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Original article

Green solvents for deoiling pumpkin and sunflower press cakes: impact on composition and technofunctional properties

Sophie Morejón Caraballo,* Harald Rohm & Susanne Struck

Chair of Food Engineering, Technische Universität Dresden, 01062, Dresden, Germany

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Summary The applicability of protein-rich press cake from mechanical seed oil production is limited because of its relatively high residual oil content. To overcome this drawback, pumpkin and sunflower press cakes were deoiled at room temperature by using two green solvents, namely ethanol and isopropyl alcohol. Hexane, which is mostly used in the plant oil industry, was used as a reference. The derived meals were analysed regarding composition as well as with respect to technofunctional properties such as water-binding capacity, water solubility, nitrogen solubility and colour. Extraction efficiencies of more than 94% were achieved once the solvents were refreshed during extraction. In contrast to pumpkin meal, solvent-specific differences in the residual oil content of sunflower press cake were discovered, which was lowest for hexane and highest for ethanol. The water-binding capacity and nitrogen solubility of the meals were improved after solvent extraction. The results indicate that it is possible to replace hexane with more sustainable green solvents such as ethanol or isopropyl alcohol to extract residual oil from sunflower and pumpkin press cake.

Keywords Nitrogen solubility, protein, sustainability, valorisation of by-products.

Introduction

Press cake (PC) from edible oil production and meal made thereof, which refers to solvent-extracted press cake, are valuable plant processing by-products that may be further utilised because of their high protein contents. In 2020/21, approx. 50 million tons of sunflower (*Helianthus annuus*) seeds were harvested worldwide, giving an amount of approx. 20 million tons of sunflower oil but also approx. 20 million tons of sunflower meal (www.statista.com). The main fraction of this sunflower oil processing by-product, showing a protein content of up to 48 g 100 g^{-1} dry matter (dm) and a dietary fibre content of 9–50 g 100 g^{-1} dm, is used as animal feed (Arrutia *et al.*, 2020). Another high-quality seed oil comes from pumpkin (*Cucurbita pepo*), with its press cake or meal containing a similar amount of protein and also being used as feed. Because of the high nutritional value and the absence of antinutritional compounds in sunflower and pumpkin press cakes, they may also be considered for human consumption (Bracher, 2019).

When oil is obtained from sunflower seeds by continuous mechanical pressing only, the resulting press cake often still contains about 16–24 g 100 g^{-1} oil (Baümler *et al.*, 2016), and similar is true for pumpkin press cake with a residual oil content of approx. 6–36 g 100 g^{-1} after pressing (Ancu a & Sonia, 2020). If the oil was processed at a temperature below 50–60 °C, it can be distributed as cold-pressed oil (Bendini *et al.*, 2011; Ancu a & Sonia, 2020). In industrial oil processing, the press cake is further extracted with solvents to take advantage of the residual oil (Baümler *et al.*, 2016). After removal of the solvent from the press cake by evaporation, the final product is the deoiled press cake, further named meal.

There is a high potential for press cake being utilised in different foods, such as bread, biscuits, snacks or dairy products, but in all cases, its technofunctional properties play an important role (Ancu a & Sonia, 2020). To improve the properties of press cake from, for instance, small-scale organic oil production for incorporation in foods, it might be important to reduce the residual oil content by solvent extraction. Exemplary, the reduction of the oil content of rice bran improved its water-binding capacity (Capellini *et al.*, 2020). In the industrial production of plant oil, a counter-flow current extraction using hexane as a solvent is commonly used to increase the yield of the

*Correspondent: E-mail: sophie.morejon_caraballo@tu-dresden.de

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extracted oil (Li *et al.*, 2014; Scharlack *et al.*, 2017). Hexane is frequently used because of its good selectivity resulting from its highly non-polar character. Additionally, the solvent can be recovered easily by subsequent evaporation and distillation (Kumar *et al.*, 2017; Calvo-Flores *et al.*, 2018). For echium seeds, it was shown that the oil yield after hexane extraction was always higher than after extraction with ethanol, except when a temperature of at least 150 °C was applied (Castejón *et al.*, 2018). However, it should be considered that hexane as a petroleum solvent is hazardous to the environment and health (Sánchez-Camargo *et al.*, 2019). Alternatively green solvents, for example alcohol, might be used. The advantage of green solvents is that they can be produced from renewable raw materials and that they are less harmful. Nevertheless, the quantity of such solvents used for oil extraction should be kept small to reduce operational costs and a negative impact on the environment, because waste treatment and recycling for the application in industrial extraction processes are not completely studied yet (Sánchez-Camargo *et al.*, 2019). Ethanol and 2-propanol (isopropyl alcohol, IPA) are both alcohols that can be prepared from biomass sources, are biodegradable and less toxic and are therefore considered as being part of the group of green bio-based solvents (Calvo-Flores *et al.*, 2018; Sánchez-Camargo *et al.*, 2019). In guides that should help in selecting solvents for chemical processes, for example the GlaxoSmithKline solvent guide (Alder *et al.*, 2016), hexane is classified as undesirable, and its substitution is requested, whereas ethanol and IPA are recommended as they only come with some minor issues regarding waste, environment, health and safety (Calvo-Flores *et al.*, 2018).

The aim of the present study was to compare the impact of press cake extraction by hexane or by two green alternatives (ethanol and IPA) on the oil and protein content of the deoiled sunflower or pumpkin meal and to evaluate technofunctional properties of the obtained material. Sequential extraction was carried out on a lab scale by varying extraction time and solid-to-solvent ratio. In previous studies, extraction was performed at 50–90 °C to determine the effect of extraction temperature on oil yield and technofunctional properties (Baümler *et al.*, 2016; Scharlack *et al.*, 2017). In this study, the extraction was done at room temperature to prevent thermally induced protein denaturation and to examine the possibility of effective low-energy extraction. The main emphasis of the study was placed on the benefits resulting from alternative solvents and on the properties of the extracted press cake as a promising side-stream for application in foods.

Materials and methods

Materials

Sunflower press cake (SPC) as a remnant of mechanical cold pressing of sunflower seeds with hulls was obtained from BIO PLANÈTE Ölmühle Moog GmbH (Lommatzsch, Germany). Before use, the pellets were ground at 12 000 rpm using a ZM 200 ultracentrifugal mill equipped with a 1 mm mesh sieve (Retsch GmbH, Haan, Germany). Pumpkin press cake (PPC) powder was obtained from Ölmühle Solling GmbH (Boffzen, Germany). Both press cakes were sieved using an AS 200 vibratory sieve shaker (Retsch GmbH), and the fraction with a particle size of 300–600 μm was used for further experiments. All solvents namely ethanol, 2-propanol and hexane were of analytical grade and obtained from VWR International GmbH (Darmstadt, Germany).

Press cake analyses

The dry matter content of native press cake (PC) and the deoiled press cake (dPC) obtained by solvent extraction was determined through drying at 103 °C until mass constancy (ULE 500, Memmert GmbH & Co. KG, Schwabach, Germany). The total nitrogen content of PC and dPC was analysed by the Kjeldahl method using a K-436 digestion system and a K-360 distillation unit (Büchi Labortechnik GmbH, Essen, Germany), and the protein content was calculated using a nitrogen conversion factor of 5.6 for sunflower (Pickardt *et al.*, 2015) and 6.25 for pumpkin (Pham *et al.*, 2017). The oil content of PC and dPC was determined by Twisselman extraction with petroleum ether using a Soxtherm extraction unit (Gerhardt GmbH & Co. KG, Königswinter, Germany). Ash content and dietary fibre content of the raw materials were analysed by incineration at 550 °C in an L9/11 muffle furnace (Nabertherm GmbH, Lilienthal, Germany) and by using an enzymatic test kit (Megazyme Ltd., Bray, Ireland), respectively.

Particle size distribution of the target fractions of SPC and PPC was determined in triplicate by laser diffraction using a HELOS/KR Multirange diffractometer (Sympatec GmbH, Clausthal-Zellerfeld, Germany), equipped with a He-Ne laser (632.8 nm, 5 mW, 2000 Hz) and a RODOS injection disperser operating at a dispersion pressure of 0.3 MPa. Particle size from 0.5 to 875.0 μm was recorded and evaluated with the PAQXOS 4.3 software (Sympatec GmbH).

Solvent extraction of press cake

For deoiling press cake by solvent extraction, a 20 g aliquot of milled and sieved PC was placed in a beaker

and mixed with the respective solvent in a solid-to-solvent ratio of 1:6 or 1:10 (w v^{-1}). The mixture was then stirred on an MS-MP8 mixing plate (witeg Labortechnik GmbH, Wertheim, Germany) at room temperature for 1 h at 200 rpm. After mixing ceased, the press cake sedimented and the supernatant was decanted. The wet press cake in the beaker was again mixed with fresh solvent in the same amount as in the first stage, and the procedure was repeated. Based on the results of preliminary trials (data not shown), total extraction time was 2 h (one change of solvent) at a solid-to-solvent ratio of 1:10 or 3 h (two changes of solvent) at solid-to-solvent ratios of 1:6 or 1:10. After the final extraction stage, solvent and press cake were separated by centrifugation (Sigma 3-30 K, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) at 10 397 ***g*** and 4 °C for 20 min. The residual wet press cake pellets were transferred to glass Petri dishes and dried in a VT 6060 M vacuum oven (Thermo Fisher Scientific, Waltham, MA, USA) connected to an MD 4C membrane vacuum pump (Vacuubrand GmbH + Co. KG, Wertheim, Germany) for 24 h at 35 °C and 20 kPa to remove residual solvents. After drying, the dry matter content of dPC obtained by drying at 103 °C was 92.6 ± 1.7 g 100 g^{-1}. All experiments were performed in duplicate with individual batches. The relative residual oil content (%) was calculated as the ratio of oil in the dPC to the oil content in the initial PC. The relative protein content (%) was calculated similarly. The extraction efficiency (%) was calculated as the difference between 100% and the relative residual oil content.

Water-binding capacity and water solubility

Water-binding capacity (WBC) and water solubility (WS) were determined following the methods of Chen *et al.* (1984) and Anderson *et al.* (1970), respectively. One g ± 0.05 g of PC or dPC sample (m_S) was weighed into a 50 mL falcon tube, and 30 g of deionised water (m_W) were added. Tzhe sample was homogenised in a vortex mixer for 30 s and allowed to rest for 30 min at 20 °C. After centrifugation at 4000 ***g*** for 10 min at 20 °C (Sigma 3-30 K, Sigma Laborzentrifugen GmbH) the supernatant was decanted, and its mass (m_{SN}) was determined. The moisture content of the supernatant x(SN) [g g^{-1}] was determined by drying at 105 °C until constant mass using an MA 30 infrared moisture analyser (Sartorius AG, Göttingen, Germany). The mass of water or solids in the supernatant (m_W (SN) or m_S (SN)) was calculated by multiplication of the mass of the supernatant with the moisture or dry matter content of the supernatant. After calculating the mass of water m_W (sed) and mass of solids m_S (sed) in the sediment by considering the moisture content x of the initial sample, WBV and WS were calculated by

$$m_W\ (\text{sed})\ [\text{gH}_2\text{O}] = m_W - m_W\ (\text{SN}) + \frac{m_S * x}{100} \quad (1)$$

$$m_S\ (\text{sed})\ [\text{gdm}] = m_S - m_S\ (\text{SN}) - \frac{m_S * x}{100} \quad (2)$$

$$\text{WBC}\ \left[\frac{\text{gH}_2\text{O}}{\text{gdm}}\right] = \frac{m_W\ (\text{sed})}{m_S\ (\text{sed})}, \quad (3)$$

$$\text{WS}\ \left[\frac{\text{g}}{\text{gdm}}\right] = \frac{m_S\ (\text{SN})}{m_S * \left(1 - \frac{x}{100}\right)}. \quad (4)$$

Nitrogen solubility index

Nitrogen solubility was analysed according to the method of Sawada *et al.* (2014) with some modifications. One g ± 0.05 g of the PC or dPC sample (m_{sample}) was dispersed in 50 g deionised water (m_{liquid}). During gentle stirring, the pH was adjusted to 6.8 ± 0.1 which was close to the initial pH of the dispersion by adding 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl. The dispersion was agitated at 200 rpm at room temperature for 2 h (MS-MP8, witeg Labortechnik GmbH) and subsequently centrifuged at 5000 ***g*** for 30 min at 4 °C (Sigma 3-30K, Sigma Laborzentrifugen GmbH). To improve the separation of the insoluble residue and the liquid part with the solubilised proteins, the supernatants were filtered through a filter paper (13 µm). The nitrogen content of the filtrate $N_{supernatant}$ (g 100 g^{-1}) was determined by the Kjeldahl method, and the nitrogen solubility index was calculated according to eqn (5). N_{sample} (g 100 g^{-1}) refers to the total nitrogen content of the initial samples:

$$\text{NSI}\ [\%] = \frac{m_{liquid} * N_{supernatant}}{m_{sample} * N_{sample}} * 100\%. \quad (5)$$

Colour determination

The colour of the samples was determined using an LUCI 100 spectral colorimeter (D65 xenon lamp, 10° observer; Hach Lange GmbH, Düsseldorf, Germany). Press cake powder was filled into Quartz glass cylinders (d = 34 mm) up to 4 mm in height and colour primaries of triplicate measurements were transferred to the CIE-Lab colour space. The colour difference ΔE shows the colour change of the press cake after solvent extraction and was calculated according to eqn (6). L_0^*, a_0^* and b_0^* are the colour values of SPC or PPC before extraction:

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2}. \quad (6)$$

Statistical analysis

For all results, arithmetic mean ± standard deviation ($n > 2$) or arithmetic mean ± half deviation range ($n = 2$) is given. Two-way ANOVA was carried out for the relative oil and protein content of dPC with one factor being the solvent, and the other being the extraction conditions. One-way ANOVA was performed for PC and dPC for each property. A Pearson correlation analysis was done for the extraction conditions and the resulting data of all dPC samples. All analyses were carried out using OriginPro2021 (OriginLab Corporation, Northampton, MA, USA).

Results and discussion

Composition and particle size of SPC and PPC

The dry matter content of SPC was 92.0 g 100 g^{-1} and consisted of 21.2 g 100 g^{-1} dm protein, 17.2 g 100 g^{-1} dm oil, 54.5 g 100 g^{-1} dm dietary fibre, 3.8 g 100 g^{-1} dm ash and 3.3 g 100 g^{-1} dm carbohydrates (calculated by difference). PPC had a higher protein content and a lower oil and dietary fibre content. The dry matter content was 92.1 g 100 g^{-1} and consisted of 61.8 g 100 g^{-1} dm protein, 15.5 g 100 g^{-1} dm oil, 18.1 g 100 g^{-1} dm dietary fibre and 7.6 g 100 g^{-1} dm ash. Because of measurement inaccuracies, the sum of compounds slightly exceeded 100 g 100 g^{-1} dm, and therefore no carbohydrates were calculated for PPC. These results are in line with Bárta *et al.* (2021) who also observed a protein content for pumpkin press cake (62 g 100 g^{-1} dm) being almost twice as high as that of sunflower press cake (37 g 100 g^{-1} dm). The protein and fibre content of sunflower press cake highly depends on the content of seed hulls which mainly consist of dietary fibre, while the kernel contains more protein (Geneau-Sbartaï *et al.*, 2008). The SPC used in this study originated from unhulled seeds, and therefore had a lower protein and a higher oil content compared to press cake from hulled seeds.

Although the preparation of both SPC and PPC included an identical sieving step, differences in particle size distribution are evident from the mean logarithmic density functions q_3*, based on the volume of the particles (Fig. 1). Compared to PPC, the volume fraction of SPC at smaller particle size (<200 µm) is lower and the amount of larger particles >200 µm is higher. This can be attributed to the presence of seed hulls and is also an indicator for a smaller specific surface area of the SPC bulk particles. In their study, Bárta *et al.* (2021) stated that the dietary fibre content of press cake with hulls increases with increasing particle size. It can therefore be assumed that the sunflower seed hulls that mainly contain dietary fibre remain in the fraction with larger particles. The higher amount of small particles in PPC is presumably due to the presence of particle aggregates that were collected in the 300–600 µm fraction but separated during sample preparation for laser diffraction measurements.

Composition of extracted press cake

As a residual moisture content in solvents is responsible for impaired extraction efficiency (Scharlack *et al.*, 2017), absolute solvents were used throughout this study. The residual contents of oil and protein after deoiling pumpkin and sunflower press cakes with the three solvents are shown in Fig. 2. The residual oil content of dSPC ranged from 0.25 to 1.10 g 100 g^{-1} dm, and extraction efficiency was on average approx. 98% for hexane and approx. 95% for ethanol. Although working at the boiling temperature of the respective solvent, Rodriguez *et al.* (2021) also showed that the extraction efficiency of sunflower press cake was higher for IPA than for ethanol. Also at elevated temperatures, Li *et al.* (2014) reported a lower oil yield when canola oil was extracted with ethanol rather than with hexane or IPA. In case of dPPC, the content of residual oil varied between 0.19 and 0.45 g 100 g^{-1} dm or, given as the fraction of residual oil to initial oil content, 1.84% on average. This is significantly lower than the residual oil in dSPC (3.45% on average). For dPPC, no significant differences concerning solvent or extraction conditions were observed, whereas, for dSPC, a significant correlation between the dielectric constant of the solvent and the relative oil content of dSPC was observed ($r = 0.69$, $P \leq 0.05$). The dielectric constant can be considered a measure of polarity and is important for the interaction between the solvent and the oil. At 20 °C, the dielectric constants ε′ for

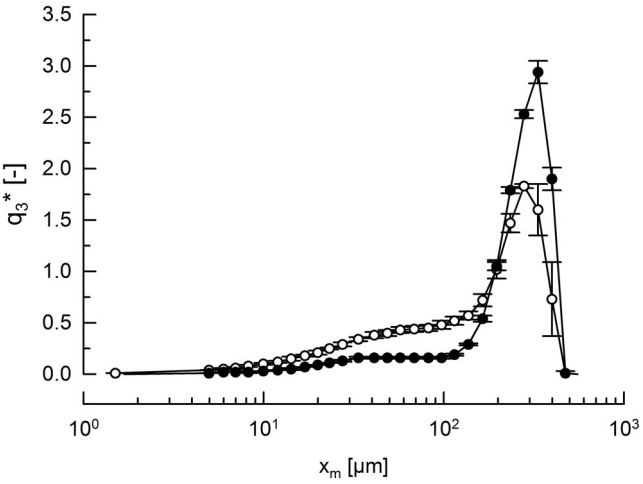

Figure 1 Logarithmic density function of the particle size of SPC (black circles) and PPC (white circles).

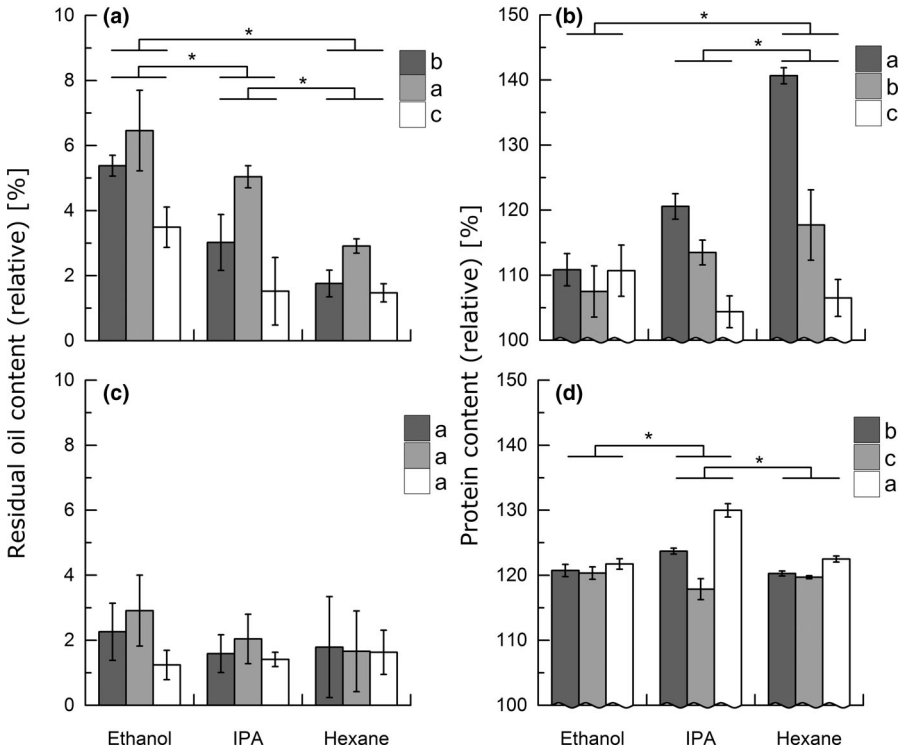

Figure 2 Relative oil and protein content of dPC from sunflower (a, b) and pumpkin (c, d); dark grey: solid-to-solvent ratio 1:6, 3 h; light grey: solid-to-solvent ratio 1:10, 2 h; white: solid-to-solvent ratio 1:10, 3 h; given are mean values with standard deviation ($n = 4$); horizontal lines with asterisks indicate significant differences among solvents; lowercase letters indicate significant differences ($P \leq 0.05$) among the extraction conditions. *$P \leq 0.05$.

hexane, IPA and ethanol are 1.87, 17.9 and 24.5, respectively (Li *et al.*, 2014). More polar solvents with a higher ε′ such as alcohols have a lower affinity to lipids with low dielectric constants which are, for instance 3.07 for commercially available edible sunflower oil and 3.17 for cold-pressed unroasted pumpkin oil (Lizhi *et al.*, 2008; Li *et al.*, 2014; Prevc *et al.*, 2015). Additionally, alcohols exhibit a lower selectivity towards oil and are therefore more likely to extract additional press cake compounds such as polyphenols, pigments and soluble sugars (Baümler *et al.*, 2016; Rodriguez *et al.*, 2021). It was shown by Baümler *et al.* (2016) that, despite the lower dielectric constant of hexane, the extraction yield of oil from sunflower press cake was higher with ethanol, but it turned out that only 69% of the extracted material was identified as oil. Beside this, other components, for example sugars such as sucrose or raffinose, were removed. The extraction efficiency of IPA is higher as it is able to open cell walls in the press cake structure, which enhances oil extraction and additionally interacts with ester groups of triacylglycerides by hydrogen bonds (Attah & Ibemesi, 1990; Tir *et al.*, 2012). Attah & Ibemesi (1990) stated that, in general, solvents with dielectric constants between 6 and 8 lead to higher oil extraction yields for different oil seeds, including pumpkin seeds, than solvents with a higher or lower dielectric constant. However, the extraction yield also depends on the type of oil and, for pumpkin seed oil, solvents with a dielectric constant of about 2 and about 20 resulted in a high oil yield as well.

Besides solvent type, both the solid-to-solvent ratio and extraction time affected the residual oil content of the press cake. For dSPC, the extraction efficiency was in the order of the extraction conditions 1:10_2 h < 1:6_3 h < 1:10_3 h. The extraction experiments with the longest total time had the highest extraction efficiencies. The impact of the solid-to-solvent ratio was inconclusive because extractions with the highest solid-to-solvent ratio of 1:10 resulted in high as well as low extraction efficiencies. Therefore, the number of repeated stages exhibited a more pronounced influence on the residual oil content than the solid-to-solvent ratio or the total amount of solvent used in the process. Although a lower total amount of solvent was used in condition 1:6_3 h than in 1:10_2 h, a lower amount of oil remained after extraction. Therefore, these conditions are favourable to save solvent. As regards dPPC, no significant differences were evident among samples extracted under different conditions.

According to Pérez *et al.* (2019), some water is necessary for solvent extraction of SPC as the extraction efficiency was higher for a press cake with a dry matter content of 87.6 or 81.1 g 100 g^{-1} than for a press cake with 94.3 g 100 g^{-1} dry matter content; consequently, intermediate dry matter contents of about 88 g 100 g^{-1} were recommended. The dry matter content of SPC and PPC used in this study was 92.0 ± 0.2 and 92.1 ± 0.2 g 100 g^{-1}, respectively, so it was above this recommended level. The removal of oil from the press cake resulted in a significant increase in its protein content. The relative protein content after extraction was, on average, 114.7% for dSPC and 121.9% for dPPC. In the study of Rodriguez *et al.* (2021) on sunflower press cake, more non-lipid material was extracted by ethanol than by IPA and, in contrast to hexane, ethanol extracted more soluble sugars. In our study, no significant difference in the relative protein content of dSPC extracted by ethanol and IPA was observed. However, extraction with hexane led to a significantly higher protein content so it can be concluded that less non-lipid material is extracted with hexane. Furthermore, more protein of SPC was extracted using the conditions 1:10_3 h, followed by 1:10_2 h and 1:6_3 h. For dPPC, the highest relative protein content was reached by extraction with IPA and the condition 1:6_3 h but, compared to dSPC, the differences were smaller.

Technofunctional properties of extracted press cake

Not only the chemical composition but also the particle size of a particular sample affects its technofunctional properties. Water-binding capacity, water solubility and the nitrogen solubility index of the deoiled press cakes are summarised in Table 1. Generally, WBC of SPC and PPC increased significantly after solvent extraction. Comparable studies on rice bran showed a higher WBC for the deoiled material than for the raw material as well (Capellini *et al.*, 2020). Depending on the solvent type, the solid-to-solvent ratio and extraction time, no significant differences in WBC among the differently deoiled SPC were observed. In general, PPC and dPPC exhibited a slightly lower WBC than SPC and dSPC, which is in line with recent data from Bárta *et al.* (2021). The WBC mainly depends on the fibre content of a sample, but proteins and carbohydrates do also contribute to this measure because they introduce polar and charged side chains that provide hydrophilic side groups where water can interact (Pérez *et al.*, 2019; Espinosa-Pardo *et al.*, 2020). As the protein content in the deoiled press cake was higher than in the raw material, this is presumably a reason for the improved water-binding capacity of the powder after extraction. Accordingly, the correlation between WBC and the relative protein content of dPPC is significant ($r = 0.87$, $P \leq 0.05$). For dPPC, a significant inverse correlation ($r = -0.70$, $P \leq 0.05$) was also found between WBC and the residual oil content. A higher oil content in dPPC, therefore, resulted in a lower WBC of the sample because the remaining oil prevents the binding of water to the powder surface.

The water solubility data showed relatively high standard deviations and, hence, no effect of deoiling on this measure was identified. However, the WS of pumpkin was higher than that of dSPC. This can be attributed to the lower particle size of PPC compared to SPC, resulting in an enhanced interface area between powder and water where soluble components can migrate into the liquid phase. Bárta *et al.* (2021) showed that milled press cake with smaller particles exhibited a higher WS, but they did not observe any significant differences between sunflower and pumpkin press cake. The WS can furthermore be influenced by the globulin and albumin sections in proteins (Bárta *et al.*, 2021). For dSPC, there is a significant positive correlation ($r = 0.82$, $P \leq 0.05$) between WS and the relative protein content which emphasises the impact of the protein on this measure.

The nitrogen solubility index can be interpreted as a measure of the degree of protein denaturation. The lower the NSI, the more denatured proteins are present in a sample as they are not soluble in water anymore (Navarro & Rodrigues, 2018). For sunflower and pumpkin press cake, NSI generally increased after solvent extraction (Table 1) which means that more soluble proteins are available in the dPC. For rice bran, macadamia and soybean press cake, it was shown that NSI was lower after solvent extraction at 40–90 °C because of thermal denaturation effects (Sawada *et al.*, 2014; Navarro & Rodrigues, 2018; Capellini *et al.*, 2020). Other studies reported an inverse relationship between extraction temperature and nitrogen solubility as plant proteins usually denature at temperatures above 65 °C (González-Pérez *et al.*, 2004; Sawada *et al.*, 2014). The contact between protein and alcohol may also decrease NSI because it destabilises the proteins by weakening hydrophobic interactions between non-polar residues and disturbs the water layer around the protein molecules (Sessa *et al.*, 1998). This effect seems to be higher with hydrated ethanol than with absolute ethanol (Sawada *et al.*, 2014). For dSPC, a negative correlation ($r = -0.76$, $P \leq 0.05$) between the dielectric constant of the solvent and the NSI was observed. The highest NSI in dSPC was reached with hexane, having the lowest dielectric constant among the used solvents. For dPPC, the samples extracted with ethanol had the highest NSI. The higher nitrogen solubility of dSPC might be attributed to their higher content of 2S albumins (approx. 20% of protein) which are soluble at the pH used in this study

Table 1 Water-binding capacity (WBC), Water solubility (WS), Nitrogen solubility index (NSI) at pH 6.8 ± 0.1 and ΔE for SPC, PPC and dPC obtained under different processing conditions

	Extraction conditions						
Materials	Solvent	Ratio	Time [h]	WBC [g H_2O g^{-1} dm]	WS [g 100 g^{-1} dm]	NSI [%]	ΔE [–]
Sunflower				4.58^{b} ± 0.26	8.01^{b} ± 3.06	12.66^{e} ± 1.22	
	Ethanol	1:6	3	6.01^{a} ± 0.18	7.64^{b} ± 0.01	13.82^{de} ± 0.17	16.4
		1:10	2	5.93^{a} ± 0.07	10.01^{ab} ± 2.40	14.91^{cd} ± 1.14	16.1
		1:10	3	6.17^{a} ± 0.15	10.09^{ab} ± 0.84	15.34^{cd} ± 0.62	16.4
	IPA	1:6	3	6.11^{a} ± 0.04	12.07^{ab} ± 1.95	16.67^{bc} ± 0.48	15.3
		1:10	2	6.21^{a} ± 0.21	11.81^{ab} ± 2.25	14.91^{cd} ± 0.33	16.2
		1:10	3	6.37^{a} ± 0.16	10.12^{ab} ± 2.33	16.27^{bc} ± 0.72	16.0
	Hexane	1:6	3	6.37^{a} ± 0.33	14.42^{a} ± 1.63	15.71^{c} ± 0.30	16.8
		1:10	2	5.98^{a} ± 0.26	12.14^{ab} ± 3.66	18.76^{a} ± 0.61	17.8
		1:10	3	5.93^{a} ± 0.21	8.39^{b} ± 1.90	17.95^{ab} ± 0.01	16.3
Pumpkin				4.29^{e} ± 0.15	15.44^{a} ± 0.63	8.54^{c} ± 0.03	
	Ethanol	1:6	3	5.12^{d} ± 0.25	12.86^{a} ± 1.15	12.30^{a} ± 0.91	29.6
		1:10	2	5.30^{cd} ± 0.11	14.58^{a} ± 2.75	10.11^{b} ± 0.49	24.3
		1:10	3	5.54^{bcd} ± 0.14	15.76^{a} ± 4.81	9.79^{bc} ± 0.38	27.3
	IPA	1:6	3	5.81^{ab} ± 0.18	12.19^{a} ± 2.29	8.37^{c} ± 0.39	27.2
		1:10	2	5.33^{bcd} ± 0.05	13.05^{a} ± 2.19	8.44^{c} ± 0.52	25.3
		1:10	3	6.11^{a} ± 0.25	13.73^{a} ± 1.13	8.66^{bc} ± 0.12	23.6
	Hexane	1:6	3	5.34^{bcd} ± 0.22	12.30^{a} ± 1.65	8.90^{bc} ± 0.36	22.0
		1:10	2	5.52^{bcd} ± 0.06	13.51^{a} ± 5.78	9.80^{bc} ± 1.05	21.8
		1:10	3	5.64^{abc} ± 0.15	11.67^{a} ± 1.74	9.33^{bc} ± 0.03	21.7

Mean values within each press cake and column with different letters differ significantly at $P \leq 0.05$.

(Mazhar *et al.*, 1998; González-Pérez *et al.*, 2005) compared to pumpkin with a 2S albumin content of approx. 6% of the total protein (Marcone *et al.*, 1998).

The L*, a* and b* colour values were 42.4 ± 0.1, 1.0 ± 0.0 and 4.4 ± 0.1 for SPC and 55.9 ± 0.4, −2.1 ± 0.1 and 23.3 ± 0.6 for PPC. To measure the degree of decolourization induced by solvent extraction, the colour difference between the untreated PC and the dPC was calculated. The largest difference was observed for L*, lightness was more pronounced for the deoiled samples compared to the native PC. The higher ΔE for pumpkin press cake indicates that its decolourization was more enhanced than that of SPC. The colour difference between native and deoiled sunflower meal ranged from 16.0 to 17.8, so it is easy to note the difference with the naked eye. The colour difference for pumpkin meals was even higher and ranged from 21.7 to 29.6. The colour difference among the extracted pumpkin meals correlated significantly ($r = 0.82$, $P \leq 0.05$) with the dielectric constant of the solvents, and was lowest for the samples extracted by hexane (low dielectric constant) and increased for samples extracted with IPA and ethanol. It can be assumed that during the extraction with ethanol or IPA, more pigments are extracted from the pumpkin press cake than with hexane.

Conclusions

Ethanol and IPA constitute a good alternative to hexane and are suitable for the extraction of oil from PC. For pumpkin PC, the relative oil content of the meal was lower than 3% regardless of solvent type and extraction conditions. No disadvantages of using a green solvent such as ethanol or IPA were recognised unless that more pigments were extracted than when hexane was used as a solvent. For sunflower PC, the residual oil content was highest with ethanol, but the extraction has been improved by adding multiple extraction steps. The meals exhibited improved techno-functional properties as well as increased protein content and could therefore be considered potential ingredients in foods. The extraction efficiency could be furthermore improved by applying a conditioning step with the aim of adjusting the dry matter content of the press cake to the recommended level before the extraction. To verify the suitability of green solvents for a more sustainable way of deoiling PC, the step of solvent recovery and reuse has to be evaluated as well. For scaling up the process, a high amount of solvent is necessary and needs to be handled, stored and recycled. Furthermore, more energy-efficient drying methods than vacuum drying should be applied in this case, but with the risk of impairing the

technofunctional properties of the deoiled meal by thermal treatments.

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Author contributions

Sophie Morejón Caraballo: Conceptualization (equal); investigation (equal); methodology (equal); writing – original draft (equal). **Harald Rohm:** Supervision (equal); writing – review and editing (equal). **Susanne Struck:** Conceptualization (equal); project administration (equal); writing – review and editing (equal).

Conflict of interest

There is no conflict of interest.

Ethics statement

Ethics approval was not required for this research.

Data availability statement

Research data are not shared.

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