

**UNIVERSITI TEKNOLOGI MARA**

**COSMO-RS SCREENING AND  
SYNTHESIS OF DEEP EUTECTICS  
SOLVENTS FOR THE EXTRACTION  
OF DELPHINIDIN-3-  
SAMBUBIOSIDE FROM *HIBISCUS*  
*SABDARIFFA***

**RAIHANAH BINTI ROSLAN**

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## ABSTRACT

The underutilization of *Hibiscus sabdariffa* (roselle), despite being rich in valuable anthocyanins such as Delphinidin-3-sambubioside (Dp3-sam), presents a missed opportunity for developing functional ingredients. Conventional extraction relies on hazardous organic solvents and long maceration periods (up to 48 h), which contradict green chemistry principles and limit industrial scalability. Although deep eutectic solvents (DESs) have emerged as greener alternatives, most reported studies employ DESs as primary solvents. Limited work has evaluated DESs as additives to water for improving selectivity towards standardised Dp3-sam while simultaneously integrating process optimization and kinetic understanding. In this study, DESs as additive in water were investigated as greener extraction media combined with irradiation-assisted extraction. A COSMO-RS screening approach was first applied to evaluate solute-solvent compatibility based on capacity, selectivity and performance index. Choline chloride(ChCl)-based DESs with betaine (Be), triethylene glycol (TEG), levulinic acid (LevA) and oxalic acid (OA) were identified as promising candidates. The selected DESs were synthesised, characterized, and subsequently incorporated as additive in water for microwave-assisted extraction and ultrasonic-assisted extraction (UAE). Response surface methodology was used to determine optimal extraction conditions, and kinetic modelling was conducted to describe mass transfer behaviour. Experimentally, ChCl:TEG (1:1) produced the highest total anthocyanin content (TAC) of 73.54 mg CGE/L at a solid-to-solvent ratio of 1:15. Under UAE conditions, 5% DESs with a particle size of 750  $\mu\text{m}$  yielded 96.83 mg CGE/L. Optimization identified 5% DESs, 60% amplitude, and 19.87 min as the best operating conditions, resulting in 100.48 CGE/L TAC with an AARD of 3.82%. Kinetic evaluation showed that the Modified Fick's Law provided the best fit (AARD 3.03%), with the  $k_w$  coefficient ranged from 0.0554 to 0.2600  $\text{min}^{-1}$  while the  $k_d$  coefficient ranged from 0.0002 to 0.1938  $\text{min}^{-1}$ , indicating washing dominance at 5% DESs with 60% amplitude and enhanced diffusion at 20% DESs and 40% amplitude. This work demonstrates that using DESs as additives rather than the main solvents, together with optimized UAE, can enhance selectivity towards standardized Dp3-sam while reducing hazardous solvents dependence and extraction time. The findings contribute a greener extraction strategy that is scientifically justified, technically scalable, and relevant for the development of stable, standardized roselle-based extracts that support safer food, nutraceutical, and colorant applications.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

The abundant *Hibiscus sabdariffa*, commonly known as roselle in Southeast Asia, has gained attention as a commodity. In Malaysia, its commercialization began through initiatives led by the Department of Agriculture (DOA) Terengganu in 1990. By 2024, roselle cultivation was largely dominated by smallholders, with plantations established across 8 out of 14 Malaysian states producing 103 million tonnes yearly (Department of Agriculture Malaysia, 2024). Roselle calyces are primarily marketed as teas, jams, and beverages, while China and India incorporated roselle more regularly into the daily diet. This demand is supported by the presence of bioactive compounds such as antihypertensive, antidepressants, and mainly antioxidants, which can offer nutraceutical and pharmaceutical benefits. However, despite rising interest, challenges remain within the value chain. The DOA strategic plan (2020-2024) highlighted growing consumer demand for herbal and organic-based products, yet adoption of improved technology among smallholders and post-harvest handling limitations continue to restrict product diversification. (Department of Agriculture Malaysia, 2020, 2024). Hence, the introduction of post-processing enhancers such as irradiation-assisted extraction might be able to solve the problem. This could open the possibility for the exploration of a variety of roselle-based products with vast formulations for consumers.

The predominant antioxidant in roselle, delphinidin-3-sambubioside (Dp3-sam) constitutes approximately 70% of the total anthocyanins (Marquez-Rodriguez et al., 2021; Shruthi et al., 2016; Sindi et al., 2014; Somaratne et al., 2025). Dp3-sam has been explored for various pharmaceuticals and nutraceuticals prospects such as for the treatment of hypertension, hyperlipidaemia, cancer along with other inflammatory diseases (Riaz et al., 2021; Riaz & Chopra, 2018). These properties highlight the importance of extracting standardized Dp3-sam efficiently. Therefore, the extraction of standardized Dp3-sam has been explored with various solvents and methods employed. Conventional extraction of standardized Dp3-sam relies heavily on volatile organic solvents such as methanol and ethanol (Chen et al., 2019; J. Tan et al., 2022). Although effective due to their selectivity, these solvents require large volumes and long