Effects of ball-milling on physicochemical, thermal and functional properties of extruded chickpea (*Cicer arietinum* L.) powder

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**ABSTRACT**

The objective of this study was to explore and compare the effects of particle size distribution (PSD) on physicochemical, functional thermal and structural properties of extruded (ECP) and raw (RCP) chickpeas powders. Chickpea powders were obtained by flour fractionating through standard sieves of various particle sizes: 80, 120, 160, and 200 mesh (<180, <125, <95, and <75 μm). Extrusion achieved a desirable degree of lightness in finest (ECP 200) powder followed by increases of yellowness and redness as compared to the finest fraction of control samples (RCP 200). The results of TGA showed better stability for ECP at 600°C with reduced particle sizes as compared to RCP at 400°C. The results of FTIR and XRD showed differences in band intensities and crystalline structures of samples. Extrusion caused microstructural changes in ECP which were elucidated by SEM. ECP exhibited higher WAC ranged from 2.80–2.71 g/g compared to RCP (1.87–1.81 g/g).

**1. Introduction**

Chickpea (*Cicer arietinum* L.), belonging to the family Fabaceae, has been documented as one of the most trivial pulses and widely consumed leguminous crop in recorded history and its use dated back to 7500 years ago in the Middle Eastern region (Lev-Yadun & Abbo, 2000). According to recent estimates, global production is about 14.2 million tonnes with an average yield of 0.96 tonnes/ha, and India is the largest producer (70% of total world production) of chickpeas followed by Australia, Pakistan and Turkey among others. (FAOSTAT, 2016). As a rich source of proteins, chickpeas are mostly consumed in developing countries, however, its demand is constantly on verge of rise globally and has made it a popular ingredient of choice for dietary purpose and industrial uses in fresh or processed forms. Chickpeas have been processed using different traditional and conventional processing methods like soaking, grinding, germination, fermentation, irradiation, roasting and frying to improve functional, sensorial, and nutritional quality (Ramirez, Cendoya, Nichea, Zachetti, & Chulze, 2018). Several epidemiological studies have concluded that consumption of pulses including chickpea along with cereals provides starch, proteins and dietary fiber to intended consumers as well as are used in animal feed to achieve a complete profile of amino acids. However, the high-temperature processing over extended periods of time may lead to undesirable changes in functional and thermolabile components of chickpeas, such as thermal degradation of polyphenols, and consequently, these changes may
adversely affect the consumer’s freedom of choice, likeness, and preference.

Particle size is an important parameter which governs the functional properties of flour and is needed in the quality evaluation of end products. Size reduction is usually carried out to produce small, medium, and large-sized flour fractions. Based on particle size distribution (PSD), flour fractions of variable particle sizes can be obtained by sieving, whereas PSD provides more profound understanding about flour characteristics (Ahmed, Taher, Mulla, Al-Hazza, & Luciano, 2016). Various published reports have already reported that PSD has exerted significant effects on quality properties of end-products or extrudates. Moreover, expansion of extrudates was improved significantly by achieving PSD within a narrow range (Carvalho, Takeiti, Onwulata, & Pordesimo, 2010). So, it is important to study each powder for its functional and structural properties to formulate products or employment in food process engineering (Ahmed, Al-Foudari, Al-Salman, & Almusallam, 2014; Ahmed et al., 2016; Cuq, Rondet, & Abecassis, 2011; de la Hera, Gomez, & Rosell, 2013).

Recently, extrusion has gained popularity in the food processing industry due to its continual advancements after its inception in the late 1800s (Bouvier & Campanella, 2014; Maskan & Altan, 2016). So, extrusion processing is more preferable to attain significant nutrients retention because its operation involves cooking at high-temperature for short intervals of time (Nikmaram et al., 2017). The changes in compositions of chickpeas after extrusion processing have also been studied by some other researchers (Bampidis & Christodoulou, 2011). Extrusion is a thermo-mechanical process for physical and chemical transformation of materials through mechanical and thermal stresses produced by heated barrels and rotating screws, and finally, the materials are shaped and formed by die-based shearing and perforated plates. The process of extrusion is commonly based on series of operations starting from the transport of sample, compression, mixing, plasticizing, shearing, melting, heating, denaturation, and texturization, etc. (Riaz, 2000). The significant sensorial properties like crispiness, mouth-feel, crunchiness, and taste are produced due to evaporation phenomenon produced at the die-exit formed by the significant pressure drop in extruder die (Horvat, Emin, Hochstein, Willenbacher, & Schuchmann, 2013). The use of extrusion has recently increased to produce foods and food products like breakfast cereals, poultry, meat, pasta, ready to eat snacks, baby foods, vegetable-based textured protein and some modified starches (Nikmaram et al., 2017). Starch gelatinization, protein denaturation, degradation of inherent toxins in foods, enhancement of iron-bioavailability and inactivation of anti-nutritional factors are the most possible effects of extrusion processing (Martínez, Calviño, Rosell, & Gómez, 2014). As usage of pulses has been growing in developed and developing countries which are resulting in the introduction of massive production of a wide variety of pulse-based foods in emerging and growing markets. Therefore, it is necessary to conduct further studies in this regard to evaluate the effects of extrusion on physicochemical properties and nutritional adequacy of prepared products.

Although several published reports are available about physical, functional, and structural exploration of chickpeas, however, the effect of sieve particle size on extruded (ECP) and raw (RCP) chickpeas powder is not reported yet. Therefore, the objective of this study was to explore and compare the effects of PSD on physicochemical, functional and structural properties of extruded and raw chickpeas powder. Moreover, thermal stability and microstructural changes were also evaluated by employing thermogravimetric and scanning electron microscopic (SEM) analyses to investigate inherent differences in extruded and unextruded chickpea samples.

2. Materials and methods

2.1. Raw materials

Chickpeas were provided by Xinjiang Tian Shan Qi Dou Biotechnology Co. Ltd. (Xinjiang, China) Sample was collected from a single lot (20 kg) and stored at room temperature (25 ± 2°C) in PET containers until further use.

2.2. Sample preparation

2.2.1. Extrusion of chickpea flour

Chickpeas were soaked for 12 h at 37°C followed by drying at 50°C until constant moisture content. Grinding was carried out using a Planetary Ball Mill (PM 100 Retsh, Germany) to prepare chickpeas flour. The flour was then conditioned to 20% moisture content and packed in polyethylene bags and allowed to equilibrate for 12 h. The extrusion was performed on a twin-screw extruder. The screw diameter, length to diameter (L/D) ratio and die diameter were 25, 16 and 6 mm, respectively. The feed rate (8 kg/h) and screw speed (250 rpm) were kept constant. The extrusion was carried out at 150°C, the temperatures of different barrel zones were 50°C, 100°C, 120°C and 150°C. The samples were collected in an aluminum tray and dried in a hot-air oven at 50°C for 24 h. After drying, they were sealed in plastic bags and stored at −18°C.

2.2.2. Sieve analysis

The extruded and raw chickpeas were ground using a Planetary Ball Mill (PM 100, Retsh, Germany) followed by micronization. In this mill, the samples were mixed with 10 mm zirconia balls (volume ratio 1:1) in a 250 mL grinding jar and milled for 15 min (at a rotary speed of 400 rpm) for three times with an interval of 30 min to avoid powder overheating. The milled sample was then passed through a series of standard sieves of variable mesh sizes, such as 80, 120, 160, and 200 mesh (<180, <125, <95, and <75 um).

2.3. Determination of particle size distribution (PSD)

The particle size distribution of the ECP and RCP was analyzed using a Malvern Mastersizer 3000 instrument (Malvern Instruments Ltd., Worcestershire, UK). Mastersizer 3000 software (version 3.63) was used to calculate the particle size distributions (PSDs) at 10% (Dv10), 50% (Dv50) and 90% (Dv90) volume distribution. All measurements were done in triplicates.

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2.4. Hunter’s color analysis

The colorimetric analysis of ECP and RCP samples was done using a Hunter Colorflex™ Lab Colorimeter (Hunter Associates, Reston, VA). Calibration of the instrument was done prior to measurements using standard black and white tile. The intensity of lightness ($L^*$), redness ($a^*$) and yellowness ($b^*$), and overall color difference ($\Delta E$) were analyzed using the CIE (International Commission on Illumination) color system. All analyses were done in triplicates.

2.5. Water activity

Both the ECP and RCP with different particle sizes were stored in a desiccator with silica gel for 24 h at 25°C. Water activity ($a_w$) of samples was analyzed by Novasina LabMaster-aw instrument (Novasina AG, Lachen, Switzerland) according to the method described by Sert, Mercan, and Dertli (2017). All measurements of water activity were made at 25°C.

2.6. FTIR analysis

The FTIR spectra of ECP and RCP samples were recorded by Nicolet™ FT-IR Spectrophotometer (Thermo Fisher Scientific, Massachusetts, United States). The sample to potassium bromide ratio (1:100) was used to make transparent pallets of both ECP and RCP samples. Spectral data were obtained within IR range of 4000 to 400 cm$^{-1}$ at 4 cm$^{-1}$ of resolution. The ATR plate was carefully cleaned using analytical grade isopropyl alcohol before using it for every next sample. All measurements were recorded thrice.

2.7. X-ray diffraction (XRD) analysis

XRD patterns of both ECP and RCP of variable particle sizes were measured by D8-advance analytical diffractometer (Bruker AXS Ltd., Germany), equipped with pixel-detector employing Cu (Kα), running at 30 kV and 10 mA. The analysis was done between 2 theta, 5° to 60° angular regions with a step length of 0.05° and step rate of 0.210/s.

2.8. Thermogravimetric analysis (TGA)

The thermal stability or measurements of mass loss as a function of temperature for both ECP and RCP samples were carried out with a thermogravimetric analyzer (TGA 2 Model: Mettler Toledo, USA), under nitrogen ($N_2$) purge. Almost 3–5 mg of each sample, placed on the pan, was analyzed within a temperature range of 25–600°C at a rate of 10°C/min.

2.9. Scanning electron microscopy (SEM)

The microstructure of ECP and RCP was examined through a scanning electron microscope (SEM) (JEOL, JSM-5410LV, Tokyo, Japan). The samples were coated with gold in a sputter coater (Structure Probe, West Chester, PA) and photographed at different magnifications (50, 250, 500 & 1000x). Particle sizes were measured by the software provided with the instrument.

2.10. Determination of water absorption capacity (WAC)

WAC was measured according to the modified method of Schoeman and Manley (2018). Three grams of each sample were weighed and dispersed in 25 mL distilled water in the pre-weighed centrifuge tube. The samples were centrifuged at 3000 × g for 25 min. The supernatant was dried in a hot-air oven for 25 min at 50°C, and the solid residues (remained after drying) were weighed. WAC of samples was expressed as gram of bound water per gram of the sample on a dry basis in accordance with Eq. (1) given below.

\[
WAC = \frac{(\text{Weight of tube with sample after drying} - \text{Weight of tube}) - \text{Weight of sample}}{\text{Weight of sample}}
\]

2.11. Determination of oil absorption capacity (OAC)

About 0.5 g of each sample was mixed with 6 mL of soya oil in a pre-weighed centrifuge tube. After a holding period of 30 min, the tubes were centrifuged for 25 min at 3000 × g. After centrifugation, the isolated oil layer was collected separately, while the tubes (possessing sediments) were inverted for 25 min to allow oil drainage prior to weighing. The OAC of samples was expressed as gram of bound oil per gram of the sample on dry basis according to Eq. (2) given below.

\[
OAC = \frac{(\text{Sample weight with tube after removing oil} - \text{Weight of tube}) - \text{Weight of sample}}{\text{Weight of sample}}
\]

2.12. Statistical analysis

All experiments were performed thrice and the results of all data were expressed with mean and standard deviation values. One-way analysis of variance (ANOVA) with post-hoc Dunnett’s t-test was used to analyze the data using
the SPSS Statistics Ver. 19.0 software (IBM SPSS, New York, USA) at significance level of \( p < .05 \). Correlation matrix was obtained by statistical analysis through Origin Pro ver. 8.0 (OriginLab Corp., MA, USA).

3. Results and discussions

3.1. Particle size distribution (PSD)

Both ECP and RCP were passed through various sieves to obtain powders of variable particle sizes and PSD was measured as shown in Figure 1. Particle sizes at 10% (Dv10), 50% (Dv50), and 90% (Dv90) volume distribution of ECP 80, ECP 120, ECP 160, and ECP 200 were (4.5 µm, 25.1 µm, 256.0 µm), (4.4 µm, 22.2 µm, 162.1 µm), (4.4 µm, 20.0 µm, 171.5 µm), and (4.3 µm, 21.4 µm, 258.4 µm), respectively, whereas the volume distributions for RCP 80, RCP 120, RCP 160, and RCP 200 were (3.5 µm, 20.8 µm, 136.1 µm), (3.3 µm, 19.1 µm, 76.3 µm), (3.3 µm, 19.0 µm, 62.5 µm), and (3.0 µm, 15.7 µm, 41.1 µm), respectively. Ahmed, Al-Attar, & Arfa (2016) have reported similar findings for the PSD model of chestnut. It was clearly evident from the results of PSD that ECP samples exhibited slightly larger size in comparison with RCP which were ball-milled under same conditions. Keeping in view the results, it could be inferred that extrusion exerted significant effect \( (p < .05) \) on grinding efficiency of the product. In support of these results, similar findings have been reported by Hareland (1994) who described variable PSD due to effects of hardness, type, processing, grinding time or technique.

3.2. Colour analysis

The trends of color values \( (L^*, a^*, b^*) \) with respect to particle size variations were almost similar for both ECP and RCP powders as shown in Table 1. The degree of lightness \( (L^*) \) showed an inverse relationship with PSD. Significant increases of lightness were observed in ECP 120 samples as compared to ECP 80, while other samples did not show any significant difference. The increase in \( L^* \) value was ranged 87.80–89.11 (ECP) and 91.81–92.22 (RCP) when the mesh sizes of sieves were varied from 80 to 200 mesh. As compared to RCP, the decreases in the lightness of ECP samples can be possibly attributed to non-enzymatic browning phenomenon induced during the extrusion process. Ahmed et al. (2016) have found the similar rises in the degree of lightness \( (L^*-values) \) because of variations in sieve particle sizes of Indian and Turkish lentil flours, which could be due to the availability of extra surface area for reflection of light. Degrees of redness \( (a^*) \) and yellowness \( (b^*) \) showed decreases from 1.61 to 1.25 and 17.90 to 15.84 (ECP); 1.10–0.93 and 17.17–16.50 (RCP), respectively, with respective decreases in sieve particle sizes from 80 to 200 mesh. Comparative overview of both ECP and RCP samples revealed that extrusion led to increases of \( a^* \)-values in chickpeas powders, while the further reduction in size caused significant \( (p < .05) \) decreasing tendencies for both \( a^* \) and \( b^* \)-values in extrudates of ECP samples. This implied that degree of yellowness was lowered in ECP as compared to control (raw samples: RCP) which could be due to loss of pigmentation during the extrusion process, while further decreases of \( a^* \) and \( b^* \) values for both ECP and RCP samples.
could be possibly due to effects of grinding and sieving. ECP showed less changes in ΔE values as compared to RCP. This implied that extrusion was not so much influential to cause significant changes in the overall color profile of ECP whereas, RCP showed higher ΔE values. The results of the correlation analysis of ECP and RCP for physicochemical characteristics are given in Supplementary Table 1. Highest correlation of 1.0 was found between similar respective parameters. Among all parameters, b* values indicated lower magnitude of correlation coefficient (r = −0.14286). Jogihalli, Singh, and Sharananagat (2017) while working on the effect of microwave roasting found almost similar trends for color values regardless of PSD.

### 3.3. Effect on water activity (aw) of extrudates and raw samples

The results of water activity (aw) are shown in Table 1. The ranges of aw were 0.46–0.48 and 0.25–0.28 for ECP and RCP, respectively. Particle size was found to have a little but insignificant (p > 0.05) effect on aw of both ECP and RCP samples. ECP 200 showed higher aw of 0.48 in comparison with RCP 200 with aw of 0.28. A slight increase in aw due to decreasing particle size could be due to the availability of extra surface area for water molecules which resulted in hydration and consequently dissolution phenomena. Overall, RCP exhibited lower aw values as compared to ECP (Gowen, Abu-Ghannam, Frias, & Oliveira, 2007). Hence, it could be inferred that extrusion caused microbial decontamination effect by virtue of controlling aw or keeping it at a constant level which may be beneficial to extend the shelf life of processed chickpeas accompanied by maximum retention of sensorial, organoleptic and physicochemical characteristics. Moreover, moisture migration can be limited due to a controlled water activity of the prepared food product comprising various ingredients. Food manufacturers and formulators usually employ aw values to predict moisture migration and evaluate possible effects of moisture migration on product properties during extended storage.

### 3.4. Effect on thermal stability of the extruded powder

The results of the TGA analysis are shown in Figure 2. The thermal stability curves provided the amount of weight loss as a function of temperature rises within the range of 50–600°C for both ECP and RCP samples of variable particle sizes. Figure 2 shows the effect of particle size on the thermal stability of ECP and RCP. TGA curves of ECP revealed a slight but non-significant difference in weight loss of extruded samples of variable particle sizes. On the other hand, there was an increase in thermal stability of RCP samples with corresponding decreases in sieve particle size. There was no marked difference between ECP and RCP samples, however, changes in particle sizes led to variations in TGA curves and both samples showed similar tendencies. While comparing both ECP and RCP, the results for ECP at 200°C were 92.67%, 93.33%, 93.86%, and 94%, while 93.83%, 93.67%, 94.91%, and 93.83% for RCP at 80, 120, 160, and 200 mesh sizes, respectively. At 400°C, it could be seen that RCP powders of 160 and 200 mesh sizes showed improved thermal stability (39.16%; 160, 43.19%; 200) as compared to ECP (33.89%; 160, 33.93%; 200). At 600°C, RCP 80 showed percentage weight of only 8.78% as compared to that of ECP 80 (20.01%). RCP 120 and 160 had weight percentages of 9.42% and 14.92% in comparison with ECP 120 and ECP 160 which showed weight percentages of 24.48% and 25.08%, respectively. Particle size significantly (p < 0.05) affected the thermal stability of ECP 200 and RCP 200. Both ECP 200 and RCP 200 had weight percentages of 25.78% and 21.92%, respectively. The reason for differences between both ECP and RCP samples could be the rearrangement or modifications in the crystalline structures owing to extrusion cooking (Martinez et al., 2014). Regardless of particle size, the pre-treatment (extrusion) probably caused starch gelatinization of ECP flours which further aggregated the crystalline structures of flour particles and consequently increased thermal stability. Weight loss in chickpea samples could be attributed to the phenomena of oxidative mass losses, organic matter desorption, and decomposition. Similar findings have been reported by Ricardi et al. (2018), and the authors described...
the weight loss tendency with rises in temperatures for chitosan samples. Furthermore, the formation of small crystal complex due to reduced particle size could be the reason for increased thermal stabilities for both ECP and RCP samples. Corresponding to these results, Ahmed et al. (2016) have reported similar results for Indian and Turkish lentil flours which were sieved at variable particle sizes.

3.5. Effects on spectral characteristics of chickpea powders

FTIR spectroscopy offers an advantage for assessing vibrational modifications in a rapid, simple, non-destructive manner with associated time saving and cost-effectiveness (Zhao et al., 2013). The results of FTIR spectroscopy of both ECP and RCP samples are demonstrated in Figure 3. Based on the vibrational patterns of the inherent functional groups in chickpeas, FTIR provided the attractive analytical advantage of evaluation of the changes in functional groups and spectral characteristics after within infrared region for both ECP and control (RCP) samples. Significant differences occurred in spectral patterns and ECP samples showed increases in band intensities as compared to RCP samples possibly due to high-temperature cooking effect of extrusion. It was also revealed that particle size significantly (p < .05) influenced the band intensities of both extruded and raw samples. ECP and RCP at 200 mesh sizes had higher band intensities as compared to samples obtained from 80 mesh. Comparison of spectra peaks of both ECP80 and RCP80 showed a marked difference in peak sharpness (Figure 3). Although the peaks of samples of small-sized particles showed resemblance, but considerable differences in peak intensities were evident from FTIR spectra. Based on the results, the spectral variations could be seen at different regions which were 1) 3700–3600 cm$^{-1}$, 2) 3650–3250 cm$^{-1}$, 3) 2935–2915 cm$^{-1}$, 4) 1760–1725 cm$^{-1}$, 5) 1690–1675 cm$^{-1}$, 6) 1615–950 cm$^{-1}$, 7) 900–500 cm$^{-1}$. The band at the region of 3700–3600 cm$^{-1}$ corresponded to non-bonded hydroxyl (–OH) group stretching in conjunction with alcoholic and phenolics groups. The region in the range of 3650–3250 cm$^{-1}$ indicated the presence of hydroxyl or amino (–NH$_2$) groups with unsaturated or aromatic olefinic compounds. This functional groups in this region were significantly affected because of size reduction and extrusion cooking which resulted in C-H stretching. The
spectral absorption in the 2935–2915 cm\(^{-1}\) region could be attributed to methylene C-H stretching. The changes in these regions were also evident from the findings of the previously published report regarding processed flours (Mridula, Goyal, & Manikantan, 2008) which were in agreement with the results of the current study. The absorptions at 1760–1725 cm\(^{-1}\) and 1690–1675 cm\(^{-1}\) regions could be ascribed to the presence of simple carbonyl compounds, such as ketones, aldehydes, esters or quinones. The major bands in the region of 1615–950 cm\(^{-1}\) provided the evidence for the presence of aryl group frequencies having C = O, C-H or C = C stretches. The peaks at 1645–1655 cm\(^{-1}\) region corresponded to olefinic unsaturation (C = C) (Coates, 2000).

The bands at 1150–950 cm\(^{-1}\) region was indicative of probably the C-H bending vibrations of aromatic compounds mostly comprised of aliphatic fluoro compounds with C-F stretching. The presence of bands in 900–500 cm\(^{-1}\) region represented out of plane C-H bending in an aromatic ring. The increases in band intensities of ECP samples at various regions can be attributed to decreasing tendency in ordered crystalline structures of chickpea powder, and these findings were further validated from microstructure and crystallinity results from SEM and XRD analyses, respectively. As evident from the FTIR spectra, the three distinct peaks were observed in the regions of 800–1200, 1600–2000, and 2700–3300 cm\(^{-1}\), respectively. FTIR gives the information pertaining to IR light–matter interaction with powdered particles. The most prominent and evident bands were in the regions of 3500 and 3000 cm\(^{-1}\) which suggested the presence of amines and amino (-NH2) groups in their compositional profiles which are usually found in internal matrices of chickpeas in various biological forms, such as peptides, amino acids, proteins, DNA, RNA and alkaloids. The IR stretching, also known as N-H stretches, of the amines (primary: RNH\(_2\)) was present at spectral regions of 3000–3000 cm\(^{-1}\) (Figure 3). Usually, the peak broadening is caused due to the existence of O-H stretches representing hydrogen bonding in functional groups. The spectral bands in the absorption region of 1650–1580 cm\(^{-1}\) usually indicate the presence of primary amines with a characteristic N-H stretching of bending vibration. This weakening effect of a band might be due to the influence of structural expansion during extrusion cooking. Higher and lower wavenumbers at this region are usually indicative of the asymmetric and symmetric N-H stretches, respectively. Secondary amines (R\(_2\)NH) normally consist of a single weak band in this region owing to the existence of only one N-H linkage. On the other hand, tertiary amines (R\(_3\)N) usually do not demonstrate any specific spectral feature in this particular region due to lack of any N-H linkage. Other notable spectral bands were indicative of the aromatic amines (C-N stretch: 1335–1250 cm\(^{-1}\)), aliphatic amines (C-N: 1250–1020 cm\(^{-1}\)) and primary and secondary amines only (N-H wag: 910–665 cm\(^{-1}\)). The banding patterns existing in the spectral range of 1500–1800 cm\(^{-1}\) indicated the fingerprint regions which were mainly ascribed to the absorption of the polyphenolic compounds, and carbonyl groups (C = O) stretches. Other chemical moieties and components which appeared at spectral regions of absorption bands of 1800–750 cm\(^{-1}\) comprised of protein components, carbohydrates, and phenolic compounds. Our results are in agreement with the findings of Kadiroğlu, Aydemir, and Akcakaya (2018) who characterized the registered chickpea varieties of
Turkish origin on the basis of functional properties and characteristic FTIR spectral features. Moreover, the authors have reported the successful application and potential of FTIR spectroscopy with enhanced reliability for prediction of the functional properties of chickpea samples in conjunction with chemometrics as an alternative of the conventional chemical analytical approach.

3.6. Effect on crystalline structures of chickpea extrudates

XRD as an analytical technique offers a unique approach in order to determine the status regarding crystallinity and amorphousness of compounds. The results produced by the XRD analysis are usually represented in the form of diffractogram which demonstrates the intensity with respect to corresponding diffraction angles (Pozo et al., 2018). The XRD patterns for RCP showed sharp peaks at 15°, 17° and 23° while ECP sample at 17° and 19°. XRD results showed significant decreases of intensities in extruded powder. Figure 4 indicated the changes in relative crystallinity and structural modifications of chickpeas. The relative crystallinity of extruded samples showed decreasing tendencies owing to decreases in enthalpy of gelatinization of starches in processed chickpeas and increased disruption of ordered structures and changes in crystal lattices of extruded samples. XRD results further validated these tendencies and confirmed the FTIR spectral properties as well. Results were compared on the basis of particle sizes of powders, and it was implied that smaller particle-sized samples exhibited higher relative crystallinity, and this phenomenon was more prominent in the case of RCP samples. ECP samples exhibited slight peak broadening which indicated that extrusion and size reduction led to the formation of small-sized powders.

Figure 4. XRD diffractograms and patterns of raw (RCP) and extruded (ECP) chickpea powders based on PSD.

Figura 4. Difractogramas XRD y patrones de polvos de garbanzo crudo (RCP) y extruido (ECP) basados en PSD.
crystallites as compared to RCP powder particles. Similar findings were observed by Bashir and Aggarwal (2017) who reported decreases in relative crystallinity associated with increases in FTIR band intensities owing to the effect of processing in irradiated chickpea starches.

3.7. Effect on microstructural attributes of chickpea extrudates

SEM analysis consists of a beam of high-energy electrons which was bombarded on surfaces of chickpea samples to elucidate external morphological features. Obtained micrographs revealed orientation of internal matrices of grains and provided information about textural and microstructural attributes as morphology determinants. The micrographs in Figure 5(a–d) demonstrated that RCP (80–200) samples were round, oval or spherical in shape and exhibited more uniformity as compared to ECP (80–200) samples as shown in Figure 5(e–h), which had an irregular shape with disrupted or non-uniform structures. There was not any obvious effect of particle morphology of powders. Moreover, flours of 200 mesh size showed striking uniformity regardless of sample type. The oval shapes in RCP micrographs provided evidence of the presence of starch granules surrounded by proteins or fibrous particulate materials which were disrupted during ball milling (Aguilera, Esteban, Benítez, Mollá, & Martín-Cabrejas, 2009; Ma et al., 2011). Furthermore, no starch granules but amorphous flakes could be seen in ECP samples formed by a mixture of protein, fiber or gelatinized starch due to extrusion processing. The swelling of starch granules or flattened surfaces were also reported by Aguilera et al. (2009) due to the effects of different cooking treatments. Structural morphology showed that extrusion caused high degree of crosslinking of proteins and starches as powder was more exposed during processing in comparison with intact granules.

Figure 5. Scanning electron micrographs with respect to PSD of; RCP-80 (a), RCP-120 (b), RCP-160 (c), RCP-200 (d) and extruded (ECP) chickpea powders ECP-80 (e), ECP-120 (f), ECP-160 (g) and ECP-200 (h) at 500 and 1000x resolutions.

Figura 5. Micrografías electrónicas de barrido de PSD de polvos de garbanzo RCP-80 (a), RCP-120 (b), RCP-160 (c), RCP-200 (d) y extruido (ECP) ECP-80 (e), ECP-120 (f), ECP-160 (g) y ECP-200 (h) en resoluciones de 500 y 1000x.
3.8. Water (WAC) and oil absorption capacities (OAC) of extruded and raw powders

The results of the WAC are shown in Table 1. Overall, there was no significant (p > .05) effect of PSD on WAC irrespective of sample type. Slightly decreasing tendencies were observed in WAC and ranged 1.81–1.87 and 2.71–2.80 g/g for RCP and ECP, respectively. ECP also exhibited lower OAC especially in the finest sample (0.65 g/g) as compared to the finest sample of RCP (1.10 g/g). Both ECP and RCP showed decreasing tendencies in OAC with increases in particle sizes (Table 1). Increase in WAC with a decrease in the opening size of sieves was also observed by de la Hera et al. (2013) for PSD of rice. WAC is an important assessment parameter for processing industry as it can influence other functional and sensorial characteristics of a product while OAC is important for determining mouth-feel and maintaining the flavor of food products (Bouvier & Campanella, 2014). According to Ahmed et al. (2016) the WAC is influenced by particle size, the amount of fiber, starch and protein present in the powder. OAC is linked with the presence of hydrophobic protein which is helpful in the binding of lipids (Kinsella & Melachouris, 1976).

4. Conclusions

In this study, particle size significantly affected structural, functional and physicochemical properties of raw (RCP) and extruded chickpea (ECP) flours. The differences were more obvious for extruded chickpea samples. Among Hunter color values (L*, a*, and b*), increases in lightness (L*) was found in the finest chickpea powders. Overall, there was no significant (p > .05) effect of particle size distribution on water absorption capacity (WAC) irrespective of sample type. Slightly decreasing tendencies were observed in WAC and ranged 1.81–1.87 and 2.71–2.80 g/g for RCP and ECP, respectively. Both ECP and RCP showed decreasing tendencies in oil absorption capacity with increases in particle sizes. Improved thermal stabilities were observed because of size reduction for both raw and extruded samples. Changes in intensities and crystallinity of raw and extruded flours were observed through FTIR and XRD analyses. The microstructure showed disruption of starch granules for extruded chickpea flour and the distribution of particles was more uniform with reduced particle size. All these results revealed that size reduction exerted significant effects and improved physicochemical and functional properties of chickpea flours which could be useful in the formulation of functional product on industrial scale by means of extrusion cooking and texturization.

Abbreviations

| Abbreviation | Definition |
|--------------|------------|
| L/D | Length to diameter |
| OAC | Oil absorption capacity |
| PET | Polyethylene terephthalate |
| PSD | Particle size distribution |
| RCP | Raw chickpea powder |
| SEM | Scanning electron microscope |
| TGA | Thermal gravimetric analysis |
| WAC | Water absorption capacity |
| XRD | X-ray diffraction |
| ΔE | Overall color difference |

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