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Valorization of spent coffee grounds by 2-methyloxolane as bio-based solvent extraction. Viable pathway towards bioeconomy for lipids and biomaterials

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Abstract – This study attempts to shed light on the efficacy of the solvent 2-methyloxolane (2-MeOx) as an alternative for hexane in defatting spent coffee grounds (SCG). Higher lipid yields were obtained with the bio-based solvent dry 2-MeOx (13.67%) and water-saturated 2-MeOx (15.84%) compared to hexane oil yield, which is of petroleum origin and is a known neurotoxin. Palmitic acid and linoleic acid were the principal fatty acids identified. The fatty acid profile of coffee oils obtained with hexane, dry 2-MeOx and aqueous 2-MeOx were similar. Lipid hydrolysis was observed in oils extracted with 2-MeOx, which warrants further investigation. The residual caffeine content in the defatted SCG was highest when hexane was used highlighting better solubility of methylxanthine compounds in the solvent 2-MeOx.

Keywords: 2-methyloxolane / spent coffee grounds / lipid / caffeine

Résumé – Valorisation des marcs de café par le 2-méthyloxolane comme solvant d'extraction biosourcé. Voie viable vers la bioéconomie pour les lipides et les biomatériaux. L'objectif de cette étude était d'évaluer l'efficacité du solvant 2-méthyloxolane (2-MeOx) comme alternative à l'hexane dans le dégraissage du marc de café (SCG). Des rendements en lipides plus élevés ont été obtenus avec le solvant biosourcé sec 2-MeOx (13,67 %) et 2-MeOx saturé en eau (15,84 %) par rapport au rendement en huile obtenu dans l'hexane (solvant d'origine pétrolière et neurotoxique). L'acide palmitique et l'acide linoléique ont été les principaux acides gras identifiés. Les profils en acides gras des huiles de café obtenues avec de l'hexane, du 2-MeOx sec et du 2-MeOx aqueux sont similaires. L'hydrolyse des lipides a été observée dans les huiles extraites au 2-MeOx. La teneur résiduelle en caféine dans le SCG dégraissé était plus élevée lorsque l'hexane était utilisé, démontrant une meilleure solubilité des composés de méthylxanthine dans le solvant 2-MeOx.

Mots clés : 2-methyloxolane / marc de café / lipide / caféine

1 Introduction

Crude oil is the world's largest traded commodity, gratifying the ever-growing demand for our energy and fuel needs. And it is no surprise that coffee, also fondly referred to as "human fuel" ranks among the top ten traded food commodities globally (Murthy and Naidu, 2012; Santos *et al.*, 2021). Europe, the largest coffee market in the world accounts for one-third of the global coffee consumption (2019). The per capita coffee consumption in the European Union (2018) was reported be 5.15 kg (green coffee equivalent). And within Europe, France is the second-largest coffee consumer making up 12% of the European consumption in the year 2018 (European Coffee Report, 2018/2019). Spent coffee grounds (SCG) are the insoluble residues generated after milling and brewing of coffee beans, and they contain significant amounts of organic compounds namely fatty acids, amino acids, polyphenols, polysaccharides and minerals (Campos-Vega *et al.*, 2015). The chemical composition (Aguilar-Raymundo *et al.*, 2019) of spent coffee grounds is shown in Figure 1.

Under the current waste management system SCG are predominantly incinerated, dumped in landfills or categorically

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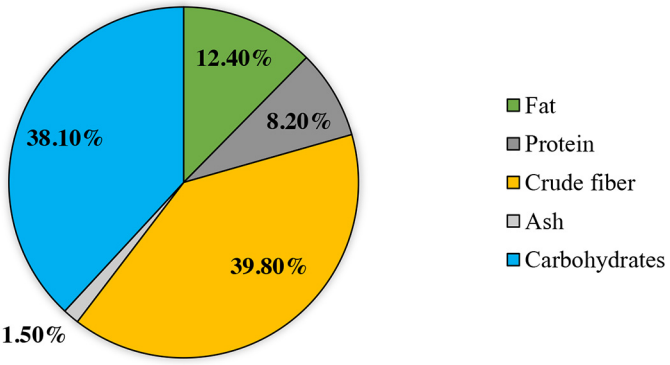

Fig. 1. Chemical composition of spent coffee grounds.

sorted with the organic fraction of the municipal solid wastes and recycled via anaerobic digestion or composting (Cameron and O'Malley, 2016; Battista *et al.*, 2020). Voluminous disposal of SCG directly in landfills without any prior pre-treatments could exacerbate global warming due to the increased emission of methane, carbon dioxide and other greenhouse gases (Atabani *et al.*, 2019).

Extraction is one of the vital tools that is used to retrieve compounds of commercial interest from complex biomasses (Chemat *et al.*, 2021). Using green extraction principles as an alternative to conventional methods is an added advantage that helps in realizing the true potential offered by a variety of plant materials. Indeed, the sustainability aspect of developing eco-friendly processes in both laboratory-scale and industrial-scale is a critical indicator that determines the success rate of such methods (Chemat *et al.*, 2019). Edible oil is ubiquitous and widely used in food, feed, cosmetic and pharmaceutical applications. Typical edible oil extraction relies heavily on hexane as solvent, which is of petroleum origin; is also a known pollutant and neurotoxin (Rapinel *et al.*, 2020). Recently, screening bio-based solvents as a potential alternative to replace hexane has been the scope of several research works. Within this domain, the solvent 2-methyloxolane, commonly known as 2-methyltetrahydrofuran was examined extensively for its usability for defatting of commercial oilseeds namely soybean and rapeseed as well as alternative lipid sources such as insects (Sicaire *et al.*, 2015; Ravi *et al.*, 2019; Rapinel *et al.*, 2020; Claux *et al.*, 2021).

Although studies on alternative techniques and bio-based solvents for lipid extraction from spent coffee grounds have been examined earlier, this study focuses on the feasibility of using dry 2-methyloxolane and aqueous 2-methyloxolane (95.5%) which is a saturated solution of water in 2-MeOx as alternatives to hexane for defatting SCG. Recycling of dry 2-MeOx is a crucial step in the industrial utilization of the solvent for oil extraction. During the recycling stage, after condensation and decantation, the resulting solvent mixture separates into an organic phase saturated with 4.5% water at 55 °C and an aqueous phase containing 2-MeOx (7%) at 55 °C. The rationale behind studying the applicability of aqueous 2-MeOx is to see whether we can bypass another drying stage (distillation) to obtain dry 2-MeOx and use aqueous 2-MeOx directly for defatting purposes (Rapinel *et al.*, 2020; Claux *et al.*, 2021). The overall lipid profile such as yield, fatty acid profile and lipid class composition of the solvent extracted crude SCG oils were compared. The residual caffeine content in the defatted SCG biomass was estimated.

2 Materials and methods

2.1 Raw material, standards and reagents

Fresh spent coffee grounds were retrieved from the local cafeteria (CROUS, Agroparc, Avignon) and immediately air-dried at 40 °C for 48 h to remove excess moisture content and stored in a dry place at ambient temperature. All solvents were of analytical grade and purchased from VWR international (Darmstadt, Germany). The solvent 2-methyloxolane A.K.A. 2-methyltetrahydrofuran was sourced from Honeywell, Sigma-Aldrich Co, St. Louis (MO, USA). The standards used for chromatography analyses were sourced from Sigma-Aldrich (USA).

2.2 Lipid extraction

The dried SCG was milled in a microfine grinder (IKA, MF 10 basic, Germany) equipped with an interchangeable sieve (hole size: Ø 1.0 mm) in order to obtain a homogenous powder. Lipid extraction with different solvents was carried out immediately after the size reduction step. A conventional soxhlet system was used to extract the lipids from the initial raw material. Two solvents hexane and 2-methyloxolane (2-MeOx) were employed for defatting the matrix. The solvent 2-MeOx was taken in its dry form and water-saturated aqueous form (2-MeOx 95.5%). Therefore, in total three solvent systems hexane, 2-MeOx (dry), and 2-MeOx 95.5% were evaluated. The solid to the solvent ratio for the extraction system was 1:10 (w/v) and the extraction was carried out for 6 h. The solvent was removed from the miscella under reduced pressure using a rotavapor (R-300, Buchi, Switzerland). The crude lipid extracts were transferred to an amber vial, flushed with nitrogen and stored at −18 °C until further analyses.

2.3 Fatty acid methyl esters (FAME) by acid-catalyzed transmethylation

Acid-catalyzed transmethylation was performed by adding 1 mL of methanolic sulfuric acid (5%) to a known quantity of the SCG lipids. The samples were spiked with internal

standard triheptadecanoin (C17:0; TAG), and the mixture was heated for 90 min at 85 °C. Post transmethylation, the mixture was brought to room temperature to which 1.5 mL of sodium chloride (0.9%, w/v) and 1 mL of hexane (GC-FID grade) were added to initiate phase separation. The mixture was vortexed for 30 s, and the organic layer was recovered and analyzed for the fatty acid profile. An Agilent (Kyoto, Japan) gas chromatography system coupled with a flame ionization detector (GC-FID) was used for the identification and relative quantitation of the fatty acid profiles. The instrument was equipped with a BD-EN14103 capillary column 30 m × 320 μm × 0.25 μm (Agilent). Helium was the carrier gas, and its velocity was set at 33 cm/s. The injection volume of the samples was 2 μL in a split mode (split ratio 1:20), and the back detector temperature was set at 260 °C. The oven temperature profile was set at 50 °C for 1 min and then increased gradually at a rate of 20 °C/min from 50 °C to 180 °C and increased from 180 °C to 220 °C at a rate of 2 °C/min. Finally, the temperature was maintained at 230 °C for 10 min before the end of each run. FAME was identified by comparing the retention time with purified FAME standard (Supelco, 37 FAME mix), and the relative quantity was estimated based on the internal standard (Breil *et al.*, 2016; Ravi *et al.*, 2019; Gharby *et al.*, 2020).

2.4 High-performance thin layer chromatography (HPTLC)

All samples (1 mg/mL) and standards (0.2 mg/mL) were prepared in chloroform and stored in the dark at −20 °C. A mixture of chloroform/methanol (2:1, v/v) was used to pre-develop HPTLC plates (silica gel 60 F254). This step was followed by drying the plates at 110 °C for 60 min on a TLC plate heater (CAMAG, Switzerland).

Lipid extracts of known quantity were spotted on 20 × 10 cm silica gel plates with an ATS 5 automatic TLC sampler. This step was followed by the development of the plates with a mixture of solvent acting as a mobile phase for elution in an ADC 2 automatic development chamber (CAMAG). For neutral lipids quantitation the mobile phase comprised n-hexane/diethyl ether/glacial acetic acid in a ratio of 70:30:2; v/v/v. The elution height was 7 cm from the origin (spot position). Finally, the plate was dipped in a revelation reagent (10 mg primuline, 160 mL acetone, 40 mL dH_2O), which was then visualized, derivatized, and scanned using a TLC scanner 3 (Breil *et al.*, 2016; Ravi *et al.*, 2019; Gharby *et al.*, 2020) equipped with WinCATs software (CAMAG).

2.5 High-performance liquid chromatography (HPLC)-UV analysis

The caffeine content in the solvent defatted SCG powders was analyzed by HPLC equipped with a UV detector (Agilent 1220 Infinity LC). Alkaloid extraction from the SCGs was realized by a simple solid-liquid extraction at 95 °C for 5 min. The supernatant was filtered using a PTFE filter (pore size: 0.20 μm) and taken in amber HPLC vials and placed in the autosampler module. The chromatographic separation was executed in a reverse-phase column (micro Bondapack C18) using an isocratic elution mixture of acidified (1% acetic acid) water (79%) and methanol (20%). The sample injection volume was 10 μL, and the volumetric flow rate of the mobile phase was fixed at 1 mL/min. Detection was carried out with a UV photometer at a wavelength of 280 nm. Various concentration of caffeine standard (3–22.5 ppm) was prepared for generating the calibration curve.

2.6 Theoretical solubility prediction of caffeine

A conductor-like screening model for real solvents (COSMO-RS) was used to theoretically calculate the thermodynamic properties of solvation without any experimental data. The solute is treated as if embedded in a dielectric medium via a molecular surface constructed around the molecule. This is a macroscopic approach using a dielectric constant of the solvent. Parameters such as σ-surface, σ-profile and σ-potential (Figs. 2a–2c) aid in estimating the solubility of the solute in the solvent system. In this case, the theoretical solubility of caffeine in the solvent systems was determined. The data was calculated in COSMOthermX'20 program (BIOVIA, Dassault systems). The standard quantum chemical method triple-valence polarized basis set (TZVP) was employed in this study and the results are expressed as log10(x_solub). More data on the solubility prediction of polar and non-polar compounds in various solvent systems can be found in relevant previous studies (Sicaire *et al.*, 2015; Breil *et al.*, 2016; Claux *et al.*, 2021).

3 Results and discussion

3.1 Effect of solvent on lipid yield

The global lipid yield from SCGs was highest in the case of aqueous 2-MeOx (15.84%), which could be attributed to the solvent's higher polarity when compared to dry 2-MeOx and hexane. Several research articles have previously reported a similar trend where dry 2-MeOx extracted more lipids from a wide array of matrices than the petroleum-based hexane solvent. As the polarity of water-saturated (aqueous 2-MeOx 95.5%) is higher than its dry counterpart, it is plausible that some polyphenols, sterols, and other unsaponifiable components were solubilized in the solvent system thereby augmenting the crude lipid yield. The increase in the lipid fraction yield in the case of aqueous 2-MeOx could also be attributed to better solubilization of polar lipids such as phospholipids in the solvent system.

The lipid extractability of the solvents hexane, dry and aqueous 2-MeOx from various biomaterials is summarized in Table 1. The data highlights the higher efficiency of the solvent 2-MeOx in terms of lipid extraction and can be considered a potential replacement for hexane. In case of oilseeds, particularly soybean, it was reported that dry 2-MeOx was able to extract 4.7% more lipophilic constituents than hexane and the 2-MeOx extracted crude soybean oil displayed superior antioxidant activity and oxidative stability. More data on the solvents origin, synthesis, characteristics, properties, efficacy and toxicity were comprehensively reviewed and detailed in a recent study.

Somnuk *et al.* (2017) compared four solvents namely hexane, anhydrous ethanol, hydrous ethanol, and methanol for their coffee oil extractability potential from SCG. The

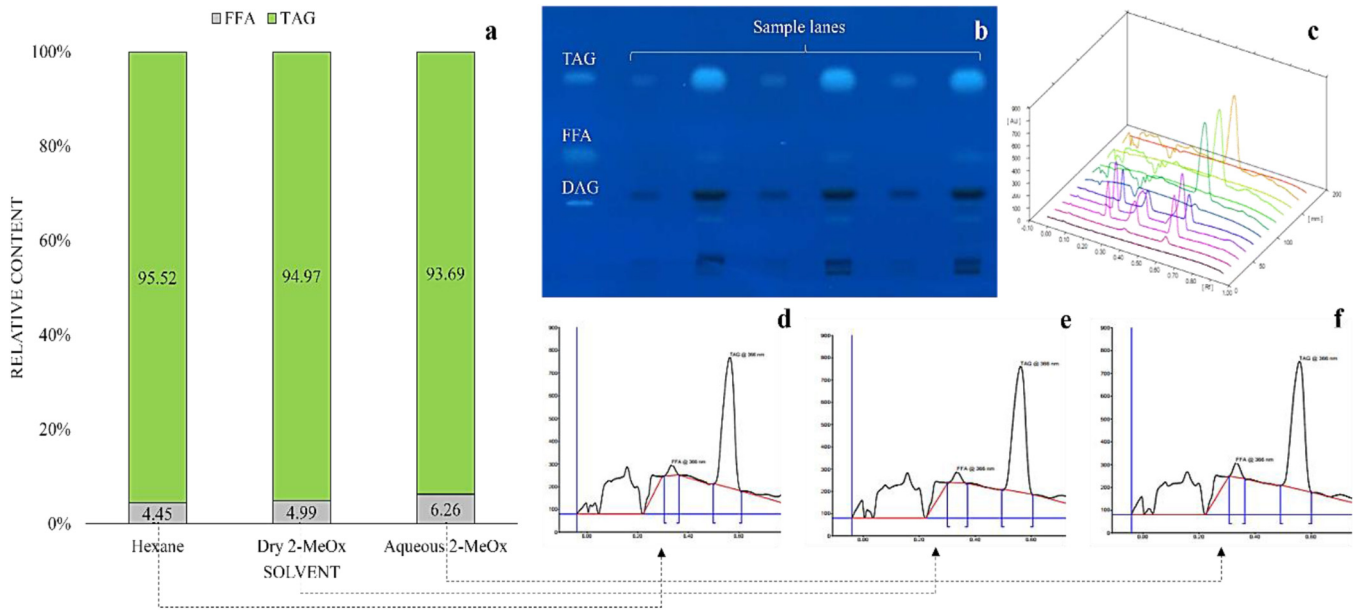

Fig. 2. (a) Lipid class composition; (b) HPTLC plate; (c) Overlay of chromatograms; (d–f) Individual chromatogram with substance assignment. TAG: Triacylglycerides; FFA: Free fatty acids; DAG: Diacylglycerides.

Table 1. Crude lipid yield of SCG and other biomaterials.

Solvent/Biomass	SCG	Soybean	Hops	Cactus seed	BSFL
Reference	This study	Claux *et al.* (2021)	Rapinel *et al.* (2020)	Gharby *et al.* (2020)	Ravi *et al.* (2019)
Hexane	12.47 ± 0.89	18.8 ± 0.1	17.9 ± 0.7	8.86 ± 0.25	32.51 ± 0.39
Dry 2-MeOx	13.67 ± 0.14	23.5 ± 0.1	20.2 ± 0.2	9.55 ± 0.12	35.83 ± 1.12
Aqueous 2-MeOx (95.5%)	15.84 ± 0.96	23.7 ± 0.1	NA	NA	NA

Results are expressed as means with their corresponding standard deviations (n = 3). 2-MeOx: 2-methyloxolane; SCG: Spent coffee grounds; BSFL: Black soldier fly larvae; NA: Not available.

extractions (maceration) were carried out at room temperature (30 °C) and reported the following coffee oil yields for the solvents studied 14.7% (hexane), 13.1% (anhydrous ethanol), 11.8% (aqueous ethanol) and 7.5% (methanol) respectively. Another study (Al-Hamamre *et al.*, 2012) comparing the coffee oil extractability of non-polar solvents such as pentane, hexane, toluene, chloroform and polar solvents such as acetone, isopropanol and ethanol reported oil yield within the range of 8.6% to 15.28%. Novel green alternatives to conventional extraction methods like accelerated solvent extraction (ASE) and supercritical carbon dioxide extractions (SCE) were investigated for oil recovery from SCGs (Muangrat and Pongsirikul, 2019). The yield obtained with different extraction techniques were as follows: ASE (solvent: propanol) – 14.02%, SCE (CO_2) – 12.11% and conventional Soxhlet (solvent: propanol) – 13.75% (Muangrat and Pongsirikul, 2019). Overall, defatting or delipification of SCGs can be executed with green extraction techniques and in case of conventional extraction systems bio-based solvent such as 2-MeOx proves to be a viable alternative exhibiting superior properties. Coffee oil extracted from SCGs possess numerous applications including biodiesel, feed ingredient, fuel in the form of pellets and also can be exploited for their antioxidant potential and inclusion in green composites (Peshev *et al.*, 2018; Leow *et al.*, 2021).

3.2 Fatty acid profile of SCG lipids

Fatty acid methyl esters of crude SCG oils were investigated (GC-FID) and the results are summarized in Table 2. The predominant fatty acids were palmitic (C16) and linoleic acid (C18:2) constituting almost 80% of the lipid fraction. The overall fatty acid profile of SCG oils extracted with hexane, dry and aqueous 2-MeOx solvents was similar. A marginal increase in relative percentage of a few fatty acids (oleic, linoleic and linolenic) was witnessed in oil extracted with dry 2-MeOx compared to hexane. The relative proportion of fatty acids in all SCG oils are indicated in decreasing order: PUFA > SFA > MUFA. Loyao *et al.* (2018) examined the potential of renewable non-polar solvents (ethyl acetate, ethanol, n-propanol and isopropanol) for lipid extraction from SCG and concluded that ethyl acetate and n-propanol enabled complete recovery of available lipids from SCG. They also found that both solvents (ethyl acetate and n-propanol) were

Table 2. Fatty acid profile solvent extracted SCG oils.

Fatty acid	Hexane	Dry 2-MeOx	Aqueous 2-MeOx (95.5%)
Tridecanoic acid (C13)	1.41 ± 0.09	1.44 ± 0.01	1.45 ± 0.02
Palmitic acid (C16)	34.94 ± 0.11	34.99 ± 0.02	35.01 ± 0.01
Stearic acid (C18)	6.89 ± 0.14	6.83 ± 0.24	6.74 ± 0.18
Oleic acid (C18:1)	7.52 ± 0.02	7.61 ± 0.05	7.53 ± 0.03
Linoleic acid (C18:2)	44.98 ± 0.89	45.04 ± 0.48	45.19 ± 0.41
Linolenic acid (C18:3)	1.36 ± 0.04	1.26 ± 0.07	1.31 ± 0.05
Arachidic acid (C20)	2.67 ± 0.09	2.61 ± 0.13	2.56 ± 0.10
Eicosenoic acid (C20:1)	0.23 ± 0.02	0.22 ± 0.02	0.21 ± 0.03
Σ SFA	45.91	45.87	45.76
Σ MUFA	7.75	7.83	7.74
Σ PUFA	46.34	46.3	46.5

Results are represented as mean ± standard deviation (n = 3). Σ SFA: Cumulative saturated fatty acids; Σ MUFA: Cumulative monounsaturated fatty acids; Σ PUFA: Cumulative polyunsaturated fatty acids.

able to extract simultaneously around 93% and 87% of the available tocopherol in SCG. Interestingly, solvent 2-MeOx exhibited higher tocopherol recovery in crude oils extracted from soybean when compared to that of hexane (Claux *et al.*, 2021). Theoretical solubility prediction results of select sterols and compounds of interest belonging to the lipid fraction in solvent system comprised of hexane and 2-MeOx have always favored the latter and is being increasingly proven with experimental results as well (Sicaire *et al.*, 2015; Breil *et al.*, 2016; Ravi *et al.*, 2019).

Vardon *et al.* (2013) analyzed the coffee oil obtained from SCG with hexane solvent through Soxhlet extraction and reported a similar fatty acid profile. Linoleic acid was the principal fatty acid with 45% followed by palmitic acid with 33.9% (Karmee, 2018). Comparable results were obtained by Somnuk *et al.* (2017) for coffee oil extracted with hexane. Whereas the fatty acid profile of SCG lipid extracted with supercritical CO_2 varied based on the extraction parameters such as temperature (40–60 °C) and pressure (175–200 bar).

Muangrat and Pongsirikul (2019) noted significant differences in the concentrations of major fatty acids namely palmitic (32.98–41.83 g/100 g) and linoleic acid (34.99–42.25 g/100 g).

3.3 Lipid class composition

Lipid class composition analysis of solvent extracted coffee oil from SCGs revealed that triacylglycerides (relative weight of the oil fraction) were the principal lipid constituent accounting for 93.69% in the aqueous 2-MeOx extract, 94.97% in dry 2-MeOx, and 95.52% in the hexane extract respectively. As shown in Figure 2a, the relative percentage of free fatty acids was higher in dry (4.99%) and aqueous 2-MeOx (6.26%) extracted oils when compared to hexane (4.45%) extracted SCG oil. This increase could be due to better extractability displayed by 2-MeOx solvent or potential hydrolysis occurring during lipid extraction as 2-MeOx is prone to absorb moisture from the biomaterial (Claux *et al.*, 2021). Nevertheless, the 4.45% of fatty acids present in the lipid fraction could have originated during the intended use of coffee powder or perhaps while drying the material before oil extraction. These results are in line with earlier findings where lipid extraction with 2-MeOx in dry and aqueous mode lead to hydrolysis of TAG into FFA, DAG, MAG (Ravi *et al.*, 2019; Gharby *et al.*, 2020; Smets *et al.*, 2021). This phenomenon can be attributed to the water affinity displayed by 2-MeOx. The extraction temperature and time also plays a significant role in triglyceride hydrolysis. Apart from hydrolysis, another plausible hypothesis that could explain the higher content of FFA in the aqueous 2-MeOx fraction is better extraction of FFA that are bound to other compounds in the SCG matrix which largely remain insoluble in apolar solvents. More data on the hydrolysis kinetics and conditions triggering the solvent-mediated lipolysis could aid in establishing preventive measures to circumvent the problem.

Previously reported data in the literature indicates that triglycerides and fatty acids are the predominant lipid class found in SCG oils. For instance, Efthymiopoulos *et al.* (2019a) reported TAG concentrations ranging between 39% and 74% whereas fatty acids ranged from 11% to 33%. Meanwhile, diglycerides and monoglycerides were also found in SCG oils but the latter was found in higher amounts (8–23%) than the monoglycerides (0–6%). Similarly, lipid profile analysis of SCG oil extracted utilizing ASE technique with hexane at varying temperatures (125–185 °C) showed that TAGs made up 45% to 64% and FFAs accounted for 27 to 35% of the lipid class (Efthymiopoulos *et al.*, 2019b). Somnuk *et al.* (2017) characterized hexane extracted coffee oil and found 81.2% of TAG, 5.93% DAG, 11.43% MAG and 0.41% FFA, respectively, in the lipid fraction. High FFA content in the coffee oil might pose serious problems in their downstream applications. For preparation of biofuels, high FFA content in the lipid fraction requires pre-treatments such as acid-catalyzed esterification and then base-catalyzed transesterification can be adopted (Al-Hamamre *et al.*, 2012). Considering the feed application of crude coffee oil, the higher acid value is undesirable as it might lead to lipid deterioration and rancidity causing digestive distress in livestock.

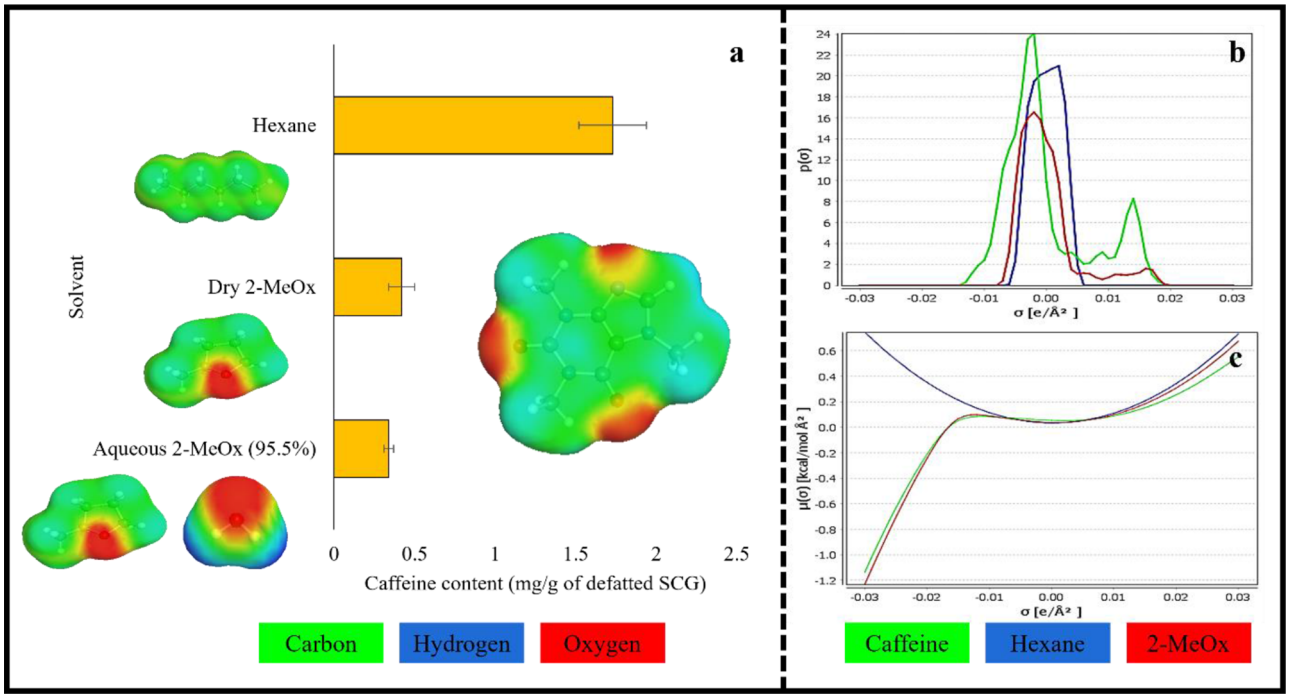

Fig. 3. (a) Caffeine content in defatted SCG along with the σ-surface of the solute and solvents; (b) σ-profile; (c) σ-potential of the solute (caffeine) and solvents (hexane, 2-MeO).

Table 3. Solubility prediction of caffeine and solvent characteristics.

Solvent/Parameters	Log (x_solub)	Log P	Boiling point (°C)	Density (g/cm^3)	Molecular weight (g/mol)
Hexane	−2.8436	3.9	68	630.24	86.18
Dry 2-MeOx	−1.5073	0.8	80	86.89	86.13

Log (x_solub): Absolute solubility of caffeine in solvent system; Log P: Partition co-efficient.

3.4 Caffeine content in defatted SCG and theoretical solubility

In this study instead of determining the caffeine content in the coffee oil, the solvent's efficacy in decaffeinating SCGs was estimated by measuring the caffeine content in the defatted SCG flour. The caffeine content in the solvent defatted SCGs residue was highest in hexane (1.73 mg/g), followed by dry 2-MeOx and measured least in aqueous 2-MeOx (95.5%) as shown in Figure 3a. Coffee oil extracted from SCGs is known to contain varying quantities of caffeine. Araújo *et al.* (2019) reported 23.06 mg caffeine in hexane extracted coffee oil from SCG.

In the same study 64.05 mg of caffeine was found in SCE oil (CO_2) and when ethanol was employed as co-solvent the caffeine content in the oil increased several fold (Araújo *et al.*, 2019). Mitraka *et al.* (2021) optimized the recovery of caffeine from SCG with ASE technique and determined the optimal values (7 min, 75 °C and ethanol: water ratio 5:95) for obtaining 30.5 ppm of caffeine concentration in the extract. The caffeine content in SCG and its recovery are dependent on two critical attributes of coffee: a) coffee type, which holds information such as geographical origin, ratio Arabica to Robusta, etc. b) nature of processing which gives insights on preparation conditions like filtration, boiling, decoction, and usage instructions recommended by the coffee maker (Peshev *et al.*, 2018).

Theoretical solubility of caffeine in solvents hexane and dry 2-MeOx was −2.84 and −1.51 respectively (Tab. 3). Values closer to 0 represent the complete solubility of the solute in the solvent system. The values obtained suggest that caffeine solubility in crude 2-MeOx (dry and aqueous) SCG extract could be relatively higher than caffeine solubility in the hexane extract. This hypothesis is supported by experimental values obtained for residual caffeine content in defatted SCG (hexane > 2-MeOx).

3.5 Non-food applications of defatted SCG: perspective

Despite the fact that the chemical composition of SCG might vary depending on a variety of parameters it predominantly comprises the following constituents: lipid, carbohydrate (cellulose, hemicellulose, polysaccharides and lignin), protein, non-protein nitrogen, tannins, fibers and other

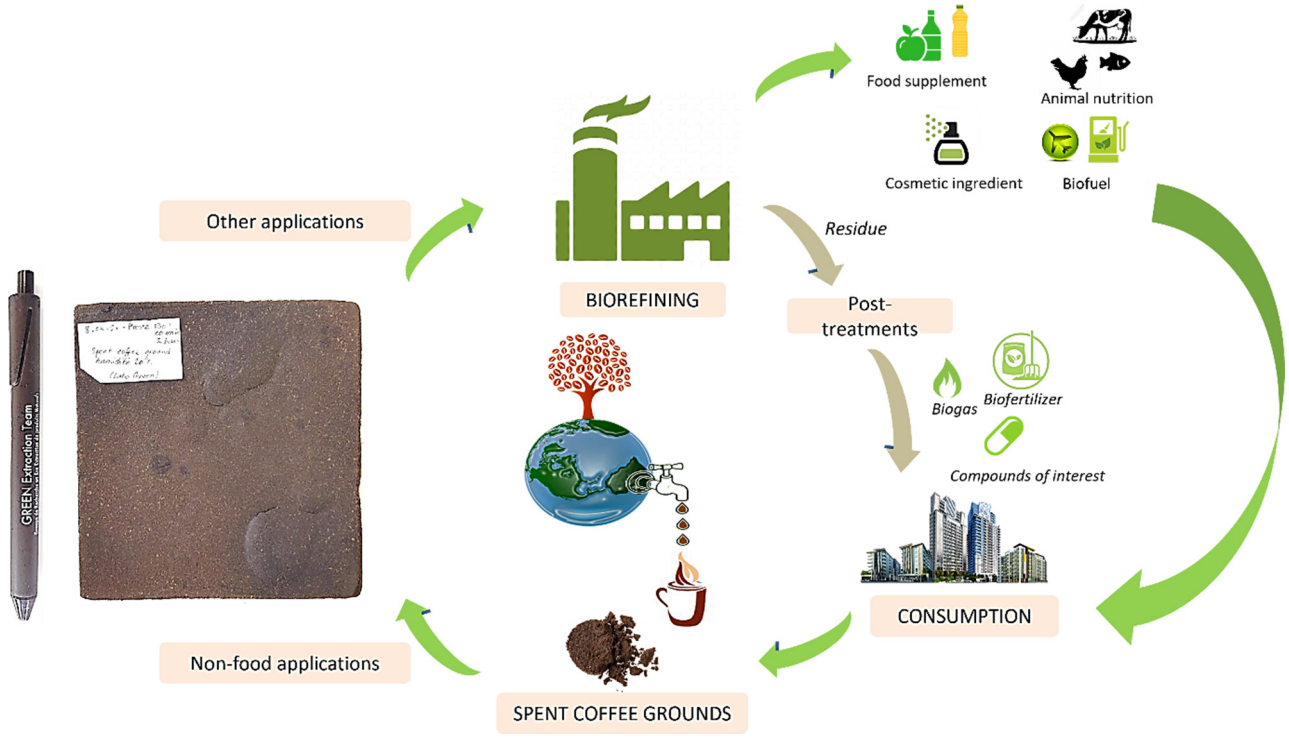

Fig. 4. Biorefinery of spent coffee grounds focusing on non-food applications of spent coffee grounds.

carbon-containing constituents (Karmee, 2018; Atabani *et al.*, 2019). Apart from fuel applications of SCG such as biodiesel, bioethanol and biogas other interesting avenues for SCG valorization include biopolymer, biocomposite fabrication, carotenoid, and bioactive compound extraction. Numerous comprehensive reviews and research articles pertinent to biorefinery, valorization and cascade utilization of SCG for food and non-food applications (Fig. 4) has been reported in literature (Vardon *et al.*, 2013; Sousa *et al.*, 2015; Georgieva *et al.*, 2018; Peshev *et al.*, 2018; McNutt and He, 2019; Atabani *et al.*, 2019). Within the purview of the biorefinery framework defatted SCG was pressed (Atelier Luma, Tarbes, France) to obtain a board-type material which when optimized can be used as a packaging alternative. Even stationaries such as enclosures for pens were fabricated where 50% of the SCG was used as ingredient in the formulation. Interestingly, coffee cups from recycled coffee grounds and other renewable resources are used for manufacturing sustainable food and beverage packaging materials and are readily available in the market for consumers (Kaffeform, Germany).

4 Conclusion

Dry and aqueous 2-MeOx prove to be potential alternative solvents for defatting SCG without impairing the inherent properties of the coffee oil and the defatted flour. The crude lipid yield ranged between 12.47% to 15.84% for solvents considered. Lipid yield was higher when solvent 2-MeOx was employed for extraction. Triglycerides (> 93%) was the principal lipid class constituent of the SCG oil. Palmitic (C16) and linoleic acids were the primary fatty acids found in the oil. Theoretical solubility of caffeine in the solvent system was also elucidated. Caffeine content was relatively higher in hexane defatted flour demonstrating the selective extractability of compounds of interest displayed by 2-MeOx.

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