Malays. J. Anal. Sci. Volume 29 Number 4 (2025): 1558

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES

Journal homepage: https://mjas.analis.com.my/

Review Article

Deep eutectic solvents as green alternative for removal of pesticides in environment and food matrices: A mini review

Nur Liyana Athirah Ahmad Hisham[1], Noorfatimah Yahaya[2], Siti Machmudah[3], Ili Syazana Johari[1] and Sazlinda Kamaruzaman[1*]

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang, 43400, Selangor, Malaysia
[2]Department of Toxicology, Advanced Medical and Dental Institute (AMDI), Universiti Sains Malaysia, 13200 Bertam Kepala Batas, Pulau Pinang, Malaysia
[3]Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

Received: 12 February 2025; Revised: 11 June 2025; Accepted: 18 June 2025; Published: 22 August 2025

Abstract
Pesticides have detrimental effects on organisms and environment. Due to extensive usage of pesticides from various group, such as triazines, organophosphates and pyrethroids in various industries, the occurrence of these pollutants had become prominent in the food matrices and environment, especially in soil and water samples. Many pesticides are detected above maximum residue limits (MRL) and threaten the well-being of humans and other living organisms. Cancer, endocrine disturbance and reproductive issues are some of the health conditions associated with the prolonged exposure to pesticides and other organic pollutants. Therefore, a lot of removal techniques had been developed and applied to ensure effective removal of these compounds. Extraction method shows promising results as it is simple, easy to design and has high relative recovery for target analytes. The utilization of deep eutectic solvents (DES) in extraction of pesticides had gained significant interest among scientists as it produced satisfactory results in addition to abiding by the principles of Green Chemistry. A wide range of pollutants are reported to be successfully removed from food, water and soil samples with the application of DES. In the present review, the focus is to discuss the extraction mainly by microextraction technique with the parameters affecting the extraction process, such as volume of DES used, temperature of solvent, pH value and extraction time were investigated.

Keywords: deep eutectic solvent, pesticides, microextraction, extractant solvent, dispersive solvent

Introduction

Background on pesticides

Pesticides are one of the emergent pollutants in the environment. Pesticides (**Figure 1**) are defined as a group of chemical and organic mixtures, including insecticides, fungicides, herbicides, plant growth regulators and others. Pesticides are heavily used in agricultural industry, public health sector and forestry to control or inhibit activity of pest. Ideally, a pesticide must be fatal to the target organisms such as to control the effect of weeds species, instead of creating issues on human beings and the environment. However, because their mode of action is not specific to one species, the usage of pesticide could result into the harming of organisms other than pests, including humans [1]. Much research had reported pesticides act as endocrine disruptors (EDs), neurodevelopmental toxicants, immunotoxicants and carcinogens in animals and humans [2,3]. For instance, several studies show long-term, persistent, chronic neurotoxicity symptoms in individuals because of acute exposure to organophosphorus pesticides [4]. Meanwhile, pesticides from the class group of organochlorines, such as aldrin, dieldrin and dichlorodiphenyltrichloroethane (DDT) can cause neurological damage, cancer, disruption of endocrine system, suppression of immune system and death [5,6]. Besides, most pesticides are highly persistence in the environment which can cause long-term exposure to human and animals.

Green chemistry and deep eutectic solvents as green solvent

Green chemistry is a concept introduced by Paul Anastas and John Warner in 1990s aiming to reduce pollution from chemicals and achieve sustainability of environments. It consists of 12 principles encouraging chemists to design chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

The introduction of green chemistry concept has result into development of various eco-friendly solvents to substitute the usage of conventional organic solvents. These organic solvents are not viable options due to their properties of having inherent toxicity and low biodegradability had contributed to the environmental pollution. Among the green solvents introduced are ionic liquid (IL) [7] and deep eutectic solvents (DES) [8]. ILs are defined as compounds completely composed of ions with melting point below 100°C. They are typically organic salts or eutectic mixture of an organic salt and an inorganic salt. ILs are often chosen as solvent due to their various properties, such as viscosity and hydrophilicity which can be tuned by the combination of different cations and anions [9]. These properties enable the application of ILs as solvents for biocatalytic processes, as extractions solvents and for electrochemical applications. However, the "greenness" of ILs have been challenged because of their toxicity and poor biodegradability.

Deep eutectic solvents (DES) are solvent developed from combinations of two or three safe components which can form homogenous eutectic mixture through hydrogen bonding interactions. The resulting eutectic mixture is characterized by having a melting point lower than that of each individual component [8]. Currently, most DES are prepared by mixing a quaternary ammonium salt with metal salts or a hydrogen bond donor (HBD) (**Figure 2**). The most common DES are based on choline chloride (ChCl), carboxylic acids, and other hydrogen-bond donors. Compared to ILs, DES are easy to prepare, less toxic, biocompatible, and biodegradable, making them solvents of choice for green chemistry. In addition, DES are customizable in which their properties can be adjusted by changing the composition of the components.

Depending on the combination of component used, DES can be hydrophilic and hydrophobic in nature. Hydrophilic DES is first introduced by Abbott et al. where they produced mixture of choline chloride and urea with the ratio of 1:2. The freezing point of the eutectic mixture is 12 °C, which is considerably lower than that of either of the constituents (mp choline chloride = 302 °C and urea = 133 °C). This characteristic enables the DES produced to be used as an ambient temperature solvent [8]. Most hydrophilic DESs are applied in many fields, including solvents or catalysts for chemical reactions [9], electrochemistry [10], pharmaceuticals [11] and separation process [12] but they are commonly water miscible and can interact with water molecules. Because water has a strong ability to form hydrogen bonds, it can destroy the hydrogen bonds between the DES components to varying degrees [12]. Therefore, the usage of hydrophilic DES in aqueous system is not possible which limits the application in analytical chemistry.

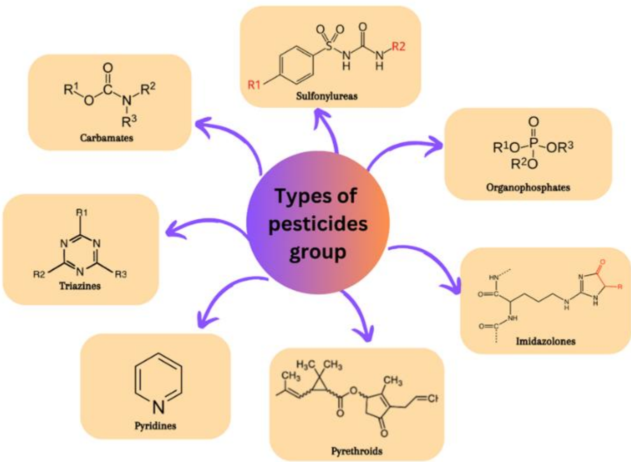

Figure 1. The different types of pesticides group

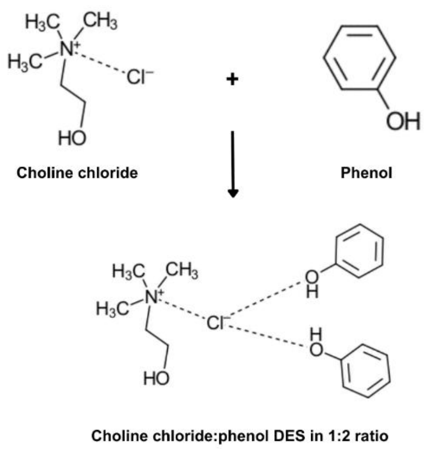

Figure 2. Formation of deep eutectic solvent between choline chloride and phenol

Mechanism of extraction using deep eutectic solvents

The mechanism of extraction method using deep eutectic solvents (DES) rely on the interaction of DES and the target analytes. The most common proposed method for removal of various contaminants including pesticides is mainly through the principle "like dissolves like" and intermolecular reactions, such as hydrogen bonding and Van der Waals force. Following the principle "like dissolves like", substances with similar polarity tend to dissolve each other. Polar solvents tend to dissolve polar solutes, while nonpolar solvents are effective at dissolving nonpolar solutes.

One of the unique properties of DES, which is tunable polarity is believed to contribute to successful extraction of pesticides and other pollutants as DES can change from hydrophilic to hydrophobic depending on combination of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) selected. For example, the application of hydrophobic DES in removals of pyrethroids in samples involve hydrogen bonding interaction between hydrophobic constituents in DES and the functional group of analytes. Pyrethroids, being relatively nonpolar, are effectively dissolved and extracted by hydrophobic DESs due to similar polarity they possess [18].

Application of deep eutectic solvent for removal of pesticides in food samples

Pesticides, defined by the World Health Organization (WHO), are chemicals used to control pests in agriculture, but their widespread use has led to residues in food and water. Some pesticides are persistent and hard to remove, prompting research into efficient removal methods. Chen et al. [13] developed a method for extracting carbendazim, thiophanate-methyl, and imidacloprid from fruit and vegetable samples by using ultrasound-assisted deep eutectic solvent extraction (UA-DES-E) and liquid-liquid extraction (LLE). The glycerol-proline DES (9:4 ratio) showed the highest extraction efficiency and it is achieved because the DES has moderate viscosity. The viscosity of solvent affects the ability of DES mixing with the sample matrix. Higher viscosity will result into slower mass transfer of target analytes. Under optimal conditions, the limits of detection ranged from 0.05 µg/mL to 0.2 µg/mL, and recovery rates were between 85.7% and 113.0%. Heidari et al. [14] used ultrasound-assisted liquid-liquid micro extraction (UA-LLME) with a DES based on choline chloride and phenol to extract phosalone and chlorpyrifos from fruit juice. The method achieved low detection limits (0.070 ng/mL and 0.096 ng/mL), high enrichment factors, and recoveries of 89.3%–116.7% for phosalone and 87.3%–109.6% for chlorpyrifos.

Using the same approach, Liu et al. [15] successfully studied the extraction of benzoylurea pesticides from tea and fruit juices by using hydrophobic DES. Hydrophobic DES are chosen in this study due to its compatibility to the benzoylurea pesticides which are hydrophobic in nature. DES used is expected to interact with the target analytes effectively as they have similar polarity. In this study, DESs were synthesized by using [P14,6,6,6]Cl as an HBA and decyl alcohol, dodecyl alcohol and tetradecyl alcohol as the HBDs. From the selection of DES prepared, [P14,6,6,6]Cl: tetradecyl alcohol was selected as the extractant solvent due to tetradecyl alcohol as the

HBD has a smaller relative standard deviation (RSD) value for the extraction recovery. Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA) were conducted to investigate the functional groups in the DES and their chemical stability. Next, central composite design (CCD) was applied to obtain the optimal extraction conditions with 10.5% salt addition, 5 min of centrifugation and 7 mL of sample volume. Relatively high extraction recoveries that ranged from 85.91%–95.12% were achieved. The limits of detection and correlation coefficients of the method were 0.30 µg L^{-1}–0.60 µg L^{-1} and 0.9992–0.9997. The above results showed that the method established in this study has good accuracy, repeatability, sensitivity, and high reliability. Socas-Rodríguez et al. [16] conducted research on application of betaine-based hydrophilic natural deep eutectic solvents (NADESs) for the evaluation of twelve pesticides in citrus and olive by-products by using ultrasound-assisted extraction with gas chromatography-mass spectrometry (GC-MS) determination. In this study, betaine is chosen as HBA as it is an alternative for choline chloride which is easily available, cheaper and less toxic. Eight NADESs were developed using betaine as the HBA and different HBD from alcohol, carboxylic acid and sugar groups were tested. Among the NADES synthesized, betaine: propylene glycol (1:4) was selected as the most adequate solvent since it provided the highest number of effectively extracted compounds and lowest number of interferences. Interferences in extraction come from other substances affecting the extraction process of target compounds. It could lead to inaccurate quantification of analytes and produce low quality data. A step-by-step optimization procedure were carried out to optimize NADESs molar ratio, volume of extraction solvent, percentage of water added to the extraction solvent, and extraction time. The dispersion of the DES extractant was achieved by using ultrasonication instead of the dispersion solvent. The study showed that relative recovery values in the range 73%–115% (RSD% < 20%) for all samples while the limits of quantification of the method were in the range of 8.5 µg/kg –128.8 µg/kg. Application of ultrasonication process in the experiment is favourable over dispersion solvent because it can produce higher extraction recovery and reduce the solvent consumption.

Mokhtari et al. [17] used a DES made from phosphocholine chloride, dichloroacetic acid, and decanoic acid to extract organothiophosphate pesticides from honey by using dispersive liquid-liquid microextraction (DLLME) technique (**Figure 3**). The study adopted the use of both extraction solvent and dispersive solvent throughout the experimental process. In DLLME, extraction solvent is mostly used to extract the analytes of interest from the samples while dispersive solvent promotes rapid transfer of analytes from the samples [19]. The method, using acetonitrile as a dispersive solvent, resulted in extraction efficiencies between 82% and 98%, with fenthion showing the highest efficiency. However, the use of acetonitrile limited its environmental appeal due to its potential to harm aquatic life, contribute to air pollution, and its persistence in the environment.

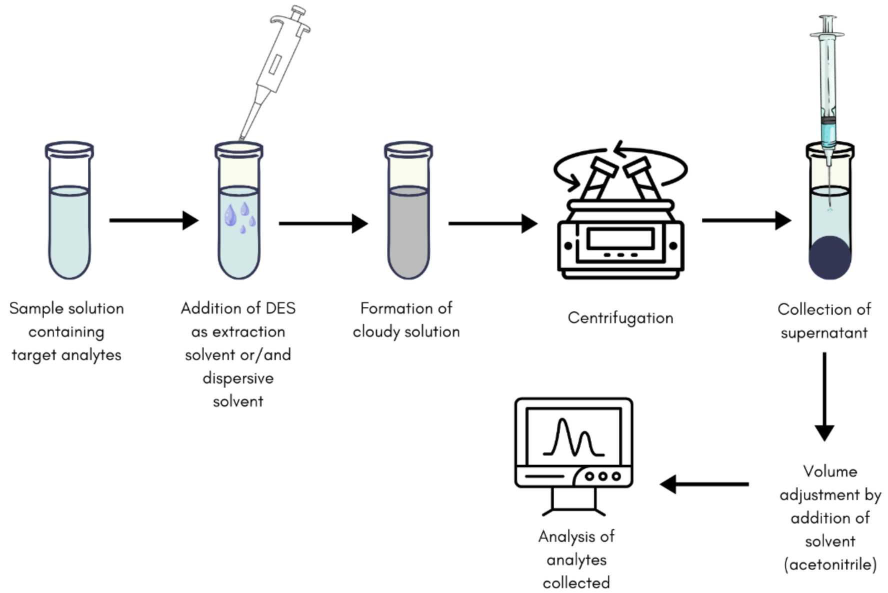

Figure 3. Dispersive liquid-liquid microextraction (DLLME) procedure

Wu et al. [18] developed a green extraction method by using deep eutectic solvent-based dispersive liquid-liquid microextraction with solidification of floating organic droplets (DES-DLLME-SFOD) for analysing the hydrophobic pyrethroid residues in cereals. The hydrophobicity of pyrethroids is contributed by the presence of non-polar hydrocarbon rings and bulky side chain within their structure. Thus, choosing compatible solvent for extraction is important to achieve good recovery. Thymol-octanoic acid, a hydrophobic DES was selected as the extractant solvent, and the method showed recovery rates of 75.6% to 87.2% for spiked cereals, with a low relative standard deviation (1.5%–3.6%). This method allows the floating solvent used for extraction to be easily collected from the aqueous phase after solidifying at low temperatures. It increases the efficiency of extraction process and provides convenience for analytes separation.

In another study, Deng et al. [20] used hexafluoroisopropanol (HFIP)-based hydrophobic deep eutectic solvents (DES) for extracting pyrethroids by using the DLLME technique. Six different DES were made with HFIP as the hydrogen bond donor (HBD) and either betaine or L-carnitine as the hydrogen bond acceptor (HBA) in different ratios. DES4 was chosen as the best extraction solvent because it produced the highest enrichment factor (EF). Enrichment factor is a way of quantifying the enrichment of a potentially contaminant-derived element in an environmental sample relative to a user-defined background composition. Higher enrichment factors indicate the extraction process is more efficient at isolating and concentrating the target compound even at trace level. L-carnitine-based DES gave higher EF than betaine-based DES, possibly because L-carnitine has more OH groups, which provide stronger hydrogen bonding with pyrethroids. The stronger the hydrogen bonding, the higher extraction recovery of target analytes. The best conditions for DLLME were 0.15 g of DES4, 1,000 µL acetonitrile, and 20-second vortex time. These conditions resulted in high EF and recovery values, with recoveries ranging from 85.1% to 109.4% and relative standard deviations (RSD) under 5.5% for intra-day and 7.5% for inter-day experiments.

Jouyban et al. [21] conducted research on application of DES in liquid phase extraction (LPE) coupled with solidification of organic droplets dispersive liquid-liquid microextraction (DLLME-SFO) technique used for determination of different classes of pesticides in milk samples. The study involved two steps of extraction process to remove pesticides from the sample and employed usage of DES as both dispersive solvent and extractant solvent. In the first step, the LPE technique, water-miscible DES, ChCl: ethylene glycol in 1:2 ratio was developed and used as an extraction solvent for extraction of pesticides residues in milk. The resultant supernatant containing analytes is then collected into a glass test tube and used in the DLLME-SFO process as dispersive solvent. Next, water- immiscible DES, decanoic acid: ChCl was added into the test tube and after the cloudy solution is formed, the test tube was placed into an ice bath for solidification. Lastly, the solid phase was collected for analysis. For the result, this method successfully produced good EFs and ERs value for the selected pesticides ranging from 320 to 445 and 64%–89% in addition to good linearity for various concentration of pesticides (13–5000 $ngmL^{-1}$) with coefficients of determination ≥0.9962.

Nemati et al. [22] conducted an investigation on the use of water–immiscible DES for extraction of pyrethroid pesticides from fruit juices in gas-controlled-deep eutectic solvent-based evaporation-assisted dispersive liquid-liquid microextraction (GC-DES-DLLME) method. In the study, three DESs prepared from different types of HBD were investigated to find the best extractant. The highest extraction yield was obtained by using ChCl: butyric acid DES and it was used in the further studies. The proposed mechanism of reaction that took place in the extraction is likely involving hydrogen bonding between ester group of pyrethroid and carboxyl group of butyric acid. To develop a highly sensitive method for extraction of pyrethroid pesticides from fruit juices, they optimized various experimental conditions. The optimal extractant volume was found to be 95 µL of ChCl: butyric acid and the pH value of samples was maintained at around pH 7 as the best ERs for the analytes were seen at the pH range of pH 4–pH 8. Changes in pH value can affect stability of pyrethroid in sample as they are more stable in slightly acidic to neutral conditions. At suitable pH value, the extraction of these pyrethroids can occur effectively. The method was validated by applying it to determine the content of pyrethroid pesticides from fruit juices. The results indicated spiked recoveries for the target pesticides in the range of 87% and 103% for all samples.

In research by Ju et al. [23], a novel vortex-assisted DLLME (VA-DLLME) method, combined with a high-throughput automatic sample addition instrument and coupled with HPLC was developed for determination of neonicotinoid pesticides. An economical and environmental-friendly DES synthesized from sorbitol and 1-methylurea was prepared in molar ratio of 1:2 and used as the extractant. However, application of 1-methylurea: sorbitol as solvent face challenges mainly because of its high viscosity. Therefore, adequate volume of water is added to its composition to reduce the viscosity. By adjusting the viscosity of DES, the rate of mass transfer of analytes can be increase significantly. Several factors affecting the extraction efficiency were individually optimized, including sample volume, extraction solvent (DES) volume, vortexing time, and extraction temperature. Under optimized conditions, the method exhibits satisfactory extraction performance for all target analytes. For instance, the LODs for thiamethoxam, imidacloprid, and thiacloprid in the rapeseed oil matrix are 5.8 μg L^{-1}, 2.9 μg L^{-1}, and 2.7 μg L^{-1}, and LOQs are 19.4 μg L^{-1}, 9.8 μg L^{-1}, and 8.9 μg L^{-1}, respectively. The technique developed was simple, inexpensive and efficient for removal of pesticides. However, the use of n-hexane in sample preparation is not favorable from the environmental view as it is toxic for living organisms.

Using similar extraction method, Zhao et al. [24] examined the extraction and preconcentration of organophosphorus pesticides (OPPs) from beverage samples by using hydrophobic DES. The DES was synthesized from choline chloride and 4-chlorophenol at different molar ratios, such as 1:2, 1:3, 1:4, and 1:5. The selection of 4-chlorophenol as HBD is good as it provides good thermal stability to the DES produced with less toxicity in comparison with its individual components. Consequently, the highest extraction recovery of analytes in the range of 69%–80% were recorded with DES of 1:4 ratio. This condition might be due to the polarity of DESs at this ratio is most similar to the analytes and enable good interaction of analytes with the DES components. In addition,110 μL of h-DESs was selected to be the best volume of extractant as the recoveries increased by the volume from 80 μL to 110 μL and achieved a good extraction recovery when DESs volume was 110 μL. However, with the further increase of DESs volume, the enrichment factor has decreased drastically and will reduce the extraction yield of target analytes. The condition is expected as the extracted analytes become more diluted in the extraction solvent at higher volume. The performance of the method is further evaluated by applying it to extract five pesticides from orange juice and green tea samples. The data showed that the ERs ranged from 71.68% to 113.18%, and RSD ranged from 1.37% to 11.92% were achieved. Based on the data, it can be concluded that hydrophobic DESs can achieve extraction and preconcentration of organophosphorus pesticides from aqueous matrices efficiently.

Soltani et al. [25] also conducted similar study where they employed the usage of hydrophobic DESs composed of thymol and vanillin for removal of pesticides residues in olive oils. Initially, several hydrophilic and hydrophobic DESs were prepared from choline chloride (ChCl), ethylene glycol, urea, thymol, vanillin, glycerol, and glucose according to the literature and tested with the proposed procedure. Among the hydrophobic DES developed, only thymol-vanillin DES in ratio 1:1 showed the properties as DES, remained in transparent liquid form while the solvents with the molar ratios of 1:2 and 2:1 were solidified after cooling to room temperature. This indicates only thymol: vanillin (1:1) achieve eutectic points which is below the individual melting point of the two substances and stable in room temperature. Besides that, the hydrophilic DESs were utilized for sample clean up prior to microextraction process. ChCl: urea along with n-hexane, acetonitrile (ACN) exhibited the highest efficiency compared to other hydrophilic DESs when being used to isolate pesticides from oil sample. This combination is able to dissolves the phenolic compounds of olive oil and can reduce the matrix effect. Reduction of matrix effect will allow quantification of analyte concentration in samples be conducted more accurately. The applicability of the method was assessed by analyzing five different oil samples. The recoveries obtained by the proposed method were in the range of 63.1%–119.4% with RSDs of 2.5%–7.4%.

Elencovan et al. [26] evaluated the application of DES as emulsifier in vortex assisted liquid-liquid microextraction (VALLME) for the determination of organophosphorus pesticides (OPPs) in honey and fruit samples. In this research, a non-ionic silicone surfactant, Miracle S240 was combined with different types of organic acids, such as hexanoic acid (HexAc), octanoic acid (OctAc), decanoic acid (DecAc) and dodecanoic acid (DodAc) in molar ratio of 1:1. All DESs were tested, and the analytical signal enhances with increasing length of the alkyl chain of HBDs. The increase in alkyl chain length is proportional to the increase in hydrophobicity of DESs prepared. The result also depicts that when only the surfactant is used as emulsifier, the extraction efficiency is low. Thus, the OPPs and SS-DodAc could possibly had strong intermolecular forces with each other, such as hydrophobic interaction and dispersion resulting in higher extraction performance. Vortex as assistant method is beneficial to shorten the mass transfer distance and increase the contact area between the sample and the hydrophobic DES. It can improve the extraction efficiency. The practicability of the proposed technique on real matrices were studied by using commercial honey, green apple, red apple and pear. The average relative recoveries of OPPs achieved from honey and fruits matrices were ranged between 83% and 109% with average RSD 1.8%–9.5% for all analytes.

Rostami-Javanroudi et al. [27] utilized properties of several novel hydrophobic DES for the determination of common acaricides in fruit juice samples by using vortex-assisted liquid phase microextraction (VALPME) method combined with high-performance liquid chromatography-ultraviolet detection (HPLC-UV). Methyltrioctylammonium chloride (MTOAC) was used as a HBA and various alcohols, such as ethylene glycol, n-butanol, glycerol, n-heptanol and n-nonanol were used as HBDs in synthesis of these hydrophobic DES. Alcohols are commonly selected as HBD due to presence of hydroxyl (-OH) group in its structure where hydrogen is attached directly to a highly electronegative atoms, causing the hydrogen to acquire a partially positive charge. The partially positive hydrogen (from the alcohol) is then attracted to the lone pair of electrons on the MTOAC, forming a hydrogen bond. In preliminary study, the ERs of the analytes showed that MTOAC: n-butanol is more effective than other solvents where it achieved 80%–=90% recovery for all analytes. Thus, it was preferred as extractant. Interestingly, in this work, no dispersion solvent was used and this led to tremendous reduction of pollution of the environment. The dispersion of the extracting solvent into tiny droplets within the aqueous sample was performed by vortex method. Moreover, relatively high extraction recoveries that ranged from 92%–107% were achieved. The VALPME technique developed was environmentally friendly in the sense that the conventional organic solvents were replaced with low toxicity, biodegradable DES. In addition, they used a dispersive solvent-free technique.

Abolghasemi et al. [28] explored the efficacy of three DES, ChCl: 4-chlorophenol, ChCl: ethylene glycol and ChCl: phenol as extraction solvent for removal of fungicides, namely penconazole, hexaconazole, cyproconazole, difenoconazole, propiconazole, triticonazole and diniconazole in fruit juice and vegetable samples. The DES produced from ChCl: 4-chlorophenol is the most effective extraction solvent as it gives the highest peak areas and extraction efficiencies for the selected analytes among the tested DESs. In the proposed method, ChCl:4-chlorophenol was added to the vial containing the sample by using micro syringe. Then, the solvent drop was suspended and exposed to the head space of the sample solution for extraction of target analytes. After extraction, the micro-drop was retracted back into the syringe and injected into the GC injection port for further analysis. The data obtained from the analysis were used to evaluate the method performance in various aspects, such as LOD, linearity, reproducibility, and repeatability. The method achieved good linearity with (R^2 >0.991 and RSD within 3.9%–6.2% for all target analytes. ChCl: 4-chlorophenol is most compatible in extraction of these triazole derivatives pesticides due to its hydrophobicity nature. The other DESs tested are hydrophilic DES and could not interact well with the triazoles pesticides which have hydrophobic bulky side chain. By abiding with 'like dissolve like" principle, the selection of DES as extraction solvent with similar properties of target analytes will increase the extraction efficiency of analytes from food samples.

Monajemzadeh et al. [29] successfully hyphenated dispersive solid phase extraction (DSPE) and DLLME technique for determination of some pesticides and their metabolite in egg samples. The researchers prepared five types of ethyldimethylammonium chloride (DEAC)-based DES to be tested in the experiment. In selection process for dispersive solvent, DEAC: propionic acid DES had been selected due to its low viscosity in comparison with DEAC: acetic acid and DEAC: ethylene glycol. Viscosity plays an important role in chemical transformations within solution by controlling the flow and the rate of mass transport. Low viscosity solvent is expected to increase extraction efficiency. In this study, in DSPE process, Fe_3O_4@MWCNTs were used as adsorbent for extraction of analytes before the magnetic particles are collected with the aid of an external magnet. The use of MWCNT nanocomposite as adsorbents helps in effective adsorption of analytes as it possesses good characteristics, such as large surface area, tunable adsorption properties, and diverse adsorption sites. As result, it allows the transfer of high concentration of pesticides from egg samples through DSPE method. The adsorbed analytes are then eluted with water-miscible DES, DEAC: propionic acid acting as dispersive solvent that increase surface contact of sample and solvent being used in the following step, the DLLME procedure. Next, water-immiscible DES, DEAC: menthol: carvacrol was added to the supernatant, followed by dispersion in NaCl solution and the resulting aliquot was collected in a syringe for analysis. The method achieved good ERs and EFs for the analytes in the ranged of 73% to 92% and 219 to 276, respectively. Overall, the work provided an environmental-friendly and effective approach for determination of pesticides in egg samples due to adoption of DES as solvent.

Daghi et al. [30] conducted research on application of metal organic framework (MOF) MIL-88A as adsorbent with various DESs as dispersive and extraction solvent for the extraction of some pesticides from fruit juices. In this study, it combined the DSPE with DLLME technique to produce high enrichment factor and extraction recovery. All DESs were prepared in the mole ratio of 1:2 for HBA: HBD. The pair of hydrophilic and hydrophobic DES, ChCl: ethylene glycol and EMAC: carvacrol showed prominent result in extraction process with highest ERs value recorded in comparison with other developed DES. ChCl: ethylene glycol is most compatible as dispersive solvent as it fits the criteria of being miscible with both water and extraction solvent thus enabling the formation of fine droplets of the extraction solvent in the aqueous phase. Following the application of both pair of DES in DLLME method, under optimized conditions, the LODs and LOQs calculated were in the ranges of 70–89 and 235 ng L^{-1}–290 ng L^{-1}, respectively. Lastly, the method when applied in real fruit juice samples, produced relative recoveries ranged from 88% to 103% at the spiked concentrations of 500 ng L^{-1} and 1,000 ng L^{-1} of each pesticide. The developed technique was environmentally friendly in the sense that it did not involve the use of organic solvents during dispersion and extraction processes.

Application of deep eutectic solvent for removal of pesticides in water and soil samples

Kachangoon et al. [31] highlighted the utilization of hydrophobic DES in DLLME method for determination of neonicotinoid insecticide residues in water, soil and egg yolk samples. The DES were prepared by combining TBABr and decanoic acid at different molar ratios of 1:1, 2:1, 3:1, 4:1, and 5:1. Decanoic acid is selected as hydrogen bond donor in this study because it contains a long hydrocarbon chain (10 carbons) that is nonpolar and repels water, making it insoluble in aqueous solutions. This property contributed to the hydrophobicity of DES produced. Consequently, ratio 3:1 is being selected as optimum ratio for the study because it possesses high stability and good extraction efficiency. Acetonitrile (ACN) was chosen as disperser solvent due to highest extraction efficiency achieved as compared to methanol and ethanol. A good disperser solvent must be miscible with the extraction solvent, hence facilitating the dispersion of the extraction solvent into tiny droplets within the aqueous sample. Other than that, several parameters for this research were investigated by using one parameter at a time method to obtain optimal condition for DLLME procedure. The established optimal conditions were found to be 100 µL of DES, 400 µL of ACN, 30 s of vortex time, and centrifugation time of 10 min with speed of 5,000 rpm. 100 µL of DES is selected as volume of extractant due to further increasing of volume contributes to dilution of analytes in sample. Consequently, less amount of analyte can be detected and quantified by using high-performance liquid chromatography (HPLC) analysis. The analytical performances of the proposed method when evaluated, showed decent performance in terms of linearity, EFs, LODs and LOQs of the analytes. For example, the obtained LODs of this method (0.001 µg·mL^{-1}–0.003 µg·mL^{-1}) is lower than the maximum residue limit (MRL) established by the European Union.

Sereshti et al. [32] investigated the application of hydrophobic liquid-polymer-based DES for extraction and multi-residue analysis of pesticides in water samples. Three new polymeric DESs, including [polyethylene glycol]: [thymol], [polyacrylic acid]: [menthol], and [polyacrylic acid]: [thymol], were prepared and examined as extraction solvent for extraction of pesticides by DLLME technique. The experiments indicated that the maximum extraction efficiency was obtained by PEG-thymol DES in the molar ratio of 2:1. The PEG: thymol DES were characterized by using FTIR and its hydrophilicity was assessed by measuring K_{ow} (octanol-water partition coefficient) with the shake flask method. The log K_{ow} value for PEG: thymol DES was obtained equal to 2.21 ± 0.01. From the analysis, the prepared DES is confirmed to be hydrophobic and carried the properties associated with hydrophobic DES as log K_{ow} is positive for lipophilic and negative for hydrophilic materials. The change in pH value of sample solution was negligible when PEG: thymol used as extractant solvent showing its low solubility in water. Thus, it could efficiently extract pesticides from the aqueous sample without interaction with water molecules.

In the following year, Sereshti et al. [33] also investigated the performance of novel hydrophobic and hydrophilic natural deep eutectic solvent (NADES) for the analysis of multiclass pesticides in water. The new hydrophilic amino acid-based, alanine: kojic acid: H_2O DES and the hydrophobic, thymol: 1-myristyl alcohol DES were prepared by using the established procedure. The alanine: kojic acid: H_2O DES were prepared in different molar ratios but only ternary mixture in the molar ratio of 1:2:5 led to creating a stable homogeneous transparent liquid. Additionally, FTIR and NMR analysis was used to characterize and confirm the presence of related functional groups, such as alkyl and aromatic groups in the structure of DES indicating successful combination between HBA and HBD. The researchers employed the usage of both DES as dispersing and extraction solvent, respectively in DLLME technique for analysis of 16 pesticides. The accuracy of the method was assessed by analyzing five different water samples. Relatively good recoveries were obtained using the method they developed. For instance, the intra-day RSDs (n =6) were 2.8%–5.4%, and the inter-day RSDs (n =3) were obtained equal to 3.7%–10.3% from analysis at three different days. A lower relative standard deviation means that the measurement of data is more precise. The technique developed conformed to the principles of green chemistry as it was simple, fast, efficient, inexpensive and environmentally friendly.

Liu et al. [34] examined the effect of using thermo-switchable DES in DLLME technique for analysis of nine pesticides. The thermo-switchable DES was synthesized by using oleic acid (OA) as HBA and lidocaine (LD) as HBD. In contrast with conventional DLLME, the proposed method involved heating of the supernatant at 40°C in water bath after addition of DES into the sample. As the temperature of the system rises and the polarity changes, the proportion of OA in the DES becomes higher, and the extractant floated on the surface of the water sample. The extractant is then collected and injected into HPLC system for analysis. The changes in temperature can directly influence the properties of DES as it alters intermolecular forces between components resulting into lower density and polarity of DES. This enables wide application of DES in extraction of pesticides and other organic compounds. The analysis showed that sufficient relative recoveries were achieved for all pesticides in different samples, in range between 66.7%–85.2%. Furthermore, the calibration curves of all analytes demonstrate good linearity, with correlation coefficients ranging from 0.9942 to 0.9995.

Pour et al. [35] successfully combined the ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME) method with solidification of floating organic droplets (SFO) to analyse pesticides residue in water sample from agricultural area. Several DES combinations were shortlisted for study but DES from combination of menthol and decanoic acid in 1:2 ratio was selected for microextraction procedure. This is attributed to the stability and density of menthol: decanoic acid. In contrast, although the 4-chlorophenol: choline chloride produced stable mixture, the high density it possesses might hinder its application in SFO method. In SFO method, it usually requires the use of DES with lesser density than water to float at the top layer of samples. The upper layer of analyte-containing DES then collected for analysis. Selection of this DES combination is good because menthol-based solvent is known with the ability to dissolve both polar and non-polar compounds. The polar hydroxyl group of menthol (HBA) allows for hydrogen bonding interactions with polar pesticides while decanoic acid with hydrophobic characteristics can interact with non-polar pesticides resulting into enhance extraction efficiency. The optimization of parameters in the research was done by using a sequential design-of-experiments strategy utilizing a 2 $(^{5-1})$ fractional factorial design (FFD) followed by central composite design (CCD). The optimization process revealed that to achieve maximum sensitivity, the optimal conditions were 2 min for sonication time, 2 min for centrifugation, and 3 min for equilibration time. Application of sequential design of experiments is recommended due to the advantages, such as more efficient than one-factor-at-a-time experiments, allowing for the estimation of factor effects at different levels of other factors and cost efficient. The overall results showed that this method achieved significantly lower LOQs, ranging from 0.3 ng/mL to 1 ng/mL, which is critical for the sensitive detection of pesticides.

Turiel et al. [36] conducted a research on choline chloride-based NADES to be used as extractant solvent in an ultrasound-assisted extraction method for triazine herbicides in soil samples. Choline chloride (ChCl) was used as hydrogen bond acceptor (HBA), and different carboxylic acids, alcohols and amines were tested as hydrogen bond donors (HBDs) in different molar ratios. From multiple combinations of HBA and HBD, three types of DES were chosen for preliminary study which are ChCl: formic acid in molar ratio 1:2, ChCl: acetic acid in molar ratio 1:2 and ChCl: 2,3-butanediol with 1:4 ratio. In preliminary study, ChCl: 2,3-butanediol depicts the best result in terms of extraction efficiency. It can be deduced ChCl: 2,3-butanediol presents a much more suitable polarity for the extraction of triazines as compared to the other DESs. Polarity of extraction solvent plays important role in extracting target analytes from sample. A polar solvent will effectively extract polar compounds while it is vice versa for non-polar solvent. In order to develop a highly sensitive method for extraction of triazine pesticides, they optimized various experimental conditions, such as temperature and extraction time. As a result, 5 min of extraction time at 60 ºC is found as optimum condition for extraction process to be carried out. The analysis showed that sufficient relative recoveries were achieved for all pesticides in different samples, in range between 87%–104.7% and low LOD calculated for the analytes. To conclude, the application of extraction technique by using ultrasonication process is a good choice as it utilized low energy and solvent consumption, improved extraction yield, and short extraction time (**Table 1**).

Future prospects and limitations

Selection of extraction solvent and its counterpart, dispersive solvent play a vital role in extraction and quantification of various organic and inorganic compounds. In the effort of complying by the green

Table 1. Summary of application of DES in extraction of pesticides in food matrices and environment

Extraction Technique	DES	Sample Matrix	Analytes	Instrument	LOD	RSD (%)	ER (%)	Ref.
Ultrasound-assisted LLE	glycerol: proline	fruit and vegetable	carbendazim, imidacloprid, thiophanate-methyl	HPLC	0.05 –0.20 mg mL^{-1}	< 5	85.7–113.0	[13]
Ultrasound-assisted LLME	ChCl:phenol	fruit juices	phosalone, chlorpyrifos	HPLC-UV	0.070–0.096 ng mL^{-1}	4.0–10.2	87.3–116.7	[14]
UA-DES-DLLME	[P14,6,6,6]Cl: tetradecyl alcohol	tea and fruit juices	diflubenzuron, flufenoxuron, triflumuron, hexaflumuron, chlorfluazuron	HPLC-UV	0.30-0.60 μg L^{-1}	1.72– 3.57	85.9–95.1	[15]
Ultrasound-assisted SLME	betaine:PPG	citrus and olive by-products	12 pesticides	GC-MS	-	< 20	73–115	[16]
DLLME	phosphocholine chloride: dichloroacetic acid: decanoic acid	honey	organothiophosphate pesticides	GC-MS	0.05–0.10 ng mL^{-1}	4–10	82–98	[17]
DLLME-SFOD	thymol: octanoic acid	cereals	pyrethroid pesticides	HPLC	2.02.7 mg kg^{-1}	< 4	75.6– 87.2	[18]
DLLME	HFIP:betaine	tea beverages and fruit juices	pyrethroid pesticides	HPLC-DAD	0.06–0.17 ng mL^{-1}	5.5–7.5	85.1–109.4	[20]
LPE and DLLME-SFO	ChCl:ethylene glycol ChCl: decanoic acid	milk	multiclass pesticides	GC-FID	0.90–3.90 ng mL^{-1}	3.8–6.9	64–89	[21]
Gas controlled evaporation-assisted DLLME	ChCl: butyric acid	fruit juices	pyrethroid pesticides	GC-MS	9–21 ng L^{-1}	< 6.9	83–92	[22]
Vortex-assisted DLLME combined with a high-throughput automatic sample addition	1-methylurea:sorbitol	edible oils	thiamethoxam, imidacloprid, and thiacloprid	HPLC	2.7–5.8 μg L^{-1}	0.3–5.5	70.0–95.2	[23]
Vortex-assisted DLLME	ChCl:4-chlorophenol	juice and green tea beverages	organophosphorus pesticides	GC-FPD	0.05–0.3 mg L^{-1}	< 12	71.6–113.1	[24]

Table 1. Summary of application of DES in extraction of pesticides in food matrices and environment (continue)

Vortex-assisted DLLME	thymol: vanillin	olive oils	16 pesticides	GC-µECD	0.01–0.08 µg kg^{-1}	6.8–9.7	63.1–119.4	[25]
Vortex-assisted DLLME	ACN/ ChCl: urea SS:dodecanoic acid	honey and fruits	organophosphorus pesticides	GC-MS	0.01– 0.09 µg L^{-1}	< 9.5	83–109	[26]
Vortex-assisted LPME	MTOAC: n-butanol	fruit juices	clofentezine, fenpyroximate and pyridaben	HPLC-UV	0.5–1.0 mg L^{-1}	2.5–5.1	85–93	[27]
Headspace single-drop microextraction	choline chloride: 4-chlorophenol	fruit juice and vegetables	triazole fungicides	GC	0.82–1.0 µg L^{-1}	3.9–6.2	93–97	[28]
DSPE combined with DLLME	DEAC: propionic acid DEAC: menthol: carvacrol	eggs	fipronil, amitraz, and cypermethrin	GC-MS	0.03–0.24 ng g^{-1}	< 10.2	73–92	[29]
DSPE combined with DLLME	ChCl: ethylene glycol EMAC: carvacrol	fruit juices	diazinon, haloxyfop–r–methyl, hexaconazole, diniconazole, and tebuconazole	GC-MS	70–89 ng L^{-1}	< 5.1	51–63	[30]
DLLME	TBABr: decanoic acid	water, soil, egg yolks	thiamethoxam, clothianidin thiacloprid, acetamiprid	HPLC	0.001–0.003 µg mL^{-1}	< 5	60–114	[31]
DLLME	PEG: thymol	water	16 pesticides	GC-µECD	0.001–0.02 µg L^{-1}	< 10.5	60.5–105	[32]
DLLME	alanine: kojic acid: water thymol: myristyl alcohol	water	multiclass pesticides	GC-µECD	0.001–0.030 µg L^{-1}	< 10.3	63.7–104.5	[33]
DLLME	oleic acid: lidocaine	water	nine organophosphorus pesticides and pyrethroids	HPLC-UV	0.16–0.81 µg L^{-1}	5.4–9.7	66.7–85.2	[34]
UA-DLLME-SFOD	menthol: decanoic acid	agricultural water	multiclass pesticides	GC-MS	-	< 15	64–119	[35]
UA-LLE	choline chloride: 2,3-butanediol	soil	triazines pesticides	HPLC-UV	0.025–0.050 µg g^{-1}	< 12	888.4–99.7	[36]

chemistry, DESs were introduced as alternative for conventional volatile organic solvents. The high biodegradability, biocompatibility, eco-friendliness, tunable properties, and presence of active groups in DESs make them the preferred solvent in a variety of solid and liquid-phase microextraction techniques. Moreover, the analytical figures, such as EF, ER, RSD, LOD and LOQ from multiple studies on DES-based DLLME are usually of higher efficiency in comparison to conventional solvents. Thus, the use of DES is seen to grow further as it is efficient and in line with green chemistry applications.

However, several limitations must be taken into consideration in application of DES as solvent. One of the challenges is in terms of the viscosity of DES. A large number of DES developed exhibit high viscosity which hinders its ability to facilitate mass transfer of analytes from samples. Consequently, it will reduce the extraction efficiency. Other than that, viscosity of solvent can impact performance of analytical instrument. For instance, in analysis using high performance liquid chromatography (HPLC) or liquid chromatography-mass spectrometry, they favor application of low viscosity solvent. High-viscosity solvents restrict flow rates and can destroy the column due to high-pressure buildup. Thus, dilution of samples or change in solvent is often applied to overcome this issue.

Next, the limitation of DES is on maintaining water contents in the composition. Most DESs, especially derived from choline chloride possess hygroscopic property, the ability to readily absorb moisture from the surrounding environment, typically at or near room temperature. The presence of water or moisture can affect the melting point, viscosity, conductivity, and other chemical and physical characteristics of DESs. The changes can take place due to disruption on the hydrogen-bonding network within the DES by water molecules. Furthermore, toxicity testing of DES has not been carried out comprehensively in the research field as majority of the research put more focus on application and performance of DES as solvent. Until now, only a small proportion of eutectic solvents have been tested on living organisms, such as in small fish, rats and cell samples. The implementation of toxicological tests needs to be expanded to support the claim that eutectic solvents are more environmentally friendly. The availability of data related to DES toxicity assessment can help in the selection of solvent combinations in future research.

Conclusion

The effective use of deep eutectic solvents (DES) as extractant and dispersive solvent in extraction of pesticides in food matrices and environments is summarized in this review paper. Occurrence of pollutants in a long period of time could result into detrimental effects on human health and endangering the environment. The development of suitable and precise removal methods could assist in mitigating these issues effectively without contributing to further pollution. The progress achieved using deep eutectic solvent in various extraction methods, such as dispersive liquid-liquid microextraction (DLLME), vortex-assisted liquid-liquid microextraction (VA-LLME) and solid phase microextraction (SPME) showed promising results and provide researchers with a viable alternative to the conventional organic solvents. The extraction process using DES is highly dependent on the condition of experiments. The type of DES used, the volume of extractant and dispersive solvent, the sonication and centrifugation time are several parameters need to be optimized to achieve good extraction efficiency. In addition, characteristics and properties of DES should be considered before extraction of target analytes. Properties such as viscosity, density and polarity directly affect the preconcentration of pesticide. Thus, choice of DES with desired physical and chemical properties must be done to maximize extraction recovery. To conclude, by employing the usage of DES, the concept of green chemistry can be followed in addition to achieving rapid and sensitive extraction of target analytes.

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