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ORIGINAL ARTICLE

## Characterization of minerals content in olive cake and bakery wastes: application in animal nutrition and bio-fuel production

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Olive cake and bakery wastes are considered as important feed ingredients that are incorporated at different levels in animal diets and can be used in bio-fuel production. Major nutrients of both feed ingredients have been characterized in the literature; however, minerals concentration and extent of variation have been overlooked. The importances of characterization of minerals content and extent of variation between different sources have a significant applications in feed industry and bio-fuel production produced from biomass pyrolysis reactions. The purpose of this study was to investigate minerals composition (Ca, Mg, K, Na, P and S) in olive cake and bakery wastes produced in Jordan and to discuss the results in relation to the average and the extent of variation with tabulated values mostly used in literature. Olive cake and bakery waste samples (twelve samples each) were collected from different olive mills and bakeries distributed in Jordan. Among all analyzed bakery wastes samples, Na had the highest average concentration (0.36%) and ranged from 0.02 to 0.67%, whereas, Mg had the lowest concentration (0.03%) and ranged from 0.01 to 0.05 %. Among all analyzed minerals in bakery wastes, Ca, K and S had the lowest CV% (16.62%, 16.57%, and 16.28%, respectively), whereas, Na had the highest CV% (69.51%). Among all analyzed olive cake samples, this study showed that K had the highest average concentration (0.75%) and ranged from 0.46 to 1.98 %, whereas, Na had the lowest concentration (0.02%) and ranged from 0.01 to 0.03 %. Among all analyzed minerals in olive cake samples, Ca had the lowest CV % (17.48%), whereas, K had the highest CV% (53.41%). It can be concluded from this study that the existed variation in minerals concentrations within the investigated by-products is necessary to recommend minerals supplementation strategies and have applied consequences on optimization bio-fuel production process. Key words: feedstock; minerals; variation; bio-fuel; nutrition

#### Introduction

Olive cake and bakery wastes are considered as industrial wastes that have been used in feed industry and on the basis of economic and environmental advantages (Al-Rugaie et al., 2011; Molina-Alcaide & Yanez-Ruiz, 2008). Minerals are considered the most variable of the nutrients commonly determined in feed ingredients (Berger, 1996; Vassilev et al., 2010). Bakery wastes and olive cake are produced from a range of food processing industries and their chemical compositions are recognized to be lacking of consistency (AL-Tulaihan et al., 2004; Arosemena et al., 1995; Guiroy et al., 2000; Ouazzane et al., 2017). From bio-fuel production prospective, accurate measuremnts of minerals and inorganic constituents of biomass are necessary to enhance pyrolysis and gasification reactions (Ouazzane et al., 2017; Suárez-Garcî a et al., 2002). Minerals in feedstock have been reported to affect thermal decomposition of biomasses, acting (especially alkaline minerals) as catalysts of some reactions such as biomass dehydration and decarboxylation reactions (Montoya et al., 2015). Commonly, as the mineral concentration in feedstock biomass increases, the bio-oil production decreases whereas gas and char production increases (Alonso et al., 2012; de Wild et al., 2011; Ranzi et al., 2011). Minerals removing from biomass by using detergent or acids have been reported to increase bio-oil production and decrease the content of reaction water (Banks et al., 2014). From feed formulation prospective, feed formulation designed for specific animal requirements requires accurate measurements of nutrients in feed ingredients including minerals. Relaying on average nutrient composition only and not variation can cause under-formulation or over-formulation which results in increase feed price and under/over achievement of nutrient specification (Saxena & Khanna, 2017). Available minerals composition in certain feed ingredients tables either not reported

(as the case in olive cake) or just report mean measurements with no indication to the variation (as the case in bakery wastes) (NRC, 1994; NRC, 2000; NRC 2007).

This work aims at determining the variation in minerals concentration in industrial by- product (olive cake and bakery waste) produced under Jordanian conditions and to compare generated results with the average tabulated measurements mainly used in literature (NRC, 1994; NRC, 2000; NRC, 2001; NRC 2007). Quantifying the variation in mineral concentrations can enhance optimization process of bio-fuel production through pyrolysis. Furthermore, quantifying the variation in minerals concentrations in feed ingredients have been reported to be helpful to recommend mineral supplementation strategies and to provide more accurate feed formulation to meet requirements in farm animals (Saxena & Khanna, 2017; Zhang & Roush, 2002).

#### Methods

Sample collection and analysis:

Olive cake samples were obtained from twelve different olive mills distributed in three Jordanian governorates: Karak, Ajloun and Irbid. Twelve bakery wastes samples were obtained from twelve bakeries distributed in Karak governorate. Olive cake and bakery wastes samples were air dried at room temperature before performing minerals analysis. Both by-products (olive cake and bakery wastes) samples were ground by using hammer mill (HM210, Erkaya, Turkey) fitted with 1 mm screen size. Milled samples were stored in nylon bags and kept in refrigerator (4 °c) until further analysis. Moisture content was determined by drying the ground material in a hot oven at 135 °C for 3 h. For mineral analysis, samples were digested by using concentrated nitric acid in microwave digestion systems (model: Multiwave 3000, Anton Parr, USA). Minerals concentration (Ca, Mg, K, Na, P, S) for each sample was analyzed by using inductively coupled plasma-mass spectroscopy (ICP-MS, Elan DRC, Perkinelmer, USA). All minerals concentrations were measured on dry mater (DM) basis and represented as an average of triplicate measurements. To compare the concentration heterogeneity among different minerals, coefficient of variation (CV %) was calculated.

#### **Results and discussion**

A detailed characterization of minerals composition is required to optimize biomass content prior to bio-fuel production through pyrolysis. Varying levels of minerals in different biomass products affected the composition and the yield of liquid thermal products after pyrolysis (Eom et al., 2012; Patwardhan et al., 2010). Enhancing pyrolysis reactions have been reported to improve the properties of bio-fuel by the removal of oxygenated compounds via water and carbon dioxide, reducing molecular weight and changing the chemical structures to products that similar to petrochemical compounds (Dickerson & Soria, 2013). The presence of metal cations have been reported to enhance the homolytic breakdown of pyranose ring bonds over the heterolytic breakdown of glycosidic linkages, consequently, increase the formation of light oxygenate decomposition products at the expense of levoglucosan formation (Lin et al., 2015). However, different alkali minerals posses different effect on pyrolysis reactions. Both Na and K have been reported to enhance secondary pyrolysis reactions; however, Mg and Ca enhanced dehydration reactions (Eom et al., 2012; Muller-Hagedorn et al., 2003; Patwardhan et al., 2010). Different anions in alkaline earth metal salts have been also reported to affect pyrolysis products (Patwardhan et al., 2010).

Table 1 shows descriptive statistics of minerals concentration (Ca, K, Mg, Na, P, S) of bakery wastes collected from twelve bakeries distributed in Karak governorate. Ca concentration in bakery wastes differed between bakeries and ranged from 0.10 to 0.17 % (Table 1). Overall average Ca concentration in bakeries wastes (0.14%) in this study was similar to the average Ca concentration (0.14%) reported in NRC (2001), approximately similar to the average Ca concentration (0.15%) reported NRC (1994), and lower than the average Ca concentration (0.18%) reported in NRC (2007). Mg concentration in bakery wastes differed between bakeries and ranged from 0.01 to 0.05% (Table 1). Overall average Mg concentration (0.03%) in bakery waste was lower than the average Mg concentration (0.05%) reported in NRC (2001) and much lower than Mg concentration (0.24%) reported in NRC (1994). K concentration in bakery wastes differed between bakeries and ranged from 0.09-0.15% (Table 1). Overall average K concentration (0.12%) in bakery waste was lower than the average K concentration (0.23%) reported in NRC (2001), lower than the average K concentration (0.15%) reported in NRC (1994), and much lower than the average K concentration (0.30%) reported in NRC (2000). Na concentration in bakery wastes differed between bakeries and ranged from 0.02-0.67% (Table 1). Overall average Na concentration (0.36%) in bakery waste was lower than the average Na concentration (0.85%) reported in NRC (2001), and was lower than the average Na concentration (1.14%) reported in NRC (1994). P concentration in bakery wastes differed between bakeries and ranged from 0.07-0.34% (Table 1). Overall average P concentration (0.20%) in bakery wastes was similar to the average P concentration (0.20%) reported in NRC (2001), was almost similar to the average K concentration (0.24%) reported in NRC (1994), and as reported (0.28%) in NRC (2007). S concentration in bakery waste differed between bakeries and ranged from 0.09-0.15% (Table 1). Overall average S concentration (0.12%) in bakery waste was slightly lower (0.17%) than the average S concentration reported in NRC (2001) and as reported (0.15%) in NRC (2000), was higher (0.02%) than the average S concentration reported in NRC (1994). Among analyzed minerals concentration in bakery wastes, it can be clearly seen that Na had the highest variation (CV%= 69.51%), whereas, S had the lowest variation (CV%= 16.28%) (Table 1).

Table 1. Descriptive statistic of minerals concentrations in bakery wastes collected from Karak governorate\*.

| Sample     | Ca (%) | K (%) | Mg (%) | Na (%) | P (%) | S (%) |
|------------|--------|-------|--------|--------|-------|-------|
| Sample 1   | 0.15   | 0.10  | 0.04   | 0.61   | 0.28  | 0.12  |
| Sample 2   | 0.10   | 0.09  | 0.01   | 0.11   | 0.22  | 0.09  |
| Sample 3   | 0.13   | 0.13  | 0.03   | 0.02   | 0.21  | 0.10  |
| Sample 4   | 0.15   | 0.14  | 0.05   | 0.54   | 0.34  | 0.11  |
| Sample 5   | 0.16   | 0.09  | 0.03   | 0.11   | 0.25  | 0.11  |
| Sample 6   | 0.13   | 0.10  | 0.03   | 0.13   | 0.28  | 0.11  |
| Sample 7   | 0.15   | 0.12  | 0.03   | 0.21   | 0.18  | 0.11  |
| Sample 8   | 0.12   | 0.13  | 0.03   | 0.66   | 0.12  | 0.11  |
| Sample 9   | 0.17   | 0.13  | 0.04   | 0.35   | 0.18  | 0.11  |
| Sample 10  | 0.16   | 0.12  | 0.03   | 0.27   | 0.15  | 0.14  |
| Sample 11  | 0.10   | 0.13  | 0.03   | 0.67   | 0.07  | 0.15  |
| Sample 12  | 0.15   | 0.15  | 0.05   | 0.66   | 0.15  | 0.15  |
| Statistics |        |       |        |        |       |       |
| Average    | 0.14   | 0.12  | 0.03   | 0.36   | 0.20  | 0.12  |
| Minimum    | 0.1    | 0.09  | 0.01   | 0.02   | 0.07  | 0.09  |
| Maximum    | 0.17   | 0.15  | 0.05   | 0.67   | 0.34  | 0.15  |
| CV%        | 16.62  | 16.57 | 32.19  | 69.51  | 37.79 | 16.28 |

\*Values are averages of triplicate measurements and expressed as % on DM basis.

Nutrients composition of bakery wastes have been reported to be variable, particularly in its fat, energy and mineral (mainly Na) contents (Arosemena et al., 1995; Saleh et al., 1996). In pyrolysis reactions, biomass samples with more added NaCl produced more furans, acids, ketones, and phenols than the samples with no NaCl (Lou et al., 2013). Therefore, it is recommended to analyze bakery wastes when obtained from new suppliers or when the source is recognized to be lacking of nutrient consistency (Arosemena et al., 1995; Guiroy et al., 2000; Mahmoud et al., 2017).

Table 2 shows descriptive statistics of minerals concentration (Ca, K, Mg, Na, P, S) of olive cake collected from twelve olive mills distributed in three governorate (Ajloun, Irbid and Karak) in Jordan. Chemical composition of olive cake (including minerals) is not reported in feed libraries mostly used by animal nutritionist. Molina-Alcaide & Yáńez-Ruiz (2008) reviewed major chemical compositions in olive cake, however, very little information is available in the literature on minerals compositions in olive cake. In this study, K had the highest average concentration (0.75%) and ranged from 0.46 to 1.98 % (Table 2). Ca had the second highest mineral concentration (0.30%) and ranged from 0.24 to 0.43 %. Previous studies showed that K was the highest and Ca the second highest mineral concentration measured in olive mill solid wastes (Barbanera et al., 2016; Buratti et al., 2016). Mg concentration ranged from 0.03 to 0.08 % with an average concentration 0.04%, while, Na concentration ranged from 0.01 to 0.03 % with an average concentration 0.02%. Approximately, similar ranges of concentrations for both Mg and Na were reported by other studies (Barbanera et al., 2016; Buratti et al., 2016). P concentration nanged from 0.04 to 0.11 % with an average concentration 0.06%.

P concentration in this study was lower than P concentration reported by Saidur (2011). S concentration also ranged from 0.04 to 0.11 % with an average concentration 0.07%. S concentration in this study was lower than S concentration reported by Suárez-Garcî a (2002). Among all analyzed minerals concentration in olive cakes samples, K had the highest variation (CV%= 53.31%), whereas, Ca had the lowest variation (CV%= 17.48%).

| Sample    | Ca (%) | K(%) | Mg (%) | Na (%) | P (%) | S (%) |
|-----------|--------|------|--------|--------|-------|-------|
| Sample 1  | 0.26   | 0.65 | 0.03   | 0.02   | 0.05  | 0.06  |
| Sample 2  | 0.27   | 0.79 | 0.04   | 0.02   | 0.07  | 0.07  |
| Sample 3  | 0.24   | 0.58 | 0.03   | 0.01   | 0.07  | 0.05  |
| Sample 4  | 0.31   | 0.71 | 0.04   | 0.01   | 0.06  | 0.07  |
| Sample 5  | 0.26   | 0.5  | 0.03   | 0.02   | 0.07  | 0.04  |
| Sample 6  | 0.29   | 0.63 | 0.03   | 0.03   | 0.08  | 0.06  |
| Sample 7  | 0.25   | 0.46 | 0.03   | 0.01   | 0.04  | 0.05  |
| Sample 8  | 0.31   | 0.61 | 0.04   | 0.01   | 0.06  | 0.05  |
| Sample 9  | 0.29   | 0.74 | 0.04   | 0.03   | 0.05  | 0.07  |
| Sample 10 | 0.30   | 0.59 | 0.04   | 0.02   | 0.05  | 0.07  |
| Sample 11 | 0.35   | 0.8  | 0.04   | 0.02   | 0.04  | 0.08  |
| Sample 12 | 0.43   | 1.98 | 0.08   | 0.02   | 0.11  | 0.11  |

**Table 2.** Descriptive statistic of minerals concentrations in olive cake collected from three governorate (Irbid, Ajloun and Karak) in Jordan\*.

| Statistics |          |       |       |       |       |         |  |
|------------|----------|-------|-------|-------|-------|---------|--|
| Average    | 0.30     | 0.75  | 0.04  | 0.02  | 0.06  | 0.07    |  |
| Minimum    | 0.24     | 0.46  | 0.03  | 0.01  | 0.04  | 0.04    |  |
| Maximum    | 0.43     | 1.98  | 0.08  | 0.03  | 0.11  | 0.11    |  |
| CV%        | 17.48    | 53.31 | 37.86 | 36.14 | 29.97 | 28.52   |  |
| 1.1.1.1    | <i>c</i> |       |       |       | 1 01  | <b></b> |  |

\*Values are averages of triplicate measurements and expressed as % on DM basis.

Average concentration values of strong cations (Na and K) in olive cake samples (0.02 % and 0.75 %, repectivley) have relatively lower concentrations compared to other forage sources such as alfalfa (0.1% and 2.37%, respectively) (NRC, 2001). Although feeding olive cake has been shown to decrease the daily cost of feeding lambs (Ben Salem et al., 2003; El Hag el al., 2002), many studies have shown that olive cake inclusion level should be minimized (Al-Jassim et al., 1997; Chabouni , 1984; Tayer et al., 1987) especially in highly producing animals. Aguilera & Molina (1986) reported that olive cake had a high lignin content and its protein content is linked with lignocellullosic ; this interaction may reduce overall olive cake nutritive value. Due to relatively low nutritive value of olive cake for animals, further research must be oriented towards bio-fuel production from olive cake. Information about chemical composition, including minerals, will facilitate recognition of any biomass for biofuel production and can also provide a guide for genetic engineers to improve biomass features (Lin et al., 2015).

#### Conclusion

The outcome of this study gives more detailed information about minerals concentrations and the variation of two major industrial by product (olive cake and bakeries wastes) produced in Jordan. This study showed existent of some variations in minerals concentrations indicating minerals composition inconsistency within both investigated by- product. Quantifying the variation in minerals concentrations of current investigated by-products is necessary to recommend nutritional supplementation strategies for animals and has applied consequences on optimization bio-fuel production process.

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