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# Caffeine, chlorogenic acid and catechin extraction from coffee cherry waste using green solvent as natural deep eutectic solvent

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**Abstract**
This research aimed to extract active substances, namely caffeine, chlorogenic acid and catechin from coffee cherries using environmentally friendly solvents based on natural deep eutectic solvent (NADES). The maximum concentration of caffeine extracted using NADES composed of choline chloride - xylose, was 264 ppm. Extraction of this substance showed varying concentrations with different composition of NADES as choline chloride with xylose > glucose > lactic acid > propylene glycol > citric acid > proline > glycerin > fructose. The maximum concentration of chlorogenic acid obtained using choline chloride-xylose, was 29.1 ppm. The extraction of chlorogenic acid indicated different concentrations with various NADES compositions using choline chloride with xylose > glucose > proline > fructose > citric acid > lactic acid > glycerol > propylene glycol. The catechin showed that the maximum extract using choline chloride-glucose with the concentration of 43 ppm.
Therefore, NADES is considered a green solvent that holds potential for application in the pharmaceutical industry for the production of various products.

*Keywods*: NADES, caffeine, chlorogenic acid, coffee cherry

## 1. Introduction

Coffee, as a global significant agricultural commodity, generates solid waste such as coffee cherries [1]. This waste has prompted numerous research studies to explore various methods of utilization, including biogas production [2,3], alcohol production, biosorbent development, and composting [1]. Typically, the active substances present in coffee cherries can be extracted using water[4,5] and organic solvents such as ethanol, acetone, methanol and octanoic acid [6-8]. The use of large quantities of organic solvents can contribute to environmental pollution. In recent years, there has been growing for sample preparation focus on green extraction that are sustainable and environmentally friendly [9].

Natural deep eutectic solvent (NADES) is developed and widely applied in various natural products. They are connected through hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). The composition of their compound involves several functional groups such as hydroxyl, carboxyl, and amino acids. As a substitute for organic solvents, NADES has several advantages such as easy preparation, high solubility, high thermal stability, and low melting point [10].

NADES is widely applied to extract the natural compounds. The extraction of phenolic compounds has been successfully with NADES [11.12]. Other application NADES for extraction such as flavonoid [13] antioxidant for anion [14], alkaloid [15], and bioactive compounds from *Cinnamomum burmannii* [16]. This research aims to explore the application of NADES in separating caffeine, chlorogenic acid and catechin from coffee cherries, with the potential for developing these compounds into pharmaceutical products. These compounds are widely used as medicines such as stimulants, analgesic and antioxidant.

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## 2. Experimental

### 2.1. NADES Preparation [1]

NADES solvents are prepared by mixing choline chloride with fructose, citric acid, glycerol, proline, glucose, xylose, propylene glycol, and lactic acid in a molar ratio (1:2) for each. The solvent preparation involved heating the mixture at 100ºC for 2 hours.

### 2.2. Extraction using NADES [17]

Extraction of active substances from coffee cherries was performed using various compositions of NADES. For each extraction, 1 gram of sample was mixed with 10 mL of NADES and stirred at 120 rotations per minute for 30 minutes. Subsequently, the mixture was filtered, and the resulting extract was analyzed by HPLC to determine the presence of caffeine, chlorogenic acid and catechin.

### 2.3. Caffeine and chlorogenic acid analysis [11]

Analysis of caffeine and chlorogenic acid using a reversed phase HPLC column was utilized to analyze a 10 mg/mL coffee extract solution. The mobile phase consisted of solvent A (50 mM acetic acid in distilled water (aqua bidest) and solvent B (50mM acetic acid in acetonitrile)

## 3. Result and Discussion

### 3.1. Caffeine analysis from coffee cherry extract in NADES

The caffeine component in coffee cherry extract in NADES was analyzed using HPLC. Identification results based on the chromatogram of coffee cherry extract using NADES, are presented in Figure 1.

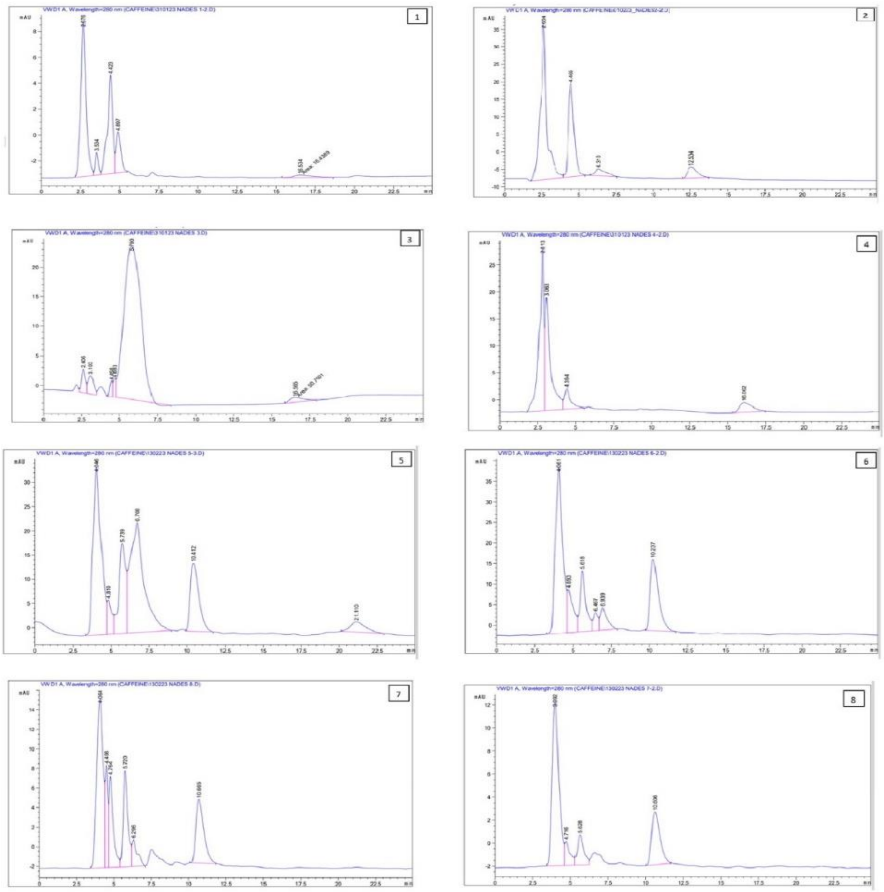

**Figure 1.** Caffeine spectrum from coffee cherry extract. NADES based on choline chloride with (1) fructose (2) citric acid (3) glycerol (4) proline (5) glucose (6) xylose (7) propylene glycol
(8) lactic acid

Figure 1 clearly the ability of NADES to separate of active compounds from coffee cherries, specifically caffeine. The chromatogram indicated the successful identification of caffeine, the active ingredient, in coffee cherry waste using NADES with different compositions. It is worth noting that this substance can

be extracted by various methods such as water extraction, supercritical $CO_2$, extraction, and organic solvents including chloroform, ethanol, methyl chloride, ethyl acetate, and acetone. Several other methods used were soxhlet, ultrasonic, and reflux extraction. To obtain caffeine in the form of a white powder, it is necessary to extract it into various solvents, followed by solvent evaporation [18]. In this research, green solvent which can extract caffeine from coffee fruit waste based on NADES, a group of sugar compounds, amino acids and organic acids, was successfully synthesized. The identification chlorogenic acid, based on the chromatogram of coffee cherry extract using NADES, are presented in Figure 2.

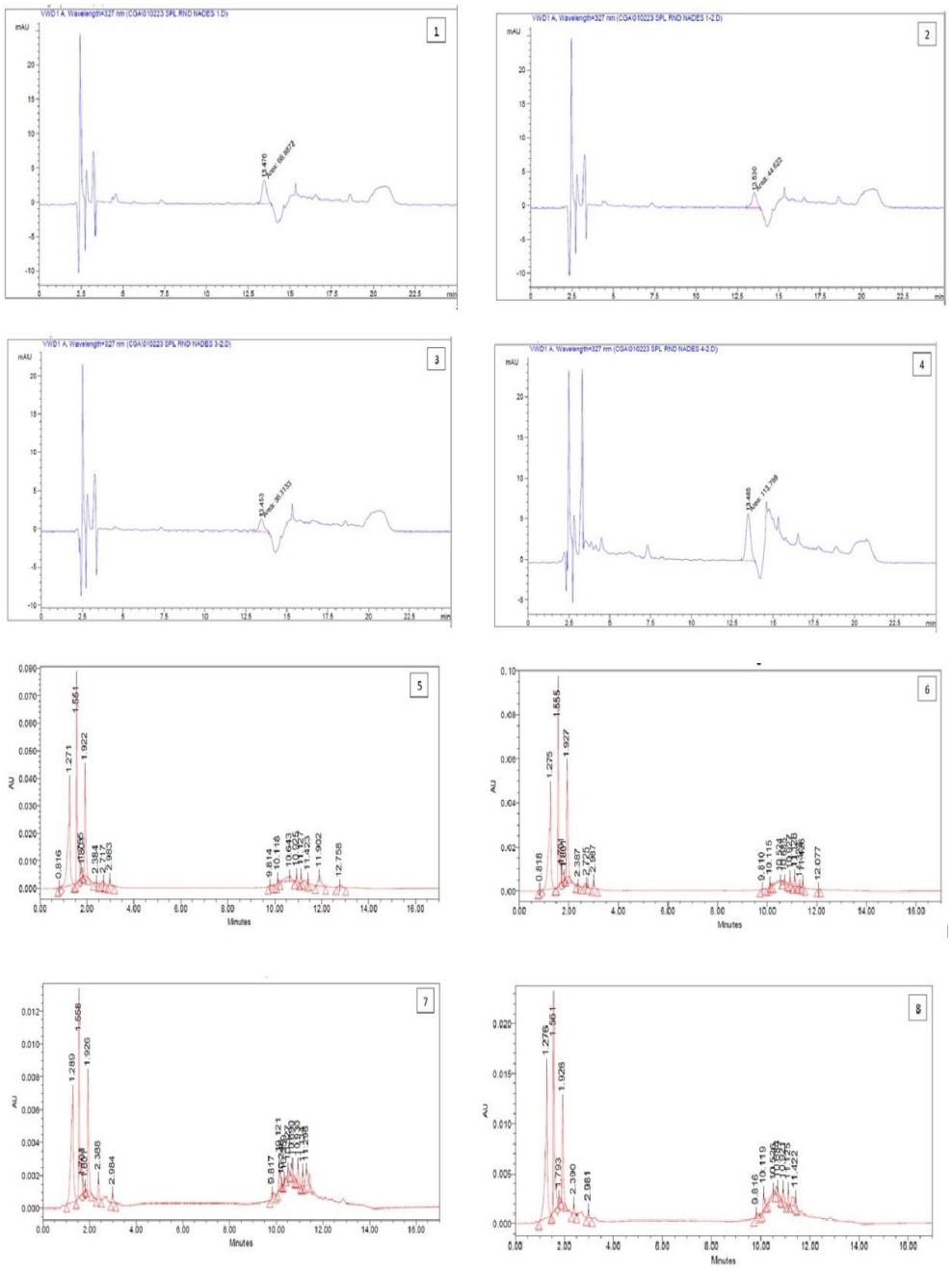


**Figure 2.** Chlorogenic acid Spectrum of Coffee Cherry Extract in NADES. NADES based on choline chloride with (1) fructose (2) citric acid (3) glycerol (4) proline (5) glucose (6) xylose (7) propylene glycol (8) lactic acid

Figure 2 clearly show the ability of NADES in extracting active compounds from coffee cherries, specifically chlorogenic acid. The chromatogram highlights the successful identification of chlorogenic acid, the active substance, in coffee cherry waste using NADES with different compositions. The result of

catechin analysis from coffee cherry extract in NADES can be seen in Figure 3.

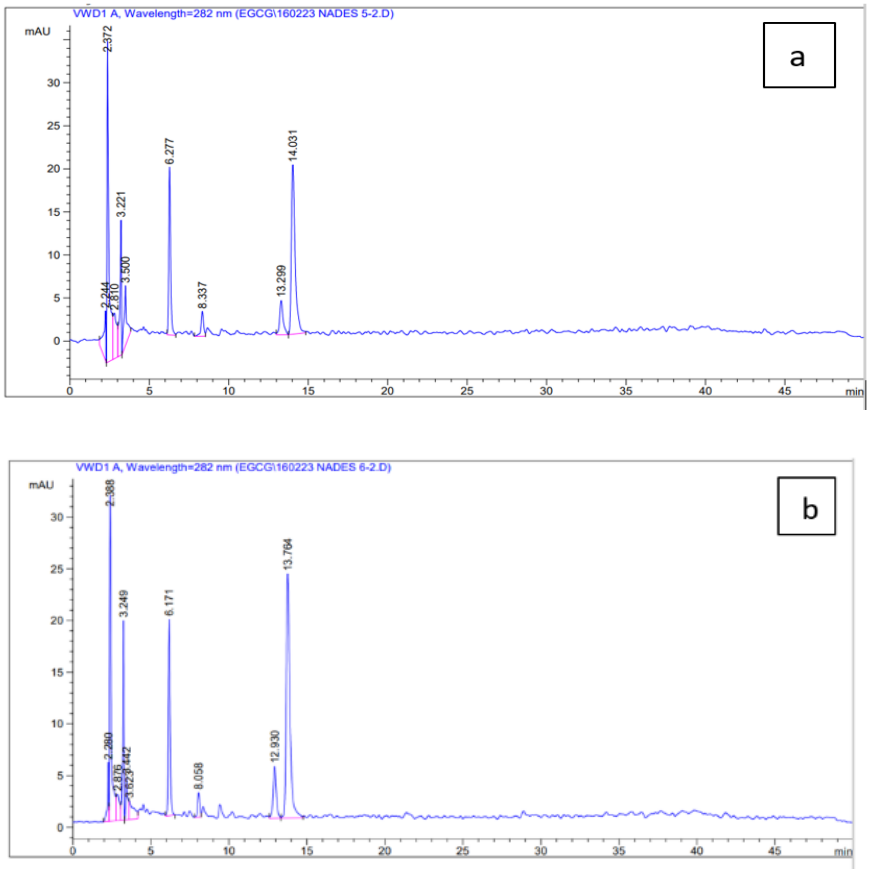


**Figure 3.** Catechin Spectrum of Coffee Cherry Extract in NADES. NADES based on choline chloride with (a) proline (b) xylose

Catechins are a class of secondary metabolite compounds that are naturally produced by plants as flavonoid class. This compound has activity as antioxidant because it has a phenolic group. In this research, NADES as green solvent was successfully synthesized as a green solvent and proved to be capable of extracting caffeine and chlorogenic acid (CGA) from coffee cherry waste, which consists of sugar compounds, organic acids and amino acids. The concentration of CGA, is shown in Table 1.

**Table 1.** Caffeine and chlorogenic acid concentration in coffee cherry extract

| Solvent | Composition | Caffeine (ppm) | CGA (ppm) | Catechin (ppm) |
|---|---|---|---|---|
| NADES 1 | Choline chloride - fructose | 15.3 | 10.0 | ND |
| NADES 2 | Choline chloride – citric acid | 73.8 | 10.0 | ND |
| NADES 3 | Choline chloride - glycerol | 32.9 | 6.0 | ND |
| NADES 4 | Choline chloride - proline | 71.8 | 21.0 | ND |
| NADES 5 | Choline chloride - glucose | 248.0 | 24.1 | 43,0 |
| NADES 6 | Choline chloride - xylose | 264.0 | 29.1 | 27,2 |
| NADES 7 | Choline chloride - propylene glycol | 81.0 | 4.8 | ND |
| NADES 8 | Choline chloride – lactic acid | 106.0 | 7.0 | ND |

Table 1 indicates that each NADES with different composition can extract caffeine from coffee cherry waste at varying concentrations. Specifically, NADES 6 with composition of choline chloride-xylose showed a maximum level of extraction at 264 ppm. This was followed by choline chloride-glucose at 248 ppm and lactic acid at 106 ppm. The sequential order of caffeine concentration extraction includes choline chloride - xylose > choline chloride - glucose > choline chloride - lactic acid > choline chloride - citric acid > choline chloride - proline > choline chloride - glycerin > choline chloride - fructose. Caffeine (1,3,7,-trimethylpurine-2,6-dione) with the molecular formula $C_8H_{10}N_4O_6$ usually accumulates in coffee beans. Its chemical structure is stable against heat and provides anti-aging, photoprotective and antioxidant properties [19]. Caffeine is classified as a nervous system stimulant drug, belonging to the alkaloid group [20] . Alkaloids are nitrogen-containing compounds in plants, which possess bitter taste and are often physiologically active in humans [18]. Caffeine is classified as a stimulus because it can increase the activity of the cardiovascular, digestive and nervous systems [20]. It has a melting point of 234 $^oC$ – 239 $^oC$. NADES with different compound compositions can extract chlorogenic acid from coffee cherry waste at varying concentrations. Specifically, NADES 6 with a composition of choline chloride showed the maximum level of extraction of this substance at 29.1 ppm. This was followed by choline chloride-glucose (24.1 ppm) and proline (21.0 ppm). The chlorogenic acid extraction include choline chloride with xylose > glucose > proline > fructose > citric acid > lactic acid > glycerol > propylene glycol. The catechin compound analyzed as epigalocatechingalate (EGCG) was obtained using NADES 5 (choline chloride-glucose) with a maximum level of 43 ppm. The next extract was followed by choline chloride-xylose with a level of 27.2 ppm.

## 4. Conclusion

NADES-based green solvent was successfully synthesized using choline chloride as HBA and compounds such as fructose, citric acid, glycerol, proline, glucose, xylose, propylene glycol and citric acid as the HBD. This solvent was applied to separate the active substances, specifically caffeine, chlorogenic acid and catechin, from coffee cherry waste. The spectrum of Caffeine and chlorogenic acid showed that the maximum extracts was obtained using choline chloride-xylose NADED, with concentrations of 264 and 29.1 ppm, respectively. The catechin showed that the maximum extract using choline chloride-glucose with the concentration of 43 ppm.

## 5. Acknowledgments

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## 6. Conflict of Interest

There is no conflict of interest

## 7. References

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