*Korean J. Chem. Eng.*, 39(5), 1299-1306 (2022)
DOI: 10.1007/s11814-021-0994-y

pISSN: 0256-1115
eISSN: 1975-7220

# Application of hydrophobic deep eutectic solvent for the extraction of aromatic compounds from contaminated water

**Abdullahi Yakubu*,***, Zaharaddeen Sani Gano**,†, Omar Umar Ahmed**, Suleiman Mohammed Shuwa*, Abdulazeez Yusuf Atta*, and Baba Yakubu Jibril***

*Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State, Nigeria
**National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria
***Dangote Fertilizer Limited, Lagos, Nigeria
(*Received 12 February 2021 • Revised 7 September 2021 • Accepted 22 October 2021*)

**Abstract**−Hydrophobic deep eutectic solvent (DES) was synthesized from TBAB and decanoic acid and used to study the extraction of aromatic hydrocarbon from contaminated water samples. DES was screened by selecting different ratios between the TBAB and decanoic acid. A ratio of 1 : 2 was observed to be the best among others and was used for the desired application. Within the temperature range of 25-70 °C, physicochemical properties such as density (944-915 kg/m$^3$), viscosity (1,636-179 mPa·s), conductivity (141-1,007 μS/cm), and pH (3.14-2.73) of the synthesized DES were determined. For the extraction study, benzene, toluene, and xylene (BTX)-doped water were used as a simulated contaminated water. Response surface methodology was employed in modeling and optimizing the effects of temperature, time, and solvent mass fraction on the extraction efficiency of the DES. Extraction efficiency of 68.1%, 70.84% and 77.73% for BTX, respectively, was recorded at optimum values of 25 °C, 60 min and 0.6 (solvent mass fraction). Extraction efficiency as high as 86.61%, 88.94%, and 92.71% for BTX, respectively, can be obtained within the design space. Effective regeneration and reuse of the DES after each extraction was carried out for five consecutive cycles; their results showed no significant decrease in their respective extraction efficiencies and recovery of the DES. This, therefore, improves the overall performance of hydrophobic DES for the extraction process.

Keywords: Remediation, Deep Eutectic Solvents, Contaminated Water, Extraction

## INTRODUCTION

Pollution of water by hazardous substances, some of which are categorized as having toxic, carcinogenic, and mutagenic properties, has continued to attract and raise environmental concerns [1]. This is because industrial wastes, crude oil spillages and other sources of waste find their way into our water bodies [2]. These waste streams contain several hazardous and toxic aromatic compounds such as benzene, toluene and xylene (BTX). BTX has been associated with detrimental health effects given its toxic and hazardous nature [3]. BTX among other aromatic contaminants has been designated as priority pollutant by the United States Environmental Protection Agency (US EPA) and the European Union (EU) lists of pollutants [1]. Previous studies carried out in most urban centers in Nigeria have shown that effluents from various industries are among the main sources of water pollution [4]. Components of crude and refined petroleum, namely aromatic contaminants such as BTX, have independently been associated with adverse human health effects by the International Agency for Research on Cancer [5].

Environmental, health and safety implications of organic pollutants are growing globally. This necessitates the need for effective, environmentally sound, energy-efficient, and economical remediation technology. One of such promising remediation techniques is solvent extraction.

Solvent extraction has been recorded as an outstanding technique because of its flexibility, low energy requirement, low operating cost, and high recovery [6]. While ionic liquids (ILs) have widely been utilized for various application and extraction purposes, the "green" character of ILs has often been questioned. This is mainly due to their poor biodegradability, biocompatibility, and sustainability [7]. Analogous to ILs are deep eutectic solvents (DESs) which are easy to synthesize, economical, and environmentally friendly when compared to ILs [8]. In contrast to ILs, DESs exhibit distinctive properties such as chemical and thermal stability, biodegradability, non-flammability, and cost effectiveness. These features account for their wide range of applications [9]. DESs are synthesized through the complexation of two or more compounds through hydrogen bonding between the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA). The aforementioned hydrogen bonding results in melting point depression. Consequently, the eutectic mixture has a melting point lower than that of the starting components [8].

Hydrophilic DESs are miscible with water, which precludes their use for separation processes of aqueous samples. Hydrophobic DES offers this advantage because it forms a clear distinct layer when applied in aqueous samples and also minimizes solvent consumption. Solvent minimization is one of the key objectives of green chemistry [10]. Previous studies have shown the successful appli-

†To whom correspondence should be addressed.
E-mail: zaharaddeenn@gmail.com
Copyright by The Korean Institute of Chemical Engineers.

cation of hydrophobic DES for extraction purposes in aqueous samples, which include extraction of volatile fatty acids (VFAs) from water [11], extraction of pesticides from water [12], extraction of polycyclic aromatic hydrocarbons [8] and micro-extraction of two auxins in water and fruit juice [13]. Although hydrophobic DESs have found applications in various fields, they have been scarcely studied in the field of BTX extraction from contaminated water [12]. Consequently, this paper aims to bridge this research gap using a hydrophobic deep eutectic solvent synthesized from tetrabutlyammonium bromide (TBAB) and decanoic acid. To achieve this, the statistical design of experiment was employed. Response surface methodology (RSM), a common technique used in design of experiment (DOE) for modeling and optimizing process parameters [14], was adopted using central composite design (CCD). Furthermore, solvent regeneration and recycling of DES were carried out to further improve the overall performance of the synthesized DES.

## EXPERIMENTAL METHODOLOGY

### 1. Chemicals

Tetrabutylammonium bromide and decanoic acid were supplied by Indiamart (India) with purity ≥97% and 98%, respectively, while benzene (≥99.7), toluene (≥99.9), and xylene (≥99.8) were supplied by Sigma-Aldrich (USA).

### 2. Synthesis of DES

A classical approach used for the selection of this DES involves the hydrophobic nature of the DES [11], sufficient difference in density between the DES and water, relatively low viscosity to facilitate the rate of mass transfer, prospects of similar DES in abating volatile organic compounds from aqueous sample [15,16], and thermal stability of the DES to loss due to degradation when subjected to elevated temperature. After background knowledge from various works of literature, DES was screened by selecting different ratios of 5 : 1, 4 : 1, 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 between the HBA and HBD. Combinations that formed no DESs were considered unsuccessful and therefore excluded, while remaining samples were critically examined to select the most stable ones. A ratio of 1 : 2 was observed to have no traces of minor to major crystal formation at the bottom of the beaker after storage. Hence, it was used for the desired application. In respect of that, hydrophobic DES of TBAB and decanoic acid was prepared by weighing appropriate amounts of TBAB and decanoic acid in a beaker with a mole ratio of 1 : 2. The mixture was mixed and heated using a hot plate coupled with a magnetic stirrer at 80 °C until a homogeneous liquid was obtained. The resulting mixture was cooled and stored at atmospheric conditions.

### 3. Determination of Physicochemical Properties

Fourier transform infrared spectroscopy (FTIR) spectra of the synthesized deep eutectic solvent were obtained using attenuated total reflectance (ATR) with spectral range of 4,000-550 $cm^{-1}$ and resolution: 2.0 (Shimadzu FTIR-8400s model). Density, viscosity, pH, and conductivity, which are the fundamental properties of the synthesized DES, were determined as a function of temperature at atmospheric pressure. The viscosity of the DES was determined using a digital viscometer (Brookfield RVDV-1 model), while density was obtained gravimetrically. The pH was obtained using (PHS-25CW Benchtop pH meter), while a conductivity test was carried out using Rohde & Schwarzhameg (HM8118) resistivity meter.

### 4. Extraction Procedure

A stock solution of BTX contaminated water was prepared and utilized for the extraction process. The stock solution was diluted to obtain working standard solutions of different concentrations. Liquid-liquid extraction was conducted using the synthesized hydrophobic DES as solvent. Contaminated water and the synthesized hydrophobic DES were contacted and mixed vigorously in closed capped vials at various conditions on a hot plate equipped with a magnetic stirrer. After extraction experiments, the resulting mixture was left to settle for clear phase separation between the DES and water. Subsequently, a separatory funnel was used to separate the DES phase and the water phase. BTX concentration in the water phase was determined using a UV spectrometer (CGOLDEWALL 722n Vis spectrometer 325-1,000 nm; 4 nm). The quantification of BTX in each sample was repeated three times to minimize unavoidable errors.

### 5. Calculation of Extraction Efficiencies

Extraction efficiencies were calculated to evaluate the performance of the hydrophobic DES by quantifying the concentration of BTX in the water rich phase after each extraction. Eq. (1) describes the extraction efficiency:

$$Y_i\,(\%) = \frac{C0 - C1}{C0} * 100 \tag{1}$$

where $Y_i$ is the extraction efficiency, C0 is the initial BTX concentration in the contaminated water in ppm, and C1 is the final BTX concentration in the water-rich phase in ppm after extraction.

### 6. Experimental Design

In the extraction process, integrating all parameters affecting the extraction efficiency often leads to a complex and tedious design. Consequently, time, temperature, and DES solvent ratio were the three variables considered.

In central composite design (CCD) a core factorial that forms a cube having two codes unit length (−1, to +1) was created to form the design space. The total number of experimental runs, N, is obtained from the summation of 2n axial runs with $2^n$ factorial runs and $n_c$ center point [17], as shown in the equation below:

$$N = 2n + 2^n + n_c \tag{2}$$

where n is the number of the independent variable. Thus, for the three variables, it involved 20 experimental runs consisting of eight factorial points, six axial points, and six replicates at the center point. Table 1 represents the range of independent variables with their

**Table 1. Range of the independent variables, codes, and their variable level**

| Variables | Codes | Units | Coded variable level | | |
|---|---|---|---|---|---|
| | | | −1 | 0 | 1 |
| Time | A | Min | 20 | 40 | 60 |
| Temperature | B | °C | 25 | 47.5 | 70 |
| Solvent mass fraction | C | - | 0.2 | 0.5 | 0.8 |

respective codes and levels used in the course of this work.

Experimental design and subsequent analyses were carried out with the statistical design software (Design Expert 7.0). Experimental runs were split into blocks of three and carried out consecutively for three days in a randomized order. The generated responses were optimized. The suitability of the model was further substantiated by the results of the analysis of variance (ANOVA). The central idea of ANOVA is to compare the variation due to the treatment (change in the combination of the variable levels) with the variation due to random errors inherent to the generated response [18].

## RESULTS AND DISCUSSION

### 1. Physical Properties of the Hydrophobic DES

Basic physical properties, such as density (Fig. 1), viscosity (Fig. 2), pH (Fig. 3), and conductivity (Fig. 4) of the hydrophobic DES, were determined in the temperature range 25-70 °C. The properties determine key parameters concerning liquid-liquid extraction, which include phase separation, mass transfer, etc. The physicochemical properties of DES are influenced by the molar ratio between the HBD and HBA as well as the choice of HBA and HBD [9]. The molar ratio of HBD to HBA is a key factor influencing the physicochemical properties of DESs and by extension their performance in various applications. Increasing the ratio of HBD to HBA would lead to a reduction of HBA concentration in the DES. This would reduce the interaction between the HBD and HBA, increase the hydrophobicity of the DES (hydrophobic nature of the HBD), and as well increase the steric hindrance between the DES and aqueous solution [11]. Consequently, this leads to a decrease in extraction efficiency.

Fig. 1 shows the density of the hydrophobic DES as a function of temperature. A linear decrease in density was observed with an increase in temperature from 25-70 °C. The linear decreasing effect on the density of the DES was probably a result of an increase in volume stemming from thermal expansion and gains in both vibrational and translational energy of the DES molecules. Similar findings were established in literature [12]. The density of DES during extraction plays a vital role in determining solvent diffusion and miscibility with other liquids [19]. In liquid-liquid extraction (LLE), an ideal extraction solvent should have qualities such as immiscibility with water and low density for easy separation [20]. Hydrophobic DES (HDES) with density equivalent to water takes longer time to separate into two phases during extraction [21]. Hence, HDES density within the range of that of water is preferred when dealing with aqueous samples. Most hydrophobic DESs exhibit lower density values than water [12]. The density is dependent on the packing and molecular organization of the DES [12].

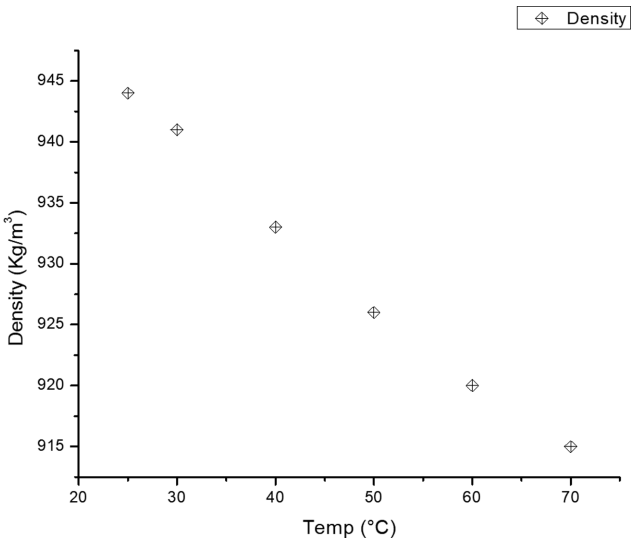



**Fig. 1. Density of the DES (TBAB: Decanoic acid (1 : 2)) as a function of temperature.**

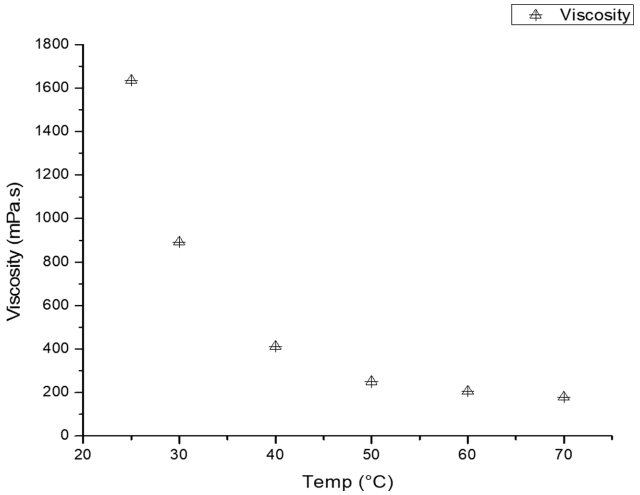



**Fig. 2. Viscosity of the DES (TBAB: Decanoic acid (1 : 2)) as a function of temperature.**

With the increase in temperature from 25-70 °C, the viscosity of the DES decreased exponentially from 1,636-179 mPa·s as shown in Fig. 2. This probably resulted from the weakening interaction effects in the hydrogen bonding, electrostatic attractions, and friction within the DES components as well as thermal expansion among the DES components with an increase in temperature. The viscosity of a substance is defined with respect to the molecular interaction and electrostatic attraction between the liquid components [17]. Therefore, DES with low viscosity is very essential for extraction applications. At a temperature of 25 °C, the DES showed a relatively high viscosity of 1,636 mPa·s (Fig. 2). This can be attributed to the extensive hydrogen bond network of the hydrogen bond donor HBD, which results in lower mobility of free species within the mixture [22]. Moreover, other forces, such as electrostatic or van der Waals interactions, contribute to high viscosities of DES at room temperature [22]. The viscosity of DESs follows an Arrhenius-like behavior as it decreases with increasing temperature [23].

As shown in Fig. 3, the pH of the DES showed a marginal decreasing effect with an increase in temperature from 3.14 at 25 °C to 2.73 at 70 °C. This may be attributed to the fact that as temperature increases, the degree of association and average speed of the molecules in the liquid increases. This generates more hydroxonium bond association of the hydrogen bond donor HBD with

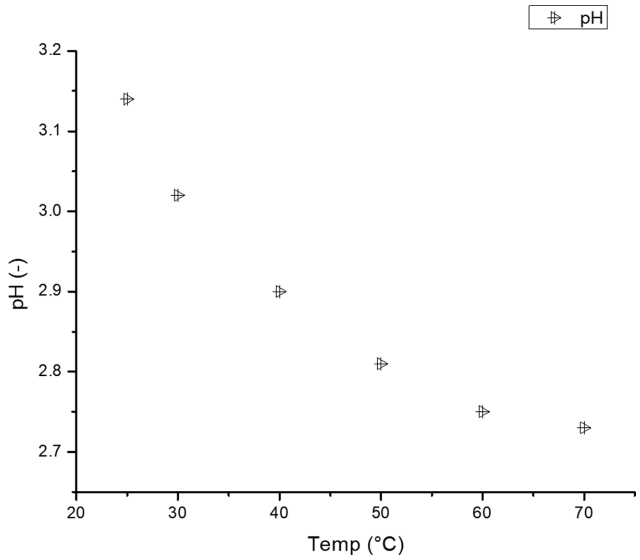



**Fig. 3. pH of the DES (TBAB: Decanoic acid (1 : 2)) as a function of temperature.**

other components [19]. Thus, the chemical potential of hydroxonium decreases, thereby decreasing the pH. Similar study on DES pH established a decreasing effect with temperature [23]. The pH of a solvent is a function of the chemical potential of hydrogen cation and temperature [19]. The chemical potential is influenced by the interaction of the ions with other species in the solvent. The hydroxonium chemical potential for DESs is determined by the hydroxonium bond association with other components, and the stronger the association of DES with another component, the higher will be the extractability of the component by DES.

Fig. 4 presents the conductivity of the DES. Conductivity was observed to increase from 141 μS/cm at 25 °C to 1,007 μS/cm at 70 °C. This is because an increase in temperature will cause a decrease in viscosity and an increase in average speed of the molecules, as well as mobility of charge-carrying species in the DES,

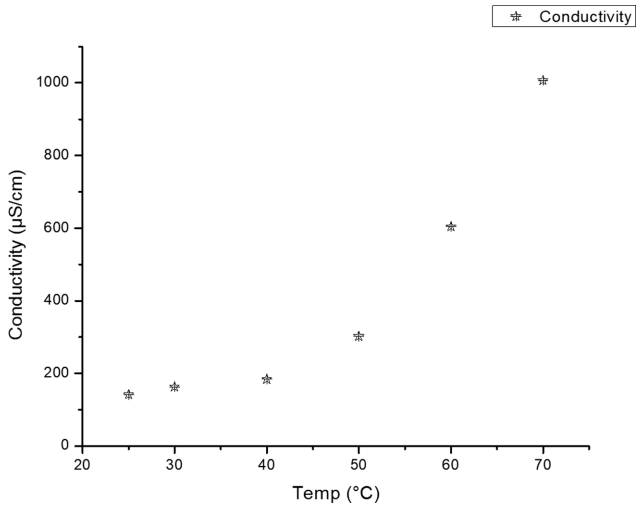



**Fig. 4. Conductivity of the DES (TBAB: Decanoic acid (1 : 2)) as a function of temperature.**

thus increasing its conductivity. Conductivity is a measure of the concentration of ions in a solution. Therefore, conductivity of DES is more related to electrochemical application than extraction application. Similar observations on temperature effect on the conductivity of DES were reported in literature [24].

Temperature effect on the physicochemical properties of the DES greatly affects phase separation, mobility, and mass transfer of the DES. This in turn affects the extraction efficiency. Extraction efficiency increases with increase in temperature, as a result of decrease in density and viscosity that enhanced the mobility and mass transfer of BTX from the aqueous phase into the DES phase. Decrease in pH with increase in temperature leads to higher extraction efficiency as a result of more hydroxonium bond association of DES with the BTX. Adeeb et al. [23] and Jibril et al. [19] in their studies developed a suitable model for temperature relationship with density, viscosity, pH and conductivity, thus:

$$\rho = a + b\,(T) \tag{3}$$

$$\mu = \mu_0 \exp\left[-E\mu/RT\right] \tag{4}$$

$$pH = a + b\,(T) \tag{5}$$

$$k = k_0 \exp\left[-E_k/RT\right] \tag{6}$$

where $\rho$, $\mu$, k is the density, viscosity, and conductivity, respectively; $\mu_0$ and $k_0$ are pre-exponential constants, a and b are constants that vary according to the type of DES, E is the activation energy, R is the gas constant, and T is the temperature in Kelvin [19,23].

The increase in temperature results in an increase in extraction efficiency, and the above Eqs. (3)-(6) correlate the physicochemical properties with temperature. Therefore, the resultant extraction efficiency can be attributed to respective changes of the physicochemical properties with temperature.

**2. Modeling and Optimization of DES Extraction of BTX**

Response surface methodology (RSM) was adopted for modelling and optimizing the operating variables affecting the extraction efficiency of the DES using central composite design (CCD). Table 2 shows the experimental design matrices and responses for the DES.

Experimental responses obtained in Table 2 were subjected to statistical analysis withy the design software. From the analysis, the best fit model describing the DES performance in extracting the BTX was quadratic. Eq. (7) represents the quadratic model describing the DES performance in extracting the BTX compound.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j \tag{7}$$

where Y represents the predicted response, $X_i$, $X_j$ are the coded variables, $\beta_0$, $\beta_i$, $\beta_{ii}$, $\beta_{ij}$ are the constant, linear, square and interaction effects of the variables, respectively.

$Y_1$, $Y_2$, and $Y_3$, respectively, represent the empirical models describing the DES extraction efficiency for benzene, toluene, and xylene all as functions of time (A), temperature (B), and solvent mass fraction (C) as shown in Eqs. (8)-(10).

$$Y_1 = 61.89 + 2.13A + 3.67B + 23.97C + 0.7AB + 0.15AC - 0.15BC - 1.79A^2 + 0.21B^2 - 4.94C^2 \tag{8}$$

**Table 2. Experimental design matrix and response results for DES performance**

| Run | Blocks | Factor 1 A: time min | Factor 2 B: temperature °C | Factor 3 solvent mass fraction | Response 1 Benzene extraction Efficiency % | Response 2 Toluene extraction Efficiency % | Response 3 Xylene extraction Efficiency % |
|---|---|---|---|---|---|---|---|
| 1 | Day 1 | 20 | 25 | 0.2 | 28.65 | 29.44 | 34.27 |
| 2 | Day 1 | 60 | 70 | 0.2 | 39.71 | 38.79 | 40.50 |
| 3 | Day 1 | 40 | 47.5 | 0.5 | 65.15 | 63.71 | 70.09 |
| 4 | Day 1 | 40 | 47.5 | 0.5 | 60.73 | 62.15 | 73.21 |
| 5 | Day 1 | 20 | 70 | 0.8 | 81.75 | 83.96 | 88.79 |
| 6 | Day 1 | 60 | 25 | 0.8 | 79.54 | 85.51 | 87.23 |
| 7 | Day 2 | 60 | 25 | 0.2 | 30.11 | 32.86 | 39.22 |
| 8 | Day 2 | 40 | 47.5 | 0.5 | 63.07 | 61.43 | 71.90 |
| 9 | Day 2 | 20 | 25 | 0.8 | 75.57 | 80.48 | 86.60 |
| 10 | Day 2 | 20 | 70 | 0.2 | 33.52 | 34.44 | 37.58 |
| 11 | Day 2 | 60 | 70 | 0.8 | 86.61 | 88.94 | 92.71 |
| 12 | Day 2 | 40 | 47.5 | 0.5 | 61.10 | 63.18 | 66.67 |
| 13 | Day 3 | 40 | 70 | 0.5 | 66.20 | 67.73 | 71.88 |
| 14 | Day 3 | 40 | 25 | 0.5 | 57.27 | 58.64 | 63.19 |
| 15 | Day 3 | 40 | 47.5 | 0.8 | 81.51 | 82.88 | 87.50 |
| 16 | Day 3 | 60 | 47.5 | 0.5 | 62.14 | 65.20 | 69.52 |
| 17 | Day 3 | 40 | 47.5 | 0.5 | 60.94 | 63.56 | 71.11 |
| 18 | Day 3 | 40 | 47.5 | 0.5 | 63.34 | 61.93 | 74.29 |
| 19 | Day 3 | 40 | 47.5 | 0.2 | 33.29 | 32.52 | 36.19 |
| 20 | Day 3 | 20 | 47.5 | 0.5 | 57.33 | 60.29 | 63.17 |

$$Y_2=62.91+2.27A+2.69B+25.37C+0.11AB+0.28AC-0.5BC+0.41A^2+0.84B^2-3.99C^2 \quad (9)$$

$$Y_3=69.92+1.88A+2.09B+25.51C+0.16AB-0.41AC+0.38BC-1.56A^2-0.38B^2-7.07C^2 \quad (10)$$

Eqs. (8)-(10) show some variations in the extraction efficiencies of BTX compounds with respect to the studied variables (time, temperature, and solvent mass fraction). A slight increasing effect is observed with increasing time of extraction, while a marginal increasing effect is observed with increasing temperature on the extraction efficiencies. This is as a result of increased mass transfer, following the fact that the amount of BTX extracted at a given time depends upon the mass transfer of the analyte from the aqueous phase into the DES phase. That being stated, the solvent mass fraction was observed to have a more pronounced increasing effect. This, therefore, suggests that the extraction performance of DES is more affected by changes in solvent mass fraction than those of temperature and time of extraction.

Model fitness parameters are presented in Table 3. From Table 3, the experimental values showed a reasonable agreement with the predicted values. From the ANOVA, the F-value (computed as the ratio of the mean square of response to mean square of error) and Prob>F values, shows that the models are significant. A lack of fit value of 0.32, 1.12, 0.95 for benzene, toluene and xylene respectively indicate a good fit of the model. The 'Lack of Fit F-value,' which is calculated as the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value [18] also signifies the suitability of the model.

Following the analysis of the variables (Temperature, time and solvent mass fraction) and how they affect the extraction performance of the DES, optimization was necessary to improve the overall efficiency of the DES. The purpose of optimization was to minimize the extraction time, which signifies the rate at which the extraction is carried out, the extraction temperature, which relates to energy consumption, and ultimately solvent mass fraction, which is the DES requirement for the extraction. The design software was used to perform optimization of the extraction variables with the utilization of the desirability function tool [25]. Optimum condition of 25 °C, 60 min, and 0.6 was established for temperature, time and solvent mass fraction, respectively. Furthermore, experimental validation was conducted at optimum extraction condition and the results are presented in Table 4. Table 4 shows a slight difference between the predicted response and experimental validation. Based on the reliability of the experimental validation, the optimum

**Table 3. Model fitness parameters**

| Model parameters | Benzene | Toluene | Xylene |
|---|---|---|---|
| $R^2$ | 0.9950 | 0.9971 | 0.9858 |
| Adjusted $R^2$ | 0.9934 | 0.9962 | 0.9814 |
| Predicted $R^2$ | 0.9892 | 0.9932 | 0.9738 |
| Associated probability (p-value) | <0.001 | <0.001 | <0.001 |
| F-value | 643.74 | 1,114.02 | 225.46 |
| Lack of fit F-value | 0.32 | 1.12 | 0.95 |
| Mean | 59.38 | 60.88 | 66.28 |
| Standard deviation | 1.53 | 1.22 | 2.74 |
| Adequate precision | 64.74 | 83.56 | 36.36 |

**Table 4. Optimum extraction conditions, predicted response, and experimental verification**

| Optimum conditions | Compounds | Predicted response (%) | Experimental verification (%) | Relative difference (%) |
|---|---|---|---|---|
| Temperature (25 °C) | Benzene | 68.1 | 67.05 | 1.05 |
| Time (60 min) | Toluene | 70.84 | 70.23 | 0.61 |
| Solvent fraction (0.6) | Xylene | 77.73 | 75.56 | 2.17 |

**Table 5. Comparison of results obtained in this work with relatively similar works reported in the literature**

| HDES | Analyte | Technique | Efficiency (%) | Ref. |
|---|---|---|---|---|
| TBAB/decanoic acid (1 : 2) | BTX | LLE | 71-78 | This work |
| TBAB/decanoic acid (1 : 2) | PAHs | SOFD-LLME[a] | 83 | [20] |
| DL-menthol/decanoic acid (1 : 1) | Benzophenone | AA-LLME[b] | 89 | [26] |
| Thymol/camphor (1 : 1) | 21 PAHs | DLLME[c] | 74 | [8] |
| [N8881]Cl/4-hydroxybenzoate (1 :2 ) | Toluene, ethylbenzene and o-xylene | SPME[d] | 89 | [27] |

[a]Solidification of floating drop liquid-liquid microextraction
[b]Air-assisted dispersive liquid-liquid microextraction
[c]Dispersive liquid-liquid microextraction
[d]Solid phase microextraction

conditions obtained were exploited and used for further experiments.

Comparison between extraction performance obtained in this work and that reported in the literature may not be directly feasible due to some discrepancies in either method of approach, experimental conditions, or contexts of experiments. However, after careful consideration of related works, it was observed that the extraction performance of hydrophobic DES used in this work looks quite promising, as shown in Table 5.

## 3. Effect of Starting Concentration

The effect of initial starting concentration of the BTX was examined to establish a relationship between the extractant and contaminant concentration. After experimenting with different initial concentrations from 100 to 500 ppm at optimum conditions, the results obtained showed only a relative increase in their respective extraction efficiency from 69.82-79.15% for benzene, 72.23-83.2% for toluene, and 76.01-89.24% for xylene, as shown in Fig. 5. This indicates that the initial starting concentration slightly affects the DES extraction efficiency. Hence, the liquid-liquid equilibrium established between the DES phase and the BTX phase determines the degree of extraction. Similar findings were reported in some related works [11].

## 4. Extraction Capacity of the DES

Fig. 6 presents the extraction efficiency of the DES for four consecutive cycles without regeneration. From Fig. 6, the extraction capacity of the DES decreases with an increase in the number of extraction cycles. This is explained by the fact that, with increasing cycles of extraction, the DES carries along with it dissolved BTX,

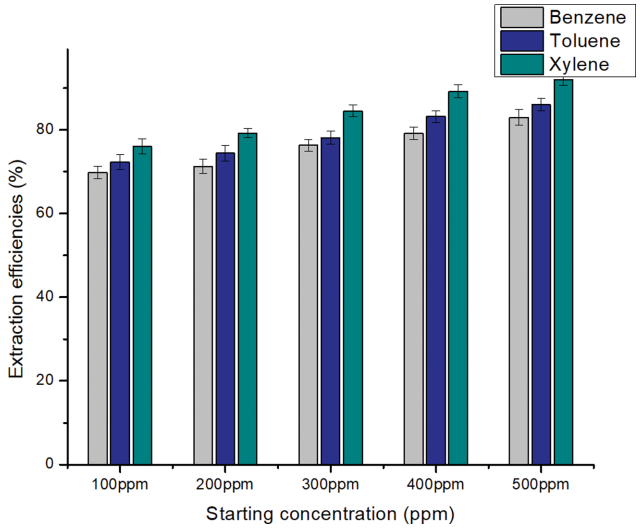



**Fig. 5. DES (TBAB: Decanoic acid (1 : 2)) performance on starting concentration of BTX.**

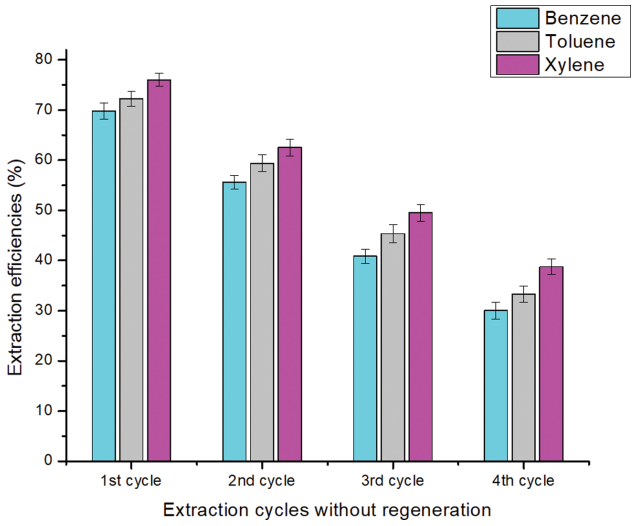



**Fig. 6. DES (TBAB: Decanoic acid (1 : 2)) Extraction capacity without regeneration.**

which limits the mass transfer of the target compounds into the DES, thereby decreasing the extraction efficiencies. Reutilization of DES to further optimize the extraction process is a key factor for the economic and environmental viability of any extraction process.

**5. DES Regeneration and Recycling**

Regeneration and recycling of DES were carried out at optimum conditions to improve the overall efficiency of the whole extraction process. Van Osch et al. [11] in their studies of the thermal decomposition of some hydrophobic DESs between five quaternary salts and decanoic acid, established that most hydrophobic DESs are thermally stable up to 400 °C. The solvent was regenerated by heating the spent solvent in a beaker at 180 °C, which was within the solvent stability range [20]. Heating of the solvent at the above-mentioned temperature (180 °C) causes the BTX compounds to vaporize, as the temperature exceeds the boiling point temperature of benzene (80.1 °C), toluene (110.8 °C), and xylene (144.4 °C) [11]. After regeneration, the solvent was allowed to cool and reused for the next cycle of extraction. Fig. 7 shows the extraction performance of the regenerated DES for five repeated stages with inter-stage regeneration of the solvent, respectively. From Fig. 7, a negligible decrease was observed in the extraction efficiency after successive regeneration cycles. This implies that, regenerated solvent was effective and can be used for multiple stage extraction.

**6. Extraction Mechanism**

Tetra-alkyl quaternary ammonium ion is an exceptional cation that effectively forms a complex with aromatic rings [28]. Fig. 8 shows the interaction between the delocalized $\pi$ electron clouds over the aromatic ring and the electron clouds of quaternary ammonium ion. Naturally, a portion of the $\pi$ electron cloud surrounds the partially positively charge H atoms in the tetra-alkyl quaternary ammonium ion, which contributes significantly to the binding of quaternary ammonium ion to the aromatic compound [28]. Cation-$\pi$ aromatic interaction facilitates the formation of a contact pair that is perhaps more stable than the ion pair between tetra-alkyl quaternary ammonium ions and anionic residue of aqueous solution [29].

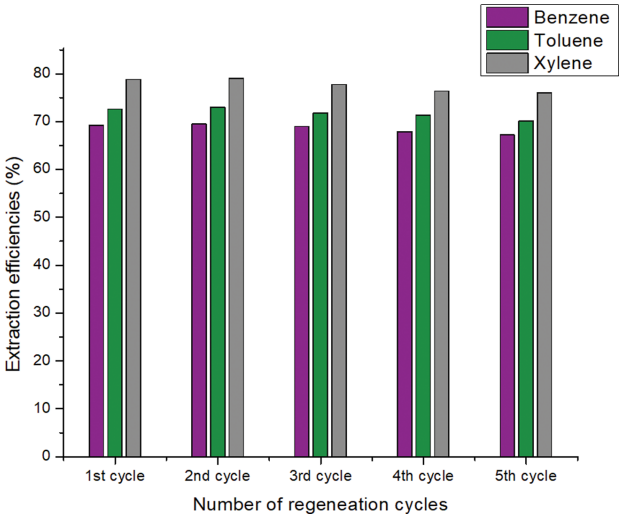



**Fig. 7. Extraction performance of regenerated DES (TBAB: Dec A (1 : 2)).**

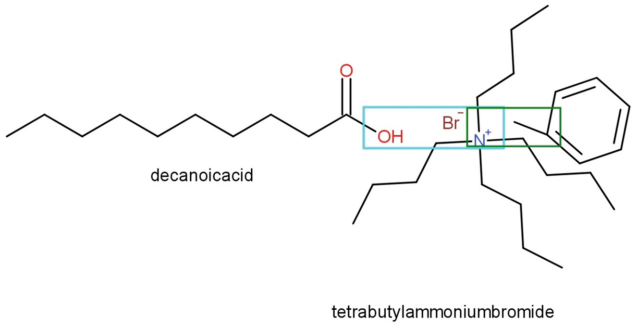



**Fig. 8. Mechanism of extraction.**

Cation-$\pi$ interactions refer to the noncovalent association between an inorganic cation or the cationic moiety of an organic molecule and the $\pi$ electrons of hydrocarbons such as alkenes, alkynes, or aromatics [30].

This stated interaction is in agreement with the proposition of Dougherty and Stauffer, that the important binding forces in the complexing of $Me_4N^+$ (tetra-methyl ammonium ion) with benzene arise from the charge-quadrupole and charge polarizability interaction [31]. Therefore, it could be concluded that the Cation-$\pi$ aromatic interaction represents the mechanism of extraction.

**7. COD Analysis on Raffinate Phase**

Extraction was performed at optimum condition of 25 °C, 60 min and 0.6 (solvent mass fraction). Chemical oxygen demand (COD) analysis of the water phase was conducted by the reactor digestion method using TNTplus™ vials. Caps from two COD digestion reagent vials were removed and volumetric pipet was used to add 2.00 mL of sample to the vial. A fresh volumetric pipet was used to add 2.00 mL of deionized water to the other vial as blank. Both vials were inverted gently several times to mix and then placed in a preheated DRB200 Reactor for two hours. After digestion, colorimetric COD determination was conducted using Spectrophotometer DR3900. The outside of the vials was cleaned with a damp towel followed by a dry one. The blank was inserted into the 16-mm cell holder and then zeroed. The sample was now Inserted and the result was 130 mg/L.

COD value of 130 mg/L indicates low level of organics in the water phase after extraction. Metcalf and Eddy [32] classified COD level of 250 mg/L as low concentration in their quantification of organics in untreated domestic waste water [32]. In addition, a compendium of waste water reuse in the eastern Mediterranean region, COD level within the range 150-200 mg/L falls within the acceptable limit [33]. Therefore, COD of 130 mg/L can be said to be relatively benign.

## CONCLUSION

The paper presents a simple, inexpensive procedure for the removal of BTX in aqueous matrices via liquid-liquid extraction using hydrophobic deep eutectic solvent (HDES). The HDES was synthesized using TBAB and decanoic acid. RSM technique was successfully used to model and optimize the key variables upon which the extraction process depends. ANOVA and model fitness parameters obtained substantiate the suitability of the developed models.

The effect of extraction variables on the DES performance shows that solvent mass fraction has a more significant effect than extraction time and temperature. Effective regeneration and reuse of the DES after each extraction, as well as its capacity, boosted the overall performance of hydrophobic DES for the extraction process. Successive reuse of DES without regeneration decreased DES performance while starting concentration of BTX was found to have a negligible effect on the extraction efficiencies of the DES. The overall results show that the DES under study has a high potential in the removal of BTX contaminants from wastewater.

## ACKNOWLEDGEMENTS

The authors appreciate the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria and the Department of Chemical Engineering, Ahmadu University, Zaria, Nigeria for financial and technical supports rendered in carrying out this research.

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

## REFERENCES

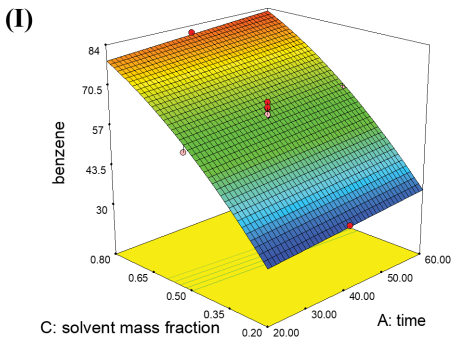
1. E. Manoli and C. Samara, *Trends Analyt. Chem*., **18**, 417 (1999).
2. N. U. Benson, J. P. Essien, F. E. Asuquo and A. L. Eritobor, *Environ. Monit. Assess*., **186**, 5519 (2014).
3. T. Khezeli, A. Daneshfar and R. Sahraei, *J. Chromatogr. A*., **1425**, 25 (2015).
4. A. M. Taiwo, O. O. Olujimi, O. Bamgbose and T. A. Arowolo, *Surface water monitoring in nigeria: Situational analysis and future management strategy, water quality monit. assess*., InTech publications, London (2012).
5. K. Z. Kponee, A. Chiger, I. I. Kakulu, D. Vorhees and W. Heiger-Bernays, *J. Environ. Health Sci. Eng*., **14**, 86 (2015).
6. L. F. Lima, J. I. R. De-Andrade, M. G. Da-Silva and M. G. Vieira, *Ind. Eng. Chem. Res*., **56**, 6326 (2017).
7. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun*., **1**, 70 (2003).
8. P. Makoś, A. Przyjazny and G. Boczkaj, *J. Chromatogr. A*., **1570**, 28 (2018).
9. M. K. I. Hadj-Kali and M. Hayyan, *J. Chem. Technol. Biotechnol*., **93**, 945 (2018).
10. Gałuszka, Z. Migaszewski and J. Namieśnik, *Trends Analyt. Chem*., **50**, 78 (2013).
11. D. J. van Osch, L. F. Zubeir, A. van den Bruinhorst, M. A. Rocha and M. C. Kroon, *J. Green Chem*., **17**, 4518 (2015).
12. Florindo, L. Branco and I. Marrucho, *Fluid Phase Equilib*., **448**, 135 (2017).
13. M. Faraji, *Microchem. J*., **150**, 104130 (2019).
14. S. Garcia, M. Gil, J. Pis, F. Rubiera and C. Pevida, *Int. J. Greenh. Gas Control*, **12**, 35 (2013).
15. A. K. Dwamena, *J. Sep. Sci*., **6**, 9 (2019).
16. B. Socas-Rodriguez, A. Santana-Mayor, A. V. Herrera-Herrerra and M. A. Rodriguez-Delgado, *Green Sustain. Process Chem. Environ. Eng. Sci*., **5**, 123 (2020).
17. Z. S. Gano, F. S. Mjalli, T. Al-Wahaibi, Y. Al-Wahaibi and I. M. AlNashef, *Chem. Eng. Process*, **93**, 10 (2015).
18. C. Montgomery and G. C. Runger, *Applied statistics and probability for engineers*, John Wiley & Sons Publications, New Jersey (2010).
19. B. Jibril, F. Mjalli, J. Naser and Z. Gano, *J. Mol. Liq*., **199**, 462 (2014).
20. S. M. Yousefi, F. Shemirani and S. A. Ghorbanian, *J. Chromatographia*, **81**, 1201 (2018).
21. J. G. P. van Osch, C. H. J. T. Dietz, J. van Spronsen, M. C. Kroon, F. Gallucci, M. V. S. Annaland and R. Tuinier, *ACS. Sustain. Chem. Eng*., **7**, 2933 (2019).
22. H. Ghaedi, M. Ayoub, S. Sufian, S. M. Hailegiorgis, G. Murshid, S. Farrukh and S. N. Khan, *Thermochim. Acta*., **657**, 123 (2017).
23. A. Hayyan, F. S. Mjalli, I. M. AlNashef, T. Al-Wahaibi, Y. M. Al-Wahaibi and M. A. Hashim, *Thermochim. Acta*., **541**, 70 (2012).
24. X. Li and K. H. Row, *J. Sep. Sci*., **39**, 3505 (2016).
25. L. Zhao and H. K. Lee, *J. Chromatogr. A*., **919**, 381 (2001).
26. D. Ge, Y. Zhang, Y. Dai and S. Yang, *J. Sep. Sci*., **41**, 1635 (2018).
27. T. Li, Y. Song, J. Xu and J. Fan, *Talanta*, **195**, 298 (2019).
28. K. S. Kim, J. Y. Lee, S. J. Lee, T. K. Ha and D. H. Kim, *J. Am. Chem. Soc*., **116**, 7399 (1994).
29. J. Gao, L. W. Chou and A. Auerbach, *Biophys. J*., **65**, 43 (1993).
30. A. Orabi and G. Lamoureux, *J. Phys. Chem. B*., **122**, 2251 (2018).
31. D. A. Dougherty and D. A. Stauffer, *J. Sci*., **250**, 1558 (1990).
32. L. Metcalf, *Waste water engineering: Treatment and reuse*, Metcalf and Eddy Inc. (2003).
33. W. H. Organization, A compendium of standards for waste water reuse in the Eastern Mediterranean Region (2006).

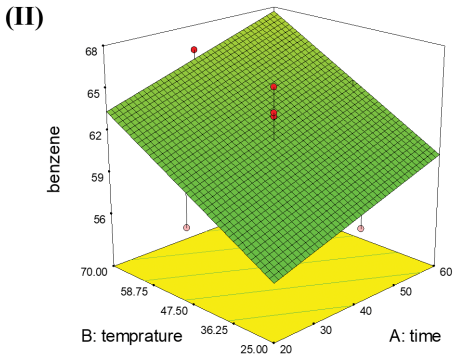
# Supporting Information

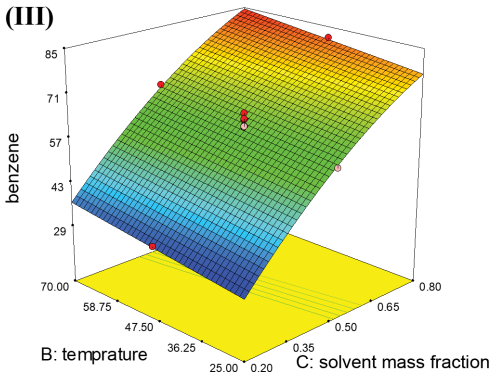
# Application of hydrophobic deep eutectic solvent for the extraction of aromatic compounds from contaminated water

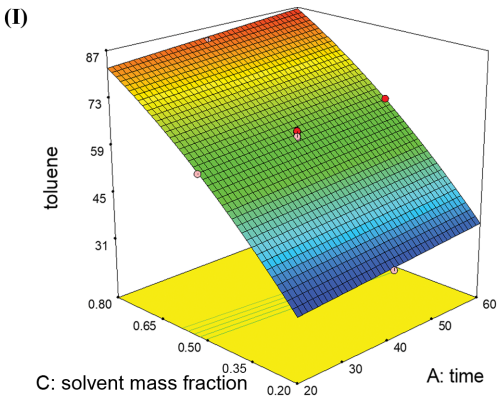
**Abdullahi Yakubu*,***, Zaharaddeen Sani Gano**,†, Omar Umar Ahmed**, Suleiman Mohammed Shuwa*, Abdulazeez Yusuf Atta*, and Baba Yakubu Jibril***

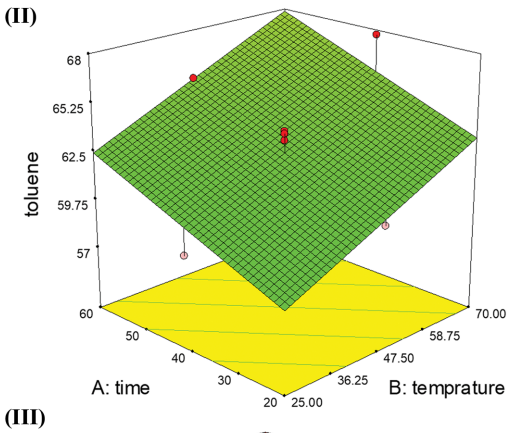
*Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State, Nigeria
**National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria
***Dangote Fertilizer Limited, Lagos, Nigeria
(*Received 12 February 2021 • Revised 7 September 2021 • Accepted 22 October 2021*)

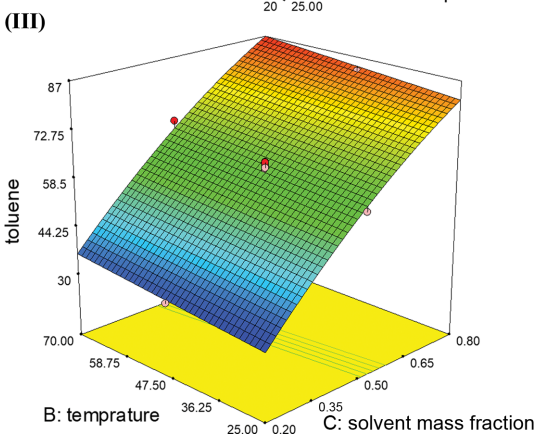


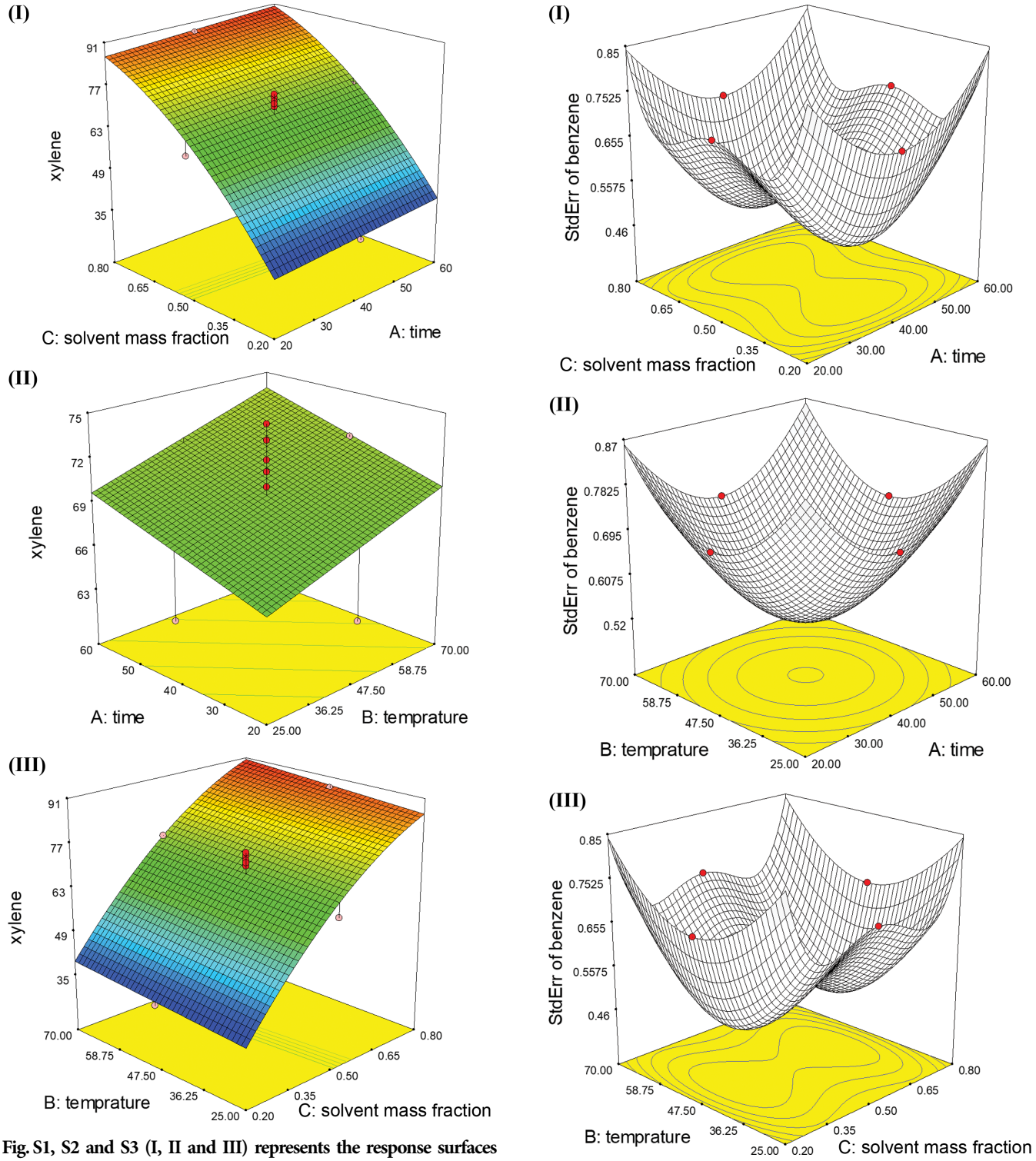
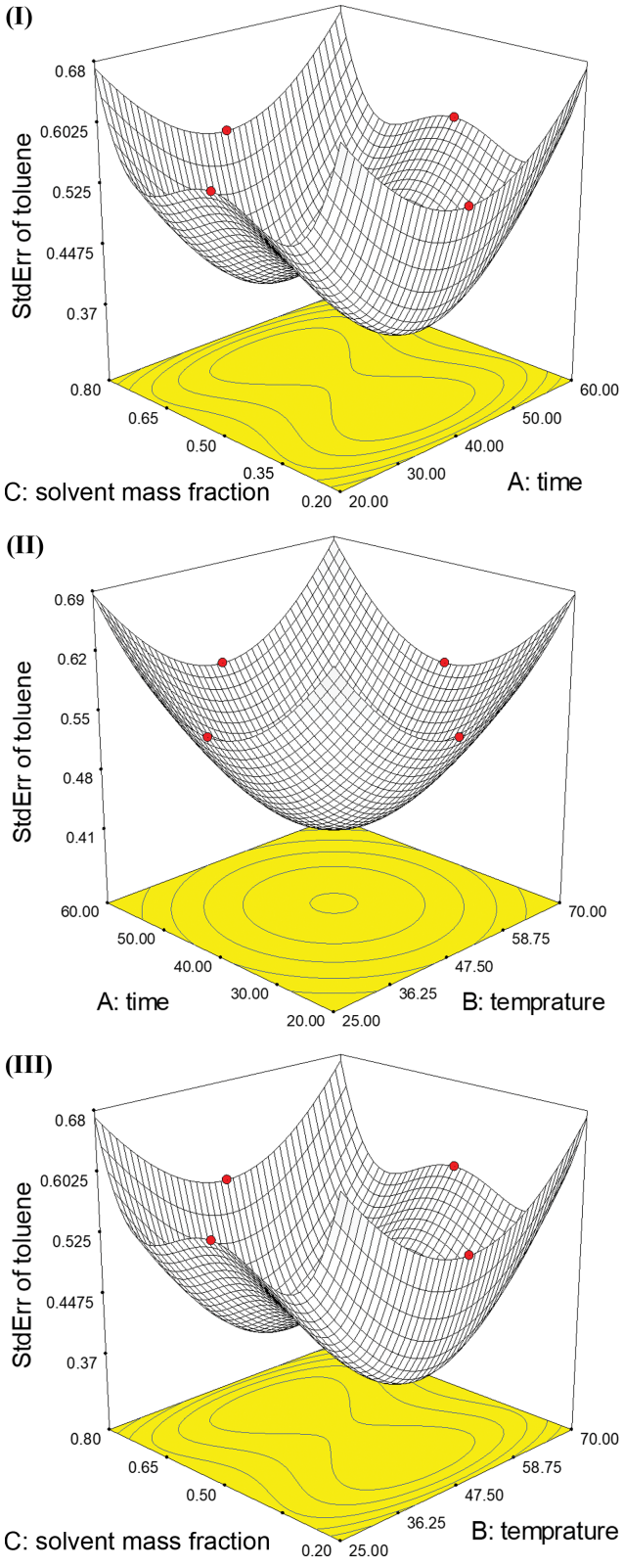



**Fig. S1, S2 and S3 (I, II and III) represents the response surfaces for benzene, toluene and xylene respectively using the central composite design obtained by plotting of: (I) the solvent mass fraction vs the extraction time, (II) the extraction time vs the extraction temperature and (III) the extraction temperature vs the solvent mass fraction.**



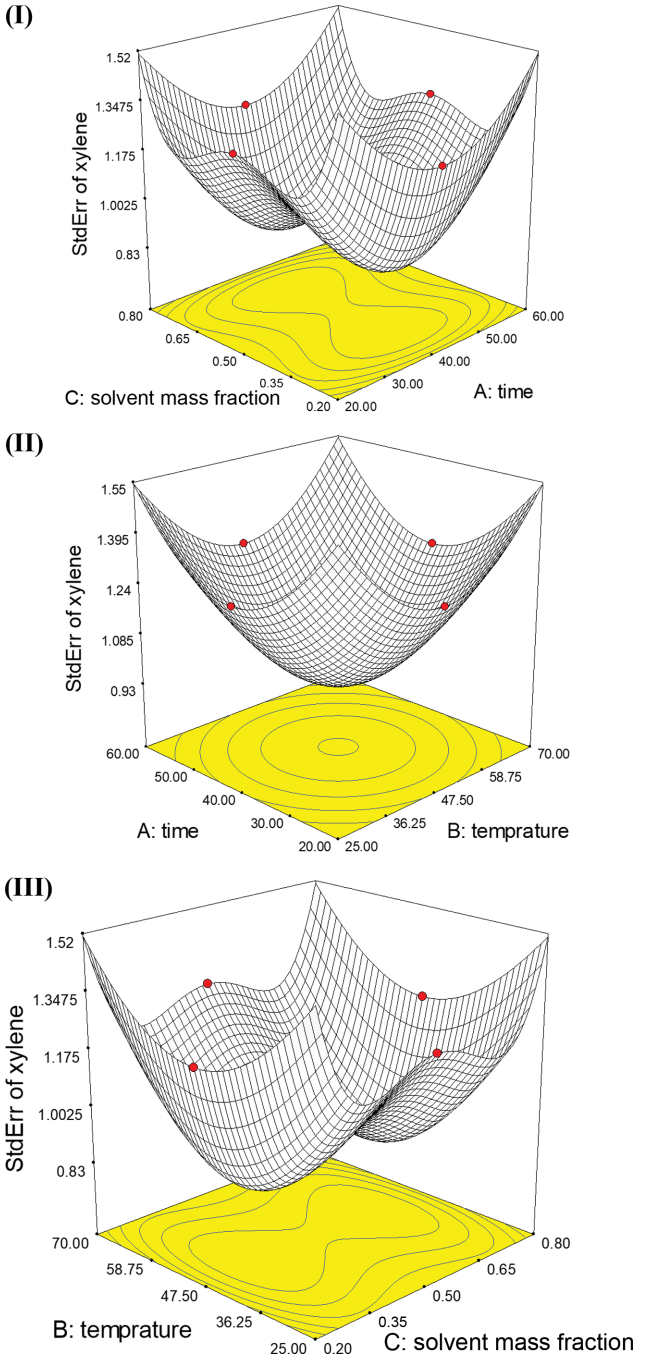




**Fig. S4, S5 and S6 (I, II and III) represents the standard error plot for benzene, toluene and xylene respectively using the central composite design obtained by plotting of: (I) the solvent mass fraction vs the extraction time, (II) the extraction time vs the extraction temperature and (III) the extraction temperature vs the solvent mass fraction.**