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Trace Determination of Iron in Real Waters and Fruit Juice Samples Using Rapid Method: Optimized Dispersive Liquid-Liquid Microextraction with Synthesized Nontoxic Chelating Agent

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Abstract

The purpose of this research was to optimize a new method for preconcentration and determination of trace iron concentrations in aqueous solutions. For this purpose, a newly synthesized ligand, 3-(3-hydroxy-2-methyl-4-oxopyridin-1(4H)-yl) benzoic acid (3-OH-3-MOPBA), was used in the dispersive liquid-liquid microextraction (DLLME) method coupled with UV–vis spectroscopy. The experiments considering input variables of extractant volume, disperser volume, salt concentration, and pH were designed with the aid of central composite design (CCD). The results were analyzed using response surface methodology (RSM). The limit of detection (LOD) was found to be 4.0 μg L^{-1} under the optimized conditions. A calibration curve with a good linearity (R^2 = 0.9986) was obtained over the concentration range of 15–800 μg L^{-1}. The relative standard deviations (RSD) were found to be around 2.1% ($n = 7$). The main advantages of the developed method are simple application, environment friendly, short time, and low cost which makes this method to be applied routinely for measuring iron in various water samples.

Keywords 3-OH-3-MOPBA · Iron · Preconcentration · Response surface methodology · UV–vis spectroscopy

Introduction

Undoubtedly, iron has an essential role in many metabolic functions in the human body. Fe is involved in a wide range of metabolic and synthetic pathways including DNA synthesis, oxygen transport and storage, mitochondrial respiration, and citric acid cycle [1, 2]. Due to the important role of iron in the human body, its disorder (overload or deficiency of iron) causes a variety of diseases [3–5]. Therefore, the determination of iron ions in trace amounts in variety of matrices, especially in aqueous samples, has been subject of many studies [6–11]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS) [12], ICP-mass spectrometry (MS) [13], inductively coupled plasma-optical emission spectrometry (ICP-OES) [14], chromatography [15], and UV–vis spectrophotometry [16–18] have been used for the speciation of iron.

Since various analytical techniques are unable to directly measure very low amounts of iron, many separation and preconcentration methods, including coprecipitation [19], solid phase extraction [20], electro-analytical methods [21], and liquid-liquid extraction [22] were manipulated. One of the methods that is widely used for preconcentration and separation metal ions and organic compounds is the dispersive liquid-liquid microextraction method [23–29]. There is a recent review article on the latest innovations and trends in liquid phase microextraction techniques [30]. The dispersive liquid-liquid microextraction techniques are derived from three-component solvent system: homogeneous liquid-liquid extraction and cloud point extraction methods [31]. It would definitely be said that the most important feature of this system is its solvent velocity. This feature is due to the high contact between the aqueous solvent and the organic solvent that causes the sample to be extracted in fractions of minutes from the aqueous phase to the organic phase [32].

In the present study, a new method for the determination of iron in small amounts by dispersive liquid-liquid microextraction method coupled with UV–vis spectrophotometry was optimized.

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While most of the chelating agent applied to measure iron is toxic, the newly synthesized ligand, 3-(3-hydroxy-2-methyl-4-oxopyridin-1(4H)-yl) benzoic acid (3-OH-3-MOPBA) [33], in this study is non-toxic and environment friendly [34]. In the previous work, we used hydroxy pyridine derivatives as a chelating agent [35]. In comparison, the main advantages of the current study include a much better limit of detection (4 μg L^{-1}), the broader dynamic range (15–800 μg L^{-1}), optimal pH (4.6) in terms of adjustment for acetate buffer, more environment friendly because of using ethanol as a disperser solvent, and ultimately the most significant advantage is that these kinds of ligands have been confirmed to be selective of iron ions in aqueous matrices.

The use of multivariate optimization has been increased in recent analytical chemistry studies [36–39]. This optimization method not only allows simultaneous analysis of several parameters contemporaneously, but also increases measurement performance and speed of analysis and, most importantly, reduces the number of experiments that consequently results in saving time and money [40]. One of the most widely used statistical methods that is used for initial multi-variable optimization is the factorial design method [41]. One of the most functionally used designs in surface response is central composite design (CCD) [42]. The CCD is an experimental design, useful in response surface methodology (RSM), for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment [43]. In this study, the effective parameters for extraction and determination of iron ions in the proposed DLLME method were optimized using CCD and RSM. The RSM explores the relationships between several explanatory variables and one or more response variables. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response [44]. The proposed optimal method is a selective method that can be used simply (because of combination with ultraviolet–visible spectroscopy) for routine determination of iron concentrations in aqueous solutions.

Experimental

Instrumentation

The absorbance of the solutions was determined by Shimadzu UV-160PC (Tokyo, Japan) spectrophotometer. The solutions were centrifuged with A Hettich EBA 200 (Andreas *Hettich GmbH & Co. KG, 78532 Tuttlingen*, Germany). Ultrapure water was prepared by a Milli-Q water purification system (Millipore S.A.S. 67120 Molsheim-France). The pH was measured by InoLab® pH meter (WTW; model 7110, Germany).

Software

MINITAB software was used for experimental design and statistical analysis (MINITAB Release 17.3.1, Minitab, Inc., Pine Hall Road, State College, PA, USA).

Chemical and Standard Solutions

Analytical grade $Fe(NH_4)(SO_4)_2\cdot 12\ H_2O$ (Merck, Darmstadt, Germany) in 1.0 mol L^{-1} HNO3 was used to prepare the stock solution (Fe^{3+} (1000 mg L^{-1})). Diluted working standard solutions were prepared every day from the stock solutions. Buffer acetate (mixing an appropriate amount of sodium acetate (analytical grade) and acetic acid solution (Merck, Darmstadt, Germany-analytical grade) (0.5 mol L^{-1})) were used to adjust the pH solutions (pH 2–8). Hydroxylamine hydrochloride solution ($NH_2OH\cdot HCl$, analytical grade) 5% (*w*/*v*) was from Merck (Darmstadt, Germany) and prepared in a 100-mL volumetric flask by dissolving 5.0 g of the reagent in distilled water. Stock solution of 3-(3-hydroxy-2-methyl-4-oxopyridin-1(4H)-yl) benzoic acid (3-OH-3-MOPBA, analytical grade) (0.0045 mol L^{-1}) was made by dissolving an adequate amount of 3-OH-3-MOPBA in 10 mL of methanol (analytical grade). All organic and inorganic reagents used in this study were obtained from Merck (Darmstadt, Germany, analytical grade (≥ 99.0%)).

Analytical Procedure

In this procedure, a mixture of 150 μL of ethanol, 600 μL of carbon tetrachloride, and 1 mL 4.5×10^{-3} mol L^{-1} of the ligand (3-OH-3-MOPBA) was injected to 5 mL of a sample of water containing 80 μg L^{-1} of iron (including 0.7 mL of reducing agent ($NH_2OH\cdot HCl$) 5% (*w*/*v*) and 1 mL of 0.5 mol L^{-1} acetate buffer (pH 4.5)). The effect of this injection is formation of a cloudy solution. Then, this cloudy solution is centrifuged at 4500 rpm for 3 min. Finally, the extraction phase was diluted in microcell 350 μL with ethanol, and the light absorption was read as absorbance at λ_{max} (546 nm) against a reagent blank.

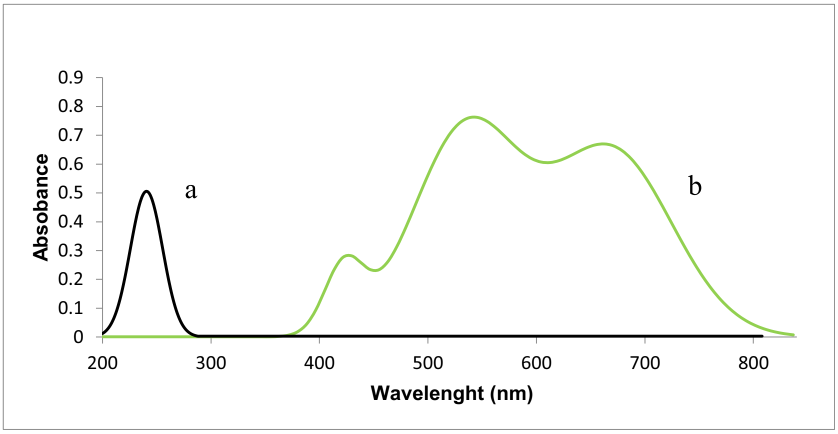
Calculations

In order to evaluate the impact of independent factors on DLLME method, extraction recovery (*R*) and enrichment factor (EF) were calculated as follows:

$$R\% = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 = EF \times \frac{V_{sed}}{V_{aq}} \times 100 \tag{1}$$

$$EF = \frac{C_{sed}}{C_0} \tag{2}$$

Fig. 1 The absorption spectrums of the reagent blank (a) and the complex (b) after proposed method. Extraction conditions: 80 μg L^{-1} of Fe^{3+}, 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, pH 4.5, 150 μL CCl_4, 600 μL ethanol, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, and 1 mL of 0.5 mol L^{-1} acetate buffer (pH 4.5)



where R% is the extraction recovery, V_{sed} is the volume of the sedimented phase, V_{aq} is the volume of the aqueous sample, and C_{sed} is the sedimented phase and was calculated from an external calibration graph obtained by conventional liquid-liquid extraction followed by spectrophotometric determination of iron ions. C_0 represents the initial analyte concentration in the aqueous sample.

Results and Discussion

A dispersive liquid–liquid microextraction procedure based on the reaction between 3-OH-3-MOPBA as a chelating agent and Fe was developed for separation and determination of iron. To find the appropriate conditions for the proposed method, multiple parameters were investigated.

In this research, parameters such as selection of extraction and disperser solvents, volume of reducing agent, and chelating agent concentration by one variable at a time and parameters such as pH, extraction, and disperser volume were optimized by response surface modeling methods. Also, the effect of the added salt concentration was optimized by both one variable at a time and response surface modeling methods, which both methods confirmed each other.

After all of the above-mentioned parameters were optimized, the extraction of iron with optimized parameters (analytical procedure) was performed.

One Variable at a Time Optimized

Selection of Wavelength

Figure 1 presents the results obtained from the analysis of the ligand and complex absorption spectra. From this graph, the two absorption bands at 546 and 662 nm could be observed (according to the extraction conditions presented in the analytical procedure): the absorption spectrums of the reagent blank (1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA) (a) and the complex (80 μg L^{-1} of Fe^{3+}, 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 150 μL CCl4, 600 μL ethanol 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent and 1 mL of 0.5 mol L^{-1} acetate buffer (pH 4.5)) after optimized DLLME technique (b).

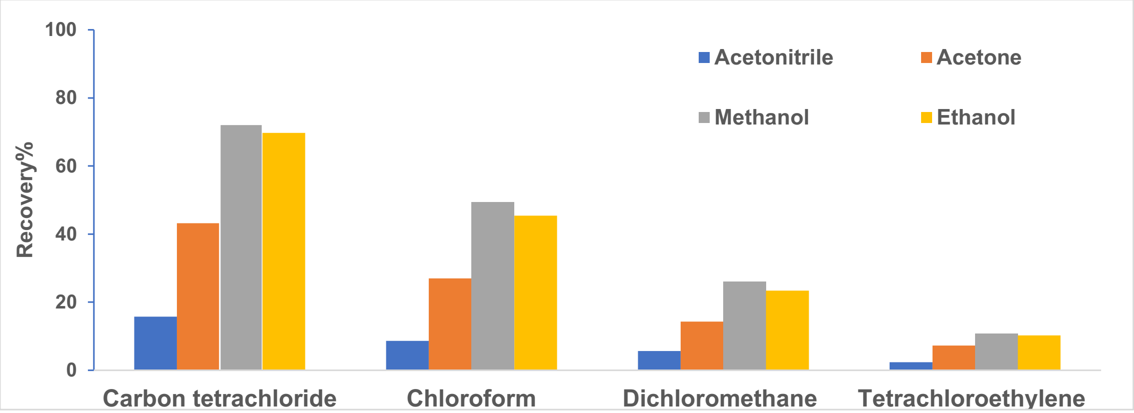


Fig. 2 Influence of extraction and disperser solvents kind on the extraction recovery of iron obtain from proposed method. Extraction conditions: 100 μL CCl4, 500 μL ethanol, 80 μg L^{-1} of Fe^{3+}, 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, and 1 mL of 0.5 mol L^{-1} acetate buffer (pH 4.5)

Table 1 Independent variables, their symbols, and levels for CCD and optimum conditions predicted

Parameters	Symbols	Levels					Predicted value[a]
		− α (low)	− 1	0 center	1	+ α (high)	
pH	A	2	3.5	5	6.5	8	4.6
Extractant solvent volume (μL)	B	80	105	130	155	180	145.6
Dispersion solvent volume (μL)	C	400	600	800	1000	1200	626.3
Salt (*w*/*v* %)	D	0	1.25	2.5	3.75	5	0

[a] The predicted value of extraction recovery by CCD is 90.24%

The observed bands (546 and 662 nm) are attributed to the formation of Fe-(3-OH-3-MOPBA) complex. The more intense band of 546 nm was selected for determination of iron concentration.

Table 2 The central composite design in various experimental and the responses

Run no.	*A*	*B*	*C*	*D*	*R*%
1	1	1	1	− 1	49.30
2	− 1	− 1	1	1	51.43
3	1	− 1	− 1	− 1	62.22
4	− 1	− 1	1	− 1	48.04
5	− 1	− 1	− 1	1	83.96
6	− 1	1	1	1	52.65
7	1	− 1	1	1	41.90
8	1	− 1	1	− 1	39.97
9	0	0	0	0	86.17
10	− 1	1	1	− 1	54.51
11	0	0	0	2	85.10
12	0	0	0	0	80.39
13	0	0	0	0	82.91
14	0	0	0	0	84.30
15	1	1	1	1	47.98
16	0	0	0	0	83.25
17	0	− 2	0	0	61.93
18	0	0	0	− 2	85.01
19	1	1	− 1	− 1	70.92
20	0	2	0	0	85.37
21	0	0	0	0	83.64
22	0	0	2	0	46.05
23	2	0	0	0	48.74
24	− 1	1	− 1	1	86.17
25	0	0	− 2	0	68.85
26	0	0	0	0	83.68
27	− 2	0	0	0	43.17
28	1	1	− 1	1	67.24
29	1	− 1	− 1	1	61.16
30	− 1	1	− 1	− 1	85.49
31	− 1	− 1	− 1	− 1	86.39

Selection of Organic Solvents

The choice of suitable organic solvents in the DLLME procedure is very important. In this study, various organic solvents including carbon tetrachloride, tetrachloroethylene, dichloromethane, and chloroform were used as extraction solvent. (experimental conditions 80 μg L^{-1} of Fe^{3+}, 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-NH_2OH·HCL as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer 150 μL and pH (4.5)). Also, organic disperser solvents such as acetone, acetonitrile, ethanol, and methanol were used. Figure 2 shows the results of using different types of extraction and disperser solvents. The ethanol and methanol extraction efficiency are approximately the same. So, ethanol was selected because it is non-toxic. Due to the fact that the mixture of ethanol and carbon tetrachloride had the best extraction efficiency, they were chosen as a disperser and extractor solvents, respectively.

Influence of the NH_2OH·HCl Concentration

To evaluate the impact of volume of hydroxylamine hydrochloride) 5%-NH_2OH·HCL (on extraction recovery, various volumes (0.1–2 mL) of reducer agent were used, while other parameters were kept constant (experimental conditions: 80 μg L^{-1} of Fe^{3+}, 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). At first, the extraction efficiency increased by increasing the volume of reducing agent to 0.7 mL. Then, a steady extraction efficiency was observed in volume of reducing agent from 0.7 to 0.9 mL. Finally, the increase in the volume of the reducing agent for higher than 0.9 mL resulted in a decrease in the extraction efficiency. Therefore, the volume of 0.7 mL was chosen as the optimum volume of the reducing agent.

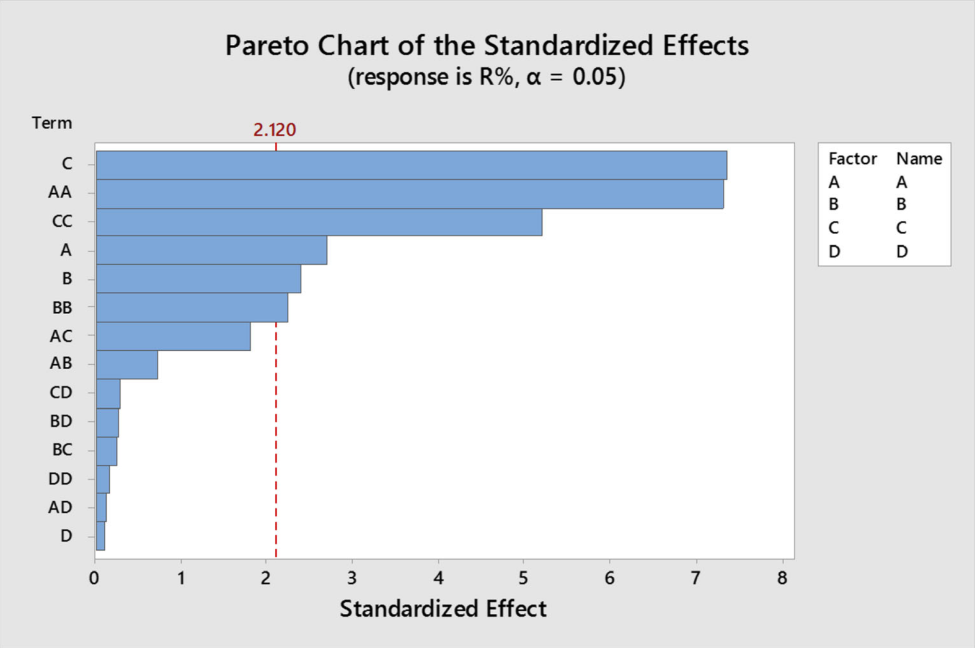


Fig. 3 Pareto chart of factorial screening experiment ($p < 0.05$). A, B, C, and D are pH, extraction solvent volume (EX), dispersive solvent volume (DIS), and salt addition (*w*/*v* %), respectively. Experimental conditions: 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, CCl_4 (extraction solvent), ethanol (disperser solvent), 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, NaCl (evaluation of ionic strength), and acetate buffer (to pH adjusted)

Influence of Salting-Out

The effect of ionic strength on the DLLME method was studied by applying different concentrations of sodium chloride (0–5% *w*/*v*), while other parameters were kept constant (experimental conditions: 80 μg L^{-1} of Fe^{3+}, 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). The results indicated that the salt addition does not affect the extraction efficiency. Therefore, all the experiments were done without increasing the salt amount. This issue has been reaffirmed with insignificant data in response surface methodology section (multi-variation optimized section).

Influence of 3-OH-3-MOPBA

The influence of chelating agent concentration on the recovery of iron ions was evaluated (0.0001–0.008 mol L^{-1}), while other parameters were kept constant (experimental conditions: 80 μg L^{-1} of Fe^{3+}, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). The recovery increased by an increase of the 3-OH-3-MOPBA concentration from 0.0005 to 0.0045 mol L^{-1}, and then it remains constant. Therefore, the 4.5×10^{-3} mol L^{-1} was selected as the optimal concentration of 3-OH-3-MOPBA.

Multi-variation Optimized

Response Surface Methodology and Selection of Optimum Conditions

In this section, after primitive optimal conditions (a number of parameters were obtained in the one variable at a time), four important factors of pH, salt concentration (NaCl), volume of extractant (CCl_4), and disperser (ethanol) solvents which affect the pre-concentration and extraction of iron ions were optimized employing the two-level full factorial by central composite design (CCD) [45]. All condition tests performed in this section are described in the analytical procedure section (80 μg L^{-1} of Fe^{3+}, 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent and acetate buffer (to pH adjusted)). The encoded and non-encoded values of experimental variables are specified in Table 1. The data from the 31 experiments (include 16 cube points, 7 center points in cube, and 8 axial points) designed by MINITAB software version 17.3.1 derived from the extraction of iron ions into DLLME method are shown in Table 2. [46]. All the experiments performed in accordance with the conditions stated in the analytical procedure section. The mathematical relations between independent variables and response are a quadratic polynomial equation as follows:

$$Y = 83.48 – 4.03\,A + 3.59\,B – 10.97\,C – 10\,A^2 – 3.07\,B^2 – 7.12\,C^2 \quad (3)$$

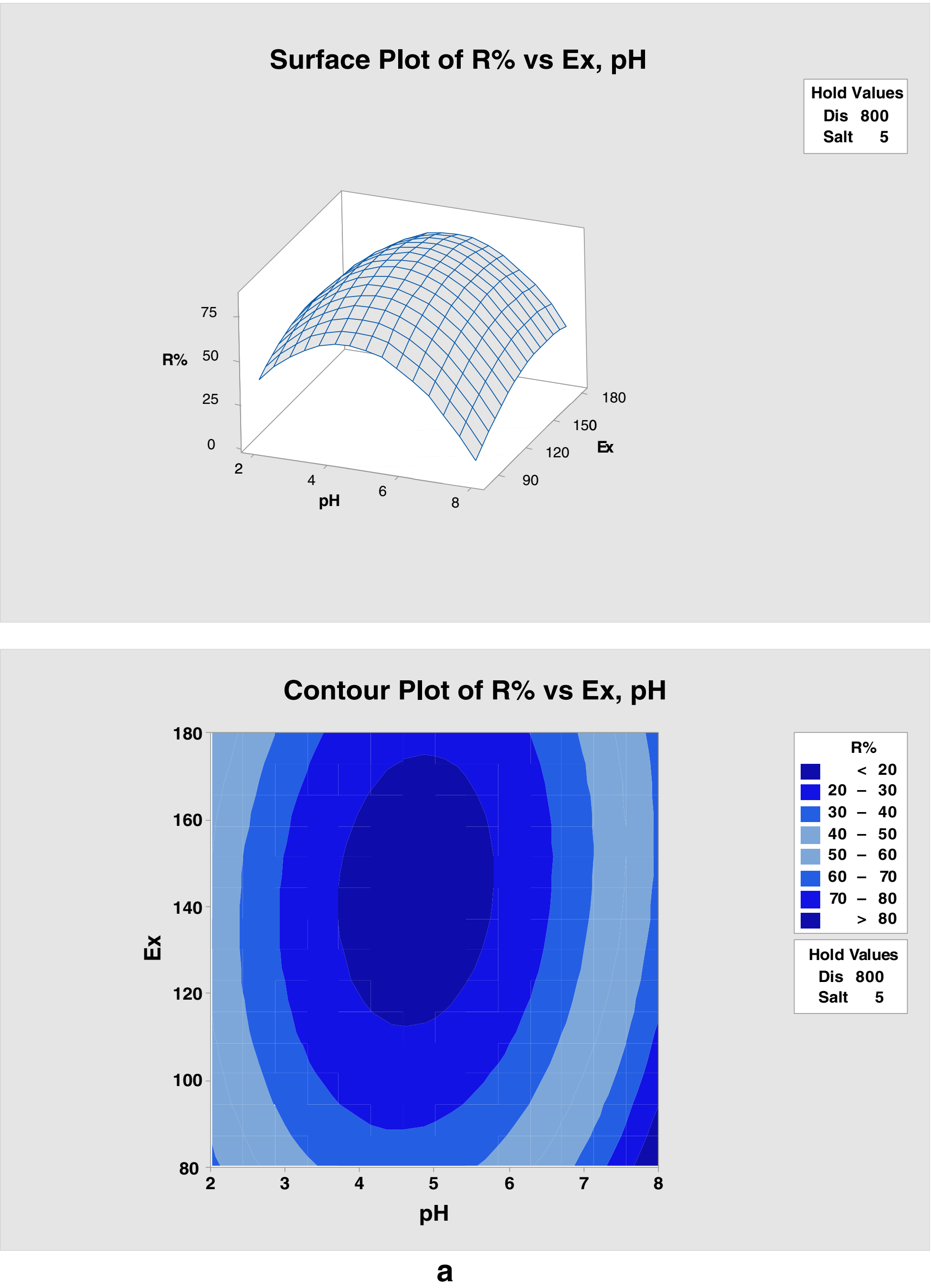


Fig. 4 2D/3D contour plots and response surface models of extraction recovery percent versus of Ex (extraction solvent volume) and pH (**a**) Dis (dispersive solvent volume) and pH (**b**). Experimental conditions: 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-$NH_2OH·HCL$ as a reducer agent, acetate buffer (to pH adjusted), NaCl (evaluation of ionic strength), CCl_4 (extraction solvent), and ethanol (disperser solvent)

where *Y* is the predicted average extraction recovery that depends on the three factors of pH, volume of extractant, and disperser solvents. *A*, *B*, and *C* are pH, extractant solvent volume (EX), and dispersion solvent volume (DIS), respectively.

Figure 3 shows the Pareto chart generated in this experiment. It is clear that DIS, pH, and EX with the lowest *p* values respectively are the most significant factors. Also, the effect of quadratic terms of pH^2, Ex^2, and Dis^2 is statistically significant on *R%*, but none of the two-way interaction is not significant on *R%* in 95% confidence level. Figure 4 illustrates the contour plot and three-dimensional surface response of extraction recovery modeling for some of the important factors. These types of curves can well illustrate the interactions between the factors. According to Fig. 4a, in the pH range of 4 to 5, and the solvent volume of the extractor of 140 μL, the extraction efficiency is maximized. Also, as shown in Fig. 4b, in the range of pH 4 to 5 and the solvent volume of the disperser, about

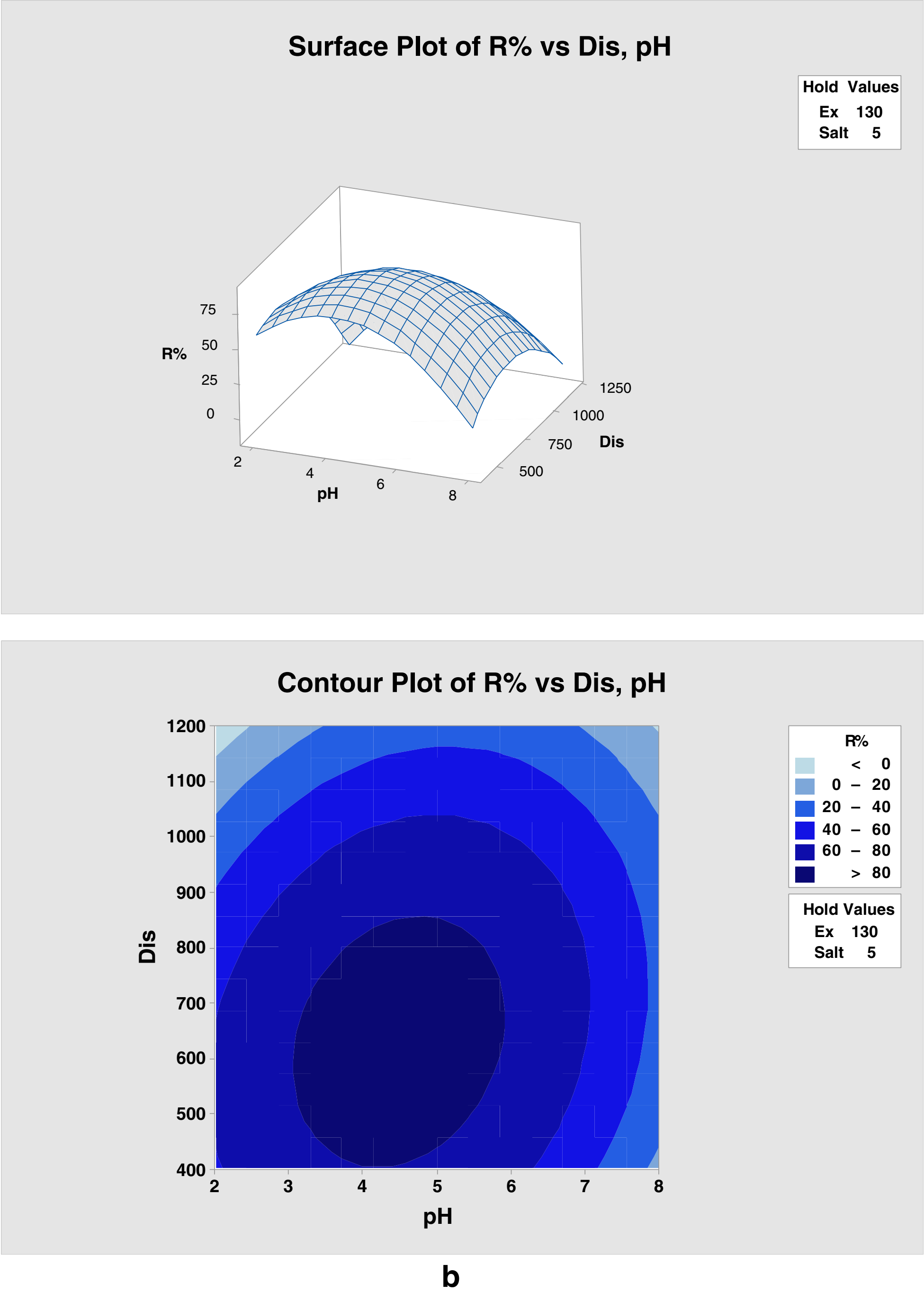


Fig. 4 (continued)

600 μL has the highest extraction amount. The optimal predicted points of the experiment conditions have been shown in the last column of Table 1. In order to evaluate the validity of the predicted model, three experiments were carried out in accordance with predicted optimal conditions, with an average extraction recovery of 87 ± 1.73 that showed good agreement between the results of the experimental results and the predicted values.

Influence of Extraction Time

Extraction time is one of the major parameters affecting the extraction efficiency. In DLLME method, it was defined as an interval between the time of injection of the mixture (disperser + extraction solvent) and the time of starting of centrifugation. For evaluating this parameter, different extraction times (0.5 to 90 min at constant experimental conditions: 80 μg L^{-1} of Fe^{3+}, 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-NH_2OH·HCL as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol) were studied. The results indicated that the extraction time has no significant effect on the extraction efficiency. This could be due to the infinitely large surface area between the extraction solvent and the aqueous phase, susceptible to extracting the uranyl ions. Therefore, DLLME technique is very fast, and this is the most important advantage of it, as reported by other researchers. In this method, centrifuging of sample solution in the extraction procedure takes the most time which is about 3 min.

Influence of Foreign Ions

There is always a great problem with coexisting ions along with environmental samples to detect metallic ions in very low amounts using instrumental techniques [47]. In order to investigate the interference of the concomitant ions, we used 5 mL of the sample containing iron ions (80 μg L^{-1}) along with different amounts of other ions (experimental conditions: 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-NH_2OH·HCL as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). As the results in Table 3 show, at a tolerable concentration of concomitant ions, less than 5% deviation in absorbance reading was observed. Therefore, the presence of coexisting ions in different amounts did not affect our optimized method.

Table 3 Interferences of foreign ions for determination of iron (80 μg L^{-1})

Coexisting ions	Tolerance ratio (*w*/*w*)
EDTA	50
SCN^-	100
Al^{3+}	300
Cu^{2+}, Sn^{2+}, Ag^+, Tartarate, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}	500
CH_3COO^-, SO_4^{2-}, NO_3^-, Cr^{2+}, Co^{3+}	800
Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}	1000

Analytical Method Validation

The analytical performance characteristics of the developed DLLME method were studied at optimal value of input variables. At optimized condition, the calibration graph with excellent linearity ($R^2 = 0.9986$) was observed for the iron concentration from 15 to 800 ng mL^{-1}. The mathematical equation of calibration curve was as $y = 0.0022x + 0.0585$ by the optimized DLLME technique (experimental conditions 80 μg L^{-1} of Fe^{3+}, 1 mL of 45 × 10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-NH_2OH·HCL as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). The limit of detection was calculated according to LOD = 3 SB/m in SB and m standard deviation of the blank and the slope of the calibration graph, respectively. LOD was observed to be 4 μg L^{-1}. To determine the relative standard deviation (RSD), iron concentration of 50 μg L^{-1} was measured ten times at optimal condition. RSD value was found to be 2.1%. The enrichment factor was 23 (8 mL of iron aqueous solution resulted in 350 μL).

The developed DLLME method was successfully tested for actual aqueous samples (spiked tap, well, and mineral waters). Real water samples were preconcentrated, and their iron concentrations were measured. The results of iron determination of real samples are shown in Table 4.

Comparison of the Proposed Method with Previous Study

The results of this study were compared with other methods by the same technique used in preconcentration and determination of iron ions. These results are shown in Table 5. In contrary to other methods, present method has a lower

Table 4 Analytical results for iron in various real water samples

Sample	Fe added (μg/L)	Fe found, mean ± SD[a] (μg/L)	Recovery (%)
Well water[b]	–	98.00 ± 0.47	–
	40	138.1 ± 0.32	100
	80	172.1 ± 0.55	97
	100	202.4 ± 0.28	102
Tap water[c]	–	33.00 ± 00.61	–
	40	67.29 ± 0.2	92
	80	111.1 ± 0.41	98
	100	125.7 ± 0.36	95
Mineral water[d]	–	Not detected	–
	40	41.97 ± 0.83	105
	80	83.57 ± 0.27	104
	100	97.00 ± 0.35	97
Fruit juice[e]	–	5.000 ± 0.95	–
	40	44.10 ± 0.95	98
	80	83.01 ± 0.95	98
	100	104.6 ± 0.95	100

[a] Standard deviation ($n = 3$)

[b] Collected from Isin Hormozgan Iran

[c] From drinking water of laboratory

[d] Aquafina mineral water bought from market

[e] Bought from market

Table 5 Comparison of the proposed method with reported methods for the determination of iron using various techniques

Instrumental technique	Preconcentration method	Complexing agent	Linear range (μg/L)	LOD (μg/L)	RSD (%)	Sample volume (mL)	Reference
Spectrophotometry	DLLME	3-(3-Hydroxy-2-methyl-4-oxopyridin-1 (4H)-yl) benzoic acid (3-OH-3-MOPBA)	15–800	4	2.1	5	Proposed procedure
Spectrophotometry	wsGA-RBFN	Methylthymol blue (MTB)	220–11,830	67	4.4	50	[48]
FAAS	DLLME	1,5-Bis (di-2-pyridilmethylen thiocarbohidrazide) (DPTH)	10–5000	9	1.85 and 4.4	10	[49]
FAAS	CPE	1,2-Tiazolylazo-2-naphthol (TAN)	25–200	10	2.1	6	[50]
FAAS	SPE	*N*,*N*0-Bis-(2-hydroxy-5-bromobenzyl)-2-hydroxy-1,3-diiminopropane	20–1000	19	1.4	25	[51]
HPLC	LLE	3,4-Dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (DHOB)	10–10,000	7	–	4	[15]
ICP-MS	Coprecipitation	–	0.5–18	ƞ 0.005	4.4	–	[19]
Spectrophotometry	DLLME	3-Hydroxy-1-(3-hydroxyphenyl)-2-methylpyridin-4 (1H)-one (3-OH-PMPO)	10–750	5	1.2–4.2	5	[35]
Spectrophotometry	Colorimetric probe	2-(2_-Pyridyl)imidazole (PIMH)	98.8–3500	102	<2	20	[52]

detection limit (4 μg L^{-1}), lower RSD (2.1%), the broader dynamic range (15–800 μg L^{-1}), higher enrichment factor (23), and shorter extraction time (3 min) (experimental conditions 80 μg L^{-1} of Fe^{3+}, 1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA, 0.7 mL 5%-$NH_2OH{\cdot}HCL$ as a reducer agent, 1 mL of 0.5 mol L^{-1} acetate buffer, pH (4.5), 150 μL CCl_4, and 600 μL ethanol). Also, due to the use of non-toxic chelating agent, our method is environment friendly [34]. According to the results, it can be said that our optimized DLLME method coupled with UV–vis spectrophotometer is a simpler and more selective method for iron determination in comparison with previously developed methods.

Conclusions

This paper describes an effective optimized method for the determination and preconcentration of iron ions in a variety of water samples. The important parameters were optimized using both one variable at a time and response surface modeling methods. In this study, parameters such as selection of extraction (CCl_4) and disperser solvents (ethanol), volume of reducing agent (0.7 mL 5%-$NH_2OH{\cdot}HCL$), and chelating agent concentration (1 mL of 45×10^{-4} mol L^{-1} of 3-OH-3-MOPBA) by one variable at a time and parameters such as pH (4.5), extraction (150 μL), and disperser (600 μL) volume were optimized by response surface modeling methods. Also, the effect of the added salt concentration was optimized by both one variable at a time and response surface modeling methods, which both methods confirmed each other.

Because of the special selectivity between the chelating agent and the iron ions (pH = 4.5), the extraction was performed with the least ion interference. The use of spectrophotometric instrumentation is one important merit of simplicity, cheapness, portability, and so on in comparison with other previous studies. The present method has lower detection limits and lower RSDs within less sample volume. Due to the low levels of organic solvents, as well as the non-toxicity of our non-toxic chelating agent, this method is considered as an environmentally friendly method. It is believed that the proposed procedure can be useful for analysis and monitoring of iron level in aqueous, environmental, and biological samples.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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