Effect of change in pH of skim milk and ultrafiltered/diafiltered retentates on milk protein concentrate (MPC70) powder properties

Ganga Sahay Meena¹ · Ashish Kumar Singh¹ · Vijay Kumar Gupta¹ · Sanket Borad¹ · Pankaj T. Parmar¹

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Abstract Poor solubility of milk protein concentrate (MPC) powders are attributed to their high protein and calcium contents. Concentration of skim milk in ultrafiltration (UF) and diafiltration (DF) increased total solids, protein and mineral contents and changed pH and ζ -potential values of the retentates that leads to milk proteins destabilization in $7\times$ UF/DF retentates. Hence, this investigation was aimed to study the effect of change in pH of skim milk (no change; native pH maintained) and DF retentates (5.85 and 7.10) with KOH, NaOH and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ on physicochemical, reconstitution, functional and rheological properties of fresh MPC70 powders. MPC70-7.10 powder had significantly higher ($P < 0.05$) solubility, but MPC70-NaOH and MPC70-5.85 showed significantly lower solubility than control. However, after two months storage at $25 \pm 1^\circ\text{C}$, control powder had significantly lower solubility (27.78% decrease) than treated powders. These changes in pH, significantly decreased calcium content and specific surface area; significantly improved viscosity, water binding, oil binding, emulsifying, foaming and buffering capacities, L^* , a^* , flowability, pH (except MPC70-5.85) and packed bulk density (except MPC70-NaOH) of treated powders over control. However, rennet coagulation time of all reconstituted powder solutions was similar. Hershel Bulkley, a best fit model, efficiently explained the pseudoplastic rheological behavior of all reconstituted MPC70 powders. This investigation had established that change in pH could improve the functional properties of MPC70 powders and is a simple, cheap,

compatible and easy to use approach. Treated MPC70 powders could replace control in several food formulations owing to their improved functional properties.

Keywords pH adjustment · Medium protein powder · Monosodium phosphate · Functional properties

Introduction

Milk protein concentrates (MPCs) are high protein milk powders which contains casein and whey proteins in the identical ratio as present in native milk. On dry matter basis, protein content of MPC powders may vary in the range of 40–89%. MPC powders are usually manufactured from skim milk by its concentration in ultrafiltration (UF) and diafiltration (DF, if required) processes to obtain desired protein to total solids ration in UF/DF retentates followed by spray drying. MPC powders containing 60–70% protein have been classified as ‘medium protein powder’ (Sikand et al. 2011) and are one of the most common type of MPC powders (Meena et al. 2017b). Popularity of MPC powders as a novel and high protein ingredient are rising globally. As per Agarwal et al. (2015), about 900 different products were developed and launched in marked using MPC as a key ingredient. MPC powders have been reported to take over the market of caseins in certain applications and could cross $\sim 40,000$ MT production by 2020 (Lagrange et al. 2015).

Most of the functional properties of MPC powders are inferior to other protein rich powders such as sodium caseinate (NaCas), whey protein concentrate (WPC) and whey protein isolate (WPI). Particularly, MPC powders have poor solubility; a vital property, considered as a prerequisite for many other functional properties and

✉ Ganga Sahay Meena
gsmndri@gmail.com

¹ Dairy Technology Division, ICAR-National Dairy Research Institute, Karnal 132001, India

crucial for the better utilization of functional potential of these powders in different food formulations (Meena et al. 2017b).

In brief, composition of skim milk and severity of its heat treatment; extent of protein concentration and temperature during UF & DF; change in calcium, protein and lactose contents, pH and zeta potential (responsible for milk proteins destabilization); drying conditions, moisture content, duration and temperature of storage favouring interaction and aggregation of different milk constituents have been reported in the literature as the key detrimental factors for solubility and other functional properties of MPC powders (Singh 2007; Baldwin 2010; Meena et al. 2017b). Poor solubility (particularly due to higher protein and calcium contents) and variability in other functional properties of MPC powders have been reported to limit their use in different food formulations (De Castro-Morel and Harper 2002; Huppertz and Gazi 2015). Moreover, poor solubility of MPC powders such as MPC80 can also lead to problem of nugget formation during cheese making, hardening of high-protein bars and sedimentation of undissolved mass during production of high protein beverages.

Different physical (sonication, ultrasound, high pressure processing, micro-fluidization etc.), chemical (addition of NaCl, KCl, various stabilizing salts and calcium chelators such as citrate, phosphate, hexametaphosphate (HMP), or ethylenediaminetetraacetic acid- EDTA, CO₂ purging etc.), and enzymes (chymotrypsin, trypsin, pepsin, cysteine protease-papain etc.) based methods have been used by the researchers worldwide to improve the solubility of MPC powders (Meena et al. 2017b), yet scientific interventions which can markedly improve its functional properties and at the same time remain extremely cost effective, easy and compatible with existing production plants, are still awaited.

Our previous studies have also assessed the effect of Na₂HPO₄ addition (pH 6.6) with and without homogenization (2500/500 psi) and diafiltration with 75 mM solution of NaCl and KCl (1:1 ratio) in 4–5× retentates and MPC60 powders (Meena et al. 2016, 2017a). Not much work have still been conducted on solubility improvement of medium protein powders. As milk proteins can be modulated to deliver the desired functional properties by changing the pH and temperatures during processing, but the change in pH of either skim milk or 7× UF/DF retentates and its impact on solubility and other properties of the resultant powders have not been studied so far. Moreover, currently Indian dairy industry is facing numerous challenges in the export of skim milk powder but continuously importing whey protein and lactose powders. Therefore, conversion of skim milk into novel and functional protein ingredients like MPC powders with improved

functional properties than ordinary SMP, will surely improve the exports and at the same time provide a preferred raw material i.e. defatted and deproteinized UF permeate for commercial lactose production.

Hence, this study was undertaken to investigate the effect of change in pH (native, acidic-5.85 and alkaline-7.10) of skim milk, ultrafiltered and diafiltered retentates with monosodium phosphate (NaH₂PO₄•2H₂O), potassium hydroxide (KOH) and sodium hydroxide (NaOH) on physico-chemical, reconstitution, functional and rheological properties of milk protein concentrate 70 (MPC70) powders.

Materials and methods

Ultrafiltration and diafiltration

Pasteurized (73 ± 1 °C/15 s) cow skim milk (PCSM, 0.14%LA) was collected from Experiential Dairy of ICAR-National Dairy Research Institute, Karnal (India) and concentrated in pilot scale UF plant having tubular module and equipped with 1.68 m² ZrO₂ membrane up to 7× concentration at constant temperature (50 ± 1 °C) and transmembrane pressure (TMP-1 kg/cm²) adopting the operational procedure reported by Meena et al. (2016), (2017a). Diafiltration (DF) experiments were performed in the same plant with similar operating parameters but at lower (30 ± 1 °C) temperature. Volume reduction (VR, %) compared to initial feed and, concentration factor (CF, quotient of initial feed volume to final retentate volume) were calculated on weight basis. During UF, permeate flux in liter per m² per hour (LMH) was directly recorded from the flow meter equipped with the UF plant. Analytical grade chemicals and rennet (*Mucor Mieheli*) were procured from Sigma-Aldrich, USA and used in this investigation.

Production of MPC70 powders

To obtain control (without any treatment) retentate, PCSM was ultrafiltered up to 7× CF and used to produce control MPC70 powder (MPC70-C). In another trail, PCSM was concentrated up to 7× CF by constantly maintaining its pH (equal to the natural pH, 6.68) with the addition of 1 N NaOH solution and spray dried to obtain MPC70-NaOH powder. PCSM was concentrated up to 7× CF without pH adjustment and diafiltered to obtain 7× DF retentates (7× DFR) using RO water equal to retentate weight. Monosodium phosphate (NaH₂PO₄•2H₂O) was added as 12% solution in 7× DFR at the rate of 20% of its TS content that reduced its pH to 5.85. NaH₂PO₄•2H₂O added 7× DFR was termed as 7× DFR-5.85. The pH of a part of 7× DFR-5.85 was increased to 7.10 with the addition of KOH

solution and resultant retentate was named as 7× DFR-7.10. MPC70-5.85 and MPC70-7.10 powders were obtained by the drying of 7× DFR-5.85 and 7× DFR-7.10 retentates, respectively. All retentates were forewarmed ($40 \pm 1^\circ\text{C}$) and spray dried in a pilot scale spray drier (SSP Pvt. Ltd. Faridabad, India; feed rate 110 kg/h; atomizer diameter-0.17 mm, single stage) at $185/85 \pm 5^\circ\text{C}$ inlet and outlet air temperatures. All experiments were conducted in triplicate. Powders were packed in metalized polyester-LDPE laminates and stored at $4 \pm 1^\circ\text{C}$ in a refrigerator until analyzed. To determine solubility after 60 days, powders were also stored at $25 \pm 1^\circ\text{C}$. The flow chart of MPC70 powders production have been depicted in Fig. 1.

Analysis of chemical composition and determination of physico-chemical, reconstititional, functional and rheological properties of MPC70 powders

Chemical constituents (TS, ash, protein, fat and calcium contents); measurement of pH and ζ -potential; physical properties such as loose bulk density (LBD, g/mL) and packed bulk density (PBD, g/mL); wettability (min), dispersability (%) and flowability in terms of angle of repose

(θ°), specific surface area (SSA, m^2/kg), median particle size distribution (d_{10} , d_{50} and d_{90} , μm), volume mean diameter ($D_{4,3}$ and $D_{3,2}$, μm), color values (L^* , a^* , b^*) and water activity (a_w); functional properties such as solubility (%), heat coagulation time (HCT, min), water binding capacity (WBC, g/g of protein) and oil binding capacity (OBC, g/g of protein), foam capacity (FC, %) and emulsion capacity (EC, %), viscosity (mPa s), rennet coagulation time (RCT), buffering capacity expressed as buffer index (dB/dH), and rheological properties of concerned PCSM, retentates and MPC70 powders were analyzed, measured and determined using standards methods as reported earlier by Meena et al. (2016) and Meena et al. (2017a). The LBD and PBD values of the manufactured powders were used to calculate compressibility index/Carr Index [CI, % = $((\text{PBD}-\text{LBD})/\text{LBD}) \times 100$] and Hausner Ratio [HR = PBD/LBD], while d_{10} , d_{90} , and d_{50} values were used to calculate the span i.e. the ratio of $(d_{90}-d_{10})/d_{50}$, that shows the width of arbitrary particle size distribution were calculated as reported by Koç et al. (2014). Here, d_{10} , d_{90} , and d_{50} are the equivalent volume diameters at 10, 50 and 90%, cumulative volume, respectively.

Fig. 1 Flow diagram for the production of MPC70 powders

Statistical analysis

Results obtained for different properties in this study (mean value, $n = 3$) were statistically analysed adopting the procedure reported by Meena et al. (2016), (2017a) by SAS Enterprise guide (5.1, 2012) developed by SAS Institute Inc., North Carolina, USA (SAS 2008).

Results and discussion

Ultrafiltration and diafiltration of PCSM and membrane flux

The changes occurred in chemical composition and zeta potential of PCSM, ultrafiltered and diafiltered retentates during ultrafiltration and diafiltration of PCSM are presented in Table 1. Significant difference ($P < 0.05$) was observed in the TS, fat, protein, ash, protein to TS and ash to TS ratio of different retentates (Table 1). However, marked increase in ash to TS ratio of 7×5.85 and 7×7.10 retentates were observed that was attributed to the addition of $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$ and KOH to adjust the pH of these retentates. The natural pH value of $1 \times$ was 6.68 that reduced to 6.33 and 6.25 in $7 \times$ UFR and $7 \times$ DFR, respectively. The decreased values of ζ -potential with increase in CF of retentates is at par with the previous reports (Huppertz and Fox 2006; Meena et al. 2016) and attributed to the decreased pH and increased calcium contents as reported by Meena (2016). With increase in CF or VR% of PCSM during UF, permeate flux reduced progressively (Fig. 2) due to concentration polarization and membrane fouling as both phenomenon have detrimental effect on flux.

Chemical composition of MPC70 powders

Chemical composition of MPC70 powders are presented in Table 1. These powders contains 92.74–96.71% TS, 60.77–68.92% protein, 7.05–17.85% ash, 0.99–1.57% calcium (Table 2) and 5.98–7.34 pH values (Table 2), respectively. The composition of MPC70-C and MPC70-NaOH was broadly similar to that reported by Crowley et al. (2014) and Huppertz and Gazi (2015). However, MPC70-5.85 and MPC70-7.10 powders have markedly different composition i.e. higher ash content that have caused relative decrease in their other constituents compared to MPC70-C and MPC70-NaOH powders. This increase in ash contents of MPC70-5.85 and MPC70-7.10 powders are ascribed to the addition of $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$ and KOH to adjust the pH of 7×5.85 and 7×7.10 retentates from which they were produced. Calcium contents of MPC70-C and MPC70-NaOH powders were

statistically at par ($P > 0.05$) with each other, however MPC70-5.85 and MPC70-7.10 powders showed significant difference ($P < 0.05$) in the calcium contents with each other and MPC70-C and MPC70-NaOH powders. According to Floris et al. (2007), calcium contents of MPC68.30-MPC72.50 powders were in the range of 1.90–2.17% which is little higher than the calcium contents observed in control and MPC70-NaOH powders in this study (Table 2). Further, addition of $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$ and KOH resulted in marked increase in total ash contents, but noticeable decrease in Ca contents of MPC70-5.85 and MPC70-7.10 powders that might be attributed to calcium chelation action of added $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$, and also due to the dilution effect resulted from the addition of $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$ and KOH itself. The ash contents of the MPC70 powders were higher than control, but lesser than that reported by (Schuck et al. 2002) for casein powders.

Physical and reconstititional properties of MPC70 powders

Physical and reconstitution properties of the manufactured MPC70 samples have been shown in Table 2. These properties play a vital roles during conveying, packaging, storage and transportation of powders; in reconstitution process and also influence consumers preference by exhibiting required nutritional, sensorial and functional attributed in the processed foods. The pH; LBD and PBD; CI; HR; θ values; wettability; dispersability; a_w ; L^* , a^* , b^* values; SSA; d_{10} , d_{50} and d_{90} ; $D_{3,2}$ or $D_{4,3}$ and span values of produced powders were observed in the range of 5.98–7.37; 0.37–0.42 and 0.54–0.59 g/mL; 28.27–32.73%; 1.39–1.49; 22.48–34.48°; 1.24–35 min; 40.74–75.43%; 0.25–0.37; 86.22–89.40, – 1.04 to – 0.47, 9.53–13.90; 60.65–123.70 m²/kg; 27.09–54.84, 71.43–123.93, 147.71–281.09 μm and 48.51–98.93 or 81.96–166.22 μm and 1.62–1.96%, respectively.

As shown in Table 2, significant difference ($P < 0.05$) among the pH values of all MPC70 powders were observed. Compared to control powder, the increase in pH of MPC70-NaOH and MPC70-7.10 were attributed to the adjustment of retentates pH during their manufacturing by the addition of NaOH and KOH, while the decrease in pH of MPC70-5.85 was attributed to $\text{NaH}_2\text{PO}_4 \bullet 2\text{H}_2\text{O}$ addition. The LBD values of MPC70 powders were significantly different ($P < 0.05$) with each other except MPC70-C and MPC70-7.10 powders that were statistically at par ($P > 0.05$) with each other. Except, MPC70-NaOH, other MPC70 powders showed non-significant difference ($P > 0.05$) among their PBD values (Table 2). The PBD values of MPC70 powders were higher than the value 0.49 g/mL, reported by Crowley et al. (2014) for MPC70 powder produced from the retentate containing 32.80% TS

Table 1 Chemical composition and ζ -potential of skim milk, ultrafiltered, diafiltered and treated retentates and reconstituted MPC70 powders

Samples		TS (%)	Ash (%)	Protein (%)	Fat (%)	Lactose (%)	Protein/TS ratio	Ash/TS ratio	ζ -potential (mV)
PCSM UF and DF retentates	1 ×	8.45 ⁿ ± 0.01	0.61 ⁱ ± 0.00	3.04 ⁱ ± 0.00	0.05 ^j ± 0.00	4.75 ^h ± 0.01	0.36 ^k ± 0.00	0.07 ^{lgh} ± 0.00	− 10.87 ^e ± 0.22
	2 ×	11.58 ^m ± 0.00	0.74 ^k ± 0.01	6.08 ^k ± 0.01	0.10 ^j ± 0.00	4.66 ^{hi} ± 0.01	0.53 ^j ± 0.00	0.06 ⁱ ± 0.00	− 9.33 ^{cd} ± 0.35
	3 ×	15.06 ^l ± 0.01	1.06 ^j ± 0.01	9.12 ^j ± 0.01	0.15 ^h ± 0.00	4.72 ^h ± 0.01	0.61 ⁱ ± 0.00	0.07 ^h ± 0.00	− 10.50 ^{cd} ± 0.51
	4 ×	18.41 ^j ± 0.01	1.33 ⁱ ± 0.01	12.16 ⁱ ± 0.01	0.20 ^g ± 0.00	4.72 ^h ± 0.02	0.66 ^f ± 0.00	0.07 ^{gh} ± 0.00	− 8.75 ^{bc} ± 0.65
	5 ×	21.95 ^b ± 0.01	1.65 ^h ± 0.01	15.20 ^b ± 0.06	0.25 ^f ± 0.00	4.85 ^g ± 0.06	0.69 ^e ± 0.00	0.08 ^{ef} ± 0.00	− 8.49 ^{abc} ± 0.56
	6 ×	25.61 ^g ± 0.01	1.9 ^g ± 0.01	18.24 ^g ± 0.01	0.30 ^e ± 0.00	5.17 ^f ± 0.02	0.71 ^d ± 0.00	0.07 ^{fg} ± 0.00	− 7.49 ^{ab} ± 0.11
	7 ×	29.18 ^e ± 0.01	2.19 ^f ± 0.03	21.26 ^e ± 0.01	0.35 ^d ± 0.00	5.38 ^e ± 0.03	0.73 ^b ± 0.00	0.07 ^{efg} ± 0.00	− 8.46 ^{abc} ± 0.22
	7 × DF	27.62 ^f ± 0.01	2.16 ^f ± 0.03	20.50 ^f ± 0.01	0.35 ^d ± 0.00	4.61 ⁱ ± 0.01	0.74 ^a ± 0.00	0.08 ^d ± 0.00	− 8.37 ^{abc} ± 0.09
MPC Powders	7 × 5.85	19.87 ⁱ ± 0.03	3.36 ^d ± 0.05	—	—	—	—	0.17 ^c ± 0.00	− 8.00 ^{abc} ± 0.30
	7 × 7.10	17.26 ^k ± 0.01	3.19 ^e ± 0.01	—	—	—	—	0.18 ^a ± 0.00	− 7.34 ^a ± 0.30
	MPC70-C	95.56 ^b ± 0.01	7.05 ^d ± 0.01	68.05 ^a ± 0.05	1.15 ^a ± 0.05	19.31 ^a ± 0.08	0.71 ^d ± 0.00	0.07 ^{fg} ± 0.00	—
	MPC70-NaOH	95.28 ^c ± 0.01	7.38 ^c ± 0.00	68.92 ^b ± 0.00	1.05 ^b ± 0.00	17.94 ^b ± 0.04	0.72 ^c ± 0.00	0.08 ^{cd} ± 0.00	—
	MPC70-5.85	92.74 ^d ± 0.01	16.57 ^b ± 0.05	60.95 ^c ± 0.00	0.97 ^c ± 0.00	14.25 ^d ± 0.01	0.66 ^g ± 0.00	0.18 ^b ± 0.00	− 10.45 ^{cd} ± 0.75
	MPC70-7.10	96.71 ^a ± 0.00	17.85 ^a ± 0.01	60.77 ^d ± 0.00	0.95 ^c ± 0.01	17.15 ^c ± 0.01	0.63 ^h ± 0.00	0.18 ^a ± 0.00	− 10.11 ^{cd} ± 0.34

Mean values ± S.E. (n = 3), values in a particular column followed by different superscripts (^{abcde} or ^{ijklm}) differ significantly ($P < 0.05$) with each other; — not determined

Fig. 2 Effect of UF concentration on permeate flux (n = 3) **a** volume reduction percent versus flux and **b** concentration factor versus flux

content (w/w). Therefore, the observed variation in LBD and PBD values of these powders than reported by Crowley et al. (2014) was attributed to the lower TS contents of the retentates used in this study (Table 1), because feed with lower TS produces higher foam and results in lower LBD values of powders due to its higher interstitial and occluded air contents and vice versa (Amaladhas and Emerald 2017). The observed difference among the loose and packed bulk densities of MPC70 powders could also be attributed to variation in feed composition that leads to change in its TS and viscosity (Meena et al. 2016), atomization behavior which could leads to alteration in several powder properties such as occluded and interstitial air contents, densities, specific surface area, mean particle size and particle size distribution. Moreover, Schuck (2013) has reported that bulk density of powdered products is a complex property which is combinedly governed by different feed and process parameters such as composition and viscosity of feed, heat treatment and air incorporation in feed during processing; type of atomizer used, particle density and size of powder particles and their occluded and interstitial air contents. Khatkar and Gupta (2012) and Schuck (2013) reported 0.27, 0.24, 0.29 g/mL LBD and 0.37, 0.29, 0.35 g/mL PBD values for dairy whitener, micellar casein isolate (MCI) and milk protein isolates, (MPI) which are lower than the values observed in this study.

The CI, HR and θ are important parameters that describe the flowability of dried powders. The CI and HR values of MPC70-C and MPC70-7.10 or MPC70-NaOH and MPC70-5.85 exhibited non-significant difference ($P > 0.05$) between them, but observed to have significant difference ($P < 0.05$) among these powders as shown in Table 2. However, θ values of all MPC70 powders were significantly ($P < 0.05$) different with each other and

considered as ‘free flowing’ powders ($\theta < 35^\circ$) as per Carr (1965) classification. However, as per CI and HR criteria, as reported in US Pharmacopeia (2006), the flow of MPC70-C and MPC70-7.10; MPC70-NaOH and MPC70-5.85 powders were poor and very poor, respectively. The observed difference in CI and HR values of MPC70 powders is accorded to the existing difference in their LBD and PBD values (as discussed above), from which these parameters were calculated and same can easily explain their lower CI values or better flowability than the reported CI value (50.50%) by Crowley et al. (2014) for MPC70 powder.

The wettability defines the capacity of powder particles to absorb water on their surface and mainly governed by the size of powder particles (Barbosa-Cánovas et al. 2005). The wettability of all the manufactured MPC70 powders differed significantly ($P < 0.05$) with each other (Table 2). MPC70-7.10 and control powders exhibited maximum and minimum wetting time as 35 and 1.24 min, respectively. The difference in particle size as supported by SSA and $D_{3,2}$ or $D_{4,3}$ (Table 2) could easily explained the variation in wettability values of MPC70 powders. Barbosa-Cánovas et al. (2005) reported that smaller powder particles have higher specific area (quotient of surface area to mass) values, difficult to get wetted individually, due to enhanced incidences of particles clumping that leads to marked increase in wettability. Further, Bouvier et al. (2013) reported that due to altered chemical composition particularly due to the presence of higher protein and fat on the surface of powder particles, MPC powders exhibits higher wetting index (> 120 s). According to Schuck (2013) other high protein powders such as MCI, MPI, NaCas, whey protein isolate, whey and micellar casein powders were

Table 2 Physical and functional properties of MPC70 powders

Samples	Physical properties											
	pH	Bulk density (g/mL)		CI, %	HR	AOR, θ	Wet., min	Disp., %	a_w	Color values		
		LBD	PBD							L^*	a^*	b^*
MP70-C	6.94 ^c $\pm$ 0.00	0.41 ^a $\pm$ 0.01	0.58 ^a $\pm$ 0.01	29.10 ^b $\pm$ 0.59	1.41 ^b $\pm$ 0.01	34.48 ^a $\pm$ 0.01	1.24 ^d $\pm$ 0.03	75.43 ^a $\pm$ 0.08	0.25 ^d $\pm$ 0.00	86.22 ^d $\pm$ 0.05	- 1.04 ^d $\pm$ 0.00	13.90 ^a $\pm$ 0.05
MP70-NaOH	7.18 ^b $\pm$ 0.00	0.37 ^c $\pm$ 0.00	0.54 ^b $\pm$ 0.00	32.11 ^a $\pm$ 0.68	1.47 ^a $\pm$ 0.01	31.23 ^b $\pm$ 0.01	31.49 ^b $\pm$ 0.00	64.76 ^b $\pm$ 0.51	0.31 ^c $\pm$ 0.00	87.74 ^c $\pm$ 0.02	- 0.65 ^c $\pm$ 0.00	11.25 ^b $\pm$ 0.01
MP70-5.85	5.98 ^d $\pm$ 0.00	0.39 ^b $\pm$ 0.00	0.59 ^a $\pm$ 0.00	32.73 ^a $\pm$ 0.64	1.49 ^a $\pm$ 0.01	25.60 ^c $\pm$ 0.01	23.33 ^c $\pm$ 0.03	51.08 ^c $\pm$ 0.30	0.36 ^b $\pm$ 0.00	89.32 ^b $\pm$ 0.14	- 0.47 ^a $\pm$ 0.01	9.53 ^d $\pm$ 0.03
MP70-7.10	7.34 ^a $\pm$ 0.00	0.42 ^a $\pm$ 0.00	0.59 ^a $\pm$ 0.00	28.27 ^b $\pm$ 0.64	1.39 ^b $\pm$ 0.01	22.48 ^d $\pm$ 0.01	35.00 ^a $\pm$ 0.00	40.74 ^d $\pm$ 0.01	0.37 ^a $\pm$ 0.00	89.40 ^a $\pm$ 0.01	- 0.56 ^b $\pm$ 0.01	9.93 ^c $\pm$ 0.01
Samples	Physical properties											
	SSA, m ² /kg		Particle size distribution, μ m				Mean diameter		Span			
			d ₁₀	d ₅₀	d ₉₀	D _{3,2}	D _{4,3}					
MP70-C	60.65 ^d $\pm$ 0.00		54.84 ^d $\pm$ 0.00	123.93 ^a $\pm$ 0.00	281.09 ^a $\pm$ 0.00	98.93 ^a $\pm$ 0.00	166.22 ^a $\pm$ 0.00	1.83 ^b $\pm$ 0.00				
MP70-NaOH	112.50 ^c $\pm$ 0.00		30.98 ^b $\pm$ 0.00	71.88 ^c $\pm$ 0.00	147.71 ^d $\pm$ 0.00	53.34 ^b $\pm$ 0.00	81.96 ^d $\pm$ 0.00	1.62 ^d $\pm$ 0.00				
MP70-5.85	117.20 ^b $\pm$ 0.00		27.72 ^c $\pm$ 0.00	75.23 ^b $\pm$ 0.00	161.95 ^c $\pm$ 0.00	51.18 ^c $\pm$ 0.00	86.60 ^c $\pm$ 0.00	1.78 ^c $\pm$ 0.00				
MP70-7.10	123.70 ^a $\pm$ 0.00		27.09 ^d $\pm$ 0.00	71.43 ^d $\pm$ 0.00	167.13 ^b $\pm$ 0.00	48.51 ^d $\pm$ 0.00	87.72 ^b $\pm$ 0.00	1.96 ^a $\pm$ 0.00				
Samples	Functional Properties											
	Calcium, %	Solubility, %		Viscosity, mPa s	WBC, g/g of protein	OBC, g/g of protein	FC, %	EC, %	HCT, min	RCT, min		
		0 day	60 days									
MP70-C	1.57 ^a $\pm$ 0.00	86.79 ^b $\pm$ 0.23	59.01 ^d $\pm$ 0.12	23.10 ^c $\pm$ 0.00	4.70 ^a $\pm$ 0.01	3.23 ^c $\pm$ 0.01	45.16 ^d $\pm$ 0.56	37.33 ^b $\pm$ 1.45	39.00 ^a $\pm$ 0.00	210.00 ^a $\pm$ 0.00		
MP70-NaOH	1.57 ^a $\pm$ 0.00	69.10 ^d $\pm$ 0.19	61.93 ^c $\pm$ 0.02	19.60 ^d $\pm$ 0.00	3.77 ^b $\pm$ 0.03	3.47 ^b $\pm$ 0.06	53.79 ^c $\pm$ 0.06	36.00 ^b $\pm$ 0.00	22.00 ^b $\pm$ 0.00	210.00 ^a $\pm$ 0.00		
MP70-5.85	1.15 ^b $\pm$ 0.00	82.66 ^c $\pm$ 0.18	73.82 ^b $\pm$ 0.11	25.20 ^b $\pm$ 0.00	2.41 ^c $\pm$ 0.06	3.58 ^a $\pm$ 0.01	112.43 ^b $\pm$ 0.49	40.00 ^a $\pm$ 0.00	13.00 ^c $\pm$ 0.00	210.00 ^a $\pm$ 0.00		
MP70-7.10	0.99 ^c $\pm$ 0.00	95.65 ^a $\pm$ 0.13	87.15 ^a $\pm$ 0.18	27.30 ^a $\pm$ 0.00	1.85 ^d $\pm$ 0.03	3.20 ^c $\pm$ 0.01	125.23 ^a $\pm$ 1.33	40.00 ^a $\pm$ 0.00	9.00 ^d $\pm$ 0.00	210.00 ^a $\pm$ 0.00		

*Mean values ± S.E. (n = 3), values in a particular column followed by different superscripts (a,b,c,d) differ significantly ($P < 0.05$) with each other

LBD loose bulk density, PBD packed bulk density, CI compressibility index, HR Hausner ratio, AOR angle of repose, Wet. Wettability, Disp. Dispersibility, SSA specific surface area, WBC Water binding capacity, OBC Oil binding capacity, EC Emulsion capacity, HCT Heat coagulation time, RCT rennet coagulation time

also have > 120 s wetting index and cannot be considered as ‘instant’ powders.

Dispersibility is defined as the ability of powder particles which enable their dispersion in water as individual particles. Dispersibility of MPC70 powders was in the range of 40.74–75.43% and significantly different ($P < 0.05$) with each other (Table 2). It was observed that dispersibility of all treated MPC70 powders was significantly ($P < 0.05$) lower than that of control powder. This decrease in dispersibility of treated powders was attributed to their smaller particle size as increase in fines particles (< 90 μm) leads to decreased dispersibility and vice versa (Singh and Newstead 1992). This decrease in size of powder particles was also supported by increase in their SSA values (Table 2). Huppertz and Gazi (2015) reported that commercial MPC samples possess dispersibility in the range of 38–100%. Further, Bouvier et al. (2013) reported that MPC and micellar casein isolates (MCI), which are rich in aggregated caseins, exhibit lower dispersibility indexes, while only 5.1 and 25.6% dispersibility values were reported in MCI and MPI by Schuck (2013).

The a_w values of treated MPC70 powders were significantly higher ($P < 0.05$) than control powder (Table 2) that might be attributed to their chemical composition (Table 1) and interaction of water with lactose, protein and salts.

Schuck (2013) reported that lightness (L^*), redness (a^*) and yellowness (b^*) values of MCI and MPI powders were 69.5, – 5.1, 12.0 and 73.5, – 5.50, 9.30, respectively. Statistically significant difference ($P < 0.05$) in color (L^* , a^* and b^*) values of control and treated MPC70 powders were observed (Table 2). In general, protein rich MPC powders are grayish-white in color compared to yellowish-white colored skim milk powders because of their different chemical makeup. The existing differences in color values of control and other treated MPC70 powders could be accorded to the varied milk constituents present in the feed and addition of NaOH, KOH and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ that also changed the composition of these powders.

The physical, reconstitution, sensory and even functional properties of powders are known to be influenced by their SSA; d_{10} , d_{50} , and d_{90} and $D_{3,2}$ or $D_{4,3}$ and span values. All these properties of control and other treated powders (Table 2) differed significantly ($P < 0.05$) with each other and might be due to different TS, salts and protein contents of their respective retentates from which these powders were manufactured. The SSA and d_{10} , d_{50} , and d_{90} values of MPC70 powder were 380 m^2/kg , 14.90, 39.60, 72.70 μm , respectively (Crowley et al. 2014) which are markedly different than the values obtained in this study and mainly attributed to higher retentate TS (32.8%, w/w) used by Crowley et al. (2014) than TS contents (< 29.18%) of the retentates used in this investigation.

Functional properties of MPC70 powders

During different food preparations, MPC powders are mainly added as high protein ingredients to improve their physical, functional, nutritional and sensorial attributes. Solubility of MPC powders is of vital importance as higher solubility leads to better expression of other functional properties of these powders and vice versa. Floris et al. (2007) reported that solubility of MPC67.10–MPC72.50 measured as nitrogen solubility index (NSI) were in the range of 60–87%. All fresh MPC70 powders showed significant difference ($P < 0.05$) in their solubility values with each other. Several factors such as composition of milk, applied unit operations (UF, heat treatment, evaporation if used and spray drying); powder composition (particularly protein, moisture and salts contents), particle size, degree of protein denaturation and storage conditions have major effect on solubility of MPC powders (Huppertz and Gazi 2015).

Solubility of fresh MPC70-NaOH and MPC70-5.85 powders were lower, while that of MPC70-7.10 powder was significantly higher ($P < 0.05$) than control powder as shown in Table 2. This marked improvement in the solubility of MPC70-7.10 powder is accorded to the adjustment of retentate pH to 7.10 by the addition of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and KOH which might have changed the ionization state of inorganic phosphate ions from HPO_4^{2-} to HPO_4^{3-} ; that has led to demineralization of casein micelles as HPO_4^{3-} form of phosphate had higher affinity towards calcium (Ahmad et al. 2009). Further, Vaia et al. (2006) reported that this phenomenon was also responsible for the decreased mineral concentrations in the aqueous phase and improved solvent quality; led to higher dissociation of casein micelles by decreasing cohesive interactions between the hydrophobic regions of caseins. Schuck et al. (2002) also produced native phosphocaseinate powder (NPCS) with 12% (w/w) sodium phosphate (pH 7.10) addition using co-drying method that led to markedly lower insolubility index (0.2 mL) in treated NPCS than of control (14.40 mL) sample. Temperature and storage period have markedly detrimental effect on the solubility of MPC powders. In this study also, solubility of all MPC70 powders decreased after two months storage and differed significantly ($P < 0.05$) with each other. At the end of studied storage period, the highest reduction in solubility was observed in control powder (27.78%) compared to only < 9% reduction in solubility values of treated MPC70 powders that clearly underlined the efficacy of pH adjustment treatments in retaining better solubility of treated powders than control during storage (Table 2). The better solubility retention in treated powders might be attributed to their different chemical composition particularly lesser calcium and modified protein–protein and protein–mineral

interactions due to their alkaline pH. Moreover, Dalgleish and Law (1988) reported that acidification of milk in the 5.6–6.0 pH range had been reported to results in swelling and dissociation of casein micelles and acts a physical method to induced changes in casein micelles. This phenomenon could explain the better solubility of MPC70-5.85 powder than control powder during storage.

The viscosity values of MPC70 powders were in the range of 19.60–27.30 mPa s (at 50 s⁻¹ and 20 °C) and showed significant ($P < 0.05$) difference among them. Maximum and minimum viscosity values were observed in MPC70-7.10 and control powders, respectively (Table 2). The increased viscosities of treated powders (except MPC70-NaOH) than that of control powder was attributed to the presence of higher number of smaller powder particles as decreased particle size leads to increased viscosity. This is also supported by SSA values of these powders (Table 2) as higher number of smaller particles results in increased SSA values of powders.

The HCT values of control and treated MPC70 powders were differed significantly ($P < 0.05$) with each other and in the range of 9–39 min that is in good agreement with the earlier reported range (i.e. 0–40 min) for commercial MPC powders by Huppertz and Gazi (2015). The maximum and minimum HCT values were observed in control and MPC70-7.10 powders, receptively. The lower HCT values of treated powders might be accorded to their pH values that were markedly away from native milk pH. It is also attributed to DF treatment that is known to reduce the heat stability of DF retentates from which MPC70-5.85 and MPC70-7.10 powders were manufactured. In ascending order the HCT values of MPC70 powders were MPC70-7.10 < MPC70-5.85 < MPC70-NaOH < MPC70-C, respectively.

According to Schuck (2011) water absorption by milk powders is of practical importance in their functionality and use as protein-water interaction had significant effects on several other functional properties of powders. Kneifel and Seiler (1993) reported that water holding is a broad term that covers a number of properties such as hydration capacity, suction potential, swelling; binding, retention, imbibing and absorption of water and used interchangeably in the literature. In simple terms, ability of milk proteins to bind water and swell in called water binding and mainly influenced by different factors such as temperature, ionic strength, pH and protein composition etc. Significant difference ($P < 0.05$) among the WBC values of produced MPC70 powders were observed. The maximum and minimum WBC values as 4.70 and 1.85 g/g of proteins were observed in control and MPC70-7.10 powders, respectively (Table 2). Water absorption for WPC, soluble and insoluble low calcium co-precipitates; NaCas and acid casein

were reported as 0.65, 2.60 and 0.75; 2.50 and 0.68 g/H₂Og⁻¹ protein by Singh (2011).

Oil binding capacity of protein powders is mainly related to their protein content and denotes the physical entrapment of oil by proteins because of their chemical modification (Zayas 1997). Similar to WBC, OBC values of manufactured powders were differed significantly ($P < 0.05$) with each other. Except MPC70-7.10 powder, MPC70-NaOH and MPC70-5.85 powders exhibited significantly improved ($P < 0.05$) OBC than control powder that is accorded to their smaller particle size (or higher SSA values) and lower LBD values as shown in Table 2. Zayas, (1997) reported that powders with smaller particle size and lower density absorb and entrap more oil and vice versa. The MPC70-5.85 and MPC70-7.10 powders were observed to have maximum and minimum OBC values, respectively (Table 2). Higher LBD of MPC70-7.10 powder could explain the minimum oil absorption by this powder than other samples.

Compared to excellent and good, foaming and emulsification properties of sodium caseinate, whey protein concentrates and isolates, these properties of calcium caseinates and MPC powders have been reported as poor by Singh (2011). Foam capacity of MPC powders is one of the important functional property of these powders. The selection and utilization of MPC powders as a high protein ingredient in bakery, confectionary, ice-creams and frozen dessert applications is governed by its foaming potential. Foam capacity values of MPC70 powders were in the range of 45.16–125.23% and significant improvement ($P < 0.05$) in FC values of treated powders than that of control powder were observed (Table 2). Minimum and maximum FC values were observed in control and MPC70-7.10 powders, respectively. This improvement in FC values of treated powders could be accorded to the adjustment of pH of the retentates with NaH₂PO₄•2H₂O, NaOH and KOH as addition of salts have been reported to improve the foaming properties of milk proteins. The FC values obtained in this study is higher than that reported by MPC60 powders by Meena et al. (2017a), but lesser than the range reported by Huppertz and Gazi (2015) for commercial samples of MPC powders.

The emulsification capacity values of MPC70 powders were varied in the range of 36–40%. Statistically, EC values of either control and MPC70-NaOH or MOC70-5.85 and MPC70-7.10 powders showed non-significant difference ($P > 0.05$) between them, but the EC values of MPC70-5.85 and MPC70-7.10 powders were significantly higher ($P < 0.05$) than remaining powders as shown in Table 2. This improvement in EC values of these powders could be accorded to their reduced calcium contents than control and MPC70-NaOH powders as Ye (2011) reported increased values of emulsion capacity and stability in MPC

Fig. 3 Titration curve (a) and buffer index (b) of alkalinization-acidification with 0.1 N HCl and 0.1 N NaOH solution of MPC70 powders (0.5% protein solution)

powders containing lower calcium contents. Further, this improvement could also be explained by different chemical makeup and smaller particle size and SSA values of these powders as reported by Meena et al. (2017a).

The RCT values of prepared MPC70 samples were observed to have non-significant difference ($P > 0.05$) among them. These reconstituted powder samples were did not coagulated till 210 min of rennet addition, thereafter, the study was discontinued. Similar findings were also reported earlier by Meena et al. (2017a) in control and treated MPC60 powders. MPC powders have been reported to remain uncoagulated after rennet addition because of their lower calcium contents. However, external addition of

calcium chloride could induce rennet coagulation in such powders. Although, MPC powders with lower calcium contents is preferred in standardization of cheese milk to overcome the problem of nugget formation in cheese.

The amount of acid and base used to induce 0.5 change in the pH of reconstituted MPC70 powders during acidification and alkalization as well as calculated dB/dpH values have been shown in Fig. 3a, b. The observed variation in dB/dpH values of control and treated MPC70 powders were attributed to their chemical makeup and adjustment of retentates pH with different salts which have resulted in their higher buffer index than control powder.

Table 3 Rheological properties of reconstituted MPC70 powder samples

Sample	Bingham			Ostwald			Herschel Bulkley			
	σ_0	η	R^2	k	n	R^2	σ_0	k	n	R^2
MPC70-C	0.908	2.66	0.986	0.323	0.318	0.794	0.983	0.000	1.153	0.995
MPC70-NaOH	0.764	3.06	0.998	0.235	0.373	0.879	0.710	0.009	0.914	0.999
MPC70-5.85	0.952	6.06	0.997	0.249	0.451	0.900	0.891	0.012	0.944	0.999
MPC70-7.10	1.200	8.09	0.984	0.447	0.400	0.779	1.469	0.001	1.192	0.985

Where σ is the shear stress (Pa), σ_0 yield stress, η viscosity (mPa s), and k consistency index (Pa-s), n flow behavior index and R^2 is the coefficient of determination

Rheological properties of reconstituted samples of powders

Bingham, Ostwald and Herschel Bulkley models (Table 3) were used to study the rheological behavior of reconstituted samples of MPC70 powders. The observed apparent viscosity of MPC70 powder solutions in descending order were: MPC70-7.10 > MPC70-C > MPC70-5.85 > MPC70-NaOH that can be easily explained by similar trend observed in their relative yield stress values (Table 3). Moreover, Herschel Bulkley models was observed to best explain the rheological behavior of these powders (maximum R^2 values) compared to other studied models.

Conclusion

Concentration of skim milk in UF at its natural pH and adjustment of retentate pH before drying altered the composition and pH of treated powders than control. Alkalization resulted from salts addition of UF retentate caused the decalcification in its casein micelles that decreased the crosslinking and interactions of calcium with caseins. This also facilitated caseins dissociation by decreasing cohesive interactions between the hydrophobic regions of casein micelles. $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ addition decreased the pH of retentate (5.85) and powder (5.98) and resulted in swelling and dissociation of casein micelles in smaller particles. Thus, the change in pH using NaOH, monosodium phosphate and KOH induced significant improvement in most of the properties of treated powders than control powder. This intervention have checked the problem of initial poor solubility and drastic decrease in solubility during storage in MPC powders. Thus, it is a cost effective, easy to use and compatible intervention. However, pH adjustment decreased protein contents in treated powders. Despite this, treated powders could replace control powder in various processed foods aiming for improved functionality of milk protein ingredients.

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