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Physicochemical and Interfacial Behavior of Demineralized Acid Whey

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Abstract: In Algeria, the quantities of whey released into the environment are changing with the growth of the cheese industries whey remains a cheese effluent and a source of serious biological pollution due to its richness in noble organic fractions (lactose and proteins), released into the environment without prior treatment (case of cheese industry of Sidi Saada, Yellel, Relizane, Algeria) whey subsequently affects the quality of freshwater ecosystems (Oued Mina). The crude acid whey is a cheese rejection comes from the manufacture of soft cheeses and fresh dough. In this context, our study focused on the control of physicochemical and interfacial properties of demineralized acid whey. The results showed that demineralisation of crude acid whey modified its physicochemical and interfacial properties. In perspective, the valorization of industrial whey has become one of the major concerns of the cheese industries.

Key words: Acid whey, ion exchange resin, interfacial properties, proteins, valorization, perspective

INTRODUCTION

The crude acid whey is aco-product and an effluent of soft cheeses and fresh dough. According to Mollea et al. (2013) global whey production was estimated at 180-190 tons/year in Algeria and in other countries of the world, this rejection accounts for about 85% of milk processed into cheese (FAO., 1995; Gana and Touzi, 2001); rejected in the environment without prior treatment (case of dairy and cheese industry Sidi Saada, Yellel, Relizane, Algeria), the latter may be a favorable factor in the biological pollution of freshwater ecosystems following its native biochemical composition (Acem and Choukri, 2016; Acem et al., 2017a, b), its valorization is an economic and ecological stake, since, one liter of the whey has a Biological Demand in Oxygen (BDO) is between 30 and 45 g/L of oxygen and therefore, requires the oxygen of 4500 L of oxygen unpolluted water (Juillerat and Badoud, 2010) making it a pollutant that can no longer be released into the environment.

Whey proteins are widely used in the food industry because they possess, inter alia, good functional properties (Bottomley *et al.*, 1990, Acem *et al.*, 2017a, b), the whey proteins have in particular the properties to retain water to act as foaming and/or emulsifying agent and to form aggregates (or gels) (Kinsella and

Whitehead, 1989; Acem and Choukri, 2016, 2017). According to Cheftel *et al.* (1985), Acem and Choukri (2012 a, b) the whey proteins have functional properties which vary according to the preparation treatments they have undergone (ultrafiltration, fixation on ion exchangers, precipitation by chemical or thermal agents).

The whey is very mineralized (8-20% of the dry matter) which can impair its transformation and its properties (Daufin *et al.*, 1998; Acem and Choukri, 2012a, b) for some applications it is therefore, important to demineralize it for example in infant formulas and in dietary applications (Hoppe and Higgins, 1992). In this context, the present study focuses on analyzing the impact of demineralization on the physicochemical and interfacial behavior of crude acid whey.

MATERIALS AND METHODS

Crude acid whey: The crude acid whey is prepared at the laboratory level using a skim Milk powder (0% MG) made from cow's milk by Fonterra Ltd., 9 Princes Street, Auckland, New Zealand (Acem and Choukri, 2012a, b) by adjusting the pH of the milk prepared 10% at the isoelectric pH of casein (Baumy and Brule, 1986); filtered by filter paper (German Folded Filters: 185 mm diameter) and stored at 4°C (Acem and Choukri, 2012a, b).

Demineralized acid whey: According to Acem and Choukri (2012a, b) the demineralized acid whey is prepared at the laboratory using the data sheet of the cation exchange resin (Amberlite IRC-86, weak acid, H⁺ counter-ion, Fluka brand, product of France). The physico-chemical tests applied to both types of whey are: Acidity (Mathieu, 1998), pH (pH meter CG 822 GHS), proteins (Lowry *et al.*, 1951), viscosity by a ball drop viscometer (Viscometer: Hoeppler BH2), the ash and dry matter content by the AFNOR (1980) method.

Dispersed system

Emulsion: The emulsion is composed of a dispersed phase (virgin olive oil: it is a virgin olive oil from trade, production 2017 brand CHIALI of Sidi-Bel-Abbes, Algeria) and a dispersing phase (whey) the dispersions are prepared in the presence or absence of sodium caseinates (stabilizing agent) and Tween 80 as surfactant (Fluka product of France) in an O/W ratio equal to 0.0526 (Acem and Choukri, 2012a, b); each mixture is homogenized at 25°C to 18000 rpm during 1 min by a homogenizer (Bomann, Stabmixer SM 354 CB-hand blender).

Foam: For the formation of the foam, 20 mL of the whey is whipped by Blinder (Bomann, Stabmixer SM 354 CB-hand blender) at 18000 rpm during 1 min. The evaluation of the whey emulsifying power was carried out by measuring the mean diameter of the fat globules of virgin olive oil (Acem and Choukri, 2012a, b) and the creaming index (Klinkesom *et al.*, 2004) and the estimation of its foaming power was made by controlling the mean diameter of the air bubbles and the foaming capacity (Martinez *et al.*, 2011) whose average diameter of the fat globules and air bubbles is observed and determined under a photonic microscope (Phywe, hund Wetzlar, Germany) using an ocular micrometer graduated from 0-10 whose graduations are distant from each other others of 0.1 μm.

Statistical analysis: The experimental data are analyzed statistically by R Software.

RESULTS AND DISCUSSION

Demineralized acid whey: Figure 1 gives the average physicochemical properties of the demineralized acid whey. Figure 1 shows that demineralization has modified the contents of controlled physicochemical parameters compared to those labeled for crude acid whey with the following values: acidity (DAW:62, CAW:38°D), dry matter (DAW:5.25, CAW:6.25 %), proteins (DAW:6.53, CAW:8.17 g/L), viscosity (DAW:1.54, CAW:1.82cP), pH (DAW:3.2, CAW:4.6) et ash (DAW:2.64, CAW:5.44 g/L).

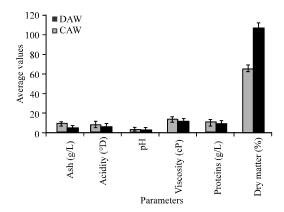


Fig. 1: Average values of the physicochemical parameters of Crude Acid Whey (CAW) and Demineralized Acid Whey (DAW)

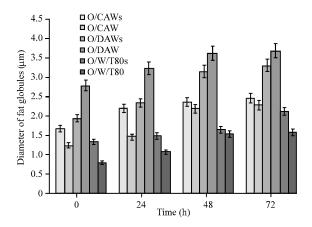


Fig. 2: Kinetics of the average diameter of the fat globules of the emulsions studied

According to Adrian et al. (1981), the viscosity depends on the temperature, the nature of the solvent, the size, the shape, the concentration, the electrical charge of the dispersed particles and their affinity for the solvent. According to Cheftel et al. (1985), the viscosity of most proteins increases in an alkaline environment. The pH and acidity values are comparable to those found by Acem and Choukri (2012a, b) the pH is a decreasing function with the acidity, the latter evolves with the composition and the high content of acid substances (Mathieu, 1998). In addition, the ash content of the crude acid whey studied is lower than that found by Croguennec et al. (2008) that they obtained the following results: 7.5 g/L for sweet whey, 12 g/L for acid whey and 9 g/L for acid whey of casein industry. According to Sottiez (1985) the variation in the dry matter content of whey depends mainly on the quality of the milk used and the process of separation of the whey.

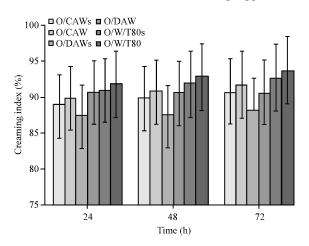


Fig. 3: Kinetics of the creaming index of the emulsions studied

Dispersed system

Emulsifying power: Figure 2 shows the kinetics of the mean diameter of the fat globules of the emulsions studied. We have noticed an increasing variability in the size of the fat globules of the studied emulsions over time (Fig. 2) emulsions based on demineralised acid whey are positioned in 5th and 6th rank after those formed, respectively of crude acid whey and Tween 80 in the presence or absence of sodium caseinate: emulsion (O/DAWs): 1.96 at time t 0 h to 3.31 μm after 72 h emulsion (O/CAWs): 1.69 at time t 0 h to 2.47 μm after 72 h emulsion (O/CAW): 1.26 at time t 0 h to 2.30μm after 72 h emulsion (O/W/T80s): 1.34 at time t 0 h to 2.12 μm after 72 h and emulsion (O/W/T80): 0.81 at time t 0 h to 1.60 μm after 72 h.

Figure 3 illustrates the kinetics of the creaming index of the emulsions over time. We have noted that the creaming index of the emulsions studied tends to grow over time (Fig. 3), the creaming index stability values have been signaled in particular in the emulsions based on demineralized whey in the presence of sodium caseinate (O/DAWs: from 87.5 after 24 h to 88.5% after 72 h) and in the absence of sodium caseinate (O/DAW: from 90.75 after 24 h to 90.9% after 72 h).

The emulsifying properties of whey proteins are due to the ability to reduce interfacial tensions between hydrophilic and hydrophobic components. They are often related to the solubility of the protein in water (Lorient and Linden, 1994). The rheological behavior of an emulsion then often depends on the viscosity of its external phase (Allouche, 2003). Anisa and Nour (2010) have shown that a negative correlation is evident between the viscosity of the external phase of the emulsion and the size of the dispersed fat globules.

There are various conflicting ideas and theories surrounding the effects of salt concentration on the

characteristics of emulsions (Lim et al., 2015). According to Lim et al. (2015) the emulsion stability is influenced by many factors such as mixing speed and mixing duration, pH of solution, temperature of solution and salt concentration. Generally, higher mixing speed and longer mixing duration would produce smaller sizes of emulsion droplets which have higher interfacial area and droplet interaction, resulting in more stable emulsions (Ashrafizadeh and Kamran, 2010).

Sakka (2003) and Yang et al. (2007) suggested that higher pH (alkaline) would give more stability to the emulsions. According to Yang et al. (2007) for oil-in-water emulsions, higher pH would promote more affinity of surfactant molecules towards aggregation, resulting in more stable emulsions. Tambe and Sharma (1993) have found that low pH values of 4-6 favoured oil-in-water emulsions while high pH values of 8-10 favoured water-in-oil emulsions they found out that for the case of oil-in-water emulsions, the stability was increased as the pH as increased from 4-6 but beyond pH 6-10, oil-in-water emulsions became less stable and on the flip side, water-in-oil emulsions were favoured.

The high or very low pH values would help in stabilizing the emulsions (Sjoblom et al., 1990). Higher tempearture will first reduce the emulsions viscosity, eventually destabilizing and breaking the emulsions (Lim et al., 2015). Mat et al. (2006) highlighted that the rate of droplet film drainage is directly proportional to the temperature. Ashrafizadeh and Kamran (2010) reported that at higher salinity of the water phase, the viscosity of oil-in-water emulsions was increased and the amount of separated water was reduced as well and that the phenomenon could be caused by salt ions acting as barriers among the oil droplets and the continuous water phase, thus, increasing the emulsions stability. Figure 4 shows the microscopic aspect of the emulsions prepared from Crude Acid Whey (CAW) and Demineralized Acid Whey (DAW).

Foaming power: Figure 5 shows the evolution of the mean diameter of the air bubbles formed from the Crude Acid Whey (CAW) and Demineralized Acid Whey (DAW). The average diameter of the air bubbles tends to increase over time for Crude Acid Whey (CAW) foam the diameter varied from 4 at time 0 min to 9.2 µm after 40 min with respect to the foam prepared from Demineralized Acid Whey (DAW) which modulated from 2.4 at time 0 min to 7.2 µm after 40 min. Figure 6 shows the evolution of the foaming capacity of the Crude Acid Whey (CAW) and Demineralized Acid Whey (DAW).

We have observed that the curves of the foaming capacity are decreasing over time for the Crude Acid Whey (CAW) foam: its foaming capacity has varied from



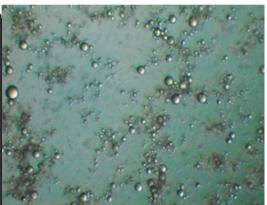


Fig. 4: Microscopic aspect (Mg:100×) of the emulsions studied at time 0 h showing the influence of demineralization of acid whey on the size of fat globules; a) Emulsion O/CAWs and b) Emulsion O/DAWs

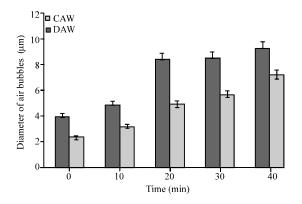


Fig. 5: Kinetics of the average diameter of the air bubbles of the Crude Acid Whey (CAW) and Deminralized Acid Whey (DAW)

112.5 at time 0 min to 83.33% after 40 min and it has modulated from 116.66 at time 0 min to 66.66% after 40 min for Demineralized Whey (DAW) foam.

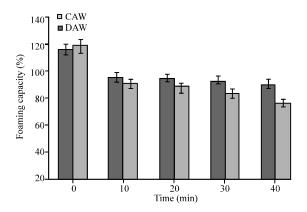


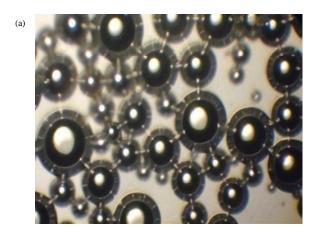
Fig. 6: Kinetics of the foaming capacity of the Crude Acid Whey (CAW) and Deminralized Acid Whey (DAW)

The foaming properties or surface activities of proteins are closely related to the protein conformational properties such as structure, size, shape and amino-acid composition (Patino and Pilosof, 2011) and external environment factors. External parameters such as pH, ionic strength and heating condition directly affect protein structure and its interfacial properties, thus, impact the foaming properties of whey protein (Phillips *et al.*, 1989, 1990, 1991; Clark *et al.*, 1994; Zhu and Damodaran, 1994; Raikos *et al.*, 2007).

Foamability of whey proteins is comparable to egg white protein which allows them to be considered as a potential replacement of egg white protein (Yang and Foegeding, 2011). The negative relationship between foaming temperature and the average foam bubble diameter was proved by research of Borcherding *et al.* (2008).

The foamability of protein can be maximized when pH is close to pI (Hailing and Walstra, 1981; Zhang et al., 2004) while higher overrun of milk protein was found with increasing pH in the range of pH>pI (Borcherding et al., 2009). Ionic strength plays an important role in determining foaming properties through affecting protein solubility and electrostatic properties (Wang, 2013).

The overrun of 5% WPI (Whey Protein Isolate) had positive relation with NaCl concentration (from 0-1 M) and with the increasing of ionic strength, the stability showed a peak and then decreased (Mott *et al.*, 1999). Zhu and Damodaran (1994) reported that foam stability reached the maximum value in the presence of low concentration of CaCl₂ (20 mM) and then decreased at higher CaCl₂ concentration. Figure 7 shows the microscopic aspect of the foams prepared with the Crude Acid Whey (CAW) and Demineralized Acid Whey (DAW).



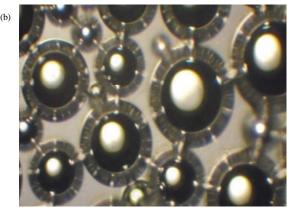


Fig. 7: Microscopic aspect (Mg:100×) of the foams studied of acid whey at time 0 min; a) CAW and b) DAW

CONCLUSION

The demineralization of the crude acid whey by the cation exchange resin has modified on the one hand its physicochemical parameters, namely the ash, proteins, dry matter, viscosity, pH and acidity content and on the other hand it has improved interfacial properties, namely its emulsifying power (the index of creaming) and foaming (the average diameter of the air bubbles and the foaming capacity).

RECOMMENDATION

In the future, our study will continue by application of the precision technical control of interfacial properties of whey as the interfacial tensiometer.

ABBREVIATIONS

- CAW: Crude Acid Whey
- DAW: Demineralized Acid Whey

- O/CAW: Emulsion of Oil in Crude Acid Whey without stabilizer
- O/CAWs: Emulsion of Oil in Crude Acid Whey with stabilizer
- O/DAW: Emulsion of Oil in Demineralized Acid Whey without stabilizer
- O/DAWs: Emulsion of Oil in Demineralized Acid Whey with stabilizer
- O/W/T80: Emulsion of Oil in Water in presence the Tween 80 and without stabilizer
- O/W/T80s: Emulsion of Oil in Water in presence the Tween 80 and stabilizer
- Mg: Magnification

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