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Development and Validation a new method for determination Iron (III) in soil sample of ishaqi irrigation project using Dispersive Liquid-Liquid Microextraction

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Abstract

In this work, simple and rapid dispersive liquid-liquid microextraction procedure was developed for determination Fe (III) levels in soil sample. The detection was carried out by using Shimazu uv-visible spectrophotometer at wavelength of 620 nm. The developed method relies on a complexation reaction between Fe (III) with methylthymol blue (MTB) in an acetate buffer at pH= 5, conducted at a temperature of 25 ^{0}C. Subsequently, a mixture of methylene chloride (for extraction) and acetonitrile (for dispersive) was then quickly injected in solution. After microextraction, the organic and aqueous phases were separated by centrifugation and the resulting blue-colored complex was measured at 620 nm. The parameters governing for extraction efficiency and complex formation were systematically identified and optimized for maximum effectiveness. Optimal experimental conditions yielded linear responses for Fe (III) concentrations between 2 and 50 µg/mL, as predicted. The results showed an intra-day variability of 0.114% and an inter-day variability of 0.698% for five measurements using a concentration of 40 µg/mL. Finally, the developed method was successfully applied for the determination of Fe (III) in different soil samples.

Keywords: DLLME determination, Bromothymol blue, spectrophotometry, soil sample, Iron (III), ishaqi irrigation project.

تطوير واثبات طريقة جديدة لتقدير الحديد (///) في عينة تربة مشروع ري الاسحاقي باستخدام طريقة التشتت السائل-السائل المايكروي

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الخلاصة

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في هذا العمل ، تم تطوير إجراء الاستخلاص الدقيق السائل السائل المشتت البسيط والسريع لتحديد مستويات الحديد الثلاثي في عينة التربة. تم الكشف باستخدام مقياس الطيف الضوئي المرئي للأشعة فوق البنفسجية Uv–visible (Shimazu) بطول موجي 620 نانومتر. تعتمد الطريقة على تفاعل تكوين معقد بين ايون الحديد الثلاثي والبروموثايمول الأزرق في محلول منظم من الخلات عند درجة حرارة 25 درجة مئوية بعد ذلك ، تم حقن خليط من كلوريد الميثيلين كمذيب استخلاص والأسيتونيتريل كمذيب مشتت بسرعة في المحلول. بعد الاستخلاص الدقيق ، تم فصل الطبقتين العضوية والمائية عن طريق الطرد المركزي وتم قياس المركب الأزرق الناتج عند 620 نانومتر. تم تحديد المعلمات التي تحكم كفاءة التكوين والاستخلاص المعقدة بشكل منهجي وتحسينها لتحقيق أقصى قدر من الفعالية. أسفرت الظروف التجريبية المثلى عن استجابات خطية لتراكيز ايون الحديد الثلاثي بين 2 و 50 ميكروغرام / مل ، كما هو متوقع. كانت قابلية التكرار خلال اليوم والتكاثر بين الأيام (عدد القياس = 5 ، التركيز = 40 ميكروغرام / مل) 0.114 و 0.698 على التوالي. أخيرا ، تم تطبيق الطريقة المطورة بنجاح لتحديد ايون الحديد الثلاثي في عينات التربة المختلفة

1. Introduction

Iron is undoubtedly a critical element in biological chemistry, serving a fundamental role in essential life-sustaining processes [1, 2]. The amount of iron required by humans varies based on factors including diet, sex and age. For instance, 0.27 mg per day for children under 6 months while 27 mg for pregnant women and for healthy adult men and women is required 8 and 18 mg, respectively [3]. However, excessive intake of iron can pose health risks [4].
According to the literature, various analytical techniques have been employed to measure iron in different matrices, including spectrophotometry [5-7], electrochemical methods [8], inductively coupled plasma optical emission spectrometry [9], capillary electrophoresis [10], polarography [11], chromatography [12], voltammetry [13] and flame atomic absorption spectrometry[14]. However, many existing methods struggle to detect iron at trace levels, requiring sample preparation and pre-concentrated before analysis. Therefore, several methods for pre-concentration such as solid-phase extraction [15], liquid– liquid extraction [16], co-precipitation [17], and cloud point extraction [18], have been developed.
Recently, researchers have developed techniques that employ low-cost and efficient organic solvents, prioritizing ease of use and reduced solvent usage [19]. Over the past decade, there has been a significant increasing advances in the field of DLLME [20]. Numerous publications have been published in this field, with a substantial number of publications highlighting its advantages including ease of use, high enrichment factor, excellent extraction performance, eco-friendly and low cost [21, 22].
Ishaqi irrigation project is one of the largest initiatives launched in Iraq during the 20th century. The area of Is'haqi project is (410 Du). The land of the project is irrigated 3 from the Tigris River by Ishaqi project with the right side of the Tigris River near Samarra Barrage. The Ishaqi project is located about 100 K to the north of Baghdad within Salah Al Dean on the right side of the Tigris River in the region south of Samarra Barrage about 25 Km as shown in **Figure 1** [23]. During the latest 20 years, there was scarcity in surface water, therefore, farmers used the groundwater for irrigation Ishaqi project area is notable by shallow groundwater, which led to many unacceptable impacts on the economic and agricultural activities. The use of shallow groundwater causes another problem such as increasing soil alkalinity and salinity, which in turn affect the main sours of life for the local people (plant production).

The objective of this study was to develop a simple, accurate and cost effective DLLME procedure for the extraction and preconcentration of Fe (III) in soil sample of ishaqi irrigation project. This method relies on the complexation reaction between Fe (III) and methylthymol blue and used UV-visible spectrophotometer for measured complex formation. Moreover, the optimal conditions that affect the formation of complex ions and the efficiency of DLLME extraction were thoroughly optimized and investigated.

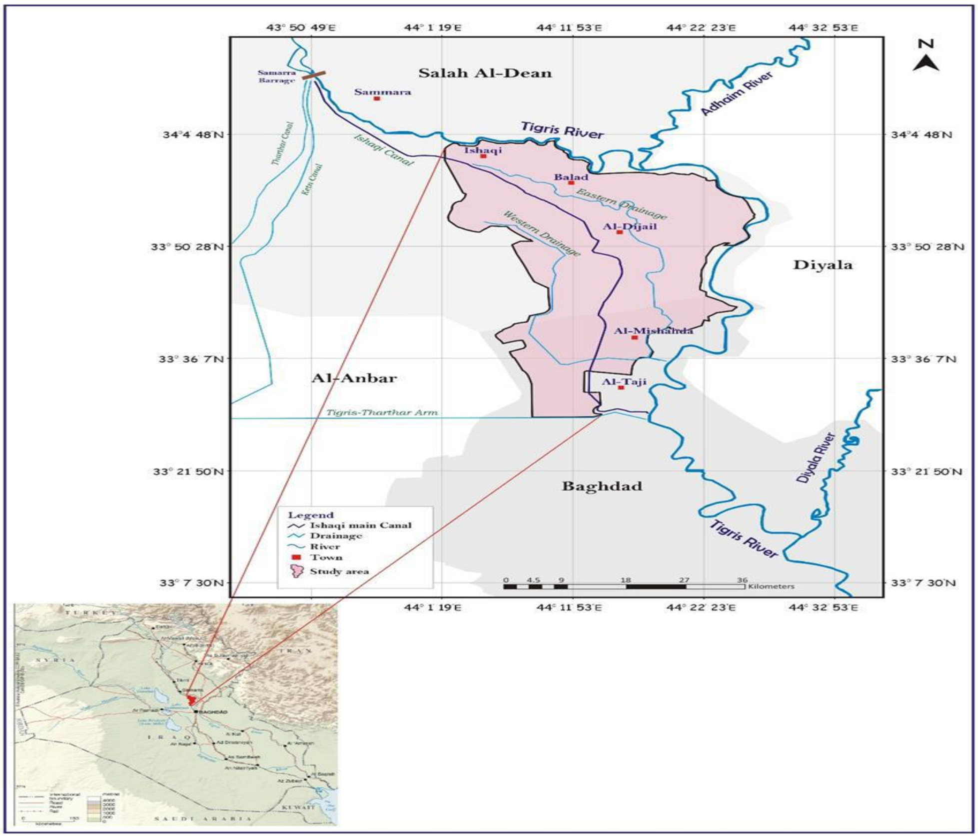


Figure 1: Location map of the ishaqi irrigation project

2. Materials and methods

2.1. Instrumentation

A Shimadzu (1800 UV–Visible, Germany) double beam spectrophotometer was employed to record absorption spectra using 10 mm matched quartz cuvettes. Hanna Instruments pH 210 pH Meter equipped with a combined glass-calomel electrode was used to measure the pH of the prepared solutions. Hotplate (China) was used for heating soil sample.

2.2. Reagents and solutions

The stock solution of Fe (III) (1000 µg/mL) was prepared by dissolving (0.100 gm) $Fe(NO_3)_3$ (This is precisely equal to 0.023 gm of Fe(III) supplied by CDH in 100 mL deionized water. Stock solution methylthymol blue was prepared by weighing an amount of methylthymol blue (supplied from Fluka) corresponding to 1000 µg/mL in 100 mL deionized water. Daily working standard solutions were prepared through dilution of stock solutions with high-purity water. Acetate buffer solution (pH= 5) was prepared by weight an amount from sodium acetate and added for it glacial acetic acid and diluted to 1000 mL with distilled water [24].

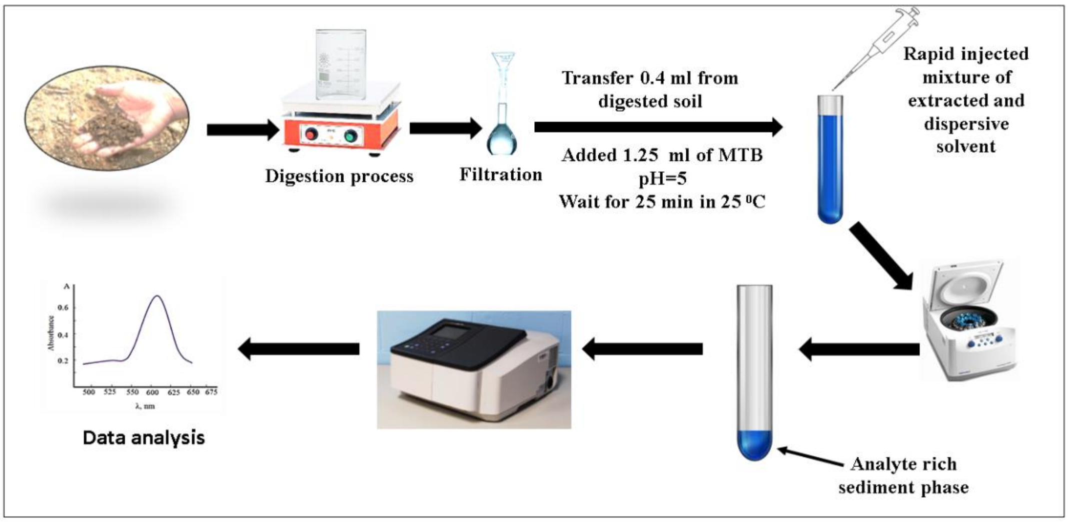
2.3. Preparation of soil sample

A total of 500g of soil samples were collected from various locations within the Ishaqi project, dried at 110 ^{0}C and weight 0.100 g of each sample and add an Aqua regia solution prepared from concentrated hydrochloric acid and concentrated nitric acid (supplied from Merck) ($3HCl:1HNO_3$) then heat until the soil dissolved. After cooling, the solution was filtered and diluted to 100 mL with distilled water. From this solution, 0.6 mL was taken, corresponding to a concentration of 40 µg/mL.

3. Experimental

3.1. General procedure for DLLME

A Fe (III) standard solution (ranging from 0.5 to 0.02 mL) was transferred into a 15 mL centrifuge tubes, followed by the addition of 1.25 mL of methylthymol blue solution. The volume was then brought to the mark with buffer solution (pH=5). The mixture was allowed to stand for 25 minutes for complex formation to occur at a temperature of 25 ^{0}C. Nest, a micro syringe was used to quickly add 1 mL of acetonitrile, which contained 0.5 mL of methylene chloride, to the solution. This made the solution cloudy. Subsequently, the mixture underwent centrifugation at a speed of 5000 rpm for a duration of 5 minutes. The extraction phase, consisting of finely dispersed droplets, accumulated at the bottom, resulting in the formation of a blue complex. The organic layer was extracted using a micro syringe and transferred to a 1 cm quartz microcell for absorbance measurement at a wavelength of 620 nm, with readings compared to a blank sample. The blank solution was prepared under identical conditions, but without adding Fe (III). Scheme 1 outlines the steps of the proposed DLLME procedure. For the determination of Fe (III) in soil sample the same procedure was used by added 0.6 mL from prepared soil sample which equivalent to 40 µg/mL. This concertation was chosen for further experiments.



Scheme 1: Show steps of suggested DLLME procedure

4. Result and discussion

4.1. Absorption spectra

Spectra were collected within a certain spectral ranging from 190 to 1100 nm. The analysis of the UV/Vis spectra for the Fe (III): methylthymol blue complex solutions revealed that the complex absorbed at 620 nm (Figure 2 A), while the highest wavelength for methylthymol blue reagent was 412 nm (Figure 2 B).

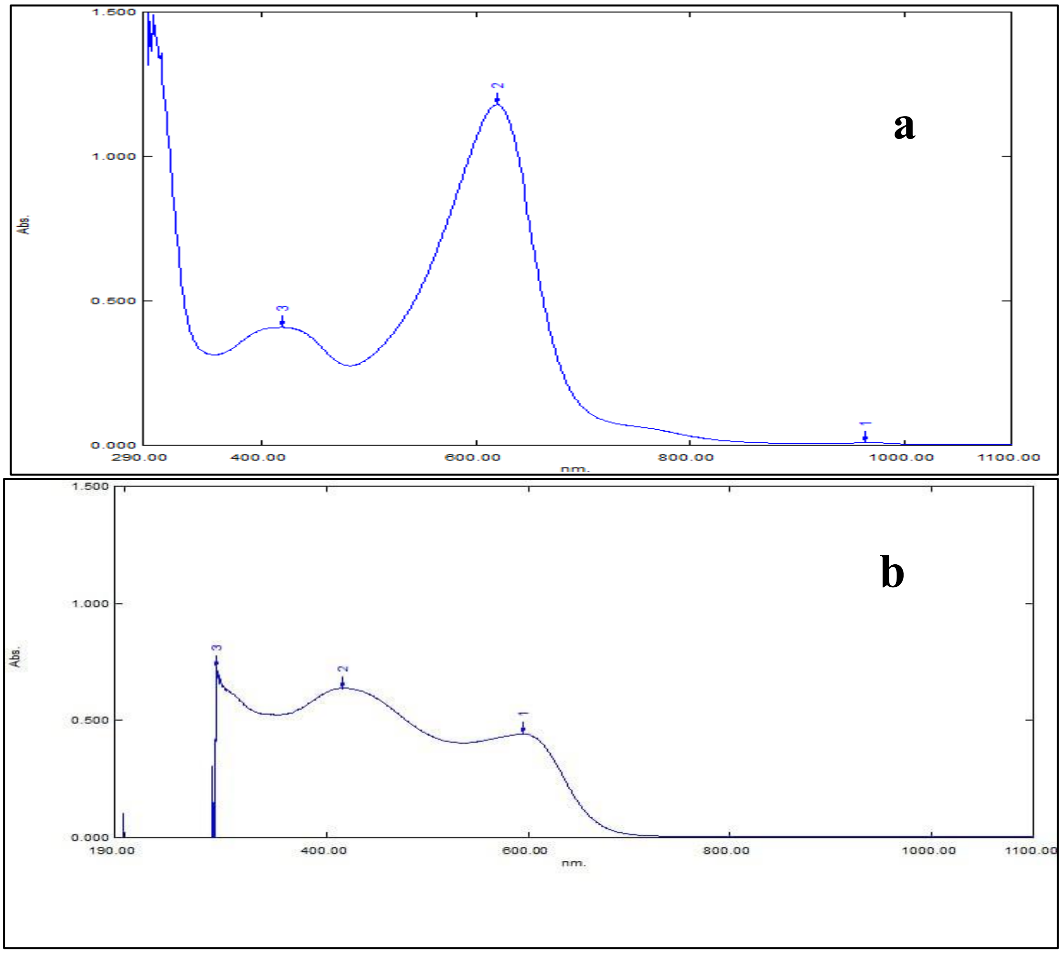


Figure 2: Show the absorption spectra of a) Fe (III) : methylthymol blue complex and b) for methylthymol blue only

4.2. Study the optimum parameters

4.2.1. Effect the concentration and volume of methylthymol blue

The impact of varying concentrations of methylthymol blue was investigated within the range of 25-200 µg/mL (1 ml volume was taken at 25 0C in 25 min). The data presented in Figure 3.A indicate that the highest absorbance was obtained at 50 µg/mL. Therefore, 50 µg/mL was adopted for the subsequent study.

The effect of volume of methylthymol blue on the formation of Fe(III): methylthymol blue complex was study. Various volumes of (0.25-2 mL) of methylthymol blue (50 µg/mL) were used. The results presented in Figure 3.B indicate that a volume of 1.25 mL yielded the highest absorbance, leading to its selection for subsequent experiments.

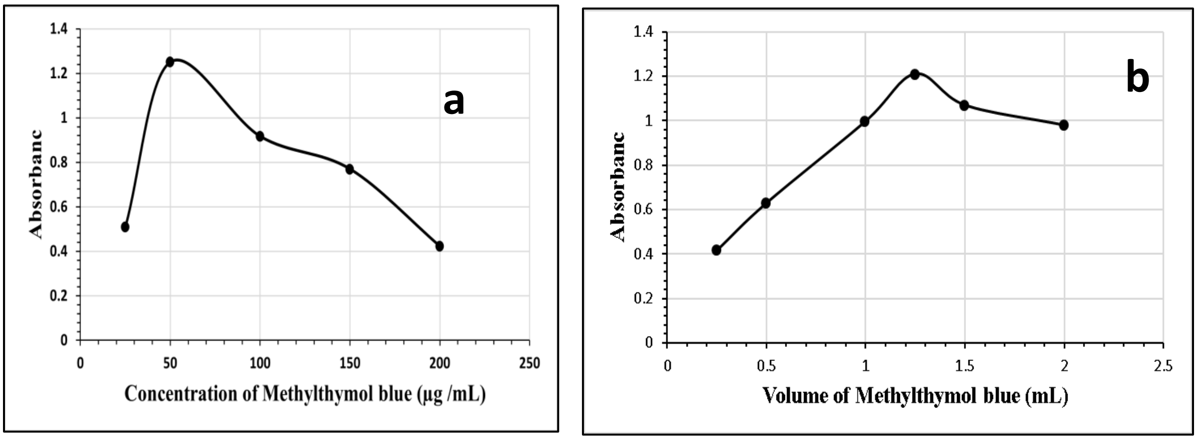


Figure 3: Study (a) Concentration of methylthymol blue (b) volume of methylthymol blue

4.2.2. Impact of temperature and reaction time

In this experiment, it is generally preferable to utilize conditions that involve the lowest temperature and the shortest reaction time [25]. We conducted an investigation to examine the impact of reaction time and temperature ranging from 5–30 minutes and 25–50 °C, respectively. Figure 4 presents data indicating that a temperature of 25 °C within a time period of 25 minutes achieved the highest reaction rate.

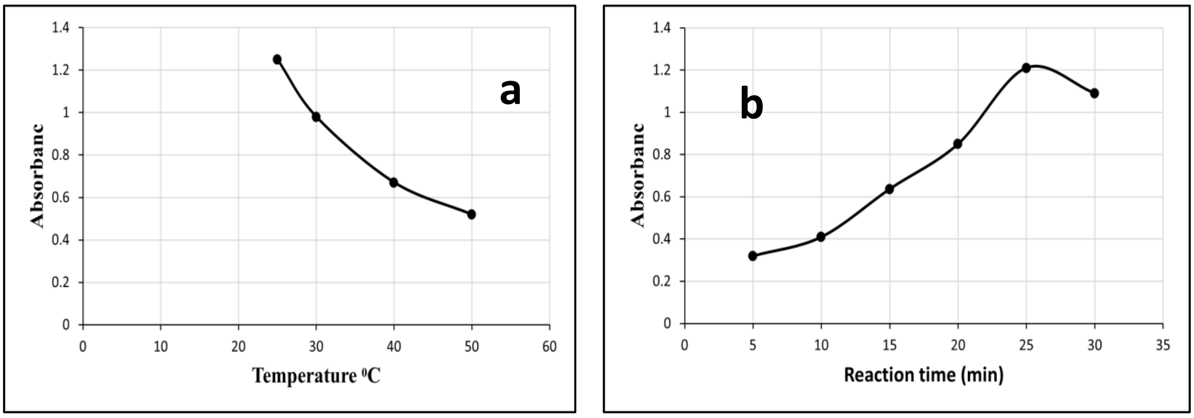


Figure 4: Show (a) maximum temperature (b) maximum reaction time

4.2.3. Effect of type of extraction and dispersive solvent

The key determinant for achieving effective extraction was the careful choice of extraction and disperser solvents. A suitable extraction solvent should possess a greater density than water, a high capacity to extract specific compounds, exhibiting limited aqueous solubility, and the ability to form small droplets when combined with a dispersing solvent[26]. We evaluated halogenated hydrocarbons such as carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), ethylene chloride, methylene chloride, and benzene as extraction solvents to achieve this objective. The primary determinant in choosing a dispersing solvent is its ability to mix well with both organic and aqueous phases. Thus, a few solvents, such as acetonitrile, methanol, ethanol, and acetone, restrict the choice of dispersive solvents [27]. The experiment involved testing various combinations of disperser solvents and extraction, as shown in Figure 5. The combination of methylene chloride and acetonitrile revealed a stable biphasic system and a stronger signal. Therefore, the methylene chloride and acetonitrile were selected as suitable combination for extracting Fe(III) ions.

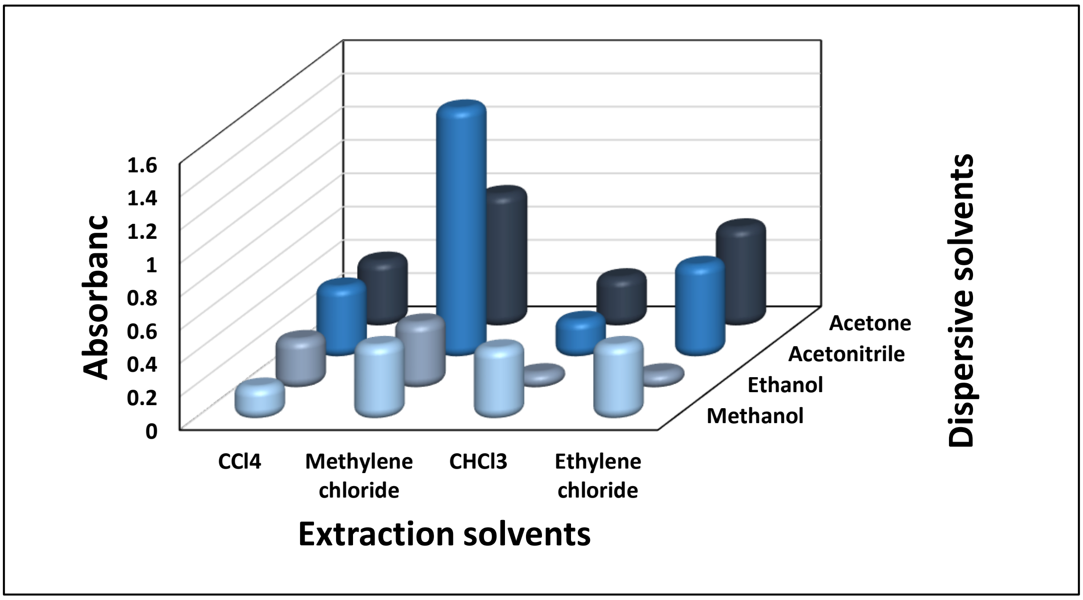


Figure 5: Type of extraction and dispersive solvent

4.2.4. Effect of Volume of extraction and dispersive solvent

The volume of the extraction solvent plays a pivotal role in the developed method, as it has a direct bearing on the efficiency of complex extraction [1]. To evaluate the effect of varying amounts of methylene chloride on extraction efficiency, different volumes (ranging from 0.1 to 1 mL) with 1.5 mL of acetonitrile and the procedure was carried out as described. As illustrated in Figure 6-A, the extraction efficiency increases significantly up to 0.5 mL. Nevertheless, for volumes exceeding 0.5 mL, the analytical signals showed a decrease. We can attribute the decrease to the solution's high viscosity. Therefore, a volume of 0.5 mL of methylene chloride was determined to be the most effective amount of extraction solvent.

The volume of the disperser solvent critically influences the formation of a turbid solution, which consists of water, extraction solvent, and disperser solvent[28]. Changing the disperser solvent's volume can also change the size of the droplets, the polarity of the water phase, and the collection of the organic phase [29]. An investigation was conducted on the volume of acetonitrile ranging from 0 to 1.7 mL, which included 0.5 mL of methylene chloride. The absorbance exhibited a gradual increase up to a volume of 1 mL, followed by a sudden decline. This decline can be attributed to the extraction solvent, which likely enhanced the product's dissolution in water, leading to a decrease in extraction efficiency. Figure 6-B illustrates this observation. Consequently, 1 mL was selected as the optimal volume for the subsequent experiments.

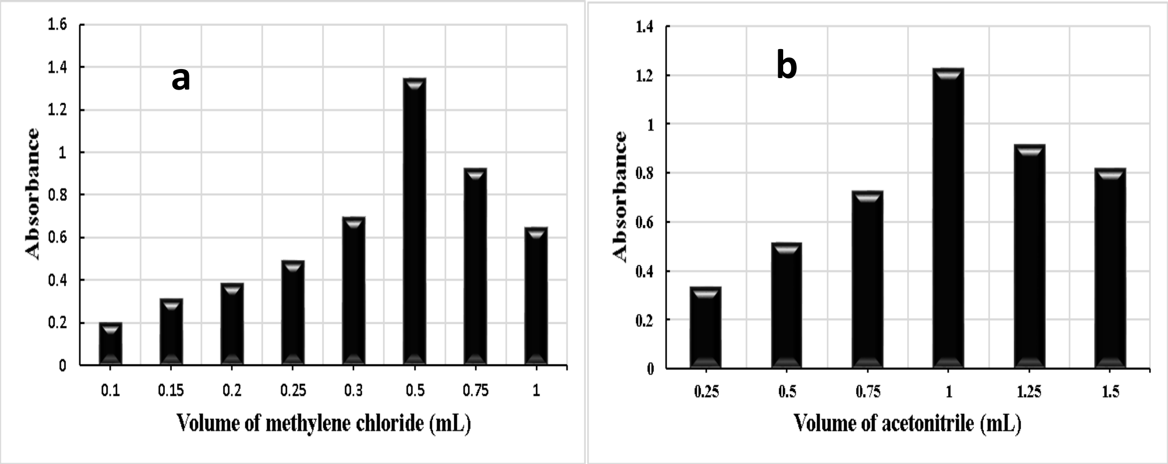


Figure 6: Show a) volume of extraction solvent b) volume of dispersive solvent

4.2.5. Study of centrifuging parameters

An investigation was conducted to assess the effects of centrifuging speed and time within the ranges of 1000–5000 rpm and 1–10 min, respectively. Initially, different speeds were tested while maintaining a consistent duration of 5 minutes. Figure 7-A indicated that a speed of 5000 rpm is optimal for effectively separating the two phases and collecting the extraction solvent. The study investigated the effect of centrifuging time on the complex's extraction efficiency at the optimized rate. We found that a duration of 5 minutes was sufficient to achieve the highest absorbance signals, as illustrated in Figure 7-B.

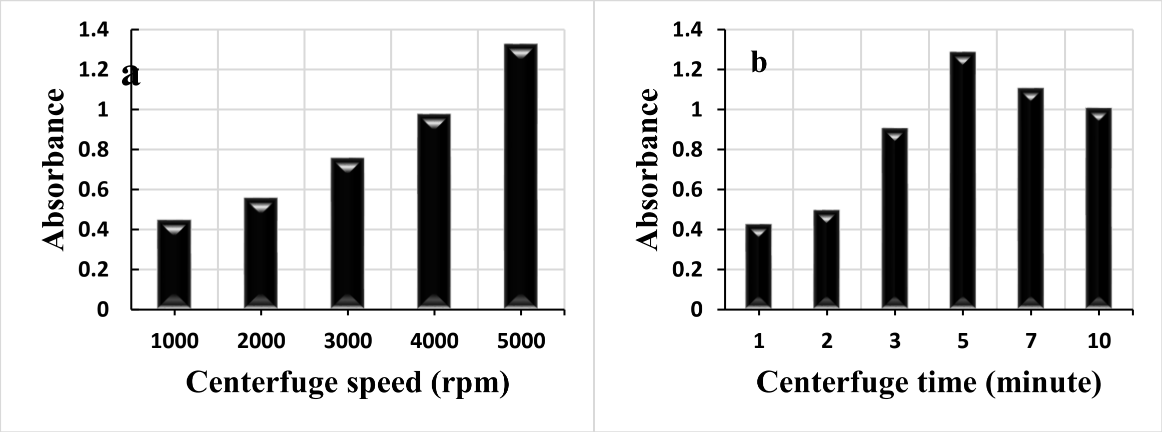


Figure 7: Shows the Centrifuge a) speed and b) Time

4.2.6. Effect of extraction time

The extraction time, which requires study and determination, is the most crucial factor in DLLME. This term is characterized as the time period between the injection of the mixture of disperser and extraction solvents from the commencement of centrifugation process [30]. We examined various extraction times, ranging from 1 to 15 minutes, to achieve this objective. The findings demonstrated that the extraction process time did not have a significant impact on the absorbance signal. A cloudy solution forms between the extraction solvent and the aqueous solution, resulting in a large surface area. As a result, the color product rapidly disperses into the extraction solvent. The greatest advantage of DLLME lies in its ability to operate without being restricted by time constraints.

4.3. Method validation

4.3.1 Calibration curve

The proposed method was evaluated under optimal conditions to determine its analytical performance. This evaluation included assessing the relative standard deviation (RSD%), linear range, limit of quantification (LOQ), coefficient of determination (R^2) and limit of detection (LOD). Table 1 presents the outcomes. The LOD and the LOQ were calculated using the formulas: 3 times the standard deviation of the blank (SB) divided by the slope of the calibration graph (m) for LOD, and 10 times the SB divided by m for LOQ. To assess the method's performance, it was tested on five solutions over the course of one day (intraday) and three different days (inter-day), each with 40 µg/mL of the analyte. Repeatability was expressed as the relative standard deviation (RSD%). The satisfactory and promising results indicate that the suggested method has a good potential for widespread application in the determination of Fe (III) at trace level in different soil samples. Figure 8 shows the calibration curve of the proposed method.

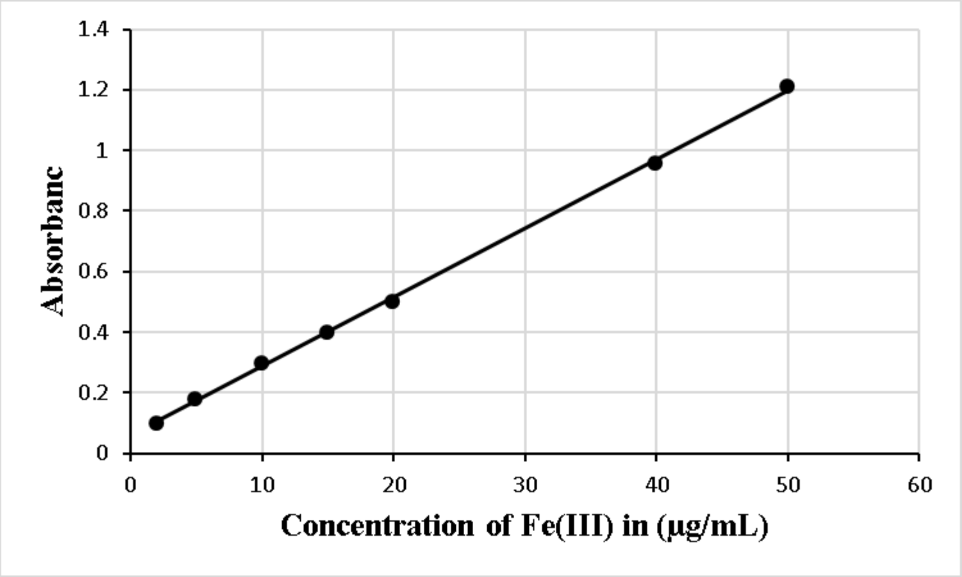


Figure 8: Calibration curves of proposed method

Table 1: The statistical parameters for determination Fe (III) by proposed method

Parameters	Standard value
Regression equation	y = 0.0226x + 0.0669
Correlation coefficient (r)	0.9992
Linearity percentage (r^2%)	99.84
Linear range (µg /mL)	2-50
LOD [a] (µg /mL)	1.327
LOQ [b] (µg/ mL)	4.424
Intra-day repeatability (RSD [c] %)	0.114
Inter-day reproducibility (RSD [c] %)	0.698
sandell's sensitivity (µg/cm^2)	0.0442

[a] Limit of detection

[b] Limit of quantification.

[c] Relative standard deviation (C=40 µg /mL, n=5)

4.3.2. Application

Performance of proposed method was evaluated by determination of Fe (III) level in soil samples of Ishaqi project. The procedure adopted on weight of 0.100 g from each soli sample in order to obtain 1000 μg /mL and take 0.6 mL from this solution to obtain 40 μg /mL. Analytical results (%Rec.) for determination of Fe (III) from different place of Ishaqi project. Table 2 displays the information. The results obtained using the proposed method demonstrate that it is suitable for detecting very small amounts of Fe (II).

The proposed method was compared with other documented methods for determining Fe(III) (Table 3). The findings demonstrated the benefits of the suggested approach concerning the linear ranges, LOD, LOQ and Sandell's sensitivity.

Table 2: Application of proposed method for determination Fe (III) in soil sample

Sample Type	**Soil sample location**	**Conc. Added μg/mL**	**Conc. Found μg/mL**	**Recovery %**
Soil 1	Soil sample from the banks of the Ishaqi River project in Balad District	40	40.01	100.03
Soil 2	Soil sample from the banks of the Ishaqi River project in Al-Taji District	40	39.27	98.18
Soil 3	Soil sample of well in Al-Nabai area	40	40.55	101.38
Soil 4	Soil sample of well in Al- Taji distract	40	40.13	100.33
Soil 5	Soil sample of well in Al- Mishahda area, right side	40	41.02	100.05
Soil 6	Soil sample of well in Al- Mishahda area, left side	40	38.42	96.05

Table 3: Comparison of linear range, LOD, LOQ and S for the determination of Fe (III) using the developed and reference methods

Method	Linearity range ($\mu g\ mL^{-1}$)	LOD ($\mu g\ mL^{-1}$)	LOQ ($\mu g\ mL^{-1}$)	S ($\mu g\ cm^{-2}$)	Samples	Ref.
SPE/ Spectrophotometry	0.02–0.45	0.002	0.006	0.51	Environmental and food	[31]
Smartphone–paper-based sensor	50–900	20	…………..	………	Water and blood plasma samples	[32]
Fluorescence	0.56-55.85	0.123	……….	………	Water, blood and tablet	[33]
Fluorescence	0.56-2.79	0.28	………	………..	Real samples	[34]
DLLME/ Spectrophotometry	2-50	1.327	4.424	0.0442	Soil	Present study

Conclusion

The present research employs a fast and effective method for preparing samples that relies on the formation of complexes between Fe (III) and methylthymol and DLLME for the preconcentration and extraction of Fe (III) from soil samples prior to their determination by Uv-visible spectrophotometer. The proposed method shows a wide concentration range from 2-50 μg/mL with a detection limit of 1.327 μg/mL and quantification limit 4.424 μg/mL. The proposed method presents numerous benefits, including simplicity, simplicity of operation, and affordability. Furthermore, the suggested method employs a minimal amount of extractant, thereby minimizing potential hazards to human health and the environment. The proposed technique was effectively employed to determine the concentration of Fe (III) in various soil samples.

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