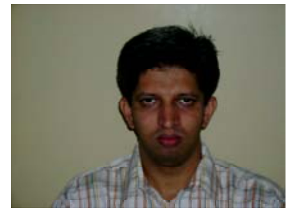
Efficacy of pullulan in emulsification of turmeric oleoresin and its subsequent microencapsulation



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Introduction

The rhizomes of the plant *Curcuma longa* L. (turmeric), a tropical herb of the Zingiberaceae family is native to southern Asia. India produces about 94% (225,000 metric tons) of the world's turmeric. Turmeric oleoresin commonly contains 30 to 45 percent curcuminoids pigments, and 15 to 20 % volatile oil. The spice extract are used in the form of liquid concentrate (Gilberston, 1971). Liquid turmeric oleoresins undergo oxidative degradation. This problem can be overcome by microencapsulation; besides, it also protects the flavors from undesirable interaction (Reineccius, 1989; Versic, 1988). To prepare microencapsulated free flowing powder by spray drying, the water-soluble component (i.e. wall material) is dissolved in water, and the oleoresin is dispersed therein. To get stable emulsions, suitable polymeric stabilizers are gum acacia, modified starch, pectin, alginate, or a proteinacious material such as gelatin or casein. Alternatively, non-polymeric emulsion stabilizers such as fatty acid partial esters of sorbitol anhydride (sorbitan or the trade name "Span") and polyoxyethylene derivatives of fatty acid partial esters of sorbitol anhydride (trade name Tween) are also used. The emulsions are homogenized and spray dried. When the stabilizer acts as an encapsulant as in the cases of the polymeric stabilizers, no extra encapsulant is need to be added to the emulsion. When non-polymeric stabilizers are used for stabilization, an encapsulant must be added from above listed polymeric stabilizers. All flavor emulsions require only polymeric stabilizers to form stable emulsion. However, but for an oleoresin polymeric stabilizer alone or in combination is not able to produce stable emulsion. It requires non-polymeric stabilizer and diluent with combination of polymeric stabilizers to act as an encapsulant. The literature on microencapsulation of oleoresins such as garlic, paparika and capsicum, all report the use of edible gums, emulsifier and diluent as wall materials

Pullulan, a neutral glucan consisting of liner polymer of maltotriosyl units connected by α-1,6 linkages, is an extra cellular microbial polysaccharide produced by an yeast like fungus, *Aureobasidium pullulans*. The rheological properties of pullulan impart thickening or bodying to food and beverage products. It also stabilizes the product (Sandford, 1982). The emulsifying properties of pullulan with gum Arabic and maltodextrin with lipids in emulsion system have been investigated (Matsumura et al., 2000). Imagi et al., (1990) and Minemoto et al., (1999) have reported on the high encapsulation activity of gum arabic, pullulan and maltodextrin. In this work, attempts have been made to form stable turmeric oleoresin emulsion with polymeric stabilizer pullulan in combination with gum arabic and maltodextrin, and further check the stability of turmeric constituents in the microcapsules prepared therefrom.

Materials & methods

Turmeric oleoresin was procured from Synthite Industrial Chemicals Ltd., Kerala. Standard curcumin was obtained from Indfrag Ltd., Bangalore. Gum arabic (GA) (Encapcia) was procured from Colloides Naturels International (CNI), France. Maltodextrin (MD) was procured from Gujarat Ambuja, Baroda.

Pullulan was obtained from Hayashibara, Okayama, Japan Optimization of turmeric oleoresin and pullulan concentration for encapsulation was carried out by varying the pullulan concentration from 0 to 5 **%** of the total solution and turmeric oleoresin (5% based on the 30 g of gum arabic). Further, the pullulan concentration was kept constant and oleoresin was varied from 5 to 20 % (based on 30% of gum arabic). The optimization was based on viscosity, emulsion particle size and emulsion stability index (ESI) (Cho et al., 2003).

Total volatiles (TV) and non-volatiles (NV) were analysed as per method reported by Ranganna (1977). Curcumin content was measured as absorbance at 425 nm by using UV spectrophotometer (Hitachi). Different ratios of gum arabic and maltodextrin (100:0 to 0:100) were used to evaluate the appropriate wall material for encapsulation of turmeric oleoresin by spray drying. The emulsions were prepared at 10 % loading of turmeric oleoresin and 1% pullulan of total solution. To evaluate the ability of these carrier materials as a flavour carrier, the spray-dried microcapsules were analyzed for entrapped curcumin content by measuring absorbance of the entrapped curcumin (Chauhan, 1999) and entrapped TV and NV by the method suggested by Maleeny**,** (1961). The samples were analyzed for 6 weeks. The percentage retention of analytes was calculated by the formula (analyte at 'X' storage time) x 100/ (analyte at zero storage time). A semi- log plot of percentage retention of all these analytes vs. time according to Cai & Corke (1998) to obtain the rate constant (k) as slope of the graph which predicted the half-life ($t_{½}$) for the retention of curcumin and TV.

Results and discussion

Emulsion studies for optimization of pullulan and turmeric oleoresin concentration
Optimization of pullulan concentration: With 5% loading of oleoresin (based on the weight of gum Arabic – which itself was used as 30 % solution), and at pullulan concentrations (0-5%) used in the study, the emulsions showed an ESI of 1 to 0.4. Hence, no interpretation about the optimal pullulan concentration (1 to 5%) for which ESI was 1 could be drawn based on the above emulsion studies. Eight of these emulsions were then selected for spray drying. It was observed that perfect microcapsules were formed at pullulan concentrations ≤ 1%. At 2%, small fibre-like structures were formed. At still higher concentrations, cobweb like structures were formed.

Optimization of turmeric oleoresin concentration: The oleoresin loading was optimized by taking 30% gum arabic with 1% pullulan of total solution. The viscosities, emulsion sizes and emulsion stability indices (ESI) at 5 to 30% oleoresin loadings based on carried material were recorded. Viscosity and mean particle size were found to increase with oleoresin loading, and the ESI at 5 & 10% loading was 1. The ESI decreased with a further increase in oleoresin concentration. Hence the optimum conditions were a 1% pullulan of total solution and 10% oleoresin based on gum Arabic.

Analysis of turmeric oleoresin and stability: The turmeric oleoresin from Synthite Industrial Chemicals, Kerala was analyzed for TV (19.73 %) and NV (80.14 %) and curcumin (30.2%). This oleoresin was stored at ambient temperature (30 ± 2°C) in a glass bottle and studied weekly for 6 weeks. The curcumin and TV content in oleoresin decreased from 30.2 % to 23.2 %, and TV decreased from 19.7% to 14.1% over a period of six weeks. Increase in the concentration of total NV was due to a decrease in the concentration of TV. The half life, $t_{1/2}$, that is the time required for the reduction of a value to 50 % of its original was calculated from the slope 'k' as $t_{1/2}=0.693/k$ by semi-log plot of % retention of curcumin and TV vs. storage time. For curcumin the $t_{1/2}$ was 16.38 weeks and total volatiles (TV) had the $t_{1/2}$ of 11.94 weeks

Analysis of entrapped curcumin, TV, NV and stability: The microcapsules of turmeric oleoresins obtained were analyzed for entrapped curcumin and entrapped TV and NV over a period of 6 weeks. Curcumin recovery decreased from 70.23 to 48.04 and TV decreased from 17.24 to 12.08% in microcapsules prepared from gum arabic supplemented with 1% pullulan (Table 1). The effect of addition of pullulan is more predominantly shown in blend having only 100% maltodextrin as encapsulant.

Carrier Materials	% Recovery[1]					
	0 week		3 week		6 week	
	A	B	A	B	A	B
GA:MD[2] (100:0)	72.23	17.24	66.57	16.78	65.13	16.40
GA:MD (80:20)	65.13	15.86	59.42	15.01	56.56	13.61
GA:MD (60:40)	62.20	15.02	55.23	14.43	45.23	13.43
GA:MD (40:60)	55.21	14.95	48.22	14.47	47.34	13.88
GA:MD (20:80)	50.31	13.64	43.21	13.08	39.74	12.41
GA:MD (0:100)	48.04	12.08	40.05	11.34	34.25	10.56

Table 1: % Recovery of curcumin and total volatiles from turmeric oleoresin entrapped in microcapsule prepared from various wall materials using 1% pullulan of total solution

[1]results are mean of three individual determinations; A: curcumin content; B: Total Volatiles

[2]GA: Gum Arabic; MD: Maltodextrin of 18 DE

The $t_{1/2}$ of microcapsule of curcumin and TV in each of the wall materials was calculated and results are seen in Table 2. Among these, microcapsules obtained using gum arabic with 1% pullulan as carrier material provided greater protection which was seen from the half values calculated. This was in agreement with the observation made by Reineccuius (1989) and Raghavan, Abharam & Shankaranarayan (1990).

Carrier materials	Half-life $T_{1/2}$ (weeks)	
	Entrapped Curcumin	Entrapped total volatile
GA:MD[1] (100:0)	38.08	76.15
GA:MD (80:20)	29.36	37.26
GA:MD (60:40)	13.64	37.26
GA:MD (40:60)	28.64	57.75
GA:MD (20:80)	19.41	43.58
GA:MD (0:100)	12.91	29.74
Turmeric	16.38	11.94

Table 2 Half life of entrapped curcumin, TV prepared from various wall material with 1% pullulan v/s turmeric oleoresin

[1]GA: Gum Arabic; MD: Maltodextrin of 18 DE

The half life of curcumin and TV in turmeric oleoresin was 16.38 and 11.94 weeks, respectively. The corresponding values for these constituents in microcapsules prepared with gum Arabic supplemented with 1 % pullulan were 38.08 weeks for curcumin, and 76.15 weeks for TV (Table 2). The reasons for the differences observed among other wall materials used need to be investigated.

Conclusion

Replacement of diluent and non-polymeric stabilizer with pullulan and its supplementation with polymeric stabilizer as an emulsifier and encapsulant gave a stable emulsion. Gum arabic supplemented with 1% pullulan proved to be a better wall material for encapsulation of turmeric oleoresin as compared to the other blends of gum arabic and maltodextrin with 1% pullulan as wall materials.

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