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Speciation of Cr (III) and Cr (VI) in Industrial Waste Water using Biphasic Extraction and Determination by LIBS

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Abstract

An aqueous, biphasic one step separation method for Cr (III) and Cr (VI) is presented in this paper. Optimization of different parameters like pH, volume of solvent etc. in the extraction experiments are carried out using standard solutions of Cr (VI) and Cr (III). Extraction efficiency for chromium species using biphasic technique is calculated by performing quantitative analysis of chromium using Laser Induced Breakdown Spectroscopy (LIBS). After biphasic extraction, LIBS spectra of $(NH_4)_2SO_4$ containing Cr are recorded by depositing and drying 20 μL of this solution on Whatman filter paper (No. 542). Quantitative analysis of LIBS spectra are performed using Cr emission line at 425.4 nm. Optimum extraction (about 90 %) of Cr (VI) is found at pH 4 and solvent volume 4mL. The optimized methodology is then used for determination of total Cr and Cr (VI) in waste water collected from leather tanning industries of Kanpur City, India.

***Keywords*:** LIBS; Biphasic extraction; Cr speciation; Cr (III); Cr (VI)

1. Introduction

Chromium is usually present in surface and ground water in either trivalent (Cr (III)) or the hexavalent (Cr (VI)) oxidation state. Cr is used in leather tanning; metallurgical processing and electroplating industries [1]. Thus the industrial wastewater of these industries is a major source of environmental contamination. While Cr (III) is considered an essential nutrient for the maintenance of glucose, lipid and protein metabolism, Cr (VI) is known to be highly irritating and toxic to humans and animals and is considered to cause cancers owing to its oxidizing potential and easy permeation in biological membranes [2, 3]. Hence it is important not only to determine total chromium but also it is necessary to quantify the different oxidation stated of Cr. According to the European Community Directive 80/778/EEC, L229/20, D48, the maximum allowable concentration for Cr in drinking water is $50 \mu g L^{-1}$[4]. The concentrations given above reflect only the total chromium content comprising a rich variety of chemical and physical species. These different chemical species have different reactivities and effects. The availability of chromium species to organisms as well as their toxic effects strongly depends on chromium species [2].

Speciation studies on chromium have been reported in literature using ion chromatographic techniques [5, 6]. While this methodology is simple, it is not suitable for field applications. Biphasic liquid extraction, performed in two-layer liquid medium composed of an organic solvent phase (polymer) and an aqueous phase (inorganic salt), is one of the promising alternatives to other solvent extraction techniques because of its outstanding advantages in separation capacities. Several methods have been reported for the quantification of the trivalent and hexavalent chromium species using different methods like ETAAS, AAS, Ion chromatography, ICP-MS, FAAS etc. after speciation using different method like membrane, Immobilized Moss, Adsorptive stripping voltammetry, Column Solid phase extraction etc. [7-12]. The major advantage of aqueous biphasic systems is the use of environmental friendly chemicals for separation. Cloud point extraction is another method for the speciation of the chromium species. Xiashi Zhu et al. have used cloud point extraction for speciation of chromium and applied ETASS for the quantification of chromium species [13]. Non-chromatographic speciation of Cr species at sub-ppb level was performed by Ignacio *et al.* and ETAAS was used for the quantitative analysis [14]. Selective solid-phase extraction of chromium species in environmental water samples was performed by Nan et al. using chromium(III)-imprinted 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS)-functionalized silica gel sorbent and the ICP was employed for the quantification [15]. A new on-line flow injection (FI) procedure for the sequential separation, pre-concentration and speciation of Cr(III)/Cr(VI) species in different matrices using solid phase extraction and flame atomic absorption spectrometry (FAAS) was reported by Serkan et al. [16].

In the present study, a biphasic separation method combined with LIBS has been optimized to obtain maximum extraction/separation efficiency between the two species of Cr. The optimized method was then applied to different industrial effluent solutions collected from the industrial area of Kanpur. Kanpur is well known for the leather industries, where chromium salts (chromium sulphate, chrome syntans, anchrome, etc.) were used for tanning purposes [1, 17, 18]. The effluents were selected to get an idea about the amounts of Cr (III) and Cr (VI) in the industrial waste as these effluents are being used for the irrigation purpose in the nearby areas of the industries. For quantification of chromium, laser induced breakdown spectroscopy (LIBS) was employed.

2. Material and Method

2.1 Reagents

A stock solution of Polyethyleneglycol (PEG) [50% w/v] with average molecular weight 2000 was prepared. A stock solution of $(NH_4)_2SO_4$ [50% (w/v)] was also prepared. Stock solution (1000 μgL^{-1}) of Cr (VI) was prepared by dissolving exact amount of K_2CrO_4. ICP standard solution of Cr (III) (1000 μgL^{-1}) was used to prepare trivalent chromium solutions. 1 M H_2SO_4 and 0.5 M NaOH solutions were prepared and used for pH adjustment in the extraction experiments. All the solutions were prepared using Millipore water with conductivity of 10^{-18} ohm-m and high purity reagents (M/s. Merck).

2.2 Biphasic Extraction

For the bi-phasic extraction, PEG and ammonium sulphate were mixed in a 60 mL separation funnel. At the same time, the chromium sample (sample for the chromium speciation) was added into the funnel. The funnel was kept on automatic shaking machine at constant speed for 10 minutes. After 10 minutes shake, the funnel was kept horizontally for 10 minutes at rest. After that PEG phase containing Cr (VI) goes up whereas the sulphate phase containing Cr (III) comes down in the funnel [19]. Thus using the separation funnel, both PEG and $(NH_4)_2SO_4$ can be separated containing hexavalent and trivalent chromium respectively.

PEG and the sulphate were taken in equal volume. The extraction procedure was carried out at different pH to get the most appropriate pH for the maximum extraction of Cr (III) and Cr (VI). Different amounts of Cr (III) and Cr (VI) were used to optimize the method.

2.3 Analytical method used for the Quantification

LIBS have several advantages over traditional analytical methods for field application as it is quick, inexpensive, and eco-friendly physical technique. Therefore quantification of chromium present in the $(NH_4)_2SO_4$ after extraction was carried out by LIBS. Small amount (20 (µL)) of the extracted solution ($(NH_4)_2SO_4$ containing Cr) was deposited on the filter paper (No. 542) and the LIBS spectra of the deposited sample was recorded. In the present work, a Q-switched Nd:YAG laser (continuum surelite III-10) was used. Second harmonic (532 nm) of Nd:YAG laser having pulse width of 4 nanosecond and repetition rate of 10Hz was focused to create the plasma on the sample surface. Emission from the plasma was collected with a collimator (Andor Collimator, CC52) and the collected emission was fed to the spectrometer (Andor mechelle 5000) equipped with intensified charged couple device (ICCD) (Andor iStar DH334T) through the optical fiber cable connected between collimator and spectrometer. Intensity and wavelength calibrations of the spectrograph-ICCD were done using the Deuterium-Halogen (DH-2000-BAL, Ocean Optics, USA) and Hg-Ar lamps (HG-1,Ocean Optics, USA), respectively. LIBS spectrum was recorded at the 10 mJ laser energy. A plano convex lens of focal length 15 cm was used to focus the laser beam on the sample surface. Gate delay and gate width were also optimized as 1µs (gate delay) and 10 µs (gate width) to get better S/B ratio.

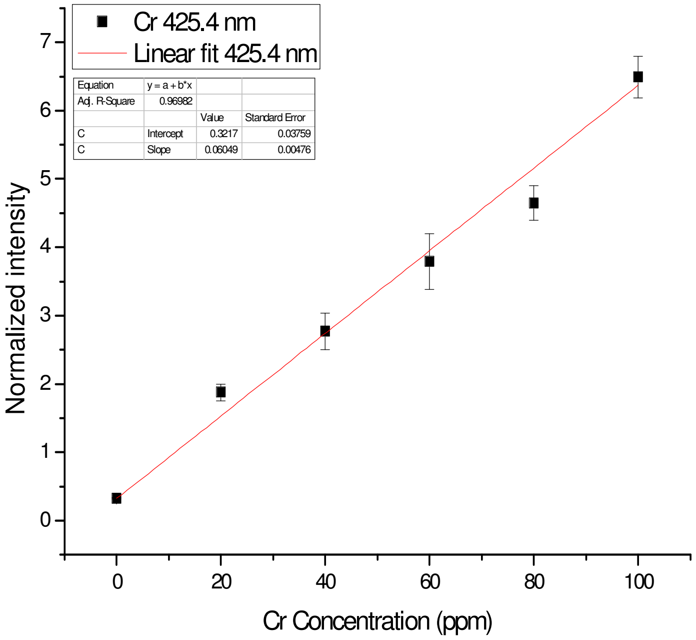

Figure 1: Calibration curve using Cr (425.4nm)

Calibration curve method was employed for the quantification of Cr present in the extracted $(NH_4)_2SO_4$ solution. To draw the calibration curve, different standard solutions having known amounts of chromium concentration were prepared in $(NH_4)_2SO_4$). 20 µL of the solution (from different concentrations) was deposited and dried using a drier on the Whatman paper (No. 542) and LIBS spectra of different standards were recorded under optimized conditions. Calibration curve was drawn for the different analyte concentrations of Cr at wavelength 425.4 nm and is shown in the Figure 1. Determination of concentration of Cr species in the industrial waste is described in the following paragraph.

For the detection and quantification of the Cr species, 20 μL of the solution from the salt phase was dried using a drier on the Whatman paper (No. 542) and LIBS spectrum was recorded. By comparing the spectral intensity of Cr (425.4 nm) in LIBS spectrum of unknown sample, amount of Cr (III) was determined using calibration curve.

3. Results and Discussion

3.1 Effect of pH

To study the effect of initial pH on the extraction of Cr species, 4 mL of PEG (50% w/v) and 4 mL of $(NH_4)_2SO_4$ (50% w/v) solutions were taken. Known amount of Cr (III) standard was mixed and extraction procedure was performed at different pH values. Concentration of the Cr present in $(NH_4)_2SO_4$ was determined by measuring spectral intensity of Cr (425.4 nm) in the LIBS spectra of the sample and comparing it with calibration curve in Figure 1. Extraction efficiency of PEG in this method is calculated using equation 1.

$$\text{Amount (\%) extracted in PEG} = \frac{\text{Amount of Cr extracted in PEG phase}}{\text{Amount of Cr taken initially in salt phase}} \text{ x } 100$$

$$= [1 - (\frac{\text{Amount of Cr present in salt phase after extraction}}{\text{Amount of Cr taken initially in salt phase}})] \text{ x } 100 \qquad (1)$$

The variation of the extent of distribution of speciation efficiency of Cr (III) at different pH is shown in the Figure 2. It is clear from the Figure 2 that the pH does not affect the extraction efficiency of trivalent chromium.

Similar extraction experiments were performed for the hexavalent chromium at different pH values and extraction efficiency for Cr (VI) is also plotted in Figure 2. It is clear from Figure 2 that maximum extraction for hexavalent chromium is achieved at pH 4.

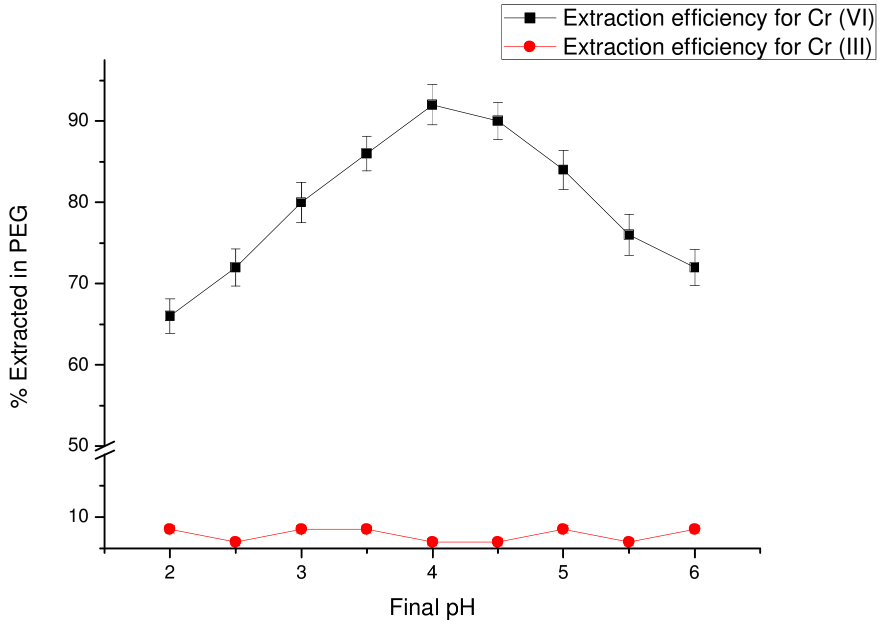

Figure 2: Variation of extraction efficiency with pH for Cr (III) and Cr (VI)

3.2 Optimization of Cr (VI) uptake by PEG

This experiment was performed to get the idea of the maximum amount of the hexavalent chromium that can be taken up by PEG. For speciation, 4 mL of each solution [PEG (50% w/v) and $(NH_4)_2SO_4$ (50% w/v)] was taken and extraction was performed for different [50µg to 250µg] amounts of Cr (VI). After extraction, the amount of the residual chromium present in $(NH_4)_2SO_4$ was determined. Amount (%) of hexavalent chromium extracted in PEG was calculated using equation 1 and the variation in amount (%) extraction with amount of Cr (VI) and Cr (III) is plotted in Figure 3. Figure 3 shows that, for 50 µg of hexavalent chromium taken initially in salt phase, extraction is more than 90%. It is also clear from the Figure 3, that on increasing the amount of hexavalent chromium, significant amount of Cr (VI) remained in $(NH_4)_2SO_4$.Thus for obtaining maximum extraction of Cr(VI), it should be less than 50 microgram in the sample to be analysed.

Similar experiment was also performed for trivalent chromium species and it was found that more than 95% of Cr (III) remained in $(NH_4)_2SO_4$ for different amounts of trivalent chromium.

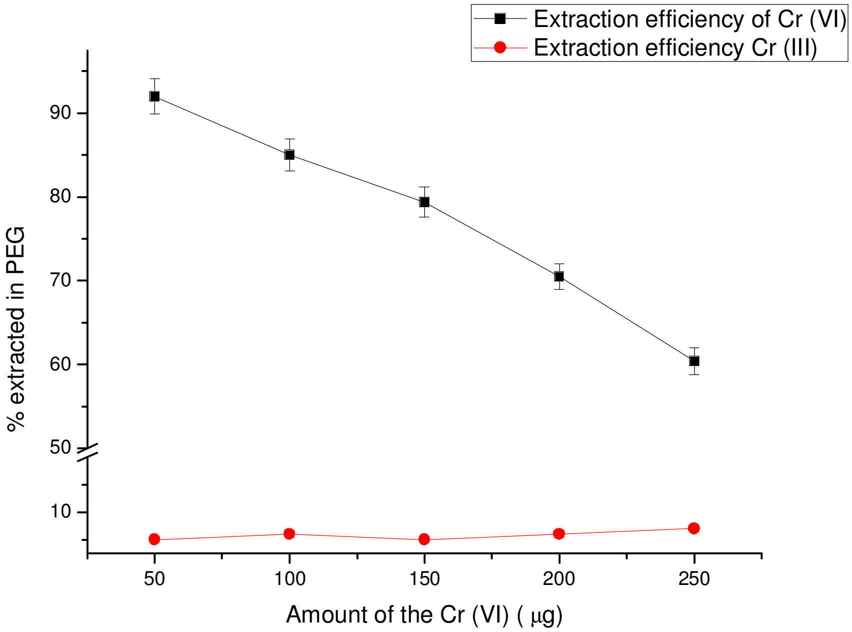

Figure 3: Variation of amount (%) extracted in PEG with amounts of Cr (VI) and Cr (III)

3.3 Optimization of volumes of PEG and $(NH_4)_2SO_4$

An experiment for the extraction of trivalent chromium was performed to get suitable amount of the solvent [PEG and $(NH_4)_2SO_4$] for maximum extraction. Amount of PEG and $(NH_4)_2SO_4$ was varied from 1 mL to 4 mL while amount of trivalent chromium was kept fixed (50 µg) during extraction. Extraction efficiency for trivalent chromium with volume of solution [PEG and $(NH_4)_2SO_4$] is shown in Figure 4. Similar experiment was done using hexavalent chromium and extraction efficiency is plotted in Figure 4.

It is observed that volume of salt phase or PEG taken initially does not affect the efficiency (%) of trivalent chromium whereas maximum amount (%) of Cr (VI) is extracted in PEG phase when 4 ml of PEG and $(NH_4)_2SO_4$ were used.

After optimization of the different parameters like pH, volume of PEG and $(NH_4)_2SO_4$, for the extraction of chromium species in solution containing Cr (VI) or Cr (III) individually, an experiment was performed to see the extraction efficiency of Cr species in a mixture containing both Cr (III) and Cr (VI). Two mixtures containing i) 75 µg Cr (III) and 75 µg Cr (VI) and ii) 100 µg Cr (III) and 50 µg Cr (VI) were prepared in tap water and extraction was performed under the optimised conditions.

The amount of Cr in the $(NH_4)_2SO_4$ was determined after extraction in the above mixtures and the results are given in Table1.

In solution 1, after extraction 75 µg should be present the $(NH_4)_2SO_4$ and rest must be in PEG. But Table 1 clearly reveal that 80 µg of Cr is present in $(NH_4)_2SO_4$. Similarly in solution 2, Cr amount in $(NH_4)_2SO_4$ is close to that of the expected amount.

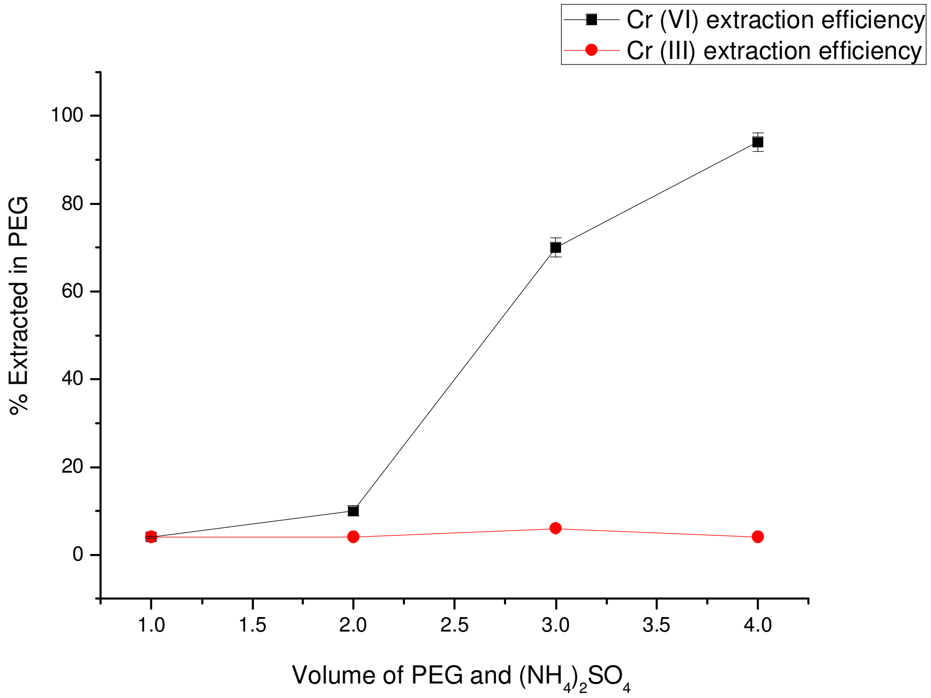

Figure 4: Amount (%) of Cr species extracted in PEG with variation in volume of PEG and $(NH_4)_2SO_4$ taken for extraction

Table 1: Cr amount expected and obtained in the salt phase after extraction

Solution	Total Cr (µg) [Cr (III) + Cr (VI)]	Expected amount of Cr in the $(NH_4)_2SO_4$ (µg)	Amount of Cr determined in the $(NH_4)_2SO_4$ after extraction (µg)
Solution 1	75+75=150	75	80
Solution 2	100+50=150	100	102

3.4 Speciation study of the industrial effluent samples

The above optimized extraction method was then applied for speciation of chromium in the samples collected from the industrial area of the Kanpur where a large number of the leather tanning industries are situated. Industrial waste water was collected (200mL) from different locations near industries like agriculture field, waste water treatment plant of Kanpur. Details of the collected samples are given in the Table 2. After collection, 20 mL dilute HNO_3 (Suprapure) was added to each sample and these were kept in the ice-box and brought to the laboratory and the experiments were performed in the laboratory within 6 hours of collection of the samples. The samples were filtered with Whatman filter paper 42 to remove the sludge from the industrial waste effluent.

To determine the total chromium amount, 20 µL of sample was deposited and dried on the whatmann filter paper, and LIBS spectra were recorded. The amount of the chromium was determined using calibration curve shown in Figure 1. Total amount of the chromium are given in Table 3.

Table 2: Details of the samples collected from the industrial area

Sample No.	**Details of the Sample**
Sample 1	Industrial waste effluent
Sample 2	Industrial waste effluent after one step of the treatment
Sample 3	Waste water from the solid waste sludge
Sample 4	After complete treatment which is used for irrigation in nearby fields.

Table 3: Total Cr Amount and Cr (III) amount in the industrial effluent samples

Sample	Total amount of Cr (µg)	Amount of the Cr (III) (µg)	% of Cr(VI) in sample
Sample 1	315	300	4.8
Sample 2	250	215	14
Sample 3	372	340	8.6
Sample 4	90	75	16.7

It is clear from Figure 3 that maximum extraction efficiency is obtained when solution (sample) contains upto 50 µg of Cr (VI). But total amount of Cr (i.e. Cr (III) + Cr (VI)) is higher (Table 3, total Cr amount) than optimized value (50 µg in 4 mL). Therefore, to get more than 90% separation of Cr (III) and Cr (VI) from industrial waste samples 1 to 3 were diluted 10 times and sample 4 was diluted 5 times. Extraction experiment was performed for all the diluted samples. After extraction, 20 µL of $(NH_4)_2SO_4$ containing Cr (III) was deposited and dried on whatmann filter paper and their LIBS spectra were recorded. A typical LIBS spectrum of the industrial effluent after extraction is shown in Figure 5. Presence of atomic lines at 425.4 nm, 427.4 nm and 428.9 nm confirms the presence of chromium in $(NH_4)_2SO_4$.

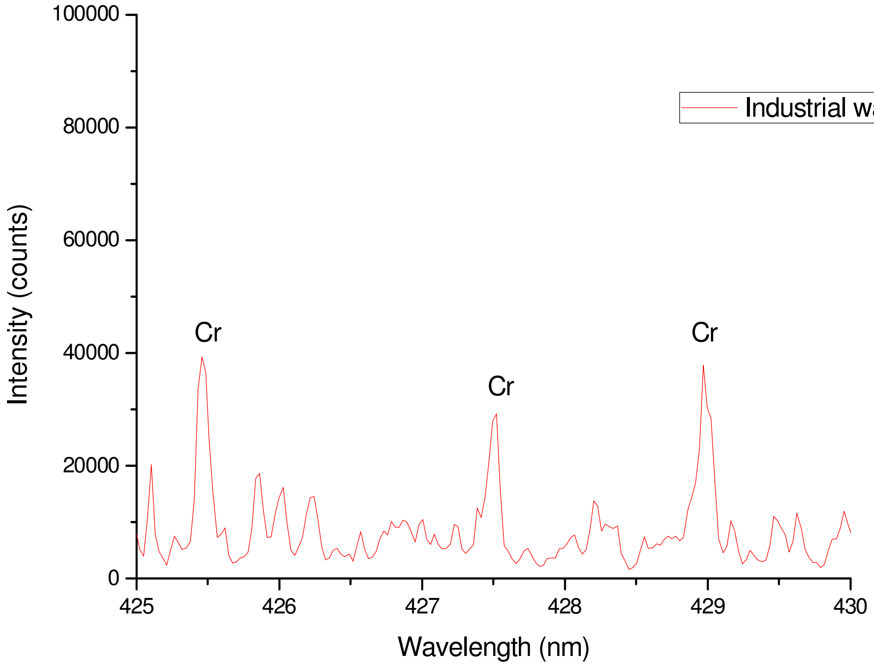

Figure 5: Presence of spectral lines of Cr in the LIBS spectrum of $(NH_4)_2SO_4$ after extraction

Amount of chromium in the $(NH_4)_2SO_4$ was determined using calibration curve method and results are given in Table 3. To determine Cr (VI), amount of chromium in $(NH_4)_2SO_4$ after extraction was subtracted from total amount of chromium obtained before extraction. Total Cr (before extraction) and Cr (i.e. Cr (III) + residual Cr (VI)) present in $(NH_4)_2SO_4$ after extraction in the collected industrial effluent samples are given in Table 3.

It is clear from Table 3 that most of Cr in the waste water is present in the form of Cr (III) species. The content of Cr (VI) species is increasing as the process of treatment of effluent continues which may be due to the high pH of the waste water samples. It can be seen that about 70% of Cr in the effluent is removed in the processing (from samples 1, 3 to 4), but still the amount of Cr present in the water used for irrigation contains significant amount of Cr when compared to the permissible limits.

4. Conclusion

An aqueous biphasic system consisting of $(NH_4)_2SO_4$ and polyethylene glycol was employed for separation of the two species of chromium (Cr) i.e. Cr (III) and Cr (VI). More than 90 to 95% separation of the Cr species was achieved by optimizing pH and volume of the PEG and ammonium sulphate. LIBS technique was employed for the quantification of chromium in different solutions. The results of the present study show that about 70% of the chromium in the industrial waste water is present in the form of trivalent chromium. This biphasic extraction method is suitable for the separation of the species of Cr in the industrial waste water at the site since it does not require elaborate experimental apparatus. Moreover using portable LIBS systems, this method can be used for the quantification of Cr (III) and Cr (VI) in the industrial waste at site which will give insight into contamination monitoring/remediation efforts. This study also indicates that the total amount of chromium is higher than the permissible limits of $50 \mu g L^{-1}$ specified by European Community Directive 80/778/EEC, L229/20, D48.

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