Development and optimization of a microwave-assisted extraction process of spent coffee grounds using betaine-glycerol Natural Deep Eutectic Solvent

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Coffee, with a global consumption of 2.25 billion cups per day, is one of the mostly consumed nonalcoholic beverages in the world and one of the most traded agricultural commodities (Roberts, 2016). The total consumption in 2019/2020 reached the amount of almost 165 million 60 kg bags (ICO, 2020). Almost 50% of the overall production is used for drinking purposes. It has been estimated that 650 kg of spent coffee grounds (SCG) are generated during processing of 1 ton of green coffee while 2 kg of wet spent coffee grounds result from the preparation of 1 kg of soluble coffee (Karmee, 2018). SCG are also produced in domestic environment in addition to the coffee industry. Hence, huge quantities of residue are produced every year, which now days in Europe, are mainly disposed in landfills (Pettinato, Casazza and Perego, 2019).

Spent coffee waste valorization includes promising applications in energy with biodiesel production and biomass briquettes (Haile, 2014), in pollutants remover as sorbent, in composites production, in construction materials, as dietary fiber, even for uses in furniture. More importantly SCG are a valuable source of several bioactive compounds, some, like chlorogenic acids and trigonelline naturally occurring and some, like melanoidins and nicotinic acid formed during brewing (Stylianou *et al.*, 2018).

Recovery of the natural antioxidants present in SCG in order to be used in nutraceuticals, implies eco-friendly techniques such as supercritical fluid, microwave and ultrasonic extractions. Microwave-assisted extraction (MAE) seems to be the most favorable due to high selectivity and yield in addition to lower time and solvents consumption (Pettinato, Casazza and Perego, 2019; Coelho *et al.*, 2021).

Along with the extraction method, the choice of solvent is crucial for the composition and quality of the final extract. Natural deep eutectic solvents (NaDES) are considered as green solvents with desirable properties. They are composed of naturally occurring metabolites, they are biodegradable, show chemical and thermal stability and can dissolve many different compounds due to their adjustable physicochemical properties. They are promising solvents for extraction processes since they offer increased extraction yields, stabilization of the obtained extracts, and protection of the extracted compounds (Koutsoukos *et al.*, 2019; Skarpalezos and Detsi, 2019; Tzani *et al.*, 2021; Tzani, A; *et al.*, 2022). Thus, the NaDES-extracts can be incorporated as obtained in final products without any purification or solvent removal steps.

The aim of this study was the development and optimization of a microwave-assisted extraction process of SCG using a NADES as a green solvent. The NADES Betaine-Glycerol (1:3) was synthesized using the simple heating and stirring method. Espresso coffee domestic residues from various commercial coffee brands of no specific variety were used. All residues were homogenized and air dried for 72 hours in a dark room. For the sake of comparison, extractions using hydroethanolic solutions and magnetic stirring were also performed.

A 3 level-4 factor Taguchi design of experiments (DOE) was implemented in order to optimize the MAE parameters. The effects of H_2O/NADES ratio (0-75% v/v), solid to liquid ratio (1-10%), extraction time (1-3 h) as well as temperature (40-60 °C) were tested. A L9 orthogonal experiment plan was applied with all combinations among factors and their levels in order to study their effect on phenolic compounds extraction. The metric of signal-to-noise (S/N) ratio was employed to find the optimum conditions. The extracts' TPC and Total Flavonoid Content (TFC) were used as the response factors. Regression analysis was used for results prediction in conditions within and beyond the design levels. Confirmation experiments were performed at optimum conditions and were in accordance to the predicted values.

Solid to liquid ratio and temperature were shown to be the most influential factors. The 1% solid to liquid ratio, 60 min and H_2O/NADES 50:50 v/v were shown to be optimum for TPC and TFC however, increasing the temperature was shown to positively affect the responses, we set out to perform an additional experiment at 90 ºC. The TPC and TFC were found to be up to 30.9±0.8 mgGAE/gSPG and 22.17±1.7 mgCATE/gSPG respectively. These conditions were also applied on spent grounds of different coffee varieties and the results are presented in Table 1.

Table 1. TPC and TFC of the extracts of different coffee varieties from MAE with H_2O/NADES 50:50v/v, 1% solid to liquid ratio at 90°C for 60 min

Coffee variety	TPC (mgGAE/gSPG)	TFC (mgCATE/gSPG)
Kenya	29.8±2.5	20.4±3.3
Ethiopia	21.5±0.2	15.8±0.6
Guatemala	21.2±2.3	18.8±1.5
Brazil	19.9±2.9	16.2±1.8
Ruanda	22.1±1.8	17.1±2.1

Among the different varieties, Kenya variety exhibits the highest TPC of 29.8 mgGAE/gSCG and TFC of 20.4 mgCATE/gSCG while all the rest varied between 19.9-22.1 mgGAE/gSPG and 15.8-18.8 mgCATE/gSPG respectively.

Overall, the use of betaine-glycerol (1:3) NaDES resulted to the highest yield of TPC and TFC (with a value of 30.9±0.8 mgGAE/gSCG and 22.17±01.7 mgCATE/gSPG respectively) while the hydroethanolic solution in the same conditions rendered 18.67±0.2 mgGAE/gSCG and 22.88±0.4 mgCATE/gSPG and the conventional method (hydroethanolic solutions, 24h, room temperature) 13.75±2.13 mgGAE/gSCG and 13.77±1.11 mgCATE/gSPG respectively.

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