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Whole Whey As A New Bulk Additive During Papermaking and Paper Coating Processes

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In Loving Memory of Late Professor Doctor ""Mohamed Refaat Hussein Mahran""

Abstract
The present work introduces whole whey as a new in bulk additive during papermaking and paper coating processes. In bulk Addition of whole whey to pulp during papermaking, as well as, paper coating with whole whey both succeeded in promoting strength of paper and decreasing its water vapor permeability in comparison to paper, which did not involve whole whey as an additive. Previous studies, by the authors and others, have shown that each of the three major components of dairy products, as an isolate, improves paper properties (protein isolates, sugars, and fat isolates). Whey is a dairy Industry byproduct -involving these three non-isolated components. Whole whey -including the three non-isolated previous mentioned components- has not been evaluated for papermaking. Using whole whey for paper improvement is more money, time, and energy saving compared to separating each component and using it alone as isolate. Moreover, such approach avoids the use of chemicals and processes required for isolation of the previous mentioned dairy components. This would increase the sustainability of both milk and paper industries by finding new uses for dairy industry byproducts and improving paper properties through natural environmentally safe additives in contrast to synthetic additives.Keywords: Lataniaverschaffeltii ,Hepatoprotctive activity, Antioxidant activity, Phenolic compounds, Flavonoids.

1. Introduction

Average composition of cow's milk (percentage of solids) is 37.5% sugars namely lactose, Protein 26.6%, and fat 28.9% (1-2). Each one of these three milk components was shown -in research articles done on each component separately as an isolate in absence of the other components- to improve paper properties either by paper coating or in bulk addition during papermaking process (3-13). Thus it would be theoretically logic that milk containing the three non-isolated components altogether would be optimum for paper improvement. However, due to food importance of milk it can not be dissipated in paper improvement. Therefore, milk Industry byproducts -involving the three non-isolated components- may be an optimum candidate for paper improvement. If such improvement proves practically it would be more money, time, and energy saving compared to separating each component and using it alone as isolate. Moreover, such approach avoids the use of chemicals and processes required for isolation of the previous mentioned dairy components. This would increase the sustainability of both milk and paper industries by finding new uses for dairy industry byproducts and improving paper properties through natural environmentally safe additives in contrast to synthetic additives. All these reasons encouraged the authors, in the present work, to evaluate an important dairy byproduct, namely whey, for paper improvement.

Whole whey -including the three non-isolated previous mentioned components- has not been evaluated for papermaking.

Moreover, previous research investigated water vapor permeability (wvp) in case of whey protein isolates, and whey lipids isolates separately, in comparison to artificial emulsions formed by mixing of both isolates. The best results were obtained for lipid-protein isolates artificial mixture (13). Therefore, it is logically expected that whole whey -which is a natural emulsion mixture of proteins and lipids- would be a simple way to improve wvp properties..

Whey is the major dairy industry by-product in the huge volume of aqueous wastes produced during cheese making. 1 kg of cheese, requires 10 kg of milk and produces 9 kg of whey. Whey disposal without treatment represents an environmental problem regarding it's huge volume and organic content. Treatment before disposing whey is not economically favorable. Thus, there is a continuous motive to finding, as much as possible, new economic environmentally uses for this main dairy byproduct. Typical composition of whey residue is 70 % sugars namely lactose, 14 % proteins, 9 % minerals, 4 % fats and 3 % lactic acid (1-2, 14-18).

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It is apparent that sugars comprise the majority of whey residue (70%). Sugars such as glucose, sucrose, and sugar industry byproducts, containing sugars, namely molasses were shown in recent research to act as strength promoters and retention aids in papermaking. The strength promoting effect of sugars succeeded to counteract the ultimate fate of deterioration in paper strength, due to addition of inorganic fillers such as kaolin. These positive improvements were attributed to several factors including adhesive effects, and sugars molecules being entrapped in the cell wall natural nanopores of cellulose fibers, during the collapse of these pores, as the fibers are dried. Sucrose and glucose molecules act as spacers, preventing the irreversible collapse of the natural nanoporous structure of cellulose fibers, which –normally – occurs during drying.. Sucrose spacers hinders the fibers to relax leading to a strain, which makes some microfibrils partially released and protrude out of the fibers. This in turn leads to more efficient entanglement of the fibers, and hence increases the strength of the prepared paper nanocomposites. In other words, a sort of fibers beating takes place. The authors called this phenomenon *incorporation beating* to differentiate it from chemical and mechanical beatings, conventionally applied to increase the strength of paper. Moreover, during paper sheet formation, the sucrose-incorporated fibers are more swollen and thicker, relative to the sucrose-free fibers. This fiber swelling decreases the size of the gaps present between the fibers, during paper sheet formation. Therefore, lesser amount of inorganic filler can escape through these narrowed gaps, during the water drainage, which occurs at paper sheet formation. Eventually, more inorganic filler is enmeshed between these swollen thickened sucrose-incorporated fibers. The authors called this phenomenon incorporation retention to differentiate it from the conventional types of retention of inorganic fillers (3-7)

Proteins comprise the second major component in whey residue (14%). Protein isolates are well established as paper strength promoters. They are used for paper coating or added to the pulp to increase paper strength and/or fillers retention. This is because the fiber-additive-fiber bond is stronger than the fiber-to-fiber bond. Protein, being natural and biodegradable, is preferred to synthetic adhesives, which pollute the environment and cause troubles in paper recycling. Protein isolates from dairy industry namely casein were of major importance in papermaking. However, their use decreased due to isolates high costs (8-11).

Fat isolates from whey , are showing promise in recent research for production of films with useful properties including mechanical properties(17-18).

On the other hand, fatty dispersions may, theoretically, help to lubricate fibers during paper sheet formation if added in bulk to the pulp during paper making process. This is based on one of the several proposed factors explaining the strength promoting effect of starch in papermaking. Such explanation proposed that starch lubricate fibers during papermaking leading to better entanglement of fibers and thus better paper sheet formation leading to stronger paper (19).

Results and Discussions: -

The pulp used for the present work was unbleached bagasse pulp produced by Alkaline sulphite process. Effects of in bulk addition of whole whey to pulp during papermaking , and coating of paper sheets with whole whey were both investigated.

The strength properties of the obtained paper are shown in Table 1. The percentage of improvement (change) is shown in Table 2. Moreover, the strength results are represented in Figures 1-5. The wvp results are shown in Figure 6.

Table 1: The tensile strength results:

	Maximum Load (N)		**Deflection at Maximum Load (mm)**		**Stress at Maximum Load (MPa)**		**Stiffness (N/m)**		**Young's Modulus (MPa)**	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Blank	6.89	1.70	1.39	0.52	3.17	0.78	524052.00	577973.46	24094.34	26573.49
25% Whey (SC)	9.82	1.01	2.25	0.24	5.46	0.56	870451.46	376521.24	48358.41	20917.85
50% Whey (SC)	10.19	1.91	2.28	0.03	5.22	0.98	28481.95	10342.90	1460.61	530.41
75% Whey (SC)	8.03	0.37	2.01	0.67	4.12	0.19	319844.98	425302.41	16402.31	21810.38
100% Whey (SC)	9.57	1.34	1.93	0.68	5.11	0.71	703828.20	673143.12	37537.50	35900.97
100% Whey (SC soaked 5 days)	5.61	0.86	1.01	0.65	2.20	0.49	68762.45	484392.77	2696.57	27010.86
25% Coated Whey (based on Original)	6.85	0.72	2.16	0.73	3.05	0.44	30300.85	508304.82	1346.70	28965.61
50% Coated Whey (based on Original)	6.61	0.58	2.68	0.80	2.75	0.39	220758.06	532216.87	9198.25	30920.36
100% Coated Whey (based on Original)	8.88	0.45	1.92	0.88	3.95	0.34	2113919.76	556128.92	93951.99	32875.11

Table 2 The percent improvement of strength due to whey application

	Maximum Load (N)		Deflection at Maximum Load (mm)		Stress at Maximum Load (MPa)		Stiffness (N/m)		Young's Modulus (MPa)	
		% improv.		% improv.		% improv.		% improv.		% improv.
Blank	6.89		1.39		3.17		524052.00		24094.34	
25% Whey (SC) in bulk addition	9.82	42.54	2.25	62.22	5.46	72.23	870451.46	66.10	48358.41	100.70
50% Whey (SC) in bulk addition	10.19	47.82	2.28	64.18	5.22	64.87	28481.95	-94.57	1460.61	-93.94
75% Whey (SC) in bulk addition	8.03	16.50	2.01	44.27	4.12	29.94	319844.98	-38.97	16402.31	-31.92
100% Whey (SC) in bulk addition	9.57	38.93	1.93	38.53	5.11	61.15	703828.20	34.31	37537.50	55.79
100% Whey (SC) soaked 5 days in bulk addition	5.61	-18.65	1.01	-27.32	2.20	-30.62	68762.45	-86.88	2696.57	-88.81
25% Coated Whey-Paper (based on Original whey solution)	6.85	-0.53	2.16	55.13	3.05	-3.85	30300.85	-94.22	1346.70	-94.41
50% Coated Whey-Paper (based on Original whey solution)	6.61	-4.10	2.68	93.05	2.75	-13.09	220758.06	-57.87	9198.25	-61.82
100% Coated Whey-Paper (based on Original whey solution)	8.88	28.87	1.92	38.42	3.95	24.58	2113919.76	303.38	93951.99	289.93

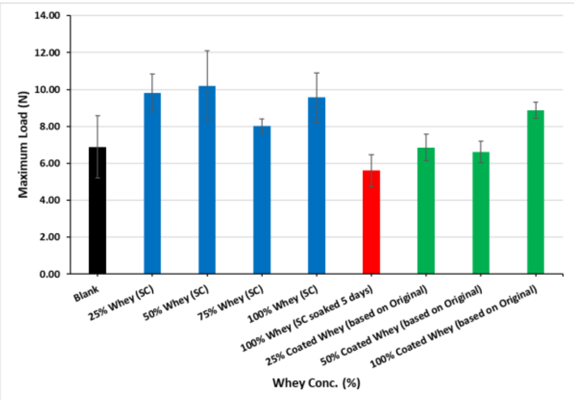

Fig1 Maximum load versus whey concentration

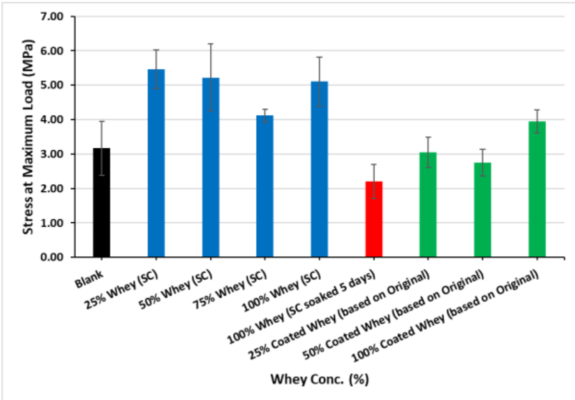

Fig3 Stress at maximum load versus whey concentration

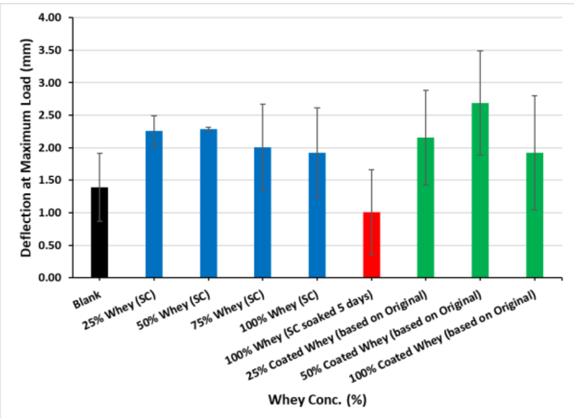

Fig2 Deflection at maximum load versus whey concentration

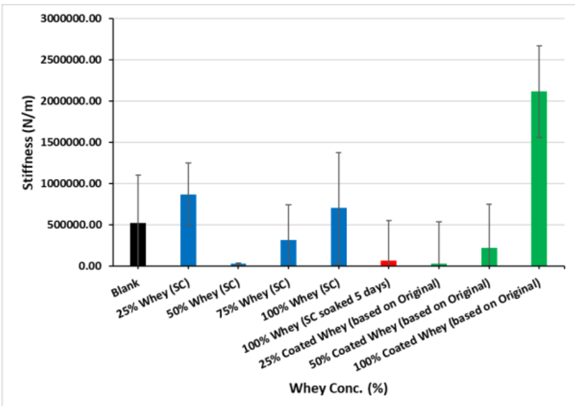

Fig4 Stiffness versus whey concentration

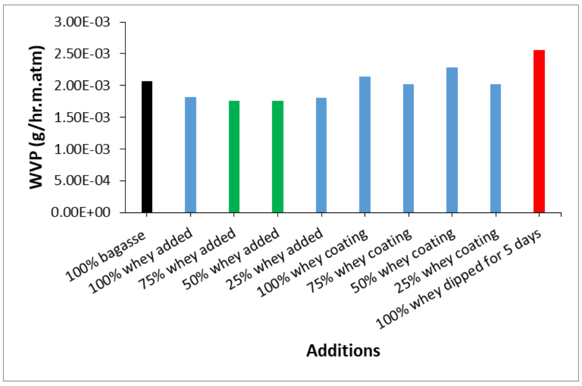

Fig5 Young's modulus versus whey concentration

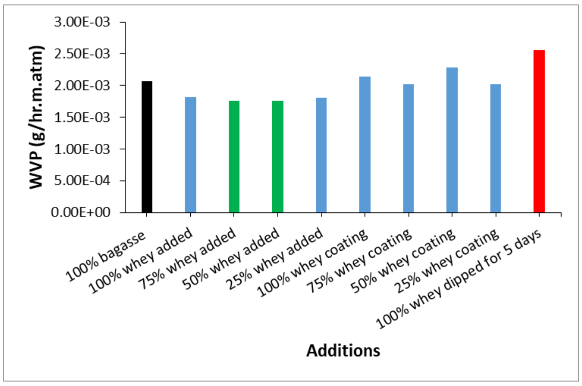

Fig 6 water vapor permeability versus whey concentration

1. Effect of In Bulk Addition of Whole Whey to pulp during papermaking on the Properties of the Produced Paper: -

It is clear from Tables 1 and 2 that in bulk addition of whole whey to the pulp improved the strength compared to the blank whole whey free paper at all addition percentages. The improvement increased gradually with increasing the percentage of added whole whey reaching maximum improvement at 50% in bulk addition relative to solid content (SC). Then the improvement decreased with increasing the percentage of added whole whey. The improvement in strength due to in bulk addition of whole Whey to the pulp during papermaking may be explained by the combined effects of the three non-isolated dairy components. The combination of sugars, proteins, and fats would lead to adhesive effects, better inter-fiber bonding, better sheet formation as shown by previous research done on each component alone in isolation (3-18). The decrease in improvement at high percentages of in bulk addition (70% and 100% relative to SC) may be attributed to disruption of fiber-to-fiber bonding by excessive whey. The maximum strength improvement at 50% addition was 47.82% improvement and the maximum load reached 10.19 N compared to the blank whole whey free paper whose maximum load was 6.89 N.

Similar pattern and interpretation may apply to wvp. Where wvp decreased with increasing percentage of added whole whey reaching maximum improvement at 50% and 75% in bulk addition relative to solid content (SC).Then the improvement decreased with increasing the percentage of added whole whey. The decrease in wvp due to in bulk addition of whole Whey to the pulp during papermaking may be explained by the combined effects of the non-isolated protein and lipid dairy components (12-13). The decrease in improvement at high percentages of in bulk addition may be attributed to disruption of fiber-to-fiber bonding by excessive whey. Allowing more water vapor to pass through the loose bonded fibers. The wvp results are represented in Figure 6.

Using lower percentages of whole whey is more economic and logistically favored. Therefore, these results confirm that whole whey is a promising in bulk additive for papermaking.

2. Effect of Extended time Soaking after In Bulk Addition of Whole Whey to pulp on the Properties of the Produced Paper: -

To further confirm the reason of decrease in strength improvement at high percentages of in bulk addition of whole whey to the pulp, the authors investigated the effect of excessive whey addition by soaking the pulp for five days into 100% whey relative to SC. This leaded to sharp decrease in strength of paper reaching a level below the strength of the blank whole whey free paper. The maximum load of this five days whole whey soaked samples was 5.61N relative to the blank whole whey free paper whose maximum load was 6.89N. Thus there was a decrease in strength by 18.65% due to excessive whey addition. Such results confirmed disruption of fiber-to-fiber bonding by excessive whey.

The same holds true for wvp which increased to a level above the wvp of the blank whole whey free paper. Indicating disruption of fiber-to-fiber bonding by excessive whey, which allows more water vapor to pass through the loose bonded fibers.

3. The Effect of Coating Paper Sheets with Whole Whey on the Properties of the Paper: -

On contrary to bulk addition, coating of paper sheets by several concentrations of whole whey solution resulted in decrease of paper strength except for coating with original undiluted whole whey solution of 100% concentration relative to whey solution. This may be attributed to the high water content of low concentrations of whey solution which dissociated the paper sheets during coating, while the low amounts of whole whey were unable to counteract the effects of water on paper sheets. However original undiluted whole whey was able to counteract the effects of water on paper sheets, and to improve the strength of the coated paper relative to the blank uncoated paper. The percentage of improvement due to coating by original undiluted 100% whole whey solution reached 28.87% relative to the blank uncoated paper sheets. The maximum load of paper sheets coated by original 100%

whole whey solution was 8.88N relative to 6.89N in case of blank uncoated paper sheets. Such improvement may be attributed to the adhesive effects of the main three components of whole whey as previously mentioned at introduction (3-18).

Using the original undiluted whole whey solution i.e. using this dairy byproduct as is for paper sheets coating is easier, more economic, and more logistically favorable than the diluting processes. Therefore, these results confirm that original undiluted whole whey is a promising strength promoting coating agent for papermaking.

Wvp decrease occurred at coating by 25% and 75% whole whey solutions as shown in Figure 6. At 25% coating solution the decrease in wvp was slight; indicating that the water content of whole whey led to some dissociation of paper sheets. Thus allowing passage of water vapor through paper sheets thereafter. At coating by 50% whole whey solution, the wvp increased. The solution dissociated the paper and the emulsion was unable to penetrate deeply into the fibers due to its higher concentration leading to higher viscosity and lower penetration ability (20). Thus minimizing it's effect on wvp. At 75% coating solution, the wvp decreased again; indicating that at this concentration the adhesive properties of whole whey counteracted the paper dissociation. At 100% coating solution, the wvp increased; indicating that too much of the dairy components may exert hygroscopic effects towards water vapor counteracting it's benefits.

4. Theoretical and Practical Significance of Results:

The practical results are in accordance with the theoretical expectations mentioned by the authors of the present work at introduction. The authors expected that whole Whey -involving the three non-isolated dairy components, namely sugars, proteins, and fats- would act as a new economic, sustainable, and environmentally safe strength prompter for paper, while decreasing its wvp.

The improvement in strength and decrease in wvp due to in bulk addition of whole Whey to the pulp during papermaking may be explained by the combined effects of the three non-isolated dairy components. The combination of sugars, proteins, and fats would lead to adhesive effects, better inter-fiber bonding, better sheet formation as shown by previous research done on each component alone in isolation (3-18).

In case of coating paper with whole whey, the strength promoting effects may be mainly attributed to adhesive effects provided by the three non-isolated dairy components. (3-18).

5. Conclusion

The results indicate that Whole whey shows Promise as strength promoter, while decreasing wvp Moreover, Using whole whey is more money, time, and energy saving compared to separating each component and using it alone as isolate. Such approach avoids the use of chemicals and processes required for isolation of the previous mentioned dairy components. This would increase the sustainability of both milk and paper industries by finding new uses for dairy industry byproducts and improving paper properties through natural environmentally safe additives in contrast to synthetic additives.

Experimental

The bagasse raw material was kindly supplied from Quena Company for Pulp and Paper, Quss, Quena, Egypt with the following chemical composition; 3.28% ash, 22.09% lignin, 37.65% cellulose, 1.81% extract, 27.97% pentosan and 3.01% SiO2. Sodium Hydroxide, Sodium Sulfite and Sodium Carbonate were kindly supplied as AR reagent from ElNaser Company Egypt and were used as it without any modifications.

Bagasse Alkaline-Sulfite pulping Methods:

Sugarcane bagasse raw material was mixed with 15% based on dry oven NaOH; 5% Na2SO3 and 2.5% Na2CO3 at (1:6) liquor ratio and heated at 160 oC for 2 hrs. Yield percent was 44%.

Preparation of hand sheets paper (HSP), in bulk addition of whole whey, and paper coating by whole whey

Sugarcane bagasse was chemically treated for removing the lignin content; to obtain unbleached pulp which used for HSP making according to the S.C.A standard, using a sheet former (S.C.A model-AB Lorentzen and Wettre). The HSP was prepared as mentioned in previous study (21). Exploration on ability of printable modified papers for the application in heat sublimation transfer printing of polyester fabric. Scientific Reports, 13(1), p.6536). In brief, about 1.2 g of bleached sugarcane bagasse was homogenized with 5 to 7 l of tab water. After a homogenizing step, the suspension is separated through a screen. A sheet of 201 cm2 surface areas and 165 mm in diameter is formed in the appliance, and then it is pressed for 4 min using a hydraulic press. The wet sheet is then collected on blotting paper, protected between two sheets. Drying of as prepared sheets is finished by using a rotary drum dryer for 4 h at 70-80 °C.

-Whole whey of different concentrations 25 ,50, 75, and 100% was added to the pulp suspension in the mixer prior to paper sheet making. In coating experiments, prepared paper sheets were coated with different concentrations of whey 25, 50, 100%.

Mechanical and Barrier characterizations of paper sheets

-Tensile strength testing is achieved utilizing a universal testing machine (LR10K; Lloyd Instruments, Fareham, UK) with a 100-N load cell at a constant crosshead speed of 2.5 cm/min in line with TAPPI

(T494-06) standard method was used to determine the mechanical properties of coated HSP with shellac in alginate and/or bentonite. The gauge length is set at 10 cm and strips of 15 mm width and 15 cm length are used for the analysis. Each HSP thickness was determined by an electronic digital micrometer before the examination. Each test was performed by using 5 specimens and the average of the results was recorded.

-Measurements of water vapor permeability (WVP) are carried out by ASTM E96/E96M-10. Before being used to seal cover aluminum cups holding 5g of anhydrous calcium chloride, paper sheets under examination are first conditioned at 50% RH and 25°C for 24 hours. Then, the uncoated side of coated paper is exposed to the dehydrated area, and the WVP is calculated using the following equation.

$$WVP = g \cdot h / t \cdot A \cdot \Delta P$$

Where (g/t) is the slope of the line drawn between the obtained weight (g) and time (t), h is the average paper thickness, A is the infiltration area, and P is the difference in partial water vapor pressure between the air inside the cup and the saturated potassium sulphate solution (98% RH) outside. The average of three repeated measurements for all samples is used to get the final WVP values.

References

1. Varnam, A., & Sutherland, J. P. (2001). Milk and milk products: technology, chemistry and microbiology (Vol. 1). Springer Science & Business Media.
2. Audicc, J. L., Chaufer, B., & Daufin, G. (2003). Non-food applications of milk components and dairy co-products: A review. Le Lait, 83(6), 417-438.
3. Fahmy, Y., Fahmy, T. Y. A., Mobarak, F., et al. (2017). Agricultural residues (wastes) For manufacture of paper, board, and miscellaneous products: Background overview And future prospects. International Journal of ChemTech Research, 10, 424-448.
4. Fahmy TYA, Mobarak F, Fahmy Y, Fadl MH, El-Sakhawy M (2006) Nanocomposites from natural cellulose fibers incorporated with sucrose. Wood Science and Technology 40(1): 77-86.
5. Fahmy TYA, Mobarak F (2008) Nanocomposites From Natural Cellulose Fibers Filled with Kaolin in Presence of Sucrose. Carbohydrate Polymers 72(4): 751.
6. Fahmy TYA (2007) Introducing molasses as a new additive in papermaking. Tappi Journal 6(8): 23.
7. Fahmy TYA (2007) Molasses as a new Additive in papermaking: for high alpha-cellulose wood pulp. Professional Papermaking 4(1): 42
8. Yang S.T., Gao F., Yin Z., Chemical modified gelatin and its application in cast coated paper, China Pulp. Paper 19 (2000) 26–31.
9. Gerna, S., D'Incecco, P., Limbo, S., Sindaco, M., & Pellegrino, L. (2023). Strategies for Exploiting Milk Protein Properties in Making Films and Coatings for Food Packaging: A Review. Foods, 12(6), 1271.
10. Fahmy TYA, Abou-Zeid RE, Fahmy Y (2014) Response of pulps of different origins to the upgrading effect of bulk added green denatured soy protein, in correlation to morphological structure & chemical composition of cellulose fibers. Nature and Science 12(4): 79-83
11. Fahmy Y, El-Wakil N A, El-Gendy A A, Abou-Zeid R E, Youssef M A (2010). Plant proteins as binders in cellulosic paper composites. International journal of biological macromolecules 47(1): 82-85.
12. Rullier-Birat, B., Bonino, J. P., Garreau, X., Menu, M. J., Gressier, M., & Ansart, F. (2013). New green coatings made from fatty acid dispersions: improvement in barrier properties of biodegradable thermoplasticized-starch substrate. Journal of adhesion science and technology, 27(1), 102-109.
13. Perez-Gago, M. B., & Krochta, J. M. (2000). Drying temperature effect on water vapor permeability and mechanical properties of whey protein− lipid emulsion films. Journal of Agricultural and Food Chemistry, 48(7), 2687-2692.
14. Zandona, E., Blažić, M., & Režek Jambrak, A. (2021). Whey utilization: Sustainable uses and environmental Approach. Food Technology and Biotechnology, 59(2), 147-161.
15. Smithers, G. W. (2008). Whey and whey proteins—From 'gutter-to-gold'. International dairy journal, 18(7), 695-704.
16. Gokhale, J.S., Tekale, D.P., Annapure, U.S. (2022). Biohydrogen Production Using Cheese Industry Waste: Current Trends and Challenges. In: Kuddus, M., Yunus, G., Ramteke, P.W., Molina, G. (eds) Organic Waste to Biohydrogen. Clean Energy Production Technologies. Springer, Singapore. https://doi.org/10.1007/978-981-19-1995-4_6
17. Arab, S. A., Kaemipoor, M., Alkhaleel, R., & Mahdian, A. (2023). Recent Trends in Developing Whey Products by Advanced Technologies. Sch Acad J Biosci, 2, 74-79.
18. Satyanarayana, S. D. V., Lavanya, M., & Priyanka, B. The Development of Dairy Business Enterprise: A review.
19. Casey JP (1962) "Pulp and Paper", Interscience Publishers Inc., New York.
20. Shtyka, O. S., Błaszczyk, M. M., & Sęk, J. P. (2016). Analysis of emulsions concentration changes during imbibition in porous sorbents. International Journal of Environmental Science and Technology, 13, 2401-2414.
21. Adel, A. M., Ahmed, N. M., Diab, M. A., El-Shall, F. N., & El-Shinnawy, N. (2023). Exploration on ability of printable modified papers for the application in heat sublimation transfer printing of polyester fabric. Scientific Reports, 13(1), 6536.