO_4^- to CrO_4^{2-} as pH changed, and the other is the competition of hydroxide ions for chelating function groups of Aliquat 336 as described above in Eq. (4).

To explore the effects of these two possible reasons, regeneration experiments were conducted under high and low Aliquat 336 dosages conditions. The Aliquat 336 dosages are 5 and 1.5 times of initial Cr(VI) molar concentration and are indicated as high and low conditions, respectively. Under the high Aliquat 336 dosage condition, no sign of Cr(VI) recovery in aqueous phase by increasing pH from 4 to around 12 (see Fig. 5). If increasing pH beyond 7 will alter the speciation of Cr(VI) from HCrO_4^- to CrO_4^{2-} in the solvent phase, the amount of Aliquat 336 required

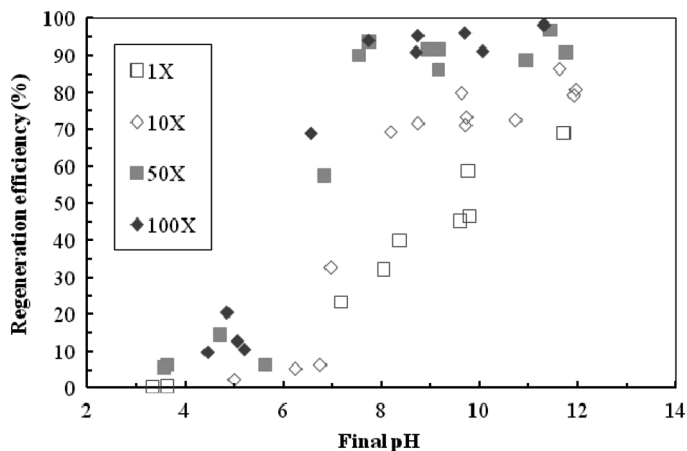


Figure 4. Cr recovery efficiency as a function of regenerant pH for various Cl^- to Aliquat 336 molar ratios. Regeneration time = 3 hrs.

for complete removal of Cr(VI) will increase 2.8 times based on 1:1 and 2.8:1 molar ratios between HCrO_4^- and CrO_4^{2-} , respectively, to Aliquat 336 shown before. Under the high dosage condition, Aliquat 336 applied is 5 times more than the initial Cr(VI) molar concentration which can meet the requirement of completed removal of CrO_4^{2-} , and no sign of Cr(VI) recovery in the aqueous phase as indicated in Fig. 5. Based on this result,

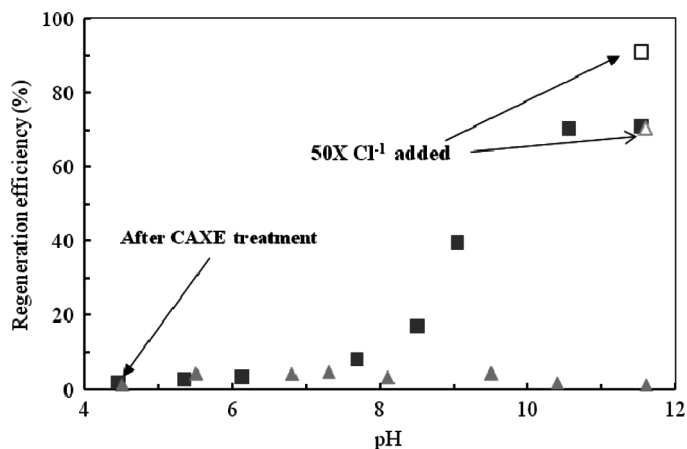


Figure 5. Cr recovery efficiency as a function of regenerant pHs under high (triangle symbols) and low (rectangle symbols) Aliquat 336 dosage. Regeneration time = 3 hrs.

one can conclude that the competition of hydroxide ions with CrO_4^{2-} for chelating function groups of Aliquat 336 is not the responsible mechanism for Cr(VI) regeneration.

On the other hand, the amount of Aliquat 336 applied under low dosage condition, i.e., 1.5 times more of Aliquat 336 than initial Cr(VI) molar concentration, is short of the dosage required for complete removal of CrO_4^{2-} , resulting in higher Cr(VI) concentration in aqueous phase at pH higher than 7. Finally, NaCl was added to the sample with the highest pH at the chloride-to-Aliquat 336 molar ratio of 50 to explore the role of chloride ions during regeneration. As shown in Fig. 5, the Cr(VI) regeneration efficiency increases dramatically to 71% under the high Aliquat 336 dosage condition with the pH increased (open triangle in Fig. 5), and additional increases (20%) in Cr(VI) regeneration efficiency can also be seen after chloride ions added for the low Aliquat 336 dosage condition (open rectangle in Fig. 5). Based on these results, the affinity of these ions with Aliquat 336 can be ordered as $\text{HCrO}_4^- > \text{Cl}^- > \text{CrO}_4^{2-} > \text{OH}^-$.

CONCLUSIONS

This study investigated the removal of Cr(VI) by CASX and regeneration/recovery of Cr(VI) from spent solvent under various experimental conditions, exploring the effects of pH, extractant/diluent ratio, solvent dosage, and competing anion concentration on Cr(VI) removal efficiency. The effect of the initial pH on Cr removal is mainly related to the dominant species of Cr(VI) in the aqueous phase, since Aliquat 336 is a quaternary ammonium salt which is not affected by the solution pH. The removal of HCrO_4^- followed the 1:1 molar ratio assumption between HCrO_4^- and Aliquat 336. However, the theoretic line based on 2:1 stoichiometric molar ratio between Aliquat 336 and CrO_4^{2-} does not fit well to the experimental data. Instead, the best Aliquat 336 and CrO_4^{2-} ratio to fit the experimental data is 2.8, indicating the possibility of hydroxide ion competing for Aliquat 336 and much weaker affinity between CrO_4^{2-} and Aliquat 336 than that between HCrO_4^- and Aliquat 336. Finally, the regeneration of Cr(VI) from the spent solvent was investigated with the effects of pH and chloride ion concentrations explored. The affinity of these ions with Aliquat 336 was ordered as $\text{HCrO}_4^- > \text{Cl}^- > \text{CrO}_4^{2-} > \text{OH}^-$ based on this study. Based on the affinity order, the alternation of Cr(VI) species to CrO_4^{2-} by raising solution pH up to 8 and the addition of chloride (50 times of the Aliquat 336 dosage applied) can achieve a satisfactory regeneration of Cr(VI) from the solvent phase.

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