APPLICATION OF HYDROPHOBIC DEEP EUTECTIC SOLVENT [DES] FOR THE EXTRACTION OF AROMATIC COMPOUNDS FROM HYDROCARBON CONTAMINATED WATER

BY

ABDULLAHI YAKUBU
(P16EGCE8061)

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DEPARTMENT OF CHEMICAL ENGINEERING,
AHMADU BELLO UNIVERSITY,
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ABDULLAHI YAKUBU,
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ZARIA, NIGERIA

APRIL, 2021

Declaration

I, Abdullahi YAKUBU, hereby declare that this dissertation entitled “APPLICATION OF HYDROPHOBIC DEEP EUTECTIC SOLVENT DES FOR THE EXTRACTION OF AROMATIC COMPOUNDS FROM HYDROCARBON CONTAMINATED WATER” was carried out by me in the Department of Chemical Engineering. The information presented in the literature was duly acknowledged in the text and no part of this dissertation was previously presented for the award of degree or diploma at any institution.

Abdullahi YAKUBU _____________ _____________
Name of Student Signature Date

Certification

This is to certify that this dissertation entitled “APPLICATION OF HYDROPHOBIC DEEP EUTECTIC SOLVENT FOR THE EXTRACTION OF AROMATIC COMPOUNDS FROM HYDROCARBON CONTAMINATED WATER” by Abdullahi YAKUBU, and registration number P16EGCE8061, meets the regulations governing the award of Master of Science (M.Sc.) degree in Chemical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literally presentation.

Dr. A. Y. Atta ______________ ______________
Chairman, Supervisory Committee Signature Date

Dr. S. M. Shuwa ______________ ______________
Member Supervisory Committee Signature Date

Dr. Z. S. Gano ______________ ______________
Member, Supervisory Committee Signature Date

Dr.J.A. Muhammad ______________ ______________
Head of Department Signature Date

Prof. S.A. Abdullahi ______________ ______________
Dean, School of Postgraduate Studies Signature Date

Dedication

To my Mother (HajiyaAminaYakubu)

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In the name of Allah, the most Merciful, the most beneficent. All praise is due to Allah (SWT), Lord of the worlds, and the Sovereign of the Day of Recompense. May peace and blessings of Allah (SWT) be upon His final prophet, Muhammad (SAW), his companions and those that follow the right path to the last day. Thanks to Allah for giving me the opportunities to complete this research work successfully.

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Abstract

Environmental pollution of water bodies by industrial effluent and other related sources containing toxic organic compounds has raised concern by different environmental protection agencies, and the urgent need for effective remediation. Hydrophobic based Deep Eutectic Solvent (DES) was synthesized and applied as extractant in the removal of aromatic hydrocarbon namely benzene, toluene and xylene (BTX) from contaminated water samples. Physicochemical properties such as density, viscosity, conductivity and pH of the synthesized DES were determined and the values were in ranges of 944-915Kg/m^3, 1636-179mPa.s, 141-1007µS/cm and 3.14-2.73 respectively, within the temperature range (25-70^{0}C). The hydrophobic DES was applied in liquid-liquid extraction to remove BTX from simulated contaminated water. Quantitative monitoring of BTX was carried out using UV spectrometer and average values are presented. Major variables that affect the extraction efficiency of the DES were optimized and efficiencies of 68.1%, 70.84% and 77.73% for BTX respectively were determined to be the optimum values at 25^{0}C 60 min 0.6 solvent mass fraction. Response surface methodology was employed as a tool in modeling and optimizing the extraction performance of the DES. The results obtained substantiate the suitability of the model developed. Extraction efficiencies as high as 86.61%, 88.94% and 92.71 % for BTX respectively was obtained from the model. These values show that the DES under study has high potential in the removal of contaminants such as BTX from waste water. Finally, effective regeneration and reuse of the DES after each extraction was carried out for 5 consecutive cycles and their results showed no significant decrease in their respective extraction efficiencies. Hence, improving the overall performance of hydrophobic DES for the extraction process.

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List of Symbol and Abbreviation

Benzene, Toluene, Xylene	BTX
Tetrabutyl Ammonium Bromide	TBAB
Deep Eutectic Solvent	DES
Liquid Liquid Extraction	LLE
Fourier Transform Infrared	FTIR
Polycyclic Aromatic Hydrocarbon	PAH
Hydrogen Bond Donor	HBD
Hydrogen Bond Acceptor	HBA
Quaternary Ammonium Salts	QAS
Environmental Protection Agency	EPA
Environmental Guidelines and Standardsfor the Petroleum Industry in Nigeria	EGASPIN
Parts Per Million	PPM
United State Environmental Protection Agency	USEPA
Naphthalene, Phenanthrene and Dibenzothiophene	NPD
Norwegian Oil Industrial Association	NOIA
Ionic liquids	ILs
Response Surface Methodology	RSM
Volatile Fatty Acids	VFA
Trioctylammine	TOA
Central composite Design	CCD
Design of Experiment	DOE
Volatile Organic Compounds	VOC
Tetrahydrofuran	THF

CHAPTER ONE

1.0 INTRODUCTION

Pollution of water by hazardous substances, some of which are categorized as having toxic, carcinogenic and mutagenic properties, has attracted and raised environmental concerns(Manoli and Samara, 1999). Most water bodies are usually the receptacle of refinery effluents, petrochemical effluents, sewage effluents, crude oil spillage (which arise from pipe lines leakage and accidental spills from tankers) and other related industrial effluent(Benson *et al*., 2014). Consequently, these effluents contain some hazardous and toxic aromatic compounds, among which are benzene, toluene and xylene (BTX). These compounds are widely used as raw materials in chemical and petrochemical industries. BTX are important organic water pollutants that require remediation(Khezeli*et al*., 2015). These aromatic compounds have also been associated with detrimental health effects as a result of their toxic and hazardous nature(Khezeli*et al*., 2015). BTX and other aromatic contaminants are listed as priority pollutants collected by the United States Environmental Protection Agency (US EPA, 2006) (Manoli and Samara, 1999). Studies carried out in most urban centers in Nigeria has shown that effluents from various industries are one of the main sources of water pollution(Taiwo*et al*., 2012). 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(Kponee*et al*., 2015)

Ionic liquids (ILs) have widely been utilized for various application and extraction purposes. Their unique properties are established and fine-tuned by selecting the appropriate components that makes up the ILs. On the other hand, the “green” character of ILs has often been questioned, due mainly to their poor biodegradability, biocompatibility, and sustainability(Abbott *et al*., 2003). Analogues to ILs are Deep Eutectic Solvents (DES), with properties similar to that of ILs, but are easy to synthesize. In addition they are more economical and environmentally friendly than ILs(Makoś*et al*., 2018). DESs are synthesized from the complexation of two or more compounds as a result of hydrogen bonding between the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA). The resulting eutectic mixture obtained suffers a freezing point depression and usually have a melting point lower than that of the starting components(Makoś*et al*., 2018).

Presently, availability of researches on hydrophobic DESs are limited, and are basically obtained by complexing (contacting and mixing) organic salts with carboxylic acids (Makoś *et al*., 2018). Hydrophobic DES have been applied for extraction purposes which include;Extraction of volatile fatty acids (VFAs) from water which gave better extraction performance than the normal conventional solvent, Trioctylammine (TOA)(van Osch *et al*., 2015). Extraction of pesticides from water with extraction efficiencies of up to 80% obtained(Florindo*et al*., 2017).Extraction of polycyclicaromatic hydrocarbons in aqueous samples with extraction efficiencies above 73%(Makoś*et al*., 2018) and Micro-extraction of two auxins in water and fruit juice samples with extraction performance of 90%(Faraji, 2019).

Response surface methodology RSMis a common technique used in design of experiment (DOE) for modeling and optimizing of process operations(Garcia *et al*., 2013) RSM tool was adopted using the Central Composite Design (CCD) because of its advantages of simplicity and ease of use. Solvent regeneration and recycling of DES were carried out to further improve the overall performance of the synthesized DES.

1.1 Problem Statement

Environmental regulations on the maximum contaminant limit of organic pollutants is becoming more stringent as a result of increased global industrialization, hence requires the need for effective, environmentally sound, energy efficient and economical remediation technology. Biodegradation which is one of the regular techniques used, suffers some setbacks because its reaction rates are kinetically influenced and controlled by several parameters which include pH, temperature, initial substrate concentration, type of inoculum added, nutrient concentration, substrate inhibition among others, thus making bioremediation technique tedious, time consuming and relatively expensive(Jo *et al*., 2008).

1.2 Justification

Aromatic contaminants in natural waters derive mainly from municipal effluents, industrial effluents and oil spillage or leakage. BTX have been listed as priority pollutants that need to be monitored in both industrial and domestic effluents and freshwater systems.

Hydrophilic DESs which are often applied for the extraction of BTX are miscible with water and requires large amount of DES as well as an emulsifier such as tetrahydrofuran (THF). Therefore, application of DES in solvent extraction involving water-based samples requires hydrophobic solvent. This in turn reduces the consumption of DES and eliminates the use of an emulsifier. Hence meeting some of the objectives of green chemistry.

Extraction processes are effectivein the removal of persistent organic pollutants.Hazardous nature and poor biodegradability, high price and toxicity of mostILs used in extraction processescalls for new generation of green solvents such as deep eutectic solvents (DESs)

1.3 Aim

The aim of this work is toremove BTX from contaminated waterusinghydrophobic deep eutectic solvents, synthesized from tetrabutlyammonium bromide (TBAB) and decanoic acid.

1.4 Objectives

The objectives of this work are to:

i. Synthesize and characterize hydrophobic DES
ii. Carry out liquid liquid extraction (LLE) of BTX compounds
iii. Model and optimize the LLE of hydrophobic DES using design of experiment (DOE)
iv. Regenerate the synthesized DES

1.5 Scope

There is no limit to the number or type of DESs that can be prepared from available chemicals, because there are a large number of salts and hydrogen bond donors that can be used to prepare these solvent mixtures. Therefore, in this work, the eutectic mixtures of tetrabutyl ammonium bromide and decanoicwasprepared, and utilized for the extraction of aromatic contaminant (Benzene, Toluene, Xylene) from simulated water.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1Hydrocarbons

A hydrocarbon is one of the simplest and primitive of organic compounds. They have varying concentrations in storm water and effluent water. Hydrocarbons in water can be found as free floating, emulsified, dissolved, or adsorbed to suspended solids(Khir Umaimah,2012). Basically hydrocarbon compounds contain only carbon and hydrogen atoms. Hydrocarbons are broken down into three main classes; aliphatic, alicyclic, and aromatics.

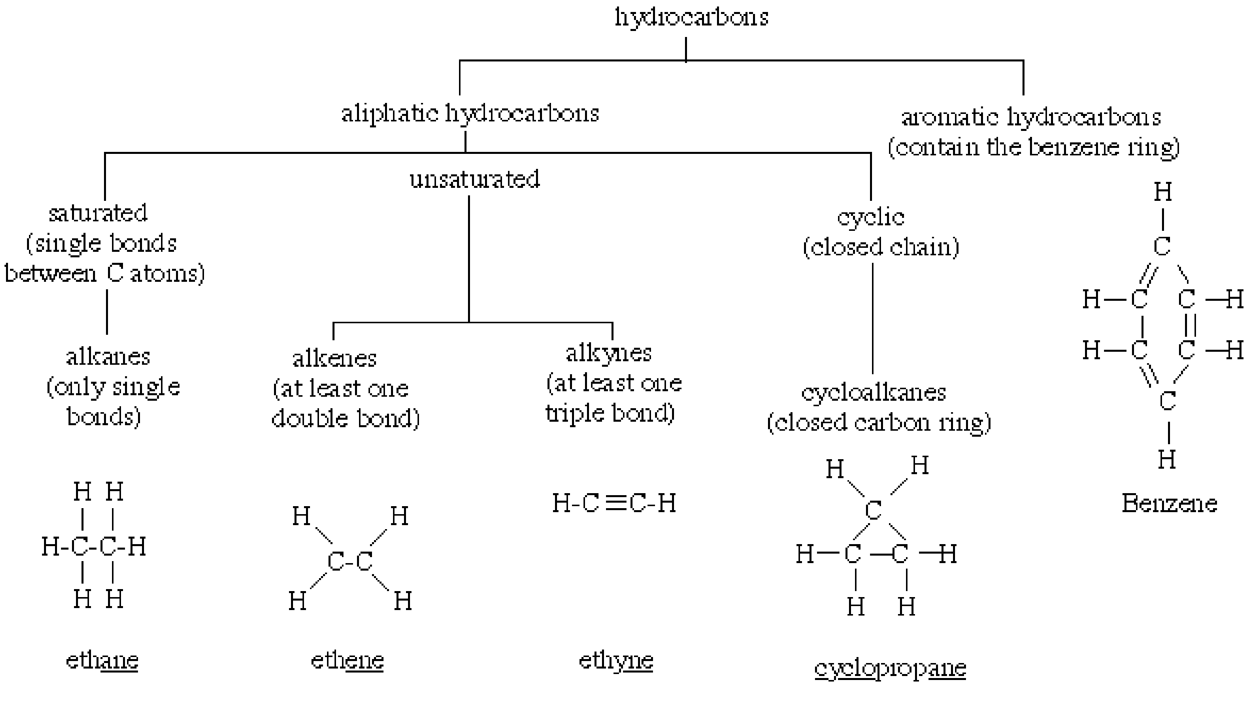


Figure2.1. Three Main Classes of Hydrocarbon(Khir Umaimah, 2012)

Aliphatic is an open chain compound, bonded in a linear chain. This hydrocarbon can be either in the saturated or unsaturated phase. Saturated aliphatics consist of single bond aliphatic while, unsaturated aliphatics consist of double and triple bond of aliphatics.Typicallyaliphatics include ethane, actelyene, and 1,2 butadiene, methane (Khir Umaimah, 2012).

Alicyclics or cyclic hydrocarbons as indicated by their name, contain rings of carbon atoms in their structures. Examples of alicyclics include cyclopropane and cyclopentane(Khir Umaimah, 2012)

Aromatic hydrocarbons typically contain at least one 6-membered benzene ring. This aromatic compound can be bonded with other aliphatic, alicyclic or with aromatic itself. As the name implies, these compounds are typically related to odour and fragrance. Benzene, toluene and xylene (BTX) are part of common aromatic compounds(Khir Umaimah, 2012).

2.2 Monoaromatic Properties and Analytical Methods

Monoaromatic compounds such as Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are classified into the groups of hazardous compounds to the environment because of their large migration abilities and toxicity (Coates *et al*., 2002). Generally, percent volumes of benzene, toluene, ethyl benzene and mixed xylenes in gasoline are 1, 1.5, 1–1.5 and 8–10, respectively (Azev*et al*., 2004). The presence of light aromatic hydrocarbons in water is an indicator of the presence of oil products. The physical and chemical properties of monoaromatic compounds are important characteristics which help in predicting the fate of these chemicals in the environment. They are summarized in Table 2.1 below.

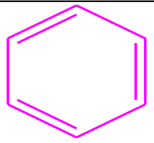
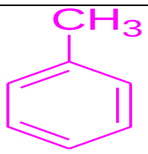
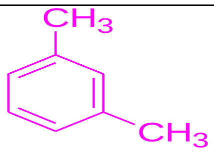
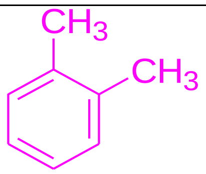
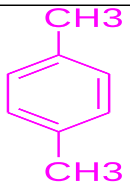
The relatively high water solubility of monoaromatic hydrocarbons demonstrates their great tendency to spread in contaminated water (Lipson and Siegel, 2000). The maximum levels BTX allowed in the United States for drinking water are 0.005, 1 and 10 parts per million (ppm) for benzene, toluene and mixed xylenes, respectively (USEPA, 2006). Generally, high vapor pressure and low molecular weight mean that the compound is more likely to volatilize out of water solution (Lee *et al*., 2004).

There are several methods that can be used to determine the content of monoaromatic hydrocarbons in a water sample. Techniques such as gas chromatography (GC) and liquid chromatography (LC) can provide quantitative, constituent-specific analysis of volatile hydrocarbons. Several reports have shown that preferred methods for determination of monoaromatic compounds in water are GC/flame ionization detector (FID) (de Nardi*et al*., 2006), GC/mass spectrometry (MS) (Wang *et al*., 2002).

The determination of monoaromatic compounds in water samples at the mg per liter level requires the preconcentration of aromatics before analysis (Demeestere*et al*., 2007). These preconcentration techniques can be classified into three families: solute concentration in a gas phase, a liquid one or on a solid. The first approach makes use of techniques such as headspace analysis or the purge and trap process. The second approach allows analyte adsorption onto a porous support, followed by desorption prior to GC injection. These techniques are recommended methods for VOC analysis in contaminated water as they are rapid, cost efficient and can be automated (Gusma*et al*., 2006, 2007)

The second way to preconcentrate volatile compounds from water samples is solvent extraction such as liquid liquid extraction. Numerous studies on detection and determination of benzene, toluene, xylenes (BTX) compounds in water by GC/MS and HPLC have been established (Farhadian *et al*., 2008). As already stated, aromatic compounds can also be detected by high-performance liquid chromatography (HPLC) fitted with an ultraviolet (UV) detector. These methods can measure constituent concentrations in the parts per billion (ppb) ranges, the lower detection limit being between 1 and 500 mg/L (Vogt et al. 2000)

Table 2.1.BTX Characteristics and Properties (Farhadian *et al*., 2008).

Properties	Benzene	Toluene	m- Xylene	o- Xylene	p- Xylene
Chemical Structure					
Chemical formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}
Molecular weight (g/mol)	78.11	92.14	106.17	106.17	106.17
Some trade names and Synonyms	Benzol 90 Pyrobenzol	Phenylbenzene Methylbenzene	m-Xylolmetaxylene	o-Xylolorthoxylene	p-Xylolparaxylene
Water solubility (mg/L) at 25 ^{0}C	178.5	532.6	161.5	171.5	181.6
Boiling point temp.(^{0}C)	80.0	110.6	139.1	144.5	138.3
Vapor pressure (mmHg) at 20 ^{0}C	95.19	28.4	8.3	6.6	3.15
Melting point temp. (^{0}C)	5.50	-94.9	-47.8	-25.2	13.2
Octanol–water partition coefficient. 25 ^{0}C (log P)	2.13	2.73	3.20	3.12	3.15

2.3Aromatic Water Contaminants

2.3.1Aromatic compounds

Aromatics are termed as mono and polycyclic aromatic compounds containing only hydrogen and carbon atoms. Dibenzothiophene, a sulphur-containing compound, is the only exception in this group(Scurtu, 2009). Due to their wide range of concentrations in hydrocarbon contaminated water, as well as their potentials for causing environmental effects, stringent conditions and maximum allowable limit have been set for these compounds. Aromatic compounds are divided into the following groups: BTEX: monocyclic aromatic compounds - benzene, toluene, ethylbenzene, and xylenes (ortho, meta and para isomers); NPD: naphthalene, phenanthrene and dibenzothiophene, including their C1-C3 alkyl homologues. These are 2-3 ring aromatic compounds; PAH: polycyclic aromatic hydrocarbons. These are represented by the 16 EPA PAHs (except naphthalene and phenanthrene that are included in the NPD group).

- BTEX

  Benzene, toluene, ethylbenzene and xylenes (BTEX) are found in high concentrations among aromatic compounds in produced water(Ghimire& Wang, 2018). They are moderately soluble in seawater, highly volatile and are biodegraded rapidly in the water environment. BTEX compounds have a low affinity for partitioning into lipid tissues of aquatic organisms. They are not persistent in sea water and are not accumulated to any degree by marine organisms(Scurtu, 2009).

- NPDs

  The most abundant compounds in NPD group are naphthalene and its alkyl homologues. Compared with the high molecular weight PAHs, naphthalenes have lower bioaccumulation potential and are rapidly biodegraded in the aquatic environment. Therefore, naphthalenes pose a relatively low environmental risk. The other compounds in this group such as dibenzothiophenes are moderately toxic, but not mutagenic or carcinogenic(Scurtu, 2009).

- PAHs

  PAHs (polycyclic aromatic hydrocarbons) have a wide range of structures and properties. The higher the molecular weight of a compound in this group the lower its solubility and the higher its potential for bioaccumulation in marine organisms(Scurtu, 2009). PAHs partition mostly in the oil droplets or particulate matter. Their toxicity is variable and depends on the particular compound, exposure (acute or chronic) and the nature of the organism exposed to PAHs. Technologies for the removal of dissolved compounds Dissolved compounds are the only hydrocarbons remaining in contaminated water after the removal of oil droplets. The most important groups of dissolved aromatic compounds that need to be removed are BTEX and light phenols (C0 – C3)(Ghimire& Wang, 2018). Heavy phenols, NPDs and PAHs with many fused aromatic rings are mostly removed with dispersed oil. Treatment methods able to remove heavy phenols, NPDs, PAHs, and as well have potential for removing of heavy metals, are given priority over the others(Scurtu, 2009).

Table 2.2. Amount of Aromatic Compound (tons) Discharge in Norwegian Sector (compiled from NOIA, 2007).

Group of Compounds	Discharge (tons)
BTEX	1826
PAH	1.1
NPD	124

Benzene, toluene and xylene (BTX) are typical volatile organic compounds (VOCs) that are constituents of petroleum and industrial solvents widely employed in producing rubbers, lubricants, dyes, detergents, and drugs(Peng*et al*., 2015). Contamination of drinking water, groundwater, and seawater with these volatile organic compounds (VOCs) poses a significant health risk to humans(Karlowatz. *et al*., 2004). Therefore, awareness of the public toward the problem of groundwater, surface water, drinking water, and seawater contamination with VOCs is of paramount importance.

Pollutants such as chlorinated hydrocarbons, aromatic hydrocarbons especially benzene, toluene, and xylenes (BTX) are among the most commonly detected organic contaminants in water(Karlowatz. *et al*., 2004).

Although conventional Drinking Water Treatment Plant (DWTP) multistep treatment processes use advanced technologies as adsorption, membrane filtration, ozonation and chlorination, none was specifically designed to remove aromatic contaminants and thus are not effective(Rodriguez *et al*., 2009).

Assessment of water is not only for suitability for human consumption but also in relation toits agricultural, industrial, recreational, commercial uses and its ability to sustain aquaticlife. Water quality monitoring is therefore a fundamental tool in the management of freshwater resources. To underpin its importance, World Health Organization (WHO), United Nations Environment Programme (UNEP), United Nations Educational, Scientific and Cultural Organization (UNESCO) and World Meteorological Organization (WMO) launched in 1977,a water monitoring programme to collect detailed information on the quality of global ground and surface water.

Table 2.3.Maximum Permissible Effluent Discharge Limits.

Compounds (ppm)	EGASPIN (2002)	EPA (2015)
Benzene	10	5
Toluene	30	10
Xylene	1000	1000

2.4 Petrochemical Wastewater

Petrochemical wastewater is a general term of wastewater associated with oil-related industries. The sources of petrochemical wastewater are diverse and can originate from oilfield production, crude oil refinery plants, olefin process plants other sporadic wastewaters(Gutiérrez *et al*., 2007; Llop *et al*., 2009).

petrochemical wastewater has been categorized to oilfield-produced wastewater, petrochemical refinery, and oily wastewater based on the originates(Ghimire& Wang, 2018). Oilfield-produced wastewater is generated in crude oil extraction from oil wells that contain high concentrations of artificial surfactants and emulsified crude oil characterized of high COD(Zou, 2015). Petroleum refinery wastewater is generated in oil refinery processes that produce more than 2500 refined products(Ghimire& Wang, 2018). The wastewater can be from cooling systems, distillation, hydrotreating, and desalting. The compositions of the refinery wastewater can vary depending upon the operational units for different products at specific time and locations. Different concentrations of ammonia, sulfide, phenols, Benzo, and other hydrocarbons are normally present in such wastewater(Santo *et al*., 2013).

2.4.1 Partitioning of organic constituents in petrochemical wastewater

Hydrocarbons present in petrochemical waste waters exist either as dispersed droplets or in the dissolved phase(Scurtu, 2009). Some compounds such as the aliphatic hydrocarbons are found predominantly in the dispersed phase due to their solubility properties, while others, such as carboxylic acids are normally found in the water phase(Scurtu, 2009). Depending on their molecular weight and structural complexity. Aromatic compounds are found in both phases. Low molecular weight aromatics, such as benzene, toluene, ethylbenzene and xylene (BTEX) and naphthalene are fairly soluble in the water phase while higher molecular weight polycyclic aromatic hydrocarbons (PAHs) are significantly less soluble and mostly remain in the dispersed oil phase. Major dissolved organic compounds present in hydrocarbon contaminated water include;

- Carboxylic acids
- BTEX
- Phenols
- PAHs
- Alkylphenols

Table 2.4. Dissolved Organic Compounds Present in Waste Water (compiled from NOIA, 2007).

Organic Compounds	% in Waste Waters
Carboxylic acid	93.6
BTEX	4.8
Phenols	0.5
PAHs	0.13
Alkylphenols (C1-C3)	0.89
Alkylphenols (C4-C9)	0.03

Table 2.5.Petroleum Refinery Waste Water Characteristics (Ishak, 2013).

Parameters	Range (ppm)
Total Organic Compounds (TOC)	184-187
Phenol	1.16-1.44
Benzene	43.31-44.36
Toluene	38.58-41.08
Xylene	30.03-33.04
Sulphide	14-17

2.5 Remediation Techniques of BTX

2.5.1Stripping

Stripping remediation technology is effective for volatile compounds such as BTEX and light phenols. Its efficiency for heavier compounds such as PAHs can be enhanced by increasing the temperature (Lawrence *et al*., 1995). Stripping is an attractive technique efficient for

BTEX treatment, it is also employed for the removal of NPDs and PAHs in the oil/gas industry(OGP, 2002). The main disadvantage of stripping is that it creates new waste streams that need further treatment such as separation of hydrocarbons from condensed vapours in steam stripping and off-gas treatment in air stripping(OGP, 2002). Costs of implementing stripping for the treatment of dissolved compounds can be very high, especially for steam stripping, which is more energy intensive(Scurtu, 2009). A large stripping column would probably be required in order to comply with the stringent effluent standards set in top water project.

2.5.2 Oxidation

Oxidation remediation technique for the treatment of dissolved organic compounds makes use of ozone and/or hydrogen peroxide for chemical oxidation. The main advantage of this technique is the relatively simple operation, while the high-energy consumption for ozone generation and the toxic waste generated by the process are the main drawbacks(Lawrence *et al*., 1995). Chemical oxidation requires long contact times for an efficient degradation of the target soluble compounds(Klasson*et al*., 2002). Advanced oxidation employs UV light and titanium dioxide as catalyst for degradation of target compounds. This method has a potential advantage over chemical oxidation, since it does not generate waste streams. However, fouling of the UV lamps and/or catalyst may be a major disadvantage of this technique(Klasson*et al*., 2002).

2.5.3 Membranes

Dissolved organic compounds as well as some heavy metals can be removed from hydrocarbon contaminated water by reverse osmosis (RO) membranes(Scurtu, 2009). This technology is more energy intensive than nanofiltration (NF) membranes, since it requires higher pressure for operation. NF-process utilizes membranes with larger pores and therefore, would be less effective than a RO-process for removal of compounds with low molecular weight(Lawrence *et al.*, 1995). However, this technique is sufficient for the removal of BTEX and light phenols. A major drawback reported for both processes (NF and RO) is membrane fouling(Lawrence *et al.*, 1995; OGP, 2002). Other disadvantages of membrane treatment are the short lifetime of membrane material and the relatively low flux rates(OGP, 2002). The concentrate generated in the process must undergo further treatment to separate hydrocarbons from water. The resulting water is recycled upstream of the pre-treatment step. A significant challenge of NF or RO operation is low recovery(Hayes & Arthur, 2004). An alternative to NF and RO is electro dialysis (ED) that utilizes an electric field as driving force for separation. Compared with NF and RO, ED has three major advantages:

- High water recovery;
- Low pressure requirement;
- Resistance to fouling.

The major drawbacks of ED are the inefficiency to remove BTEX and naphthalenes as well as the high-energy costs(Hayes & Arthur, 2004). Membrane distillation (MD) can separate two liquid phases using an evaporation/condensation process. Proper operation of this technique requires that the temperature on the feed/concentrate side of the membrane is higher than on the effluent/permeate side(Scurtu, 2009).

2.5.4 Adsorption

Adsorption technique can be carried out with adsorbents that can or cannot be regenerated. It is more cost-efficient to use adsorption media with regenerative properties, especially if a low-cost on-site regeneration method is available. Activated carbon is an established adsorbent usually employed in municipal and industrial wastewater treatment(Scurtu, 2009). Although the spent carbon was reported to be regenerated on-site by wet air oxidation, it is mainly regenerated off-site(Hayes & Arthur, 2004). Ranck*et al.* (2002) investigated the utilization of a surface modified zeolite (SMZ) to remove BTEX compounds from contaminated water. The spent surface modified zeolite was successfully regenerated by air sparging. However, this regeneration method is problematic, since it transfers the pollutant from the water phase to the gaseous phase (off-gas from air sparging). The off-gas stream requires further treatment before being released into the atmosphere.

2.5.5 Biological Treatment

Removal of dissolved aromatic compounds can also be achieved in aerobic or anaerobic bioreactors. Depending on the nature of biomass growth, biological treatment can be divided in suspended growth (activated sludge) and attached growth (biofilm) processes(Santo *et al.*, 2013).

Attached growth processes utilize carriers, on which microorganisms establish a biofilm, feeding on the organic compounds and nutrients available in water(Scurtu, 2009). Biofilm systems are usually more compact processes and therefore, the footprint and volume requirements would be lower than in the case of activated sludge processes. This is a significant advantage, since stringent footprint and weight requirements are in place on offshore platforms. Different reactor configurations have been used for the treatment of aromatic compounds. The most common technologies are fluidized bed reactors (FBR), moving bed biological reactors (MBBR), submerged fixed film reactors (SFFR) and fixed film activated sludge (FAS)(Pruden*et al.*, 2003). All these types of systems are based on fixed film approach, which can retain larger concentrations of biomass, therefore increasing microbial degradation when operated as continuous processes(Pruden*et al.*, 2003).

2.5.6 Extraction

Extraction technique has recorded outstanding performance in the removal of aromatic compounds from contaminated water. Conventional extraction methods include solvent extraction, soxhlet extraction, ultrasonic agitation/sonication etc. Modern extraction methods include solid phase extraction-SPE, liquid liquid extraction LLE, supercritical fluid extraction (SCF), microwave assisted extraction (MAE) and Membrane Extraction (ME)(Scurtu, 2009). Liquid liquid extraction (LLE) which involves the partitioning of an analyte between an organic solvent and aqueous solution has been widely used for the extraction aromatic compound from aqueous samples. Improved versions of LLE include microscale solvent extraction-MSE, single drop micro extraction-SDE, and Continuous liquid-liquid extraction-CLLE(Scurtu, 2009).

2.6 Principle of Liquid Liquid Extraction.

Liquid liquid extraction stands out amongst other separation techniques because of its ease, simplicity, speedand wide scope. Further advantages of the extraction method overother separation methods lies in the clean separation, simple apparatus, short period of operation and application ofthe method both to trace and macro levels of metals.

Liquid liquid extraction, also known as partitioning, is essentially a technique in which two immiscible liquids are used to isolate compounds from one another base on their difference in solubility. Liquid liquid extraction comprises a step of mixing (contacting) followed by a step of phase separation. Both steps are important criteria in the selection of extraction solvent and modes of operation. Thus, while vigorous mixing is favorable to the transfer of the solute from one solvent to the other, it may also impair the ease of phase separation after equilibrium. The distribution of a solute intwo immiscible phases involves a continuous interchange of solutemolecules across the interface in terms of interfacial film diffusion.

The interfacial tension is one of the fundamental physical properties of liquid/liquid interface. It is defined as the force per unit length that is required to increase the contact surface of two immiscible liquids. The units of the interfacial tension are dyne cm–1. It determines the droplet form and the force retaining the droplet and reflects the interfacial concentration of substances directly. Equilibrium is reached when the chemical potential of the extractable solute is the same in the two phases. Practically, this rule leads to the definition of a "distribution coefficient", K, as follows

$$K = C1/C2 \qquad (2.1)$$

where C1 and C2 are the equilibrium concentrations of the solute in the organic and aqueous phases respectively. The distribution coefficient is an expression of the relative preference of the solute over the solvents.

Complex formation is one of the essential factors,determining the magnitude of the distribution ratio value (Coates, 2006). Thus it can be said that the π complexation between the quaternary salts and the BTX compound leads to the removal of the BTX compounds from the aqueous phase into the DES phase.

2.7Deep Eutectic Solvents (DES)

In 2002, Abbott and co-workers have reported a new generation of ionic solvents. Formation of these solvents occurs through complexation of quaternary ammonium salts with hydrogen bond donors(Abbott *et al.*, 2003). Hydrogen bonding between the halide anion and the hydrogen donating moiety results in a charge delocalization. This in turn results in a deep depression of the freezing point (as compared to the individual components). This effect is most prominent at the eutectic composition of the QAS:HBD mixture. Hence these novel solvents were named Deep Eutectic Solvents. In contrast to traditional IL's (for example Ethyl imidazolium chloride – $AlCl_3$), DES are generally not considered to be ionic liquids. Although they do offer a fully ionic environment, DES unlike IL's can be obtained from non–ionic species (Christopher, 2015). In terms of industrial applications, eutectic solvents have significant advantages over traditional IL's. Many of DES's display physico-chemical properties similar to those of imidazolium based IL's. Their other notable advantages are low price (result of usually cheap components and 100% atom economic synthesis process), inertness towards air and water (thus eliminating the application barrier of $AlCl_3$ based

liquids), low toxicity and biodegradability reported for many of these solvents (Christopher, 2015). Abbott and co-workers had so far identified four types of DES. Three of them are based on the general formula of$R1R2R3R4N^+X^- \cdot Y^-$.

Type I DES

Y = MX → solvent example = ChCl: $ZnCl_2$

Type II DES

Y = MX · n H_2O → solvent example = ChCl: $CrCl_3$× 6 H_2O

Type III DES

Y = R5Z → solvent example = ChCl: $CONH_2$ (where Z = $CO(NH_2)_2$, COOH, ROH)

Type IV DES is composed during the complexation of metal chlorides with different hydrogen bond donors.

MX + HBD → solvent example = $CO(NH_2)_2$: $CrCl_3$ × 6 H_2O

Types I → III formulations patterns share the similar complexation pathway, which can be generally described by the following equilibrium:

cation + anion + complexing agent → cation + complex anion

or

cation + anion + complexing agent → anion + complex cation

2.7.1 Preparation of deep eutectic solvents

Since the first paper on DESs was published in 2003(Abbott. *et al*., 2003), many papers have reported the preparation of DESs as a new type of green solvent. An increasing number of DESs have been prepared by many researchers. DESs can be prepared by mixing a HBA and HBD at a suitable temperature. In 2003, Abbot obtained the first DES by an interaction of choline chloride (melting point 302°C) with urea (melting point 133°C). This combination of solid starting materials produced a eutectic mixture that was liquid at ambient temperature (melting point 12°C for a molar ratio of 2:1) and exhibited unusual solvent properties(Abbott. *et al*., 2003). Hydrogen bonds or even van der Waals forces interfere with the ability of the initial compounds to crystallize. HBAs can shield the charge when in the vicinity of certain HBDs, and a DES will then be obtained(Harris, 2009).

A large number of different compounds have been used in the synthetic process of DESs as HBA and HBD(Tang, 2014). The most common DESs were based on choline chloride (ChCl), carboxylic acids, and other HBD, such as urea, citric acid, succinic acid, and glycerol. ChCl is the most common HBA used extensively in many studies. Recently, an increasing number of different compounds have been used in the preparation of DES as a HBA, such as an inorganic salt ($ZnCl_2$ and $FeCl_3$) and organics (betaine, glucose, citric acid etc.). From 2003, the first DES was obtained at 80°C and stirred until a homogeneous liquid formed, and this synthetic method was then applied in the preparation of DESs(Abbott. *et al*., 2003). In 2009, Gutiérrez prepared a DES by a freeze-drying method. In this method, urea and ChCl at a 2:1 molar ratio with a 5 wt% solute contents were prepared by mixing separate aqueous solutions of urea and ChCl. Subsequently, the mixed solutions were frozen (at 77 and 253 K) and freeze-dried to produce a clear viscous DES. In 2015, Gano*et al*. reported the formation of $FeCl_3$-based DES and $FeCl_3$-based DES and their use in the extractive desulfurization of liquid fuel. More DESs are expected to be discovered in follow-up studies.

2.7.2 Properties of deep eutectic solvents

The properties of DES, as ILs analogues in green chemistry, are a very important factor. The physicochemical properties of DESs are similar to conventional ILs, such as low vapor pressure, but they are cheaper to produce, due to the lower cost of the required raw materials and the simplicity of synthesis. The physical properties of DESs govern their potential applications, and intermolecular interactions between the components affect these properties.

DESs exhibit different physicochemical properties such as freezing point, viscosity, conductivity, and pH, among others, can be prepared. Owing to their promising applications, many efforts have been devoted to the physicochemical characterization of DESs.

2.8Application of Deep Eutectic Solvents in Aromatic Separation and Extraction

Aromatic hydrocarbons are the basic materials in the chemical industry and are applied widely in the production of fibers, plastics, pesticides, medicines, preservatives, explosives, etc. On the other hand, most aromatic hydrocarbons are harmful to human health. From a human health point of view, it is beneficial to remove all aromatic hydrocarbons from chemical products or decrease their amount. BTX are included in the European Union (EU) and the US Environmental Protection Agency (US EPA) priority pollutant list because of their mutagenic and carcinogenic properties(Khezeli*et al*., 2015). Because of the low solubility of BTX, their amount in environmental water samples is traceable. Therefore, a pre-concentration/separation step is needed before the determination of these compounds by chromatographic methods. LLE is a simple, convenient, and widely applicable method for the pre-concentration of analytes from aqueous matrices(Khezeli*et al*., 2015).

Ghanemi*et al*., 2015 applied ChCl/oxalic acid (ChCl/Ox) to the extraction of eight polycyclic aromatic hydrocarbons (PAHs) using a minimum volume of cyclohexane. The extracted PAHs were purified and measured by HPLC with fluorescence detection (FL). The optimized conditions wereChCl/Ox (1:2) at 55°C for 30 min, which is a considerably lower temperature than that used in classical and current methods. The simplicity of the procedure, high extraction efficiency, short analysis time, and use of safe and inexpensive components suggest that the proposed method has high potential for routine trace of PAH. Khezeli*et al*., 2015 used an emulsification liquid–liquid microextraction based on the DES (ELLME-DES) in the extraction of benzene, toluene, xylene (BTX), and seven polycyclic aromatic hydrocarbons (PAHs) from water samples.

Table 2.6. Related Works

S/N	Author	Title	Findings	Remarks
1	Duchez*aet al.*, 2008	Monoaromatics removal from polluted water through bioreactors	Microbial degradation of BTEX was established by aerobic biofilm processes.	Possible pollutant loss through gas stripping. Some VOC were resistant to biodegradation
2	KhirUmaimah,2012	BTX treatment from petrochemical wastewater using Pseudomonas Putida	The optimum condition for Pseudomonas Putida to achieve the highest percentage of BTX removal was established	Only xylene satisfied the required standard. BTX removal was dependent on many parameters
3	Khezeli*et al.*, 2015	Emulsification liquid-liquid micro extraction of BTX and seven PAHs from water sample	A homogeneous solution was formed during extraction. THF was introduced into the homogeneous solution to provide a turbid state and to create phase separation.	Synthesized DES was hydrophilic and thus requires an emulsifying agent.
4	Florindo*et al.*, 2017	Development of hydrophobic DES for extraction of pesticides from aqueous environments	Hydrophobic DESs were prepared for the extraction of pesticides from water. Extraction efficiencies of up to 80% were obtained.	Optimum condition for the extraction was not reported. Solvent regeneration was not studied. Target compound was not BTX
5	Lima*et al.*, 2017	Fixed Bed Adsorption of BTX Contaminants from Monocomponent and Multicomponent Solutions using a Commercial Organoclay	Removal capacity obtained in monocomponentsystems were31.25 % for benzene, 15.27% for toluene and 38.30% for p-xylene. while for Multicomponent system, the highest percentage removal value of 36.657% was obtained for p-xylene.	Low BTX extraction efficiencies

CHAPTER THREE

3.0 EXPERIMENTAL METHODOLOGY

3.1 Chemicals

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

3.2 Materials for the Preparation of Contaminated Water

Benzene, Toluene and Xylenes were acquired from the Department of Chemical Engineering, Ahmadu Bello University (ABU), Zaria. Deionized water was gotten from National Research Institute for Chemical Technology (NARICT), Zaria. Deionized water was used for the preparation of simulated aromatic contaminated water with the target compound (BTX) at a concentration of 9mg/L, 20mg/L and 50mg/L for Benzene, Toluene and Xylene respectively.

3.3 Preparation of DES

The DES was prepared following one of the standard experimental methods of mixing appropriate mass of the compounds (50g/w of TBAB and 53.44g/w of decanoic acid, making a ratio of 1:2), followed by heating and stirring at a particular temperature until a clear homogeneous liquid was formed, as described by Abbott *et al*., 2003. The hydrogen bond donor (HBD), decanoic acid, was first weighed on a weighing balance as well as the hydrogen bond acceptors (HBAs), and the quaternary ammonium salts. The required amount of HBA and HBD were mixed in a beaker in the ratio 1:2. The mixture was then heated and stirred with a magnetic stirrer on an electric hot plate at a temperature of 80°C and 300rpm respectively until a clear homogeneous liquid was formed. The wall of the beaker was rinsed with the

DES inside the beaker to ensure that the entire solid was converted to the liquid phase for maximum yield. After the rinsing, the beaker was further heated to 80 °C until a clear homogeneous liquid was obtained. Afterwards, the DES was maintained and stored at room temperature.

3.4 Liquid-Liquid Extraction Method

Liquid-liquid extractions were conducted using the prepared hydrophobic DESasextractants at 30 °C. Aromatic contaminated water containing BTX was prepared as stated above. A relatively high concentration of BTX (0.08 g/L) in the starting deionized water solution was used in this work. An equal mass of contaminated water and the prepared hydrophobic DES was put in contact and vigorously stirred, at room temperature, and then left to settle for 2hours, to ensure complete separation of the phases. Subsequently, the both top (DES-rich phase) and bottom (water-rich phase) were carefully separated by means of a separating funnel. The concentration of the BTX in the water-rich phase was determined using UV spectrophotometer.

3.5 Determination of BTX Concentration using UV Spectrophotometer

The spectrophotometer was switched on and the lamps were allowed to warm up for an appropriate period of time (3 min) in order to stabilize.Deionized water was used as blank by filling a clean cuvette with the deionized water, and then the outside surface was wiped with a clean cotton wool to remove any fingerprints.

The cuvette was covered to prevent ambient air from entering and then inserted into the spectrophotometer. The absorbance of the blank was measured and recorded, after which it was zeroed to form the basis for the subsequent samples. The wavelength range set for the BTX, as gotten from NIST was within 190-280nm. The blank was discarded and the cuvette was rinsed twice with BTX water sample to avoid dilution. The cuvette was 75% full with the BTX water sample and then inserted in the spectrophotometer in the correct orientation and the absorbance was measured.

The same procedure was repeated three times for each sample to minimize error. The average was taken and the amount of BTX was quantified using the absorbance of different concentration samples to create a calibration curve by plotting a graph of analyte concentration vs absorbance following the Beer's Law

3.6Characterization of Deep Eutectic Solvent

Fourier transform infrared spectroscopy (FTIR) spectra of the synthesized deep eutectic solvent was obtained using attenuated total reflectance (ATR) with spectral range 4000-550 cm^{-1} and resolution: 2.0 (Shimadzu (Europe) 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 carried out using digital viscometer (model RVDV-1), while density was obtained gravimetrically. pH was obtained using (PHS-25CW Benchtop pH meter) while conductivity test was carried out using Rohde &Schwarzhameg (HM8118) resistivity meter.

3.6.1 Density

The empty density bottle was dried and weighed in a weighing balance, after which it was 80% filled with the DES and covered with a stopper. The weight of the density bottle, DES and the stopper was also recorded. The thermometer of the bottle and the stopper were properly aligned and the temperature of the bottle was adjusted in a thermostatic bath. The density of the DES was then calculated from the relationship

Density = Mass of DES / Volume of DES(3.1)

3.6.2 Viscosity

The viscosity of the DES was measured digitally with a model (RVDV-1) viscometer. The tube of the viscometer was filled with the DES until the rotating spindle was completely immersed in the DES. The tube was placed on a hot plate and the viscosity of the DES at respective temperatures (30 to 70 °C) were recorded from the display on the viscometer.

3.6.3 pH

The pH meter was checked and put on the pH measurement mode. The meter was calibrated with a neutral pH buffer solution. Distilled water was used as the buffer solution. The pH electrode was dipped into the DES and stirred with a magnetic bar for 1minute to ensure even distribution. The pH was recorded from the display when the pH reading was stable.

3.6.4 Ionic Conductivity

The conductivity of the DES was calculated from the resulting resistance using the resistance meter (ROHDE & SCHWARZ HAMEG/HM8118 Programmable LCR bridge) at frequency 120Hz.

The resistance was computed using equation 3.2.

$$\rho = \frac{Rs\ A}{d}. \qquad (3.2)$$

Where;

ρ = resistance

Rs = resistivity

A = area

D = diameter

The diameter of the tube containing the DES was evaluated using a Vernier caliper and was used to calculate the area.

Hence, conductivity (σ) $= {}^{1}\!/_{\rho}$(3.3)

3.7Calculation of Extraction Efficiency

After each extraction experiment, the BTX concentration in the raffinate phase was evaluated in terms of the extraction efficiency of the DES.

Thus, the extraction efficiency of the DES is expressed as

$$\text{Extraction efficiency } Y_i (\%) = \frac{C_0 - C_1}{C_0} * 100 \qquad (3.4)$$

Where

$C_0$is the initial BTX concentration in the contaminated water in g/L

C_1 is the final BTX concentration in the raffinate phase in g/L after extraction with DES

3.8Experimental Design

Due to the fact that incorporating all the experimental factors that affect extraction efficiency would lead to a challenging design, this study was limited to only three factors which were time, temperature and DES mass fraction.

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, was obtained from the summation of 2n axial runs with 2^n factorial runs and n_c center point as shown in equation 3.5

$$N = 2n + 2^n + n_c (3.5)$$

Where n is the number of independent variable. Thus, for the tree variables, a total number of 20 experimental runs consisted of eight factorial points, six axial points and six replicate at the center point.

Table 3.1. Range of Independent Variables for Experimental Design

Variables	Range
Temperature (^{o} C)	30 to 70
Time (min)	20 to 120
Solvent mass fraction	0.25 to 0.9

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

4.1 Physical Properties of the Hydrophobic DES

Basic physical properties such as density, viscosity, conductivity and pH of the hydrophobic DES were determined in the temperature range 25-70^{0}C. The aforementioned properties determine the key parameters with respect to liquid-liquid extraction which include phase separation, mass transfer, etc.

4.1.1 Density

The density of DES during extraction plays a vital role in determining solvent diffusion and miscibility with other liquids(Jibril*et al*., 2014). Most hydrophobic DESs exhibit lower density values than water(Florindo*et al*., 2017). The density is dependent on the packing and molecular organization of the DES(Florindo*et al*., 2017). Figure 4.1 shows the density of the hydrophobic DES as a function of temperature. A linear decrease in density was observed with increase in temperature from 25^{0}C-70^{0}C. The linear decreasing effect on the density of the DES was due to probably volume increase produced by increased mobility due to thermal expansion and gains in both vibrational and translational energy of the DES molecules(Jibril*et al*., 2014). Similar findings were established in literature (Abbott *et al*., 2003; Florindo *et al*., 2017; Gano *et al*., 2015; Jibril *et al*., 2014).

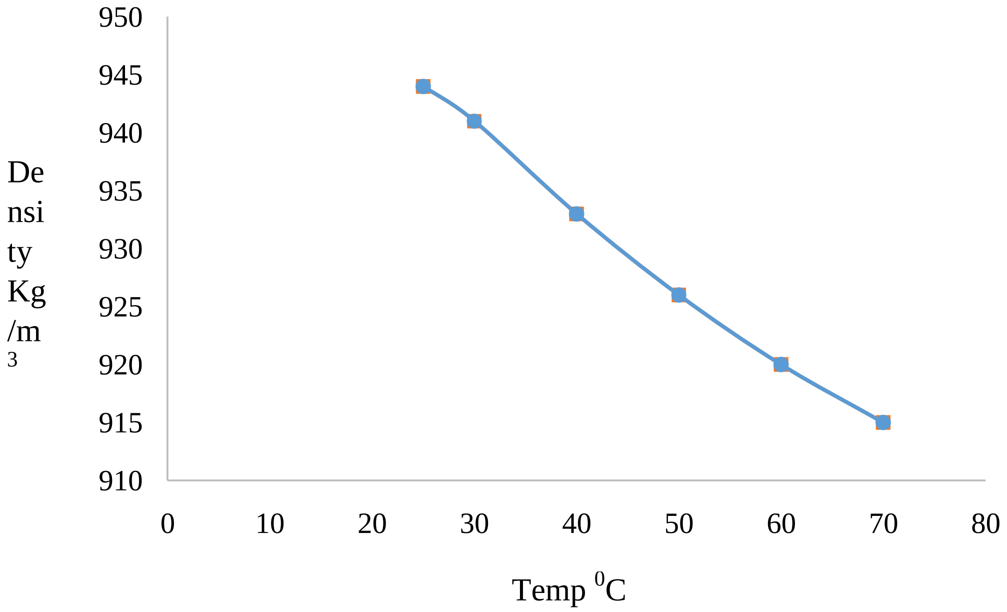


Figure 4.1. Density of The DES as a function of temperature

4.1.2 Viscosity

The viscosity of a solvent is defined with respect to the molecular interaction and electrostatic attraction between the liquid components(Gano*et al*., 2015). Therefore, DES with low viscosities is very essential for extraction applications. At a temperature of 25^0C, the DES showed a relatively high viscosity of 1,636mPa.s. This can be attributed to the extensive hydrogen bond network of the hydrogen bond donor HBD, which results in a lower mobility of free species within the mixture(Ghaedi*et al*., 2017). Moreover, other forces such as electrostatic or van der Waals interactions contributes to high viscosities of DES at room temperature(Ghaedi*et al*., 2017). The viscosity of DESs follows an Arrhenius-like behavior as it decreases with increasing temperature(Jibril*et al*., 2014). With an increase in temperature from 25 - 50^0C, the viscosity of the DES decreased exponentially from 1,636 to 179mPa.sas shown in Figure 4.2. This probably results from the weakening interaction effects in the hydrogen bonding, electrostatic attractions and friction within the DES components with increase in temperature(Jibril*et al*., 2014), and thermal expansion among the DES components is more pronounced within the temperature range of 25 - 50^0C(Dannie *et al*., 2015). Similar findings were observed in related works(Gano*et al*., 2015; Jibril *et al*., 2014).

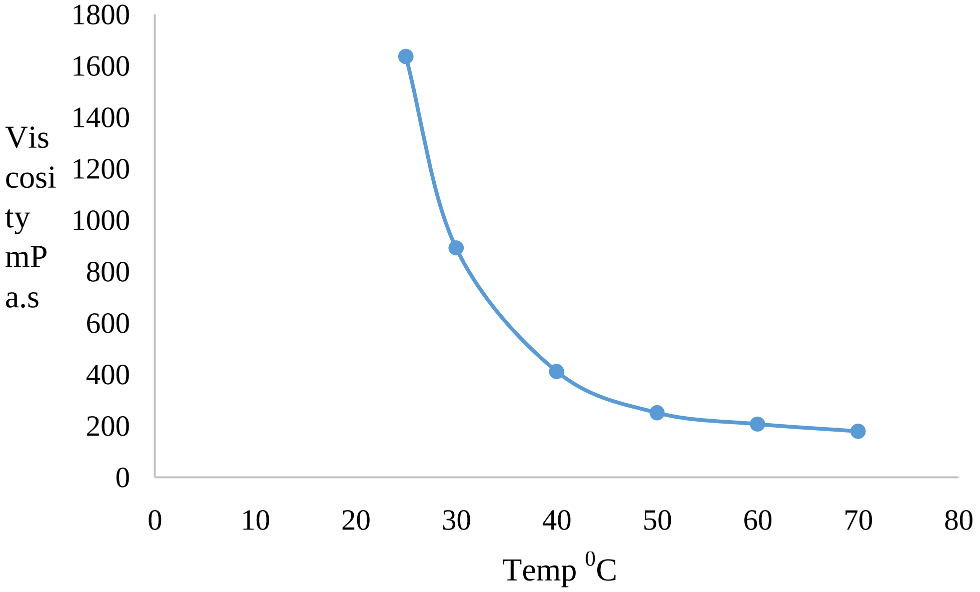


Figure 4.2. Viscosity of the DES as a function of temperature

4.1.3 pH

pH of a solvent is a function of the chemical potential of hydrogen and temperature(Jibril*et al*., 2014). The chemical potential is influenced by the interaction of the ions with other species in the solvent(Jibril*et al*., 2014). The hydrogen chemical potential for DESs is determined by hydrogen bond association with other component, and the stronger the association of DES with another component, the higher would be the extractability of the component by DES(Gano*et al*., 2015). As shown in Figure 4.3, the pH of the DES showed a marginal decreasing effect with increase in temperature from 3.14 at 25^{0}C to 2.73 at 70^{0}C. This may be attributed to fact that as temperature increases, the degree of association increases, causing an increase in molecular vibrations which result in more hydrogen bond association of the hydrogen bond donor HBD with other components. Thus, the chemical potential of hydrogen decreases(Jibril*et al*., 2014) and therefore, pH also decreases.

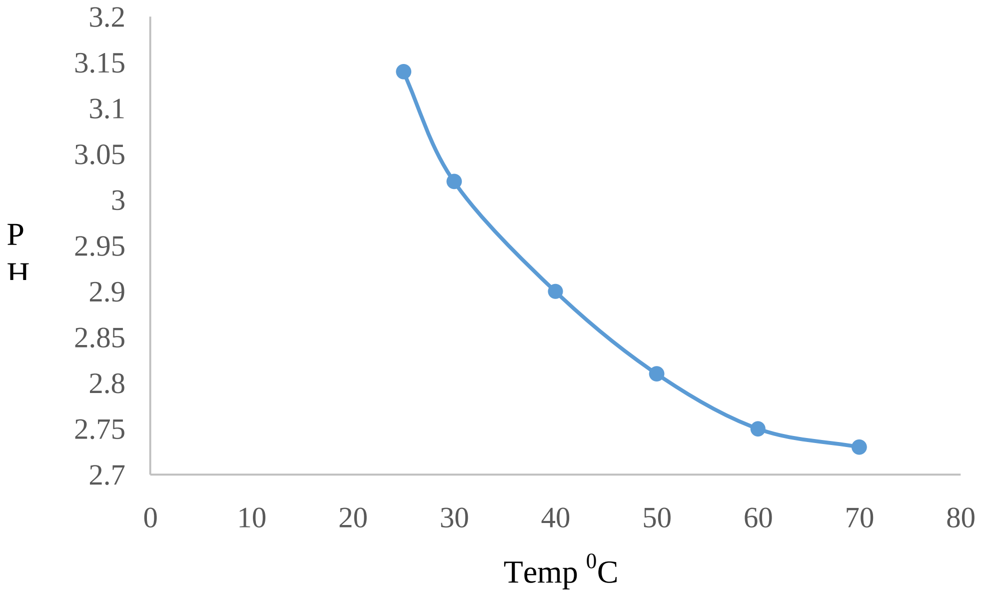


Figure 4.3.pH of the DES as a function of temperature

4.1.4 Ionic conductivity

Conductivity is a property of the material medium that determines the speed of a transport phenomenon. The transport can be of electric charge, heat or of mass. The conductivity of DES is more related to electrochemical application than extraction applications(Gano*et al*., 2015). From Figure 4.4, the conductivity of the DES was observed to increase from 141µS/cm at 25^{0}C to 1,007µS/cm at 70^{0}C. This is due to the fact that increase in temperature will cause a decrease in viscosity and an increase in molecular vibrations as well as mobility of charge carrying species in the DES, thereby increasing its conductivity. Similar observations on temperature effect on conductivity of DES were reported in the literature(Li and Row, 2016).

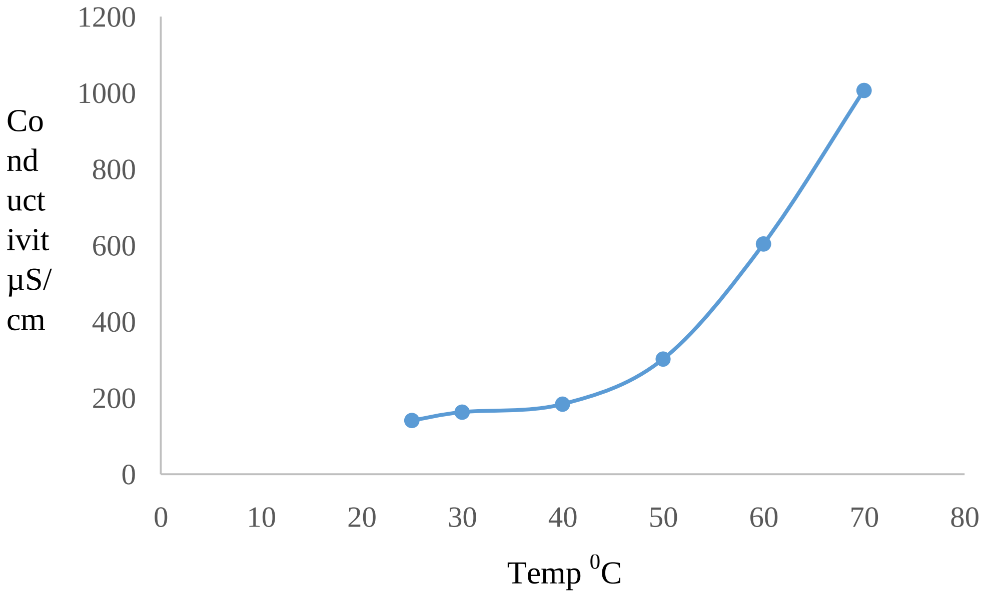


Figure 4.4. Conductivity of the DES as a function of temperature

4.2 Modelling and Optimization using Experimental Design

Response surface methodology (RSM)is a common technique used in design of experiment (DOE) for modeling and optimizing of process operation. The tool was employed to model and optimize the variables affecting the extraction efficiency of the DES using central composite design (CCD). Experimental design and subsequent analysis were carried out with a statistical design software (Design Expert 7.0). Experimental runs were split into blocks of three and carried out consecutively for 3 days in a randomized order. Table 4.1 shows the experimental design matrices and responses for the DES.

Table 4.1. Experimental Design Matrix and Response Results for DES Performance

Run	Blocks	Factor 1 A: time Min	Factor 2 B: temperature ^{0}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

4.2.1 Model development and statistical analysis

Experimental responses obtained in Table 4.1 was subjected to statistical analysis in the design software. From the analysis, the best fit model describing the DES performance in extracting the BTX was quadratic. Equation 4.1represent the quadratic models describing the DES performance in extracting the BTX compound.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i}^{n} \beta_{ii} X^2{}_i + \sum_{i=1}^{n}\sum_{j=1}^{n} \beta_{ij} X_i X_j \qquad (4.1)$$

Y represent the predicted response

X_i, X_j are the coded variables

β_0,β_i,β_{ii},β_{ij} are the constant, linear, square and interaction effects of the variables, respectively.

Model fitness parameters are presented in Table 4.2. From the table, the experimental values showed a reasonable good agreement with the predicted values. 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(Montgomery and Runger, 2010). 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. 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(Montgomery and Runger, 2010)" also signifies the suitability if the model. From Table 4.2, 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.

Table 4.2.Model Fitness Parameter.

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	1114.02	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

4.2.2 Effect of extraction variables on DES extraction

Equations (4.2) – (4.4) below shows variations in the extraction efficiencies of BTX compounds with respect to the studied variables (time, temperature and solvent mass fraction).

$$Y_1 = 61.89 + 2.13A + 3.67B + 23.97C + 0.7AB + 0.15AC - 0.15BC - 1.79A^2 + 0.21B^2 - 4.94C^2 \quad (4.2)$$

$$Y_2 = 62.91 + 2.27A + 2.69B + 25.37C + 0.11AB + 0.28AC - 0.5BC + 0.41A^2 + 0.84B^2 - 3.99C^2 \quad (4.3)$$

$$Y_3 = 69.92 + 1.88A + 2.09B + 25.51C + 0.16AB - 0.41AC + 0.38BC - 1.56A^2 - 0.38B^2 - 7.07C^2 \quad (4.4)$$

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).

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 due to increased mass transfer, because the amount of BTX extracted at a given time depends upon the mass transfer of analyte from the aqueous phase into the DES phase(Gano*et al.*, 2015). Solvent mass fraction was observed to have a more pronounced increasing effect. Hence, extraction performance of the DES is more affected by changes in solvent mass fraction than temperature and time of extraction.

4.2.3 Optimization of extraction variables

Having analyzed some major variables potentially affecting the extraction performance of the DES, optimization was necessary to improve the overall efficiency of the DES.

optimizationwas aimed at minimizing extraction time which signifies the rate at which the extraction is carried out, minimizing extraction temperature which relate to energy consumption and ultimately solvent mass fraction which is the DES requirement for the extraction. The design software was used for optimization of the extraction variables using the desirability function tool(Zhao and Lee, 2001). Experimental verification was conducted at optimum extraction condition and the results showed an insignificant difference in comparison with the optimized results. Based on the reliability of the experimental verification, the optimum conditions obtained was exploited and used for further experiments.

Table 4.3.Optimum Extraction Conditions, Results and Experimental Verification.

Desirability	0.649
Extraction temperature (^{0}C)	25
Extraction time (mins)	60
Solvent mass fraction	0.6
Benzene extraction (predicted, %)	68.1
Benzene verification (measured, %)	67.05
Relative difference (%)	1.05
Toluene extraction (predicted, %)	70.84
Toluene verification (measured, %)	70.23
Relative difference (%)	0.61
Xylene extraction (predicted, %)	77.73
Xylene verification (measured, %)	75.56
Relative difference (%)	2.17

4.3 Extraction Capacity of DES

Reutilization of DES to further optimize the extraction process is a key factor for economic and environmental viability of any extraction process(Gano*et al*., 2015). Therefore, reutilization of the DES in extracting BTX compounds under the optimum condition for four consecutive cycles was conducted. Figure 4.5 presents the extraction efficiency of the DES for four consecutive cycles without regeneration. From Figure 4.5, It can be seen that 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 which limits the mass transfer of the target compounds into the DES, thereby decreasing the extraction efficiencies.

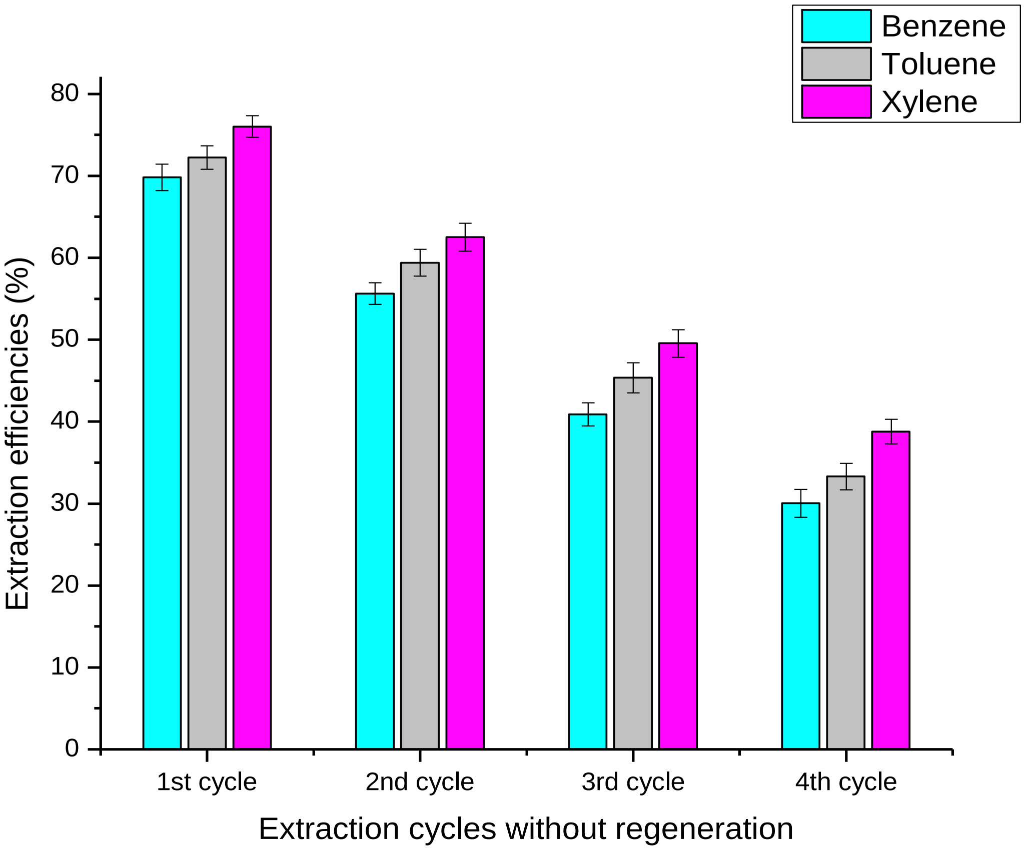


Figure 4.5. DES Extraction Capacity Without Regeneration

4.4 Effect of Starting Concentration

The effect of initial starting concentration of the BTX was examined to ascertain the extent of the DES solvent. After experimenting different initial concentration from 100 to 500ppm 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 Figure 4.6. These obtained results indicate that the initial starting concentration slightly affects the DES extraction efficiencies. Hence, the liquid-liquid equilibrium established between the DES phase and the BTX phase determines the degree of extraction (Florindo *et al*., 2017). Similar findings were reported on some related works(Gano*et al*., 2015; van Osch *et al*., 2015).

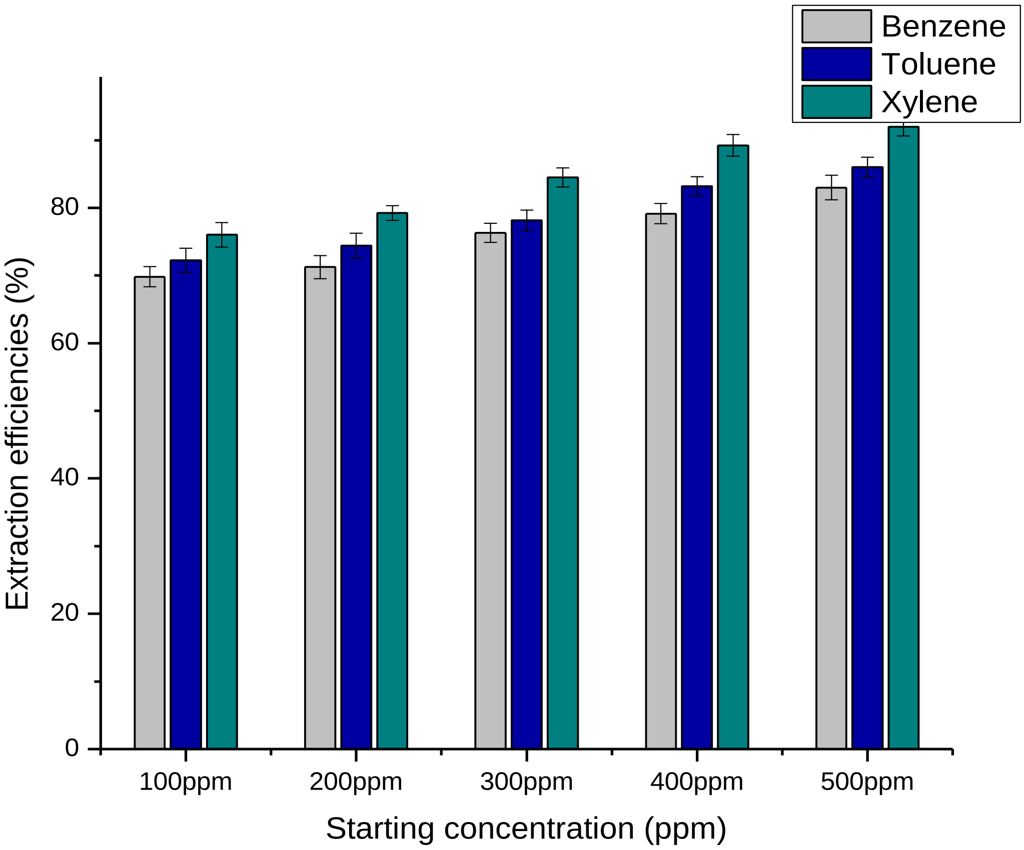


Figure 4.6. DES Performance on Starting Concentration of BTX

4.5 DES Regeneration and Recycling

Regeneration and recycling of DES was carried out at optimum conditions in order to improve the overall efficiency of the whole extraction process. Dannie *et al*, (2015) 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 at high temperatures up to 400 ^{0}C. The solvent was regenerated by heating the spent solvent in a beaker at a temperature of 180 ^{0}C which was within the solvent stability range(van Osch *et al.*, 2015). Heating of the solvent at the above-mentioned temperature (180 ^{0}C) causes the BTX compounds to vapourize, as the temperature exceeds the boiling point temperature of benzene (80.1 ^{0}C), toluene (110.8 ^{0}C) and xylene (144.4 ^{0}C)(Dannie *et al.*, 2015). Thereafter the regenerated solvent was allowed to cool and reused for the next cycle of extraction. Figure 4.7 shows the extraction performances of the regenerated DES for five repeated stages with inter stage regeneration of the solvent respectively. From Figure 4.7, negligible decrease was observed in the extraction efficiencies after successive regeneration cycles. Fourier transform infrared spectroscopy FTIR was conducted on each of the regenerated DES to confirm that the regeneration process did not alter the structure of the DES.

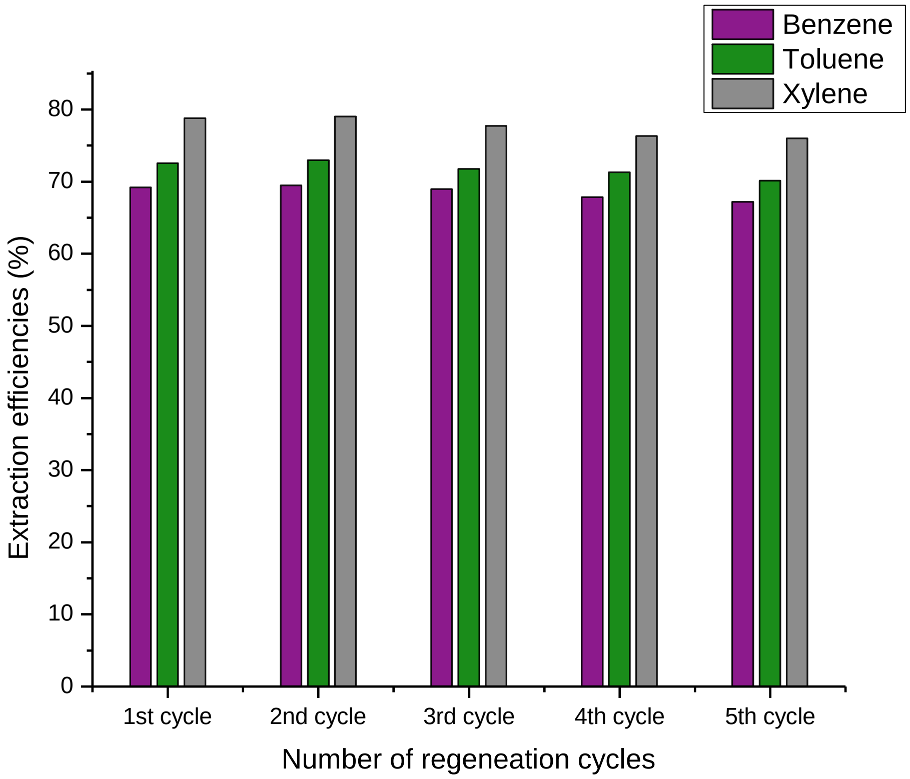


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Figure 4.7. Extraction Performance of Regenerated DES

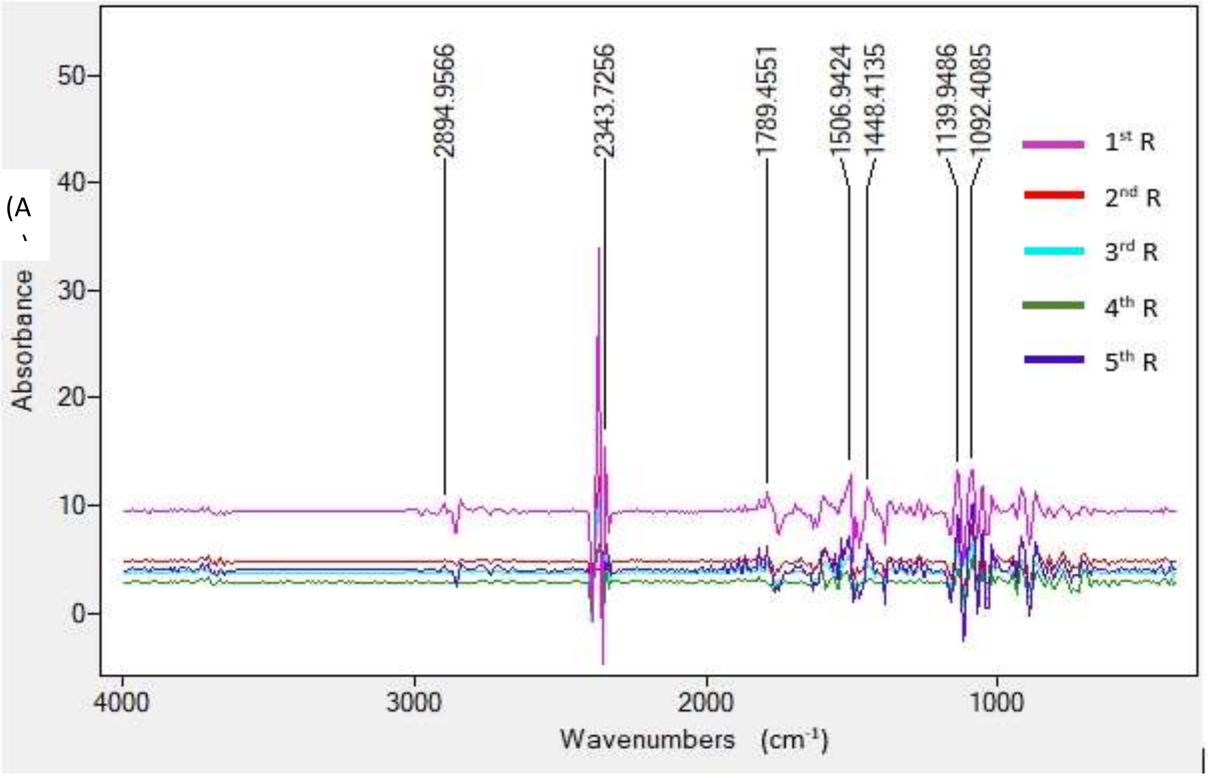


Figure 4.8. FT-IR Spectra of Regenerated DES

The FTIR spectra of regenerated DES for the five successive regenerations are shown in Figure 4.8. Absorption bands at 2895and 1789 cm^{-1} can be ascribed to O-H stretching vibrations and C=O stretching in the COOH of the carboxylic acid respectively(Duchezaet *al*., 2008). sp^{3} C-H bendingin butyl ligands of the quaternary salt could be associated with the peaks appearing at 1507 cm^{-1}(Zhang *et al*., 2012), while absorption bands at 1466 cm^{-1} and between the ranges of 1100-1200 cm^{-1} can be attributed to the N–H bending and C-N stretching vibrations of the quaternary amine present in TBAB respectively(Coates, 2006; Gano *et al*., 2015). This in turn implies that the functional groups present in both the decanoic acid and the TBAB were not destabilized and did not fall outside the required ranges of their absorbance bands.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The work presents a simple inexpensive procedure for the determination of BTX in aqueous matrices using liquid-liquid extraction (LLE) together with UV spectrometer (LLE-UV spec). Synthesized hydrophobic DES between TBAB and decanoic acid was used as extractants in contrast with ionic liquids. DES proffers the advantages of biodegradability, availability, low price, ease of synthesis and low toxicity. LLE was proven to be effective in removal of organic pollutants from water and its suitability in detecting low level of aromatic compounds. RSM technique was successfully used to model and optimize the key variables which the extraction process depends upon. ANOVA and model fitness parameters obtained substantiates the suitability of the developed models. Effect of extraction variables on the DES performance shows that solvent mass fraction has more significant effect than extraction time and temperature. Successive reuse of DES without regeneration for 5 cycles decreased the DES extraction efficiencies of BTX from 69-26% for benzene, 72 -28% for toluene and 76-33% for xylene while starting concentration of BTX was found to have a slightly increasing effect on the extraction efficiencies of the DES from 69.82-79.15% for benzene, 72.23-83.2% for toluene and 76.01-89.24% for xylene.Effective regeneration and reuse of the DES after each extraction was carried out for 5 consecutive cycles at optimum conditions and their respective extraction efficiencies where in the range 67-69% for benzene, 70-72% for toluene and 76-79% for xylene. The hydrophobic DES was therefore effective in eliminating the target BTX compound, as its regeneration and optimization yielded positive results.

5.2 Recommendations

The following recommendations should be considered based on this research work.

1. Polycyclic aromatic hydrocarbons with many rings (4 or more) should be explored to ascertain the effectiveness of this technique on them
2. The use of threecomponents DES should also be explored to enable an extensive application of DES in remediation purposes
3. Application of this technique to real environmental samples should be conducted to test its effectiveness.
4. More researches in the application of hydrophobic DES for environmental remediation should be carried out in Nigeria.
5. Research fund should be made available for environmental remediation researches in Nigeria

REFERENCES

Azev, V S, V E Emel'yanov, and F V Turovskii. (2004). "Automotive Gasolines. Long-Term Requirements for Composition and Properties." *Chemistry and Technology of Fuels and Oils* 40 (5): 291–97.

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*(1), 70-71.

Benson, N. U., Essien, J. P., Asuquo, F. E., & Eritobor, A. L. (2014). Occurrence and distribution of polycyclic aromatic hydrocarbons in surface microlayer and subsurface seawater of Lagos Lagoon, Nigeria. *Environmental monitoring and assessment, 186*(9), 5519-5529.

Christopher., J. Z. (2015). *Electrochemical concentration gradients in Deep Eutectic Solvents* [PhD Thesis].47-75

Coates, J. (2006). Interpretation of infrared spectra, a practical approach. *Encyclopedia of analytical chemistry: applications, theory and instrumentation*. 6-18

Coates, John D, Romy Chakraborty, and Michael J McInerney. 2002. "Anaerobic Benzene Biodegradation—a New Era." *Research in Microbiology* 153 (10): 621–28.

Demeestere, K., Dewulf, J., De Witte, B., Van Langenhove, H. (2007). Sample preparation for the analysis of volatile organic compounds in air and water matrices. *Journal of Chromatograph A*, 1153, 130–144.

Dannie J G P, van Osch, Lawien F Zubeir, Adriaan van den Bruinhorst, Marisa A A Rocha, and Maaike C Kroon. 2015. "Hydrophobic Deep Eutectic Solvents as Water-Immiscible Extractants." *Green Chemistry* 17 (9): 4518–21.

De Nardi, I.R., Zaiat, M., Foresti, E.(2007). Kinetics of BTEX degradation in a packed-bed anaerobic reactor. *Biodegradation*, 18(1), 83–90.

Ducheza, D., Farhadiana, M., Vachelarda, C. d., & Christian., L. (2008). Monoaromatics removal from polluted water through bioreactors—A review. *Water research*, 42(6-), 1325-1341.

Faraji, M. (2019). Novel hydrophobic deep eutectic solvent for vortex assisted dispersive liquid-liquid micro-extraction of two auxins in water and fruit juice samples and determination by high performance liquid chromatography. *Microchemical Journal, 150*, 104-130.

Farhadian, M., Duchez, D., Vachelard, C., & Larroche, C. (2008). Monoaromatics removal from polluted water through bioreactors—A review. *Water research, 42*(6-7), 1325-1341.

Florindo, C., Branco, L., & Marrucho, I. (2017). Development of hydrophobic deep eutectic solvents for extraction of pesticides from aqueous environments. *Fluid Phase Equilibria, 448*, 135-142.

Gano, Z. S., Mjalli, F. S., Al-Wahaibi, T., Al-Wahaibi, Y., & AlNashef, I. M. (2015). Extractive desulfurization of liquid fuel with FeCl3-based deep eutectic solvents: experimental design and optimization by central-composite design. *Chemical Engineering and Processing: Process Intensification, 93*, 10-20.

Garcia, S., Gil, M., Pis, J., Rubiera, F., & Pevida, C. (2013). Cyclic operation of a fixed-bed pressure and temperature swing process for CO2 capture: Experimental and statistical analysis. *International Journal of Greenhouse Gas Control, 12*, 35-43.

Ghaedi, H., Ayoub, M., Sufian, S., Hailegiorgis, S. M., Murshid, G., Farrukh, S., & Khan, S. N. (2017). Experimental and prediction of volumetric properties of aqueous solution of (allyltriphenylPhosphonium bromide—Triethylene glycol) deep eutectic solvents. *Thermochimica acta, 657*, 123-133.

Ghimire, N., & Wang, S. (2018). Biological treatment of petrochemical wastewater. In *Petroleum Chemicals-Recent Insight* (pp. 55-74). IntechOpen.

Gusma ˜o, V.R., Chinalia, F.A., Sakamoto, I.K., Varesche, M.B. (2007). Performance of a reactor containing denitrifying immobilized biomass in removing ethanol and aromatic hydrocarbons (BTEX) in a short operating period. *J. Hazard. Mater*. 139 (2), 301–309.

Gusma ˜o, V.R., Martins, T.H. Chinalia, F.A., Sakamoto, I.K., Thiemann, O.H., Varesche, M.B.A. (2006). BTEX and ethanol removal in horizontal-flow anaerobic immobilized biomass reactor, under denitrifying condition. *Proc. Biochem*. 41 (6), 1391–1400

Gutiérrez, E., Caldera, Y., Fernández, N., Blanco, E., Paz, N., & Mármol, Z. (2007). Thermophilic anaerobic biodegradability of water from crude oil production in batch reactors. *Revista Técnica. Facultad de Ingeniería. Universidad de Zulia, 30*(2).

Ghanemi Kamal, Helalat–Nezhad, Zahra, and Mehdi Fallah–Mehrjardi. 2015. “Dissolution of Biological Samples in Deep Eutectic Solvents: An Approach for Extraction of Polycyclic Aromatic Hydrocarbons Followed by Liquid Chromatography-Fluorescence Detection.” *Journal of Chromatography A* 1394: 46–53.

Harris., C. R. (2009). *Physical properties of alcohol based deep eutectic solvents.* [PhD Thesis, University of Leicester]. 38-80.

Hayes, T., & Arthur, D. (2004, October). Overview of emerging produced water treatment technologies. In *11th Annual International Petroleum Environmental Conference, Albuquerque, NM* (Vol. 201512).

Ishak, S., & Malakahmad, A. (2013). Optimization of Fenton process for refinery wastewater biodegradability augmentation. *Korean Journal of Chemical Engineering* 30(5), 1083-1090.

Jibril, B., Mjalli, F., Naser, J., & Gano, Z. (2014). New tetrapropylammonium bromide-based deep eutectic solvents: synthesis and characterizations. *Journal of Molecular Liquids, 199*, 462-469.

Jo, M.-S., Rene, E. R., Kim, S.-H., & Park, H.-S. (2008). An analysis of synergistic and antagonistic behavior during BTEX removal in batch system using response surface methodology. *Journal of hazardous materials, 152*(3), 1276-1284.

Karlowatz., M., Kraft., M., & Mizaikoff. (2004). *Simultaneous Quantitative Determination of Benzene, Toluene, and Xylenes in Water Using Mid-Infrared Evanescent Field Spectroscopy*.

Khezeli, T., Daneshfar, A., & Sahraei, R. (2015). Emulsification liquid–liquid microextraction based on deep eutectic solvent: an extraction method for the determination of benzene, toluene, ethylbenzene and seven polycyclic aromatic hydrocarbons from water samples. *Journal of Chromatography A, 1425*, 25-33.

Khir Umaimah., B. M. (2012). *BTX Treatment from Petrochemical Wastewater Using Pseudomonas Putida* (Doctoral dissertation, UMP). 5-16.

Klasson, K. T., Tsouris, C., Jones, S. A., Dinsmore, M. D., Walker, A. B., DePaoli, D. W., Yiacoumi, S., Vithayaveroj, V., Counce, R. M., & Robinson, S. M. (2002). Ozone treatment of soluble organics in produced water. *Petroleum Environmental Research Forum Project*. 4-98.

Kponee, K. Z., Chiger, A., Kakulu, I. I., Vorhees, D., & Heiger-Bernays, W. (2015). Petroleum contaminated water and health symptoms: a cross-sectional pilot study in a rural Nigerian community. *Environmental Health, 14*(1), 1-8.

Lawrence, A. W., Miller, J. A., Miller, D. L., & Hayes, T. D. (1995). Regional assessment of produced water treatment and disposal practices and research needs. *SPE/EPA Exploration and Production Environmental Conference.*373-383

Lee, C.K., Chao, H.P., Lee, J.F., (2004). Effects of organic solutes properties on the volatilization processes from water solutions. Water Res. 38 (2), 365–374.

Lima, L. F., de Andrade, J. R., da Silva, M. G., & Vieira, M. G. (2017). Fixed bed adsorption of benzene, toluene, and xylene (BTX) contaminants from monocomponent and multicomponent solutions using a commercial organoclay. *Industrial & Engineering Chemistry Research*, *56*(21), 6326-6336.

Li, X., & Row, K. H. (2016). Development of deep eutectic solvents applied in extraction and separation. *Journal of separation science, 39*(18), 3505-3520.

Llop, A., Pocurull, E., & Borrull, F. (2009). Evaluation of the removal of pollutants from petrochemical wastewater using a membrane bioreactor treatment plant. *Water, air, and soil pollution, 197*(1-4), 349-359.

Lipson, D., Siegel, D.I.(2000). Using ternary diagrams to characterize transport and attenuation of BTX. Ground Water 38 (1), 106–113

Makoś, P., Przyjazny, A., & Boczkaj, G. (2018). Hydrophobic deep eutectic solvents as “green” extraction media for polycyclic aromatic hydrocarbons in aqueous samples. *Journal of Chromatography A, 1570*, 28-37.

Manoli, E., & Samara, C. (1999). Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *TrAC Trends in Analytical Chemistry*, *18*(6), 417-428.

Montgomery, D. C., & Runger, G. C. (2010). *Applied statistics and probability for engineers*. John Wiley & Sons.

Norwegian Oil Industry Association (NOIA). Environmental report (2007) http://www.olf.no/getfile.php/Dokumenter/Publikasjoner/Miljørapporter/080805 OLF (accessed on the 5th of December 2019).

OGP. (2002). Aromatics in produced water: Occurrence, fate and effects and treatment. *Report No., 1*(20-324).

Peng, C., Lee, J. W., Sichani, H. T., & Ng, J. C. (2015). Toxic effects of individual and combined effects of BTEX on Euglena gracilis. *Journal of hazardous materials*, *284*, 10-18
.

Pruden, A., Sedran, M., Suidan, M., & Venosa, A. (2003). Biodegradation of MTBE and BTEX in an aerobic fluidized bed reactor. *Water Science and Technology, 47*(9), 123-128.

Ranck, J Michael, Robert S Bowman, Jeffrey L Weeber, Lynn E Katz, and Enid J Sullivan. 2005. “BTEX Removal from Produced Water Using Surfactant-Modified Zeolite.” *Journal of Environmental Engineering* 131 (3): 434–42.

Rodriguez, C., Van Buynder, P., Lugg, R., Blair, P., Devine, B., Cook, A., & Weinstein, P. (2009). Indirect potable reuse: a sustainable water supply alternative. *International journal of environmental research and public health*, *6*(3), 1174-1203.

Santo, C. E., Vilar, V. J., Bhatnagar, A., Kumar, E., Botelho, C. M., & Boaventura, R. A. (2013). Biological treatment by activated sludge of petroleum refinery wastewaters. *Desalination and Water Treatment, 51*(34-36), 6641-6654.

Scurtu, C. T. (2009). Treatment of produced water: targeting dissolved compounds to meet a zero harmful discharge in oil and gas production. 5-77.

Taiwo, A. M., Olujimi, O. O., Bamgbose, O., & Arowolo, T. A. (2012). Surface water quality monitoring in Nigeria: Situational analysis and future management strategy. *Water quality monitoring and assessment, 13*, 301-320.

Tang, B., Bi, W., Zhang, H., & Row, K. H. (2014). Deep eutectic solvent-based HS-SME coupled with GC for the analysis of bioactive terpenoids in Chamaecyparis obtusa leaves. *Chromatographia*, *77*(3-4), 373-377.

USEPA (US Environmental Protection Agency), (2006). Edition of the drinking water standards and health advisories. EPA 822-R-06-013, Washington, DC.

van Osch, D. J., Zubeir, L. F., van den Bruinhorst, A., Rocha, M. A., & Kroon, M. C. (2015). Hydrophobic deep eutectic solvents as water-immiscible extractants. *Green Chemistry, 17*(9), 4518-4521.

Vogt, F, M Tacke, M Jakusch, and B Mizaikoff. (2000)c. “A UV Spectroscopic Method for Monitoring Aromatic Hydrocarbons Dissolved in Water.” *Analytica Chimica Acta* 422 (2): 187–98.

Wang, Z., Li, K., Fingas, M., Sigouin, L., Menard, L. (2002). Characterization and source identification of hydrocarbons in water samples using multiple analytical techniques. J. Chromatogr. A 971, 173–184.

Zhang, Q., Vigier, K. D. O., Royer, S., & Jerome, F. (2012). Deep eutectic solvents: syntheses, properties and applications. *Chemical Society Reviews, 41*(21), 7108-7146.

Zhao, L., & Lee, H. K. (2001). Application of static liquid-phase microextraction to the analysis of organochlorine pesticides in water. *Journal of Chromatography A*, *919*(2), 381-388.

APPENDIX A

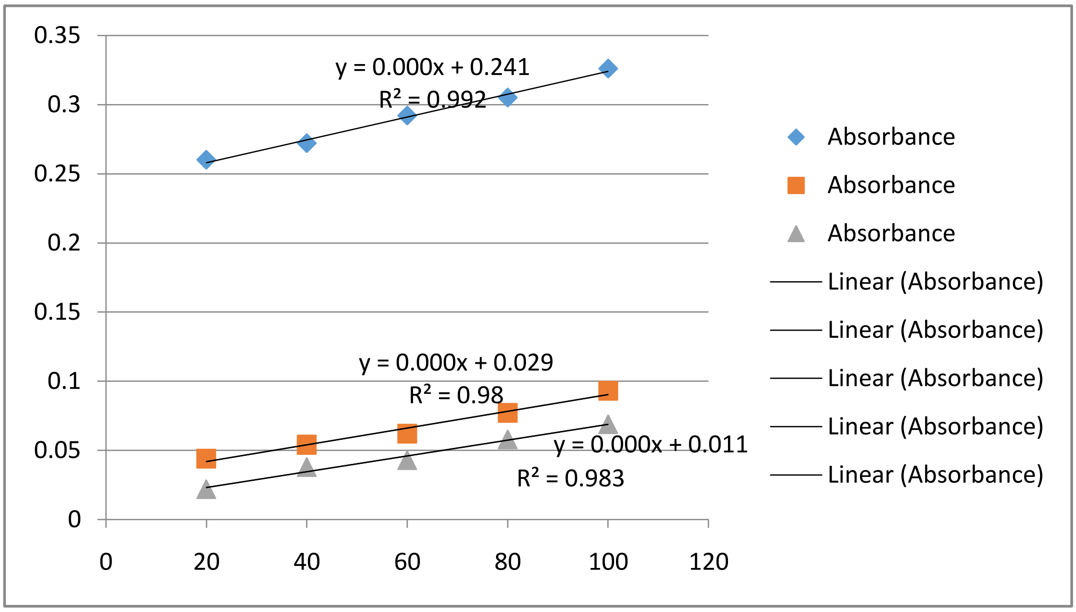


Figure A1. BTX Calibration Curve for 20- 100ppm

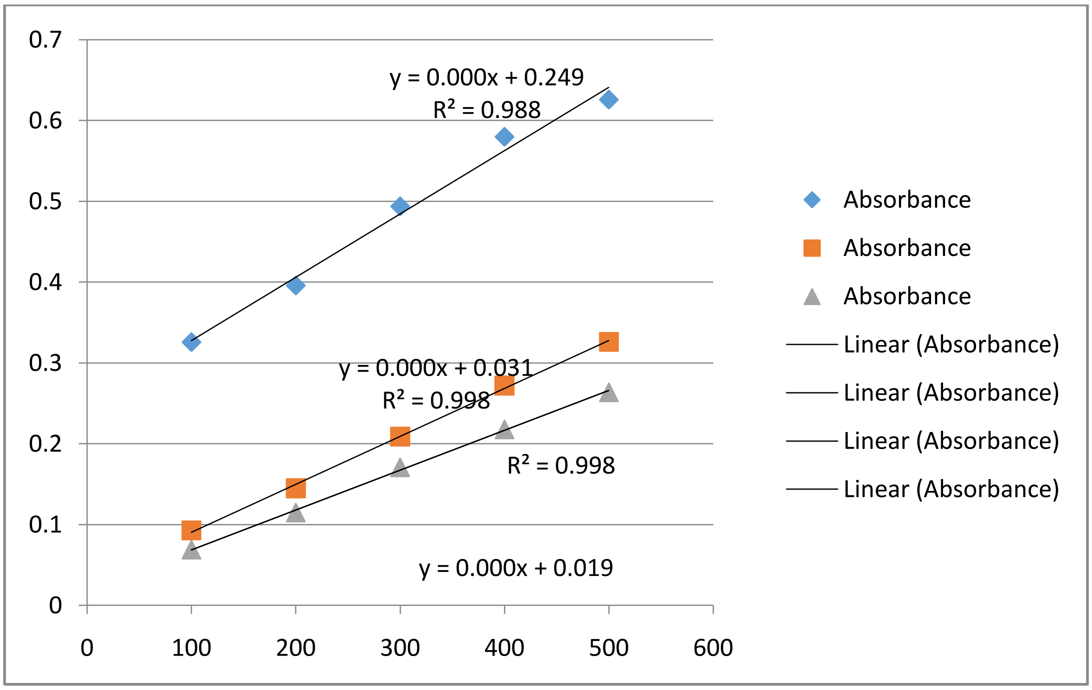
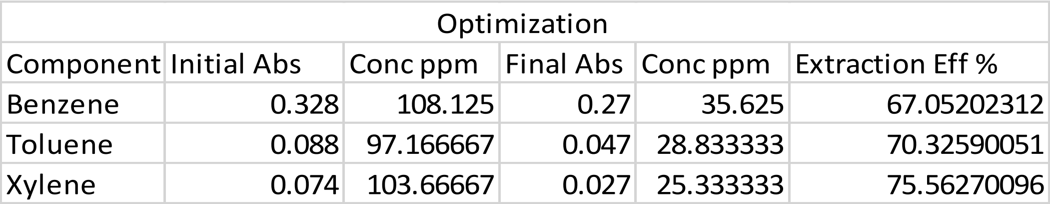


Figure A2. BTX Calibration Curve for 100- 500ppm

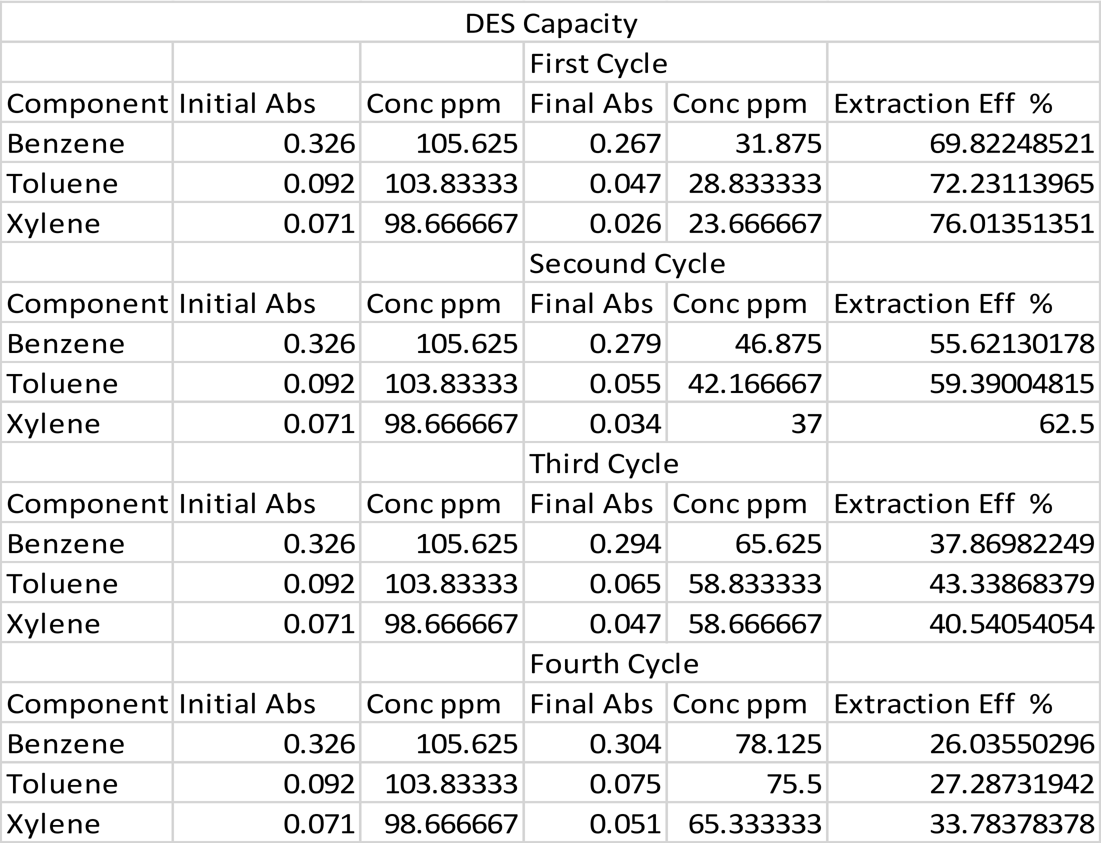
APPENDIX B

Table B1.Extraction Efficiencies Computation for the Optimum Values



Optimization					
Component	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.328	108.125	0.27	35.625	67.05202312
Toluene	0.088	97.166667	0.047	28.833333	70.32590051
Xylene	0.074	103.66667	0.027	25.333333	75.56270096

Table B2.Extraction Efficiencies Computation for the DES Capacity

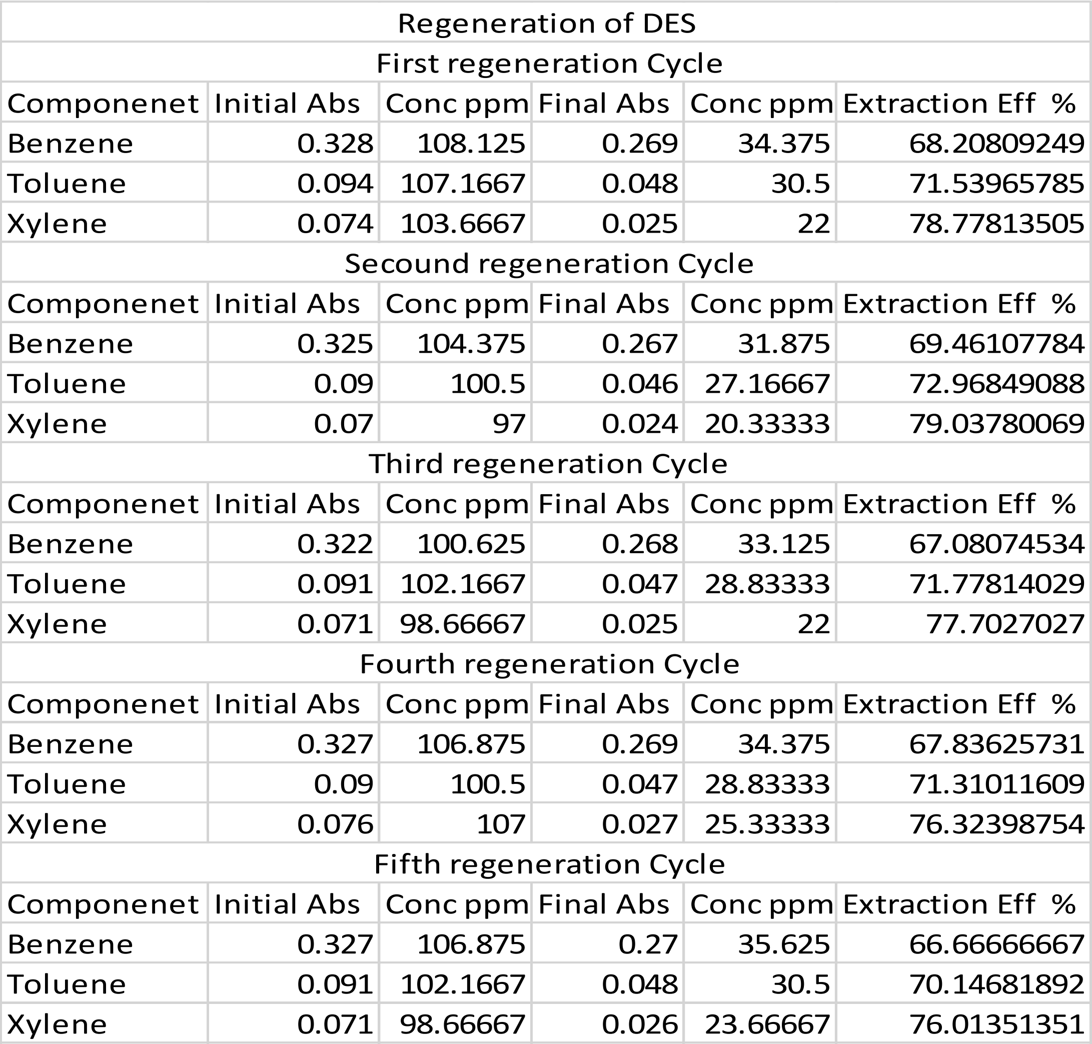


DES Capacity					
			First Cycle		
Component	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.326	105.625	0.267	31.875	69.82248521
Toluene	0.092	103.83333	0.047	28.833333	72.23113965
Xylene	0.071	98.666667	0.026	23.666667	76.01351351
			Secound Cycle		
Component	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.326	105.625	0.279	46.875	55.62130178
Toluene	0.092	103.83333	0.055	42.166667	59.39004815
Xylene	0.071	98.666667	0.034	37	62.5
			Third Cycle		
Component	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.326	105.625	0.294	65.625	37.86982249
Toluene	0.092	103.83333	0.065	58.833333	43.33868379
Xylene	0.071	98.666667	0.047	58.666667	40.54054054
			Fourth Cycle		
Component	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.326	105.625	0.304	78.125	26.03550296
Toluene	0.092	103.83333	0.075	75.5	27.28731942
Xylene	0.071	98.666667	0.051	65.333333	33.78378378

Table B3.Extraction Efficiencies Computation for Different Concentration Levels

Effect of starting Concentration					
Starting Conc (100 ppm)					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.326	105.625	0.267	31.875	69.82248521
Toluene	0.092	103.8333	0.047	28.83333	72.23113965
Xylene	0.071	98.66667	0.026	23.66667	76.01351351
Starting conc (200 ppm)					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.412	203.5	0.296	58.5	71.25307125
Toluene	0.148	194.8333	0.061	49.83333	74.4225834
Xylene	0.123	207	0.041	43	79.22705314
Starting conc (300 ppm)					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.493	304.75	0.307	72.25	76.29204266
Toluene	0.209	296.5	0.07	64.83333	78.13378302
Xylene	0.171	303	0.043	47	84.48844884
Starting conc (400 ppm)					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.575	407.25	0.333	104.75	74.27869859
Toluene	0.273	403.1667	0.081	83.16667	79.37164117
Xylene	0.224	409	0.048	57	86.06356968
Starting Conc (500 ppm)					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.656	508.5	0.334	106	79.15437561
Toluene	0.334	504.8333	0.082	84.83333	83.19577418
Xylene	0.275	511	0.047	55	89.23679061

Table B4.Extraction Efficiencies Computation for Different Regeneration Cycles



Regeneration of DES					
First regeneration Cycle					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.328	108.125	0.269	34.375	68.20809249
Toluene	0.094	107.1667	0.048	30.5	71.53965785
Xylene	0.074	103.6667	0.025	22	78.77813505
Secound regeneration Cycle					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.325	104.375	0.267	31.875	69.46107784
Toluene	0.09	100.5	0.046	27.16667	72.96849088
Xylene	0.07	97	0.024	20.33333	79.03780069
Third regeneration Cycle					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.322	100.625	0.268	33.125	67.08074534
Toluene	0.091	102.1667	0.047	28.83333	71.77814029
Xylene	0.071	98.66667	0.025	22	77.7027027
Fourth regeneration Cycle					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.327	106.875	0.269	34.375	67.83625731
Toluene	0.09	100.5	0.047	28.83333	71.31011609
Xylene	0.076	107	0.027	25.33333	76.32398754
Fifth regeneration Cycle					
Componenet	Initial Abs	Conc ppm	Final Abs	Conc ppm	Extraction Eff %
Benzene	0.327	106.875	0.27	35.625	66.66666667
Toluene	0.091	102.1667	0.048	30.5	70.14681892
Xylene	0.071	98.66667	0.026	23.66667	76.01351351

APPENDIX C

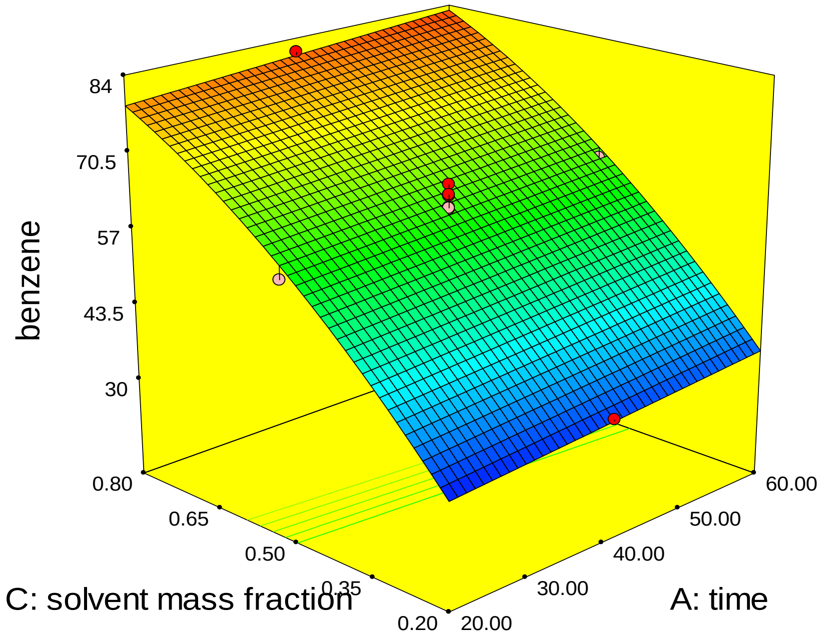


Fig. C1 (I)

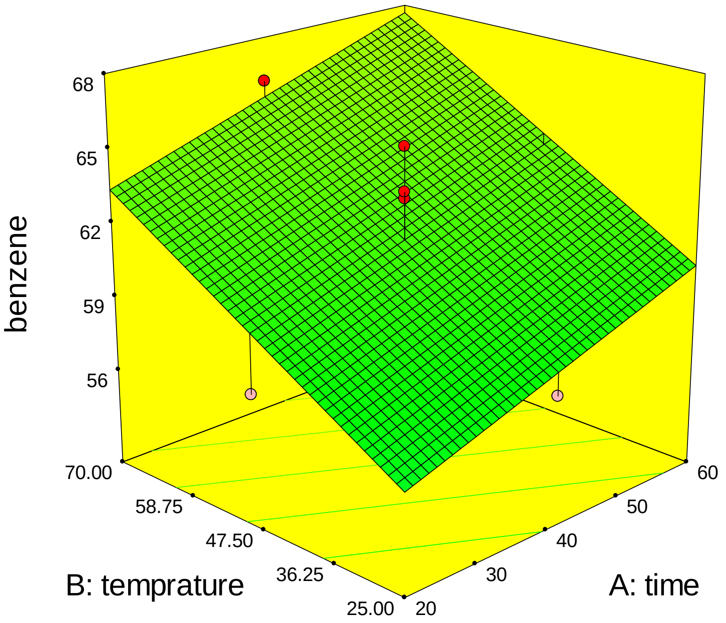


Fig C1 (II)

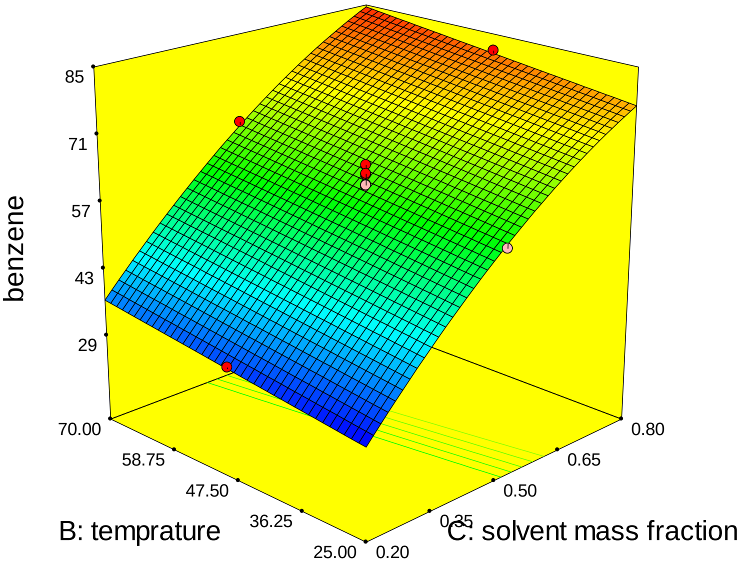


Fig C1 (III)

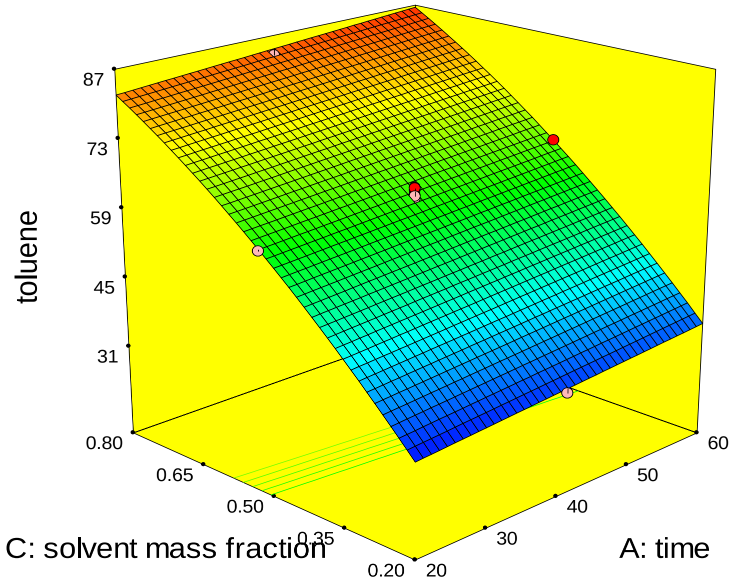


Fig C2 (I)

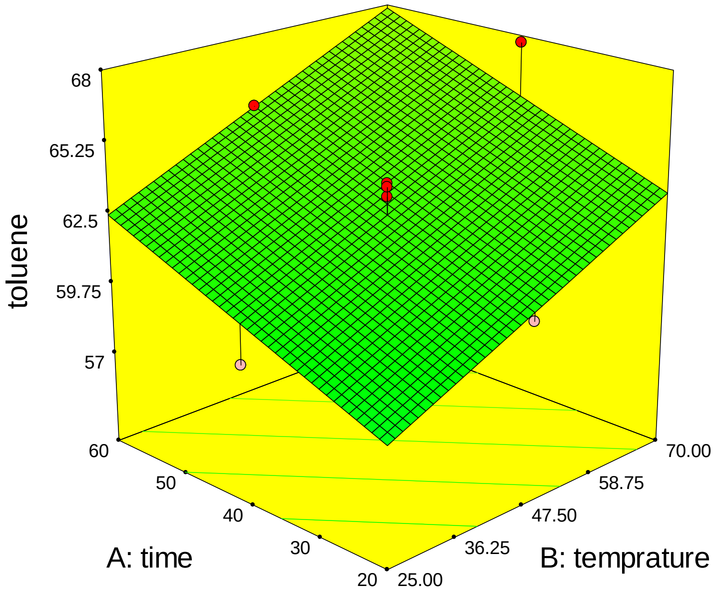


Fig. C2 (II)

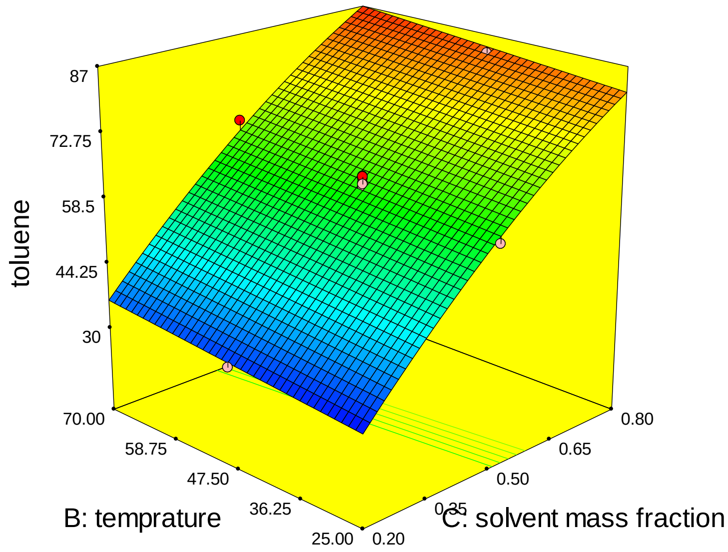


Fig. C2 (III)

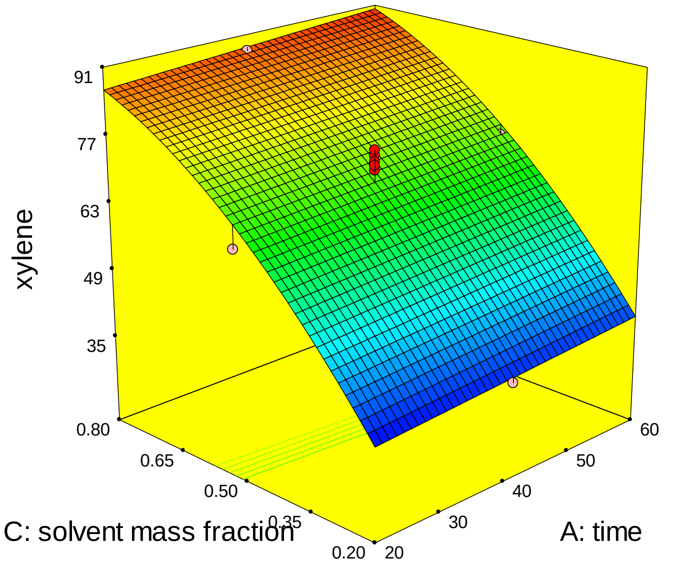


Fig. S3 (I)

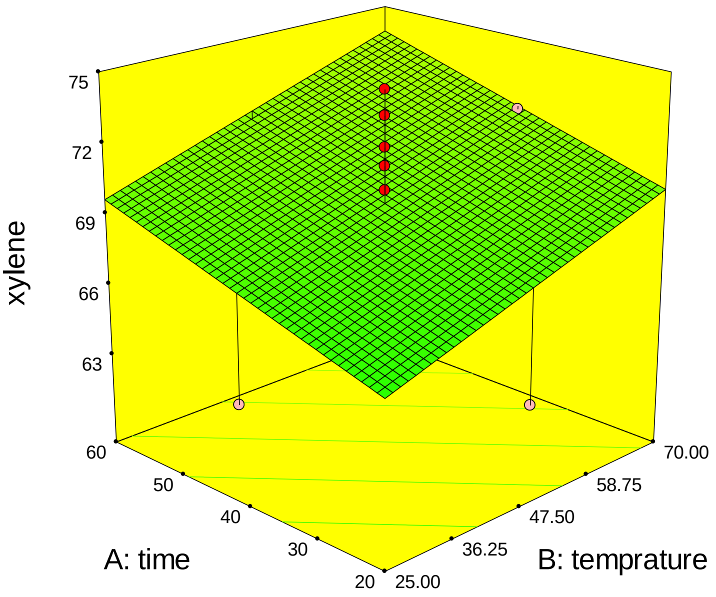


Fig C3 (II)

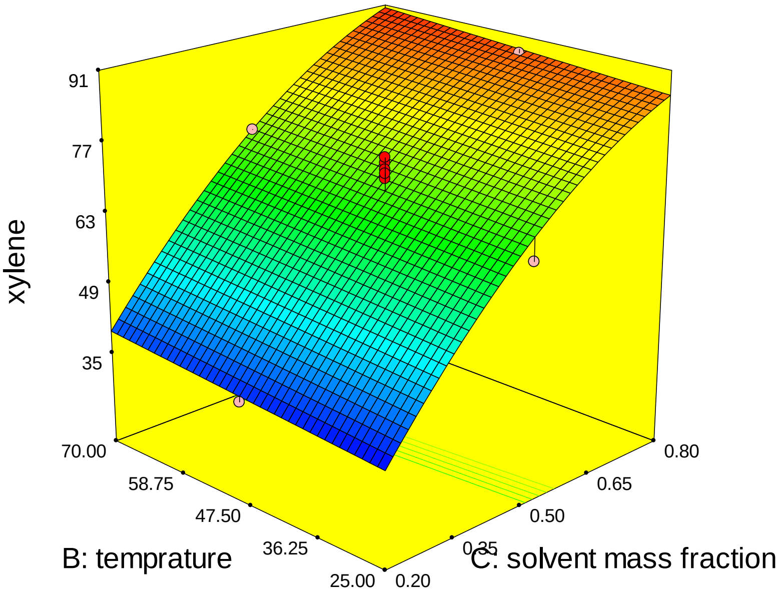


Fig C3 (III)

Figure C1, C2 and C3 (I, II and III) represents theresponse 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.

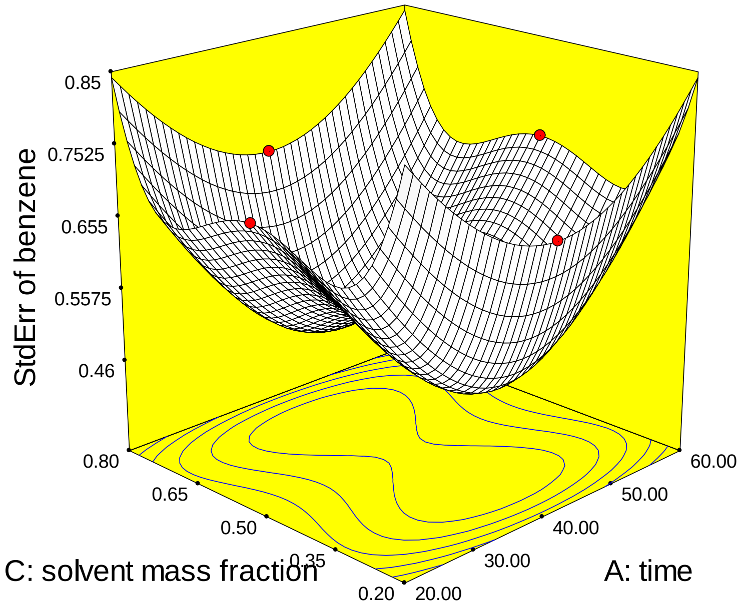


Fig. C4 (I)

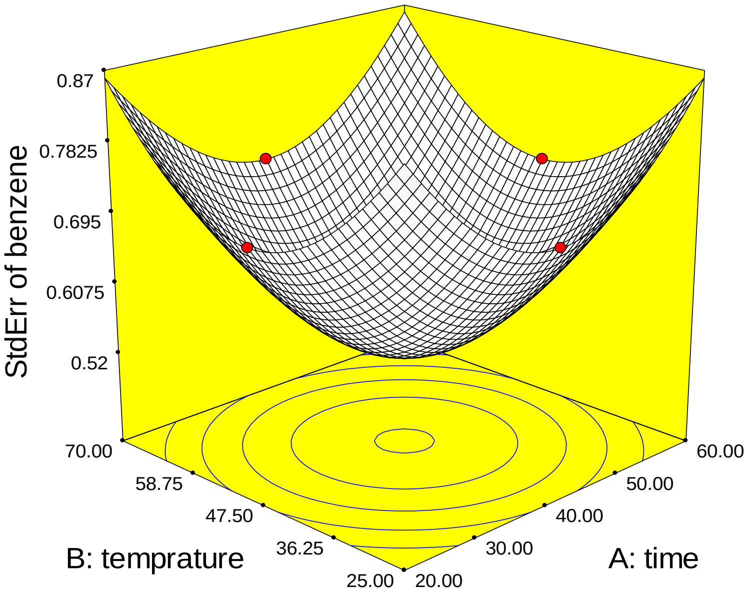


Fig.C4 (II)

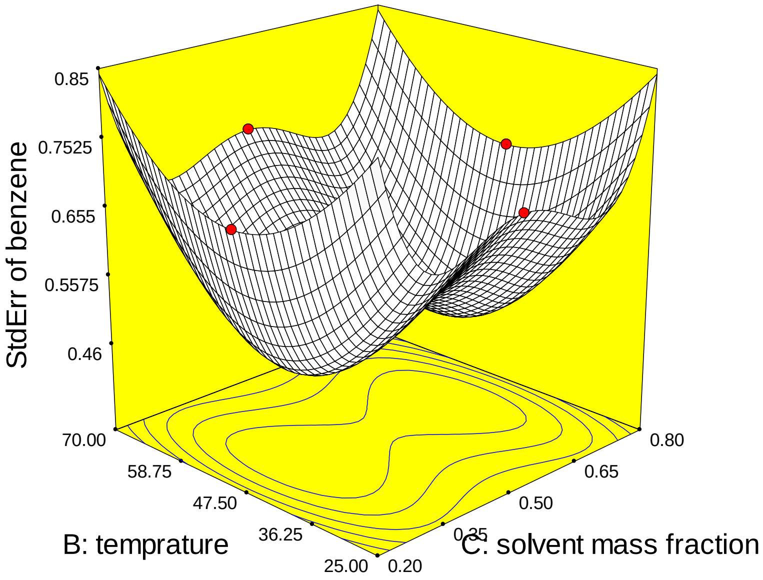


Fig. C4 (III)

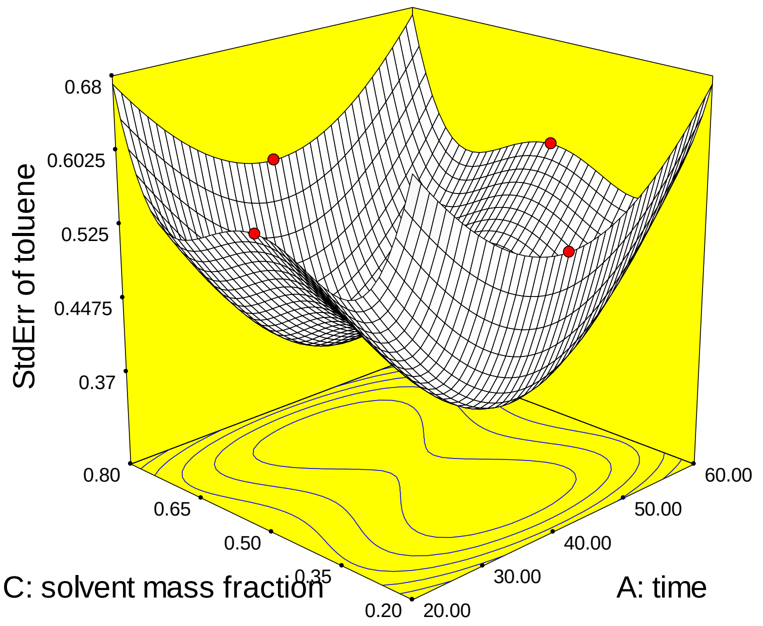


Fig. C5 (I)

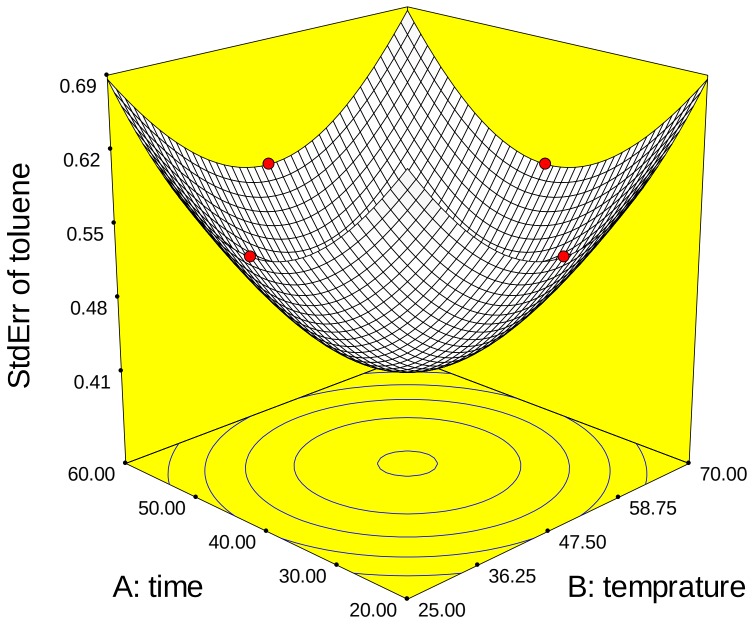


Fig. C5 (II)

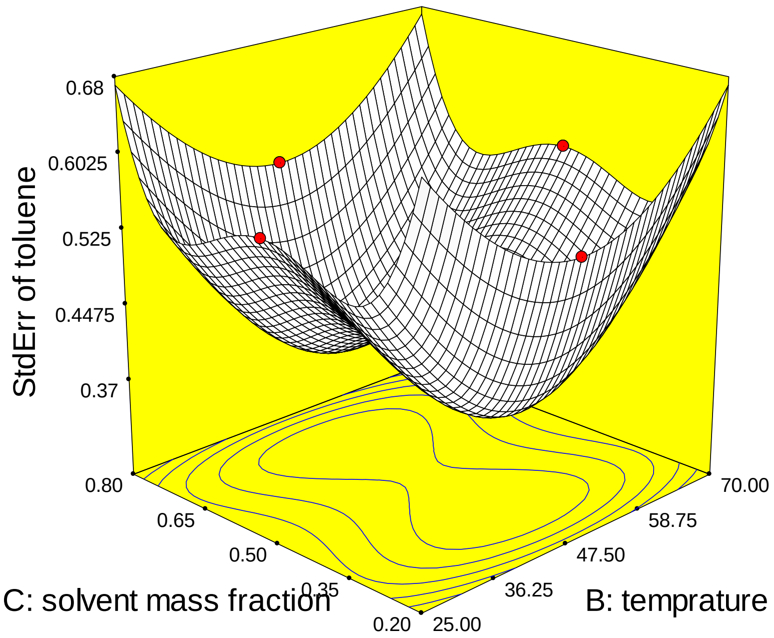


Fig. C5 (III)

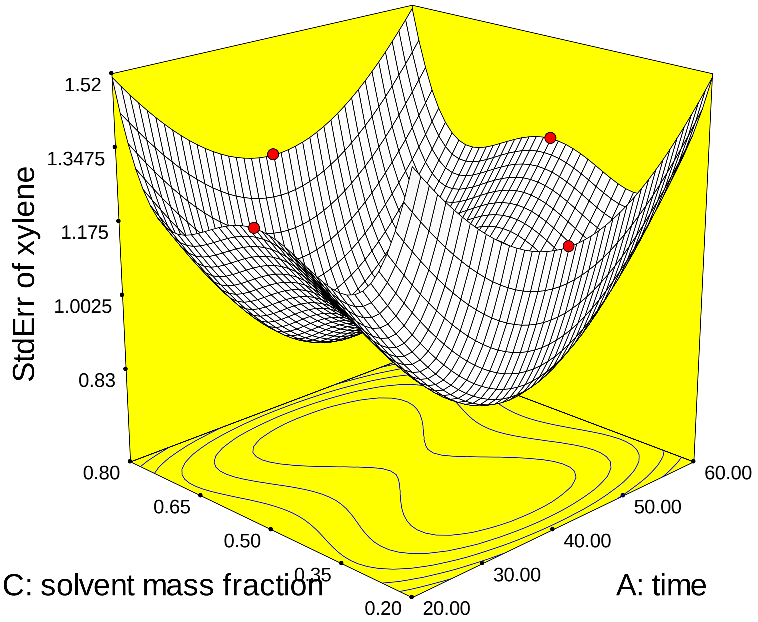


Fig. C6 (I)

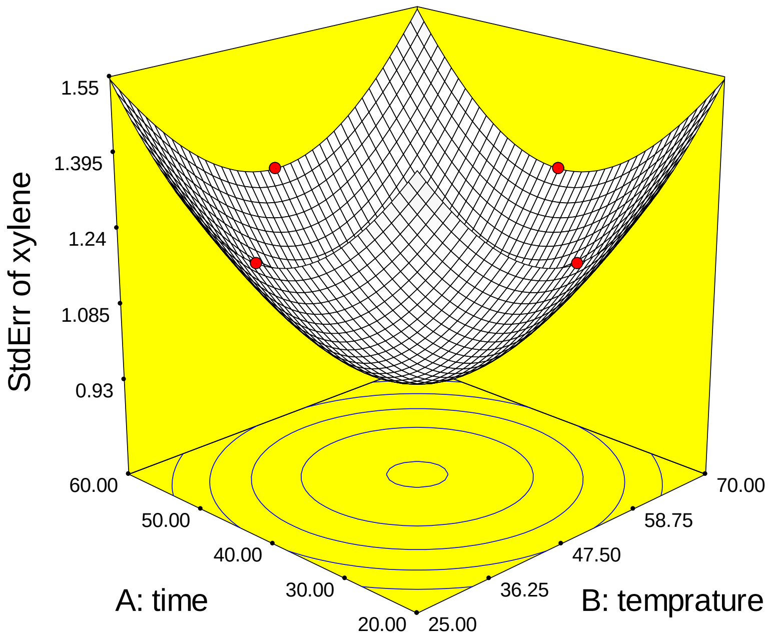

StdErr of xylene
1.55
1.395
1.24
1.085
0.93
60.00
50.00
40.00
30.00
20.00
A: time
25.00
36.25
47.50
58.75
70.00
B: temprature

Fig. C6 (II)

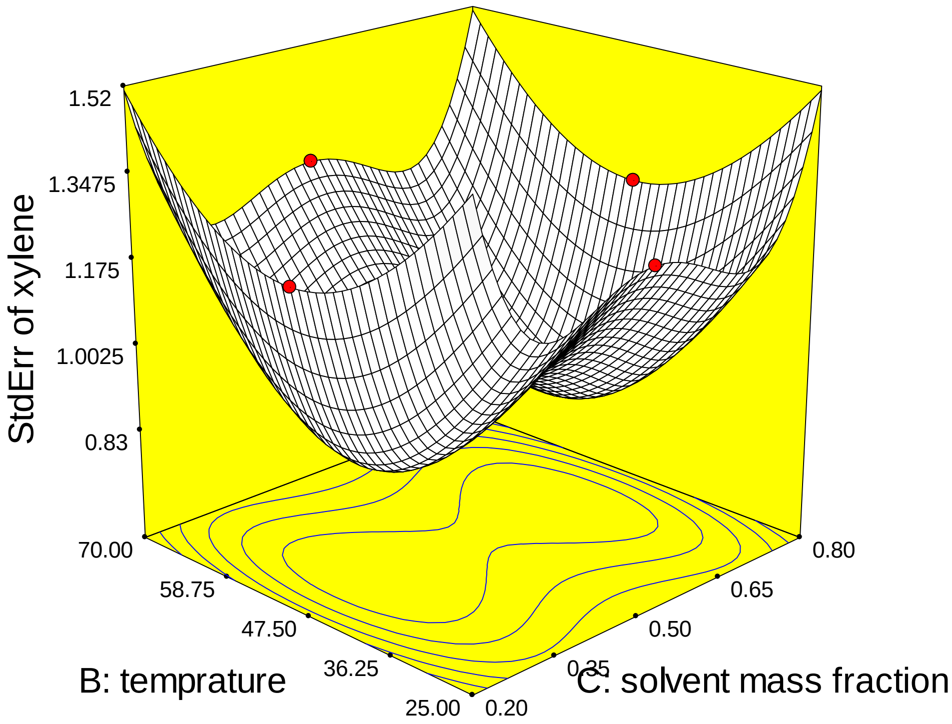

StdErr of xylene
1.52
1.3475
1.175
1.0025
0.83
70.00
58.75
47.50
36.25
25.00
B: temprature
0.20
0.35
0.50
0.65
0.80
C: solvent mass fraction

Fig C6 (III)

Figure C4, C5 and C6 (I, II and III) represents thestandard 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.