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Minimisation of Waste via the Valorisation of Spent Coffee Grounds into High-Value Products

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Spent coffee grounds (SCG) valorisation can produce high-value products to supply cosmetics, petroleum and pharmaceutical industries among others. An overview of the various products achievable from spent coffee grounds valorisation are established, while the effect of temperature, reaction time and solid-to-liquid loading ratio on the yield of caffeine extracted from SCG was investigated. The best extraction solvent between (i) dichloromethane, (ii) 1-ethyl-3-methylimidazolium chloride (IL) and (iii) water was established. Characterisation of SCG using Technical Association of the Pulp and Paper (TAPPI) methods was carried out. Variations of parameters were established using the Box-Behnken design of experiment (DOE) which varied the investigated parameters; (i) temperature (88 – 120 ºC), (ii) reaction time (15 - 35 min) and (iii) solid-to-liquid loading ratio (5 g SCG per 10 -25 mL). The conventional extraction method used dichloromethane as the extraction solvent, whereas the green method used the ionic liquid and water in a Parr pressure reactor. High performance liquid chromatography (HPLC) quantified the yield of extracted caffeine. Recrystallised caffeine is analysed using scanning electron microscopy (SEM), transition electron microscopy (TEM) and energy dispersive spectroscopy (EDS) for its structural properties, crystalline structure and physical analysis, while differential scanning calorimetry (DSC) established the purity of extracted caffeine achieved from each extraction solvent. The expected yield of caffeine is between 4.67 and 8.0 mg/g SCG. According to this experimental methodology, at 120 ºC, 25 min reaction time and 25 mL solvent volume the extraction yield ranged from 2.83 to 3.67 mg/g SCG.

1. Introduction

Spent coffee grounds are solid residues obtained in large quantities on the completion of coffee brewing processes, considered hazardous waste when released directly into the environment since the oils and other compounds make the soil acidic, causing damage and contamination to the surroundings while contributing to the greenhouse effects. SCG production is continuously increasing proportional to the global world population, hence justifying the need to utilize the waste while minimising waste build up in landfill sites, pollution and contamination and simultaneously extracting specific components for the production of high-value products from a cheap but highly potential source (Rodrigues et al., 2014). SCG is renewable and reliable in nature; wide availability; sustainability; cheap and cost efficient source; the presence of large amounts of organic compounds; numerous health and environmental benefits.SCGs composition includes lignocellulosic materials that require to be broken down and digested by enzymes, chemicals or a pre-treatment step being required to overcome the hindering lignin limitations during extraction processes. SCG composes of large amounts of fatty acids, amino acids, polyphenols, minerals and polysaccharides proving its capabilities to produce a wide variety of low, medium and high value products such as food additives, pharmaceutical products, caffeine, bio-sorbents, fertilizer, livestock feed, composts, cosmetics and biofuels while reducing its harmful environmental impacts, waste build-ups and carbon footprint. According to Girotto (2018), SCGs contain carbohydrates, proteins and many other rich chemical components which were not extracted from the coffee bean when brewed. Chiang et al. (2018) highlighted the main challenges of caffeine extraction being high energy intensive conventional pre-treatment methods and low yields of caffeine, hence the need to develop a novel technology system. This study will establish the best operating conditions for caffeine extraction in a Parr pressure reactor. Extraction using

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ionic liquids in a Parr pressure reactor is advanced green and sustainable technology for the future. Valorising SCG into high quality caffeine is of great benefit to the medicinal field.

1.1 Caffeine

As early as 1820, caffeine has been part of innumerable cultures. Bisht and Sisodia (2010) described caffeine as “a wonder gift to medicinal science.” It is naturally occurring in over 60 plants including tea leaves, cola nuts, cocoa pods and coffee beans. Caffeine’s solubility in water is 1 g per 46 mL of water. Therefore, we can gather that an excess amount of caffeine remains in the already brewed, waste coffee beans (Lin and Hu, 2018). Caffeine’s ($C_8H_{10}N_4O_2$) IUPAC name is 1,3,7-trimethylxanthine appears as a white crystalline powder with a melting point range of 234 - 236.5 °C. Caffeine has pharmacological effects on humans and animals. It has a bitter taste and can also be used as a sharp flavouring additive. Caffeine has a wide variety of uses, such as a stimulant to the central nervous system (CNS), cardiac heart muscles, and respiratory system; acts as a diuretic; stimulation the mind, and alertness levels; increases concentration; increases individual sporting ability, better absorption of medication; reduction of inflammation and heart related diseases. 10 g of caffeine is considered the lethal dose of caffeine. The recommended daily consumption of caffeine is 200 to 400 mg, which equates to two to four cups of coffee (Petre, 2023). Like any other drug, the over consumption of caffeine can lead to severe side effects such as headaches; muscle cramps; insomnia; raised blood pressure; amplified stress levels; urinary infections and dehydration.

1.2 Ionic Liquids

Biomass is considered an abundant renewable and environmentally friendly source, but it is still of great interest to produce green energy and bioproducts from these lignocellulosic materials (Xiao et al., 2018). The commonly used conventional solvents require to be replaced by solvents that are less toxic, less flammable and less polluting since these are a few of the major challenges the chemical industry faces. Ionic liquids (IL) are sometimes called green solvents mainly because ILs have negligible vapour pressure, are non-flammable, have minimal vapours and atmospheric environmental spills are avoided. These characteristics make ILs much safer and environmentally suitable compared to that of conventional volatile organic compounds. The use of ILs is growing immensely due to global environmental factors, sustainability practises and environmentally friendly procedures present. The use of ILs is highly advantageous due to the wide variety of solvents available, easily amendable properties, negligible vapour pressure, non-flammable therefore lower risks, compounds can be separated due to the vapour pressure differences and their high stability against temperature and electrochemical decomposition property.

2. Factors Affecting Extraction of Caffeine from Spent Coffee Grounds

Coffee is the most popular beverage in the world. The coffee brewing process is an important step in achieving the quality of the final product, and the extraction method used during brewing affects the bioactive compounds released. The composition of the coffee varies depending on the brewing method, particularly in chlorogenic acids and caffeine content. Many factors affect the coffee brewing process, including taste, strength and aroma. Factors such as the type of coffee, brewing time, temperature, water type, pressure, degree of roasting, coffee-to-water ratio, stirring, and volume of coffee solution potentially impact caffeine content and the amount of caffeine leftover in the coffee grounds.

2.1 Particle size of coffee grinds

Grinding coffee to reduce grinds to finer particles increases the surface area during extraction, leading to increased release of volatile and non-volatile compounds in the brewed solution (Akiyana et al. 2015). Finer particles increase the contact surface area for direct contact during the extraction process, which in turn increases the permeability of chemicals and substances released into the water. This process also influences the extraction yield of caffeine, making it faster and reducing the overall extraction time Cordoba et al. (2019).

2.2 Brewing/reaction time

Coffee brewing time depends solely on the brewing method, since different coffee qualities are obtained (Nhan and Phu, 2012). The shortest brewing time contrasts with a distinctive property of espresso machines (3 times for 13 s or a total of 42 s) or the longest cold brewing time of 282 or 420 min. According to the study by Ludwig (2014), the highest caffeine concentration of 7.908 g/L while the lowest value recorded by Rao et al. (2020) was 1.036 g/L. If only brewing time is considered as an influencing variable on the caffeine extraction, the coffee prepared in the coffee machine over a shorter period had significantly higher caffeine content than the cold brew coffee, despite the shorter brewing times. Therefore, it is evident that high caffeine yields can be achieved through shorter brewing times when other influencing factors are met.

2.3 Pressure

Pressure can significantly affect the extraction process and yield. Caprioli et al. (2015) investigated the effect pressure (7, 9, 11 bar) has on the caffeine content of both Arabica and Robusta brewed coffee. Maximum caffeine yields (10.303 g/L) were obtained at 7 bar and a water temperature of 92 °C.

2.4 Temperature

When water flows through coffee grinds, bioactive substances are released into the brew. Water temperature has a significant impact on the amount of caffeine released into the coffee solution, as caffeine is moderately soluble in water at 20 °C (1.46 mg/mL). The solubility of caffeine increases at 80 °C to 180 mg/mL and peaks at 100 °C, extracting 670 mg/mL Espresso coffee machines work at temperatures between 92 °C and 94 °C, with a pressure of 7 bars. Caetano et al. (2012) studied the influence temperature had on caffeine extraction, and noticed an increased level of caffeine when the temperature was increased from 88 °C to 92 °C. Further increasing the temperature to 98 °C showed less caffeine extracted regardless of the high pressure used. Caprioli et al. (2014) concluded that the best conditions for caffeine extraction were at 92 °C and 7 bar. Salamanca et al. (2017) showed that lowering the temperature from 93 °C to 88 °C reduced the caffeine yield. Rao et al. (2016) and Angeloni (2016) confirmed by using the same operating conditions, confirmed that lower temperatures slow down the extraction of caffeine.

2.5 Solid-to-Solvent loading ratio

Increasing the volume of organic extraction solvent is expected to increase the extraction yield of the caffeine as more solutes come into contact with the coffee grounds. The solid to solvent ratio has a significant impact as it allows for reaching the optimal extraction point with the highest extraction yield (Angeloni et al., 2016).
Characterisation of the SCG is done using the Technical Association of the Pulp and Paper Industry (TAPPI), a method established SCG composition as cellulose (12.4%), hemicellulose (39.1%) which consists of 3.6% arabinose, 19.07% mannose and 16.43% galactose, together with lignin (23.9%), fat (2.29%), proteins (17.44%) and dietary fibres (6.46%). Experimental runs were established using the Design of Experiment. The parameters investigated were water, dichloromethane and 1-ethyl-3-methylimidazodium chloride as extraction solvents with varying (i) solid-to-solvent loading ratios; (ii) reaction time and reaction temperatures.

3. Materials and Methodology

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3.1 Extraction of caffeine using a Parr pressure reactor

A Parr pressure reactor allows reactions at higher temperatures (500 ºC) and pressures (5,000 psi). The reactor vessel consists of a 50 mL Teflon beaker into which spent coffee grounds and the extraction solvent was inserted. Nitrogen gas was used for pressurisation inside the reactor with a set pressure limit of 7 bar. Extraction occurs from the point at which the SCG is wet and the water-soluble components leave the solid phase and enter the liquid phase. After exiting the Parr reactor, the solution is filtered and evaporated using a rotary evaporator to remove the extraction solvents prior to HPLC analysis and quantification.

3.2 Crude extraction and recrystallisation of the extracted caffeine

After extraction in the Parr pressure reactor, the solution is cooled down using an ice water bath before purification of the crude caffeine is necessary to achieve solid powder caffeine. 5 g of sodium chloride and 0.25 g of calcium hydroxide is added to the filtrate to remove any water present. Solid-liquid extraction was performed followed by liquid-liquid extraction (LLE) (Figure 1a), where the caffeine is extracted using dichloromethane, water or the 1-ethyl-3-methylimidazodium leaving the less dense solvent at the top. Caffeine is to be recovered from the organic phase by evaporation of the solvent (Figure 1b). The evaporation will produce crude caffeine (Figure 1c). The organic layer is treated with magnesium sulphate ($MgSO_4$) to remove water and remove any emulsions present. Thereafter, the crude caffeine extract is washed with ethanol and dried to remove any impurities that were in the aqueous layer, which are further processed to form crystals of pure white caffeine (Figure 1d). Removal of the solvent was done using a rotary evaporator, equipped with a lukewarm water bath connected to a cold tap. Dichloromethane evaporated at 39.6 ºC, leaving the crude caffeine behind. The IL organic later was washed three times with ethanol, and thereafter evaporated.

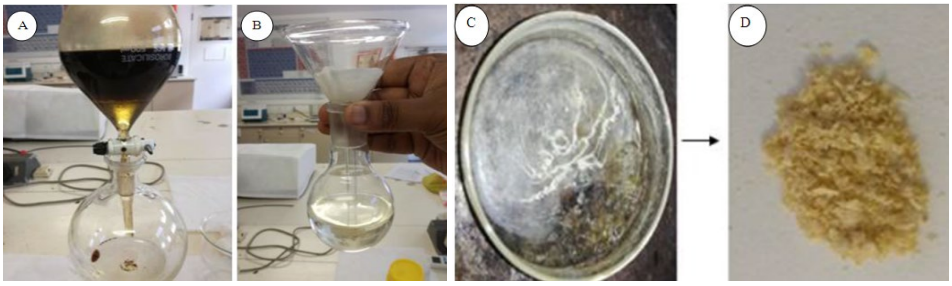

Figure 1: Image of (a) liquid-liquid extraction of caffeine and solvent, (b) organic phase containing caffeine , (c) extracted crude caffeine and (d) extracted powder caffeine

4. Analysis of extracted caffeine

The 99 % pure caffeine standard was obtained from Merck (Germany) and diluted to concentrations of 200 ppm standard solutions. The retention time of the caffeine standard and the corresponding peak area were determined using HPLC, Shimadzu system. A Germin 5 C18 reversed phase column (5 m OD, 4.6 m ID and 150 mm length) was used at 25 ºC. Sample injections were 2 mL volume using an isocratic elution with a mixture of 0.1 % acetic acid in water (solvent A) and acetonitrile (solvent B). The constant solvent flow of 0.5 mL/min with an A/B ratio of 90/10 (v/v) for 30 min was applied. The caffeine was detected using a UV visible diode at a wavelength of 272 nm. The purity of the extracted samples and the surface structure was also analysed using scanning electron microscopy (SEM). SEM provided information about surface topography, microstructure, chemistry and composition of the SCG. Differential scanning calorimetry (DSC) was used to determine the purity of the extracted caffeine samples against the caffeine standard using the melting points (Figure 2). 1-2 g of caffeine sample and the caffeine standard were placed on a sample holder with integrated temperature sensors. The samples were maintained at the same temperature for a period of time. Each sample was inserted into the sample holder under a nitrogen flow of 60 mL/min and at a heating rate of 5 ºC/min.

5. Results and Discussion

To establish the purity of the extracted caffeine sample against the standard, the melting points of the samples were analysed. According to the literature, 100 % pure caffeine has a melting point of 234 °C – 236.5 °C (ChemicalBook, 2021). The blue line in Figure 2 indicates that the 99 % pure caffeine standard used has a melting point of 233.51 °C. The caffeine extracted using IL had a melting point of 226. 52 °C, concluding that the sample had a purity of 96 %, almost as pure as the standard sample used. The caffeine extracted using water had a melting point of 212.28 °C, achieving 90 % purity. The caffeine extracted using dichloromethane achieved the lowest melting point and the lowest grade of caffeine; at 200.5 °C and 85 % purity.

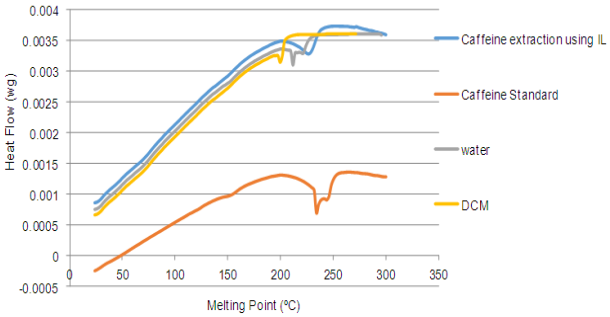

Figure 2: Graphical representation of the cumulative melting point of extracted caffeine samples

The extracted powdered caffeine was analysed against the pure caffeine standard. Figure 3 compares the pure caffeine (Figure 3a) to the caffeine extracted using 1-ethyl-3-methylimidazolium (Figure 3b); which appears clean and similar in shape and structure to the standard caffeine, also showing that the particles have the same crystallinity, structure and almost the same particle size of 10 µm and 8.75 µm, respectively. The same crystallinity and structure indicate that the entire extraction process was successful in obtaining a clean, uncontaminated sample. Comparing Figure 3c, the IL during extraction against water, it is shown that the caffeine was released, but was unable to fully separate. Oily substances were present surrounding the caffeine

molecules which decreased the purity of the caffeine achieved. Assuming that water was not efficient to remove any impurities and contaminants present, hence the lower grade of 90 % pure caffeine was achieved. The caffeine extracted using dichloromethane (Figure 3d) illustrated that the caffeine was less crystalline, appearing very small and thin. The oily substance released could have possibly hindered the proper formation of caffeine crystals.

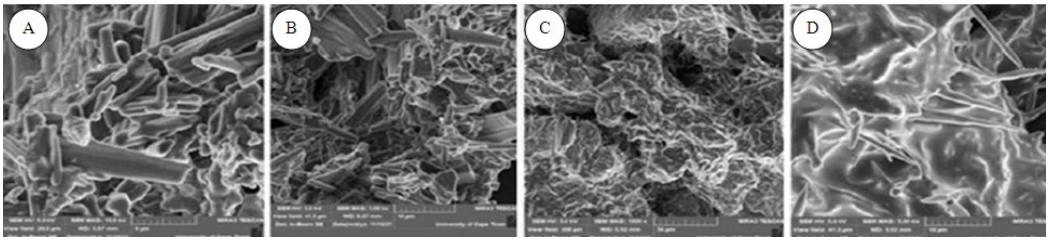

Figure 3: SEM micrographs of a) pure 100 % caffeine standard, (b), caffeine extracted with IL (c) caffeine extracted with water and (d) caffeine extracted with DCM

Quantification of caffeine using HPLC distinguished the relationship between reaction time, temperature and solid-to-liquid loading ratio against the extraction yield. The selection of the best extraction solvent was determined by the highest caffeine yield. At 88 ºC with 15 min extraction time and 17.5 mL extraction solvent, 337 mg/L and 439 mg/L of caffeine were extracted using water and dichloromethane respectively. Maintaining the extraction temperature of 88 ºC, with a longer extraction time of 25 min and solvent volume of 10 mL, the yield increased to 513.62 mg/L and 609.80 mg/L respectively. To test the effect of the solid-to-solvent loading ratio, 25 min reaction time with a 25 mL solvent was used, which yielded a higher caffeine content of 563.31 mg/L and 673.04 mg/L respectively. It was evident that the caffeine yield increased as the reaction time increased from 15 min to 25 min, and the solvent volume increased from 10 mL to 25 mL In order to analyse the effect of reaction time, the lowest temperature of 88 ºC was maintained with a longer reaction time of 35 min, and an average solid-to-solvent loading ratio of 17.5 mL. The caffeine yield was almost equal to that of a 15 min reaction time, indicating that reaction time is crucial in achieving the highest yield possible. This also proved that a longer extraction time does not mean a larger yield. Extraction conditions of 88 ºC, 25 min and 25 mL extraction solvent, dichloromethane extracted 673 mg/L caffeine, 636 mg/L using 1-ethyl-3-methylimidazolium and 566 mg/L using water. (Figure 4a)

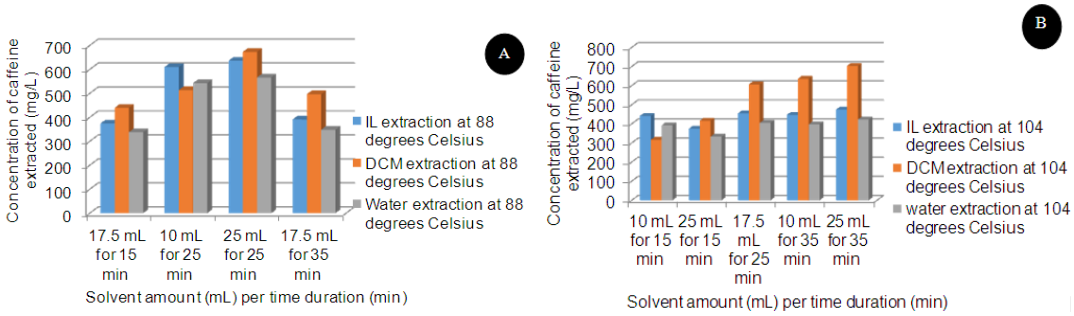

Figure 4: Cumulative extractions results obtained using various solid-solvent ratios and time durations (a) at 88 ºC; (b) at 104 ºC.

Increasing the reaction temperature from 88 ºC to 140 ºC a reaction time of 15 min, varying the solvent ratio from 10 mL and 25 mL, and extracted caffeine ranged from 316.54 mg/L to 441. 17 mg/L. This amount was lower than the yield extracted at 88 ºC with a 15 min reaction time, and 10 mL solvent volume. The same temperature of 104 ºC with a 25 min reaction time yielded a slight increase in caffeine extractions of 455 mg/L – 606.66 mg/L. However, this yield still did not exceed the value achieved by using 88 º C reaction temperatures. It was evident that at 104 ºC the highest caffeine yields were not achievable. Increasing the reaction time to 35 min at 104 ºC, the same yields that were achieved at lower temperatures and time were achieved. It can see that 104 ºC was not efficient in the caffeine extraction process (Figure 4b). Since water boils at 100 ºC, it is more likely caffeine would be achievable above 100 ºC, hence the effect of 120 ºC on caffeine extraction was analysed. At 120 ºC, 10 mL and 25 mL solvent volume yielded lower yields than 88 ºC. It is possible to state that using too high temperatures made the solvent evaporate, before allowing it to react with the SCG in the Parr pressure reactor. Increasing the reaction time to 25 min showed much higher yields of caffeine. At 120 ºC

with 10 mL and 25 mL solvent volume, the highest caffeine yield of 530.12 mg/L – 726.22 mg/L was extracted, proving these conditions were the best for caffeine extraction (Figure 5). At 120 ºC, 25 min of reaction time and 25 mL solvent volume, the IL extracted the highest caffeine yield of 726.22 mg/L, followed by water and dichloromethane extracting 646.33 mg/L and 566.12 mg/L respectively.

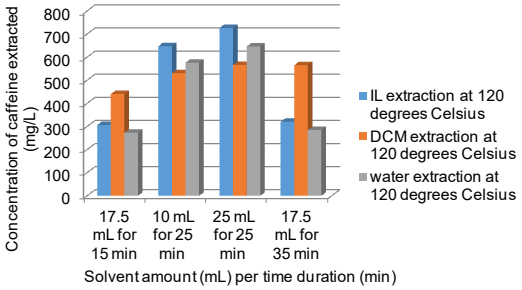

Figure 5: Cumulative extractions results obtained using various solid-solvent ratios and time durations at 120ºC

6. Conclusion

The routine home brewing and coffee percolations leave behind a major amount of caffeine in the coffee grounds. With technology and green processes, it was possible to use sustainable methods to extract the remaining caffeine. Dichloromethane and 1-ethyl-3-methylimidazolium chloride have great extraction potential; however 1-ethyl-3-methylimidazolium chloride extracted a higher yield of caffeine compared to water and dichloromethane. At 120 ºC, 25 min reaction time and 25 mL volume, caffeine extracted using IL, water and DCM was 726.22 mg/L, 646.33 mg/L and 566.12 mg/L respectively. At these conditions, a caffeine recovery of 60% was extracted. Using an ionic liquid continues the green engineering and sustainability principles of engineering. Caffeine is a much needed and valuable product in the healthcare, food and medicinal sectors that can be recovered from waste.

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