Research Article

Salting-Out Assisted Liquid-Liquid Extraction of Cr (VI) from Water Samples before Its Determination by UV-Vis Spectrophotometry

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This paper proposes salting-out assisted liquid-liquid extraction for selective extraction of a Cr (VI)-1,5-diphenylcarbazide complex before its determination by UV-Vis spectrophotometry. Parameters affecting the complexation process and the extraction efficiency of the method were studied. The highest extraction efficiency was obtained when acetonitrile was used as an extraction solvent and $(NH_4)_2SO_4$ was used as a salting-out agent. Under optimum conditions, the calibration curve constructed at seven concentration points exhibited good linearity from 0.015 to 2.00 mg/L with a 0.9973 coefficient of determination. The method's detection and quantification limits were 0.004 and 0.015 mg/L, respectively. The method showed a 5.8 enrichment factor. The intra- and inter-day precisions studied at two concentration levels (0.75 and 1.25 mg/L) showed relative standard deviation values of <9.0. The recoveries of the spiked water samples at the two concentration levels ranged from 88.0 ± 2.5 to 97.3 ± 0.1%. The method demonstrated negligible interferences (<5%) for Fe, Cu, V, and Cd up to 500 mg/L. The findings showed that the method is simple, rapid, efficient, and selective to be used as an alternative procedure for analyzing Cr (VI) from water and other related matrices.

1. Introduction

Chromium (Cr) is a toxic contaminant that has attracted attention due to its widespread use in industries [1]. Cr and its salts are used in electroplating, tanning, dyeing, mining, cement manufacture, metallurgy, and chemical industries. Thus, effluents discharged from these industries can elevate the amount of Cr in an environment, especially in surface and ground waters. In the environment, Cr mainly occurs as trivalent chromium, Cr (III), and hexavalent chromium, Cr (VI), which have different physicochemical properties and toxicities [2]. Cr (III) is beneficial in trace amounts. It is used for glucose, protein, and fatty acid metabolisms. However, Cr (VI) is a highly toxic or an extremely carcinogenic agent [3].

Depending on the pH of the aquatic environment, Cr (VI) occurs as H_2CrO_4, $HCr_2O_7^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} [4]. For instance, it occurs as CrO_4^{2-} from the pH of 6.5 to 14 [4], which spans the pH range of normal biological [5] and environmental water [6] systems. CrO_4^{2-} ions can enter cells via the sulphate/phosphate anion-transport system. In cells, it can be converted to Cr (III) by cellular reductants that involve the multi-step electron transfer process [4, 7] and formation of intermediate species that can damage DNA, disrupt transcription, and cause genotoxicity and malignant alterations in the cell [2–4]. Cr (III) can also be converted to Cr (VI) in an oxidizing medium but this is less likely to happen. Environmental contamination due to Cr is thus related to Cr (VI) species. It has carcinogenic and mutagenic effects in humans and inhibits growth and development as well as survival time of fish and plants among the living organisms [2–4, 8]. Owing to its toxicity, the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have set the maximum permitted limits for Cr (VI) in groundwater and drinking water at 0.1 mg/L and 0.05 mg/L, respectively [9].

Different analytical techniques can be used for the determination of total Cr and its species such as Cr (III) and Cr (VI) and these techniques were reviewed by Jyothi et al. [10] as well as Dawra and Dabas [11]. Among these techniques, the spectrophotometric method is extensively used for the determination of Cr (VI), mainly after chelating with 1, 5-diphenylcarbazide (DPC) [12–18]. However, before its instrumental determination, sample preparation involving extraction and preconcentration of the low-level concentration of Cr (VI) from real samples is necessary.

Classical sample preparation methods such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) have been used for extraction and preconcentration of Cr (VI) from different sample matrices [10, 11]. Nevertheless, these methods have several inherent drawbacks including use of high volumes of toxic organic solvents, generation of large volumes of wastes, and long processing times. In the last few decades, various modern sample preparation methods that use small volumes of pure or mixtures of organic solvents have been reported as selective, sensitive, and environmentally benign alternatives for extraction and preconcentration of Cr (VI) from various samples [9, 12–19].

For instance, among the modern sample preparation methods, surfactant-assisted dispersive liquid-liquid microextraction (SA-DLLME) [18], ultrasound-assisted supramolecular solvent DLLME [19], in-syringe magnetic stirring-assisted DLLME [20], deep eutectic solvent-based DLLME [16], solid phase microextraction (SPME) using a polyethylene terephthalate (PET) nanofiber film as adsorbent [13], solid phase extraction using thermally reduced graphene (TRG) modified SiO_2 as adsorbent [14], dispersive solid phase extraction (DSPE), using Zn-Al-layered double hydroxide intercalated with L-alanine (ZnAl-ALA-LDH) as adsorbent [9], and salt-assisted liquid-liquid microextraction using the hydrophilic ionic liquid as an extraction phase (SALLME-IL) [17] have been recently reported for extraction and preconcentration of Cr (VI) from various samples. Development of other simple, less expensive, and environmentally friendly alternative methods for extraction and preconcentration of Cr (VI) before its determination by instrumental techniques is still crucial.

In the last few decades, salting-out assisted liquid-liquid extraction (SA-LLE) or homogeneous liquid-liquid extraction (HLLE) has gained much attention as a simple and greener sample preparation method for analysis of different organic and inorganic pollutants [21]. The method usually uses pure or a mixture of water-miscible organic solvents such as acetone, acetonitrile, ethanol, and isopropanol as extraction solvents. In the procedure, a homogeneous phase formed between the aqueous sample and the water-miscible extractant is separated into biphases by the addition of salting-out agents or inorganic salts such as $K_4P_2O_7$, K_2HPO_4, K_3PO_4, K_2CO_3, $MgSO_4$, NaCl, and $(NH_4)_2SO_4$ [21–30]. The method uses small volumes of less toxic organic solvent, as well as commonly available inorganic salts and laboratory apparatus.

The aim of the current study was to optimize SA-LLE for extraction of Cr (VI) from water samples before its determination by UV-Vis spectrophotometry. Before the SALLE procedure, Cr (VI) reacts with DPC in a highly acidic solution to form a red-violet Cr (VI)-DPC complex whose absorbance is monitored at 540 nm.

2. Materials and Methods

2.1. Chemicals and Reagents. All chemicals and reagents used were of analytical grades. Potassium dichromate ($K_2Cr_2O_7$) (Sigma-Aldrich), 1, 5-diphenylcarbazide (DPC) (Kiran light laboratories, Mumbai, India), organic solvents: acetonitrile and ethanol (Sigma-Aldrich), methanol and acetone (CARLO ERBA, Paris, France), sulphuric acid (H_2SO_4) (Merck, Darmstadt, Germany), phosphoric acid (H_3PO_4) (Riedel-de Haen, Germany), nitric acid (HNO_3) (Blulux laboratories, Faridabad, India), potassium dihydrogen phosphate (KH_2PO_4) and dipotassium hydrogen phosphate (K_2HPO_4) (Beijing Chemical Reagents Company, China), ($NH_4)_2SO_4$ (Fisher Scientific Company, Pittsburgh, USA), and NaCl, $MgSO_4$, and Na_2CO_3 (BDH Chemicals Ltd, England) were used in this study.

A stock standard solution of Cr (VI), 1000 mg/L, was prepared by dissolving 2.83 g of $K_2Cr_2O_7$ in 1000 mL of 0.01 mol/L of HNO_3. The solution was stored in an amber bottle at 4°C and used for a maximum of two days. The intermediate standard solution of 100 mg/L was prepared by dilution of the stock solution. Then, 5 mg/L was prepared by dilution of the intermediate solution to prepare the desired concentration level for the daily use and preparation of the seven concentration levels: 0.25, 0.5, 0.75, 1, 1.25, 1.5, and 2 mg/L for the construction of calibration curve. Similarly, a stock solution of the chelating agent, DPC, 1000 mg/L, was prepared by dissolving it in acetone and kept at 4°C in an amber bottle when it was not in use. Phosphate buffer (pH = 6) was prepared by dissolving KH_2PO_4 and K_2HPO_4 in distilled water. Other solutions such as 2 mol/L of HNO_3, 3 mol/L of H_2SO_4, and 3 mol/L of KOH were also prepared in distilled water.

2.2. Instruments and Apparatus. Double beam UV-Vis spectrophotometer (SPECORD 200 PLUS, Analytik Jena, Germany), centrifuge (1790_{xg}, 4000 r/min) (Gemmy Industrial Corporation, Taiwan), Whatman no. 542 filter paper (Whatman International Ltd, England), 15-mL falcon centrifuge tubes, 1-cm quartz cuvette, and a medical syringe with B. Braun Sterican needle 21 G × 4¾ (0.80 × 122 mm BL/LB) (B. Braun Melsungen AG, Melsungen, Germany) were used during this study.

2.3. Water Samples Collection. The tap water sample was taken from the Jimma University's Analytical Chemistry Research Laboratory. The river water sample was collected from the Hawetu River (a river that crosses Jimma town) and well water sample was collected from the Abba Hassan area in Jimma town. All water samples were filtered using a Whatman filter paper to remove suspended materials and placed in a refrigerator when not used for analysis.

2.4. SA-LLE Procedure. A 5 mL aqueous sample containing 2 mg/L of Cr (VI) was transferred to a 15-mL falcon tube. Then, 0.5 mL of 0.032 mol/L of H_2SO_4 and 0.4 mL of 1000 mg/L of DPC were added, respectively. After the formation of the Cr (VI)-DPC complex, the pH of the sample was adjusted using the phosphate buffer. Subsequently, an extraction solvent and salt were separately added. The mixture was then vigorously shaken until the added salt was completely dissolved and then centrifuged to enhance the phase separation. Finally, the upper organic phase containing the target analyte was carefully withdrawn and transferred into a quartz cuvette for the subsequent UV-Vis analysis at 540 nm. The enrichment factor (EF) and differences in absorbance signals were used to evaluate the extraction efficiency of the method. The EF was obtained from the ratio of analyte concentration in the upper (organic) phase to the initial concentration in the aqueous phase, which is mathematically expressed as follows:

$$EF = \frac{C_{ex}}{C_{spiked}}, \tag{1}$$

where C_{ex} and C_{spiked} are the concentrations of Cr (VI) in the extraction phase and spiked in the aqueous sample, respectively.

3. Results and Discussion

The method under the study is based on the reaction of Cr (VI) with DPC in a strongly acidic solution. In this reaction, Cr (VI) is reduced to Cr (III) and DPC is oxidized to DPCN. The newly created species react to form a red-violet colored complex [4]. In this study, the Cr (VI)-DPC complex has been extracted using a water-miscible organic solvent in the presence of an appropriate amount of inorganic salt. The addition of inorganic salt helps to weaken the solvation force between the water-miscible organic solvent and the aqueous sample, which could result in the formation of a biphasic system [20]. In the process, the Cr (VI)-DPC complex migrates into the organic phase due to the hydrophobic nature of the ligand [12, 16]. Finally, the absorbance of the extracted and enriched analyte was monitored at 540 nm. Figure 1 shows the absorption spectra of 0.75 mg/mL Cr (VI) solution, DPC, and Cr-DPC complex recorded from 400 to 700 nm.

3.1. Optimization of the SA-LLE Procedure. To achieve efficient extraction, factors affecting the formation and subsequent extraction of the complex were investigated. Accordingly, variables that affect the formation of the complex (pH of the sample and volume of DPC) as well as its extraction by the proposed method (type and volume of organic solvent, types and amount of salt, and extraction time) were optimized using the one-variable-at-a-time method. The stability of the complex and the effect of interferences of various ions including Fe, Cu, V, and Cd were also studied.
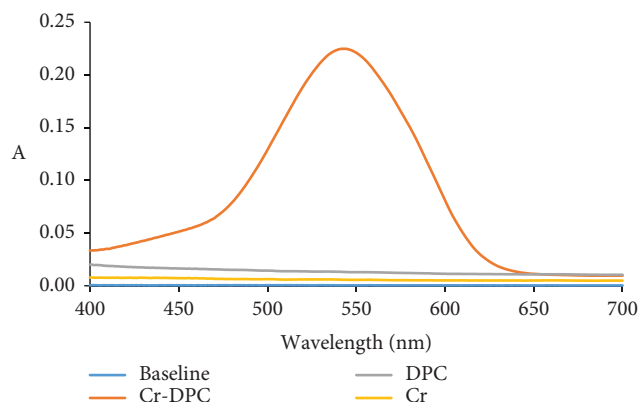

FIGURE 1: The spectra of 0.75 mg/mL Cr (VI) solution, DPC, and Cr (VI)-DPC complex.

3.1.1. Effect of pH. The pH of the aqueous solution is one factor that affects both the Cr (VI) complexation and the subsequent extraction process. The complexation reaction usually occurs in a strongly acidic solution [13, 16, 17]. However, according to literature, the Cr (VI)-DPC complex can be extracted at different pH values [16, 17]. Thus, the effect of pH was investigated from 1 to 7. The experiment was performed after the complex formation in acidic media (i.e., in 0.0032 mol/L of H_2SO_4). The results showed that extraction efficiency was increased as the pH of the sample increased up to pH 2 and remained constant up to pH 3. However, it declined at higher pH values (Figure 2). At pH values higher than 5, the color of the complex disappeared completely, indicating the instability of the complex at pH > 5. The observed extraction efficiency at pH 2 and 3 could be due to the established suitable conditions, allowing for the extraction of the complex either by pairing it with the appropriate ions [12, 16] or in hydration form [14]. Thus, pH 2 was chosen as the optimum value throughout the study.

3.1.2. Effect of DPC Concentration. To extract the available Cr (VI) ions, an appropriate amount of DPC should be added to the sample solution. To determine the optimum, different volumes (100–600 μL) of 1000 mg/L of DPC were added to the sample solution containing 2 mg/L of Cr (VI). Figure 3 shows the effects of the volume of DPC on the extraction efficiency of the method. It was observed that as the volume of the DPC increased, the absorbance of the resulting extracts increased up to 400 μL, and then, became constant with the addition of higher volumes. This implies that at a lower volume, below 400 μL, the ligand added is not enough to consume the available Cr (VI), indicating the presence of excess Cr (VI) in the solution. Therefore, 400 μL of 1000 mg/L DPC was selected for further studies.

3.1.3. Selection of a Suitable Organic Solvent. The organic solvent used for SA-LLE should be water-miscible, exhibit suitable hydrophobicity for phase separation upon the addition of salt, and selectively extract the target analyte
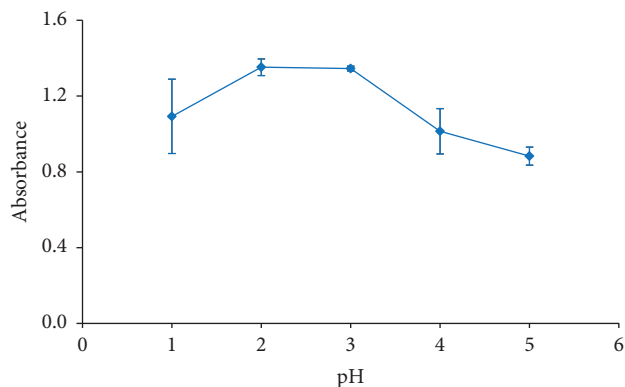
FIGURE 2: Effect of the pH. Experimental conditions: sample volume: 5 mL, Cr (VI): 2 mg/L, DPC: 1000 mg/L (400 μL), acetonitrile: 1.5 mL, $(NH_4)_2SO_4$: 3 g, and extraction time: 3 min.
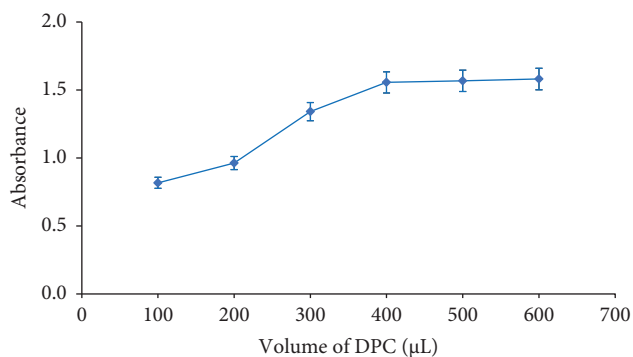

FIGURE 3: Effect of DPC volume. Extraction conditions: pH: 2, sample volume: 5 mL, Cr (VI): 2 mg/L, DPC: 1000 mg/L (400 μL), acetonitrile: 1.5 mL, $(NH_4)_2SO_4$: 3 g, and extraction time: 3 min.

[17, 21]. In this study, four solvents, including acetonitrile, acetone, ethanol, and methanol were evaluated. Among these solvents, only acetonitrile and acetone induced phase separation upon the addition of salt. Compared to acetone, acetonitrile extract showed higher extraction efficiency. Literature also showed that acetonitrile is the most commonly used solvent in the SA-LLE procedure [21–30]. Therefore, acetonitrile was selected as an extraction solvent in further experiments.

3.1.4. Effect of Acetonitrile Volume. To obtain high extraction efficiency, an appropriate volume of the extraction solvent should be used. Accordingly, to obtain the optimal volume, varied volumes of acetonitrile ranging from 0.5 to 3 mL were investigated. The findings demonstrated that the highest extraction efficiency was obtained when 1.5 mL of acetonitrile was used (Figure 4). Clear phase separation was not obsrved when 0.5 mL of acetonitrile was employed. However, when higher volumes (>1.5 mL) were used, the extraction efficiency of the method decreased, and this might have happened due to dilution resulting from the higher volume of the organic phase obtained after extraction [16]. Thus, 1.5 mL of acetonitrile was chosen as the optimal extraction volume.
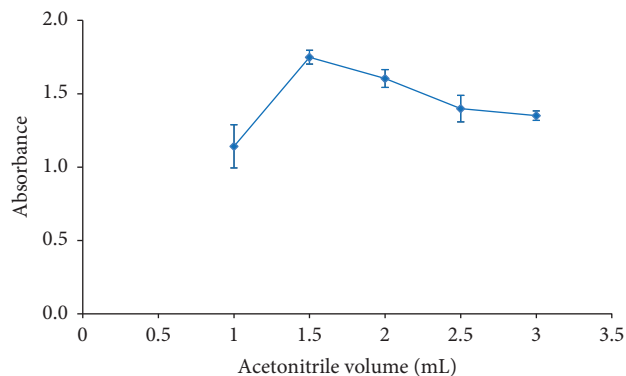

FIGURE 4: Effect of the extraction solvent volume. Extraction conditions: pH: 2, sample volume: 5 mL, Cr (VI): 2 mg/L, DPC: 1000 mg/L (400 μL), acetonitrile: 1.5 mL, $(NH_4)_2SO_4$: 3 g, and extraction time: 3 min.

3.1.5. Effect of the Salt Type and Amount. In SA-LLE, the use of an appropriate salt type is required to obtain a proper phase separation between the water-miscible organic solvent and the aqueous sample. Various salts have different degrees of phase separations [17, 21]. In the present work, four salts: NaCl, $MgSO_4$, Na_2CO_3, and $(NH_4)_2SO_4$ were evaluated, using 2 g of each salt, as potential salting-out agents. All the studied salts have induced phase separation. However, $(NH_4)_2SO_4$ gave reliable and reproducible phase separation than other salts and thus, it was chosen for further experiments.

The amount of the added salt must be sufficient to exhaustively separate the organic solvent from the aqueous phase. The influence of the amount $(NH_4)_2SO_4$ was studied by adding 0.5–3.5 g (10–70%, *m/v*) of $(NH_4)_2SO_4$. Phase separation was not observed when <1.5 g of $(NH_4)_2SO_4$ was added to the sample. As can be seen from Figure 5, the extraction efficiency of the method increased as the amount of the added salt increased up to 3.0 g and then slightly decreased when a higher mass, 3.5 g was used. The slight decrement observed at 3.5 g of $(NH_4)_2SO_4$ could be due to the adsorption of the complex on the undissolved particles of the salt since it was not completely dissolved. In addition, a decrease in the extraction efficiency on the addition of salt above 3 g could be due to an increase in the viscosity of the solution which reduces the transfer of the analyte from aqueous to organic phase [27]. Therefore, 3 g of $(NH_4)_2SO_4$ was used for further experiments.

3.1.6. Effects of Extraction Time and Stability of the Complex. During the extraction process, a large amount of SO_4^{2-} was introduced into the sample solution from the salting-out agent, $(NH_4)_2SO_4$. The Cr (VI)-DPC complex would be salted-out from the aqueous sample with an organic solvent, acetonitrile, due to the high hydration capacity of SO_4^{2-} ions and the hydrophobic character of the chelating agent. Shaking of the sample solution enhances the interaction between its constituents by increasing SO_4^{2-} ion hydration and analyte transfer to the organic phase [26]. The influence of mixing time (shaking time) was investigated from 1 to
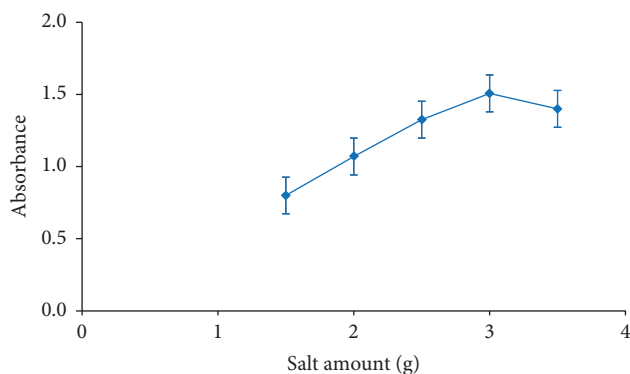
FIGURE 5: Effect of salt amount. Extraction conditions: pH: 2, sample volume: 5 mL, Cr (VI): 2 mg/L, DPC: 1000 mg/L (400 μL), acetonitrile: 1.5 mL, $(NH_4)_2SO_4$: 3 g, and extraction time: 3 min.

11 min at 2 min intervals. The results indicated that the extraction efficiency was increased with the extraction time up to 3 min and then, remained constant on extending the extraction time. Thus, 3 min was chosen for further study.

The stability of the Cr (VI)-CPD complex in the acetonitrile was evaluated from 20 to 160 min by measuring the absorbance of the extract at 20 min intervals. The extract was kept in the dark when not used for analysis. It was observed that the absorbance of the complex was nearly constant up to 120 min, but it steadily dropped after 120 min. In agreement with the previous report [16], we performed absorbance measurement in 30 min after extraction.

3.1.7. Effect of Interfering Ions. The DPC reagent specifically reacts with Cr (VI). However, in water samples, coexisting metal ions can interfere with the reaction and thus, may influence its analysis. As a result, the selectivity of the method was evaluated by separately spiking 50–500 mg/L of potentially interfering ions: Cu (II), Fe (III), V (VI), and Cd (II) into a sample containing 2 mg/L of Cr (VI). These metal ions were selected based on earlier reported literature [16, 17, 23]. Any interfering ion is considered to be tolerable if it causes variation of the absorbance signal by < 5% [1, 16]. The relative recovery (%RR) which was obtained by multiplying the ratio of the absorbance of the extracted sample containing the interfering ions to the absorbance of the extract of the original (interfering ions free) sample by 100% was used for evaluation of the interfering ions. The results of the study are presented in Table 1.

It was observed that both Fe (III) and Cu (II) ions affected the extraction efficiency of the method in a similar manner, i.e., extraction efficiency decreased when their concentrations were increased. Generally, the presence of the studied ions at all studied concentration levels (up to 500 mg/L), did not cause a significant change in the intensity of Cr (VI)-DPC color and its absorbance values, indicating that they could not interfere with the analysis of Cr (VI) by the proposed method.

TABLE 1: Effect of interferences for determination of 2 mg/L of Cr (VI) with DPC.

Concentration added, mg/L	%RR ± RSD in the presence of interfering ions			
	Fe (III)	Cu (II)	V (V)	Cd (II)
0	100 ± 1.8	100 ± 2.1	100 ± 0.8	100 ± 2.2
50	97.8 ± 1.7	95.6 ± 0.9	97.5 ± 6.4	96.8 ± 3.7
100	99.0 ± 1.8	97.1 ± 0.7	98.5 ± 3.8	97.8 ± 0.3
200	96.6 ± 1.5	96.0 ± 0.6	97.7 ± 4.0	103.2 ± 2.6
300	95.3 ± 0.9	98.8 ± 0.5	104.4 ± 0.9	103.3 ± 0.1
500	96.3 ± 0.5	96.0 ± 4.9	98.7 ± 3.8	104.7 ± 3.0

TABLE 2: Intraday and interday precisions (RSD) of the proposed method.

Spiked concentration, mg/L	Intraday ($n = 12$)	Interday ($n = 15$)
0.75	0.5	6.2
1.25	1.3	8.7

TABLE 3: Recovery studies.

Spiked concentration, mg/L	Tap water	River	Well water
0.75	97.3 ± 0.1	89.0 ± 8.7	90.0 ± 4.7
1.25	94.8 ± 0.1	88.0 ± 2.5	91.0 ± 1.1

3.2. Method Validation

3.2.1. Evaluation of Analytical Performance Characteristics. Seven concentration levels from 0.25 to 2.0 mg/L were used for the construction of a calibration curve. By using the optimum conditions, each concentration level was extracted in duplicate and each extract was analyzed in triplicate. The calibration curve was obtained by plotting the absorbance against Cr (VI) concentration. The obtained calibration curve had a linear equation of $y = 0.4264x + 0.088$ with the coefficient of determination, R^2, 0.9973. The LOD and LOQ of the method determined by multiplying the ratio of the standard deviation of the blank ($n = 10$) with the slope of the calibration curve by 3 and 10 were 0.004 and 0.015 mg/L, respectively. The EF of the method was 5.8.

3.2.2. Precision Study. The precision of the proposed method was investigated in terms of intra-day precision (repeatability) and inter-day precision (within-lab reproducibility) by spiking the sample at two concentration levels: 0.75 and 1.25 mg/L. Intra-day precision was studied by extracting each concentration level in duplicates, twice in a day (morning and afternoon). Inter-day precision was also evaluated for five consecutive days. In both cases, the absorbance of each extract was recorded in triplicates. The results of precision studies are presented in Table 2. The findings showed that the proposed method has a satisfactory precision, RSD < 9, for extraction of Cr (VI) after complexing with DPC before its spectroscopic determinations.

TABLE 4: Comparison of the proposed SA-LLE with other related methods.

Methods	Sample volume (mL)	LDR (mg/L)	R^2	LOQ (mg/L)	RSD	%RR	Ref
DSPE using ZnAl-ALA-LDH-FAAS	50	0.02–0.70	0.9979	0.0236	<3.0	88.5–110.1	[9]
Electrospun nanofibrous PET adsorbent-UV-Vis	25	0.0018–0.06	0.9923	0.0018	<4.0	96.9–99.1	[13]
TRG modified SiO_2 composite-UV-Vis	25	0.0013–0.04	0.9930	0.0013	<8.0	92.6–109.9	[14]
DLLME-DES-UV-Vis	10	0.005–0.20	0.9978	0.005	<5.0	90.0–98.2	[16]
SA-LLE-IL-FAAS	10	0.003–0.15	0.9994	0.004	<2.0	97.6–102.4	[17]
SA-DLLME/UV-Vis	5	0.005–0.10	0.9976	0.005	<5.2	83–102	[20]
SA-LLE-UV-Vis	5	0.015–20	0.9973	0.015	<9.0	88.0–97.3	Current study

DSPE, dispersive solid phase extraction; FAAS, flame atomic absorption spectroscopy; LDR, linear dynamic range; PET, polyethylene terephthalate; ZnAl-ALA-LDH, Zn-Al layered double hydroxide intercalated with L-alanine; SA-LLE-IL-FAAS, salt-assisted liquid-liquid microextraction with ionic liquid; SA-DLLME, surfactant-assisted dispersive liquid-liquid microextraction.

3.3. Analysis of Real Sample and Recovery Studies. The applicability of the method has been evaluated by analyzing tap, river, and well water samples and performing recovery studies. Recovery studies were conducted by spiking the water samples with concentration levels earlier used for the precision studies. The obtained recoveries ranged from 88.0 ± 2.5 to 97.3 ± 0.1 (Table 3), indicating the acceptance of the method for analysis of Cr (VI) from water samples and other related matrices. From the studied samples, the river water sample contained 0.06 mg/L of Cr (VI) but the tap and well water samples either had no Cr (VI) at all or had it at levels that were below the LOD of the method.

3.4. Comparison of the Proposed Method with Other Reported Methods. The optimized SA-LLE-UV-Vis' method was compared with other reported methods employed for extraction and determination of Cr (VI) from water samples (Table 4). The results demonstrated that the proposed method has comparable analytical performance characteristics such as linearity, precision, and recoveries. In addition, the method offers a short analysis time and uses small sample and extraction solvent volumes.

4. Conclusion

In this work, we proposed the SA-LLE procedure for extraction of Cr (VI) from water samples before determining it by UV-Vis spectrophotometry. The method involved complexing the Cr (VI) with DPC. Various parameters influencing the complexation process and extraction efficiency of the method were thoroughly studied. Under the optimal conditions, 1.5 mL of acetonitrile and 3.0 g of $(NH_4)_2SO_4$ were used as the extraction solvent and salting-out agent, respectively. The method has demonstrated satisfactory analytical performance characteristics such as linearity, precision (intra- and inter-day precisions), and recovery values. The findings also showed that the presence of metal ions, including Cu (II), Fe (III), Cd (II), and V (V) could not interfere with the analysis of Cr (VI), indicating the selectivity of the proposed method for analysis of Cr (VI) from water samples and other related matrices.

The method also showed comparable analytical performance characteristics such as linearity, precision, and recoveries with other earlier reported methods. However, the SA-LLE method is rapid and uses small sample volumes, conventional laboratory apparatus, and a small volume of less toxic organic solvent, which is available in any research laboratory. Therefore, the proposed SA-LLE procedure could be used as another alternative method of analyzing Cr (VI) from environmental water and other related matrices.

Data Availability

The data sets used and/or analysed during the current study are available from the corresponding author upon request.

Disclosure

The article is extracted from the MSc thesis of the first author, which was previously released online on Jimma University repository: https://repository.ju.edu.et/handle/123456789/5827.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

Authors' Contributions

AG and FW designed the research work and guided the experimental work. JD conducted the experimental work. GJM wrote the manuscript.

Acknowledgments

References

[1] A. Lace, D. Ryan, M. Bowkett, and J. Cleary, "Chromium monitoring in water by colorimetry using optimised 1, 5-diphenylcarbazide method," *International Journal of Environmental Research and Public Health*, vol. 16, no. 10, p. 1803, 2019.

[2] M. Tumolo, V. Ancona, D. De Paola et al., "Chromium pollution in European water, sources, health risk, and remediation strategies: an overview," *International Journal of Environmental Research and Public Health*, vol. 17, no. 15, p. 5438, 2020.

[3] A. Sharma, D. Kapoor, J. Wang et al., "Chromium bioaccumulation and its impacts on plants: an overview," *Plants*, vol. 9, no. 1, p. 100, 2020.

[4] R. Milačič and J. Ščančar, "Cr speciation in foodstuffs, biological and environmental samples: methodological approaches and analytical challenges- a critical review," *TRAC Trends in Analytical Chemistry*, vol. 127, Article ID 115888, 2020.

[5] E. Hopkins, T. Sanvictores, and S. Sharma, "Physiology, acid base balance," in *StatPearls*, StatPearls Publishing, Treasure Island, FL, USA, 2023.

[6] Who, *WHO/SDE/WSH/07.01/1: pH in Drinking-Water: Revised Background Document for Development of Who Guidelines for Drinking-Water Quality*, World Health Organization, Geneva, Switzerland, 2007.

[7] S. H. Pezzin, J. F. L. Rivera, C. H. Collins, and K. E. Collins, "Reduction of Trace quantities of chromium (VI) by strong acids," *Journal of the Brazilian Chemical Society*, vol. 15, no. 1, pp. 58–65, 2004.

[8] S. Prasad, K. K. Yadav, S. Kumar et al., "Chromium contamination and effect on environmental health and its remediation: a sustainable approaches," *Journal of Environmental Management*, vol. 285, Article ID 112174, 2021.

[9] V. dos Santos Azevedo Leite, B. G. L. de Jesus, V. G. de Oliveira Duarte et al., "Determination of chromium (VI) by dispersive solid-phase extraction using dissolvable Zn-Al layered double hydroxide intercalated with L-alanine as adsorbent," *Microchemical Journal*, vol. 146, pp. 650–657, 2019.

[10] N. R. Jyothi, N. Mohammad Farook, M. Cho, and J. Shim, "Analysis and speciation of chromium in environmental matrices by various analytical techniques," *Asian Journal of Chemistry*, vol. 25, no. 8, pp. 4125–4136, 2013.

[11] N. Dawra and N. Dabas, "Advances in spectrophotometric determination of chromium (III) and chromium (VI) in water: a review," *International Journal of Environmental Analytical Chemistry*, 2022.

[12] T. Simonova, V. Dubrovina, and A. Vishnikin, "Speciation of chromium through aqueous two-phase extraction of complexes of Cr (III) with 4-(2-pyridylazo) resorcinol and Cr (VI) with 1, 5-diphenylcarbazide," *Journal of the Serbian Chemical Society*, vol. 81, no. 6, pp. 645–659, 2016.

[13] H. Sereshti, F. Amini, and H. Najarzadekan, "Electrospun polyethylene terephthalate (PET) nanofibers as a new adsorbent for micro-solid phase extraction of chromium (VI) in environmental water samples," *RSC Advances*, vol. 5, no. 108, pp. 89195–89203, 2015.

[14] H. Sereshti, M. Vasheghani Farahani, and M. Baghdadi, "Trace determination of chromium (VI) in environmental water samples using innovative thermally reduced graphene (TRG) modified SiO$_2$adsorbent for solid phase extraction and UV-Vis spectrophotometry," *Talanta*, vol. 146, pp. 662–669, 2016.

[15] K. K. Onchoke and S. A. Sasu, "Determination of hexavalent chromium (Cr (VI)) concentrations via ion chromatography and UV-Vis spectrophotometry in samples collected from Nacogdoches wastewater treatment plant, East Texas (USA)," *Advances in Environmental Chemistry*, vol. 2016, Article ID 3468635, 10 pages, 2016.

[16] M. Pourmohammad, M. Faraji, and S. Jafarinejad, "Extraction of chromium (VI) in water samples by dispersive liquid–liquid microextraction based on deep eutectic solvent and determination by UV–Vis spectrophotometry," *International Journal of Environmental Analytical Chemistry*, vol. 100, no. 10, pp. 1146–1159, 2020.

[17] B. Majidi and F. Shemirani, "Salt-assisted liquid-liquid microextraction of Cr (VI) ion using an ionic liquid for preconcentration prior to its determination by flame atomic absorption spectrometry," *Microchimica Acta*, vol. 176, no. 1-2, pp. 143–151, 2012.

[18] H. R. Sobhi, E. Azadikhah, M. Behbahani, A. Esrafili, and M. Ghambarian, "Application of a surfactant-assisted dispersive liquid-liquid microextraction method along with central composite design for micro-volume based spectrophotometric determination of low level of Cr (VI) Ions in Aquatic samples," *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, vol. 202, pp. 36–40, 2018.

[19] M. Tuzen, A. Elik, and N. Altunay, "Ultrasound-assisted supramolecular solvent dispersive liquid-liquid microextraction for preconcentration and determination of Cr (VI) in waters and total chromium in beverages and vegetables," *Journal of Molecular Liquids*, vol. 329, Article ID 115556, 2021.

[20] C. Henríquez, B. Horstkotte, P. Solich, and V. Cerdà, "In-syringe magnetic-stirring-assisted liquid–liquid microextraction for the spectrophotometric determination of Cr (VI) in waters," *Analytical and Bioanalytical Chemistry*, vol. 405, no. 21, pp. 6761–6769, 2013.

[21] S. F. Hammad, I. A. Abdallah, A. Bedair, and F. R. Mansour, "Homogeneous liquid–liquid extraction as an alternative sample preparation technique for biomedical analysis," *Journal of Separation Science*, vol. 45, no. 1, pp. 185–209, 2022.

[22] S. Xie, W. Song, C. Fu, C. Yi, and X. Qiu, "Separation of acetone: from a water miscible system to an efficient aqueous two-phase system," *Separation and Purification Technology*, vol. 192, pp. 55–61, 2018.

[23] I. M. Valente, L. M. Gonçalves, and J. A. Rodrigues, "Another glimpse over the salting-out assisted liquid–liquid extraction in acetonitrile/water mixtures," *Journal of Chromatography A*, vol. 1308, pp. 58–62, 2013.

[24] J. Zhang and X. Xiong, "Salting-out assisted liquid–liquid extraction (SA-LLE) in LC-MS bioanalysis," in *Sample Preparation in LC-MS Bioanalysis*, W. Li, W. Jian, and Y. Fu, Eds., pp. 68–75, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2019.

[25] Y. Q. Tang and N. Weng, "Salting-out assisted liquid–liquid extraction for bioanalysis," *Bioanalysis*, vol. 5, no. 12, pp. 1583–1598, 2013.

[26] A. M. Hyde, S. L. Zultanski, J. H. Waldman, Y. L. Zhong, M. Shevlin, and F. Peng, "General Principles and strategies for salting-out informed by the Hofmeister series," *Organic Process Research & Development*, vol. 21, no. 9, pp. 1355–1370, 2017.

[27] R. Rezaeepour, R. Heydari, and A. Ismaili, "Ultrasound and salt-assisted liquid–liquid extraction as an efficient method for natural product extraction," *Analytical Methods*, vol. 7, pp. 3253–3259, 2015.

[28] R. Heydari and M. Mousavi, "Simultaneous determination of saccharine, caffeine, salicylic acid and benzoic acid' in different matrixes by salt and air-assisted homogeneous liquid-liquid extraction and high-performance liquid chromatography," *Journal of the Chilean Chemical Society*, vol. 61, no. 3, pp. 3090–3094, 2016.

[29] R. Heydari, Z. Lotfi, and M. Ramezani, "Simultaneous determination of zidovudine and lamivudine in plasma samples using miniaturized homogenous liquid–liquid extraction and high-performance liquid chromatography," *Journal of Analytical Chemistry*, vol. 73, no. 11, pp. 1105–1110, 2018.

[30] M. Heydarzadeh, M. H. Givianrad, R. Heydari, and P. Aberoomand Azar, "Salt-assisted liquid–liquid extraction in microchannel," *Journal of Separation Science*, vol. 42, no. 20, pp. 3217–3224, 2019.