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Valorization of spent coffee grounds – A new approach

D. Peshev[a,*], D. Mitev[b], L. Peeva[c], G. Peev[a]

[a] University of Chemical Technology and Metallurgy, Department of Chemical Engineering, 8 Kl. Ohridsky Blvd., 1756 Sofia, Bulgaria
[b] REGPOT-2012-2013-1 NMP INERA Project, Institute of Solid State Physics-BAS, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
[c] Chemical Engineering and Chemical Technology, Imperial College London, Exhibition Road, London SW7 2AZ, UK

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ABSTRACT

It is established that from well selected spent coffee grounds by water extraction and subsequent extract nanofiltration one can obtain valuable products as permeate and retentate fractions. The obtained permeate is of high caffeine concentration and is potentially applicable in soft and energy drinks production. The retentate has main characteristics (antioxidants concentration, caffeine content and browning index) suitable for its application as coffee drink or ingredient in food technologies.

The conditions of the two processes allowing such separation are described and discussed: water/spent coffee grounds ratio, temperature and duration of extraction; membrane, pressure, modes of filtration and degree of feed volume reduction. The results obtained outline the elements of a new approach for valorization of spent coffee grounds avoiding the permeate treatment to powdered caffeine and extending the area of retentate applicability.

The study encourages further investigations for practical realization of the approach.

1. Introduction

Coffee is the second largest traded commodity after petroleum [1]. Its production, processing and consumption generate enormous amount of residues. Spent coffee grounds (SCG) are particularly attracting increasing interest due to the following reasons:

- They contain large number of organic compounds (more than 1000 individual components) which can be classified in carbohydrates, proteins, lipids, minerals, non-protein nitrogeneous and phenolic compounds, and can be considered as potential functional ingredients for the food industry [2]. Caffeine (CF), diterpene alcohols cafestol and kahweol, and polyphenols with chlorogenic acid (CA) as major representative are of special attention because of their physiological effects [3];
- Their granulometry allows quick removal of the respective substances from the matrix by a convenient solvent;
- They are waste mainly from the production of instant coffee and brewing process easily available in huge quantity (6 million tons per year [4]) at low price.

Various applications of SCG are well known: as fuel in the form of pellets [4], in production of biofuels [5] and adsorbents for gaseous emissions [6], as a source of compounds of the above mention groups, antioxidants for example [7]. After target compounds isolation the residues have been utilized for energy production [8].

The investigations aiming at more complex valorization of SCG are only a few [2]. For such a purpose combinations of several separation methods should be applied and particularly membrane technology should be included allowing separation at molecular level. Nanofiltration technology was shown to be a more economical alternative to reverse osmosis for concentration of coffee extracts [9] or capable for their fractionation [10]. Brazinha, Cadima and Crespo [11] employed nanofiltration aiming at valorization of SCG. They combined solid-liquid extraction with several membrane processes seeking to produce dry fractionated extract with high caffeine concentration for the needs of cosmetics and energy food segments. For this reason they used low liquid to solid ratio (from 8.6 to 4) and long time of extraction. They also added 3 g L^{-1} citric acid in the water employed as solvent.

In our opinion valorization of SCG regarding caffeine utilization can be obtained if a sufficiently concentrated permeate is achieved and directly utilized for production of soft drinks or hair-restorer shampoo. The US Food and Drug Administration (FDA 2006) defines caffeine as a generally recognized as safe substance, but limits its concentration in

Abbreviations: BC, batch concentration; BCC, brown-coloured compounds; CA, chlorogenic acid; CF, caffeine; DFVR, degree of feed volume reduction; GAE, gallic acid equivalent; HPLC, high performance liquid chromatography; MET, membrane extraction technology; RSD, relative standard deviation; SCG, spent coffee grounds; SS, steady-state; TPC, total phenolic content; abs, absorption of light; rpm, rotations per minute

* Corresponding author.
E-mail addresses: d.peshev@uctm.edu (D. Peshev), dpmitev@issp.bas.bg (D. Mitev), l.peeva@imperial.ac.uk (L. Peeva), georgiapeev@gmail.com (G. Peev).

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carbonated beverages up to 0.02% (appr. 200 mg L^{-1}) [12]. However the amount in many brands detected analytically is considerably lower: from 2.8 to 62 mg L^{-1} in beverages (Regular Cola, Diet Cola, Lemon Cola) marketed in Riyadh city [12]; from 44 to 46 mg L^{-1} in Pepsi Cola, Mountain Dew, etc. in Yenagoa, Nigeria [13]. In another study values from 32.4 to 133.3 mg L^{-1} are reported [12]. The energy drinks are generally richer in caffeine and the reported concentrations vary in wider limits reaching even values higher than 200 mg L^{-1} [12,13].

To the best of our knowledge the caffeine concentrations in the brands of hair-restorer shampoo are not announced. One can suppose that it varies in the range at which the caffeine positive effects have been observed [14,15], i.e. 10–50 mg L^{-1}.

Such an approach will allow to avoid the reverse osmosis and drying, as well as the addition of citric acid in the proposed technology [11] and to improve the economics of caffeine recovery. The approach realization has sufficient resources: (i) use of SCG with higher caffeine content; (ii) more complete extraction at lower liquid to solid ratio and higher temperature; (iii) lower membrane rejection of caffeine, etc. Regarding the latest, the membranes used in [11] rejecting from 13 to 26% of caffeine can be replaced with more convenient ones, fulfilling the requirements for use in food technologies as well.

Regarding the first resource it should be reminded that the caffeine content in SCG depends not only on the sort of the coffee (place of origin, ratio Arabica to Robusta, etc.) but also on how it has been processed (filtered, boiled or to prepare espresso type coffee) and what coffee maker model has been used to this aim [16]. The same is true for the total phenolic content (TPC). Zuorro and Lavecchia [8] reported that in SCG collected from coffee bars TPC was 17.75 mg GAE g^{-1} but in that recovered from coffee capsules it was 21.56 mg GAE g^{-1}. Therefore SCG have to be taken from well-known and not accidental places.

There are serious contradictions concerning the duration of the extraction process. In [8] the time of the designed experiments varied from 60 to 120 min. Times from 30 min to 6 h were reported in [11]. Boyadzhiev et al. [16] reported that total phenolic content reached maximum at 20 min and then decreased. The same behaviour displayed chlorogenic acid with maximum after 90 min. As far as the extraction kinetics depends on many other factors like temperature, liquid to solid ratio, coffee particles dimensions, etc., the duration should be sufficient to allow direct utilization of caffeine solution obtained as permeate from SCG extract nanofiltration at a reasonable price. For the producer of drinks and shampoos the price will be reasonable if it is lower than the price of trade caffeine used in theirs technologies. Such a price can be achieved easier if a complete utilization of SCG is realized including retentates from the nanofiltration process and energy produced from the extracted SCG. It is well established that the extracts of SCG are rich of phenolic compounds which together with the contained brown-coloured (Maillard) compounds, both exhibit antioxidant activity. Therefore the retentates may be useful as functional ingredients in foods [2]. Moreover, retentates can be used as partly decaffeinated coffee drinks if they have properties similar to those of regular coffee brews. The preservation of TPC in membrane fractionated coffee extracts during storage up to at least 10 days in airtight glass containers found in [17] is encouraging the idea of direct caffeine and phenolic compounds utilization as products of a SCG extract nanofiltration processing. The present paper aims at an experimental assessment of this idea.

2. Materials and methods

2.1. Materials

The spent coffee grounds as well as the short and long coffee brews were obtained from a local cafeteria situated at the University of Chemical Technology and Metallurgy, Sofia, Bulgaria. They originated from one and the same “Carraro” brand of medium roasted blend of 50% Arabica and 50% Robusta (Caffè Carraro S.p.A., Schio, Italy), processed with Belogia 4all D/2 Espresso Machine (EUROGAT Thessaloniki, Thessaloniki, Greece; temperature of the pressurized water about 92 °C). Two separate batches of SCG were collected in the course of the study, each one during a day. After the collection, each batch was immediately subjected to drying at temperature of 60 °C. The coffee powder was stored in hermetic containers until use.

The commercial nanofiltration membrane of type ”Microdyn Nadir NP030 P” (80–95% retention of $NaSO_4$; molecular weight cut off around 400 Da) kindly supplied by MICRODYN-NADIR GmbH (Regional office Greece) was used. It was preliminary tested for rejection of caffeine (MW = 194.2 Da) and chlorogenic acid (MW = 354.3 Da) from water solutions and values of 2.0% and 75.7% respectively were obtained [18].

Microfiltration cellulose acetate membrane filter disks with pore size of 0.45 μm and diameter of 90 mm (Chemplus Scientific Ltd., China) were supplied by Biotechlab Ltd., Bulgaria.

All reagents used were of analytical grade quality: Folin-Ciocalteu’s phenol reagent, gallic acid, anhydrous sodium carbonate, ammonium acetate, chlorogenic acid (min. 95%), methanol, acetonitrile, anhydrous caffeine, dichloromethane were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Distilled water (water still GFL Type 2004, Burgwedel, Germany) was used throughout the work.

2.2. Instrumentation and equipment

An S-22UV/Vis spectrophotometer (Boeco, Germany) was used for determination of the spectral absorbance at different wavelengths. Quartz cuvettes of 3 mL capacity with optical path of 10 mm were used throughout the work. A quaternary pump Agilent 1100/1200 HPLC system equipped with diode array detector was used for determination of caffeine and chlorogenic acid concentrations in SCG extracts. A 270 mL dead-end filtration cell (METcell, Evonik Membrane Extraction Technology, London, UK) with membrane area of 54 cm^2, and maximum working pressure of 69 bar, applied by compressed nitrogen was used for lab scale nanofiltration experiments. MaxiMem cross flow filtration system (PS Prozesstechnik GmbH, Basel, Switzerland) equipped with a flat sheet membrane module for polymeric membranes (retentate channel dimensions of 260 mm length, 80 mm width, and 1.2 mm height; membrane area of 215 cm^2), operating at pressure up to 60 bar created by membrane pump, was used for determination of scaling-up effects. A laboratory scale extractor was used for treatment of SCG with water at controlled elevated temperature consisting of 1 L four-neck round bottom flask equipped with a blade propeller (diameter of 50 mm) operated at regulated revolutions (500 rpm). The SCG particle size distribution was determined by means of Camsizer XT particle analyzer (Retsch, Germany) with dynamic measuring range from 1 μm to 3 mm. The option for air pressure sample dispersion was used in order to avoid fine particles agglomeration.

2.3. Analytical methods

2.3.1. Total phenolic content (TPC)

A spectrophotometric assay of TPC was applied using a modified version of Folin-Ciocalteu method [19,20]. Corresponding amount of the phenolic/reductive coffee extract (0.020–1.000 mL) was diluted to 7 mL with an appropriate volume of distilled water. Then 0.5 mL of Folin-Ciocalteu’s reagent was added and after thorough shaking the sample was allowed to stay for 10 min prior to addition of 2.5 mL of 10% (w/w) aqueous sodium carbonate solution. The colorization reaction developed in 20 min at room temperature. Afterwards the specific absorbance at 760 nm was measured. An identical mixture without coffee extract was used as a blank sample. The total phenolic/reducing contents were rated as mg (gallic acid equivalent, GAE) per kg of initial extract sample, through the calibration line obtained for gallic acid standard solutions (Fig. 1).