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Reconsideration of Whey Clarification Using Chitosan and Decalciumphosphation Using Thermal Treatment

Nabiollah Kamyabi

Islamic Azad University-Ayatollah Amoli Branch, Iran

Abstract: The pretreatment of whey by removing fat and inorganic matters, i.e. Calcium and Phosphor is generally conducted to increase the permeate flux of ultrafiltration membrane while concentrating whey protein and to improve the quality of the final product, i.e. Whey Protein Concentrate (WPC). In this study, to perform an effective pretreatment process by removing the fat content, a chemical pretreatment by using Chitosan were tested through which several operation parameters, i.e. Chitosan concentration, pH and centrifuge resident time were investigated and resulted 0.015-0.02%, 4.4 and 5 min, respectively, as the optimum condition. Physical pretreatments, i.e. Industrial Centrifugal Separator and lab-scale Centrifuge, were investigated as well. For removing Calcium and Phosphor thermal pretreatment in three different temperatures and resident times were investigated and resulted an up to 65% and 47% calcium and phosphor removal, respectively.

Key words: Whey · Pretreatment · Decalciumphosphation (DCP) · Clarification · Chitosan · Thermal Treatment

INTRODUCTION

Whey is a byproduct of cheese and Casein production. About 85 to 90% of loading milk into the cheese production unit would leave the unit as whey. Whey is comprised of 50% of milk dry materials. The dry materials of whey are consisted of Lactose, Proteins, Fats, Inorganic Matters and Vitamins [1]. Sweet Whey, one of the major kinds of whey, contains about 64 g/l of dry matter. The dry matter has about 72% of Lactose and 12.5% of protein [1]. In fact, the most valuable constitute of whey is protein which could be extracted by denaturing process, membrane ultrafiltration, or chromatography [2].

To efficiently concentrate protein by applying membrane ultrafiltration, it is necessary to remove the fat, Calcium and Phosphor. In fact, these factors would cause fouling in ultrafiltration membrane and decrease the permeate flux [1]. Also, the presence of fat and its oxidation would result in an undesirable flavor of WPC and would reduce its functionality properties too [3].

The existence of Calcium and Phosphor ions would change the ionic environment and would cause solute-solute reactions and solute-membrane reactions. Calcium is the major material responsible for fouling in dairy industry. This is not only because of the sedimentation of Thri-Calcium-Phosphate but also because of this fact that Calcium ions would form a salt bridge between membrane and proteins and expedite the membrane fouling by protein [12].

In the following sections, we would discuss the methods of fat, Calcium and Phosphor removal.

Fat Removal: Generally, there are two main methods for removing the whey fat content. One is the physical method which benefits from equipments such as centrifugal separator and microfiltration membrane. However, because some of the fats are soluble in whey, chemical treatments are inevitable to cause the sedimentary compounds which would later be removed by employing conventional physical treatments such as centrifugal clarification and microfiltration membrane refining [4].

In one study nine different physical methods were investigated in which centrifugal clarifier in both one-pass and recycle procedure, lasting for about 20 and 30 minutes, microfiltration membranes, pore sizes of 0.6 and 1 ìm and gravitational sedimentation were employed. It is presented as the most efficient methods for fat removal using one-pass centrifugal clarifier and microfiltration membrane, pore size of 0.6 ìm, simultaneously [15].

Corresponding Author: Nabiollah Kamyabi, Islamic Azad University-Ayatollah Amoli Branch, Iran.
Tel: +98-9126436136, Fax: +98-1212517209.

In other studies, three different sedimentary additives, i.e. Calcium Chloride [16], Phosphorous salts [14] and Chitosan [4], were suggested to remove colloidal and soluble whey fats.

Calcium Chloride would not be an effective additive even for the same solutions of whey, due to the impossibility to detect its optimum amount in which its minimum amount could make maximum fat removal. It would, also, produce secondary sludge, cause more energy expenses, due to it high process temperature (40-50 °C) and intensify membrane fouling [14].

Applying Phosphorous salts would not be a good choice too because it would remove the proteins, by denaturation of proteins, cause more energy expenses, for its high process temperature (50-60°C) and decline the functionality aspects of the final product, i.e. emulsifying and foaming [17].

At last, Chitosan is proposed as a very successful absorbent which could effectively remove the turbidity without conventional problems of other sedimentary materials [17].

Decalciumphosphation (DCP): The common methods for elimination of whey salts are Ion Exchange, Electordialyses, Nanofiltration and Thermal Treatmend [2]. Although Ion Exchange is a very efficient method in removing the ions and it can almost remove all the ions, it is very expensive. In fact less expensive methods are more desirable whereas Calcium and Phosphor ion removing is also a desired aim [8].

Electrodialysis is a good choice when low ion elimination is considered. But, if a high amount of ion elimination is aimed, the energy consumption will not be economically reasonable. It is generally performed for up to 50% ion elimination [7]. So, it would not be a correct choice for high range of Calcium elimination with low expenses.

Nanofiltration membrane is especially permeable to Sodium and Potassium Chloride salts. Nevertheless, it is not good enough in removing Calcium and other ions [9]. Finally, Thermal Treatment is considered as the most economical process for salt removing and it is formally used for Calcium and Phosphor elimination. By applying an appropriate condition, i.e. pH, temperature and Calcium & Phosphor content, it would form a strong sedimentary compound which would be later removed physically by centrifugal separators [2].

In this study, Chitosan is tested again with some new point of views with a thorough investigation. Thermal Treatment is also investigated in three different conditions: 80°C & 3.5 min, 80°C & 7 min and 60°C & 30 min. to find out the optimum condition as the aim of this study a point should be sought that result in the most and cheapest removal with the least side effects on final product.

MATERIALS AND METHODS

Fat Removal by Chitosan: At first, Whey was subjected to an industrial centrifugal separator (Westfalia centrifugal separator, 4500 rpm) and after removing most of its insoluble fats it changed to be the whey without cream. Then for elimination of soluble fats Chitosan was added at 25°C to the whey without cream. Before doing the following processes, it is better to solve Chitosan in an acid, preferably an organic acid. The acid must be diluted to 10% by water and after that Chitosan must be added to the solution with a ratio of 1% w/v. Using acid as solvent has two major merits. First, it would change Chitosan structure into aqueous state. Second, it would modify the pH of solution. We can employ acids such as Acetic acid, Citric acid and Chloric acid [17].

The pH of whey would be fixed by using Chloric acid (1 Molar). The solution was leaved for 10 minutes (and regarding the environment air it could be continuously stirred in order to ease the formation of Lipid-Chitosan compounds). Then, it was entered into a lab scale centrifuge with 1200 rpm with different resident times. The value of turbidity of the clarified solution was measured with a spectrophotometer in 500 Nm.

Three main parameters were examined, namely: the resident time in centrifuge vessel, the pH of the solution and the concentration of Chitosan. To prevent excessive and unnecessary experiments, we used the optimum results of each previous experiment.

Decalciumphosphation by Thermal Treatment: First, the pH of whey solution was changed, from 6.4 to 8 by adding 10% Sodium Hydroxide at a constant temp of 10°C. Then, the solution was separately entered into two different warm water baths. In the first one, it was heated to 80°C and was leaved in it for 3.5 and 7 minutes [10]. The resident time for the second bath was 30 minutes in a temperature of 60 °C [11]. Afterwards, these two solutions were clarified by a lab scale centrifugal separator. Then, they were cooled to 10 °C. Finally, we modified the pH of whey to the primary level (i.e. 6.4) by adding Citric Acid in order to make it ready for the ultrafiltration unit.

Methods and Equipments for Measurement: Kjeldahl method was used to measure the amount of protein and the Jerber method was employed to calculate the fat content. For pH, Mettler pH-meter (Toledo MP220) was utilized. Also, to evaluate the percentage of dry matter, a Mettler, Halogen HG63, was applied. Finally, for turbidity measuring, a Unico UV 2100 spectrophotometer was used.

RESULTS AND DISCUSSION

Clarification Experiment: Regarding Jerber test, the fat content of the final whey was zero. Therefore, to evaluate the exact trace of fat residue, the dry matter of the whey solution, both before and after the clarification process, is measured.

pH Experiment: In this experiment, the effect of pH on both turbidity and the percentage of dry matter at a constant Chitosan concentration and the centrifuge process resident time are investigated.

Figure (1) shows that when pH increases from 4.1 to 4.4, both the amount of dry matters and turbidity would drastically decline and the supernatant solution would almost change into a crystalline, transparent solution. However, when pH is 4.7 the turbidity would rise. In fact, the minimum level of turbidity would happen when pH is about 4.4. So, this pH is the optimum level of pH for sedimentation or coagulation.

Chitosan Concentration: To find the minimum required amount of Chitosan to achieve a maximum fat elimination, the turbidity of the supernatant solution as a function of Chitosan concentration, at pH=4.4 and centrifuge resident time= 5 minutes, is investigated.

Figure (2) demonstrates that by increasing the concentration of Chitosan, both the amount of dry matter and the extent of turbidity will decline. In fact, when Chitosan concentration is about 0.015% w/v, the turbidity of whey would be reduced 90%. When pH is 4.4, the results show that adding 0.015 - 0.02% w/v of Chitosan would completely eliminate the Lipid content of whey solution.

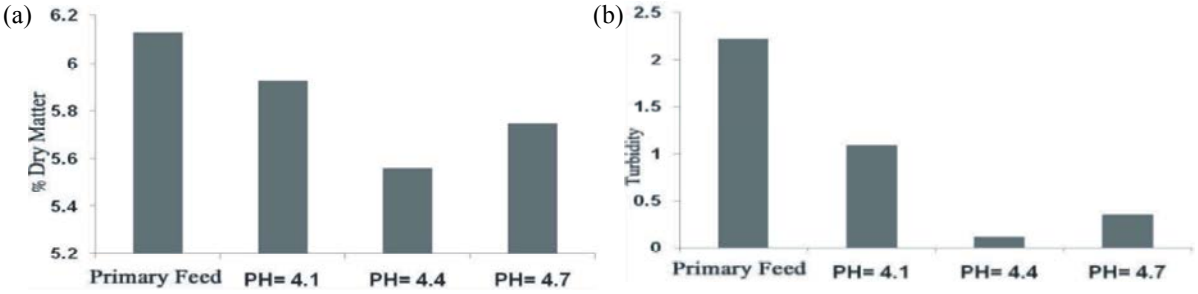

Fig. 1: Diagram (a) shows the relation between dry matter percentage and pH change when Chitosan concentration=0.02% and centrifuge resident time=5 minutes, diagram (b) shows relation between Turbidity and pH change under the same conditions.

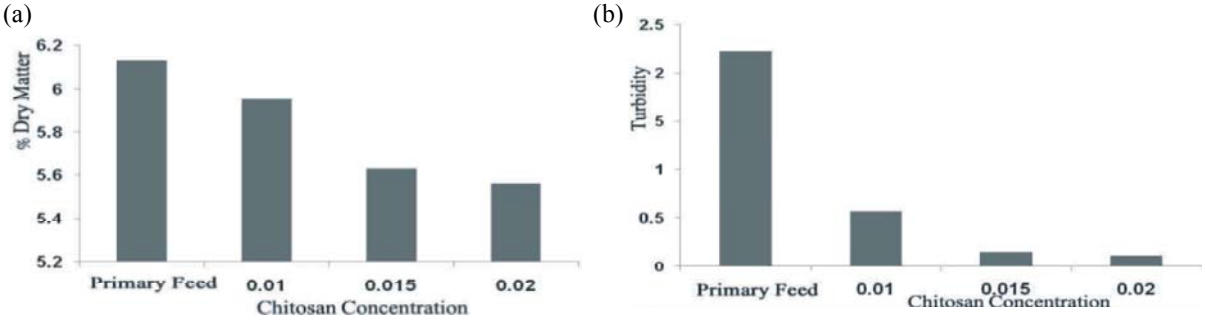

Fig. 2: Diagram (a) shows the relation between dry matter percentage and Chitosan concentration when pH=4.4 and centrifuge resident time=5 minutes, diagram (b) shows relation between Turbidity and Chitosan concentration under the same conditions

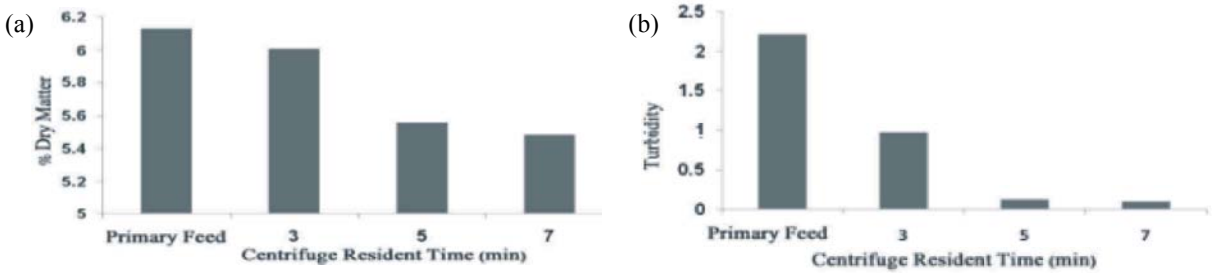

Fig. 3: Diagram (a) shows the relation between dry matter percentage and centrifuge resident time when pH=4.4 and Chitosan concentration=0.015%, diagram (b) shows relation between Turbidity and centrifuge resident time under the same conditions

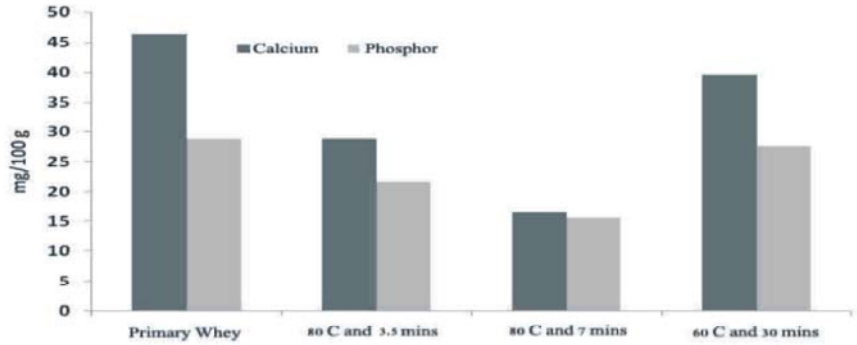

Fig. 4: The change of Phosphor and Calcium concentration for different thermal treatment processes

Centrifuge Resident Time: To discover the optimum resident time needed for centrifuge process, we examined a solution with 0.015% w/v Chitosan in whey at pH=4.4.

Figure (3) clearly shows that both the turbidity level and the amount of dry matter would decrease with a rise in resident time. When we increased the centrifuge resident time from 3 minutes to 5, the change was notable.

However, extending the centrifuge resident time from 5 minutes to 7 did not cause a considerable change. This result would demonstrate that the main parts of the Chitosan-Lipid complex would be separated in 5 minutes and in the next two minutes; the amount of separated materials would be very low. Therefore, we have found that 5 minutes is the optimum value for centrifuge resident time.

Clarification by Chitosan: When pH is 4.4, the process of coagulation of Lipids by Chitosan is an electrostatic reaction. In fact, Chitosan is a poly-glucosamine polymer that the PK of amine group of glucosamine is 6.3 [6]. When the solution pH is 4.4, Chitosan would have a high amount of positive charge that would result in an electrostatic reaction with the minus charge of Lipids. On the other hand, at pH=4.4, the major proteins of whey (namely: bovine serum albumin, Alpha-lactalbumin and beta-lacto-globomine) have positive charges that would prevent any electrostatic reaction between them and Chitosan [5, 2]. Moreover, because these proteins are very soluble at their Isoelectric points, which is about 4.4 [7], the coagulation of Lipid-Chitosan would be a very selective procedure.

Finally, because the clarified whey does not contain any suspended materials, the UF process would be conducted more efficiently. Therefore, it is possible to eliminate by 80-90% water from whey without a notable loss of flux rate. In addition, because we do not use any salts except during pH stabilization stage, the amounts of inorganic matters in the final product of protein concentrate would be low which should be considered as a leading merit of this method for whey clarification.

Regarding the toxicity figures reported by the Chitosan producer, it would be dangerous for human only if it reaches a concentration of 16 g/kg of human body [3, 6]. Therefore, the remained Chitosan in the final whey solution would not be harmful. However, because Chitosan is insoluble at pH=7, the remained Chitosan at final product could be eliminated by changing the pH of final solution into 7 and employing a filtration unit.

Decalciumphosphation (DCP): Figure (4) demonstrate that the optimum temperature in order to reach the maximum efficiency in thermal treatment is 80°C. Furthermore, if we double the resident time, the level of removed Calcium Phosphate will be doubled too. In this temperature, the level of removed Calcium and Phosphor would be about 65% and 46% respectively that is clearly higher than the other methods. Also, to obtain better result, we can extend the temperature and the resident time, but regarding the procedure of protein denaturation, these were the only values reported in previous papers.

CONCLUSION

By conducting lab scale pretreatment process, it is demonstrated that to remove fat from whey, completely, the chemical methods are also necessary for coagulation of colloidal compounds along with physical methods (namely: employing centrifugal separator and microfiltration membrane).

As a result, to reach 90% of turbidity elimination, Chitosan is approved to be the best sedimentary agent if it is employed with a concentration, whey solution pH and centrifuge process time of 0.015-0.02%, 4.4 and 5 minutes, respectively.

Also, to eliminate Calcium and Phosphor, thermal treatment is presented to be the most efficient method in a temperature and a resident time of 80°C and 8 minutes, respectively.

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