



Simple and selective extraction process for chromium (VI) in industrial wastewater

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ABSTRACT

A simple and relatively green method has been developed for the determination of chromium based on the extraction of chromium (VI) as its ion-association complex with tetrabutylammoniumiodide (TBAI) in acidic medium. The ion-pair is extracted using isobutylmethylketone (MIBK) as the solvent. The concentration of the extracted chromium (VI) in the organic layer was measured spectrophotometrically at a wavelength maximum of 366 nm and the organic layer was characterized using FT-IR spectroscopy. The influence of various analytical parameters such as pH, aqueous phase volume, equilibration time, interfering ions etc. has been studied in detail. The extracted chromium (VI) was back extracted into the aqueous phase to the non-toxic chromium (III) using ascorbic acid. The calibration graph was linear in the range of 0–2 $\mu\text{g mL}^{-1}$ chromium (VI) with a relative standard deviation of 2.4%. A detection limit of 0.25 μg in 25 mL aqueous phase volume could be achieved and the validity of the proposed method has been checked by applying it to synthetic mixtures, spiked water sample, electroplating wastewater and certified reference material BCR[®]-715.

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1. Introduction

The increasing concern about environmental pollution has stimulated active research in the study of the toxicology of heavy metals. Removal and determination of trace metals in agricultural, environmental and metallurgical samples have become increasingly important. In this context, there has been a significant advancement in the growth of the analytical chemistry of various metals. Chromium is no exception to this and it is present in the environment in different forms. The most common oxidation states are +3 and +6. Chromium (VI) finds extensive use in electroplating and chromium (III) finds its application in leather tanning. Chromium (III) is an essential nutrient required for normal glucose metabolism, whereas chromium (VI) is highly carcinogenic [1].

In view of the toxic nature of chromium (VI), development of methods for the removal of chromium assumes significant importance. The widely employed analytical techniques for the removal of chromium (VI) include liquid–liquid extraction (LLE) and solid phase extraction (SPE). Solid phase extraction has been explored in detail for the removal of chromium [2–11]. Even though, chromatographic methods were found to be useful for the speciation of chromium, some of the procedures were often found to be time consuming and the mutual separation as well as separation from

the matrix constituents was found to be tedious. Moreover, a close control of the experimental conditions is required for reproducible results. Among the various techniques, solvent extraction has come to the forefront as a popular technique due to its elegance, simplicity and applicability to trace and macro amounts of metal ions. In addition, the adsorption at the phase boundaries is minimum and equilibrium is attained very rapidly. Moreover, this technique allows easy control of the volume of the aqueous and organic phases and hence is of great significance when coupled with a suitable analytical method for the determination of many metal ions.

Solvent extraction is used in chemical industries to purify chemical elements, in environmental waste management and in the nuclear industry for the reprocessing of spent nuclear fuels [12].

Islam and Biswas [13] have reported the extraction of chromium (III) with bis(2-ethyl hexyl phosphoric acid) in benzene. The recovery of chromium from electroplating wastewater has been achieved by converting Cr (VI) to Cr (III) using Di-(2 ethyl hexyl phosphoric acid) as the reagent [14]. Trace amounts of chromium (VI) were extracted with diphenylcarbazide using isoamylalcohol as the solvent and 87–115% of spiking recovery could be achieved in water samples [15]. A review of the extraction of chromate and dichromate with functionalized calixarenes has been reported [16]. The separation of chromium (III) and chromium (VI) by a combination of solvent extraction and ion-exchange using zephyramine and TiO_2 has also been studied [17]. Liquid membrane containing triphenyl phosphine has been used for the extraction and transport of chromium [18]. A potentiometric Rhodamine-B based sensor has been studied [19] for the selective extraction of chromium based

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on the Rhodamine-B-chromate ion-association complex in a PVC membrane. A detection limit of $0.2 \mu\text{g mL}^{-1}$ could be attained by this method. Mixed extractants such as DEHPA, TBP, LIX79 and trioctylamine have been explored for the removal of chromium (VI). An extraction efficiency of 84% could be achieved [20]. Synthetic resins such as Dowex M4195 [21] and diaion SP-850 [22] have also been utilized for the removal of chromium in water samples.

Shinde and Khopkar [23] studied the extraction of chromium (VI) with 4-methyl-3-pentene-2-one and subsequent determination as its diphenylcarbazide complex. The extracted chromium was stripped using ammonia solution. Various spectrometric methods have been used in the solid phase extraction for chromium and other metal ions [24–27]. Long chain amines and quaternary ammonium salts have been used to study the extraction behavior of many metal ions [28]. Tribenzylamine has proved to be a good extractant for the removal of Cr (VI) from tannery effluents [29]. The equilibrium composition of trioctylmethylammoniumchloride with aqueous chromium (VI) has been investigated in detail [30].

In this context, tetrabutylammonium ion is one such reagent which has been used to study the extraction behavior of metal ions [31]. The specific extraction of chromium with tetrabutylammoniumbromide (TBAB) using MIBK as the solvent has been applied for the determination of chromium in water samples [32]. The extracted ion-pair was back extracted into an acidic diphenylcarbazide solution and subsequently determined by spectrophotometry. The speciation of chromium by ion-pair chromatography with post column spectrophotometric detection has been reported [33]. In this method, phosphate buffer containing tetrabutylammonium bromide was used as the eluent. Venkateswaran and Palanivelu [34] reported the extraction of Cr (VI) with 95% recovery using TBAB in dichloromethane.

A survey of the literature reveals that long chain amines and surfactants are versatile extractants [35–36] for many metal ions. Moreover, literature reports reveal that tetrabutylammonium iodide has not been explored as an extractant for the speciation of chromium in wastewater. This led to the development of a method for the extraction of chromium (VI) in acidic medium as its ion-pair with tetrabutylammoniumiodide (TBAI). The extracted ion-pair could be back extracted with ascorbic acid and converted to relatively less toxic chromium (III) species. The various analytical parameters that influence the extraction have been studied in detail and the method has been applied to study the recovery of chromium in various synthetic mixtures, well water, electroplating wastewater and BCR[®]-715 certified reference material.

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Triple distilled water (TDW) was used in the preparation of the solutions. A stock solution of $1000 \mu\text{g mL}^{-1}$ chromium (VI) solution was prepared from potassium dichromate (Central Drug House Limited, New Delhi, India). A working solution of $10 \mu\text{g mL}^{-1}$ was prepared by appropriate dilution. Sulfuric acid (Qualigens fine chemicals, Mumbai, India) of 1 mol L^{-1} was prepared by appropriate dilution. Isobutylmethylketone (Sisco Research Laboratories, Mumbai, India) was used as the solvent for extraction studies. A 2% solution of tetrabutylammoniumiodide (Himedia Research Laboratories, Mumbai, India) was prepared by dissolving 2 g in 100 mL TDW. A 5% solution of ascorbic acid, NaOH (0.5 mol L^{-1}) and Na_2SO_3 (0.1 mol L^{-1}) (S.D. Fine Chemicals, Mumbai, India) were prepared in TDW. 0.25 g of diphenylcarbazide (S.D. Fine Chemicals) solution was prepared in 100 ml acetone to check the presence of Cr (VI) in aqueous phase as per the standard procedure.

2.2. Instrumentation

A JASCO V-576 model UV-vis spectrophotometer was used to record the absorbance. An Elico LI-127 model pH meter was used for pH measurements. The FT-IR studies were performed using a Shimadzu spectrometer.

2.3. Procedure for solvent extraction of chromium (VI)

A 1 mL volume of $10 \mu\text{g mL}^{-1}$ chromium (VI) solution was mixed with 4 mL of 1 mol L^{-1} sulfuric acid and 4 mL of TBAI solution in a 60 mL separating funnel. The aqueous phase volume was maintained at 10 mL. The resulting ion-association complex was extracted for 5 min with 10 mL of MIBK. The phases were separated and the absorbance of the organic phase was measured at wavelength maximum of 366 nm against a reagent blank. The percentage of extraction (E) was calculated using the relation

$$D = \left(\frac{E}{100 - E} \right) \times \frac{V_{\text{aq}}}{V_{\text{org}}}$$

where D is the distribution ratio, V_{aq} , and V_{org} refer to the volume of aqueous and organic phase, respectively.

2.4. Calibration, validation and application of the proposed method

The calibration graph was linear in the range $0\text{--}2 \mu\text{g mL}^{-1}$ chromium (VI) with the best fit equation $A = 0.953C - 0.0784$ and a correlation coefficient of 0.99. The method was validated through recovery test and determining the concentration of chromium in the reference material BCR[®]-715 (Industrial effluent wastewater) obtained from the European commission-joint research centre-institute of reference materials and measurements (EC-JRC-IRMM, Geel, Belgium).

The electroplating wastewater sample was collected from an electroplating unit in Chennai, India and the well water sample was collected from our campus. The wastewater sample was diluted and the extraction procedure was applied as mentioned above.

3. Results and discussion

3.1. Effect of various solvents on the extraction of chromium

The extraction of Cr (VI) was investigated using various solvents such as toluene, xylene, isoamylalcohol, hexane, cyclohexane and isobutylmethylketone. The % extraction of chromium (VI) with the above mentioned solvents is given in Table 1. The studies indicated that the ion-association complex of chromium (VI) with tetrabutylammoniumiodide could be extracted quantitatively only with MIBK as the solvent.

3.2. Effect of pH

The effect of pH on the extraction of the ion-pair was investigated in the range 2.0–8.0. The percentage extractions at different

Table 1
Percentage extraction of Cr (VI) with various solvents.

Name of the solvent	% of extraction
Hexane	0
Cyclohexane	0
Xylene	55
Toluene	64
Isoamylalcohol	79
Isobutylmethylketone	99

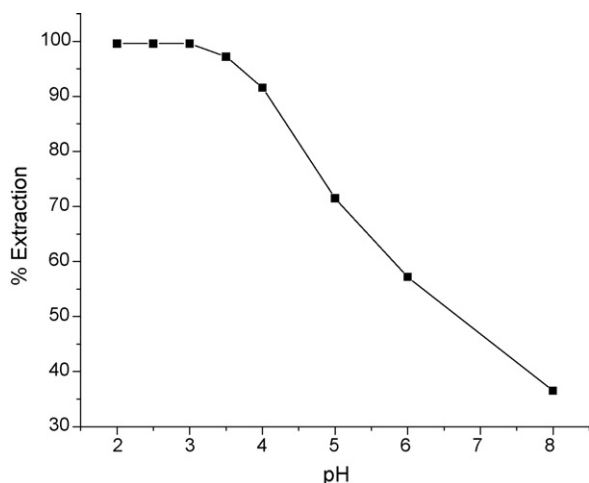
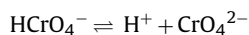
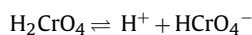
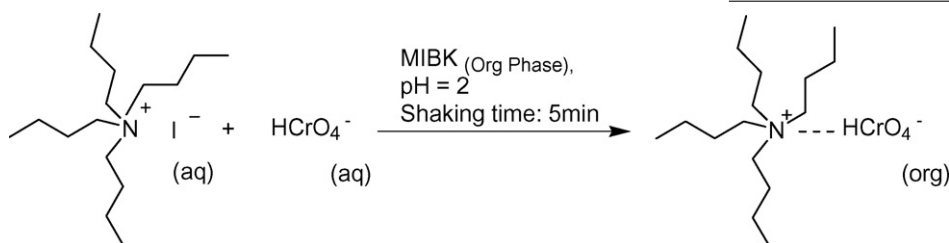


Fig. 1. Effect of pH.

pH values are shown in Fig. 1. The results indicate that the metal ion forms an ion-pair with TBAI in the pH range 2–3 and the various probable equilibrium reactions (at 25 °C) at this acidic pH is represented as follows:



At low pH the chromium exists only as oxo-anion species, which is easily hydrolyzed in aqueous solution depending on the pH of the medium. The peaks relevant to the charge transfer bands of chromate (at 258 and 349 nm) were not observed, whereas the absorbance peak of the organic phase was observed at the wavelength maximum of 366 nm. This shift in wavelength confirmed that CrO_4^{2-} species does not form an ion-pair with TBAI and hence the percentage extraction decreases at higher pH. The shift in the wavelength is due to the TBA^+ (tetrabutylammonium cation)– HCrO_4^- ion-association complex and this fact is also supported by the FT-IR studies of the ion-pair formed in the organic phase. Solvation energy and lipophilicity of the quaternary amine plays a vital role in the extraction. TBAI interacts with HCrO_4^- through electrostatic attraction. When a molecule of lipophilic TBAI is enveloped by water, the surrounding water molecules enter into a cage like structure over the greater part of its molecular surface and this being a thermodynamically unfavorable event, the lipophilic TBAI is driven out of the aqueous phase as its ion-pair with HCrO_4^- to the organic phase. The formed ion-association complex is transferred from aqueous phase to the organic phase through mass transfer. The schematic representation of ion-pair formation is shown below.



3.3. FT-IR studies on the extracted ion-pair

Hoffmann et al. [37] analyzed the IR spectrum of chromium as a function of pH. By changing the total chromium concentration, the relative mole fraction of the various chromate species

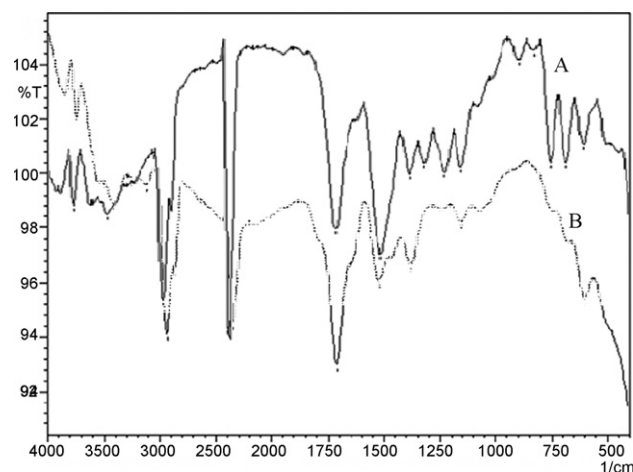
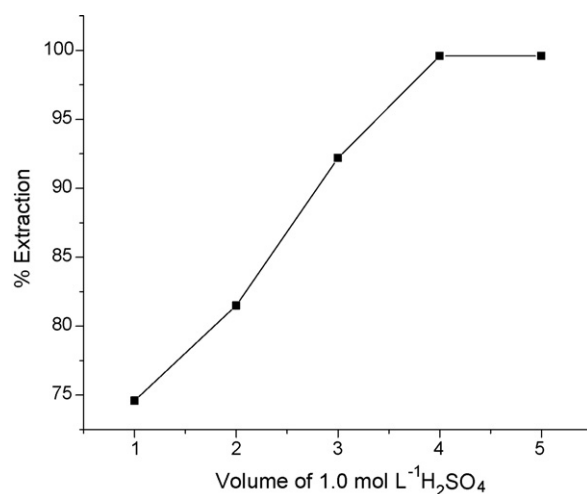


Fig. 2. FT-IR spectrum of (A) ion-pair formation; (B) organic phase after stripping with ascorbic acid.

Fig. 3. Effect of varying the volume of 1 mol L⁻¹ sulfuric acid.

changes accordingly. They have also reported that the HCrO_4^- stretching vibrations would appear at 891 cm^{-1} and the peak intensity varies with respect to the concentration. The FT-IR spectrum of organic phase for the sample extraction is shown in Fig. 2. Generally quaternary ammonium salt does not show a prominent peak for nitrogen in FT-IR. The remaining peaks in the spectrum correspond to the various types of $-\text{C}-\text{H}$ vibrations of methyl, methylene group of solvent and tetra butyl group in TBAI along with the carbonyl stretching vibration of MIBK.

There is no peak relevant to iodine or its derivative compound, but one new peak appears at 891 cm^{-1} . The new peak shows the presence of HCrO_4^- and it further confirms the ion-association with TBAI. The peak intensity in the spectra shows HCrO_4^- species is the predominant species and not CrO_4^{2-} at low pH values.

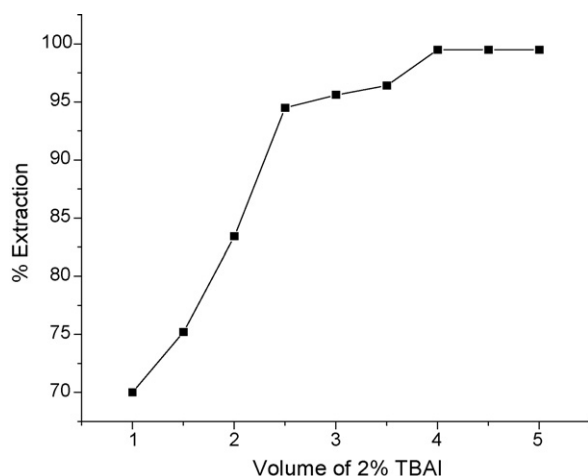


Fig. 4. Effect of varying the volume of tetrabutylammoniumiodide (TBAI).

3.4. Effect of varying the volume of 1.0 mol L⁻¹ sulfuric acid

The volume of 1.0 mol L⁻¹ sulfuric acid was varied from 1 to 5 mL and the extraction studies were carried out as before maintaining an overall aqueous phase volume of 10 mL. The results are shown in Fig. 3. There was an increase in the percentage extraction with the increase in the volume of sulfuric acid and reached saturation at 5 mL of 1.0 mol L⁻¹ sulfuric acid. The predominant species at acidic pH is HCrO₄⁻ and this anion forms an ion-pair with tetrabutylammoniumiodide.

3.5. Effect of varying the volume of tetrabutylammoniumiodide

The volume of 2% tetrabutylammoniumiodide was varied from 1 to 5 mL and the extraction studies were carried out as mentioned in the general procedure for solvent extraction. The results are presented in Fig. 4. The percentage extraction was found to be maximum in the range 3.0–4.0 mL of 2% tetrabutylammoniumiodide solution. Beyond 4 mL, there was no significant change in the extraction of the ion-pair.

3.6. Variation of equilibration time

The extraction studies were carried out for varying lengths of time ranging from 2 to 10 min. The aqueous phase volume was maintained at 10 mL and the absorbance of the organic layer was measured against a reagent blank. An optimum equilibration time of 5 min was sufficient for the extraction of the ion-pair.

3.7. Effect of aqueous phase volume

The aqueous phase volume was varied from 10 to 30 mL and the extraction studies were carried out as before. The resulting ion-pair of chromium (VI)-tetrabutylammoniumiodide was equilibrated for 5 min with 10 mL of MIBK. The absorbance of the organic phase was measured against a reagent blank at 366 nm. It is evident from Fig. 5 that the system could tolerate an aqueous phase volume of up to 25 mL. Beyond 25 mL aqueous phase volume, there was a significant reduction in the percentage extraction.

3.8. Nature of the extracted species

The nature of the extracted species was ascertained from the plot of log D vs log [ion pairing agent]. The results are given in Fig. 6. From the best linear fit, the slope was found to be 1.01, which confirms the 1:1 stoichiometry of the ion-pair.

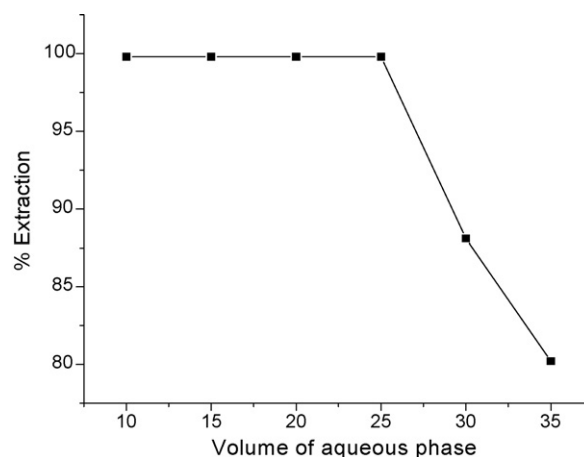


Fig. 5. Effect of aqueous phase volume.

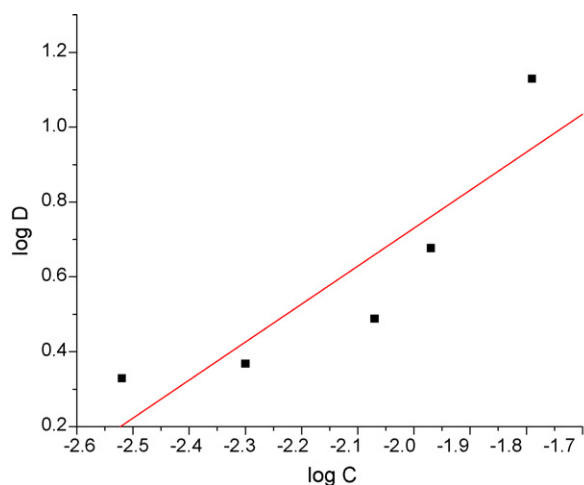


Fig. 6. Stoichiometry of the complex (log D vs log [ion pairing agent]).

3.9. Re-extraction of chromium (VI) from the organic phase

The re-extraction of chromium (VI) from the organic phase was studied using various stripping agents like ascorbic acid, NaOH and Na₂SO₃, respectively. The objective of the study is to reduce the carcinogenic chromium (VI) to the less toxic chromium (III).

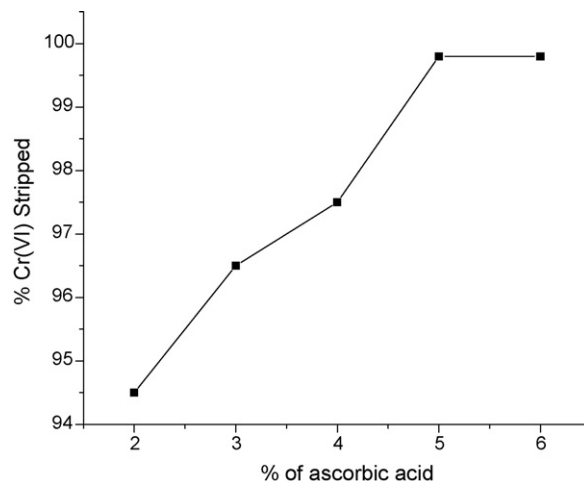


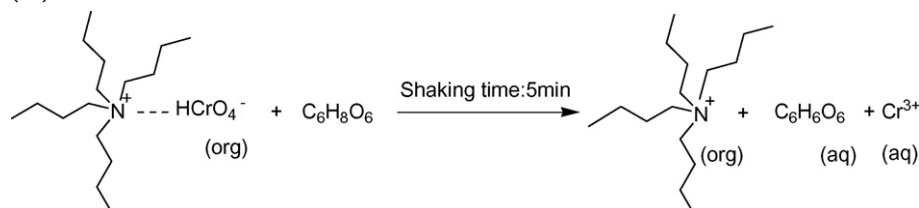
Fig. 7. Effect of varying the percentage of ascorbic acid.

Table 2
Effect of diverse ions [aqueous volume of 10 mL containing 1 $\mu\text{g mL}^{-1}$ Cr (VI)].

Ions	Remarks
Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^-	No Interference
Fe^{2+} (250 μg), Cu^{2+} (500 μg), Hg^{2+} (500 μg) SO_4^{2-} (500 μg) ^a	Interfered at 1 mg level

^a The figures in brackets are the tolerance limits.

species, and regeneration of organic phase. The separated organic phase containing chromium (VI) was equilibrated with 10 mL of the above mentioned stripping agents. It was observed that there was a significant reduction in the absorbance of the organic layer with ascorbic acid than the other two reagents. After stripping the Cr (VI) from organic phase, the resulting tetrabutylammonium cation in the organic phase could be associated through weak attractive forces like electrostatic or van der Waals or dispersive forces with MIBK. The effect of varying the percentage of ascorbic acid is shown in Fig. 7. It is evident from the figure that the reduction was the maximum with 5% ascorbic acid. This shows that ascorbic acid acts as an effective reducing agent to convert chromium (VI) to chromium (III).



The above fact was also confirmed using FT-IR studies. The spectrum (Fig. 2) clearly shows the absence of the prominent peak due to HCrO_4^- which indicates that Cr (VI) is completely reduced to Cr (III) and transferred to the aqueous phase.

3.10. Calibration, precision and detection limit

The calibration graph was linear in the range 0–2 $\mu\text{g mL}^{-1}$ of chromium (VI), with a correlation coefficient of 0.99. The precision studies were carried out at 1 $\mu\text{g mL}^{-1}$ level of chromium (VI)

Table 3
Recovery studies in synthetic mixtures.

Synthetic mixtures	Composition of synthetic mixtures	Concentration of Cr(VI) recovered ($\mu\text{g mL}^{-1}$)	Recovery (%)
SM1	Cu^{2+} (500 μg), Co^{2+} (1000 μg), Cl^- (500 μg), Cr^{6+} (1 $\mu\text{g mL}^{-1}$)	0.96	96
SM2	Cu^{2+} (500 μg), Ni^{2+} (500 μg), Zn^{2+} (500 μg), Cr^{6+} (1 $\mu\text{g mL}^{-1}$), SO_4^{2-} (500 μg)	0.97	97
SM3	Cu^{2+} (500 μg), Mg^{2+} (500 μg), Ni^{2+} (500 μg), Cr^{6+} (1 $\mu\text{g mL}^{-1}$), NO_3^- (1000 μg)	0.97	97
SM4	Hg^{2+} (500 μg), Ca^{2+} (1000 μg), Zn^{2+} (1000 μg), Cr^{6+} (1 $\mu\text{g mL}^{-1}$), SO_4^{2-} (250 μg)	0.98	98

Table 4
Recovery studies for total chromium in spiked well water sample.

Sample	Cr(III) added(μg)	Cr(VI) added(μg)	Total chromium found (μg)	Recovery (%)
Well water	5	2	6.9	98.6
	2	5	6.9	98.6
	5	10	14.8	98.7

Table 5
Analysis of chromium (VI) in electroplating wastewater (Aqueous volume 10 mL).

Sample	Concentration of Cr(VI) added ($\mu\text{g mL}^{-1}$)	Concentration of Cr(VI) found ($\mu\text{g mL}^{-1}$)	RSD (%)	Recovery (%)
Electroplating wastewater	0	142.0	2.4	
	2	140.8	2.2	97.8
	5	144.2	2.4	98.1

Table 6
Analysis of chromium in certified reference material (Aqueous volume 10 mL).

Sample	Certified ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$) ^a
BCR® -715	1.00 \pm 0.09	0.98 \pm 0.05

^a Average of three determinations.

by carrying out 10 separate determinations. The relative standard deviation (RSD) was found to be 2.4%. A detection limit of 0.25 μg in 25 mL aqueous phase volume (taken at three times the standard deviation of the blank) could be achieved.

3.11. Effect of diverse ions

The effect of various diverse ions on the extraction of the ion-pair was investigated at varying concentrations maintaining an overall aqueous phase volume of 10 mL. Varying amounts of ions were added to the test solutions containing a known concentration of Cr (VI). The results are presented in Table 1. Iron (II), copper,

mercury and sulfate interfered at 1 mg level but other ions did not interfere in the proposed method. However, these ions (such as iron (II), copper, mercury and sulfate) did not interfere at concentrations below 1000 μg in a total aqueous phase volume of 10 mL. The tolerance limits of these ions are also given within the brackets in Table 2. At high concentrations, anions such as sulfate, chloride and phosphate caused a decrease in the percentage extraction. This is due to the competition between the anions and HCrO_4^- for the ion-pair formation with TBAI.

Table 7
Comparison of the proposed method with some of the reported solvent extraction methods.

No.	System	Medium	Method	Recovery (%)	Det. limit	RSD (%)	Reference
1	Cr(VI)-Aliquat336-SO ₄ ²⁻	Mixture of Kerosene & Xylene	Spectrophotometry	97	–	–	[38]
2	Cr(VI)-Aliquat336-NO ₃ ⁻	Mixture of Kerosene & Xylene	Spectrophotometry	55	–	–	[38]
3	Cr(VI)-Aliquat336-Cl ⁻	Mixture of Kerosene & Xylene	Spectrophotometry	95	–	–	[38]
4	Cr(VI)-TBAB	CH ₂ Cl ₂	Spectrophotometry	95	–	–	[34]
5	Cr(VI)-capriquat	CCl ₄	AAS	90	–	–	[39]
6	Cr(VI)-Zephiramine	CHCl ₃	AAS	79	–	–	[39]
7	Cr(VI)-Aliquat336	Xylene	Spectrophotometry	100	–	–	[40]
8	Cr(VI)-Alamine336	Xylene	Spectrophotometry	100	–	–	[40]
9	Cr(VI)-TBAB	(NH ₄) ₂ SO ₄	AAS	93–98	60 µg/L	3.2	[41]
10	Cr(VI)-DPC	Isoamylalcohol	AAS	90–110	0.024 µg/L	8–49	[15]
11	Cr(VI)-TBA	Toluene	Spectrophotometry	98.5	0.08 µg/mL	4.5	[29]
12	Cr(VI)-TBAI	MIBK	Spectrophotometry	99	0.25 µg/25 mL	2.4	Present work

TBAB, tetrabutylammoniumbromide; DPC, diphenylcarbazine; TBA, tribenzylamine; TBAI, tetrabutylammoniumiodide.

3.12. Recovery study in synthetic mixtures

The proposed method was applied to study the recovery of chromium (VI) in various synthetic mixtures containing varying concentration of other ionic species. The results are presented in Table 3. As can be seen from the table, it is evident that the recovery of chromium (VI) is quantitative (>95%) with a relative standard deviation of 2.2% for five replicate measurements.

3.13. Application studies

The proposed method was applied to study the recovery of chromium in spiked well water and electroplating wastewater sample. The electroplating wastewater sample had the following characteristics: pH 2.4, calcium: 82 mg L⁻¹, magnesium: 56 mg L⁻¹, chloride: 1210 mg L⁻¹ sulfate: 920 mg L⁻¹. The recovery of chromium was found to be quantitative with an average relative standard deviation of 2.4% and the results are presented in Tables 4 and 5.

3.14. Analysis of chromium in certified reference material

The validity of the proposed extraction process was checked by applying it to BCR[®]-715 (Industrial effluent wastewater). The total chromium in the sample was analyzed after oxidation with peroxide–sodium hydroxide mixture. The results are presented in Table 6. The values obtained by the developed method were in good agreement with the certified value.

3.15. Comparative performance in the recovery of Cr (VI) with existing methods

The comparison of the present method with some of the existing solvent extraction procedures for Cr (VI) in the literature is given in Table 7. Most of the reported methods have some drawbacks such as usage of the toxic chlorinated solvents and third phase formation. The proposed method is better than the previously reported methods in terms of high percentage of recovery, reusability, detection limit and RSD values. Moreover, the present method is simple, facile, greener and does not have the drawback of third phase formation.

4. Conclusion

The proposed method for the extraction of Cr (VI) is simple, green, shows good sensitivity and selectivity. Isobutylmethylketone was found to be the most suitable solvent for extraction. The calibration graph was linear up to 2 µg mL⁻¹ Cr (VI), with a detection limit of 0.25 µg in 25 mL aqueous phase volume. The extracted ion-pair was quite stable under the experimental conditions and the experimental parameters studied are not highly critical. The extracted

chromium (VI) could be stripped using 5% ascorbic acid to the less toxic chromium (III) species. The proposed method was applied successfully to study the recovery of chromium in various synthetic mixtures, well water and electroplating wastewater and validated by certified reference materials (BCR[®]-715). The low relative standard deviation indicates the validity and accuracy of the method in real samples.

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