To appear in: International Journal of Recycling of Organic Waste in Agriculture (IJROWA)

Online ISSN: 2251-7715 Print ISSN: 2195-3228

Received: 19 Jan 2024 Revised: 22 Apr 2024

Accepted: 02 Jul 2024

DOI: 10.57647/ijrowa-b5y0-qf23

ORIGINAL RESEARCH

Biorefinery potential of coffee silverskin: Composition and applications

Elena M. Anchugova [1,*], Elena V. Udoratina [2], Elena G. Kazakova [2], Anastasiia O. Nosova [3], Mayya V. Uspenskaya [3],Tatiana N. Shchemelinina [1]

[1] Institute of Biology of Komi Science Centre of the Ural Branch of the Russian Academy of Sciences, 28 Kommunisticheskaya st., 167982 Syktyvkar, Komi Republic, Russia

[2] Institute of Chemistry of Komi Science Centre of the Ural Branch of the Russian Academy of Sciences, 48 Pervomayskaya st., 167000 Syktyvkar, Komi Republic, Russia

[3] Chemical Engineering Center, ITMO University, 49, Kronverksky avenue, Saint Petersburg, 197101, Russia

*Corresponding author email: anchugova@ib.komisc.ru

Abstract

Purpose: Achievements in biotechnology have paved the way for the efficient utilization of agricultural and industrial waste, presenting potential opportunities for sustainability and resource optimization. One such waste that has been studied is coffee silverskin (CS), the only waste generated during the coffee roasting process. This paper aims to analyze the potential of CS for biorefinery and explore its value enhancement through biotechnology.

Method: The study employed various analytical techniques, including elemental analysis, chromatography methods, and Fourier transform methods, to characterize the CS biomass. Additionally, three formulations for wet granulations of a biofertilizer were prepared to valorize the silverskin. Empirical formulas were used to assess the fatty acid content and key parameters of CS biodiesel precursor.

Results: The results revealed that CS, when enriched with microalgae and bindered with glauconite, becomes high-value amendment rich in essential macro- and micronutrients. The optimal biofertilizer composition suggested a ratio of three parts of CS, one part of glauconite, and 5 parts of the *Chlorella vulgaris* microalgae suspension with the liquid-to-solid ratio of 1.28. The higher heating value, the cetane number, the iodine value, the viscosity, and the density of precursors obtained comply with the requirements of the standard EN 14214.

Conclusion: The CS was found to contain significant amounts of palmitic and linoleic acid, which are known to be value-added components in cosmetic formulations and biodiesel production. The high macro and micro-nutrient contents of CS, make it an attractive opportunity to adopt a circular bioeconomy model in the agricultural sector. By transforming organic waste, the coffee roasting industry can achieve the goal of Zero Waste, contributing to a more sustainable and environmentally friendly approach.

Key words: Coffee silverskin, Biofertilizer, Fatty acids, Biodiesel, Lignin, Carbohydrates

Introduction

The concept of biorefinery is based on the efficient use of biomass and waste materials, converting them into a spectrum of valuable products. This approach aligns with the principles of a circular economy, where waste is minimized, and resources are kept in use as long as possible. The coffee industry, being one of the largest agricultural sectors globally, generates a significant amount of waste, including coffee silverskin (CS) – a thin integument that directly covers the seed and is completely removed during roasting of coffee beans. Since each ton of roasted beans produces approximately 7.5–8.3 kg of CS, its disposal presents an ecological challenge due to its low bulk density (Alves et al. 2017). However, its biological origin, renewability, and complex chemical composition make it a promising candidate for reuse and refinement into added-value products. By converting CS, not only can the ecological problem associated be mitigated, but also economic benefits can be generated.

According to the literature, the potential CS applications are indeed vast and promising. Jiménez-Zamora et al. (2015) have identified various bioactive compounds in CS, including phenolic compounds, flavonoids, and caffeine. These compounds have been found to possess antioxidant, antimicrobial and anti-inflammatory properties, making them potentially valuable for the development of functional ingredients in the pharmaceutical industry and in various food formulations, such as breads and cakes with high dietary fiber contents, nutraceutical yogurt (Ateş and Elmacı 2019**Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.**; Bertolino et al. 2019). The potential utility of CS as a substance for eliminating caffeine, toxic metals, and dyes from wastewater has been demonstrated. The porous structure and extensive surface area of the material contribute to its efficacy as an adsorbent (Benitez et al. 2019). Consequently, this implies that CS could be employed in water treatment procedures, thereby mitigating pollution and enhancing water quality.

In the agriculture realm, CS can serve as a sustainable alternative to chemical fertilizers and a feed for ruminants *in vitro* (Hoseini et al. 2021). This aligns with the global trend adopting sustainable and environmentally friendly agricultural practices. Moreover, potential applications of CS in the fabrication of various materials such as low- and

high-density polyethylene, cellulose-reinforced materials, and packaging materials represents a promising avenue for exploration (Garcia and Kim 2021). The inclusion of CS to bioplastics enhances the value of the waste and facilitates the production of environmentally friendly materials, in contrast to petroleum-based plastics that are neither renewable nor biodegradable. However, the chemical modification of CS to increase its hydrophobic properties and compatibility with the polymer matrix is crucial for obtaining composites with acceptable mechanical and barrier properties. The development of CS-based nanomaterials is another area of interest. While there are reports on nanocrystals extracted from CS and their application in reinforcing polylactic acid nanocomposite films, more research is needed (Sung et al. 2017). Additionally, CS has been the object of study for its potential as an energy source. It consists of substantial quantities of cellulose, hemicellulose, and lignin, which can be transformed into bioethanol through diverse conversion technologies (Mirón-Mérida et al. 2021). The other potential alternative to fossil fuels is biodiesel, which currently faces high feedstock costs. Feedstock alone accounts for 70–80% of the final cost of biodiesel. As the CS is completely renewable, its application may improve current knowledge of fuel cycle performance as described by Gülüm (2022, 2023).

Thus, research is underway worldwide evaluating the sustainability and cost-effectiveness of CS as an animal feed additive, a component in composites and nanomaterials, and a source of bioactive compounds, inexpensive adsorbents, and fermentation products such as enzymes, flavor and aroma ingredients for food products. CS is a promising source seen as an alternative biomass that is intended to be utilized in the future, with potential applications in a wide range of sectors. However, it is worth noting that there are several challenges that require careful consideration. These include the necessary for more research to fully understand its properties and characteristics and to develop efficient methods for its processing. With the adoption of a circular bioeconomy model, the maximum value can be extracted through biotechnological transformation, turning the waste into valuable goods.

According to the bibliometric analysis carried out by Ranjbari et al. (2022), one of the most emerging biomass research areas in the literature dedicated to the circular bioeconomy is the valorization of spent coffee grounds. The CS is largely outside the scope of researchers despite the huge amount of waste. The main research hotspots within the CS biomass sub-field in the literature are bioactive compounds, composting and fermentation media. Thus, several recycling applications such as lignin-carbohydrate association as a natural barrier to degradation, organo-mineral fertilizers, and biodiesel seem lacking in the literature. To address the gap in the field of CS biorefinery, this work aims to explore the potential of CS, focusing on its chemical composition and applications to fully utilize this by-product.

Materials and methods

Materials

CS samples were obtained from the roasting process of green coffee beans at Coffee Plus LLC (Syktyvkar, Russia). The *Chlorella vulgaris* suspension was obtained from the collection SYKO A (WDMC Number: 1125) of the Institute of Biology of Komi Science Centre of the Ural Branch of the Russian Academy of Science. Binders, including potato starch, bentonite, and glauconite, for the purpose of conducting granulation experiments were kindly provided by Bioecobalance LLC (Syktyvkar, Russia). To ensure that the experimental procedures were conducted under optimal conditions all the reagents used were of analytical grade.

Experimental design

To allow for the investigation of the effects of different binder agents and liquid-to-solid ratios on the wet granulation process this experimental setup using a single screw pelletizing mill to facilitate pellet consolidation CS as a precursor

was mixed with binder agents: starch, bentonite, glauconite, in a suitable ratio. After having been obtained by preblending, three formulations were wetted using the *Chlorella vulgaris* suspension as a granulation liquid and distilled water as a control. The wetted preblends were then transferred to the mill. During the process of the control CS granulation the liquid-to-solid ratio ranged between 0.5 and 1 to determine the optimal one. After the granulation process, the produced pellets were sampled at the outlet of the mill. To remove any remaining solvent, the pellets were tray dried at room temperature.

Analytical methods

The chemical composition was analyzed using methods generally accepted in the chemistry of plant raw materials. Moisture content was determined by drying (not less than 4 hours at 105 °C). The total ash content was carried out in two stages: firstly, to char 2.5 g of the sample thoroughly at 250 °C; and finally ashing at 800 °C for 3 hours in the muffle furnace (LV 9/11 P330, Nabertherm, GmbH). To identify the resin content, 4 g of the air-dried sample was put in the extraction thimble and inserted into the extractor. The sample was refluxed with ethyl acetate for two hours at a gentle heat. After the extraction solvent had been siphoned into a preweighed Erlenmeyer flask, the solvent was subsequently removed by distillation on a steam bath. The amount of resinous substances was determined by weighing. Kürschner cellulose was determined by the threefold extraction of approximately 2 g of the CS sample with 100 ml of the mixture of nitric acid and ethanol (1:4) followed by boiling for one hour. The Klason lignin content was determined by acid hydrolysis with 72% sulfuric acid at 24–25 °C for 2.5 hours, followed by dilution to a 3% acid concentration and low boiling for one hour as modified by Komarov. Pectin substances were isolated by sequential extraction according to Shakhmatov et al. (2020). The raw material sample was sequentially extracted with water (extracted thrice at 70 °C for 2 hours); with hydrochloric acid solutions (thrice at 70 °C and at pH 3.5 for 2 hours) and with 0.7% solution of $(NH_4)_2C_2O_4$ (thrice for 2 h, 70 °C). Hemicelluloses were extracted after a three-step extraction of pectin substances using a 7.0% KOH solution containing 10 mM/l $NaBH_4$, thrice for 2 h, 23–25 °C. The fractions from each extraction were collected separately, centrifuged, and concentrated. Polysaccharides were precipitated with a fourfold volume of 96% ethanol. The resulting precipitates were separated by centrifugation, dissolved in water, dialyzed against distilled water, and dried by lyophilization. The result was a set of five polysaccharide fractions. The mass fraction of pentosans was determined by the method based on the formation of furfural from pentosans when treating the material with a solution with a 13% mass fraction of hydrochloric acid while heating and determining the removed furfural by spectrophotometric method using orsinol as reagent. The mass fraction of proteins was calculated from the amount of nitrogen, which was determined by elemental analysis in the Vario MICRO Cube analyzer (Abacus Analytical Systems, GmbH). The mass fraction of condensed tannins (polyphenolic compounds) was determined by gravimetric method based on their condensation reaction with formaldehyde catalyzed by acid.

FTIR spectra of the lignin-carbohydrate complex components were recorded on a Shimadzu IR Prestige-21 spectrometer (Japan) with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1} using a DLATGS detector. The method of KBr pellet pressing was used for sample preparation. Elemental analysis was performed using a CHNS elemental analyzer Vario MICRO cube (Germany). The elemental composition of the mineral content of the material under study was determined by X-ray fluorescence spectroscopy (XRF-1800 X-ray fluorescence spectrometer, Shimadzu, Japan).

The quantitative chemical analysis of acid-soluble forms of heavy metals was conducted via atom emission spectroscopy with inductively coupled plasma atomic emission spectrometry using Spectro Cyros CCD (Spectro Analytical Instruments, Germany) as described by Vasilevich (2018). For the subsequent determination of heavy

metals, the CS samples were mineralized using a Minotaur-2 microwave digestion system (Lumex, Russia) through the addition of a 10:1 mixture of concentrated HNO_3 and H_2O_2.

All analytical surveys using chromatographic methods were performed in the Chromatography Core Facility of the Institute of Biology (Syktyvkar, Russia). The extraction of *n*-alkanes and polycyclic aromatic hydrocarbons (PAH) from the CS samples was performed using the ASE-350 Accelerated Solvent Extractor (Thermo Fisher Scientific, USA), as described by Yakovleva et al. (2022). One gram ground samples were placed into extraction cell and extracted thrice with the mixture of methylene: acetone (1:1) under temperature of 100 °C. The sample obtained was concentrated by the Kuderna-Danish apparatus to a final volume of 1–2 ml where upon 3–5 ml of *n*-hexane was added. To separate alkanes, the sample obtained was purified from polar organic compounds by column chromatography with 2 g silica gel 60 (Fluka 60741, Sigma-Aldrich) as a sorbent. 20–25 ml of an *n*-hexane eluate collected was concentrated using the Kuderna-Danish apparatus at 85 °C to a volume of 2 ml. The qualitative and quantitative analysis of the alkane fraction was performed with a Finnigan Trace DSQ (Thermo Scientific, USA) gas chromatograph and mass spectrometer in the selective ion monitoring (SIM) mode. The SIM scan was performed on three ions with masses 57, 71, and 85, which are characteristic of the *n*-alkanes. Identification of *n*-alkanes and determination of their retention properties were performed preliminarily in the total ion current mode using mass spectra and reference standards (Alkane Standard Solution C_8–C_{40}, Sigma-Aldrich, USA). The quantitative content of *n*-alkanes was determined by the internal standard method (*n*-decane, 0.05 mg/ml). To separate the PAH fraction the extracts were purified by the column chromatography using activated neutral aluminum oxide 90 (Brokmann grade II, Macherey-Nagel, Germany). The eluates obtained were concentrated as mentioned above and 3 ml of acetonitrile was added. After having been evaporated to a volume of 1–2 ml the sample concentrates were analyzed by the reversed phase HLPC in a gradient mode and spectrofluorimetric detection (Lumex, Russia). A standard solution EPA 610 polynuclear aromatic hydrocarbon mixture containing 16 priority PAHs (Supelco, USA) was used to provide absolute quantification of each hydrocarbon.

To maximize the lipid extraction and to reduce the solvent consumption the CS lipids were extracted and methylated with a one-step method. 5 ml of methanol and 0.7 ml of HCl (36.5%) were added to the 15 ml glass vial containing 168 mg of the CS sample and the vial was tightly sealed with a Teflon lined cap (Xiao et al. 2012). The methylation reaction was conducted by incubation at 95 °C for 90 min with shaking the contents every 30 min. After cooling to room temperature, 5 ml of distilled water and 0.5 ml of toluene containing the internal standard (*n*-hexadecane, 0.05 mg/ml) were added to the vial and fatty acid methyl esters (FAME) formed were extracted for 5 min and then analyzed directly by GC–MS.

The GC–MS analysis was conducted on a Crystal-5000.2 gas chromatograph (Chromatec, Russia) with flame ionization detector, equipped with a 30 m × 0.32 mm × 0.25 μm quartz capillary column HP-FFAP (Agilent, USA). Helium was used as a carrier gas under the column head pressure of 60 kPa. The oven temperature program was ramped from 110 to 260 °C at 5°C/min. The injector and the detector were set at 280 °C and 250 °C, respectively. The split ratio was 1:30.

A FAME standard mix (BAME Mix, Supelco, USA) containing 26 FAMEs was used to provide absolute quantification of each fatty acid (FA). The cetane number (CN), the iodine value (IV), and physicochemical properties of the biofuel produced were estimated based on the composition and content of individual FA according to empirical equations, as follows:

$$DU = MUFA + 2 \times PUFA \quad (1)$$

Where DU is the degree of unsaturation, MUFA is the amount of monounsaturated fatty acids; and PUFA is the amount of polyunsaturated fatty acids.

$$IV = \sum \frac{254 \times D_i \times N_i}{M_i} \quad (2)$$

$$CN = 46.3 + \sum \frac{5.458 \times M_i}{560 \times N_i} - 0.225 \times IV \quad (3)$$

In equations 2 and 3 D_i is the number of double bonds in the FAME, M_i is the molecular mass of the ester, and N_i is the percentage of the particular ester in the sample.

$$\text{LCSF} = (0.1 \times \text{C16:0}) + (0.5 \times \text{C18:0}) + (1 \times \text{C20:0}) + (1.5 \times \text{C22:0}) \quad (4)$$

Where LCSF is the long-chain saturated factor, *Cn* is the percentage of the particular saturated ester mentioned.

To estimate the density (ρ), and the kinematic viscosity (υ) the equations from 5 to 6 were applied.

$$\rho = \sum N_i \times \left(0.8463 - \frac{4.9}{Mw_i} + 0.0118 \times D_i\right) \quad (5)$$

$$\ln \upsilon = \sum N_i \times (-12.503 + 2.496 \times \ln Mw_i - 0.178 \times D_i) \quad (6)$$

Here, Mw_i is the molecular weight of the particular ester, and D_i is the number of double bonds in the FAME.

The higher heating value was calculated using the equation developed by the Channiwala and Parikh (2002) for estimation of wood and biomass fuel properties according to their elemental composition:

$$HHV = 0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times Ash \quad (7)$$

Results and discussion

Applications based on the lignin-carbohydrate complex of the CS

As any plant material, CS is a multi-component biomass consisting of components, including polymeric lignin-carbohydrates, low-molecular weight extractive substances, and mineral parts. CS can be used as a lignin-carbohydrate product (without separation into components), can be separated into individual components (carbohydrates, lignin), which can be used as individual products given their specific properties or chemically modified to obtain derivatives based on them, with subsequent applications (Garcia and Kim 2021). The CS chemical composition and the quantitative content of its components are shown in Figure 1.

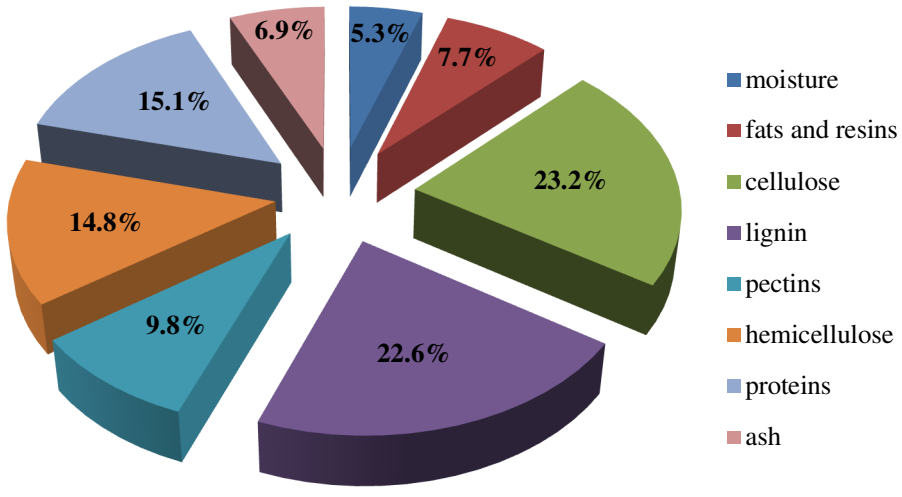

Figure 1. The CS sample chemical composition

The carbohydrate part of CS, including cellulose, hemicellulose, and pectin substances, is approximately 50% of its weight. Cellulose is the dominant structural component in the polysaccharide complex, accounting for 23.2% of the mass, followed by alkali soluble hemicelluloses (14.8%) and water-soluble pectin polysaccharides with a mass fraction of 9.8%. Pentosans such as xylans and arabinans, belong to hemicelluloses; their mass fraction in CS is 10% (not shown in the diagram). The second main component of CS is an aromatic polymer lignin with a mass fraction of 22.6%. CS contains a significant amount of proteins (15.1%). The number of low-molecular weight substances extractable with organic solvents, such as ethyl acetate, is 7.7%, and the number of mineral substances is 6.9%.

As shown above, CS contains significant amounts of non-cellulose polysaccharides (PS). Five PS fractions were isolated from the previously defatted CS by sequential extraction with water (PS_{H2O}), aqueous solutions of hydrochloric acid (PS_{HCl}), ammonium oxalate ($PS_{(NH4)2C2O4}$), and potassium hydroxide (PS_{KOH}). Table 1 shows the polysaccharide fractions yield (with a total content of 27% in CS). It was found that the alkali soluble fraction represented by hemicelluloses (15%) and the aqueous fraction represented by pectins (approximately 7%) were the dominant ones. The mass fractions of the PS_{HCl} and oxalate fractions were considerably smaller – 0.8% and 1.6%, respectively.

Table 1. Fractions of non-cellulose polysaccharides of CS

Fraction	**Extracting agent**	**Content, wt.%**
PS_{H2O}	Water	7.32
PS_{HCl}	Hydrochloric acid	0.81
$PS_{(NH4)2C2O4}$	Ammonium oxalate	1.63
PS_{KOH}	Potassium hydroxide	14.84
PS_{insol}	Alkali-insoluble	2.85
Total PS		27.44

The main components isolated from CS were identified by the FTIR spectroscopy method (Figure 2). The FTIR spectra are typical for each component. Absorption bands are observed in the IR spectrum of cellulose: 3420 cm^{-1} (OH groups), 2900 cm^{-1} (CH2-, CHO groups), 1000–1200 cm^{-1} (C–O–C and C–O in the pyranose ring). Non-cellulose polysaccharides and lignin showed absorption bands of low intensity in the range of 1630–1734 cm^{-1} corresponding to the vibrations of carbonyl (C=O) and carboxyl (COON) groups, respectively, are typical for. This indicates that some of these components are residually present in the cellulose isolated from the CS by Kürschner-Hanak method.

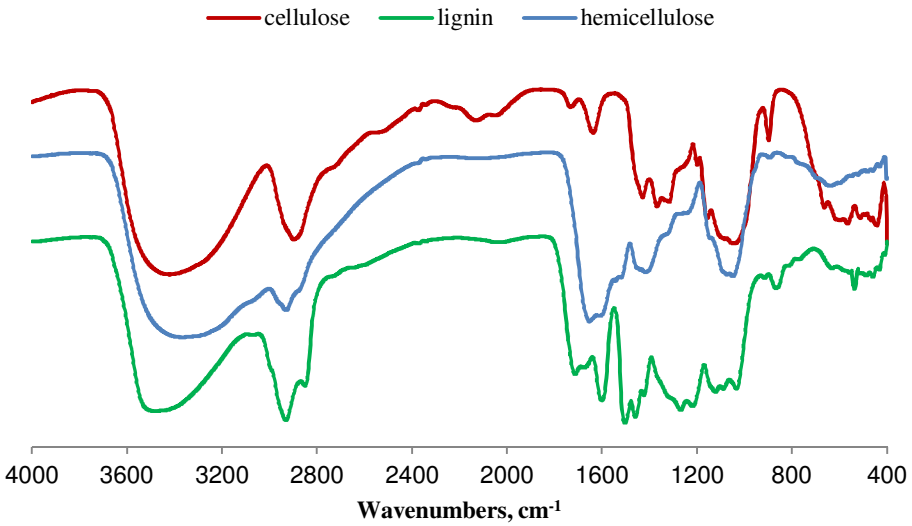

Figure 2. FTIR spectra of cellulose, lignin and hemicelluloses isolated from CS

In addition, a broad, intense absorption band in the range of 1600–1650 cm^{-1} and a band of lower intensity at 1415 cm^{-1} are observed in the IR spectra of the hemicellulose fraction isolated from CS by water-alkali solution, indicating a noticeably high content of carbonyl and methoxy groups in hemicelluloses. In the IR spectra of pectin (aqueous fraction, IR spectrum not shown), an additional band at 1728 cm^{-1} (galacturonic acid) was observed, as well as intense bands in the range of 1421–1332 cm^{-1} due to internal deformation vibrations of the methyl group.

In the IR spectra of lignin isolated by the sulfuric acid method, distinctive absorption bands were observed: two prominent bands at 2931 cm^{-1} and 2850 cm^{-1} (asymmetric and symmetric stretching vibrations of C–H bonds in methyl and methylene groups), absorption bands at 1510, 1460, and 1270 cm^{-1} (skeletal vibrations of the benzene ring), absorption bands at 1400 cm^{-1} and 1000 cm^{-1} (vibrations of aryl-alkyl ethers, mainly by vibrations of methoxy groups). Bands of strong intensity at 1715 and 1600 cm^{-1} were observed, correlated with the stretching vibrations of C=O in the COOH and COOR groups, unconjugated and conjugated to the aromatic ring, respectively.

This shows that CS can be used as a raw material to produce cellulose for industrial use, lignocellulosic intermediate products, that can be potentially used in the production of paper packaging, to produce powder lignocelluloses (additives) in biocomposites (for example, synthetic matrix modifiers), as well as a substrate for microorganisms. Moreover, it is a source of valuable hemicelluloses and pectin polysaccharides with potential biological and physiological activity, which makes their use in crop farming, animal husbandry and forestry promising.

Lignin obtained from coffee silver skin is a considerable resource that allows coffee silver skin to be used as raw material for bioprocessing plants, where the lignin can be separated from other components and chemically treated to produce valuable products such as low-molecular weight biochemicals. Various applications of lignin are widely known, such as an additive to composite materials, antioxidants, adsorbents especially, of heavy metal ions, and anticarcinogenic agents (Fedoros et al. 2022; Wang et al. 2022).

CS fatty acids as a cosmetic ingredient

CS has also been a focus of study for the cosmetic field most often as an exfoliant due to its texture and gentle abrasive properties (Alves et al. 2017). Rodrigues et al. (2016) reported for the first time the successful use of silverskin as a

cosmetic active ingredient with similar results to hyaluronic acid in the improvement of skin hydration and firmness. Moreover, to provide viscosity and consistency or lubricating and protective properties, lipids of the CS may substitute for mineral oils and waxes obtained from the purification of crude petroleum. Fatty acids of CS are increasingly applied as emulsifiers in cosmetic formulations due to the rheological similarities with mineral oil and the absence of toxicity.

This study showed the diverse composition of fatty acids found in the CS. The data in Table 2 clearly demonstrate the presence of both saturated and unsaturated fatty acids with an even number of carbon atoms from C12:0 to C22:0. The mean FA composition was primarily composed of saturated fatty acids (SFA) (70%), followed by polyunsaturated (23.3%) and monounsaturated (6.7%) ones.

Table 2. The fatty acid composition of the CS sample

Fatty acid		**The concentration (µg/g)**	**Content (%)**
Lauric	C12:0	<5.0	0.1
Myristic	C14:0	279.5	4.1
Myristoleic	C14:1	<5.0	0.1
Palmitic	C16:0	2294.6	33.4
Palmitoleic	C16:1	13.9	0.2
Stearic	C18:0	428.1	6.2
Oleic	C18:1(9)	109.7	1.6
Vaccenic	C18:1(11)	339.0	4.9
Linoleic	C18:2	1528.2	22.2
Linolenic	C18:3	73.3	1.1
Arachdic	C20:0	794.7	11.6
Behenic	C22:0	999.8	14.6
SFA		–	70.0
MUFA		–	6.7
PUFA		–	23.3
DU		–	53.3
LSCF		–	39.94

The FAME profile analysis revealed that palmitic acid (C16:0) was the predominant fatty acid, accounting at 33% of the total composition, followed by linoleic acid (C18:2 n-6) at 22%, behenic acid (C22:0) at 14%, and arachidic acid

(C20:0) at 12%. These findings align with the results obtained by (Angeloni et al. 2020). However, the relative percentages differed from those reported by Toschi et al. (2014) and Costa et al. (2018), who found linoleic acid to be predominant in the profile. Bessada et al. (2018) suggested that these variations in the FA profile could serve as potential chemical markers to differentiate CS from different geographical origins, even within the same coffee species.

Both linoleic and palmitic acids have been recognized as valuable compounds for cosmetic formulations. For instance, linoleic acid (C18:2) is a natural component of sebum and its application for oily skin has been shown to improve the activity of sebaceous glands, unblock pores, and reduce comedos. Palmitic acid exerts multiple essential biological functions at cellular and tissue levels, making it a fundamental constituent for the synthesis of soap and cosmetics (López-Linares et al. 2021). Furthermore, due to the very high content of palmitic acid, the CS lipid profile is more suitable for biodiesel production, rather than for use in the food industry, despite the fact that CS is low in fat. The distinctive feature of the CS FAME was that it had a low degree of unsaturation (DU) and high long chain saturated factor (LCSF).

CS-based biodiesel

One of the most important thermal parameters of biomass fuels, indicating their energy content, is the higher heating value. HHV indicates the maximum amount of energy that can potentially be extracted from biomass. The CS HHV was 15.64 MJ/kg, which is typical for biomass. Parikh et al. (2005) observed an HHV of 18.71 MJ/kg for coffee chaff. However, according to Tseng et al. (2020), the higher the proportion of CS in solid biofuel blends, the higher the hygroscopicity of the biofuels, which was unfavourable for storage. CS can be successfully utilized to produce biodiesel, and an experimental study found that the newly created coffee husk biodiesel fuel can be used in internal combustion engines and make up to 30% in the mixture with conventional diesel fuel without any substantial engine modifications (Emma et al. 2022).

The physical properties of the CS biodiesel precursor have been found to comply with European standards, as well as specifications of biodiesel standards worldwide. These properties included the cetane number (CN), iodine value (IV), higher heating value, (HHV), kinematic viscosity (ν), and density (ρ).

The cetane number is an important indicator of combustion quality, and a value of 62 for the CS biodiesel precursor suggested good ignition characteristics. This fell within the suitable range of 50–65, as stated by (Du et al. 2022). Therefore, the precursor exhibited favorable combustion properties.

Iodine value is a measure of the degree of unsaturation of biodiesel fuel. A higher IV indicates a higher level of unsaturated esters. The CS precursor had an IV of 49 g I_2/100 g, which was below the upper limit of 120 g I_2/100 g. This indicated that the CS biodiesel precursor contained a moderate level of unsaturated esters, making it suitable for use.

The kinematic viscosity of the biodiesel obtained was found to be 4.3 mm^2/s, which was expected to be one-third that of the original CS oil (Lanjekar and Deshmukh 2016). The precursor, containing 33.44% of palmitic acid (C16:0) belonged to the category of long-chain saturated oils and usually has higher viscosity compared to unsaturated oils. However, it is worth mentioning that the kinematic viscosity of biodiesel is an indicator of fuel atomization quality and droplet size, and it can be adjusted by blending it with conventional diesel fuel.

Fuel density (ρ) is another essential factor that greatly affects the energy content in the combustion chamber and the engine performance. The density of the CS biodiesel precursor was found to be 0.87 g/l, which fell within acceptable range for biodiesel fuels (Mairizal et al. 2020).

Based on these properties, it was concluded that the CS biodiesel precursor complied with European standards. However, it is important to note that biodiesel standards and specifications may vary in different regions, so it is recommended to verify the specific standards applicable to the intended usage area.

CS-based organo-mineral fertilizer

The Zero Waste approach covers the utilization of CS as a valuable source of biomass and active substances, enabling the creation of fertilizers for organic farming and substrates for solid-state fermentation (Hoseini et al. 2021; Russo et al. 2022). While CS has been mentioned as an amendment in numerous studies, only a limited number of studies have delved into assessing whether its agrochemical quality aligns with the necessary criteria to be classified as a fertilizer. Further exploration is needed to determine the viability of CS as a potential fertilizer and its compatibility with organic farming practices. Contents of carbon, hydrogen, and nitrogen revealed were in the range typical for lignocellulosic materials reported that potassium is the most abundant mineral element in the CS, followed by calcium, magnesium and phosphorus (Ballesteros et al. 2014; González-Moreno et al. 2020). This study perceived that the trend of chemicals was Ca > K > Mg > P (Table 3), which agreed with (Martuscelli et al. 2021). However, applying the CS directly to agricultural practices proved difficult because of the extremely low bulk density of this waste.

Table 3. Main chemical characteristics of CS and CS-based fertilizers revealed

	pH $_{H2O}$	C %	N %	C/N	P_{tot} %	K_{tot} %	Ca_{tot} %	Mg_{tot} %	S %	H %	Reference
CS	–*	43.1	2.99	14.4	0.12	2.11	0.94	0.31	0.28	–	(Ballesteros et al. 2014)
CS	8.5	53	5.1	11	0.4	3.3	2.2	0.8	1.2	–	(González-Moreno et al. 2020)
CS	4.96	46.3	2.4	19.3	0.08	1.91	3.36	0.72	0.31	5.86	This study
CS composted	8.49	64.5	1.8	35.8	1.78	1.87	2.14	3.73	–	–	(Picca et al. 2023)
CS fertilizer	4.81	38.1	2.06	18.5	1	22	9.6	3.5	0.24	6.1	This study

* – no data available.

Studies have been conducted on the production of biofertilizer pellets with CS as the precursor. The optimum liquid-to-solid ratio for pellet agglomeration during the control process was 1.7. Insufficient amount of binder provided poor integrity of the pellets. On the other hand, redundant moisture content provided a plasticizing effect on the pelletizing process resulting in shape deviations and fragile agglomerates not resistant to transport and storage. Following this, formulations of preblends with binder agents were considered that could facilitate pellet consolidation. The most common and cheap binders were tested to improve the composition as described: starch – formulation 1, bentonite – formulation 2, glauconite – formulation 3. The ratio of binder to precursor was determined by a pelleting test with various additives (ranging from 100 g to 1 kg of binder liquids). The higher friability was achieved using starch and

bentonite, but pellets exhibited worse cylindricity the following optimal biofertilizer composition was established after the formulation 3 test run: CS: glauconite : *Chlorella vulgaris* microalgae suspension (1 kg : 0.33 kg : 1.7 l) with the liquid-to-solid ratio of 1.28. The obtained pellets are presented in Figure 3.

Figure 3. The biofertilizer pellets obtained

Main chemical characteristics of the fertilizer enriched with microalgae were clearly different compared to CS. A decrease in the C/N ratio was observed, with the pelleted fertilizer showing a C/N ratio approximately two times lower than the compost obtained by Picca et al. (2023). This may result in an increase in crop biomass and a decrease in mineral soil N retention after application of the organo-mineral amendment, as per the model of van der Sloot et al. (2022). Table 4 provides further details on the achieved beneficial agronomic properties.

To evaluate the potential effectiveness and safety for valorization purposes of the integument under study the levels of saturated and polycyclic aromatic hydrocarbons, heavy metals and micronutrients were assessed. Table 2 compares levels of various toxicants and micronutrients in the CS sample. *N*-alkanes in plants are thought to be formed by elongation of a preformed fatty acid, followed by loss of the carboxyl carbon. The content of 0.9 mg/g of saturated alkanes in the sample was consistent with (Polidoro et al. 2018) mentioning the high representability of the saturated hydrocarbons (0.83 mg/g). Being obtained as a result of high-temperature roasting of coffee beans, CS should be analyzed for the PAHs content that could have formed by the incomplete combustion of organic matter. It has been reported that phenantrene, benzo[a]pyrene and antracene form near 220 °C, while a higher temperature near 250–260 °C is necessary for the generation of pyrene and chrysene (Binello et al. 2021). The very first screening of PAHs was conducted by Nolasco et al. (2022) and found higher concentrations for low molecular weight PAHs. It was also crucial to manage levels of heavy metals and micronutrients to prevent potential risks of application while ensuring the availability of essential nutrients. While the above-mentioned researchers reported higher levels for lead and nickel, Nzekoue et al. (2022) observed potentially toxic and carcinogenic heavy metals including arsenic, cadmium, lead, and mercury, which can cause various health hazards. Concerning microminerals, iron resulted to be the most concentrated in the CS with levels of 150 mg/kg followed by aluminum (69.0 mg/kg). Furthermore, the analysis revealed high levels of essential micronutrients, such as manganese (57 mg/kg) and copper (38 mg/kg). These findings are consistent with previous studies, highlighting the significance of monitoring heavy metal and micronutrient levels in CS.

Table 4. Levels of toxicants and micronutrients in the CS sample

	This study	(Nolasco et al., 2022)	(Nzekoue et al., 2022)
Polycyclic aromatic hydrocarbons, ng/g			
Naphthalene	0.0	40	–*
Acenaphthene	0.0	60	–
Fluorene	1.0	30	–
Fluoranthene	12.8	20	–
Pyrene	25.2	20	–
Chrysene	1.6	<10	–
Benzo[b]fluoranthene	0.0	10	–
Benzo[k]fluoranthene	0.3	<10	–
Benzo[a]pyrene	1.2	<10	–
Dibenzo[a,h]anthracene	1.4	20	–
Heavy metals, mg/kg			
Arsenic (As)	0.053	0.04	0.1
Cadmium (Cd)	0.052	0.05	0.07
Total Chromium (Cr)	0.25	0.86	0.23
Mercury (Hg)	nd**	0.02	0.05
Nickel (Ni)	0.20	1.78	0.7
Lead (Pb)	0.379	2.63	0.3
Micronutrients, mg/kg			
Manganese (Mn)	57	22.9	46.7
Copper (Cu)	38	58.6	37.9
Cobalt (Co)	0.30	1.02	0.2
Zinc (Zn)	9	7.08	31.9
Iron (Fe)	150	349	238
Aluminum (Al)	69	–	89

* – no data available;

** – not detected.

Conclusion

Indeed, the CS utilization in various biological processes presents a dual advantage. Firstly, it provides an alternative, sustainable source to produce value-added products such as biodiesel, biofertilizers, and biocomposites. Secondly, it helps solve environmental pollution problems by offering a beneficial use for what is otherwise considered waste from the coffee roasting process.

The functional composition of CS rich in cellulose and lignin makes it an excellent raw material for the production of paper packaging and lignocellulose powders. These materials can be used in the creation of biocomposites, which are increasingly sought after in various industries due to their biodegradability and lower environmental effect compared to conventional materials. The fatty acid composition of CS, particularly its high content of palmitic acid, makes it a

suitable substrate for biodiesel production. The biodiesel produced complies with the European standards, indicating its potential as a renewable energy source. In prospective research, the employment of machine learning techniques might be explored for addressing prediction challenges associated with in the field of engine studies and cost analysis.

The potential of CS as a biofertilizer is significant. With the application of effective biotechnology, it was transformed into a sustainable and cost-effective soil amendment, contributing to the enhancement of soil fertility and crop productivity. Subsequent research will assess the efficacy of applying CS biofertilizer to soil, examining its influence on soil properties and plant growth and development. This aligns with the increasing global demand for environmentally friendly and economically viable agricultural practices.

In conclusion, the CS utilization in these biological processes not only adds value to this by-product of coffee production but also contributes to sustainable development by reducing waste and promoting the use of renewable resources.

Author contributions: The authors confirm the study conception and design: T.N. Shchemelinina, E.M. Anchugova; data collection: E.M. Anchugova, Elena V. Udoratina, Elena G. Kazakova; analysis and interpretation of results: E.M. Anchugova, E.V. Udoratina, E.G. Kazakova, A.O. Nosova, M.V. Uspenskaya, T.N. Shchemelinina; draft manuscript preparation: E.M. Anchugova, A.O. Nosova. The results were evaluated by all authors, and the final version of the manuscript was approved.

Acknowledgements: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the frameworks of the State tasks no. 1021051101411-4-1.6.23 and no. 122040600027-6. The authors are thankful to the Eco-analytical laboratory of the IB FRC Komi SC UB RAS, to Dr. Elena Patova and Dr. Irina Novakovskaya, the curators of the collection of microalgae living cultures SYKO A of the IB FRC Komi SC UB RAS. Coffee Plus LLC is gratefully acknowledged for providing coffee silverskin. The authors also thank Bioecobalance LLC for kindly providing the materials for the study.

Funding: This study was funded by the Ministry of Science and Higher Education of the Russian Federation (the State tasks no. 1021051101411-4-1.6.23, and no. 122040600027-6).

Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the reported work.

References

Alves RC, Rodrigues F, Antónia Nunes M, Vinha AF, Oliveira MBPP (2017) State of the art in coffee processing by-products. In: Galanakis CM (ed) Handbook of coffee processing by-products. 1st edn. Academic Press, London Elsevier, pp 1–26. https://doi.org/10.1016/B978-0-12-811290-8.00001-3

Angeloni S, Scortichini S, Fiorini D, Sagratini G, Vittori S, Neiens SD, Steinhaus M, Zheljazkov VD, Maggi F, Caprioli G (2020) Characterization of odor-active compounds, polyphenols, and fatty acids in coffee silverskin. Molecules 25:2993. https://doi.org/10.3390/molecules25132993

Ateş G, Elmacı Y (2019) Physical, chemical and sensory characteristics of fiber-enriched cakes prepared with coffee silverskin as wheat flour substitution. J Food Meas Charact 13:755–763. https://doi.org/10.1007/s11694-018-9988-9

Ballesteros LF, Teixeira JA, Mussatto SI (2014) Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. Food Bioprocess Technol 7:3493–3503. https://doi.org/10.1007/s11947-014-1349-z

Benitez V, Rebollo-Hernanz M, Hernanz S, Chantres S, Aguilera Y, Martin-Cabrejas MA (2019) Coffee parchment as a new dietary fiber ingredient: Functional and physiological characterization. Food Res Int 122:105–113. https://doi.org/10.1016/j.foodres.2019.04.002

Bertolino M, Barbosa-Pereira L, Ghirardello D, Botta C, Rolle L, Guglielmetti A, Borotto Dalla Vecchia S, Zeppa G (2019) Coffee silverskin as nutraceutical ingredient in yogurt: its effect on functional properties and its bioaccessibility. J Sci Food Agric 99:4267–4275. https://doi.org/10.1002/jsfa.9659

Bessada SMF, Alves RC, Costa ASG, Nunes MA, Oliveira MBPP (2018) *Coffea canephora* silverskin from different geographical origins: A comparative study. Sci Tot Environ 645:1021–1028. https://doi.org/10.1016/j.scitotenv.2018.07.201

Binello A, Cravotto G, Menzio J, Tagliapietra S (2021) Polycyclic aromatic hydrocarbons in coffee samples: Enquiry into processes and analytical methods. Food Chem 344:128631. https://doi.org/10.1016/j.foodchem.2020.128631

Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81:1051–1063. https://doi.org/10.1016/S0016-2361(01)00131-4

Costa ASG, Alves RC, Vinha AF, Costa E, Costa CSG, Nunes MA, Almeida AA, Santos-Silva A, Oliveira MBPP (2018) Nutritional, chemical and antioxidant/pro-oxidant profiles of silverskin, a coffee roasting by-product. Food Chem 267:28–35. https://doi.org/10.1016/j.foodchem.2017.03.106

Du J, Yuan R, Hu R, Zhang H, Qi Y, Zhang W (2022) Biodiesel production from *Momordica cochinchinensis* (Lour.) Spreng seed oil. Fuel 314:123047. https://doi.org/10.1016/j.fuel.2021.123047

Emma AF, Alangar S, Yadav AK (2022) Extraction and characterization of coffee husk biodiesel and investigation of its effect on performance, combustion, and emission characteristics in a diesel engine. Energy Convers Man-X 14:100214. https://doi.org/10.1016/j.ecmx.2022.100214

Fedoros EI, Tyndyk ML, Popovich IG, Anikin IV, Yurova MN, Gubareva EA, Pigarev SE, Panchenko AV, Solovyev ND, Anisimov VN (2022) Assessment of antitumor activity of BP-C1, a platinum-based anticancer agent with a lignin-derived polymeric ligand, in autochthonous induced and spontaneous carcinogenesis rodent models. J Trace Elem Med Biol 73:127013. https://doi.org/10.1016/j.jtemb.2022.127013

Garcia CV, Kim YT (2021) Spent coffee grounds and coffee silverskin as potential materials for packaging: A review. J Polym Environ 29:2372–2384. https://doi.org/10.1007/s10924-021-02067-9

González-Moreno MA, García Gracianteparaluceta B, Marcelino Sádaba S, Zaratiegui Urdin J, Robles Domínguez E, Pérez Ezcurdia MA, Seco Meneses A (2020) Feasibility of vermicomposting of spent coffee grounds and silverskin from coffee industries: A laboratory study. Agronomy 10:1125. https://doi.org/10.3390/agronomy10081125

Gülüm M (2022) Effects of compression ratio, blending ratio and engine speed on fuel cost, performance and exhaust emissions of a diesel engine fueled with bio-derived alternative fuels. Sustain Energy Technol Assess 53A:102464. https://doi.org/10.1016/j.seta.2022.102464

Gülüm M (2023) Performance, combustion and emission characteristics of a diesel engine fuelled with diesel fuel + corn oil + alcohol ternary blends. Environ Sci Pollut Res 30:53767–53777. https://doi.org/10.1007/s11356-023-26053-x

Hoseini M, Cocco S, Casucci C, Cardelli V, Corti G (2021) Coffee by-products derived resources. A review. Biomass Bioenergy 148:106009. https://doi.org/10.1016/j.biombioe.2021.106009

Jiménez-Zamora A, Pastoriza S, Rufián-Henares JA (2015) Revalorization of coffee by-products. Prebiotic, antimicrobial and antioxidant properties. LWT 61:12–18. https://doi.org/10.1016/j.lwt.2014.11.031

Lanjekar RD, Deshmukh D (2016) A review of the effect of the composition of biodiesel on NO_x emission, oxidative stability and cold flow properties. Renew Sust Energy Rev 54:1401–1411. https://doi.org/10.1016/j.rser.2015.10.034

López-Linares JC, García-Cubero MT, Coca M, Lucas S (2021) A biorefinery approach for the valorization of spent coffee grounds to produce antioxidant compounds and biobutanol. Biomass Bioenergy 147:106026. https://doi.org/10.1016/j.biombioe.2021.106026

Mairizal, AQ, Awad S, Priadi CR, Hartono DM, Moersidik SS, Tazerout M, Andres Y (2020) Experimental study on the effects of feedstock on the properties of biodiesel using multiple linear regressions. Renew Energy 145:375–381. https://doi.org/10.1016/j.renene.2019.06.067

Martuscelli M, Esposito L, Di Mattia C, Ricci A, Mastrocola D (2021) Characterization of coffee silver skin as potential food-safe ingredient. Foods 10:1367. https://doi.org/10.3390/foods10061367

Mirón-Mérida VA, Barragán-Huerta BE, Gutiérrez-Macías P (2021) Coffee waste: A source of valuable technologies for sustainable development, in: Bhat R (ed) Valorization of agri-food wastes and by-products. 1st edn. Academic Press, London, pp 173–198. https://doi.org/10.1016/B978-0-12-824044-1.00009-X

Nolasco A, Squillante J, Velotto S, D'Auria G, Ferranti P, Mamone G, Errico ME, Avolio R, Castaldo R, Cirillo T, Esposito F (2022) Valorization of coffee industry wastes: Comprehensive physicochemical characterization of coffee silverskin and multipurpose recycling applications. J Clean Prod 370: 133520. https://doi.org/10.1016/j.jclepro.2022.133520

Nzekoue FK, Borsetta G, Navarini L, Abouelenein D, Xiao J, Sagratini G, Vittori S, Caprioli G, Angeloni S (2022) Coffee silverskin: characterization of *B*-vitamins, macronutrients, minerals and phytosterols. Food Chem 372:131188. https://doi.org/10.1016/j.foodchem.2021.131188

Parikh J, Channiwala SA, Ghosal GK (2005) A correlation for calculating HHV from proximate analysis of solid fuels. Fuel 84:487–494. https://doi.org/10.1016/j.fuel.2004.10.010

Picca G, Plaza C, Madejón E, Panettieri M (2023) Compositing of coffee silverskin with carbon rich materials leads to high quality soil amendments. Waste Biomass Valorization 14:297–307. https://doi.org/10.1007/s12649-022-01879-7

Polidoro ADS, Scapin E, Lazzari E, Silva AN, dos Santos AL, Caramão EB, Jacques RA (2018) Valorization of coffee silverskin industrial waste by pyrolysis: From optimization of bio-oil production to chemical characterization by GC × GC/qMS. J Anal Appl Pyrolysis 129:43–52. https://doi.org/10.1016/j.jaap.2017.12.005

Ranjbari M, Shams Esfandabadi Z, Quatraro F, Vatanparast H, Lam SS, Aghbashlo M, Tabatabaei M (2022) Biomass and organic waste potentials towards implementing circular bioeconomy platforms: A systematic bibliometric analysis. Fuel 318:123585. https://doi.org/10.1016/j.fuel.2022.123585

Rodrigues F, Matias R, Ferreira M, Amaral MH, Oliveira MBPP (2016) *In vitro* and *in vivo* comparative study of cosmetic ingredients coffee silverskin and hyaluronic acid. Exp Dermatol 25:572–574. https://doi.org/10.1111/exd.13010

Russo ME, Procentese A, Montagnaro F, Marzocchella A (2022) Effect of enzymes adsorption on enzymatic hydrolysis of coffee silverskin: Kinetic characterization and validation. Biochem Eng J 180:108364. https://doi.org/10.1016/j.bej.2022.108364

Shakhmatov EG, Toukach PV, Makarova EN (2020) Structural studies of the pectic polysaccharide from fruits of *Punica granatum*. Carbohydr Polym 235:115978. https://doi.org/10.1016/j.carbpol.2020.115978

Sung SH, Chang Y, Han J (2017) Development of polylactic acid nanocomposite films reinforced with cellulose nanocrystals derived from coffee silverskin. Carbohydr Polym 169:495–503. https://doi.org/10.1016/j.carbpol.2017.04.037

Toschi TG, Cardenia V, Bonaga G, Mandrioli M, Rodriguez-Estrada MT (2014) Coffee silverskin: Characterization, possible uses, and safety aspects. J Agric Food Chem 62:10836–10844. https://doi.org/10.1021/jf503200z

Tseng CH, Jhou SY, Chen YC (2020) Integrating spent coffee grounds and silver skin as biofuels using torrefaction. Renew Energy 148:275–283. https://doi.org/10.1016/j.renene.2019.12.005

van der Sloot M, Kleijn D, De Deyn GB, Limpens J (2022) Carbon to nitrogen ratio and quantity of organic amendment interactively affect crop growth and soil mineral N retention. Crop Environ 1:161–167. https://doi.org/10.1016/j.crope.2022.08.001

Vasilevich RS (2018) Major and trace element compositions of hummocky frozen peatlands in the forest–tundra of Northeastern European Russia. Geochem Int 56:1276–1288. https://doi.org/10.1134/S0016702918100129

Wang T, Jiang M, Yu X, Niu N, Chen L (2022) Application of lignin adsorbent in wastewater treatment: A review. Sep Purif Technol 302:122116. https://doi.org/10.1016/j.seppur.2022.122116

Xiao L, Mjøs SA, Haugsgjerd BO (2012) Efficiencies of three common lipid extraction methods evaluated by calculating mass balances of the fatty acids. J Food Compos Anal 25:198–207. https://doi.org/10.1016/j.jfca.2011.08.003

Yakovleva EV, Gabov DN, Vasilevich RS, Dubrovskiy YA (2022) Polycyclic aromatic compounds in plants and peat in the peatlands of the European part of Russian Arctic. Plant Soil 475:581–603. https://doi.org/10.1007/s11104-022-05397-2