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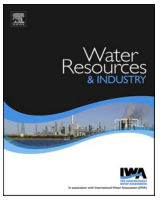

Natural deep eutectic solvent based ultrasound assisted liquid-liquid micro-extraction method for methyl violet dye determination in contaminated river water

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ABSTRACT

Simple and green natural deep eutectic solvent (NADES) based ultrasound assisted liquid-liquid micro-extraction (UA-LLME) method was developed for extraction and determination of methyl violet dye in contaminated river water samples using UV/Vis spectrophotometry. Choline chloride - decanoic acid based natural deep eutectic solvent was used for extraction. Important analytical parameters like pH, deep eutectic solvent volume/phase ratio, tetrahydrofuran volume, sonication time, and temperature were optimized. Limit of detection (LOD) and limit of quantification (LOQ) were 2.20 μg/L and 7.34 μg/L respectively. Relative standard deviation was 2.35–3.21%. Linearity of method was investigated in a concentration range 10–400 μg/L. Enrichment factor was calculated as 20. For 20 mL sample, the optimized parameters were as deep eutectic solvent volume 1.5 mL, tetrahydrofuran volume was 0.6 mL, pH = 6, sonication time 2 min. The optimized method was tested for extraction of methyl violet in real water samples confirming its applicability in routine environmental analysis.

1. Introduction

Dyes are frequently used in different industries, such as cosmetic, leather, paper, and plastic, for the coloration of their final product. The effluent from industries containing dyes, may cause environmental hazards and its accumulation in human body may affect the human life via food chain [1,2]. A large number of dyes are produced every year and mostly used in industries. Most of the dyes are toxic in nature and are a serious threat for natural ecosystem. Textile industry uses stable and hardly degradable dyes. There are over 100 thousand commercially available dyes, of which azo dyes account for roughly 70% by weight. Over 1 million tons of dyes are produced annually [3]. Azo group containing dyes are serious threat for the aquatic environment. The toxicity and level of

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contamination of these dyes became a critical task for researchers. Due to their complicated aromatic structures and synthetic origin, these dyes are very difficult to treat biologically [4,5].

Methyl violet (MV) contains a secondary amine group having different colors at different pH [6]. MV is a cationic dye [7] and soluble in water, methanol, diethylene glycol, ethanol and dipropylene glycol [8]. Methyl violet is used in textile, plastic, and food industries, paper dyeing, leather dyeing and printing inks [8–13]. The direct contact with methyl violet can cause pain, congestion and may cause skin and eye irritation whereas inhalation of MV may cause irritation in respiratory and gastrointestinal systems [13,14].

A large number of extraction methods are available for dyes extraction such as liquid–liquid extraction [15–17], solid phase extraction (SPE) [18,19], cloud point extraction [20], co precipitation method, liquid phase micro-extraction [21–23], and many other methods have been investigated for determination of dyes in different matrices.

Zhang et al., reported dispersive liquid-liquid micro-extraction method for MV [24]. Xie et al., developed method for MV detection in fish using HPLC–VIS [25]. Hakami et al., developed an UHPLC-MS method for analysis of MV in water samples [26]. Wei et al., have reported a Poly(deep eutectic solvent)-functionalized magnetic metal-organic framework based method [27]. Liang et al., developed IL-based micro-extraction (SPE) method based on functionalized MNPs for determination of MV in environmental samples [28]. These methods are associated with one or other problems. A critical study of these methods and the problems associated with these methods have been described in details in section 3.2.4. Use of green solvents for analysis is getting great attention of researchers which are less/non-toxic, biodegradable, cheaper, and tunable solvent that can be used in extraction methods [16,29–31]. Deep eutectic solvents (DESs) are rapidly emerging as a new class of green, sustainable, and tunable solvents due to their unique characteristics over conventional organic solvent such as low-cost, lower toxicity [16,32,33], biodegradable [34], high extraction efficiency [35], and ease of formation [36,37]. DESs can offer unique physiochemical interactions with analytes [38–40]. On this basis they can provide high selectivity of extraction as well as other separation processes [41,42].

Because of the distinct properties, DESs were selected as green solvents for effective extraction of methyl violet. The developed method is easy, time saving and “greener” as compared to other methods. The method was validated and applied for methyl violet extraction and analysis in aqueous medium.

2. Materials and methods

2.1. Material and reagents

Analytical grade methyl violet, tetrahydrofurane (99%) and choline chloride (98%) were obtained from DAEJUNG (Korea). Tetrahydrofuran (THF) of analytical grade was used directly without any purification or dilution. Hydrochloric acid (38%), methanol and sodium hydroxide were purchased from Sigma Aldrich (Germany). Hydrochloric acid (0.1 M) and ammonium hydroxide (0.1 M) were prepared and used for pH adjustment.

2.2. Instrumentation

UV–visible spectrophotometer (UV-1900i) produced by Shimadzu (Burladingen, Germany) was used for absorbance measurements. Vortex F202A0175 (VELP SCIENTIFICA, Pakistan) was used for shaking. Additional instruments were ultrasonic bath with 30 kHz ultrasonic frequency made by IK/UTSB (Lahore, Pakistan) and pH meter ORION STAR A329 (Thermo Fisher USA). Water deionizer Millipore (MERCK Germany) was used for water purification.

2.3. DES preparation

Choline chloride (ChCl) was used as a hydrogen bond acceptor (HBA), while ethylene glycol, phenol, glucose, malonic acid, and decanoic acid were used as hydrogen bond donor (HBD). DES-1 was obtained by mixing choline chloride with ethylene glycol a molar ratio (1:1). With a gentle stirring a clear solution was obtained. DES-2 was obtained by mixing choline chloride and phenol with a molar ratio (1:2) followed by mild heating at 50–60 °C for 30 min to get a clear transparent liquid. DES-3 was obtained by mixing choline chloride and glycerol with molar ratio of 1:2. The mixture was stirred with magnetic stirrer and heated at mild temperature (50–60 °C) for 30 min. DES-4 was obtained by mixing choline chloride and malonic acid with molar ratio (1:2). The mixture was heated at mild temperature (50–60 °C) until a clear liquid was obtained. DES-5 was obtained by simple mixing choline chloride and decanoic acid with a molar ratio (1:1).

2.4. Sample preparation and extraction procedure

Water samples were collected from Mardan River almost 0.5 km from the away from Rashakai industrial estate. Water samples were filtered with Whatman filter paper (pore size 90 mm) and stored in plastic bottles for further laboratory experiments. A 20 mL water sample was added to a falcon tube. A 2 mL of methyl violet (500 μg/L) was added to the sample (analyte concentration 45.45 μg/L). A 1.5 mL of DES was added to sample followed by sonication for 2 min at room temperature. A 0.6 mL of tetrahydrofuran was added to the mixture and the sample was mixed with vortex for 2 min. The sample was centrifuged until a clear analyte rich deep eutectic solvent layer was obtained. The separation of methyl violet was clearly visible with naked eyes. A deep eutectic solvent layer was separated in a separate vial and diluted with methanol up to 3 mL. The final sample was analyzed using UV–Visible spectrophotometer.

2.5. Validation assays and calculation formulas

Efficiency of deep eutectic solvent and optimization of parameters were studied as a function of RE%. The % recovery was calculated as follows:

$$RE\% = \frac{C_{quant}}{C_{expect}} \times 100 \quad (1)$$

In this equation C_{quant} is the methyl violet concentration experimentally determined in spiked sample and C_{except} is the expected concentration (calculated concentration). According to the Association of Analytical Communities (AOAC), LOD is the lowest concentration of analyte that can be detected with equitable precision, while LOQ is the lowest concentration of analyte, which can be quantitatively determined with suitable equitable precision [43]. In this method LOD and LOQ were calculated using the following equations

$$LOD = \frac{3 \times SD}{m} \quad (2)$$

$$LOQ = \frac{10 \times SD}{m} \quad (3)$$

In this equation, SD is the residual standard deviation of linear curve and m is the slope [44]. Residual standard deviation was calculated using ANOVA statistical analysis in excel. The enrichment/pre-concentration factor is the number of times the analytical signal is enhanced relative to analyte signal without pre-concentration [34,45] or in other words, it is the ratio of concentration of analyte in extracted DES layer and concentration in the starting sample. The EF factor was calculated by using the following equation.

$$EF = \frac{C_f}{C_i} \quad (4)$$

In this equation C_f is the final concentrations of analyte in deep eutectic solvent phase and C_i is the initial concentration of analyte in the sample before extraction/pre-concentration.

The relative standard deviation (RSD%) (also sometimes called coefficient of variation (CV)) iswidely used in analytical chemistry to express the precision and repeatability of an assay. RSD% was calculated using the following formula.

$$RSD(\%) = \frac{SD}{C_m} \times 100 \quad (5)$$

where SD is the standard deviation and C_m is the mean concentration value in real samples.

2.6. Analysis of UV-VIS absorption spectra

Methyl violet dye has lambda max value 590 nm as pure solution. However, there could be a possible shift in λ_{max} due to some

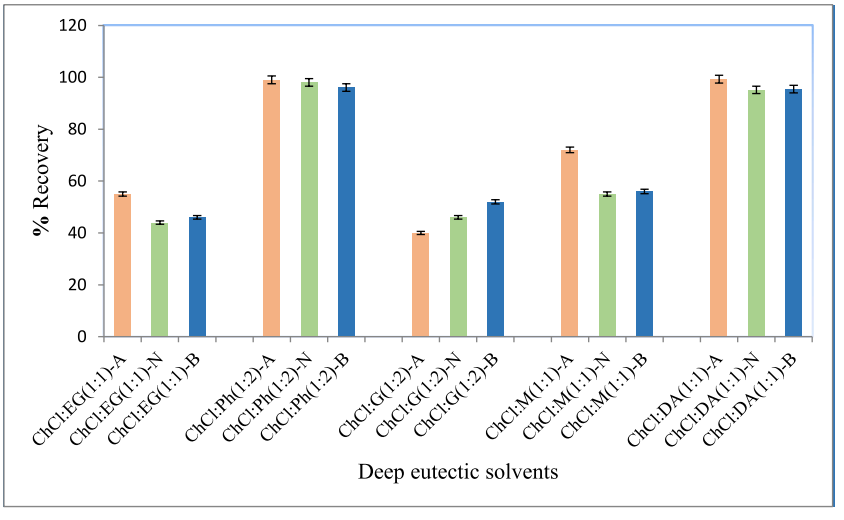

Fig. 1. Selection of suitable extractant (DES). ChCl: Choline chloride, EG: Ethylene glycol, Ph: Phenol, G: Glycerol, M: Malonic acid, DA: Decanoic acid (A: acidic, N: neutral, B: basic). Sample volume: 20 mL, Methyl violet concentration: 45.45 μg/L, Tetrahydrofuran volume: 0.6 mL, Sonication time (excess): 10 min, Centrifugation time (excess): 10 min. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

factors, such as pH [46] or DES presence [47]. Therefore, λ_{max} was determined for methyl violet in DES extracted phase. The absorbance was scanned from 400 nm to 750 nm. A minor change in the lambda max was observed. Maximum absorbance was observed at 600 nm. Therefore, this wavelength was selected as λ_{max}. The UV-VIS spectrum is given in Fig. S2.

3. Results and discussion

3.1. Optimization of extraction and sample preparation parameters

3.1.1. Selection of suitable extracting solvents

Deep eutectic solvents, as a novel class of environmentally friendly solvents, were studied as extractive media for pre-concentration of target analyte because they were the least hazardous, easy to make, highly selective, inexpensive, and readily available [40,48,49]. The extraction efficiency of the analyte is mainly affected by the composition of deep eutectic solvents and the nature of HBA and HBD. The deep eutectic solvents used for extraction should meet with few requirements, such as high affinity for specific analytes, liquid state at room temperature, no interference in analytical signal, different density comparing to matrix media (for example to water), high stability, and low solubility in the matrix (in this case in aqueous medium) [16,34,35,40]. In this study 5 different deep eutectic solvents s were prepared. All the deep eutectic solvents were prepared with their eutectic ratio of HBA and HBD. A RE% was investigated for each deep eutectic solvent in acidic (A), neutral (N) and basic (B) medium. Maximum RE% obtained for each DES is given in Fig. 1. Maximum recovery (≥99%) was observed for two deep eutectic solvents s. i) Choline chloride and phenol (1:2) and ii) Choline chloride and decanoic acid (1:2). Toxicity of phenol is questioned, so deep eutectic solvents made of choline chloride and decanoic acid (1:2) was selected as suitable for further optimization.

3.1.2. Effect of pH value

The pH value is an important parameter while performing extraction from aqueous medium. The electrostatic interactions between chemical species can be enhanced or diminished depending on the pH of the aqueous solution. As a result, the pH has a direct impact on how much of the analyte is transferred to the DES phase [35,37]. In addition, pH affects the extraction efficiency of DESs [34]. The effect of pH on the transfer of methyl violet from the aqueous phase to the DES phase was studied. For detail study of pH effect on the extraction efficiency of DES, a pH of the medium was adjusted from 2 to 10 using hydrochloric acid for acidic medium and sodium hydroxide for basic medium. The pH of the sample was monitored using portable pH meter. Fig. S3 shows results for pH optimization stage. Maximum RE% was observed in slightly acidic medium (pH = 6). pH = 6 was selected as optimum pH.

3.2. Optimization of solvents

Choline chloride is a quaternary ammonium salt that can act as a phase transfer agent, facilitating the transfer of the analyte from the aqueous phase to the DES phase. Decanoic acid is a medium-chain fatty acid with a alkane hydrophobic chain that can interact with the hydrophobic regions of the analyte molecule, thus promoting its solubility in the organic phase. Choline chloride and decanoic acid (1:2 M ratio) deep eutectic mixture provide a hydrophobic solvent, having specific interactions also with polar analytes. This results in a solvent with high solvating power for polar analytes like methyl violet, while also being easily separated from the aqueous phase.

The possible interactions involved in choline chloride and decanoic acid based deep eutectic solvent and methyl violet are likely to be a combination of hydrogen bonding, ion-dipole, and van der Waals forces. Choline chloride can form hydrogen bonds with the oxygen and nitrogen atoms in the methyl violet molecule, while the decanoic acid can interact with the hydrophobic regions of the analyte. The polar and non-polar interactions can work together (in synergy) to facilitate the dissolution of the analyte in the deep eutectic solvent.

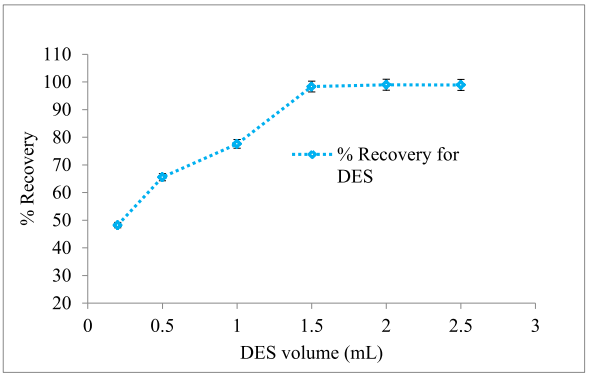

Fig. 2. Volume optimization for DES. DES: (Choline chloride and decanoic acid (1:2)), Sample volume: 20 mL, Methyl violet concentration: 45.45 μg/L, pH = 6, Tetrahydrofuran volume: 0.6 mL, Sonication time: 2 min, Centrifugation time: 2 min. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Furthermore, methyl violet is a cationic dye, so it can interact with the anionic choline chloride counter-ion through ion-dipole interactions. These interactions can help to solvate the dye and promote its transfer from the aqueous phase to the DES phase.

Phase ratio for DES was optimized by changing the volume of DES from 0.2 mL to 5 mL. Obtained results are presented on Fig. 2. Maximum recovery was obtained for 1.5 mL DES volume for 20 mL of sample. Tetrahydrofuran is an aprotic solvent, which was used in this study to enhance phase separation [16]. This aprotic solvent (THF) tend to interact readily with water than DES. After interaction with tetrahydrofuran molecules, interaction between DES and water decreases, resulting in their self-aggregation and separation. Haq et al., suggested a plausible mechanism of DESs self-aggregation that involves π–π overlap, followed by hydrogen bonding between functional groups of DES and other charge transfer interactions [16,37,50]. Volume of tetrahydrofuran was also optimized. For 20 mL of sample with methyl violet concentration 45.45 μg/L, the volume of tetrahydrofuran was changed from 0.2 mL to 1.2 mL. Maximum % recovery was achieved for addition of 0.8 mL. This volume was selected as optimum volume for further optimization.

3.3. Optimization of sonication and centrifugation time

Sonication treatment induces micro-circulation effect that significantly enhances the mass transfer between both phases [51]. Additionally, sonication treatment has been reported to improve the solvents extractability of materials at low temperatures [52,53]. This positive effect in respect to extraction based on DES was also reported in previous study [16]. Sonication is an essential step in this DES-based extraction method. Time for sonication was optimized for maximum RE%. Time for sonication was changed from 0.2 min to 4 min. With 2 min sonication time maximum % recovery was achieved. Therefore 2 min time was selected as optimum time for sonication. Results for time optimization for sonication are given in Fig. 3.

After sonication the mixture spontaneously started to separate to DES phase and aqueous phase. The phase separation process was enhanced by centrifugation. 2 min (4000 rpm) was found sufficient for complete phase separation.

3.4. Analytical performance of the developed method

This new method was validated in terms of limit of detection, limit of quantification, linearity, precision, and RE%. Limit of detection (LOD) and limit of quantification (LOQ) were 2.20 μg/L and 7.34 μg/L respectively. Relative standard deviation (RSD%) was calculated as 1.35% based on residual standard deviation for standard curve. While RSD% for real sample was 2.35–3.67% (n = 3) for 20–30 μg/L. Inter day precision (%RSD) was 0.45–0.54%. Linearity of method was investigated in a concentration range 10–400 μg/L. Enrichment factor was calculated as 20. Fig. 4 reveals results for calibration curve.

3.5. Effect of external ions

This method is based on spectrophotometric determination which can be affected by interference from a complex matter. DES-based extraction not only increases the sensitivity but also minimize the effect of possible interferences. DESs are considered as a highly selective extraction media; however, effect of external ions was still investigated to evaluate this possibility. Theselectivity was investigated under optimized conditions by evaluating interference effect for Na^{+}, Ca^{2+}, Al^{3+}, Zn^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and CO_3^{2-} ions. Table S1 illustrates results for interference study. It was observed that the external ions are not affecting the interference in extraction or spectrophotometric determination. Final findings from this experiment reveal that this method is highly selective.

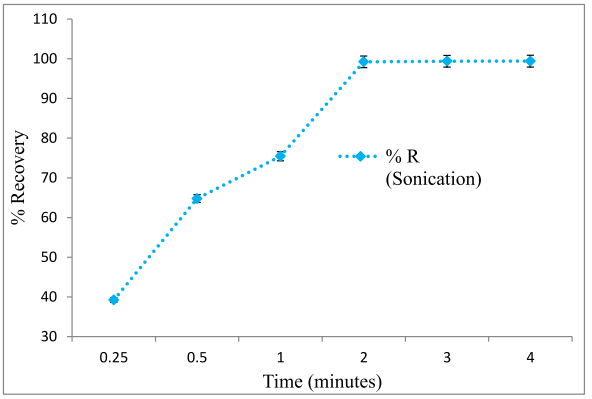

Fig. 3. Time optimization for sonication. DES: (Choline chloride and decanoic acid (1:2)), Sample volume: 20 mL, Methyl violet concentration: 45.45 μg/L, pH = 6, DES volume: 1.5 mL, Tetrahydrofuran volume: 0.6 mL, Centrifugation time (excess): 10 min. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

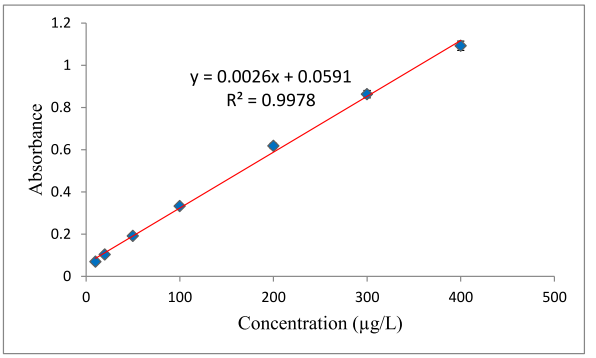

Fig. 4. Calibration curve for methyl violet. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.6. Application of the method

Contaminated water from industrial estate was selected to evaluate the validity and applicability of the method. Water samples were collected from Mardan River approximately 0.5 km away from Rashakai industrial estate. A map for sample location is given in Fig. S1. Water samples were filtered and stored in plastic bottles for laboratory experiments. Standard addition is the recommended method to evaluate the recovery for analysis of analyte in real samples. Therefore, standard addition method was followed for this experiment. The samples were spiked with 10 µg/L, 20 µg/L, and 30 µg/L of the standard solution. The results of this study are presented in Table 1. The %RSD was calculated for each sample with n = 3. This part of the studies revealed, that the recovery for real samples was between 98.6 and 100.07%. In river water no MV was found. However, in contaminated river water where industrial effluents were included, a 3.83 µg/L of methyl violet was determined.

3.7. Comparison with existing methods

The developed method has been compared with recently reported methods in literature for methyl violet dye determination. Extraction procedure, instrumentation, limit of detection, relative standard deviation, linearity range, and sample applications were compared (See Table 2). Estimated time was calculated for extraction procedure excluding the time for analysis and solution preparation. This new method required least time (<10 mints) for extraction procedure. Zhang et al., reported dispersive liquid-liquid micro-extraction method for methyl violet [24]. The reported method is simple and rapid, however the use of toxic and expensive chemicals (1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6])) is the major disadvantage. XIE et al., developed method for methyl violet detection in fish using HPLC–VIS [25]. The method is effective at low concentration in biological samples. Disadvantage of the method is the longer time consumption for sample preparation (≈50 min). Furthermore 2,3-dichloro-5, 6-dicyano-1,4-benzoquinone (DDQ) poses modest toxicity concerns [54]. Hakami et al., developed an UPLC-MS method for methyl violet analysis in environmental samples [26]. A hydrogen peroxide is used in the method for modification of biomass. The method involves advanced instrumentation (UHPLC–Mass Spectrometry) which is not frequently available in routine analysis labs. Furthermore, this required a very long time for extraction procedure (>90 min). Wei et al., have reported a DES based method in which the extraction time was 2 h [27]. This method involves the synthesis of functionalized magnetic MOF composites, which is complicated, and time consuming as compare to DES synthesis. Furthermore the use of MOF nanoparticles may cause toxicity for humans and environment [55]. Liang et al., developed ionic liquid-based microextraction method combined with functionalized MNPs solid phase extraction for analysis of methly violet [28]. The method is effective at low concentrations and required moderate time for extraction (≈20 min). However, the use of toxic chemical in this method is questionable. Secondly the use of nanoparticle (MNPs, Fe_3O_4@SiO_2@[Hpy]NTf_2)) is making the extraction process more complicated.

Currently described, new method is based on green natural deep eutectic solvents having no negative impact on environment or

Table 1
Real sample application of method.

Sample	Methyl violet added (µg/L)	Methyl violet found (µg/L)	Recovery (%)	RSD% (n = 3)
River water	0.00	<LOD	–	–
	10	9.86	98.60	2.62
	20	19.82	99.10	2.38
	30	28.81	99.36	3.21
River water (Contaminated)	0.00	3.82	–	–
	10	13.83	100.07	3.67
	20	23.80	99.91	2.35
	30	33.78	99.88	2.36

Table 2
Comparative study.

Extraction method	Instrumentation	LOD (μg/L)	RSD (%)	Linearity range (μg/L)	Estimated time (minutes)	Samples	Reference
[a]TC-IL-DLLME	[b]HPLC	0.03	7.6	0.2–20.0	≈20	Water	[24]
Oxidation	HPLC-VIS	0.10	5.1–12.3	0.5–10.0 μg/Kg	≈50	Fishes	[25]
[c]IACP							
[d]SPE, cartridges	[e]UHPLC–Mass Spectrometry	8.00	1.3–2.8	32–1000	>90	Environmental sample	[26]
[f]P(DES)-FMMOF	UV–Visible spectrophotometry	23.97	0.4	–	>120	Fishes	[27]
[g]MSPE	HPLC-UV	0.04	0.3–4.5	–	≈20	Water	[28]
[h]DES-LPME	UV–Visible spectrophotometry	2.20	1.4	10–400	<10	Contaminated water	*This method*

[1]MCPE: Magnetic cloud point extraction.
[a] TC-IL-DLLME: Temperature-controlled ionic liquid dispersive liquid–liquid micro-extraction.
[b] HPLC: High performance liquid chromatography.
[c] IACP: Immunoaffinity column purification.
[d] SPE: Solid phase extraction.
[e] UHPLC: Ultra high performance liquid chromatography.
[f] P(DES)-FMMOF: Poly(deep eutectic solvent)-functionalized magnetic metal-organic framework.
[g] MSPE: Magnetic solid phase extraction.
[h] DES-LPME: Deep eutectic solvent based liquid phase micro-extraction.

human. Deep eutectic solvents are not only green but are very easy to prepare by simply mixing two components. Method required no heating and was performed at room temperature. This method required least time for extraction (<10 min) among all the reported methods in literature. Furthermore, the method required no complicated instrumentation.

4. Conclusions

This work presents a DES-based method for extraction of methyl violet dye from aqueous matrix followed by spectrophotometric detection and quantification. Among tested DESs, the one made of choline chloride and decanoic acid (1:2) was selected as optimal green solvent for sample preparation. It was concluded, that choline chloride and decanoic acid based DES can be successfully used for extraction of methyl violet dye from aqueous medium for its spectrophotometric analysis. The RE% for this approach was >99% with linearity range 10–400 μg/L. The method is highly sensitive with limit of detection (LOD) 2.20 μg/L (ppb level) with relative standard deviation of 2.35–3.21%. Method was tested for real water samples. No significant interference in respect to existing ions was observed. The advantage of developed method relates to shortened extraction time and robustness - as no heating or sophisticated instrumentation are required. The use of green solvents is a big advantage of this method over the other methods reported in literature. To the best of our knowledge, this is a 1st ever reported DES-based direct method for the analysis of methyl violet dye. The method can be used for methyl violet detection and quantification in contaminated water samples at μg/L level.

Credit statement

Hameed Ul Haq: Conceptualization, Investigation, Methodology, Validation, Writing original draft, Investigation, Writing - review & editing. Azmat Wali: Sample collection, Formal analysis, Optimization. Faisal Safi: Sample collection, Formal analysis. Muhammad Balal Arain: Conceptualization, Methodology, Investigation, Supervision. Lingshuai Kong: Writing - review & editing. Grzegorz Boczkaj*: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wri.2023.100210

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