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Liquid−Liquid Extraction of Chromium(VI) with Tricaprylmethylammonium Chloride Using Isoamylalcohol as the Diluent and Its Application to Industrial Effluents

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A simple liquid−liquid extraction (LLE) method has been developed for the separation and determination of chromium in industrial wastewater. The Cr(VI) is held by electrostatic attraction as an ion-association complex of $HCrO_4^-$ with tricaprylmethylammonium chloride and extracted into the organic phase using isoamylalcohol (IAA) as the diluent. The extract was clear without any third-phase formation. The effects of various experimental parameters that affect the extraction process have been examined in detail. The organic phase containing the metal extractant could be regenerated using ascorbic acid as the reducing agent. The organic phases were characterized with Fourier transform infrared (FT-IR) studies. The method was applied to the extraction of chromium from synthetic effluents, real wastewater samples, and a certified reference material.

1. Introduction

The global concern for heavy metal pollution requires the development of simple and eco-friendly methods for detoxification. Chromium is one such heavy metal that requires considerable attention. Environmental contamination due to chromium arises mainly from the electroplating, tannery, and dyeing industries.[1,2] Solid phase and liquid−liquid extraction are widely used techniques for the detoxification of chromium.[3−7] Solvent extraction techniques find excellent utility in the recovery of industrially important metals.[8,9] In addition, this technique finds extensive application in the reprocessing of spent nuclear fuels.[10] Chelating agents such as crown ethers,[11] diphenylcarbazide,[12] and di-2-ethylhexylphosphoric acid (D2EHPA)[13] are known to be versatile extractants for metals.

Liquid ion-exchangers, especially long-chain amines, offer even more selectivity for various metals including chromium.[14−17] In this context, tricaprylmethylammonium chloride commercially known as Aliquat-336 is an important extractant which is a room temperature ionic liquid[18,19] and has been explored as a supported liquid membrane by many researchers for the removal of chromium.[20−22] More recently, Aliquat-336 has even found excellent application in the extraction of cephalosporin antibiotics.[23]

Most of the reported extraction techniques with Aliquat-336 involve solvents such as toluene,[24] xylene,[25] and chloroform.[26] In solvents such as kerosene, tributylphosphate and isodecanol are used as modifiers to avoid third-phase formation.[27,28] The objective of the present work is to detoxify chromium from wastewater using Aliquat-336 as the extractant with greener and more environmentally benign diluents. Isoamylalcohol (IAA) serves as a relatively eco-friendly alternative solvent for Aliquat-336 that has not been reported to date for the extractive separation of chromium.

In this paper, we report on a study of the extraction behavior of chromium with Aliquat-336 using IAA as the diluent. The effect of various experimental parameters and the subsequent application to real effluent samples is discussed in detail. Considerable emphasis is also placed on the regeneration of the organic phase for the process to be greener.

2. Experimental Section

2.1. Chemicals. All reagents were of analytical grade. Milli-Q water (MQW) (Elix 3, conductivity 0.12 $\mu S\cdot cm^{-1}$) was used in the preparation of solutions. A portion of 2.826 g of potassium dichromate (Merck, India) was diluted to 1000 mL with MQW to give a 1000 $\mu g\cdot mL^{-1}$ chromium(VI) solution. A working

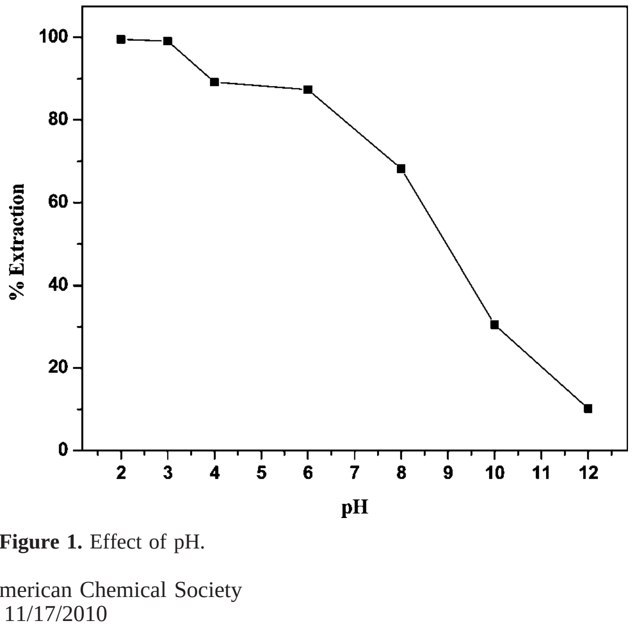

Figure 1. Effect of pH.

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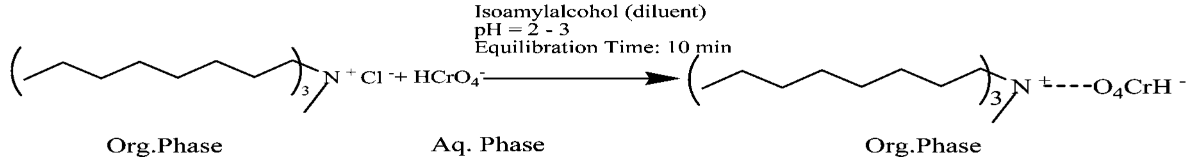
Scheme 1. Mechanism of Chromium Extraction



solution of 10 μg·mL^{-1} was prepared by appropriate dilution. Sulfuric acid (Qualigens Fine Chemicals, Mumbai, India) of 1 mol·L^{-1} was prepared by appropriate dilution. Sodium hydroxide, sodium sulfite, and ascorbic acid (Merck, India) of the required concentrations were prepared by appropriate dilution with MQW. IAA, cyclohexane, methyl isobutyl ketone (MIBK), and *n*-hexane were procured (Merck, India) and used in the experiments without further purification. A 0.124 mol·L^{-1} solution of Aliquat-336 (Merck, India) was prepared by dissolving the appropriate amounts of reagent using IAA as the diluent. Real wastewater samples were collected from electroplating and tannery units in Tamil Nadu (India). BCR-715 (Certified Industrial Waste Water Effluent) was procured from the European Commission-Joint Research Centre-Institute of Reference Materials and Measurements (EC-JRC-IRMM), Geel, Belgium.

2.2. Instrumentation. A JASCO V-650 model UV−visible spectrophotometer was used to measure the concentration of chromium, and 1 cm matched quartz cells were used for the absorbance measurements. The Fourier transform infrared (FT-IR) characterization was performed using a Prestige IR-20 Shimadzu FT-IR spectrometer. An Elico LI-127 model pH meter was used for the pH measurements.

2.3. Extraction of Chromium. A 1 mL volume of 5 μg·mL^{-1} chromium(VI) solution was acidified to pH 2 with 1 mol·L^{-1} sulfuric acid in a 60 mL separating funnel. The aqueous phase volume was maintained at 10 mL and equilibrated for 10 min with 10 mL of 0.124 mol·L^{-1} Aliquat-336 in IAA. The % extraction was calculated by measuring the concentration of chromium in the organic and aqueous layers. The percentage extraction (*E*) was calculated using the relation

$$E = 100D/(D + (V_{\mathrm{aq}}/V_{\mathrm{org}}))$$

where D is the distribution ratio, which is $[\mathrm{Cr}]_{\mathrm{org}}/[\mathrm{Cr}]_{\mathrm{aq}}$, and V_{aq} and V_{org} refer to the volume of the aqueous and organic phases, respectively. Cr(III) was not extracted under the above conditions. Cr(VI) was quantified by measuring the concentration in the aqueous phase spectrophotometrically by the standard diphenyl carbazide method at 540 nm as well as by measuring the absorbance of the ion-association complex at 335.4 nm against the reagent blank. The organic phase containing Cr(VI) was stripped with ascorbic acid to the less toxic Cr(III) in the aqueous phase and subsequently oxidized to Cr(VI) with alkaline H_2O_2 and further estimated by the standard diphenylcarbazide method.

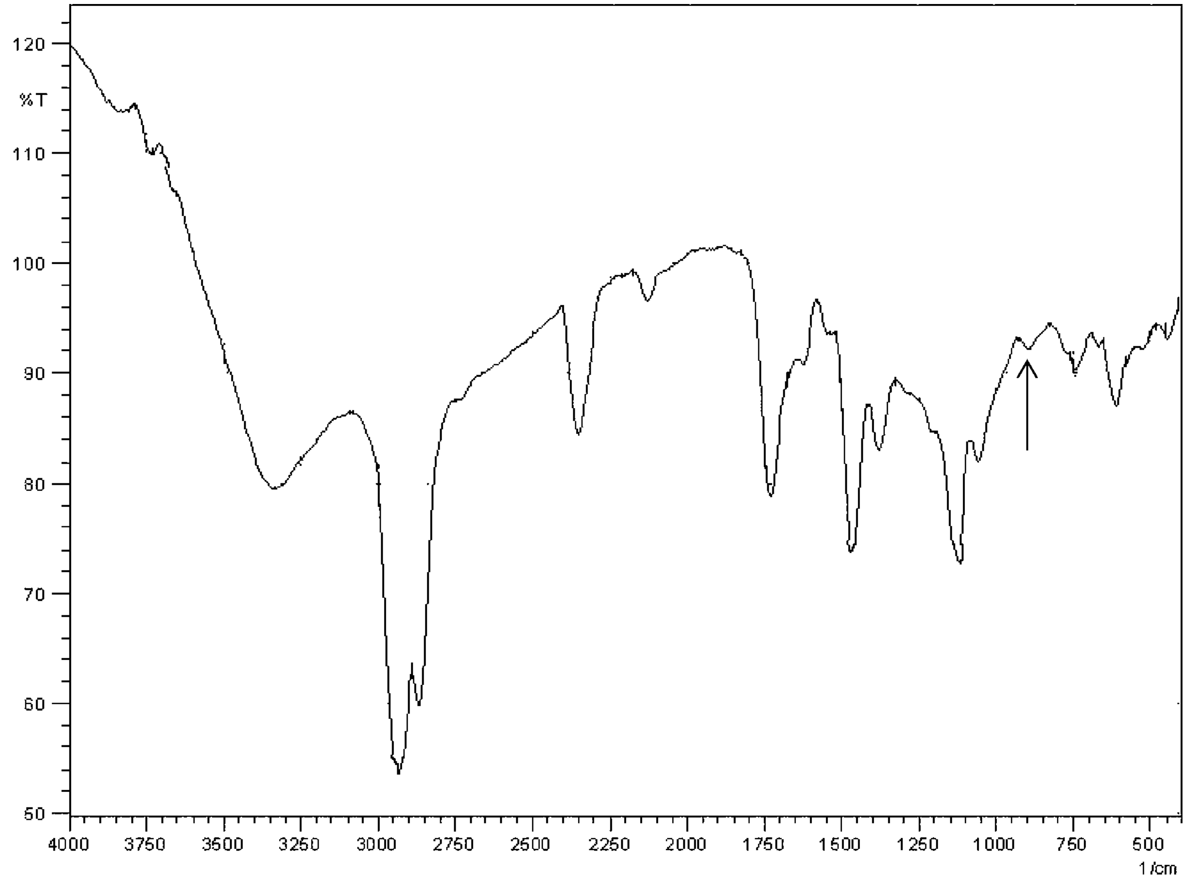


Figure 2. FT-IR spectrum of the Cr(VI)−Aliquat-336 ion pair in the organic phase.

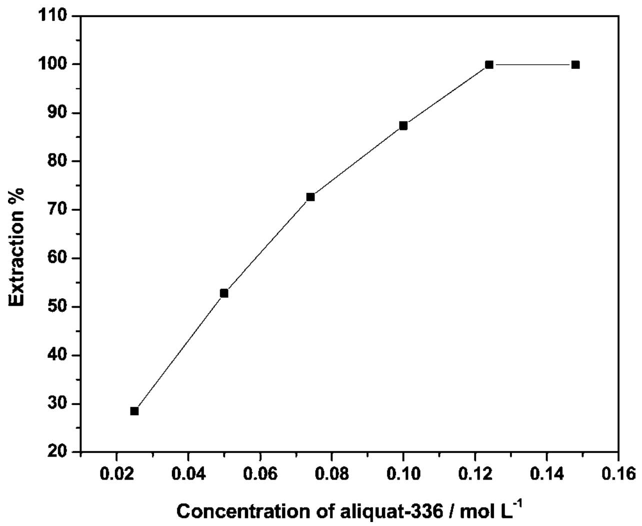


Figure 3. Effect of concentration of Aliquat-336.

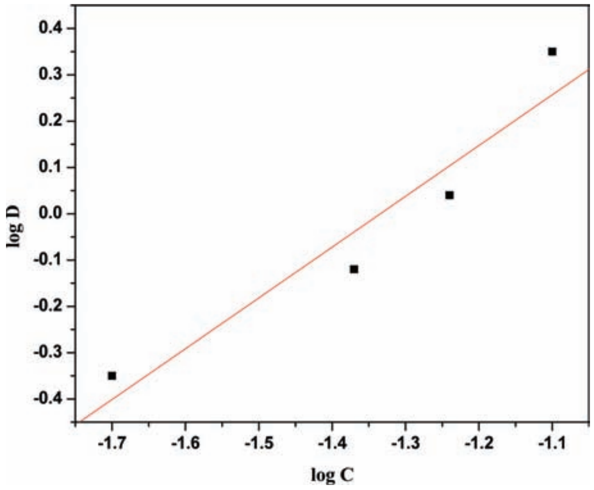


Figure 4. Stoichiometry of the extracted ion pair.

3. Results and Discussion

3.1. Choice of Diluents for Aliquat-336. As mentioned in the Introduction, Aliquat-336 has been used as an extractant with various diluents. Under the experimental conditions, the extraction efficiency studied in some solvents was found to increase in the order cyclohexane (extract very turbid) < *n*-hexane (62 %) < MIBK (73.5 %) < IAA (99.5 %). Among these solvents, IAA has the highest efficiency of extraction, and also with a view to impart a greener aspect to the process, IAA was explored as the diluent. The extraction was found to be quantitative, and the extract was clear without any third-phase formation.

3.2. Optimum pH for Extraction. The extraction efficiency mainly depends on the pH of the aqueous medium. Ion association complexes are known to be more stable in acidic media. It is well-known that Cr(VI) exists mainly as $HCrO_4^-$ and $Cr_2O_7^{2-}$ in acidic medium and as CrO_4^{2-} in alkaline medium.[29] The percentage extraction with varying pH is shown in Figure 1. The results indicate that the extraction is at a maximum in the pH range 1.5 to 3.

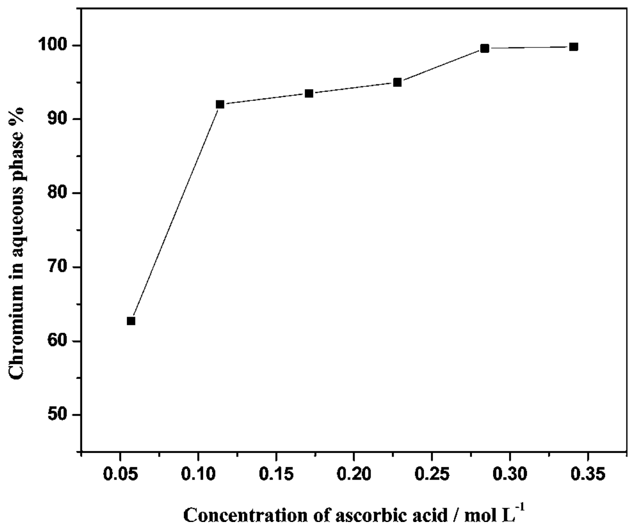


Figure 5. Percentage of chromium in the aqueous phase against the ascorbic acid concentration.

A reduction in the extraction efficiency is observed at alkaline pH since the chromate oxyanion does not form a stable ion pair with tricaprylmethylammonium chloride in the organic phase. The hydrolysis of the metal ion at alkaline pH would also influence the extraction efficiency. This was further confirmed from the FT-IR study of the organic extract.

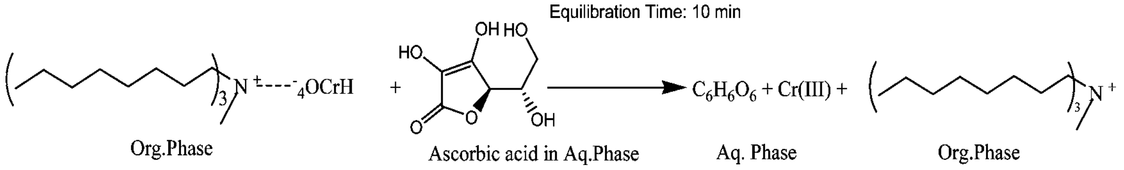
3.3. Mechanism of Extraction. In high molecular weight amines, such as tricaprylmethylammonium chloride when equilibrated with an aqueous phase containing complex anions ($HCrO_4^-$), the exchange of anions between the phases occurs, and the metal is extracted as an ion pair with the tetraalkylammonium cation. The ion-association complex is held by relatively weak electrostatic forces but is stable enough to be effectively extracted leading to greater stability in the organic phase than in the aqueous phase. The mechanism of extraction can be represented as in Scheme 1.

3.4. Characterization of the Extracted Ion Pair. An FT-IR spectrum of the extract is shown in Figure 2. A new peak at 895 cm^{-1} corresponding to the Cr−O stretching in $HCrO_4^-$ [30] along with other characteristic peaks such as C−N and C−H for Aliquat-336 shows that Cr(VI) is extracted as an ion pair of $HCrO_4^-$ in acidic media.

3.5. Variation of Equilibration Time. The time required for the extraction studies was varied from (2 to 15) min. The maximum extraction efficiency was achieved within (8 to 10) min of equilibration.

3.6. Effect of Concentration of Tricaprylmethylammonium Chloride. The concentration of tricaprylmethylammonium chloride was varied in the range of (0.03 to 0.15) $mol \cdot L^{-1}$. The percentage extraction increases with an increase in the concentration of Aliquat-336 and is at a maximum at 0.124 $mol \cdot L^{-1}$ (Figure 3).

Scheme 2. Mechanism of Regeneration of Extractant



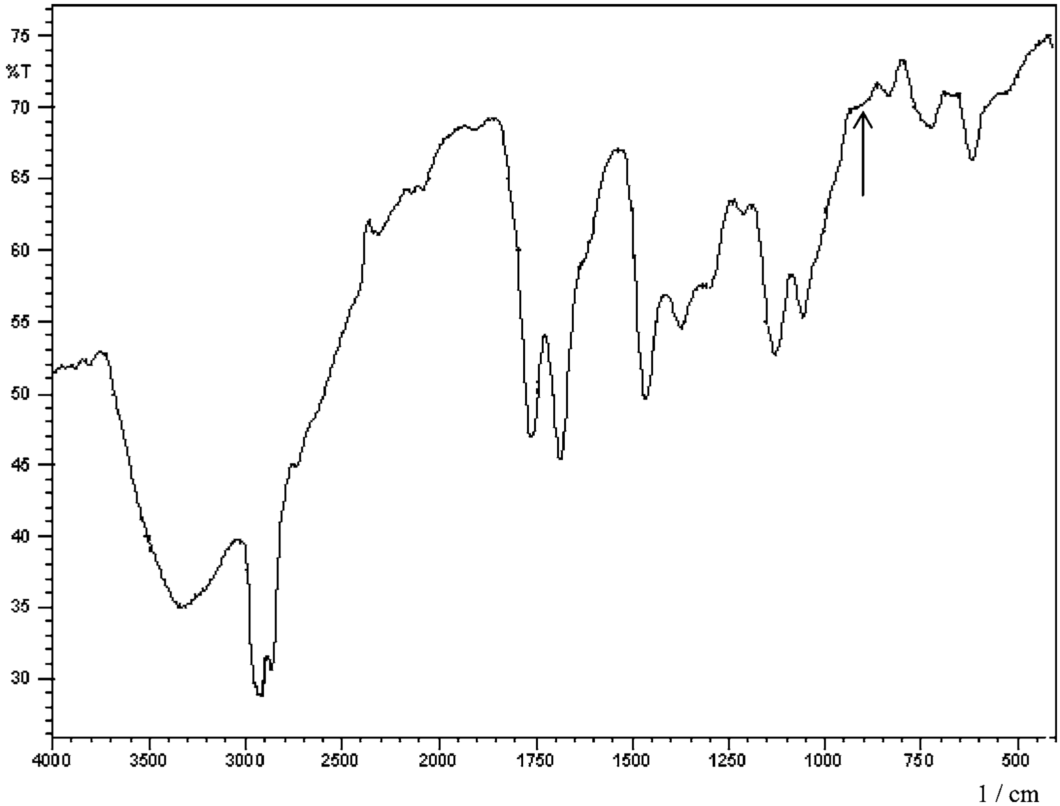


Figure 6. FT-IR spectrum of the organic phase after the reduction of Cr(VI) with ascorbic acid.

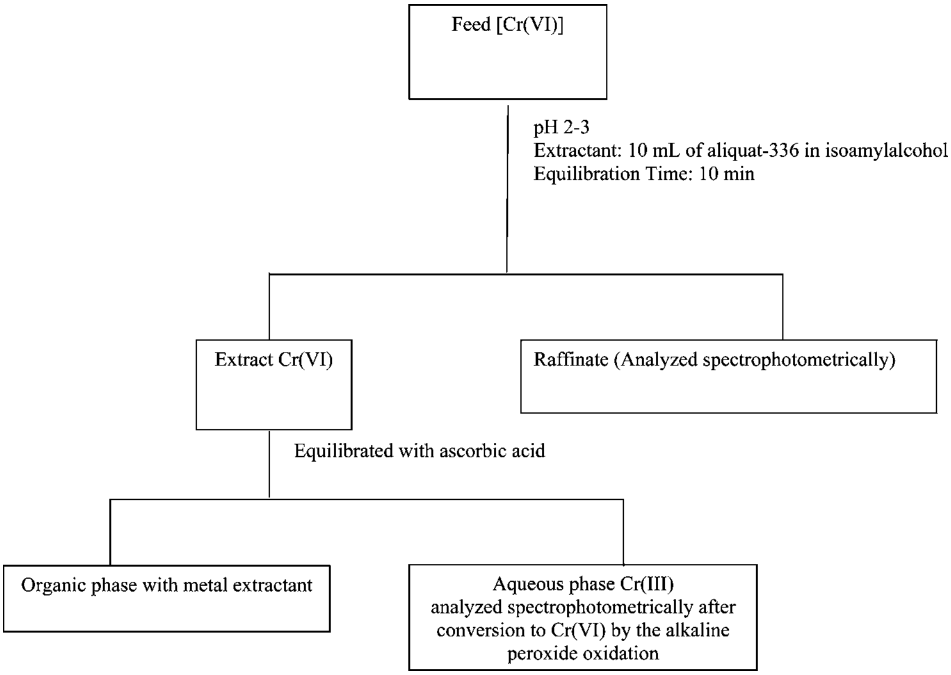


Figure 7. Scheme for the extraction process and regeneration.

3.7. Effect of Sample Volume. The aqueous phase sample volume was varied from (10 to 50) mL while maintaining an overall Cr(VI) concentration of 2.5 $\mu g \cdot mL^{-1}$. The % extraction decreases beyond a sample volume of 40 mL.

3.8. Stoichiometry of Extracted Species. The stoichiometry of the extracted species was ascertained by measuring the distribution ratio of Cr(VI) at varying concentrations. A plot (Figure 4) of the log(distribution ratio) against the log[Aliquat-336] gave a straight line with slope nearly 1.0, indicating a 1:1 stoichiometry of the ion-association complex ($HCrO_4^{-} ... {}^{+}NR_4$).

3.9. Regeneration of the Metal Extractant. The regeneration of the metal extractant was studied with ascorbic acid (0.28 $mol \cdot L^{-1}$), Na_2SO_3 (0.1 $mol \cdot L^{-1}$), $NaNO_2$ (0.1 $mol \cdot L^{-1}$), and NaOH (0.5 $mol \cdot L^{-1}$), respectively.[15] Except for sodium hydroxide, the other reagents have the ability to reduce the toxic Cr(VI) to the less toxic Cr(III). However, it was observed that, when the organic phase was equilibrated with the above reagents, ascorbic acid was found to be the most effective. The reduced Cr(III) in the aqueous phase was oxidized with peroxide in an alkaline medium to Cr(VI), and the concentration of

Table 1. Extraction Efficiency (%) of Chromium(VI) in Various Synthetic Effluents (μg)

sample	metal ions	composition	extraction efficiency
synthetic effluent 1	Cu^{2+}	250	95.2 ± 0.4
	Zn^{2+}	700	
	Cr^{6+}	10	
	Fe^{3+}	150	
	SO_4^{2-}	1250	
	Mg^{2+}	1000	
	Ca^{2+}	1500	
	NO_3^-	750	
	PO_4^{3-}	1000	
synthetic effluent 2	Cr^{6+}	20	97.3 ± 0.2
	Fe^{3+}	50	
	SO_4^{2-}	1500	
	Cr^{3+}	200	
	Ca^{2+}	1000	
	Cu^{2+}	150	
	NO_3^-	250	
	Cl^-	100	
	Mg^{2+}	1000	

chromium was measured spectrophotometrically in acidic medium by the standard diphenylcarbazide method. The effect of the ascorbic acid concentration against the percentage of chromium in the aqueous phase is shown in Figure 5. The ability of the above reagents was found to decrease in the order ascorbic acid (98 %) > sodium hydroxide (38 %) > sodium sulfite (20 %) > sodium nitrite (12 %).

3.10. Mechanism for Regeneration of Metal Extractant. Ascorbic acid disturbs the ion pair equilibrium between the organic and the aqueous phase, effectively reduces the chromium from the +6 oxidation state to the less toxic +3 state, and is brought to the aqueous phase as shown in Scheme 2.

Chromium(VI) reacts with ascorbic acid by undergoing a three-electron reduction mechanism to the less toxic chromium(III) and dehydroascorbic acid.[31−33] The above mechanism was further supported through FT-IR studies of the regenerated extract (Figure 6). A marked difference in spectral characteristics was observed after the reduction process. The spectrum clearly shows the absence of the prominent peak obtained at 895 cm^{-1} for $HCrO_4^-$ in the extraction of the ion pair. This confirmed that Cr(VI) is reduced to Cr(III) by ascorbic acid. The regenerated metal extractant in the organic phase could exist in the form of electrostatic interaction with the lone pair of electrons present in the −OH group of the solvent. The organic phase could be reused for at least 12 cycles with good precision and reproducibility. The overall scheme for the extraction and regeneration is shown as a flowchart (Figure 7).

3.11. Statistical Treatment of the Data. The calibration was linear up to 3 $\mu g \cdot mL^{-1}$. The detection limit was defined as three times the standard deviation of the blank and was found to be 0.015 $\mu g \cdot mL^{-1}$. The precision studies were carried out with 10 replicate measurements at the 3 μg level in a 10 mL aqueous volume, and the relative standard deviation was found to be 3.5 %.

3.12. Selectivity of Extraction Process. The selectivity of the extraction process was investigated by studying the effect of various cations and anions at varying concentrations in a sample volume of 30 mL. The commonly encountered cations in effluent samples such as Fe(II), Cu(II), Pb(II), Ni(II), and

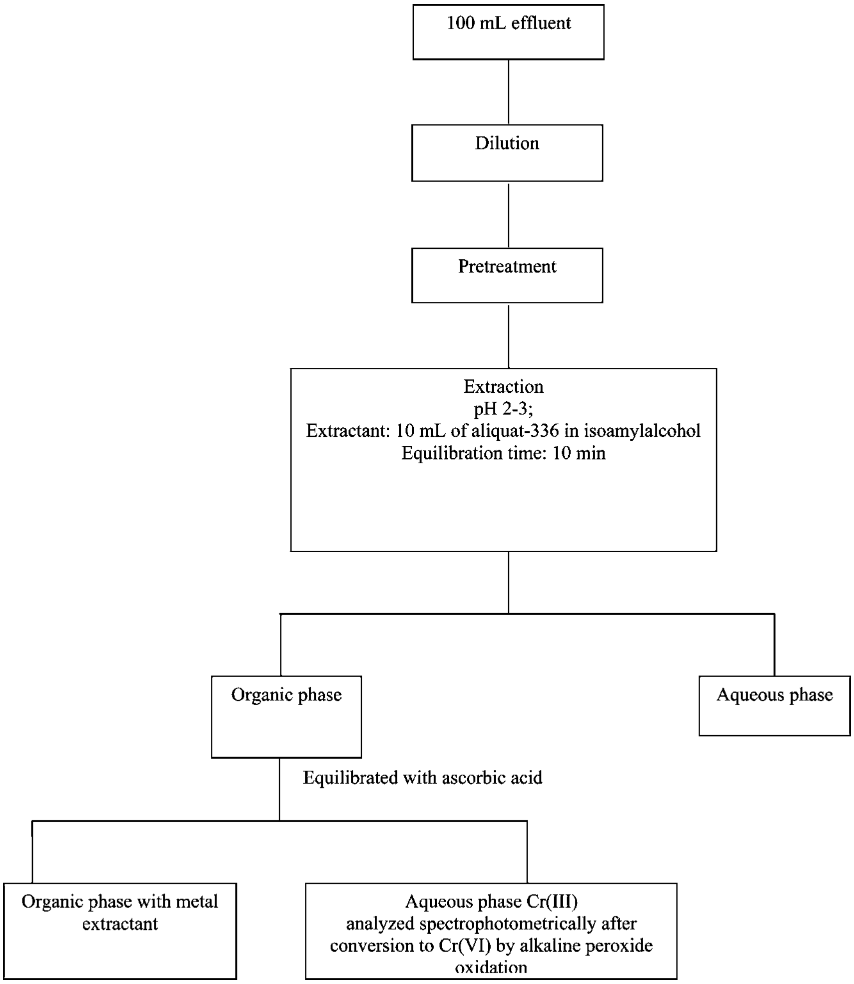


Figure 8. Scheme for the extraction process in effluent samples.

Table 2. Extraction Efficiency (%) of Chromium (μg·mL^{-1}) in Real Industrial Effluents

sample	total chromium present in the collected sample	total chromium found by proposed method	extraction efficiency
tannery effluent	524	503.04	96 ± 0.3
electroplating wastewater	225	216.45	96.2 ± 0.5

Fe(III) interfered significantly at higher concentrations (> 1000 μg). Cations such as Ca(II), Mg(II), Zn(II), Cd(II), Hg(II), and Co(II) were not coextracted with chromium(VI). Anions such as nitrate, phosphate, chloride, and sulfate caused serious interference above 750 μg in the 30 mL.

3.13. Application to Synthetic Effluents. Varying concentrations of synthetic effluents were prepared to test the efficiency of the extraction process. The synthetic samples were prepared in such a manner so as to match real wastewater effluents. It is evident from the results shown in Table 1 that an average extraction efficiency of > 95 % could be attained. The encouraging results led to the assessment of the extraction efficiency in real wastewater samples.

3.14. Performance Efficiency in Real Wastewater Samples. The efficiency of the extraction process was tested in tannery effluents and electroplating wastewater. The tannery effluent was highly concentrated and dark green in color since the major constituent of tannery effluent is Cr(III). The electroplating wastewater sample was brown in color. A 100 mL volume of the effluent samples was diluted to 1000 mL. The effluents were pretreated with H_2O_2 at 60 °C to remove organic matter.[34] The excess peroxide was removed by washing with water. Subsequently, the Cr(III) was oxidized to Cr(VI) with alkaline peroxide. The required working range was obtained with further appropriate dilution and extracted in an acidic medium with Aliquat-336. The procedure adopted in the real samples is summarized in Figure 8. The average extraction efficiency of total chromium in both of the samples was found to be in the range (96 ± 0.3) % (Table 2). Under the optimized experimental conditions, in a single extraction 30 μg of Cr(VI) could be quantitatively extracted (> 95 %) maintaining an aqueous to organic phase (A/O) ratio of 1:1. Higher amounts of Cr(VI) in the given aqueous volume can be removed by increasing the number of stages of extraction or by changing the organic to aqueous phase (O/A) ratio.

3.15. Validity of the Extraction Process Using a Certified Reference Material (BCR-715). The method was validated by analyzing a certified industrial wastewater effluent (BCR-715). The certified concentration of total chromium in the sample is (1.00 ± 0.1) μg·mL^{-1}. The total chromium present in the sample was analyzed after oxidation of the sample with alkaline peroxide. The extraction study resulted in a total chromium concentration of (0.97 ± 0.2) μg·mL^{-1}.

4. Conclusions

The proposed extraction method is simple and demonstrates the prospective application of tricaprylmethylammonium chloride using environmentally benign IAA as the diluent. The separation of the phases was clear without any third-phase formation. The efficiency of the extraction process was tested successfully in synthetic as well as real effluent samples and also validated using a certified wastewater sample. The organic phase could be regenerated by converting the toxic Cr(VI) to the less toxic Cr(III) with ascorbic acid. The regenerated metal extractant could be used for 12 cycles without appreciable loss in the performance efficiency. The aqueous phase containing Cr(III) was collected and stored in polypropylene bottles and will be used in further studies of other speciation methods which we are currently developing for chromium removal from various sources.

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