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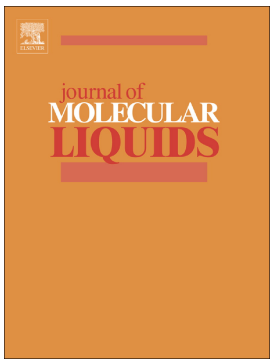

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PII: S0167-7322(19)32114-2
DOI: https://doi.org/10.1016/j.molliq.2019.111242
Article Number: 111242
Reference: MOLLIQ 111242

To appear in: *Journal of Molecular Liquids*

Received date: 13 April 2019
Revised date: 9 June 2019
Accepted date: 25 June 2019

Please cite this article as: S. Sadeghi and A. Davami, A rapid dispersive liquid-liquid microextraction based on hydrophobic deep eutectic solvent for selective and sensitive preconcentration of thorium in water and rock samples: A multivariate study, Journal of Molecular Liquids, https://doi.org/10.1016/j.molliq.2019.111242

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A rapid dispersive liquid-liquid microextraction based on hydrophobic deep eutectic solvent for selective and sensitive preconcentration of thorium in water and rock samples: A multivariate study

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Abstract

Thorium and its compounds are highly toxic and cause severe damage to bone and kidney through long term exposures. Conventional methods of Th(IV) detection are complicated and costly. In this study, we developed a new dispersive liquid-liquid microextraction (DLLME) based on hydrophobic deep eutectic solvent (HDES) for preconcentration of Th(IV) in water and rock samples prior to UV-Vis. spectrophotometric detection. The microextraction procedure was carried out by applying thorin as a chelating agent, cethyltrimethyl ammonium bromide (CTAB) as an ion pairing agent and a DES consisted of 1-hexyl-3-methylimidazolium and salicylic acid components as an extraction solvent. Central composite design (CCD) was applied to obtain the best condition of the microextraction procedure. The developed method is a green, facile, fast, selective and sensitive that could detect Th(IV) in the concentration range of 10 - 600 ng mL^{-1} with a limit of detection (LOD) and preconcentration factor of 2.1 ng mL^{-1} and 59, respectively. The relative standard deviation of five replicates measurements of Th(IV) at 100 ng mL^{-1} was 1.7%. Finally, the proposed method was successfully applied to the analysis of Th(IV) in water and rock samples, and desirable results were obtained.

Keywords: Thorium; Dispersive liquid-liquid microextraction; Central composite design; Hydrophobic deep eutectic solvent; Spectrophotometry

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1. Introduction

Thorium [Th(IV)] as the radioactive element exists on monazite sand, soil, rock, plant, atmosphere and water. It has extensive applications for various industries such as metallurgy, optic, ceramic and especially in nuclear energy sources [1, 2]. People who are exposed to thorium through food, air and water are at risk of bone fractures and liver and kidney failure. According to the World Health Organization (WHO), concentration of Th(IV) in drinking water should be below 20 μg L^{-1} [3]. Hence, there is a considerable attention to develop, simple, sensitive and selective methods for determination of Th(IV) in environmental samples. Conventional techniques for detection of low concentration of Th(IV) are usually based on inductively coupled plasma-atomic emission spectrometry (ICP-AES)[4], inductively coupled plasma-mass spectrometry (ICP-MS)[5], capillary zone electrophoresis [6], ion chromatography [7] and X-ray fluorescence spectroscopy [8]. Although these techniques provide reliable results, they require daily maintenance, well-controlled experimental conditions, costly instruments and in some cases time consuming. Because of simplicity, relatively low cost, and availability in most laboratories, UV-Vis. spectrophotometry may be effectively used as a reliable and an alternative technique to determination of Th(IV). However, it suffers from low sensitivity and matrix interferences in determination of analytes in real samples. Due to these drawbacks, separation and preconcentration are trivial steps in trace analysis of metal ions. Several preconcentration approaches such as solid phase extraction (SPE) [9], liquid-liquid extraction (LLE) [10], cloud point extraction (CPE) [11] and flotation [12] have been established for the determination of Th(IV). But, these methods are tedious, provide insufficient preconcentration, consume a large amount of toxic organic solvents, time-consuming and produce secondary labs' waste that limits their applications. To overcome these drawbacks, miniaturized extractions such as liquid phase microextraction (LPME) [13] and solid phase microextraction (SPME)[14] have been developed. Until now, various miniaturized liquid phase extraction was developed such as emulsification microextraction (EME), single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), in situ solvent formation

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microextraction (ISFME) and dispersive liquid–liquid microextraction (DLLME) [15]. These methods provides important benefits to extraction of analytes such as simplicity, less consumption of toxic solvents, high preconcentration factor, being an environmental friend method and combine with different analytical measurement techniques. Among the LPME methods, DLLME is well-developed method to optimize microextration process. In this method, a mixture of a water-immiscible solvent and a small amount of a water miscible solvent as an extraction and disperser solvents, respectively, is injected rapidly into the sample tube to produce fine droplets of the extractant which are dispersed entirely in the aqueous phase and increases mass transfer of the analyte into the extraction solvent. Finally, the extraction phase can be settled in the bottom of the tube which may be removed by a syringe [16]. Great efforts also were made in DLLME to use less amount of organic extraction solvent or elimination of disperser solvent to simple phase separation by air-assisted DLLME or ultrasound assisted DLLME. Also, to accelerate elmulsification procedure, vortex assisted DLLME was introduced whereby the extraction solvents are dispersed into aqueous samples by vortex mixing [15]. Thus, these methods simplify the operation and speed up the extraction procedure. Instead of organic solvents, different types of extraction solvents such as supramolecular solvents, switchable solvents, ionic liquids, and deep eutectic solvents have been used in DLLME for extraction and preconcentration of heavy metal ions [17]. Utilization of new DLLME based on surfactants as surfactant-assisted DLLME (SA-DLLME), ion pair-based surfactant assisted microextraction (IP-SA-ME), and surfactant-enhanced emulsification microextraction (SE-ME) combined with ultrasonic radiation, vortex agitation, and solidification improvements have been reported [15, 17]. Few methods are reported in the literature for separation and preconcentration of Th(IV) using various DLLME methods and several chelating agents. Elmasry et al. used supramolecular solvent-based liquid-liquid microextraction method for preconcentration of thorium(IV) in various environmental samples [13]. Veyseh and Niazi applied flotation-assisted homogeneous LLME for determination of thorium in water samples [5]. Hydari

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and Ramazani reported a new stirring assisted LLME for the analysis of trace amount of thorium ions [18].

Room temperature ionic liquids (RTILs) are a novel class of green solvents consisted of an imidazolium or pyridinium cation and organic or inorganic anion which have been considered as an alternative for the organic solvents [19]. Most of the hydrophobic RTILs are contained $[PF_6]^-$ as an hydrophobic anion but it produces toxic HF and POF_3 compounds by hydrolysis. Besides, these solvents are expensive and non-biodegradable [20]. In recent years, deep eutectic solvents (DESs) have been used as green solvents for extraction of different compounds. DESs are consisted of two or more components including a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), which can be associated with each other at moderate temperature via hydrogen bonding interaction result in a eutectic mixture with lower melting point than each component [21]. DESs offer solvents with excellent physiochemical properties such as non-flammable, negligible vapor pressure, extensive liquid range and thermal stability similar to RTILs. However, facile syntheses, cost effective, not require to furthering purification, biodegradability and biocompatibility make them potential alternatives to replace conventional organic solvents as well as traditional ILs [22-24]. Most of the DESs are hydrophilic that limits their applications as extractants to recover of analytes from aqueous solutions. Recently, some literatures have been reported on production of hydrophobic DESs for extraction of inorganic or organic targets from water samples [21]. Habibollahi and coworker applied hydrophobic DESs as the extraction solvent in DLLME based on the solidified deep eutectic solvent for extraction of heavy metal ions in soil and vegetables irrigated with treated municipal wastewater [25]. Akramipour et al. extended the 1-octyl-3-methylimidazolium chloride and 1-dodecanol as hydrophobic extraction solvent of vortex assisted DLLME based on the freezing of deep eutectic solvent, and applied it for speciation of organic/inorganic mercury and total mercury in blood samples [26]. Zhu et al. demonstrated that hydrophobic DESs could be used as an extraction solvent in LLME to analysis of synthetic pigments in beverages [27].

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Investigation of main factors that control a process via minimal experiments associated with confident results is desirable in each study. In the most conventional multifactor experiments, optimization process is usually performed by changing a single factor in each step while all other factors are set at constant levels (one factor at a time). Besides, a large number of experiments should be performed that consuming high amount of materials and times without considering the interactions between factors. To overcome these drawbacks, response surface methodology (RSM) has been applied. The main benefits of RSM include determination of significant factors, interactions among factors and reducing the number of experiments [28].

In the present study, we persuaded to evaluate a new hydrophobic DES as a green solvent in a simple, selective and sensitive DLLME approach for the microextraction of Th(IV) in aqueous solution for the first time. RSM based central composite design (CCD) was employed for optimization of the most significant variables in the DLLME procedure. The validity of the developed method was checked by determining Th(IV) in water and rock samples.

2. Experimental

2.1. Chemical and reagents

All of the reagents used in the present work were of analytical grade and supplied by Merck (Darmstadt, Germany). 1-methylimidazole, 1-bromobutane, 1-bromohexane, salicylic acid (SA) and benzoic acid (BA) were used to synthesize DESs. $Th(NO_3)_4.5H_2O$, cetyltrimethylammonium bromide (CTAB) and sodium salt of 2-(2-hydroxy-3, 6-disulfo-1-naphthylazo)-benzenearsonic acid (thorin) were applied as the analyte, ion pairing and chelating agents, respectively. The stock standard solution of Th(IV) (1000 mg L^{-1}) was prepared by dissolving a suitable amount of thorium salt in deionized water. The working standard solutions were freshly prepared by diluting the stock solution with deionized water. The pH of the solution was adjusted with 0.1M HCl or NaOH.

2.2. Instrumentation and software

Absorption measurements were performed with a UV-Vis. spectrophotometer 2510-PC (Shimadzu, Japan) equipped with a 1 cm quartz microcell (0.35 mL). The pH values were

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determined with BP3001 benchtop (Trans instruments, Singapore) pH meter with a combined glass electrode. For the phase separation a centrifuge model EBA20 (Hettich, Germany) was used. A Magnetic stirrer (Heidolph, Germany) and a R2062 rotary evaporator (Heidolph, Germany) were employed in the synthesis of DESs. Deionized water was obtained from Aqua max water purification system (Young–Lin, South Korea). The central composite design was accomplished with the Design-Expert®Software Version 10-Stat-Ease (Minneapolis, USA).

2.3. Synthesis of DESs

In the first step, the 1-hexyl-3-methyl imidazolium bromide ([HMIM]Br) and 1-butyl-3-methyl imidazolium bromide ([BMIM]Br) were synthesized according to the previous report [29]. Briefly, an appropriate amount of 1-methylimidazole and an excess amount of 1-bromohexane or 1-bromobutane were poured into a round bottom flask and the mixture refluxed at 80 °C for 48 h until a viscous liquid was produced. Finally, the products were washed three times with ethyl acetate and dried under vacuum at 80 °C. In the second step, to synthesize a DES, a HBA and a HBD in certain molar ratio were mixed in a screw-capped bottle and stirred at room temperature until a homogeneous liquid was formed. In this study, seven DESs (DES-1 to DES-7) were prepared by employing two HBAs, namely [HMIM]Br and [BMIM]Br which could be combined with salicylic acid (SA) or benzoic acid (BA) as HBDs with the different molar ratios (Table S1).

2.4. Preparation of real samples

Two types of water samples were used including river water (Band-e Dareh, Birjand, Iran) and seawater (Oman Sea, Chabahar, Iran). These water samples were collected, filtered through a 0.45 µm membrane and finally stored at 4°C before use.

The rock sample was collected from Shah-Kooh area (Nehbandan, South Khorasan, Iran). The digestion of rock sample was performed as the following: 5 g of rock sample were weighted and transferred into a Teflon reactor containing 50 mL concentrate HF. The reactor was heated at 100 °C to digest the sample completely. Then, the sample was heated slowly to evaporate the solvent and thereafter, cooled down to room temperature. In order to dissolution the residue, a mixture

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containing 5 mL HNO_3 (65%, w/v) and 5 mL HCl (37%, w/v) was added. Finally, the mixture was diluted to 50 mL with deionized water and was applied to the DLLME process.

2.5. DLLME procedure

An aliquot of 10 mL sample or standard solution containing 250 ng mL^{-1} of Th(IV) (pH 3.2), thorin (60 µM) as chelating agent, CTAB (50 µM) as ion pairing agent and $NaNO_3$ (0.5%, w/v) to adjust ionic strength, were introduced to a conical bottom centrifuge tube. Then, 170 µL of [HMIM]-SA (DES-4) as hydrophobic extraction solvent was injected into the solution and immediately was shaken manually for 1 min. During shaking, fine droplets of the DES were produced so that the red color ternary complex Th(IV)-thorin-CTAB could simplify transfer from aqueous solution to the DES phase. To separate two phases, the cloudy solution was centrifuged at 3500 rpm for 5 min. Then, the aqueous phase was removed by a syringe, and the settled phase was diluted to 500 µL with acidic ethanol and transferred to the cuvette. The absorbance was recorded in the wavelength range from 450 to 650 nm against a blank solution which was prepared in the same way without the analyte for control. The calibration curve was constructed based on the measurement of absorbance against the different extracted concentration of Th(IV).

2.6. Experimental design methodology

In the present study, a design of experiments based on CCD was employed. Based on the preliminary experiments, four independent variables were found that affected performance of the microextraction process, i.e. sample pH, the concentration of thorin, the concentration of CTAB and the amount of DES. In this design, the absorbance of the extracted complex of Th(IV)-thorin-CTAB was considered as the analytical response. The effects of independent variables and their interactions on the response were studied in five levels and three blocks. Other variables such as the concentration of $NaNO_3$ (0.5%, w/v), extraction time (1 min), centrifuge time (5 min) and centrifuge speed (3500 rpm) were set at fixed values. The high and low levels of each variable were selected according to the preliminary experiments (Table 1). The coded values of the variables in

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the CCD matrix and their corresponding responses are presented in Table S2. All experiments were performed in a random manner using 10 mL sample solution containing 250 ng mL^{-1} Th(IV).

3. Results and discussion

In this study, thorin was used as a selective chelating agent for Th(IV) microextraction. The hydrated free thorium is positive charge, and the charge of free thorin is negative due to the loss of the sulfonic acid hydrogens in acidic media at pH< 6. Thus, the complex of Th(IV)-thorin has the negative charge and could not extract into the hydrophobic extraction solvent. Therefore, the presence of an ion pairing agent with the positive charge was necessary [30]. For this purpose, CTAB was used as ion pairing agent that could facilitate interaction of Th(IV) with Thorin and resulted in an association of Th(IV)-thorin-CTAB. This association was very insoluble in the aqueous phase but could easily extract into hydrophobic extraction solvents. The UV-Vis. absorption spectra of Thorin, Th(IV)-Thorin, Thorin-CTAB and Th(IV)-Thorin-CTAB complex after DLLME are presented in Fig. 1. Thorin exhibited an absorption spectrum with a maximum wavelength of 473 nm. It is obvious that Th(IV)-Thorin complex or Th(IV)-CTAB extracted poorly in the hydrophobic solvent, while in the presence of the CTAB, an ion-pair complex of Th(IV)-thorin-CTAB was produced which extracted into the DES; providing a significant increase in the absorption with a red shift in the maximum wavelength to 515 nm. Thus, the hydrophobic DES could extract the ternary complex efficiently.

3.1. Selection of DES

The choice of DES as the extraction solvent is a crucial step in designing the DLLME method. The proper DES should have low solubility in aqueous solution, high affinity to extract the target analyte and easily disperse into aqueous solution. In this work, four types of DES in similar molar ratio (1:1) including [HMIM]-BA (DES-1), [BMIM]-BA (DES-2), [BMIM]-SA (DES-3) and [HMIM]-SA (DES-4) were employed. The prepared hydrophobic DESs were evaluated for the extraction of Th(IV) from diluted aqueous solutions. The results (Fig.2) demonstrated that

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[HMIM]-SA provided the highest extraction of Th(IV) among the used DESs. Therefore, [HMIM]-SA was selected for further experiments.

After selection of an appropriate DES as extraction solvent, four DESs of [HMIM]-SA with different molar ratios of [HMIM] to SA (1:1, 2:1, 1.5:1, 1:1.5; DES-4 to DES-7) were prepared and examined for the extraction of Th(IV). As seen in Fig.3, changing the molar ratio of [HMIM]Br to SA from 2:1 to 1:1 led to an increase in extraction efficiency and absorbance of the extracted and remained nearly constant at molar ratio of 1:1.5. Therefore, the [HMIM]-SA with 1:1 molar ratio (DES-4) was chosen as the best composition of extraction solvent in further experiments.

3.2. Statistical evaluation of the proposed procedure

The effectiveness of the developed regression model based on independent variables, and the interactions between the variables was evaluated by the analysis of variance (ANOVA). The high F-value (121.45) and low P-value (<0.0001) of ANOVA in Table S3 suggesting the model was significant. The lack of fit (LOF) P-value of 0.14 was more than the critical value (0.05), meaning that the LOF was not significant relatives to the pure error. The suggested second-order polynomial equation that approximated the relationship between the independent variables and the response in terms of coded variables could be expressed as the following equation (Eq. 1):

$$\text{Absorbance} = +0.520 + 0.019A + 0.034B + 0.012C + 0.022D + 0.019AB - 0.021BC - 0.013BD - 0.015CD - 0.074A^2 - 0.025B^2 - 0.025C^2 - 0.020D^2 \quad (1)$$

where linear coefficients (A, B, C and D), quadratic coefficients (A^2, B^2, C^2 and D^2) and the interaction coefficients (AB, BC, BD and CD) were significant in the microextraction process of Th(IV). The value of the coefficient of determination suggests that the proposed polynomial model is suitable to analyze the importance of individual variables, and interaction effects of the selected variables in the response. According to ANOVA results, the predicted and adjusted R^2 values (0.9495 and 0.9797) were in reasonable agreement which implied an excellent relationship between the response and the fitted model. The value of adequate precision, defined as a signal-to-noise ratio, for the model was significantly greater than 4 (41.8), indicating to suitability of the

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model(Table S3).The predicted values versus actual data are also shown in Fig. 4A. As it can be observed, the most actual values were lying on a straight line, which represented an excellent relationship between the fitted model and actual data. Also, the random pattern of residual values versus the predicted values indicated the high efficiency of the model for good presentation of actual data (Fig. 4B). In addition, Fig. 4C illustrated a normal distribution of residuals in which they were along a straight line approximately.

3.3. Interaction effects through response surface plots

Response surface plot shows relationship between independent and dependent (response) variables and their effects on response graphically in two (2D) or three (3D) dimensions and finding the optimum amounts of the variables that maximize the response. The response surface plots were depicted the influence of two significant factors on the response in the experimental range, while other factors were remained fixed at their central levels (Fig. 5). The observed curvatures of the 3D response surface showed that there was a possible interaction between the individual factors. Fig. 5A illustrates the effect of interaction of thorin concentration and pH on the response.

The sample pH played a vital role in formation of the metal-chelate-ion pair complex which in turn affects the extraction efficiency. In the acidic pH, the complex of thorin-Th(IV) is stable, so the pH range of 2-4 on the formation the Th(IV)-thorin-CTAB complex was examined. As it can be seen from Fig. 5A, the absorbance was increased with the elevation of pH from 2.0 to 3.2 and then decreased from 3.2 to 4.0. This could be justified by the fact that at higher pH values than 3.2, the complex was probably incompletely formed or hydrolyzed. Thus, pH of 3.2 was chosen for further experiments. Also, the effect of thorin concentration as chelating agent on the absorbance of the complex was explored. According to Fig. 5A, the absorbance was raised up with increasing of thorin concentration from 25 to 60 µM in the pH range of 2.0-3.2 and thereafter, the absorbance was nearly constant probably due to complete formation of the Th(IV)-thorin-CTAB complex in this pH range. Consequently, the concentration of 60 µM thorin was selected as the optimum

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amount. CTAB as cationic surfactant enhanced the extraction of the complex to the DES extractor through electrostatic interaction with Th(IV)-thorin complex. Thus, in the concentration range of thorin from 25 to 60 µM, with increasing the CTAB concentration from 30 to 50 µM, the strength of non-covalent interactions amplified, resulted in high extraction to the DES. The excess concentration of CTAB more than 50 µM, diminished stability of the ternary complex and the absorbance was decreased (Fig. 5B). As aforementioned, the ternary complex of Th(IV) was hydrophobic and could extract from aqueous solution to the small volume of DES as an extractor phase. Thus, volume of DES affects the concentration of the extracted complex. Fig. 5C shows the interaction of DES volume and CTAB concentration on the response. According to Fig. 5C, with increasing the concentration of CTAB from 30 to 50 µM, the absorbance raised up due to the complete formation of the ternary complex of Th(IV)-thorin-CTAB and more extraction to the DES phase in the volume range of 100-170 µL. At higher DES volumes over than 170 µL, a slight decreasing in the absorbance was observed because of raising the sedimented phase volume. Thereby, the optimum DES volume of 170 µL was set for the rest of experiments. Fig. 5D demonstrated that increasing the concentration of thorin from 25 to 60 µM and DES volume from 100-170 was necessary for the complete extraction of the ternary complex into the extractor phase. Based on the CCD results, the optimum conditions were: thorin concentration 60 µM, concentration of CTAB 50 µM and DES volume 170 µL. The predicted response with the optimum conditions of variables was 0.537. In order to confirm the predicted response, experiments were repeated five times at the optimum conditions. The average response of Th(IV) with the confidence level of 95% was found to be 0.549 ± 0.006, that was in good agreement with the predicted response.

3.4. Analytical figures of merit

The analytical performance of the established method was evaluated in terms of the linearity, precision and recovery. Under the optimal conditions, the calibration curve for the determination of Th(IV) was linear in the concentration range from 10 to 600 ng mL^{-1} with the correlation

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coefficient of 0.9992 and a limit of detection (LOD) 2.1 ng mL^{-1} which was calculated based on $3S_b/m$ (where S_b and m are the standard deviation of the blank and the slope of calibration curve, respectively). Also, the precision of the method described as relative standard deviation (RSD%) for five replicate measurements of Th(IV) at 100 ng mL^{-1} was 1.7%. The preconcentration factor which was calculated from the ratio of initial Th(IV) sample volume (10 mL) and the sedimented DES volume (170 µL) obtained 59.

3.5. Interference studies

The influence of possible interferent cations and anions on the microextraction process was also investigated. Binary solutions containing 250 ng mL^{-1} of Th(IV) and different concentrations of interfering ions were prepared and analyzed by the proposed method. The highest concentration of the added interfering ions that caused a variation of greater than ± 5% on the absorbance of the analyte is defined as the tolerance limit. The results are available in Table 2. It can be observed that a large excess of most cations and anions tested have no significant effects on the determination of Th(IV). Zr^{4+} and Cu^{2+} ions didn't interfere in the extraction and determination of Th(IV) up to 500 and 300 fold excess by using masking agents of tartaric acid and thiourea at 2×10^{-3} M, respectively. Interference of Fe^{3+} ions was eliminated using ascorbic acid (5×10^{-3} M) in the recommended procedure. Uranium didn't interfere in the microextraction of Th(IV) up to 17500 ng mL^{-1}

3.6. Analysis of real samples

To assess the applicability of the developed method, monitoring of Th(IV) in river and sea waters, under optimum conditions were evaluated. Since there was no Th(IV) detected in the samples, the waters were spiked with Th(IV) at four concentration levels of 20, 50, 100 and 300 ng mL^{-1} and the analyses were performed in three replicates. The recoveries of Th(IV) ions in water samples were ranged in 92.5 % - 109.4 % (Table 3), indicating that the matrices of the water samples had a negligible effect on the performance of the developed method. Also, the developed method was applied to find the amount of Th(IV) in rock sample for triplicate analyses and assessed with the analysis by ICP-AES. The statistical significance of difference in the obtained

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results were evaluated by Fisher F-test and student t-test (Table 4). The comparison of the precisions achieved by F-test indicated to not differ in those obtained in a statistically significant manner. In addition, the mean concentration of Th(IV) in rock sample achieved by the two methods was compared by t-test. The calculated t-value at 95% confidence level, 2.45, was lower than the critical t-value (Table 4), meaning that there was no significant priority between the two available methods. Thus, the proposed method was suitable for determination of Th(IV) in rock sample.

3.7. Comparison with other methods

The suggested method was compared with some reported extraction methods of Th(IV) based on UV-Vis. spectrophotometric determination [13, 30-33] and the results are represented in Table 5. It is obvious that the developed method has a wide linear range, comparatively low detection limits, high precision, and suitable preconcentration factor. As well, this method is a rapid, simple, selective, sensitive and green microextraction method that doesn't need to disperse the toxic organic solvents by heating or ultrasonic treatment to accelerate and shorten the extraction process which distinguishes it from other microextraction methods.

3.8. Conclusions

For the first time, a combination of a selective and straightforward DLLME method based on using hydrophobic DES for microextraction of Th(IV) from water and rock samples coupled with UV-Vis. spectrophotometric detection was developed. The hydrophobic DES was synthesized from [HMIM]Br and SA that make it potential alternative to replace with the chlorinated organic solvent as an extraction solvent. Surface response methodology based on CCD was successfully employed for the simultaneous investigation of effective variables on the response. The proposed method is rapid, easy, sensitive, cost effective and efficient for separation and preconcentration of thorium. The performance of this method was tested for extraction and determination of Th(IV) in spiked water and rock samples and the obtained results demonstrated the method is accurate and reliable and suitable for the determination of Th(IV) in environmental samples at trace level.

Acknowledgments

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Authors are grateful to the Research Council of the University of Birjand for supporting this work.

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Figure captions

Fig. 1 Absorption spectra of Thorin, Th(IV)-Thorin-CTAB, Thorin-CTAB, and Th(IV)-Thorin after microextraction: Conditions: pH 3.2; Sample volume, 10 mL; Th(IV), 250 ng mL^{-1}; Thorin, 60 µM; CTAB, 50 µM; DES, 170 µL, [HMIM]- SA DES with molar ratio of 1:1.

Fig. 2 Effect of type of DES on the microextraction of Th(IV) ions. Conditions: pH 3.2; Sample volume, 10 mL; Th(IV), 250 ng mL^{-1}; Thorin, 60 µM; CTAB, 50 µM; DES, 170 µL, DES with molar ratio of 1:1.

Fig. 3 Effect of composition of [HMIM]-SA on the microextraction of Th(IV) ions. Conditions: pH 3.2; Sample volume, 10 mL; Th(IV), 250 ng mL^{-1}; Thorin, 60 µM; CTAB, 50 µM; DES, 170 µL.

Fig. 4 (A) A plot of predicted response against observed response. (B) A plot of the internally studentized residuals vs. the predicted response. (C) Normal probability plot of residuals for the absorbance.

Fig. 5 The 3D central composite design curves for investigation of the effects of variables on analytical response: (A) Effect of the concentration of thorin and pH on the absorbance. (B) Effect of the concentration of CTAB and concentration of thorin on the absorbance. (C) Effect of the DES volume and concentration of CTAB on the absorbance. (D) Effect of the DES volume and concentration of thorin on the absorbance.

Figure 1

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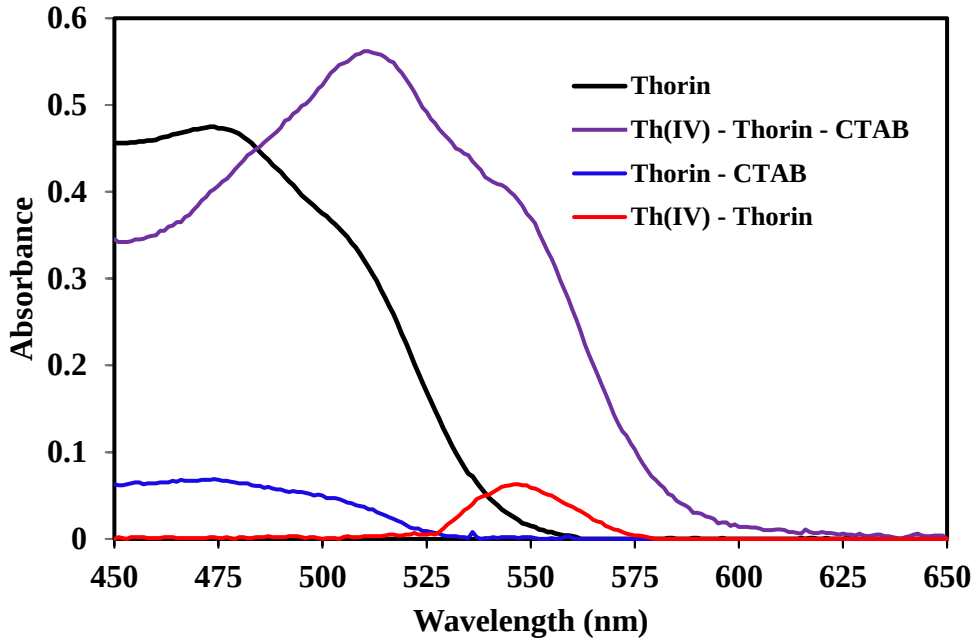

Figure 2

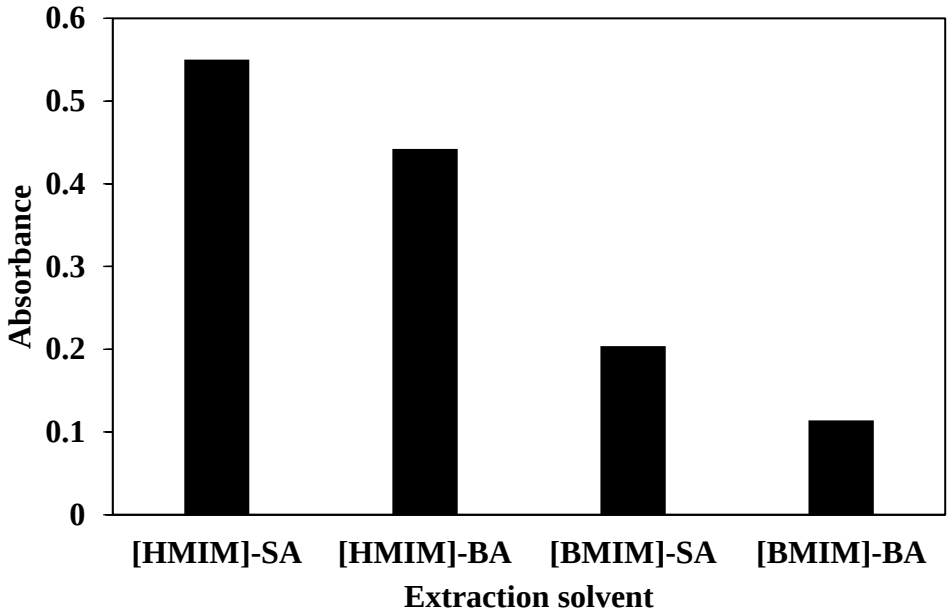

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Figure 3

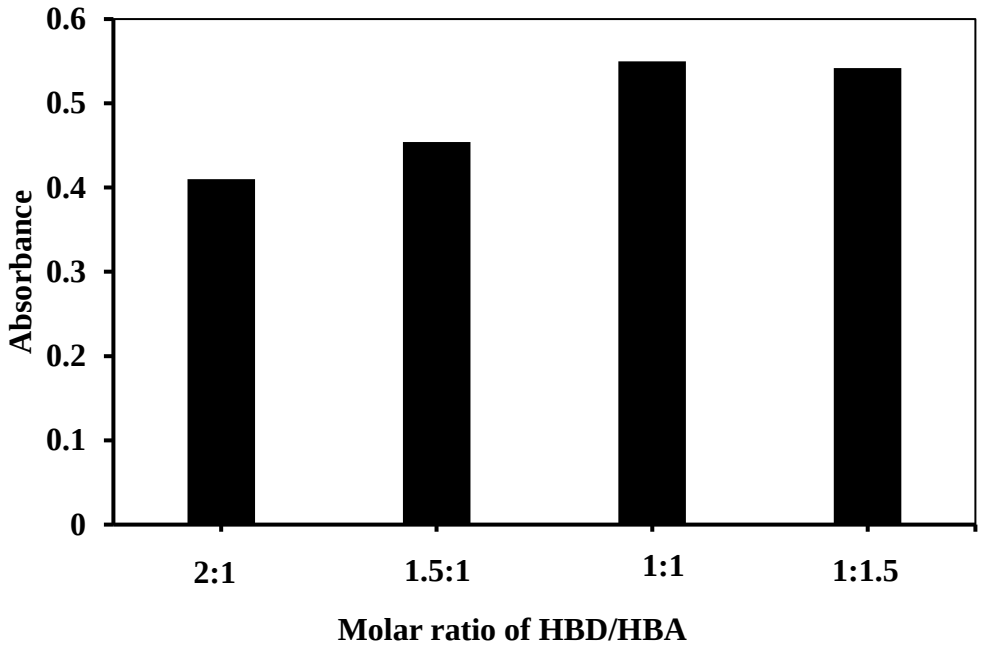
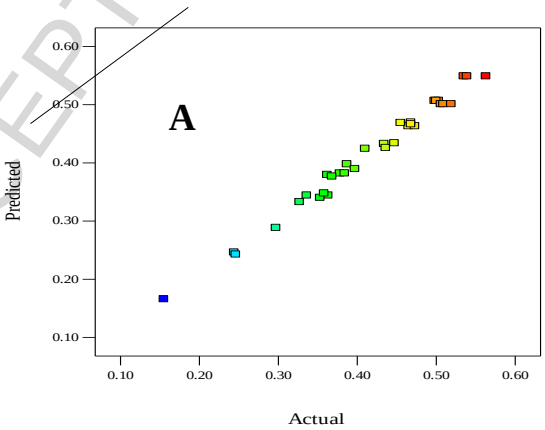


Figure 4



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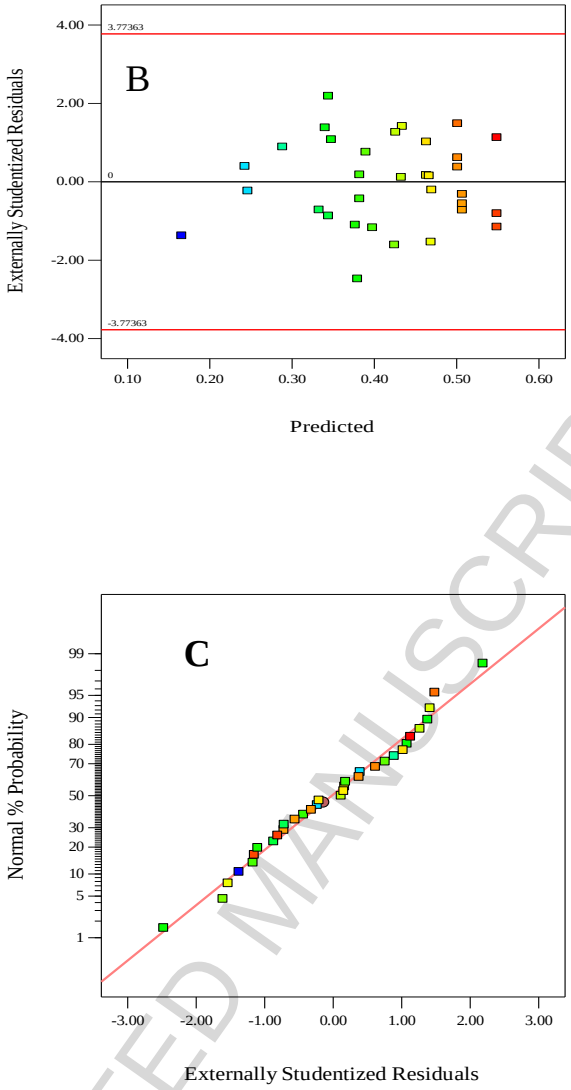

Figure 5

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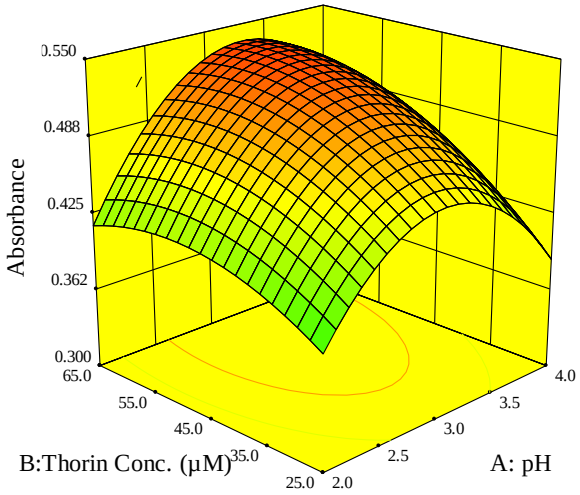
(A)



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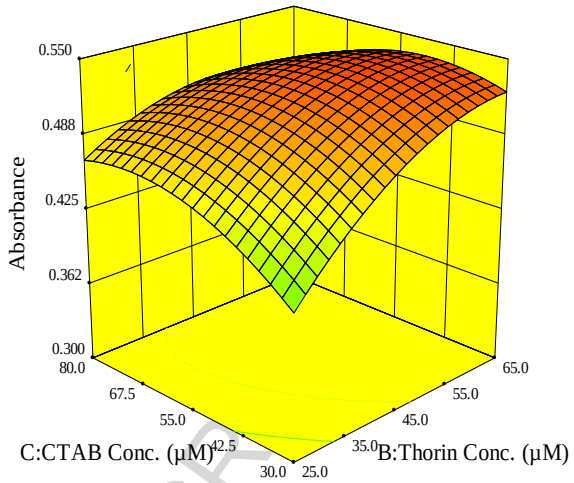

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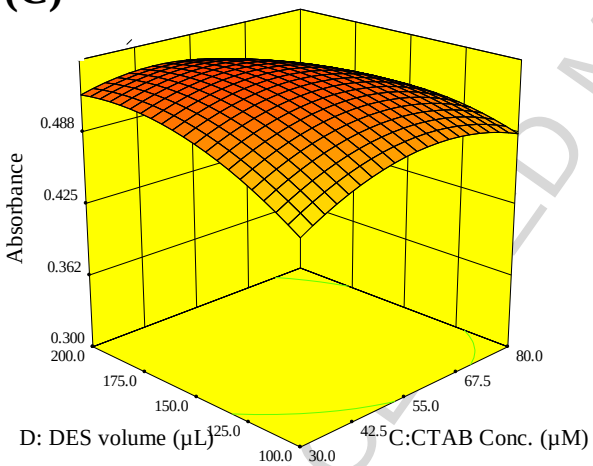

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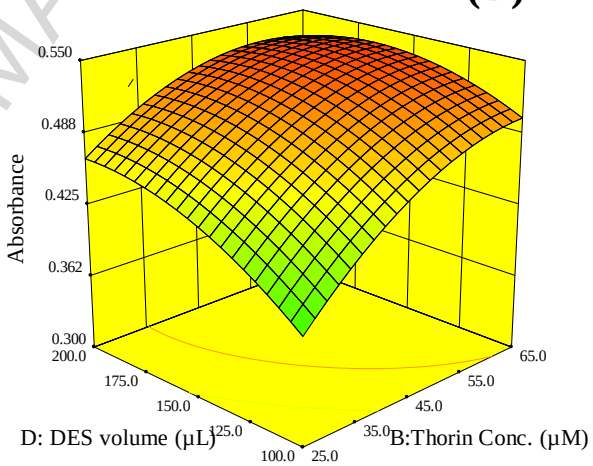

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Table 1. Variables and levels used in the central composite design

Variable	Symbol	Coded variable levels				
		-α	-1	0	+1	+α
pH	A	1	2	3	4	5
Concentration of thorin (μM)	B	5	25	45	65	85
Concentration of CTAB (μM)	C	5	30	55	80	105
Amount of DES (μL)	D	50	100	150	200	250

Table 2. Effect of interfering ions on the absorbance 250 ng mL^{-1} Th(IV) from the aqueous solution

Ion	Added as	Tolerance Limit	Ion	Added as	Tolerance Limit
Na^{+}	$NaNO_3$	1000	Cd^{2+}	$Cd(NO_3)_2.6H_2O$	800
K^{+}	KNO_3	1000	Co^{2+}	$Co(NO_3)_2.6H_2O$	800
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	1000	SO_4^{2-}	Na_2SO_4	700
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	1000	[c]Zr^{4+}	$ZrCl_4$	500
Ba^{2+}	$Ba(NO_3)_2$	1000	MoO_4^{2-}	$Na_2MoO_4.2H_2O$	500
Al^{3+}	$Al(NO_3)_3.2H_2O$	1000	WO_4^{2-}	$Na_2WO_4.2H_20$	500
Mn^{2+}	$Mn(NO_3)_2$	1000	VO_3^{-}	$NaVO_3.H_2O$	400
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	1000	[d]Cu^{2+}	$Cu(NO_3)_2.3H_2O$	300
Pb^{2+}	$Pb(NO_3)_2$	1000	Ta^{5+}	$TaCl_5$	300
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	1000	Gd^{3+}	Gd_2O_3	250
Fe^{2+}	$Fe(NO_3)_2.9H_2O$	1000	Er^{3+}	Er_2O_3	250
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	1000	Ho^{3+}	$Ho(NO_3)_3.6H_2O$	150
[b]Fe^{3+}	$Fe(NO_3)_3.9H_2O$	1000	Ce^{3+}	$Ce(NO_3)_3.6H_2O$	120
NO_3^{-}	$NaNO_3$	1000	La^{3+}	$La(NO_3)_3.6H_2O$	120

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Cl^-	NaCl	1000	UO_2^{2+}	$UO_2(NO_3)_2.6H_2O$	70
Sr^{2+}	$Sr(NO_3)_2$	800			

[a]Amount of foreign ion/amount of Th(IV).
[b] Masked with ascorbic acid 0.005 M.
[c] Masked with tartaric acid 0.002 M.
[d] Masked with thiourea 0.002 M.

Table 3. Analytical results for Th(IV) monitoring in water sample

Sample	Added (ng mL^{-1})	Founded (ng mL^{-1})	Recovery %
River water	20	18.5 ± 1.5	92.5
	50	50.3 ± 1.6	100.6
	100	95.3 ± 2.1	95.3
	300	311.5± 2.9	103.8
Seawater	20	20.1 ± 0.9	100.5
	50	54.7 ± 2.3	109.4
	100	106.2 ± 2.8	106.2
	300	320.0 ± 3.0	106.7

Table 4. Determination of Th(IV) in rock sample by the proposed method and comparison with the ICP-AES method

Sample	Th(IV) found (µg g^{-1})		Relative error (%)
	Proposed method	ICP-AES method	
Rock	55.51 ± 1.41	57.70 ± 0.90	3.79

$t_{Crit.} = 2.78$; $t_{Calc.} = 2.26$
$F_{Crit.} = 39.0$; $F_{Calc.} = 2.45$

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Table 5. A comparison between the analytical data of the suggested method with the other extraction methods based on UV-Vis. spectrophotometry for the determination of Th(IV) ion.

Preconcentration technique	Extraction solvent	LOD (ng mL $^{-1}$)	Linear range (ng mL $^{-1}$)	RSD (%)	Extraction time (min)	Ref.
SsLLME[a]	1-decanol/THF	0.40	20-100	1.4	5	[13]
VALLME[b]	Chloroform	7.50	20-240	2.8	3	[30]
CPE[c]	Triton X-114	-	10-1000	2-5	130	[31]
CPE	Triton X-100	0.16	0.5-15	1.6	5	[32]
CPE	Triton X-114	1.40	5-100	1.8	15	[33]
DES-DLLME	[HMIM]-SA	2.10	10-600	1.7	1	This work

[a]Supramolecular solvent-based liquid-liquid microextraction
[b]Vortex-assisted liquid–liquid microextraction.
[c]Cloud point extraction

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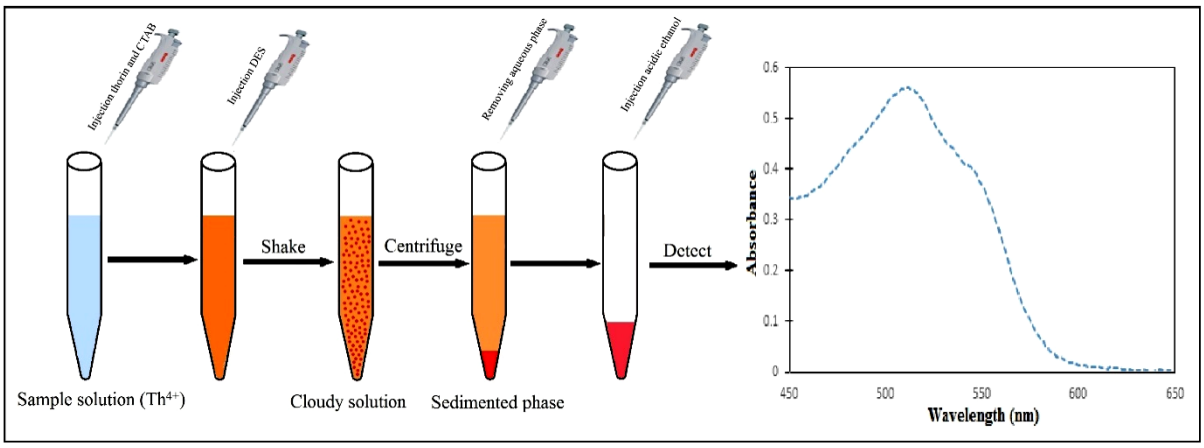
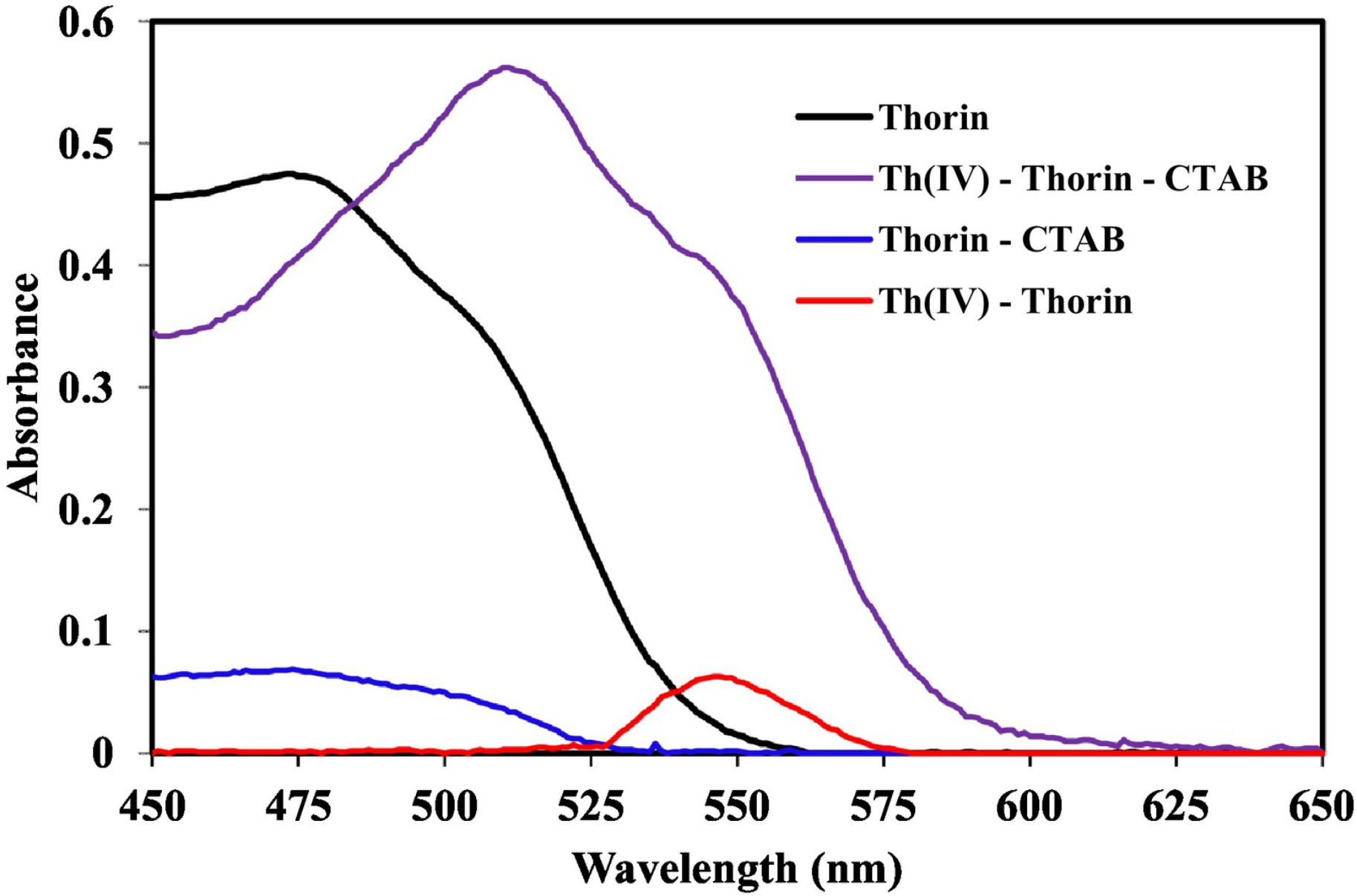
Graphical abstract



Research Highlights

- New hydrophobic, low cost and nontoxic DESs were synthesized.
- For the first time, the using of DESs as extraction solvent for DLLME of Th(IV) has been reported.
- Fast, excellent selectivity, sensitivity and green microextraction are prominent properties of this method.
- RSM based on CCD was applied for optimization of significant variables.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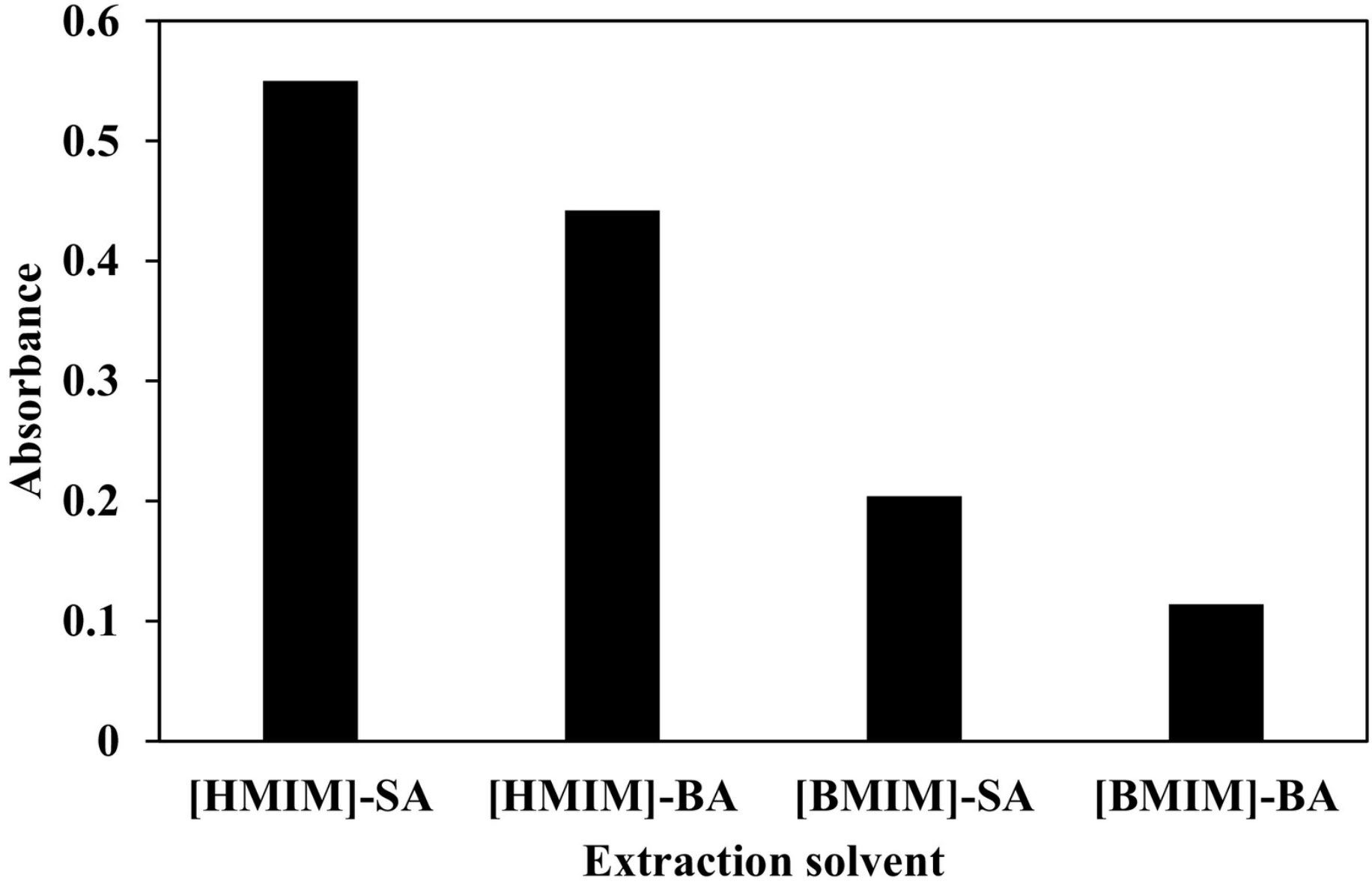
0.5
0.4
0.3
0.2
0.1
0
Absorbance
450
475
500
525
550
575
600
625
650
Wavelength (nm)
Thorin
Th(IV) - Thorin - CTAB
Thorin - CTAB
Th(IV) - Thorin

Figure 1


0.6
0.5
0.4
0.3
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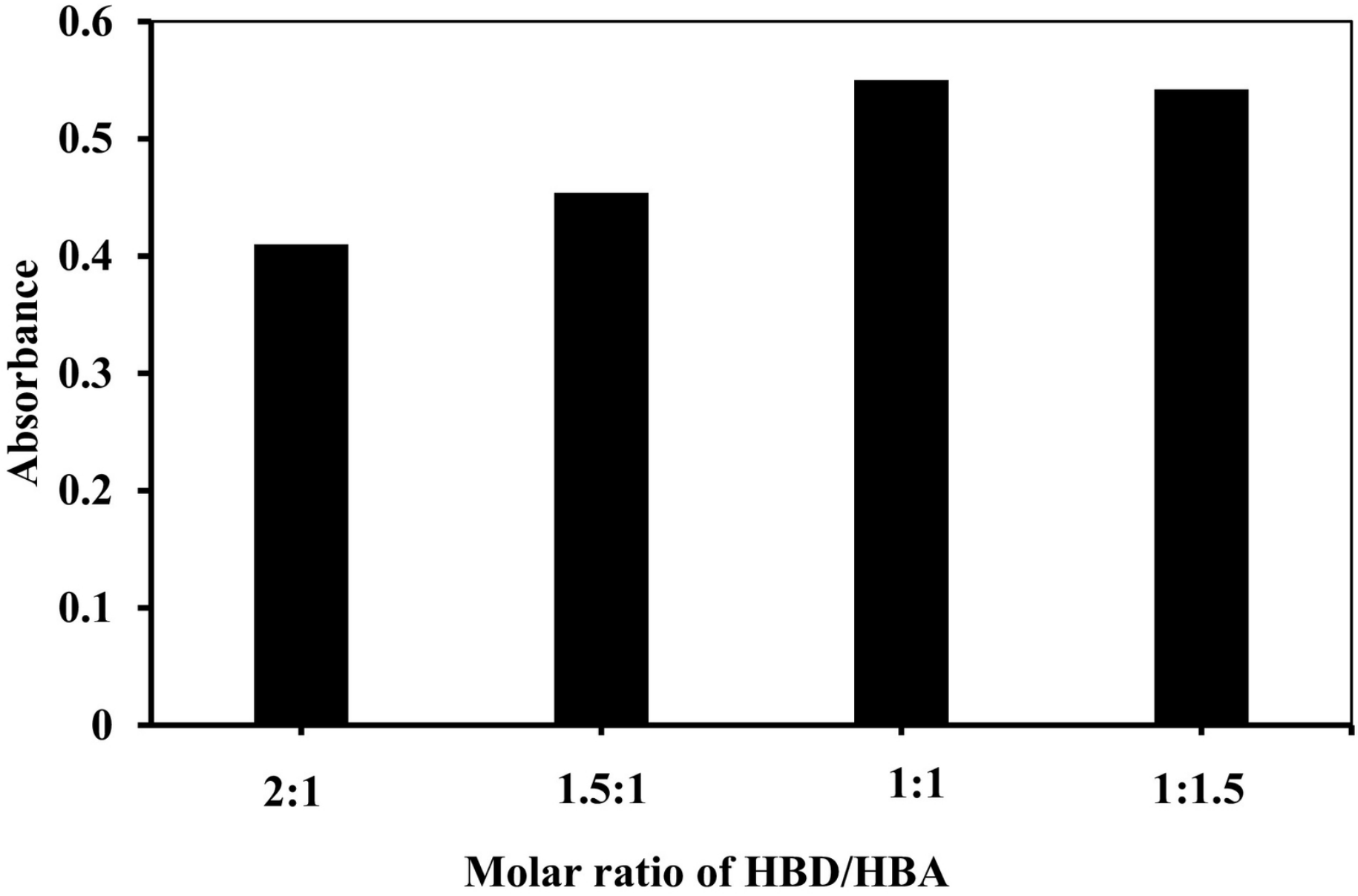
0
Absorbance
[HMIM]-SA
[HMIM]-BA
[BMIM]-SA
[BMIM]-BA
Extraction solvent

Figure 2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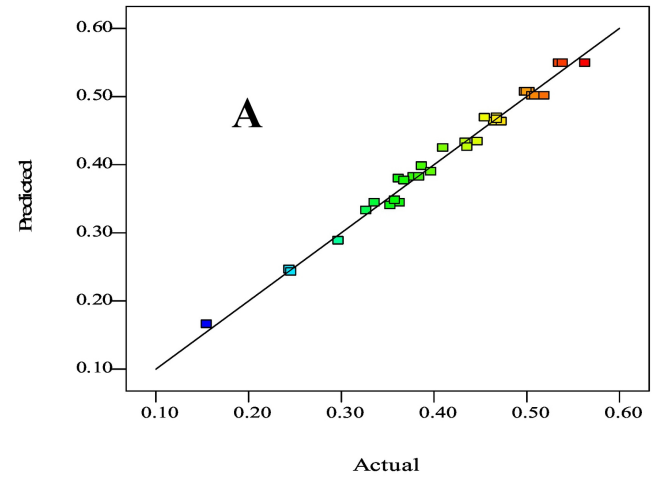
0.5
0.4
0.3
0.2
0.1
0
Absorbance
2:1
1.5:1
1:1
1:1.5
Molar ratio of HBD/HBA

Figure 3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Predicted
Actual
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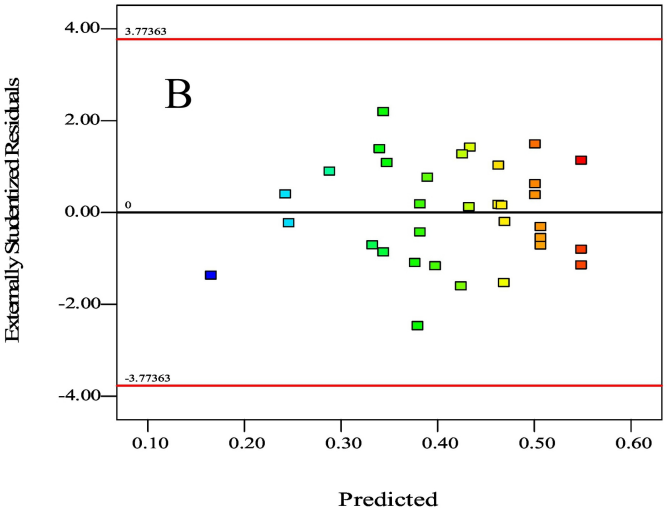
0.20
0.30
0.40
0.50
0.60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Externally Studentized Residuals
Predicted
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0
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0.20
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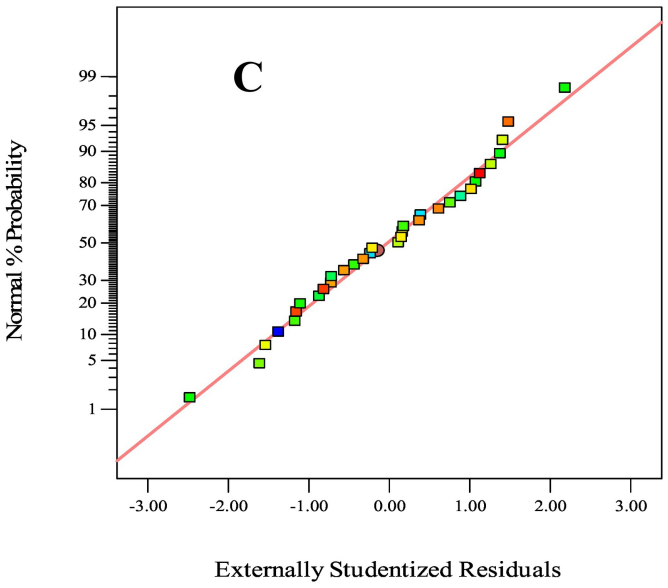
0.40
0.50
0.60


C
Normal % Probability
Externally Studentized Residuals
99
95
90
80
70
50
30
20
10
5
1
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-2.00
-1.00
0.00
1.00
2.00
3.00

Figure 4

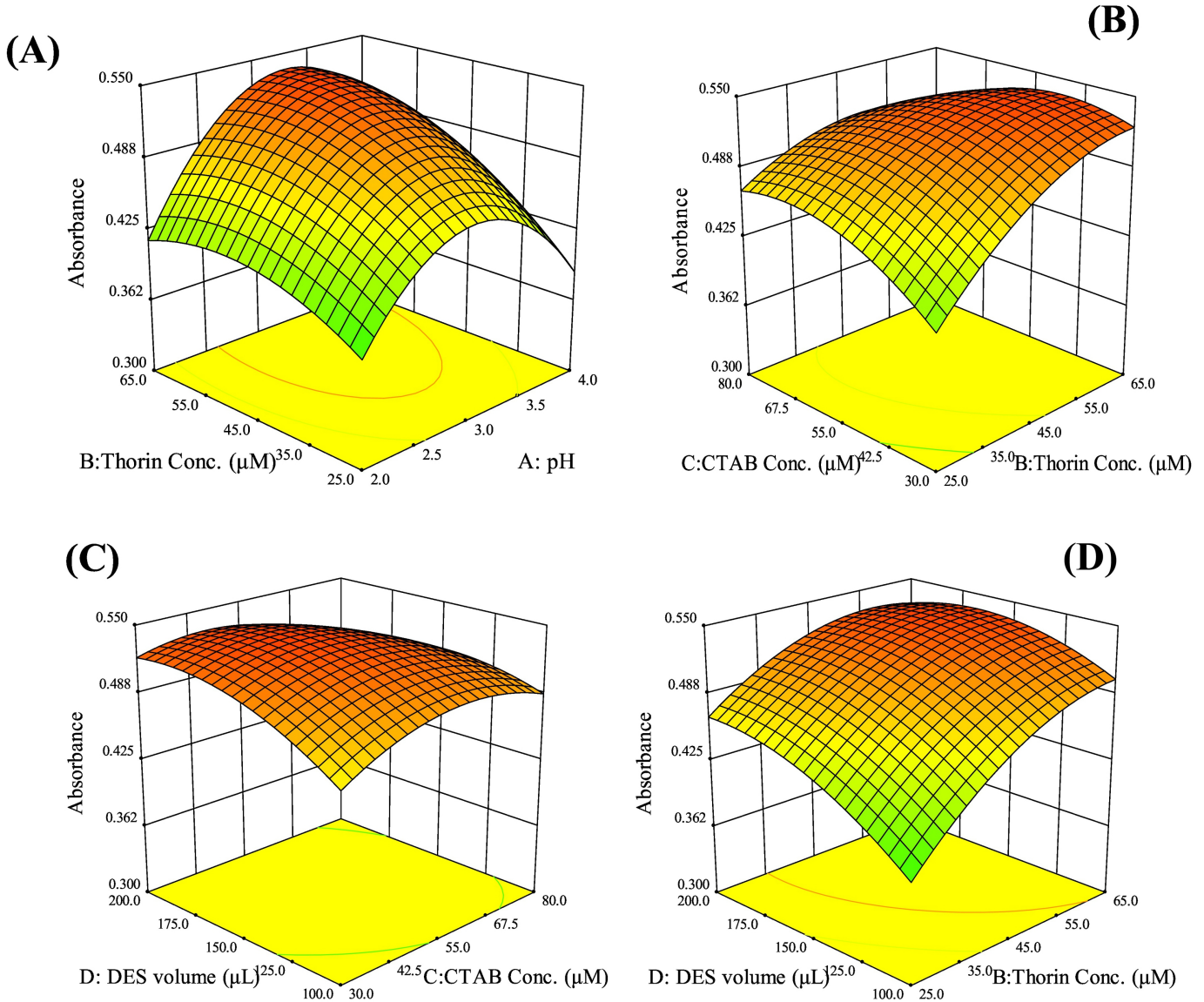
(A)
Absorbance
0.550
0.488
0.425
0.362
0.300
B:Thorin Conc. (µM)
65.0
55.0
45.0
35.0
25.0
A: pH
2.0
2.5
3.0
3.5
4.0
(B)
Absorbance
0.550
0.488
0.425
0.362
0.300
C:CTAB Conc. (µM)
80.0
67.5
55.0
42.5
30.0
B:Thorin Conc. (µM)
25.0
35.0
45.0
55.0
65.0
(C)
Absorbance
0.550
0.488
0.425
0.362
0.300
D: DES volume (µL)
200.0
175.0
150.0
125.0
100.0
C:CTAB Conc. (µM)
30.0
42.5
55.0
67.5
80.0
(D)
Absorbance
0.550
0.488
0.425
0.362
0.300
D: DES volume (µL)
200.0
175.0
150.0
125.0
100.0
B:Thorin Conc. (µM)
25.0
35.0
45.0
55.0
65.0

Figure 5