Gadolinium Quantification From Wastewater By Vortex Assisted-Dispersive Liquid-Liquid Microextraction Using Novel Hydrophobic Deep Eutectic Solvent And Spectrophotometry

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***Abstract*—Gadolinium (Gd), a significant rare earth element, is gradually recognized as a contaminant in industrial wastewater. This is largely due to its widespread use in electronics manufacturing and medical imaging. Because gadolinium persist in the environment and can potentially harm ecosystems, effective and sustainable analytical methods are crucial for its monitoring and removal. This research introduces an environmentally friendly analytical method for the preconcentration and spectrophotometric determination of Gd ions in industrial wastewater using Vortex-Assisted Dispersive Liquid-Liquid Microextraction (VA-DLLME) with a novel Deep Eutectic Solvent as the extractant. In this process, Alizarine Red S (ARS) acts as a complexing agent at a pH of 5. Subsequently, a hydrophobic deep eutectic solvent is used to extract theses bound gadolinium ions. The Gd-ARS complex was subjected to vortexing at 2800 rom for 30 sec, facilitating to complete extraction of the complex into a non-aqueous phase. Various parameters were carefully analyzed to improve the extraction efficiency of gadolinium. The analytical performance showed consistent results, with linearity ranging from 14.5- 115 µg/L, a detection limit of 3.13 µg/L, and a quantification limit of 10.43 µg/L. The enrichment factor was established at 50. The method also demonstrated high precision (RSD-1.56%) and accuracy, confirmed through recovery studies in wastewater matrices with spiked gadolinium. In the analysis of real wastewater samples, this approach exhibited good sensitivity and selectivity for quantifying Gadolinium.**

***Index Terms*—Gadolinium, Rare Earth Element, Dispersive liquid-liquid microextraction, Deep Eutectic Solvent, UV-Visible Spectrophotometry.**

I. INTRODUCTION

Rare earth elements are of growing importance to modern society, driven by their critical role in numerous advanced technological applications[1]. These elements possess distinct chemical and physical properties, which making them key components across different high technology areas like renewable energy, electronics and medical applications[2][3]. The global increase in the use of rare earth elements, gadolinium, has recently brought about significantly environmental issues and challenges of valuable resource recovery[4]. Gadolinium is key for industrial and medical uses due to its unique magnetic and optical properties[5]. It is widely utilized as a contrast agent in magnetic resonance imaging, and is also incorporated into catalyst, alloys, phosphors, nuclear reactors and electronic devices[6][7][8]. However, the increasing discharge of gadolinium into medical and industrial wastewaters raises environmental concerns[9,10].

The presence of gadolinium in industrial wastewater is a serious concern for several reasons. Although gadolinium in its metallic form is not highly toxic, but its ionic and complexed compounds, specifically those used in MRI contrast agents can accumulate in aquatic systems and it can enter the food chain[11–13]. The determination of Gd in aquatic environments raises questions regarding its long-term effects on organisms, human health and ecosystems[14–17]. The increasing environmental contamination is largely due to the inability of conventional wastewater treatment systems to effectively remove rare earth elements. Therefore, effective methods are needed for the selective extraction and preconcentration of

gadolinium from complex wastewater matrices to control the pollution and recovery of these valuable rare earth resources.

Among the various separation techniques, solvent extraction has emerged as an effective technique for the selective estimation and recovery of transition metals and rare earth elements from secondary sources, such as industrial wastewater. This approach is chosen for its effectiveness in separating target analytes from complex matrices[18].

The traditional classical solvent extraction method faces several limitations. It is labor-intensive and time-consuming, requiring highly pure organic solvents. Additionally, the disposal of used organic solvents poses environmental challenges, complicating the process[19]. Miniaturised microextraction methods have emerged as alternatives to conventional solvent extraction methods for instance dispersive liquid-liquid microextraction (DLLME)[20,21], cloud point extraction[22], liquid-phase microextraction[23,24], solid phase microextraction[25], hollow fiber phase microextraction[24] and solid floating organic drop microextraction[26]. These have been developed which utilize a limited amount of extracting agents and involve a minimal number of processing steps.

Mohammad Razaee et.al 2006, have established a novel, simple, quick and effective microextraction method called dispersive liquid-liquid microextraction (DLLME). This innovative technique can effectively concentrate both inorganic as well as organic analytes from aqueous media[27]. Conventional DLLME methods have limitations and attributes that reduce their compatibility with the green analytical sample preparation process principles[21]. The DLLME approach involves the swift injection of blend of dispersing and extraction solvents into aqueous samples containing the target analytes, resulting in the formation of a turbid solution. This cloudiness is attributed to the dispersion of minute droplets of the extraction solvent within the sample solution. The centrifugation of the sample results in the sedimentation of the droplets at the bottom of the test tube[28]. The analyte in the sedimented phase is determined using different detection methods. The most widely employed analytical techniques coupled with DLLME for the detection and quantification of rare earth elements include Inductively couples plasma-quadrupole mass spectrometry (ICP-QMS)[29], Inductively coupled plasma- optical emission spectrometry[30], Inductively coupled plasma-mass spectrometry (ICP-MS)[31]. UV-Visible spectrophotometry[32] also commonly used detection method in combination with DLLME for detecting metal ions, however it is not used to quantify the rare earth elements. These techniques require complex sample pretreatment and expensive instrumentation.

The DLLME approach has been further enhanced through the modification of DLLME with integration of vortex-assisted techniques[33]. This study investigates the feasibility of employing a simple vortex-assisted dispersive liquid-liquid microextraction technique for the detection and quantification of rare earth metals. Determining the gadolinium concentration at trace or even ultra-trace levels often necessitates a reliable preconcentration step[34]. The proposed method utilises a vortex mixer to achieve efficient dispersion of the extractant, eliminating the need for a disperser solvent. In contrast to the commonly used hazardous organic solvents in standard DLLME procedures, hydrophobic deep eutectic solvent was used.

Deep eutectic solvents (DES) are formed by combining a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). The DES were initially detailed in the academic publications authored by Abbott and coworkers[35]. In this research work, biodegradable deep eutectic solvents were utilized as the extractants. Eugenol, an effective hydrogen bond donor, was combined with various ammonium salts to synthesize hydrophobic DES.

Eugenol based deep eutectic solvent was initially documented for the microextraction of Sudan dyes[36]. DES offer several advantages, including ease of preparation, environmental friendliness, biodegradability, and low toxicity. Hydrophobic DESs are particularly useful in replacing traditional hazardous organic extraction solvents in DLLME for metal ion detection in aqueous samples[32]. They can serve as effective extraction media and can be easily synthesized without purification[37][38][39]. This study reports the first known implementation of the novel eugenol based deep eutectic solvent vortex-assisted dispersive liquid-liquid microextraction technique for the detection and quantification of gadolinium from industrial waste water samples. To the best of our knowledge, this method has not been previously employed for the analysis of gadolinium by eugenol based DES VA-DLLME method from

industrial waste water sample. The present study utilised deep eutectic solvent-based VA-DLLME coupled with UV-Visible spectrophotometry to analyse gadolinium ions in industrial waste water, owing to its simplicity and cost-effectiveness.

II. EXPERIMENTAL

2.1 Materials and reagents

In this work, we focused on establishing a reliable spectrophotometric methodology for the quantitative assessment of Gadolinium ions in aqueous media. A standard stock solution of Gadolinium (1000 mg/mL) was prepared utilizing a certified Gadolinium standard solution obtained from Sigma-Aldrich (Mumbai, India). This standard solution was then serially diluted with double-distilled water to produce the necessary µg/mL standard solutions of Gd ions. Key chemicals for this study, Eugenol and Alizarin Red S (3,4-dihyfroxy-9,10-dioxo-9,10-dihydroxyanthracene-2-sulphonate), were procured from Loba Chemicals (Mumbai, India) and quaternary ammonium salts were sourced from Spectrochem. All other analytical grade reagents and solvents employed in the experimental procedures were acquired from S.D. Fine-chem (Boisar, India). Double-distilled water was consistently used throughout the experimental procedure. Industrial wastewater originated from Tarapur M.I.D.C, Maharashtra.

2.2 Instrumentation

The Gadolinium metal complex underwent a comprehensive analysis utilizing UV-Visible spectrophotometry (Shimadzu Analytical, India) in conjunction with a microcuvette to determine various parameters of complex. For uniform sample homogenization, vortex agitation was performed using a vortex apparatus (Remi, India). Centrifugation via a centrifuge apparatus (Remi, India) facilitated the separation of the extracted phase. A pH measurement device (Thermo Scientific, India) was utilized to carefully monitor the pH levels of both the blank and analyte samples.

2.3 Synthesis of DES

In the present study, six hydrophobic DES based on the Eugenol (hydrogen bond donor) and containing different quaternary ammonium salts, (A) Benzyl triethyl ammonium chloride, (B) Benzyl triethyl ammonium bromide, (C) Benzyl trimethyl ammonium chloride, (D) Benzyl trimethyl ammonium bromide, (E) Benzyl tributyl ammonium chloride, (F) Benzyl tributyl ammonium bromide, were synthesized. The hydrophobic DES were synthesized by mixing in 3:1 molar ratio of Eugenol to salt (C). The components were mixed and heated to 55° C until a clear, homogenous liquid was obtained, which was allowed to cool at room temperature for analytical characterization. Fourier Transform Infrared Spectroscopy (FTIR) was used to study the structural features of the synthesized deep eutectic solvents; with comprehensive spectral data presented in the Figure 1. The formation of DES was confirmed by strong intermolecular hydrogen bonding between the quaternary ammonium salts and eugenol, was evidenced by red shift in the -OH group stretching vibration from 3500 cm^{-1} in pure eugenol to the 3300-3100 cm^{-1} region in the DESs, indicate that longer and stronger hydrogen bonds formed within the eutectic mixture. These finding confirmed that the DES was successfully prepared.

2.4 Va-Dllme Of Gd (III)

A preconcentration procedure was executed before analytical measurements. This preconcentration step was performed in 15 mL calibrated conical tube. Initially, a 10 mL aqueous solution containing 86.10 µg/L of Gadolinium ions was complexed with 250 µL of ARS acting as a chelating reagent at a pH range of 5-6. Then resulting Gadolinium complex was efficiently extracted by rapidly injecting 200 µL of DES via syringe. The mixture was homogenized by vortex agitation for 1 minute at 2800 rpm, which dispersed the DES into fine microdroplets within the solution, creating cloudy emulsion. Following this the sample underwent centrifugation at 5000 rpm to sediment the extracted phase. The concentrated sedimented phase was carefully isolated using a syringe and analyze using UV-Visible spectrophotometer with microcuvette. This dispersive liquid-liquid microextraction technique significantly improves extraction process by increasing the interfacial surface area and allowing rapid, almost complete analyte recovery.

2.5 Application to real samples

The proposed method was rigorously applied to industrial wastewater samples from Tarapur M.I.D.C., Maharashtra. To ensure accurate analysis, these samples were initially filtered through a 0.45 mm

cellulose membrane and subsequently stored in pre-cleaned glass bottles. A wastewater sample was taken without pretreatment before determination using VA-DLLME procedure. The method's accuracy was confirmed by measuring the recovery of rare earth elements in spiked water samples. This validated the Gadolinium ion extraction method's effectiveness across various wastewater types, proving its practical use for environmental monitoring. The VA-DLLME method showed good recovery rates for Gadolinium in complex wastewater, which suggesting its potential for routine analysis.

III. RESULTS AND DISCUSSION

The successful implementation of reliable analytical performance, particularly within complex sample matrices, requires meticulous optimization for any proposed methodology. The VA-DLLME method, while rapid, efficient and effective, required further optimization of specific factors to enhance its overall efficiency and applicability. This optimization initiative precisely investigated key factors, including solution pH, the precise concentration and quantity of the chelating agent, the selection and volumetric dosage of the extraction solvent, optimal vortex agitation duration, specific centrifugation parameters, the influential role of salt addition, and the potential for interference from co-existing foreign ions. The optimization procedure adhered to a one-variable-at-a-time approach. All experiments consistently performed in triplicate to ensure robust and reproducible results. The resultant enrichment factor and extraction recovery, both indispensable for validating analytical performance. The extraction recovery and enrichment factor (EF) were calculated employing the subsequent equations (1) & (2)[40,41]

$$\% \text{ Recovery} = \frac{C_{des}}{C_0} \times 100 \quad (1)$$

$$EF = \frac{V_{sample}}{V_{sediment}} \quad (2)$$

C_{des} and C_0 are the concentrations of the analyte in the DES phase after extraction to the original analyte concentration. V_{sample} and $V_{sediment}$ are the volumes of sample and sedimented phase, respectively.

3.1 pH Effect

The pH was identified as vital parameter that influenced the percent recovery and the formation of the Gadolinium-Alizarine Red S (ARS) complex during the VA-DLLME procedure. Gadolinium was found to form a stable complex with ARS under acidic conditions, facilitating its efficient extraction. Consequently, the impact on the Gd-ARS complex formation and the recovery was studied across the series of 2.0 to 9.0 (adjusted by 0.1 mol L^{-1} HCl and NaOH). The Gadolinium recoveries increased as the pH was elevated from 2.0 to 5.0, reaching optimal values within the pH range of 5.0 to 6.0 these findings are displayed in Figure 2. Subsequent optimization studies were conducted at a pH of 5.0. Adjusting the pH can also influence the stability of analytes during the extraction process. By optimizing the pH, the stability of these analytes was observed up to 24 hours. The extension of analyte stability directly contributes to more precise and reliable analytical measurements, enhancing the overall robustness and reproducibility of the analytical method.

3.2 Study of Absorption Spectra

In this study, a UV-Visible spectrophotometer was utilised to optimized parameters. Spectrophotometric analysis of the Gadolinium complex was performed to characterize its absorption spectrum. The maximum absorption wavelength was determined to be 600 nm, with measurement referenced against a reagent blank as shown in Figure 3.

3.3 Effect of amount of ARS (Chelating reagent)

The Gd (III) ion forms a complex with Alizarin Red S, and the impact of ARS concentration was examined using a 0.01% to 0.1% solution, as depicted in Figure 4. It is evident that the absorbance was observed to rise proportionally with increases in the chelating reagent concentration up to 0.1% and alizarin red S was subsequently selected for further studies. Similarly, the volume of the chelating reagent demonstrated significant effects on the extraction efficiency of Gadolinium. As the reagent volume was increased from 50 to 400 µL, the Gd recovery exhibited a corresponding rise, ultimately plateauing around 250 µL. The optimal volume of alizarine red S required for effective complexation and extraction of Gd was approximately 250 µL as shown in Figure 5.

3.4 Selection of DES

Selecting a suitable extraction solvent is essential for efficiently separating the analyte from the sample

matrix. The current study investigated the performance of various deep eutectic solvents as potential extraction. Consequently, a deep eutectic solvent labelled as DES C (Benzyl trimethyl ammonium chloride) was chosen as the extracting solvent to be used in further investigations. Furthermore, the volume of DES-C ranging from 25 µL to 400 µL were analysed under optimal experimental conditions. The finding revealed that a DES C volume of 200 µL displayed the maximum percentage of extraction, leading to selection of 200 µL of DES-C for subsequent extractions as shown in Figure 6.

3.5 Effect of Vortex Time

The efficiency of analyte extraction is fundamentally dependent on the rate of mass transfer from the sample solution to the extraction phase. As such, determining the optimal agitation times for dispersion is a critical step in maximizing the transfer of the analyte from the aqueous phase to the organic phase. This optimization step is instrumental in enhancing the overall effectiveness of the extraction procedure. To achieve sufficient dispersion for maximum extraction of the Gd-ARS complex, am appropriate vortex time was required. The impact of vortex duration on extraction efficiency was evaluated by changing the duration from 10 seconds to 90 seconds, while other experimental variables remained constant, as shown in Figure 7. The outcomes revealed that the extraction effectiveness increased as the vortex period was extended, with the absorbance showing the most significant change up to 30 seconds of vortexing, beyond 30 seconds, the absorbance did not change significantly, indicating that the Gd-ARS complex had been effectively dispersed and extracted within this duration. Therefore, 30 second was selected as the optimal vortex period to maximize the extraction, as it provided a balance between efficient dispersion and time-effectiveness.

3.6 Centrifugation parameter

After agitation using a vortex shaker at 2800 rpm under optimized conditions, the Gd-ARS complex was successfully extracted into the DES phase. To enable effective separation of Gd-enriched DES phase for further analysis, the sample underwent centrifugation at an optimal speed of 5000 rpm for 30 seconds. This rapid centrifugation step facilitated efficient separation and maximum extraction, causing the sedimented portion to accumulate at the base of centrifugation tube. The isolated DES phase, containing the Gd-chelate complex, was then removed using a syringe and subjected to UV-Visible spectrophotometric analysis. The separation of Gd-ARS complex in the DES phase was determined to be both effective and complete within the given centrifugation parameters.

3.7 Effect of salt concentration

The study investigated the impact of incorporating varying sodium chloride concentrations in the sample solution on extraction efficiency. This analysis explored the effect of salt addition on the extraction process. While the introduction of salts can potentially enhance the extraction of metal complexes and decrease their solubility in aqueous media due to the salting out effect, the present study evaluated the effects of 2.5%, 5 % and 10% NaCl, KCl, Na2SO4 and NaNO3 on an 86.10 µg/L Gadolinium solution. The findings revealed that incorporating these salts did not enhance the extraction efficiency compared to when no salts were added.

3.8 Effect of metal interference

The impact of matrix constituents on the determination of analyte elements using instrumental techniques should be evaluated through preconcentration/separation procedures. Certain foreign ions can form stable complexes with ARS and the salt components in real environmental samples, potentially interfering with the proposed method for Gd (III). Consequently, the influence of common coexisting ions on the VA-DLLME of Gd (III) ion was investigated. The effects of the scrutinized matrix were assessed independently. The results for percentage recovery, as presented in

Table *1*, indicate that elevated concentrations of these interfering ions did not affect the recovery of Gadolinium, demonstrating the high selectivity and lack of interference in the method following the established protocol, the solutions containing 86.10 µg/L of Gadolinium was spiked with varying concentrations of foreign ions and processed using the developed method. Thiocyanate was employed as a masking agent to mitigate the interference of Fe (II), but higher levels of these elements did impact the method.

3.9 Analytical figures of merits and validation of VA-DLLME method

The VA-DLLME method coupled with UV-Visible spectrophotometry, evaluated remarkable analytical performance under optimal conditions. The study investigated key analytical parameters, including limit of quantification (LOQ), relative standard deviation (RSD), limit of detection (LOD), and enrichment factor (EF). The calibration curve demonstrated linearity over the 14.5 to 115 µg/L concentration range for Gd (III) ions, with a corelation coefficient of 0.9996. the intraday precision, expressed as the relative standard deviation, was 1.56% based on 10 replicate measurements at 86.10 µg/L Gd (III). The quantification limit and detection limit were determined to be 10.43 µg/L and 3.13 µg/L, respectively using established calculation methods. Additionally, the enrichment factor was found to be 50. The analytical figures of merit for the VA-DLLME method are summarized in Table 2.

3.10Comparison with reported methods:

This study represents DES based VA-DLLME conjunction with spectrophotometry for the analysis of waste-water. The proposed method employs an environment-friendly DES extraction solvent and vortex assistance, offering selective analysis of Gadolinium to previous studies. Specifically, it exhibits a linear range of 14.5 to 115 µg/L, a limit of detection of 3.13 µg/L, and a relatively low relative standard deviation (RSD) of 1.56%. These favourable analytical figures of merit provide an alternative to methods relying on hazardous organic solvents, as detailed in the comparative information presented in Table 3.

3.11 Analysis of real sample

The developed DLLME technique was employed to analyses waste-water gathered from various industrial manufacturing sites. The untreated waste-water subjected to the established VA-DLLME procedure. Quantification of the analyte concentrations in the samples was achieved through the use of calibration curve generated for pure aqueous standards that underwent the same VA-DLLME process. The analytical findings for these specimens are presented in Table 4. The proposed method's reliability was verified by directly analyzing the samples using the spike method, and the results demonstrated a good alignment with the expected outcomes. The recovery of Gadolinium from industrial waste-water was examined using four samples of different weights. As the spiked Gadolinium concentration increases from 0 to 15 µg/mL, the amount of Gadolinium found in each corresponding increases, indicating successful recovery of Gadolinium from the waste-water. The recovery rates for each sample ranged from 97.3% to 101.20% indicating the proposed method's effectiveness and reliability.

IV. CONCLUSION

This research presents a green approach utilizing novel biodegradable Eugenol-based deep eutectic solvents as extracting agents for the vortex-assisted dispersive liquid-liquid microextraction of Gadolinium as Gd-ARS complexes. The proposed VA-DLLME method utilized in conjunction with UV-Visible spectrophotometric analysis, which has demonstrated its reliability and cost-effectiveness for quantifying the concentration of Gadolinium in waste-water compared to previous studies, as shown in Table 3. The method exhibits excellent potential for accurately determining the concentration of Gadolinium in these industrial waste-water. The advantages of proposed approach include its simplicity, favourable linearity range, and high recovery rate. Furthermore, the microextraction based method utilizing DES as the extracting solvent, along with vortex-assisted extraction and low waste generation, make this green analytical technique for the detection of Gadolinium in waste-water. This method offers a convenient and comprehensive solution for lab-scale analysis of gadolinium in industrial waste water, combining environmental sustainability, analytical reliability, and cost-effectiveness. The current study represents the novel eugenol-based DES to employ VA-DLLME spectrophotometry technique for detecting and quantifying Gadolinium in industrial waste-water.

Figures and Tables

Figure 1-FT-IR analysis of the synthesized Deep Eutectic Solvent.

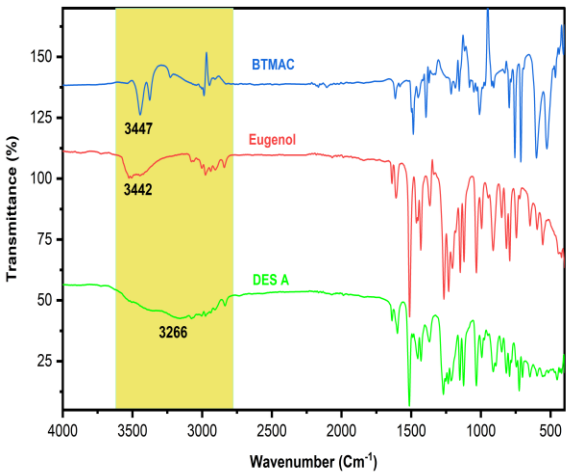
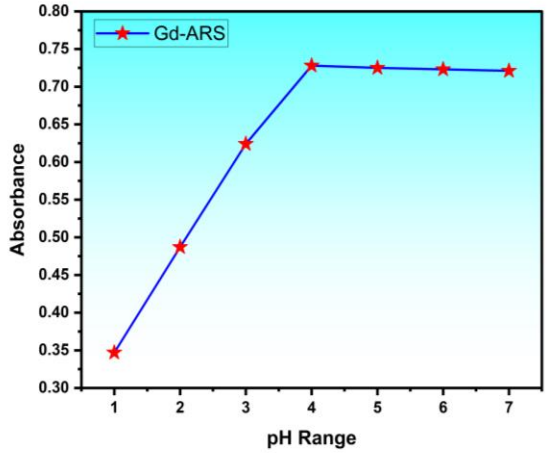
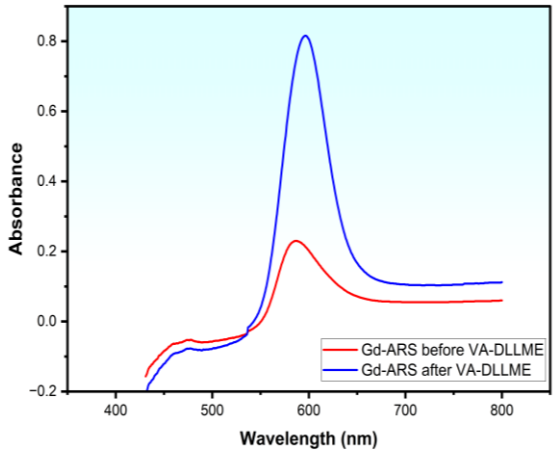


Figure 2- Effect of pH



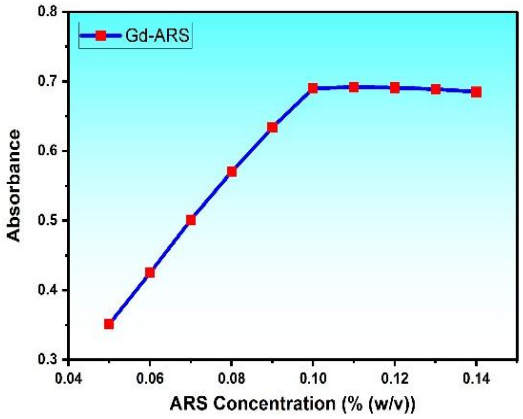
Conditions: λmax – 600 nm, Gd (III) ions- 86.10 µg/L, ARS- 0.1% w/v, Vortex- 0.5 minutes, Centrifugation- 0.5 minutes, DES- 200 µL-1. DLLME- Dispersive Liquid-Liquid Microextraction; ARS- Alizarin Res S; DES- Deep Eutectic Solvent; VA-Vortex Assisted.
The error bars represent the standard deviation (n=3)

Figure 3-Absorption spectra for Gd-ARS complex after and without VA-DLLME.



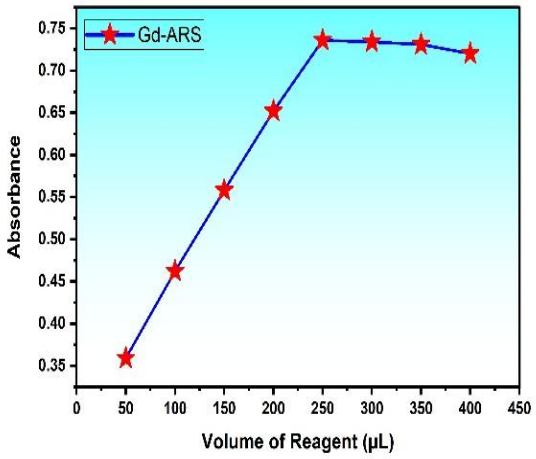
Conditions: λmax – 600 nm, Gd (III) ions- 86.10 µg/L, pH-5.0, ARS- 0.1% w/v, Vortex- 0.5 minutes, Centrifugation- 0.5 minutes, DES- 200 µL-1. DLLME- Dispersive Liquid-Liquid Microextraction; ARS- Alizarin Res S; DES- Deep Eutectic Solvent; VA-Vortex Assisted.
The error bars represent the standard deviation (n=3)

Figure 4-Optimizing the concentration of chelating reagent ARS



Conditions: λmax – 600 nm, Gd (III) ions- 86.10 µg/L, pH-5.0, ARS- 0.1% w/v, Vortex- 0.5 minutes, Centrifugation- 0.5 minutes, DES- 200 µL-1. DLLME- Dispersive Liquid-Liquid Microextraction; ARS- Alizarin Res S; DES- Deep Eutectic Solvent; VA-Vortex Assisted.
The error bars represent the standard deviation (n=3)

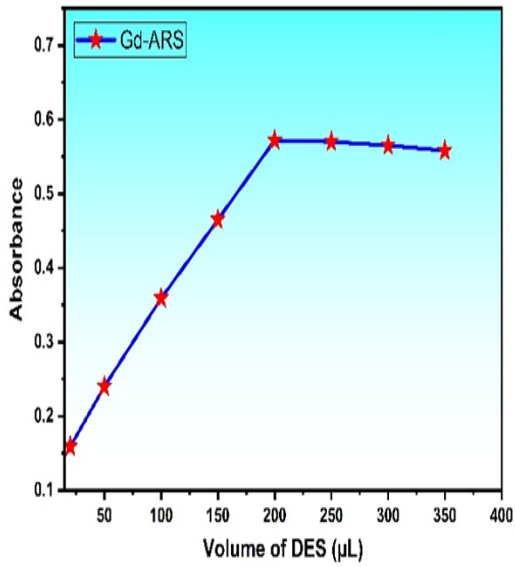
Figure 5-Optimizing the volume of chelating reagent ARS



Conditions: λmax – 600 nm, Gd (III) ions- 86.10 µg/L, pH-5.0, ARS- 0.1% w/v, Vortex- 0.5 minutes, Centrifugation-0.5 minutes, DES- 200 µL-1. DLLME- Dispersive Liquid-Liquid Microextraction; ARS- Alizarin Res S; DES- Deep Eutectic Solvent; VA-Vortex Assisted.

The error bars represent the standard deviation (n=3)

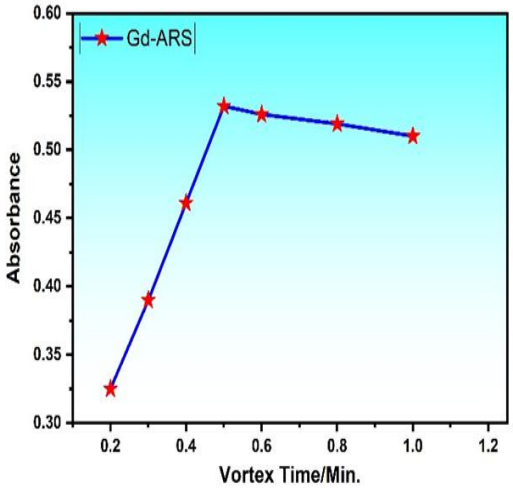
Figure 6-Optimizing the volume of extraction solvent



Conditions: λmax – 600 nm, Gd (III) ions- 86.10 µg/L, pH-5.0, ARS- 0.1% w/v, Vortex- 0.5 minutes, Centrifugation-0.5 minutes, DES- 200 µL-1. DLLME- Dispersive Liquid-Liquid Microextraction; ARS- Alizarin Res S; DES- Deep Eutectic Solvent; VA-Vortex Assisted.

The error bars represent the standard deviation (n=3)

Figure 7-Optimizing the volume of vortex time



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The error bars represent the standard deviation (n=3)

Table 1: Interference effect of some matrix ions on percent recoveries of Gd (III), pH:5, ARS: 0.1% w/v, DES: 200 µL (Relative error ±5%).

Metal Interference	Proportion	Recovery %
Cu (II)	1:300	98.2
[a]Ni (II)	1:90	92.1
Zn (II)	1:90	90.6
[b]Cr (VI)	1:90	90.2
Co (II)	1:150	104.7
[C]V (V)	1:90	91.2
Mg (II)	1:60	96.7
Ca (II)	1:90	91.5
Hg (II)	1:30	98.4
[a]Fe (III)	1:120	91.8
SO_4^{2-}	1:60	97.8
$S_2O_3^{2-}$	1:450	108.8
F^-	1:30	99.1
Br^-	1:300	109.5
Cl^-	1:60	99.6
I^-	1:30	96.5
PO_4^{3-}	1:150	98.6

[a]Masked with 0.6 mg thiosulphate, [b]Masked with 0.7 mg oxalic acid, [c]Masked with thiourea.

Table 2 : Analytical figure of merits.

Parameter	Analytical figures
Determination coefficient (R^2)	0.9996
Linear Range	14.5 to 115 µg/L
Limit of detection (LOD*) (n=10)	3.13 µg/L
Limit of quantification (LOQ*) (n=10)	10.43 µg/L
Relative standard deviation (RSD) (n=10)	1.56%
Enrichment factor	50

*LOD and *LOQ based on 3.3 and 10 σ criterion, respectively.

Table 3 : Comparative assessment of separating and analytical techniques for Gadolinium and other REEs.

Separating/analytical technique	Samples	REE quantified by method	Solvents	References
DLLME/ICP-QMS	Ground water	14 REEs	Aliquat ®336 (tricaprylmethylammoniumchloride)	[29]
DLLME/ICP-MS	Spent catalyst	Ga, La, Tb, Tm, Y, Yb	Ethanol Chloroform	[31]
D-SPE-DLLME/ETV-ICP-MS	Lake water, River water	14 REEs	Carbon tetra chloride	[42]

LL-DLLME/ICP-MS	Water samples	14 REEs	Acetone Carbon tetra chloride	[43]
VA-DLLME/ICPMS/ ICP-OES	Tap Water, Ground Water, Sea water	Eu, La, Nd, Yb, Gd	Butan-1-ol	[33]
VA-DLLME/ Spectrophotometry	Industrial Waste Water	Only Gadolinium	Hydrophobic DES	Present work

ICP-OES: Inductive couple plasma optical emission spectroscopy, REE- rare earth element, ICP-QMS- Inductively coupled plasma-quadrupole mass spectrometry, ETV-ICP-MS- Electrothermal vaporization-inductively coupled plasma mass spectrometry.

Table 4: Determination of gadolinium in industrial waste-water.

Waste-water sample	Gadolinium amount		Recovery
	Spiked in µg/mL	Found* in µg/mL	(%)
Sample A	0	0.95 ± 0.15	-
	2	2.94 ± 0.35	99.6
	4	4.93 ± 0.35	99.59
Sample B	0	1.02 ± 0.24	-
	2	3.03 ± 0.49	100.3
	4	5.08 ± 0.36	101.2
Sample C	0	0.98 ± 0.51	-
	2	2.90 ± 0.13	97.3
	4	4.90 ± 0.20	98.3
Sample D	0	0.9 ± 0.49	-
	2	2.85 ± 0.05	99.15
	4	5.02 ± 0.11	100.8

*Mean± Standard deviation (n=5)

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Declaration of interest statement

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

REFERENCES

[1] R.K. Jyothi, T. Thenepalli, J.W. Ahn, P.K. Parhi, K.W. Chung, J.Y. Lee, Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste, J. Clean. Prod. 267 (2020) 122048. https://doi.org/10.1016/J.JCLEPRO.2020.122048.

[2] V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis,

recycling, and environmental impact, Geosci. Front. 10 (2019) 1285–1303. https://doi.org/10.1016/J.GSF.2018.12.005.

[3] M. Duchna, I. Cieślik, Rare Earth Elements in New Advanced Engineering Applications, in: Rare Earth Elem. - Emerg. Adv. Technol. Util. Resour. Procure., IntechOpen, 2023. https://doi.org/10.5772/intechopen.109248.

[4] X. Zhao, F. Khelifi, M. Casale, A. Cavallo, E. Padoan, K. Yang, G.A. Dino, Critical Raw Materials Supply: Challenges and Potentialities to Exploit Rare Earth Elements from Siliceous Stones and Extractive Waste, Resour. 2024, Vol. 13, Page 97 13 (2024) 97. https://doi.org/10.3390/RESOURCES13070097.

[5] M.M. Khalifa, W.I. Mortada, M.M. El-defrawy, A.A. Awad, Selective separation of gadolinium from a series of f-block elements by cloud point extraction and its application for analysis of real samples, Microchem. J. 151 (2019). https://doi.org/10.1016/j.microc.2019.104214.

[6] C. Ramprasad, W. Gwenzi, N. Chaukura, N. Izyan Wan Azelee, A. Upamali Rajapaksha, M. Naushad, S. Rangabhashiyam, Strategies and options for the sustainable recovery of rare earth elements from electrical and electronic waste, Chem. Eng. J. 442 (2022). https://doi.org/10.1016/j.cej.2022.135992.

[7] J. Sousa, J. Pinto, H. Barbosa, D.S. Tavares, R. Freitas, T. Trindade, J. Rocha, E. Pereira, Efficient Recovery of Gadolinium from Contaminated Waters Using Manganese Ferrite Nanoparticles, Recycling 10 (2025) 57. https://doi.org/10.3390/RECYCLING10020057/S1.

[8] L. Blomqvist, G.F. Nordberg, V.M. Nurchi, J.O. Aaseth, Gadolinium in Medical Imaging—Usefulness, Toxic Reactions and Possible Countermeasures—A Review, Biomol. 2022, Vol. 12, Page 742 12 (2022) 742. https://doi.org/10.3390/BIOM12060742.

[9] J. Ognard, J.A. Barrat, F. Cotton, A. Mian, S. Kremer, Y.Y. Sitoh, S. Verclytte, R. Loffroy, R. Tripier, Z. Alavi, D. Ben Salem, A roadmap towards pollution prevention and sustainable development of Gadolinium, J. Neuroradiol. 48 (2021) 409–411. https://doi.org/10.1016/J.NEURAD.2021.08.002.

[10] P. Ebrahimi, M. Barbieri, Gadolinium as an Emerging Microcontaminant in Water Resources: Threats and Opportunities, Geosci. 2019, Vol. 9, Page 93 9 (2019) 93. https://doi.org/10.3390/GEOSCIENCES9020093.

[11] J. Rogowska, E. Olkowska, W. Ratajczyk, L. Wolska, Gadolinium as a new emerging contaminant of aquatic environments, Environ. Toxicol. Chem. 37 (2018) 1523–1534. https://doi.org/10.1002/ETC.4116.

[12] S. Piarulli, J.A. Riedel, F.N. Fossum, F. Kermen, B.H. Hansen, B. Kvæstad, P.A. Olsvik, J. Farkas, Effects of gadolinium (Gd) and a Gd-based contrast agent (GBCA) on early life stages of zebrafish (Danio rerio), Chemosphere 350 (2024) 140950. https://doi.org/10.1016/J.CHEMOSPHERE.2023.140950.

[13] W. Gwenzi, L. Mangori, C. Danha, N. Chaukura, N. Dunjana, E. Sanganyado, Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants, Sci. Total Environ. 636 (2018) 299–313. https://doi.org/10.1016/j.scitotenv.2018.04.235.

[14] G. Jeric B., M.H. Wang, C.F. Chen, C.W. Chen, C. Di Dong, Rare earth elements as emerging contaminants in marine ecosystems: Bioaccumulation and ecological implications, J. Environ. Manage. 394 (2025) 127465. https://doi.org/10.1016/J.JENVMAN.2025.127465.

[15] S. Hong, Y. Zhang, Q. Zhang, Z. Su, G. Hu, L. Wang, S. Yu, X. Zhu, G. Jia, Health risks of rare earth elements exposure: Impact on mitochondrial DNA copy number and micronucleus frequency, J. Environ. Sci. 151 (2025) 150–160. https://doi.org/10.1016/J.JES.2024.01.054.

[16] X. Wang, F. Wang, L. Yan, Z. Gao, S. Yang, Z. Su, W. Chen, Y. Li, F. Wang, Adverse effects and underlying mechanism of rare earth elements, Environ. Heal. A Glob. Access Sci. Source 24 (2025). https://doi.org/10.1186/S12940-025-01178-3.

[17] S. Piarulli, B.H. Hansen, T. Ciesielski, A.L. Zocher, A. Malzahn, P.A. Olsvik, C. Sonne, T. Nordtug, B.M. Jenssen, A.M. Booth, J. Farkas, Sources, distribution and effects of rare earth

elements in the marine environment: Current knowledge and research gaps, Environ. Pollut. 291 (2021). https://doi.org/10.1016/j.envpol.2021.118230.

[18] D. Hendrati, H. Bahti, U. Pratomo, C. Wulandari, R. Fauzia, S. Wyantuti, Solvent Extraction and Stripping of Gadolinium (III) from Samarium (III) and Europium (III) Using D2EHPA as Extractant, in: European Alliance for Innovation n.o., 2020. https://doi.org/10.4108/eai.11-7-2019.2297444.

[19] SUSTAINABLE SEAWEED TECHNOLOGIES :cultivation, biorefinery and, (2020). https://www.researchgate.net/publication/344241625_Sustainable_seaweed_technologies (accessed October 24, 2024).

[20] M. Rezaee, Y. Yamini, M. Faraji, Evolution of dispersive liquid-liquid microextraction method, J. Chromatogr. A 1217 (2010) 2342–2357. https://doi.org/10.1016/j.chroma.2009.11.088.

[21] H. Faraji, Advancements in overcoming challenges in dispersive liquid-liquid microextraction: An overview of advanced strategies, TrAC - Trends Anal. Chem. 170 (2024). https://doi.org/10.1016/j.trac.2023.117429.

[22] X. Wen, P. Wu, L. Chen, X. Hou, Determination of cadmium in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction, Anal. Chim. Acta 650 (2009) 33–38. https://doi.org/10.1016/j.aca.2009.01.053.

[23] O. Stashkiv, V. Vasylechko, G. Gryshchouk, I. Patsay, Solid phase extraction of trace amounts of praseodymium using transcarpathian clinoptilolite, Colloids and Interfaces 3 (2019). https://doi.org/10.3390/colloids3010027.

[24] S. Dadfarnia, A.M. Haji Shabani, Recent development in liquid phase microextraction for determination of trace level concentration of metals-A review, Anal. Chim. Acta 658 (2010) 107–119. https://doi.org/10.1016/j.aca.2009.11.022.

[25] B. Hu, M. He, B. Chen, Z. Jiang, Separation/preconcentration techniques for rare earth elements analysis, Phys. Sci. Rev. 1 (2016). https://doi.org/10.1515/psr-2016-0056.

[26] S. Chen, X. Cheng, Y. He, S. Zhu, D. Lu, Determination of the rare earth elements La, Eu, and Yb using solidified floating organic drop microextraction and electrothermal vaporization ICP-MS, Microchim. Acta 180 (2013) 1479–1486. https://doi.org/10.1007/s00604-013-1091-7.

[27] M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, J. Chromatogr. A 1116 (2006) 1–9. https://doi.org/10.1016/J.CHROMA.2006.03.007.

[28] D. Han, K.H. Row, Trends in liquid-phase microextraction, and its application to environmental and biological samples, Microchim. Acta 176 (2012) 1–22. https://doi.org/10.1007/s00604-011-0678-0.

[29] K. Chandrasekaran, D. Karunasagar, J. Arunachalam, Dispersive liquid-liquid micro-extraction for simultaneous preconcentration of 14 lanthanides at parts per trillion levels from groundwater and determination using a micro-flow nebulizer in inductively coupled plasma-quadrupole mass spectrometry, J. Anal. At. Spectrom. 27 (2012) 1024–1031. https://doi.org/10.1039/c2ja30066d.

[30] M.H. Mallah, F. Shemirani, M. Ghannadi Maragheh, Use of dispersive liquid-liquid microextraction for simultaneous preconcentration of samarium, europium, gadolinium and dysprosium, J. Radioanal. Nucl. Chem. 278 (2008) 97–102. https://doi.org/10.1007/s10967-007-7220-1.

[31] J.C. Ramos, D.L.G. Borges, Simultaneous determination of six rare earth elements in geological and spent catalyst samples using electrothermal vaporization inductively coupled plasma mass spectrometry following dispersive liquid-liquid microextraction, J. Anal. At. Spectrom. 32 (2017) 1893–1904. https://doi.org/10.1039/c7ja00153c.

[32] Y. Dilip, P. Laxman, J. Suhas, N. Arundhati, C. Mrunmayi, Hydrophobic deep eutectic solvent-based vortex-assisted dispersive liquid–liquid microextraction with UV–visible spectrophotometry for copper determination in waste printed circuit boards, Int. J. Environ. Anal.

Chem. (2024) 1–14. https://doi.org/10.1080/03067319.2024.2352169.

[33] F.O. Leme, L.C. Lima, R. Papai, N. Akiba, B.L. Batista, I. Gaubeur, A novel vortex-assisted dispersive liquid-phase microextraction procedure for preconcentration of europium, gadolinium, lanthanum, neodymium, and ytterbium from water combined with ICP techniques, J. Anal. At. Spectrom. 33 (2018) 2000–2007. https://doi.org/10.1039/c8ja00252e.

[34] B. Hu, M. He, B. Chen, Z. Jiang, Separation/preconcentration techniques for rare earth elements analysis, Phys. Sci. Rev. 1 (2016). https://doi.org/10.1515/PSR-2016-0056/MACHINEREADABLECITATION/RIS.

[35] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixturesElectronic supplementary information (ESI) available: spectroscopic data. See http://www.rsc.org/suppdata/cc/b2/b210714g/, Chem. Commun. (2003) 70–71. https://doi.org/10.1039/b210714g.

[36] D. Ge, Z. Shan, T. Pang, X. Lu, B. Wang, Preparation of new hydrophobic deep eutectic solvents and their application in dispersive liquid-liquid microextraction of Sudan dyes from food samples, (n.d.). https://doi.org/10.1007/s00216-021-03337-0/Published.

[37] O.E. Plastiras, E. Andreasidou, V. Samanidou, Microextraction techniques with deep eutectic solvents, Molecules 25 (2020). https://doi.org/10.3390/molecules25246026.

[38] E. Majidi, H. Bakhshi, Hydrophobic deep eutectic solvents characterization and performance for efficient removal of heavy metals from aqueous media, J. Water Process Eng. 57 (2024). https://doi.org/10.1016/j.jwpe.2023.104680.

[39] R. Liu, X. Liu, J. Li, X. Yin, Y. Yang, Bifunctional hydrophobic deep eutectic solvents for selective recovery of Sm and Co from waste SmCo permanent magnets, J. Ind. Eng. Chem. 130 (2024) 191–202. https://doi.org/10.1016/j.jiec.2023.09.023.

[40] M.R. Jamali, Y. Assadi, R. Rahnama Kozani, Determination of trace amounts of palladium in water samples by graphite furnace atomic absorption spectrometry after dispersive liquid-liquid microextraction, J. Chem. (2013). https://doi.org/10.1155/2013/671743.

[41] Q. Wu, Q. Chang, C. Wu, H. Rao, X. Zeng, C. Wang, Z. Wang, Ultrasound-assisted surfactant-enhanced emulsification microextraction for the determination of carbamate pesticides in water samples by high performance liquid chromatography, J. Chromatogr. A 1217 (2010) 1773–1778. https://doi.org/10.1016/j.chroma.2010.01.060.

[42] X.Q. Guo, X.T. Tang, M. He, B.B. Chen, K. Nan, Q.Y. Zhang, B. Hu, Dual dispersive extraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for determination of trace REEs in water and sediment samples, RSC Adv. 4 (2014) 19960–19969. https://doi.org/10.1039/c4ra01576b.

[43] I. Çelik, D. Kara, C. Karadaş, A. Fisher, S.J. Hill, A novel ligandless-dispersive liquid-liquid microextraction method for matrix elimination and the preconcentration of rare earth elements from natural waters, Talanta 134 (2015) 476–481. https://doi.org/10.1016/j.talanta.2014.11.063.