

Deep Eutectic Solvent Coupled with High Performance Liquid Chromatography for Extraction of Bisphenols and Phthalates from Selected Freshwater Source in Selangor, Malaysia

(Pelarut Eutektik Dalam Digandingkan dengan Kromatografi Cecair Berprestasi Tinggi untuk Pengekstrakan Bisfenol dan Phthalat daripada Sumber Air Tawar Terpilih di Selangor, Malaysia)

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ABSTRACT

Bisphenol A (BPA) and phthalates (PAEs) are endocrine disrupting chemicals that are abundantly found in the environment. These chemicals leach from polycarbonate plastics and epoxy resins into the environment when exposed to heat. Human exposure to these chemicals causes various health issues; hence, the detection of BPA and PAEs has become more sensitive, and thus it is the most important environmental issue to be reduced due to consequences on human health. This research aimed to determine the optimum parameter of extraction process for BPA and PAEs from water samples by using deep eutectic solvent (DES) coupled with high performance liquid chromatography-ultraviolet spectroscopy (HPLC-UV). Water samples for BPA and PAEs extraction were from various rivers and lakes in Selangor. The solvent used in the DES was a mixture of decanoic acid and tetrabutylammonium iodide. The extraction parameters that have been studied are molar ratio i.e., 1:2, 1:3 and 1:4, extraction time i.e., 10, 15 and 20 min, extraction temperature i.e., 50, 60 and 70 °C and solvent volume i.e., 3, 6 and 9 mL. The optimum molar ratio of solvent and extraction time were 1:2 and 20 min, respectively. The best extraction temperature and volume of solvent with the highest recovery rate were 70 °C and 3 mL. Sungai Kuang shows the highest bisphenol-A concentration of 23.9613 µg/L while Sungai Nada has the highest benzyl-butyl phthalates concentration of 73.6834 µg/L. Sungai Damansara shows the highest dibutyl phthalates concentration of 7.3163 µg/L. In conclusion, data obtained in this research will contribute a new knowledge in the Sustainable Development Goals 6, which is clean water and sanitation because the world is progressing to increase access to clean drinking water and sanitation. There are also some other endocrine disrupting chemicals (EDC) such as disinfection byproducts and pesticides which is more suitable to be extracted from water samples using solid phase microextraction due to low contamination in water. It is very important to research, detect and extract the bisphenol and phthalates from water sources as these pollutants might cause health issues and environmental pollutions which cannot be resolved in future due to its smaller size and its existence in large quantity.

Keywords: Bisphenols; deep eutectic solvent; freshwater; Phthalates

ABSTRAK

Bisfenol A (BPA) dan phthalat (PAEs) adalah bahan kimia yang mengganggu sistem endokrin yang banyak terdapat di alam sekitar. Bahan kimia ini meresap daripada plastik polikarbonat dan resin epoksi ke dalam persekitaran apabila

terdedah kepada haba. Pendedahan manusia kepada bahan kimia ini menyebabkan pelbagai masalah kesihatan; Oleh itu, pengesanan BPA dan PAE telah menjadi lebih sensitif dan merupakan isu alam sekitar yang paling penting untuk dikurangkan kerana kesannya terhadap kesihatan manusia. Kajian ini bertujuan untuk menentukan parameter optimum dalam pengekstrakan BPA dan PAE daripada sampel air dengan menggunakan pelarut eutektik (DES) dianalisis dengan kromatografi cecair berprestasi tinggi- spektroskopi ultraungu (HPLC-UV). Sampel air untuk pengekstrakan BPA dan PAE adalah dari pelbagai sungai dan tasik di Selangor. Pelarut yang digunakan dalam DES ialah campuran asid dekanolik dan tetrabutylammonium iodida. Nisbah molar optimum pelarut dan masa pengekstrakan masing-masing ialah 1:2 dan 10 min. Suhu pengekstrakan dan isi padu pelarut terbaik dengan kadar pemulihan tertinggi ialah 50 °C dan 10 mL. Kepekatan tertinggi BPA dan PAE yang dikesan dalam sampel air ialah 0.0256 mg/L BPA di Sungai Kuang. Kesimpulannya, data yang diperoleh dalam penyelidikan ini akan menyumbang satu pengetahuan baharu dalam Matlamat Pembangunan Lestari 6 (SDG 6) iaitu air bersih dan sanitasi kerana dunia semakin berkembang untuk meningkatkan akses kepada air minuman dan sanitasi bersih.

Kata kunci: Air tawar; bisfenol; phthalat; pelarut eutektik dalam

INTRODUCTION

Plastic is an invention that is widely used in modern society. It has many applications in various industries and daily life. However, plastics have some unbounded chemicals called bisphenol A (BPA) and phthalates (PAEs) which are primarily used as plasticizers that can leach into the surrounding environment, especially when in contact with lipophilic substances or exposed to mechanical and thermal stress (Rayees et al. 2020; Rouse et al. 2021). Phthalate is an organic chemical that is produced by double esterification of 1,2-benzenecarboxylic acid and is added to plastics and many other consumer products because it increases flexibility, longevity, durability and transparency (Rayees et al. 2020). On the other hand, bisphenol A is a molecule which is widely used for packaging as it is malleable and workable in plastic polymers.

The main exposure can occur by ingestion, inhalation, intravenous, and dermal (Catarina et al. 2021). BPA and PAEs contain similar toxicogenomics and health effects (Sher & Steven 2012). Due to high exposure to these contaminants, the migration of these compounds might cause human health risk. One of them is that BPA might disrupt the human endocrine system (Yvette 2021). BPA can imitate and interfere as natural hormones in the body. It can also behave similarly as other hormones. This causes concern because even though it appears in small amount, it may cause developmental and biological impacts as the balance of hormones is very sensitive. Furthermore, exposure of these contaminants might cause cardiovascular problems, such as heart diseases, heart attack, hypertension, and peripheral artery disease (Catarina et al. 2021).

Since frequent exposure of these compounds to humans through food, drinks, and water supplies are in very small amount, the Food and Drugs Administration (FDA) has considered it as safe (Yvette 2021). The main challenge of detecting the EDC is it exist in a small size and in a very low concentration in water samples. Several extraction techniques were used for the extraction of BPA and PAEs from water samples. The conventional methods such as are liquid-liquid extraction (LLE), solid phase extraction (SPE), headspace solid phase microextraction and matrix solid phase dispersion has some challenges in detection of bisphenol and phthalates (Xia et al. 2018).

This technique has challenges in terms of higher consumption of organic solvents and high cost for LLE as well as specialty and skill disadvantages for SPE (Xia et al. 2018). However, DLLME has a low sensitivity, requirement of three solvents, limited choices of solvent and requires additional centrifugation as a part of the technique (Tan et al. 2018). The most suitable extraction technique for BPA and PAE is ultrasonic assisted extraction (UAE) because it is simple, low cost, requires less solvent, with high purity, high selectivity and high extraction efficiency (Panzella et al. 2020). This technique is also suitable for green solvent usage.

DES is a green technology, which is an alternative for conventional organic solvent (Biernacki et al. 2020). DES dominated conventional organic solvent in extraction process in terms of less toxicity, less explosive and less negatively impact humans, animals, and plants. DES is a hybrid system which is made up of two or three cheap and safe components, that may be solid or liquid. The eutectic solvent has a lower melting point than its

individual component. These components are capable of interacting with each other through hydrogen bond interactions to form a eutectic solvent. This hybrid system is made of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). The physicochemical properties of DES are highly depending on various combinations of HBA and HBD which provides unique interactions through hydrogen bonding or anion exchange during extraction process. Most of DES are generally hydrophilic due to hydrogen bonding formation ability between HBD and HBA and thus dissolve rather easily in water.

The hydrophilic compounds in DES can dissolve in the aqueous phase according to their solubility. This will reduce DES stability which causes the hydrophobic DES became an alternative for hydrophilic DES. Hydrophobicity of DES is strongly affected by structure of individual components HBD and HBA. In general, the longer alkyl chain in both HBA and HBD provide to the lower solubility of individual components as well as DES in aqueous phase. Patrycja, Edyta and Jacek (2020) proposed that terpenes and long chain ammonium and phosphonium salts in combination with long chain organic acids indicate the high stability in aqueous samples such as tetrabutylammonium $[N_{4444}]$ chloride with decanoic acid (1:2). To achieve a higher extraction yield, factors that affect efficiency of the extraction process need to be considered, such as HBA/HBD ratio of eutectic solvent, extraction temperature, volume of solvent and extraction time (Yongjing et al. 2019).

This research aims to determine the optimum parameter of ultrasonic-assisted extraction process to extract BPA and PAEs by using DES from different water samples from selected rivers and lakes in Selangor which is simple, cost saving and rapid. Decanoic acid and tetrabutylammonium iodide-based DES is used to implement the concept of green chemistry. The extraction temperature, time, solvent molar ratio and volume of solvent are chosen and still crucial to be analyzed because these parameters are the main factors that affect the extraction yield (Liu et al. 2022; Shang et al. 2018). The optimization was conducted with

different parameters, such as solvent molar ratio at 1:2, 1:3 and 1:4, extraction time of 10 min, 15 min and 20 min, extraction temperatures at 50 °C, 60 °C and 70 °C and different volumes of solvent at 3 mL, 6 mL, and 9 mL. HDES uses a high volume of chemicals without dilution or minimizer will cause to negative effect to the environment and human health. Therefore, only three points are chosen to also minimize the usage of HDES and its negative effects towards environment, human health as well as to save chemical cost.

METHODS AND MATERIALS

CHEMICALS AND REAGENTS

Tetrabutylammonium iodide, decanoic acid, bisphenol A (BPA), benzyl butyl phthalate (PAE 2), and dibutyl phthalate (PAE 3) were purchased from Sigma-Aldrich, Germany. Figure 1 show the chemical structure of tetrabutylammonium iodide (Dejanovic 2018; Naik et al. 2019).

METHODS

The extracted BPA and PAEs from the final extraction process were analyzed with HPLC-UV. HPLC Brand Agilent, USA was used to measure concentrations of BPA and PAEs in the water samples. Waters C18 Column of 5 μ m was used for sample preparation at wavelength between 210 and 280 nm. Meanwhile, 10 μ L of sample was injected into the system for analysis in isocratic elution at 1mL/min under room temperature. Analysis was carried out for 17 min with a mobile phase which consisted of water/acetonitrile (40:60, v/v).

WATER SAMPLE COLLECTION

Water samples were collected using mineral water bottles from selected rivers and lake in Selangor, Malaysia as shown in Table 1. Figure 2 shows the location of selected sample area in google map. The samples were kept in a freezer until the extraction was carried out. Table 1 shows the information about the collected samples.

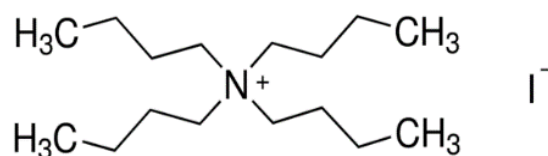


FIGURE 1. Chemical structure of tetrabutylammonium iodide

The control sample is prepared by adding 10 ml of stock solution of each kind of phthalates and bisphenols to form 10 ppm of standard solution which is diluted by 10 mL of distilled water.

DEEP EUTECTIC SOLVENT PREPARATION

Decanoic acid (HBD) and tetrabutyl ammonium (N_{4444}) iodide (HBA) were weighed accurately at 1.108 g and 1.033 g, respectively, to obtain a molar ratio of 1:2 and mixed in a beaker. Due to lack of availability [N_{4444}] iodide was chosen as HBA instead of [N_{4444}] chloride. The decanoic acid is initially in crystalline state and will melt quickly when it is withdrawn from container due its melting point is 31.6 °C at room temperature which makes it hard to handle. Therefore, solid crystalline of [N_{4444}] iodide which is easy to handle should be added to the decanoic acid in the beaker. The mixture is then heated at a temperature of 70 °C using heat source until a homogenous yellow liquid was observed (Wang et al. 2020) as shown in Figure 3 (Ling & Hidanoto 2022). The sample should be added to the HDES for extraction process very quickly as the HDES starts to solidifies when the temperature decrease.

PROCEDURE OF ULTRASONIC-ASSISTED EXTRACTION (UAE)

Figure 4 shows the illustration of procedure of ultrasonic-assisted extraction (Phongsirirux, 2017). Water samples of 5 mL were added to the prepared solvent. The beaker which contained a mixture solvent and water sample was placed in a water bath of sonicator. The sonicator was used to generate an ultrasonic effect to the solvent that contained the sample. After 10 min, the beaker was withdrawn from sonicator when a mixture of two layers was observed, as shown in Figure 5. The cloudy layer was separated from the mixture and stored in a vial for further analysis.

This procedure was repeated for optimization of extraction process at different parameters, such extraction temperature at 50 °C, 60 °C, and 70 °C, extraction time of 10 min, 15min, and 20 min, volumes of solvent at 3 mL, 6 mL, and 9 mL and molar ratio of solvent at 1:2, 1:3, and 1:4. Since HDES uses a high volume of chemicals without dilution or minimizer, it will give negative impact to the environment and human health. Therefore, only three points are chosen for optimization to reduce the negative effects towards environment and human health as well as to save chemical cost.

TABLE 1. Information of water samples

Location of water sample	Sample label	Sampling date
Sungai Damansara	SD	3rd August 2022
Sungai Kuang	SK1	3rd August 2022
Sungai Kuyoh	SK2	4th August 2022
Sungai Langat	SL	4th August 2022
Sungai Nada	SN	4th August 2022
Sungai Timbun	ST	3rd August 2022
Tasik Bukit Jalil	T1	4 th August 2022
Tasik Seksyen 9 Kota Damansara	T2	4 th August 2022
Tasik Kelana Jaya	T3	3rd August 2022
Tasik Biru Sungai Buloh	T4	3 rd August 2022

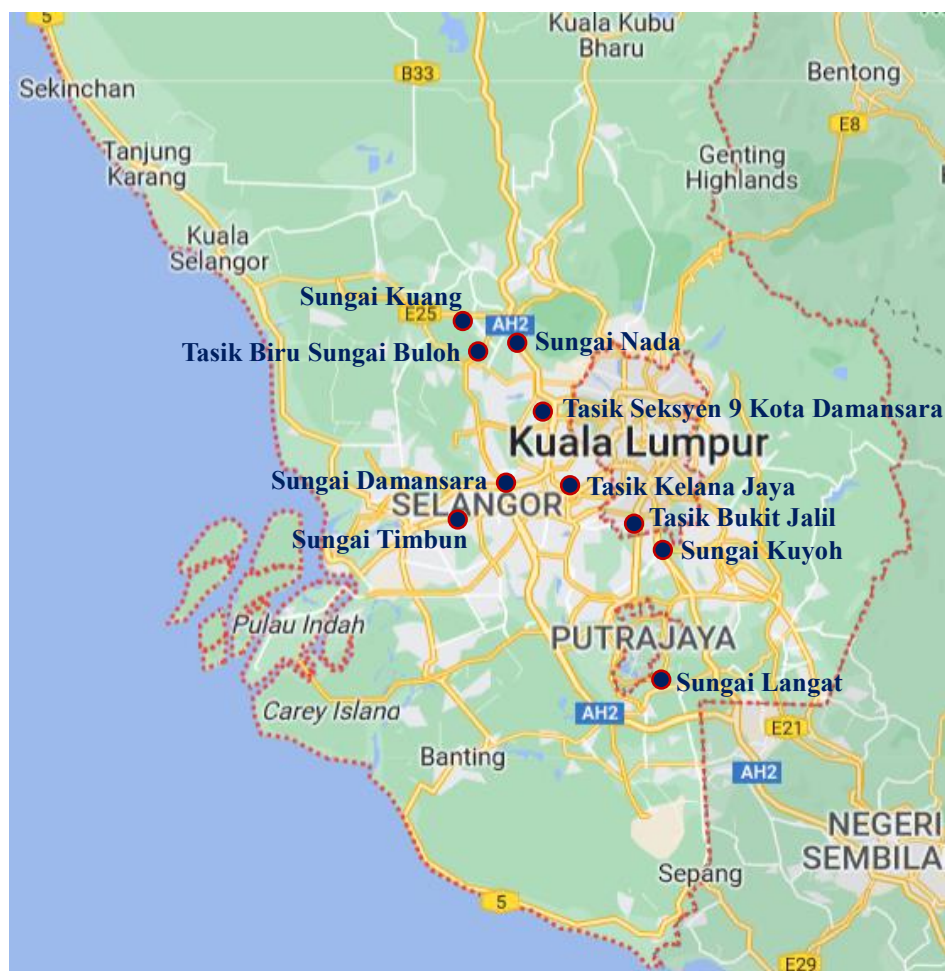


FIGURE 2. Location of samples in google map

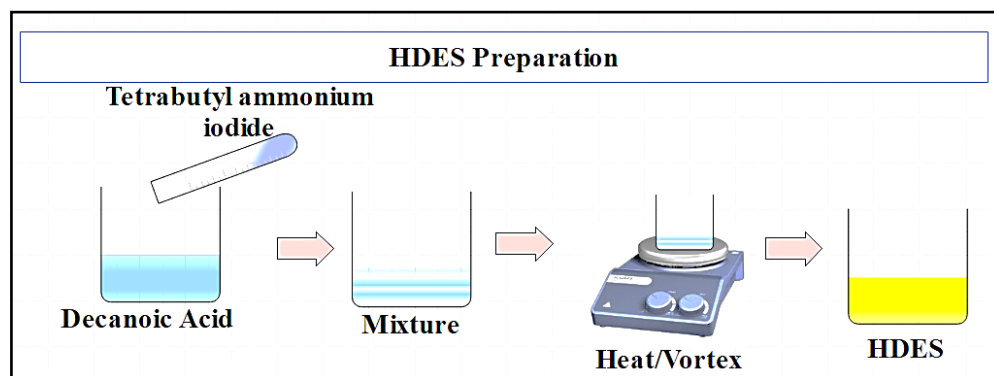


FIGURE 3. General procedure of HDES preparation

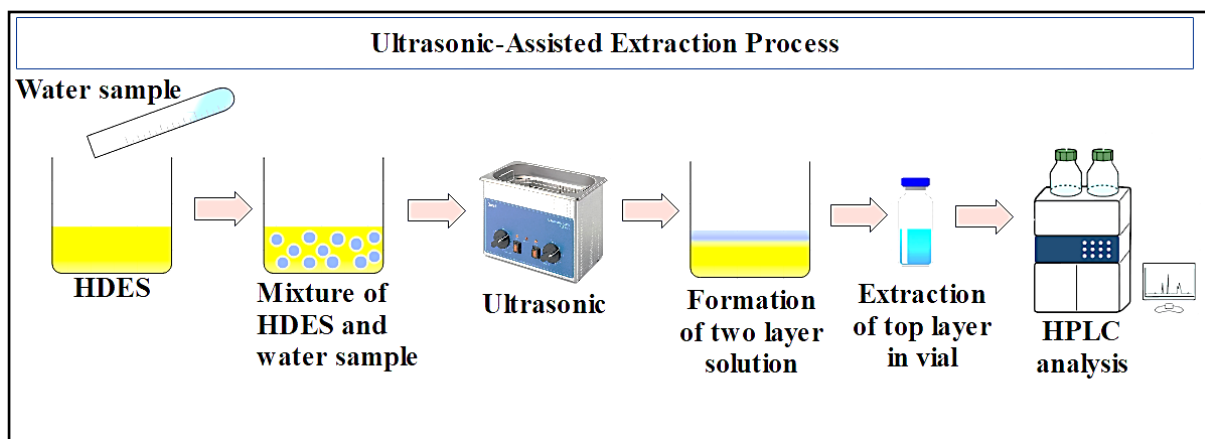


FIGURE 4. General procedure of deep eutectic solvent extraction process



FIGURE 5. Formation of two layers of deep eutectic solvent

RESULTS AND DISCUSSION

CALIBRATION CURVE

The linearity of the method was analyzed by constructing a calibration curve. A set of dilutions of 2, 4, 6, 8, and 10 ppm were prepared from standard solution of 100 ppm to obtain a calibration curve. Figure 6 shows the calibration curve based on the peak area versus the respective concentrations of analytes based on data in Table 2. In addition, equation of the best fit line, the gradient and correlation coefficient of trendline (R^2) is displayed on the graph. The LOD and LOQ value has been calculated

for concentration range 2-10 mg/L which has R value of 1 for all the analytes as well as LOD and LOQ range is between the proposed value by Patrycja, Edyta and Jacek (2020). This shows that this method is sensitive to the analytes at the best conditions.

OPTIMIZATION OF DEEP EUTECTIC SOLVENT
EXTRACTION PROCESS MOLAR RATIO OF SOLVENT

Different molar ratios were analyzed to determine the optimum molar ratio for BPA and PAEs extraction process, such as 1:2, 1:3, and 1:4 as shown in Table 3.

TABLE 2. Information of calibration curve for each analyte

Analytes	Concentration Range (mg/L)	Slope	y-intercept	R^2	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
BPA	2-10	539.46	332.67	1	0.45	1.36
PAE 2	2-10	993.64	2892.10	1	0.87	1.64
PAE 3	2-10	512.11	2395.8	1	0.33	1.00

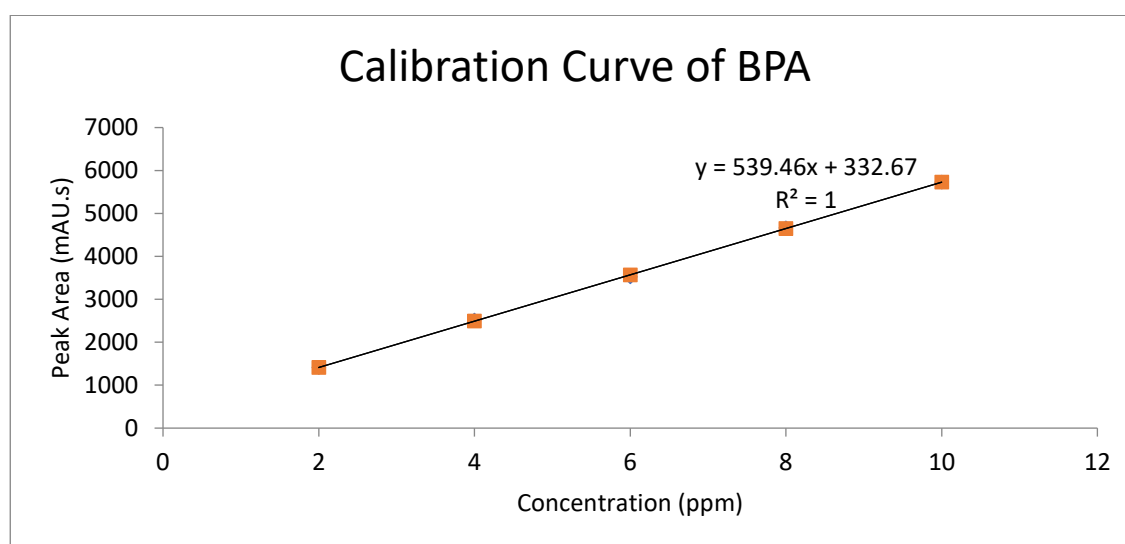


FIGURE 6. Calibration curve of BPA

Figure 7 shows the results for molar ratio 1:2 at wavelength 210 μm . Among the three ratios, 1:2 showed the highest peak area of 97.82 %, followed by ratio 1:3 with 69.31% and the lowest peak was indicated by ratio of 1:4, which was 63.19%. Therefore, the best molar ratio of tetrabutylammonium iodide to decanoic acid obtained was 1:2.

Density is important parameter in extraction processes. Based on Patrycja, Edyta and Jacek (2020) HDES should have higher or lower density than water. HDES that has similar density as water has a disadvantage of extended separation time into two phases during extraction. Therefore, HDES densities smaller or higher than water is preferred. As the tetraalkyl quaternary ammonium (HBA) and organic acids (HBD) chain increases, the density decreases which will increase the extraction yield. Therefore, the molar ratios of 1:2, 1:3, and 1:4 were chosen to be analyzed, which has a HDES density of 726.9 kg/m^3 , 759.1 kg/m^3 , and 780.9 kg/m^3 , respectively, that was lower than the density of water (997 kg/m^3).

Similarly, a study conducted by Emanuelle et al. (2017) proposed that a decreasing HDES molar ratio

of 1:2 gave the highest yield. This is because 1:2 has the lowest density among the other molar ratio which is further away from the density of water. The decrease in the density of solvent will also decrease the viscosity of the solvent which will increase the extraction yield. The relatively low viscosity values of HDES attributed to the presence of lower hydrogen bond network between HBA and HBD, which will lead to higher mobility of free species within the HDES. This will increase the extraction rate. Furthermore, this ensured the usage of lower amount of solvent, cost and generation of waste.

EXTRACTION TEMPERATURE

Extraction was performed at different temperatures to determine the optimum extraction temperature, such as 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$ and 70 $^{\circ}\text{C}$. Table 4 shows results for different extraction temperatures at wavelength 254 μm . Figure 8 shows the chromatogram of temperature of 70 $^{\circ}\text{C}$. Among the three temperatures, 70 $^{\circ}\text{C}$ showed the highest peak area of 79.95%, followed by 60 $^{\circ}\text{C}$ with 79.62% and the lowest peak area was shown by 50 $^{\circ}\text{C}$, which was 72.10%.

TABLE 3. Peak area of solvent molar ratio

Molar ratio	Peak area (%)
1:2	97.82
1:3	69.31
1:4	63.19

TABLE 4. Peak area of extraction temperature

Temperature (°C)	Peak area (%)
50	72.10
60	79.62
70	79.95

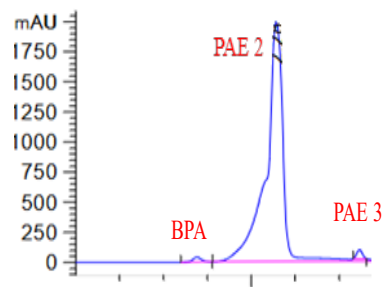


FIGURE 7. HPLC chromatogram of solvent ratio of 1:2

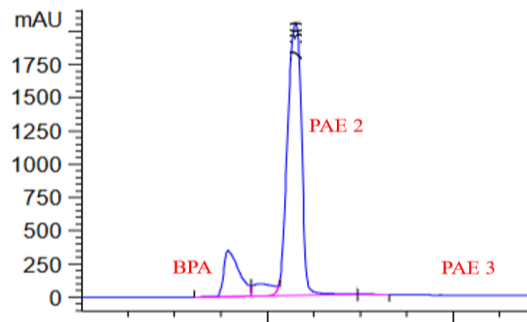


FIGURE 8. Chromatogram of extraction temperature 70 °C

Basically, increasing temperature will reduce the viscosity of the extraction mixture which will increase the mobility and average kinetic energy of the particles. It will also increase the interaction between the particles and speed up the extraction rate as well as the extraction yield. This result is valid because Chia et al. (2019) conducted a similar study that showed temperature of 70 °C gave the highest extraction yield by using ultrasonic-assisted extraction. Similarly, Seol et al.

(2022) proposed that the optimal temperature that was close to 70 °C has the highest yield in ultrasound-assisted extraction of glycyrrhizic acid from licorice.

EXTRACTION TIME

Several extraction times were analyzed such as 10 min, 15 min, and 20 min. Figure 9 shows the results for all the extraction time at wavelength of 254 μm . Figure 10

shows the chromatogram of extraction time of 20 min. Among the extraction times, 20 min showed the highest peak area of 91.45%, followed by 15 min with 88.23%, and the lowest peak was showed by 10 min, which was 88.09%. The optimum extraction time obtained was 20 min. This is because as the extraction time increases, the extraction yield increases too due to the prolonged interaction between the solvent and the targeted analytes in the compound. However, it is better to maintain the extraction time between 20-30 min.

This is because the extraction period that is more than 30 min might cause oxidation or degradation of targeted analytes which also encouraged by higher extraction temperature. The result can be validated by comparing the study conducted by Buanasari et al. (2018) proposed that the extraction yield continued to increase from 15 min to 30 min by using ultrasonic-assisted extraction. The longer the extraction time, the higher the yield. However, it was also proposed that extraction for more than 30 min would decrease the yield. Yue et

al. (2022) also proposed that an optimum extraction time of 20 min gave a better yield in the extraction of effective components from *Phellodendron chinense* C.K. Schneidby using deep eutectic solvent.

VOLUME OF SOLVENT

In this research, hydrophobic deep eutectic solvent was used, which was tetrabutylammonium iodide (HBA) with decanoic acid (HBD). This was because ionic DES made up of hydrophobic components have a greater stability in aqueous samples as compared to hydrophilic DES due to the long chain of ammonium salt and decanoic acid (Patrycja, Edyta & Jacek 2020). Three different volumes of solvent were analyzed, such as 3 mL, 6 mL, and 9 mL. Figure 11 shows results for different solvent volumes at wavelength of 254 μm . Figure 12 shows the chromatogram of solvent volume of 3 mL. The solvent volume of 3 mL showed peak areas of 79.27%, while 6 mL of solvent showed 80.03%, and the 9 mL of solvent showed 80.15%.

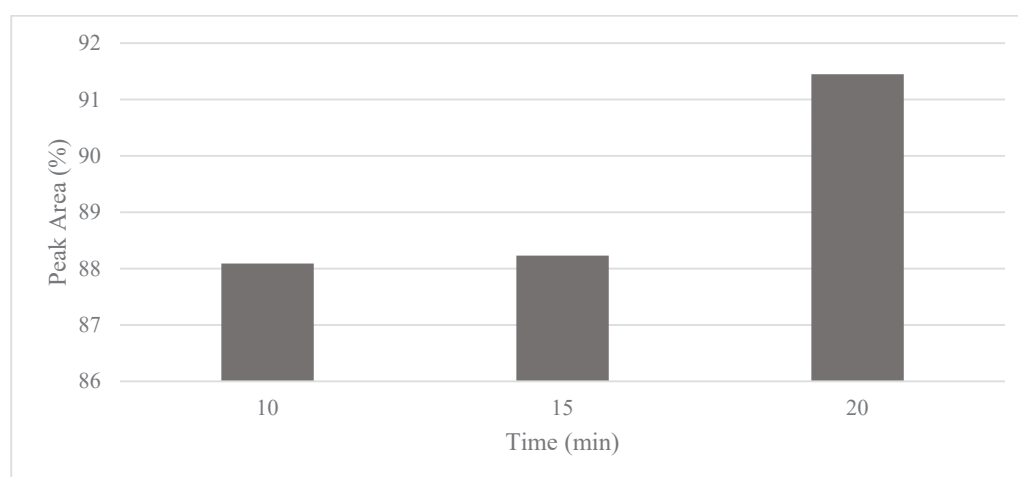


FIGURE 9. Peak areas of different extraction time

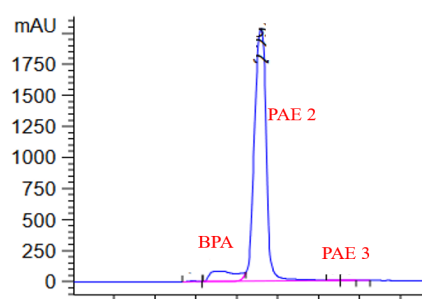


FIGURE 10. Chromatogram of extraction time of 20 min

As the volume of solvent increases, the extraction rate increases. This is because increasing volume will increase the concentration gradient between the surface and the interior targeted analytes. The higher the volume of solvent, more solvent particles can interact with the water molecule and the targeted analytes by enlarging the contact surface (Patrycja, Edyta & Jacek 2020). This will increase the extraction rate as well as speed up the extraction process. Based on the result obtained, since the three volumes showed almost the same peak areas, 3 mL was chosen as the optimum solvent volume to avoid wastage of solvent in the experiment and due to limited amount of solvent.

METHOD VALIDATION

Water samples were collected from several rivers in Selangor and spiked with 10 mg/L of BPA/PAEs. Based on Figures 13 and 14, BPA was detected at 3.152 min, while PAE 2 was detected at 13.417 min and PAE 3 was detected at 14.495 min.

The concentration of BPA/PAE in sample was calculated by using the following equation:

$$\text{Conc. sample} =$$

$$\frac{\text{Peak Area of sample.}}{\text{Peak Area of standard}} \times \text{concentration of standard}$$

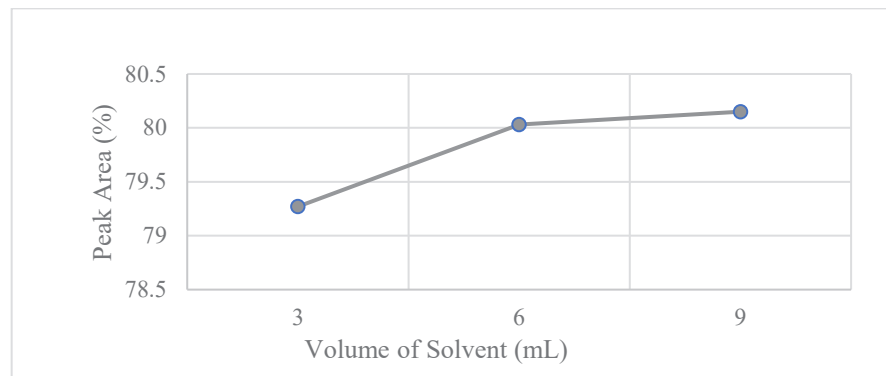


FIGURE 11. Peak areas of different volumes of solvent

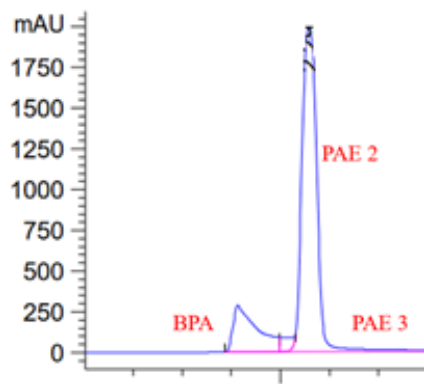


FIGURE 12. Chromatogram of solvent volume of 3 mL

Based on the result in Table 5, Sungai Kuang had the highest BPA concentration (23.9613 $\mu\text{g/L}$), Sungai Nada had the highest benzyl butyl phthalates concentration (73.6834 $\mu\text{g/L}$) and Sungai Damansara had the highest dibutyl phthalates concentration (7.3163 $\mu\text{g/L}$). The higher concentration of BPA in Sungai Kuang was due to a plastic processing company that is located upstream of the river. Any solid/liquid wastes produced from that company might be the reason for this. Furthermore, Sungai Nada is accumulated with large amounts of plastic rubbish and debris from

housing areas and restaurants, which might also cause the leach of a large amount phthalates when exposed to sunlight. High concentration of PAE in Sungai Damansara is mainly caused by food and beverage factories, commercial centers, storm water releases from residential areas, and public sewage treatment plants. Based on the chromatograph and calculation, it confirmed that bisphenol A and phthalates occur in the river and lake waters, but at a very low concentration. Therefore, the developed method was valid and acceptable.

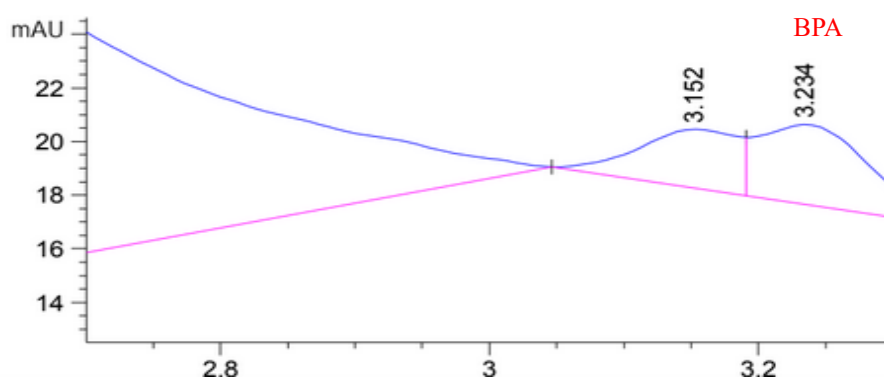


FIGURE 13. Chromatogram of Sungai Nada water sample at 3.152 min

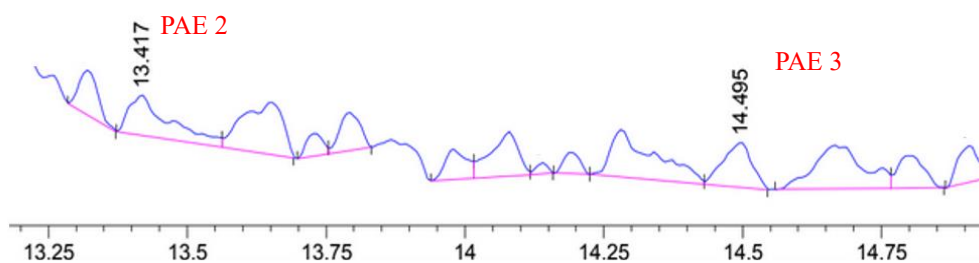


FIGURE 14. Chromatogram of Sungai Nada water sample at 13.417 min and 14.495 min

TABLE 5. Concentration of bisphenol A, benzyl butyl phthalates (PAE 2) and dibutyl phthalates (PAE 3)

Location of water sample	Sample label	Concentration of BPA ($\mu\text{g/L}$)	Concentration of PAE2 ($\mu\text{g/L}$)	Concentration of PAE3 ($\mu\text{g/L}$)
Sungai Damansara	SD	23.0689	2.6010	7.3163
Sungai Kuang	SK1	23.9613	5.599	0.5527
Sungai Kuyoh	SK2	13.2003	44.6701	1.5225
Sungai Langat	SL	17.3666	69.3841	0.8171
Sungai Nada	SN	15.0605	73.6834	0.4016
Sungai Timbun	ST	22.8780	34.9154	0.8086
Tasik Bukit Jalil	T1	21.7770	0.9350	1.7851
Tasik Seksyen 9 Kota Damansara	T2	23.4719	3.3150	1.1819
Tasik Kelana Jaya	T3	15.0906	3.1761	0.8957
Tasik Biru Sungai Buloh	T4	23.8194	2.5471	5.2088

MECHANISM OF INTERACTION BETWEEN
TETRABUTYLAMMONIUM IODIDE AND DECANOIC ACID
IN THE FORMATION OF HDES

During mixing of tetrabutylammonium iodide (HBA) and decanoic acid (HBD), the HBA and HBD components reacted and interacted with each other through hydrogen bonding. Figure 15 shows the illustration of formation of tetrabutylammonium-decanoic acid-based HDES mechanism and its hydrogen bonding interaction. It shows clearly the formation of hydrogen bond interaction between iodine ion of HBA and OH group of HBD. This mechanism of HDES would further react with bisphenol A and phthalates in the extraction process, as shown in Figure 14 (Ling & Hadinoto 2022).

COMPARISON OF DEVELOPED HPLC-UV METHOD WITH
OTHER METHOD FOR DETERMINATION OF BISPHENOL A
AND PHTHALATES

The present developed method was compared with

other developed methods. Based on comparison in Table 6, HPLC-UV gave better recovery of 90%-98% as compared to other developed methods, which also involve bisphenol A and phthalates. It also had a higher limit of detection range which is 0.22 - 0.8 $\mu\text{g/L}$. Among the other method, HPLC-UV has the lowest relative standard deviation (RSD) which is lower than 6.7%. Based on the LOD calculation performed by using Microsoft Excel regression method, the LOD of BPA, PAE 2 and PAE 3 are 0.45 $\mu\text{g/L}$, 0.87 $\mu\text{g/L}$ and 0.33 $\mu\text{g/L}$, respectively, which was within the LOD range proposed by Patrycja, Edyta and Jacek (2020). The LOQ of BPA, PAE 2, and PAE 3 are 1.36, 1.64, and 1.00, respectively, which is also within the proposed value by Patrycja, Edyta and Jacek (2020). Therefore, the developed method was valid and reasonable.

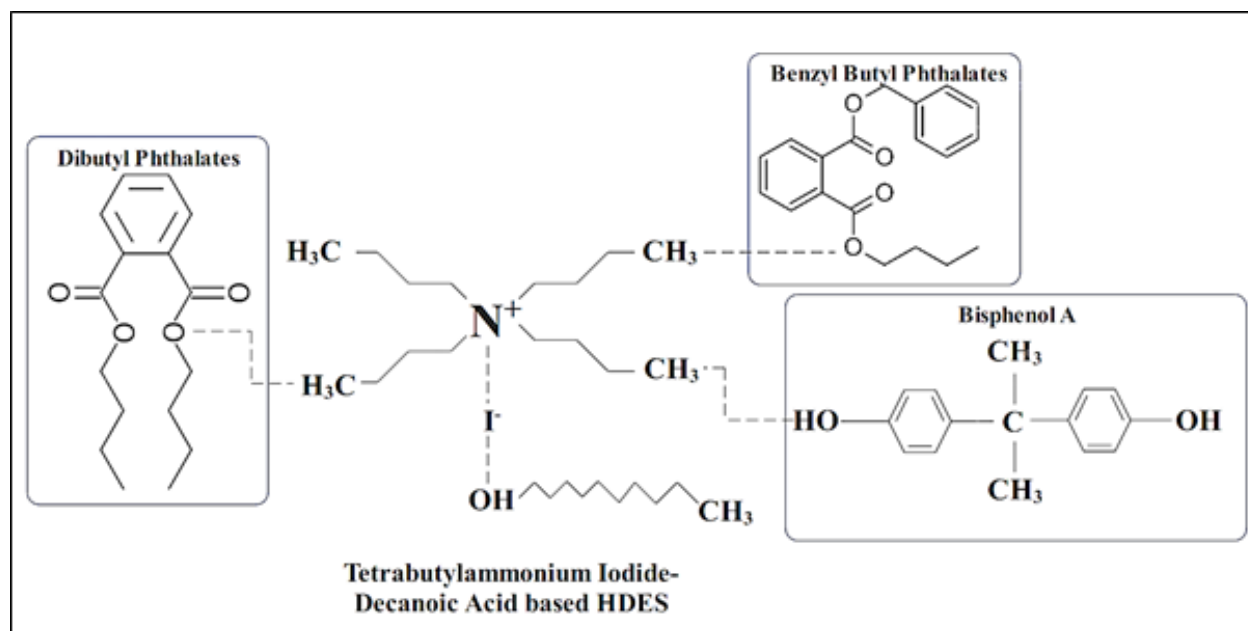


FIGURE 15. Mechanism of interaction between tetrabutylammonium iodide-decanoic acid-based HDES, bisphenol A and phthalates

TABLE 6. Comparison of HPLC-UV with other method

Analysis method	Analytes	Matrix (Amount)	Extractant (Molar Volume), (Volume)	Disperse (Volume)	%RSD	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)	References
UPLC-MS/MS	Bisphenol S, Bisphenol B, Bisphenol A	Canned fruit (0.5 g)	Methol: undecanol (1:2), (300 μL)	Acentonitrile (400 μL)	<4.6	0.0015 – 0.003	0.15- 0.16	
GC-MS	DEP, DBP, DEHP, BPA, DEHA	Polyethylene packed injection solutions (5 mL)	Menthol: decanoic acid (1:2), (65 μL)	Aspiration/dispersion (4 cycles)	<7	1.7-8.3	5.1-25	
HPLC-PDA	BPA, BP, EE, DEST, 4-NP	Water (5 mL)	Nonanoic acid: decanoic acid: dodecanoic acid (1:1:1), (200 μL)	Aspiration/dispersion (6 cycles)	<7	0.96– 2.3	1.5-4.5	El-Deen & Shimizu (2021)
HPLC-UV	DPP, BPP, DBP, DCHP, DEHP, DINP, DIDP, diisopentyl phthalate, di-n-pentyl phthalate, BPF, BPA, BPB, naphthalene, biphenyl,	Water (10 mL), tea infusions (5 mL), soft drinks (20 mL)	Menthol: acetic acid (1:1), (100 μL), Menthol: dodecanoic acid (3:1), (100 μL)	Manual vigorous shaking (1 min), Aspiration/dispersion (9 cycles)	<22	0.16– 0.75	1.2-4.8	
HPLC-UV	Bisphenol-A, Bisphenol-AF, Tetrabromobisphenol-A, 4-tert-octylphenol	Tap water, lake water and river water	Methyl trioctyl ammonium chloride: decanoic acid (1:2), Tetrabutylammonium chloride: decanoic acid (1:2), Tetra-n-butylammonium chloride: decanoic acid	-	2.6-6.7	0.22 – 0.8	0.73- 1.77	Patrycja, Edyta & Jacek (2020)

CONCLUSION

Bisphenol and phthalates were extracted from water sample using decanoic acid-tetrabutylammonium iodide based HDES. The operating parameters was optimized to give a highest extraction yield such optimum solvent molar ratio of 1:2, extraction temperature of 70 °C, extraction time of 20 min and solvent volume of 3 mL. Based on the water samples collected from various matrices in Selangor, Sungai Kuang shows the highest bisphenol-A concentration of 23.9613 µg/L. Sungai Nada has the highest benzyl-butyl phthalates concentration of 73.6834 µg/L and Sungai Damansara shows the highest dibutyl phthalates concentration of 7.3163 µg/L. It can be concluded that all the rivers have higher concentration of bisphenol-A compared to phthalates and Sungai Nada is the most polluted river among other river. This shows the occurrence of BPA and PAE in river and lake water.

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