Investigation the Physicochemical Properties and Stability of W/O Emulsion

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(Received on 8th January 2013, accepted in revised form 27th June 2013)

Summary: The study aims to investigate the stability of W/O emulsions with respect to coalescence time. The various concentrations of water were dispersed in oil phase (soybean oil). The compositions of organic and aqueous phases were varied by adding emulsifier (Monoglyceride), sodium chloride and thickening agent (mango's pulp). The technique employed for the mixing of two phases was homogenization. The Emulsion Stability Index (ESI), Viscosity changes, separation of organic and aqueous phases as a function of storage time have been studied. It has been found that monoglyceride increases the stability and decreases the emulsion stability index (ESI) and also decreases the viscosity changes with storage time while electrolytes and mango's pulp encourage the coalescence process and enhance the instability of the system. On the other hand the system that contained all the organic and aqueous ingredients showed high stability.

Key Words: W/O Emulsion, Emulsion Stability Index (ESI), Viscosity, Storage Time, Optical Microscopy.

Introduction

An emulsion is a colloidal mixture of two immiscible liquids where one of the liquid dispersed in the form of droplets throughout the other**.** Generally water-in-oil emulsions are thermodynamically unstable, due to large area of oil and water interface which provides positive free energy which causes instability in such system [1, 2]. On the other hand different types of W/O emulsions are used in as bakery fat, cakes, cookies, breads, pastries, and face creams [3, 4]. The stability of water-in-oil emulsion system depends on the rate of coalescence. The properties of the interfacial film will determine the stability of emulsions. The coalescence of droplets in the emulsion is initiated by the collision of droplets. The coalescing droplets can be deformed by the contact zone of the droplets which are flattened [5]. Between the droplets a sphere of an uneven thin liquid film develops which influences the stability of the droplets [6]. Some attractive and repulsive forces are also present in the emulsion system. These forces determine whether droplets coalesce, aggregates or rebound [7]. The attractive forces play important role. If these forces are predominant, the system becomes unstable, and the film of the emulsion becomes thin. At a critical film thickness, the film might rupture and cause coalescence in the emulsion. When the repulsive forces are predominant the droplets repel each other and coalescence cannot occur easily. Coalescence kinetics is governed by collision frequency and the coalescence probability and this process restricts the applications of food as well as in cosmetics industries [8, 9, 10].

The stability of emulsion is very important for various industrial processes. It is very difficult to maintain the stability of an emulsion [11, 12]. Many attempts have been made to make emulsion stable, such as, by using emulsifier, salts and polymers [13]. The addition of protein/ polysaccharides may increase the viscosity of aqueous phase and so increase the viscosity and stability of W/O emulsions [14]. Further by using different devices for emulsification, the effect of salt on the particle size distribution, effect of water contents on sedimentation and coalescence process have been investigated with respect of coalescence time [15, 16].

Previously we have investigated the impact of various parameters over the quality and stability of oil-in-water and water-in-oil systems [17-21]. In this attempt we investigated the stability of W/O emulsions with storage time. The emulsion stability index (ESI) and change in viscosity were measured daily as a function of storage time till the organic and aqueous layers were separated from each other. A model has presented in order to study the instability mechanism with special reference of coalescence process in W/O emulsions.

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Results and Discussion

ESI Measurement

In the current investigation, the effects of different concentrations of water over the stability of water-in-oil emulsion were studied, using fixed amounts of emulsifier (monoglyceride), sodium chloride and the mango's pulp. These studied were made as a function of storage time. The emulsion stability index (ESI) of different water contents in water-in-soybean oil is plotted as a function of storage time (Fig. 1). The figure shows that ESI increases with storage time. This increase could be due to the occurrence of the sedimentation and then coalescence processes with storage time. The shelf life of such system could not maintain and hence the system might separate. It could be observed that the emulsion stability index increased after 48 hours but was found to be higher at the 72 hours and hence the two layers were started to separate from each other, later. It could be due to the occurrence of coalescence processes, increased after 24 hours and might occur due to reduction of the distance between the droplets and between the droplets and the interface [22]. The main cause of separation of two layers was the separation of water layer which measures the emulsion stability [23]. Further it was investigated that the separation occurred more easily in higher contents of water due to increased coalescence/ sedimentation process. To study the effect of emulsifier over the ESI of the emulsion, Monoglyceride was added to the system. The figure (Fig. 2) shows that ESI increases slowly with the storage time indicating that monoglyceride played an important role of emulsifier and retarded the movement of the droplets hence separating the two layers easily [24]. The figure (Fig. 3) shows that ESI increased with addition of NaCl resulting in the separation of water from oil fastly, favoring the coalescence process [25]. The role of mango's pulp as a thickening agent was also investigated (Fig. 4). The figure shows that in the presence of mango's pulp the ESI increased with the increase of storage time and mango's pulp was found not to be helpful in the stability of emulsion thereby showing increased sedimentation. It was also investigated that pulp was soluble into the water and so hydrophilic attraction was found to be increased with mango's pulp resulting in the increased concentration of the aqueous phase. To study the role of all ingredients, a mango's pulp/salt/monoglyceride/w/o emulsion was prepared. The data was plotted as a function of storage time in Fig. 5 showing that ESI gradually increased with storage time. It could not only be the effect of monoglyceride alone but salt also might increase the stability of emulsions and reduce the ESI, in combination. The NaCl solution might increase the efficiency of emulsifier molecules to the surface of droplet and hence protecting the droplet against coalescence. The ESI increased with increase of contents of water and not by all the ingredients. It was explained previously that the increase of water contents might increase the separation rate due to the increase of water layer which might cause separation [23].

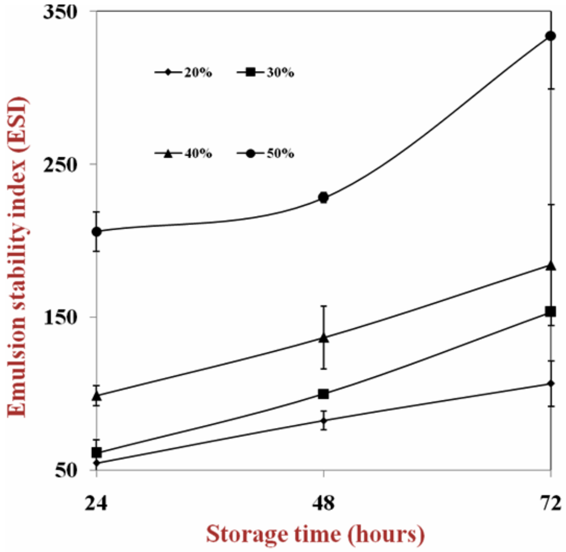


Fig 1: ESI of W/O emulsions as a function of storage time. (20-50% water contents)

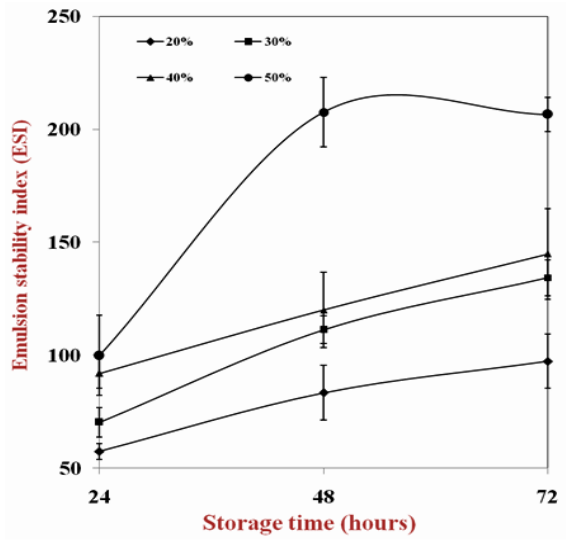


Fig. 2: ESI of W/O emulsions as a function of storage time. (0.05% Monoglyceride).

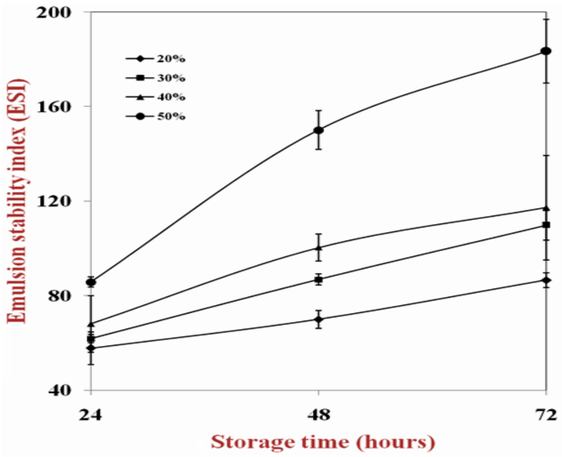


Fig. 3: ESI of W/O emulsions vs storage time (0.3% NaCl).

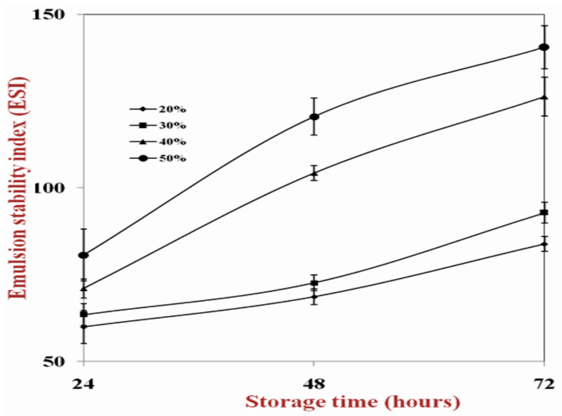


Fig. 4: ESI of W/O emulsions vs. storage time. (20-50% water contents; 0.5% mango's pulp in oil phase).

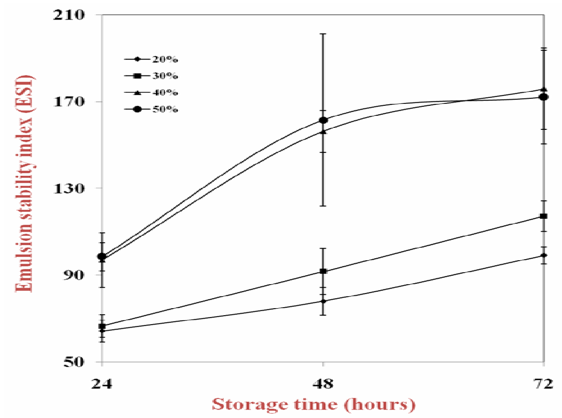
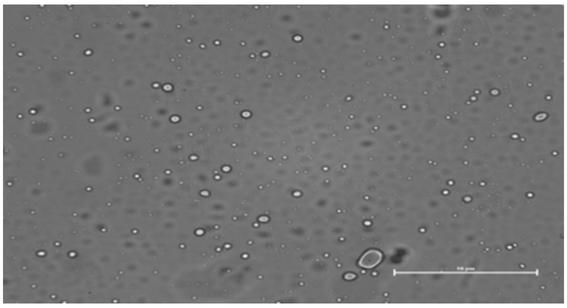


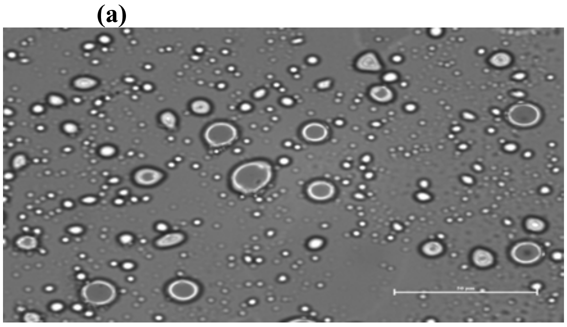
Fig. 5: ESI of W/O emulsions as a function of storage time. (20-50% water contents; Sodium Chloride and mango's pulp is 0.3% ; 0.5% Monoglyceride is 0.05% in oil phase).

Microstructures of W/O emulsions

The optical micro-structures of fresh and stored W/O emulsions are displayed in Fig. 6ab, thereby differentiating between the two images (fresh and stored). It was observed that there was no droplet attraction found in fresh emulsion as compared to the stored one (after 48 hours). Some droplets were found to be close to each other which might attribute to the fusion leading to the coalescence of emulsion (image b).



(a)



(b)

Fig. 6: Microstructures of 20% W/O emulsion having 0.05% monoglyceride (a) after emulsification (b) after 2 days of emulsification.

Change in Viscosity Measurement

The W/O emulsions were prepared using different contents of water. The change in viscosity is plotted as function of storage time (Fig. 7). The figure shows that there was an increased change in viscosity by increasing the storage time. This effect might be due to the viscosity change with storage time. The droplets might recombine together through flocculation/sedimentation processes causing coalescence due to gravity. The figure shows that viscosity changed slowly with storage time in the presence of monoglyceride (Fig. 8). The monoglyceride may form a protective layer on the W/O emulsion so the separation might be discouraged. It could be observed that monoglyceride might be deposited at the interfacial film between water droplets and oil phase thereby imparting the viscosity for a longer time hence stabilizing the water droplets and avoiding the coalescence mechanism [25]. The figure shows that the change in viscosity increased in the presence of NaCl which might be due to increased attraction between water and salt molecules [26]. The phenomenon could be explained by following equation [27].

$$P_g = \varphi_i \rho_w + (1 - \varphi_i)\rho_\circ \quad (3)$$

where

P_g = Density of the globule
ρ_o = Density of oil
ρ_w = Density of the water
φ_i = Internal droplet volume fraction

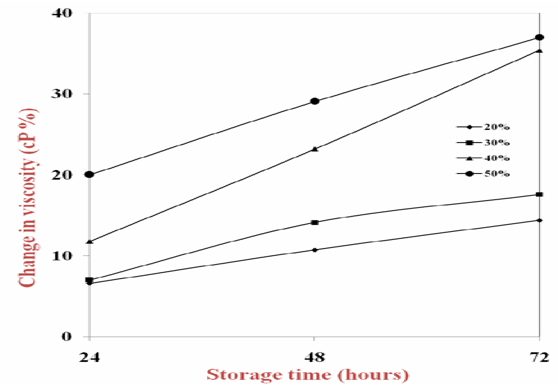


Fig. 7: Change in viscosity of W/O emulsions as a function of storage time. 20-50% water contents).

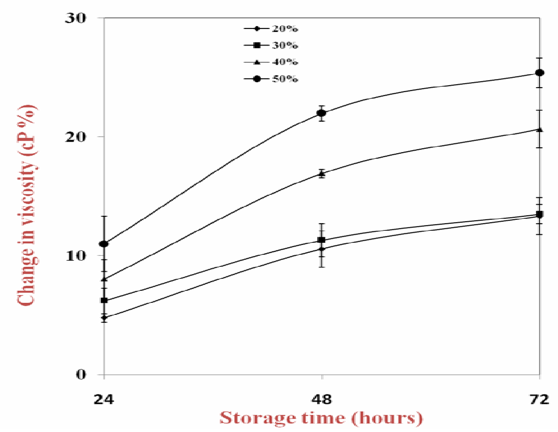


Fig. 8: Change in viscosity of W/O emulsions as a function of storage time. (20-50% water contents 0.05% Monoglyceride in oil phase).

The figure (Fig. 10) shows that the mango's pulp increased the viscosity of the emulsion but did not act as a stabilizer in W/O emulsion. The effect of all ingredients over the change in viscosity of mango's pulp/salt/monoglyceride/w/o emulsion was studied (Fig. 11). The figure shows that the viscosity of emulsion was found to be high and the change in viscosity took place very slowly. The effect may be due to the fact that mango's pulp might increase the viscosity and the system remains viscous for longer time [28]. The figure (Fig. 12ab) shows the separation of aqueous as well as organic layers with storage time. The trend of separation of different systems was found to be the same but the separation of these phases was different with storage time. The systems containing salt and mango's pulp increased the separation rate with the storage time. By adding the emulsifier and/or all other ingredients (mango's pulp/salt/monoglyceride/w/o emulsion) the separation rate was found to be slower. The reduction in the rate of separation might be due to the interaction of monoglyceride and salt thereby reducing the surface tension. The separation of aqueous phase was found to be higher as compared to organic layer as the separation of aqueous layer may cause the instability of W/O emulsions [23, 29].

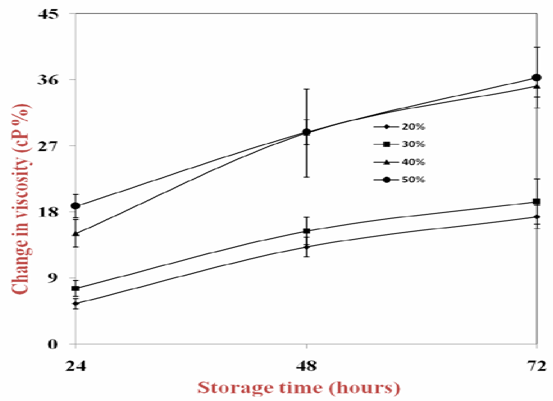


Fig. 9: Change in viscosity of W/O emulsions as a function of storage time.(20-50% water contents 0.3% NaCl in aqueous phase).

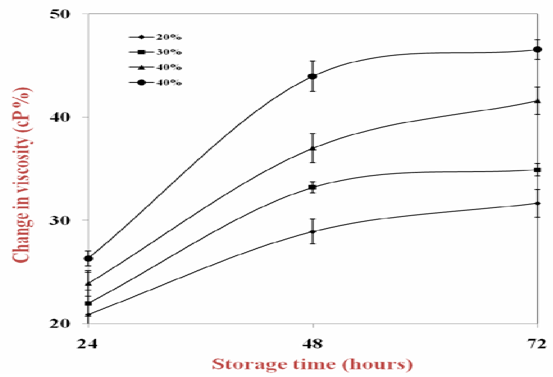


Fig. 10: Change in viscosity of W/O emulsions as a function of storage time (20-50% water contents 0.5% mango in aqueous phase).

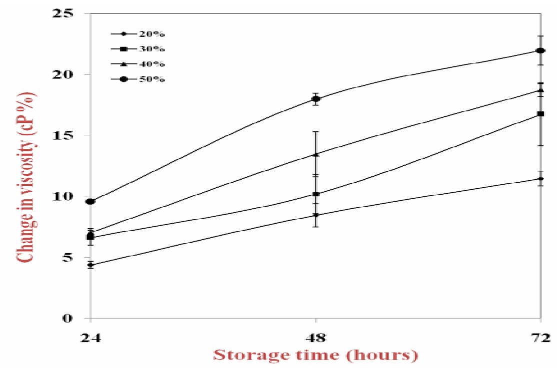
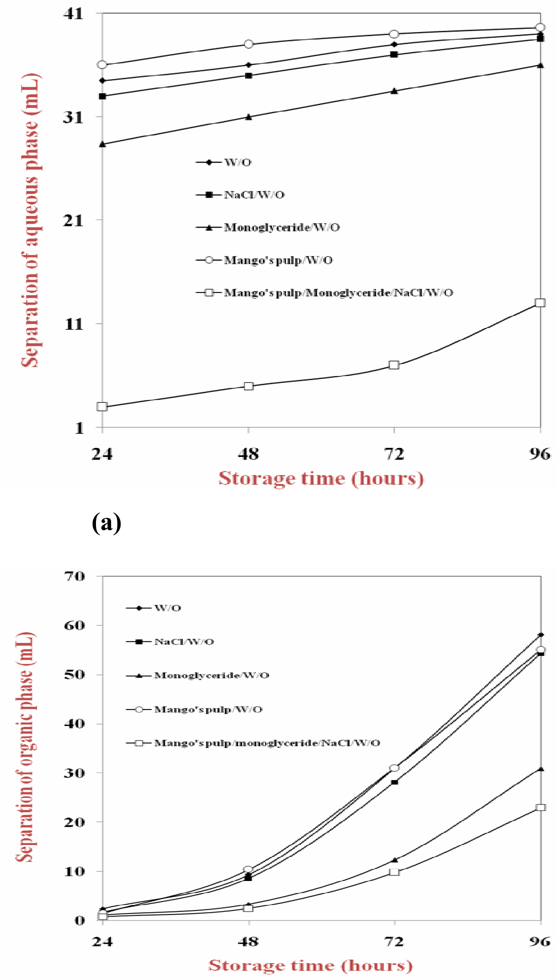


Fig. 11: Change in viscosity of W/O emulsions as a function of storage time. (20-50% water contents, 0.3% NaCl, 0.5% mango's pulp in aqueous phase, 0.05% Monoglyceride).



(a)

(b)

Fig. 12: Separation of phases of 40% W/O emulsions (a) aqueous phase (b) organic phase with storage time.

Experimental

Materials

Soybean oil was used in the study purchased from the local market. The surfactant, glyceryl monostearate, was obtained from Oleofine Organic SDN Shah Alam seianger Darul Ehsan, Malaysia. The water used for the preparation of emulsion, was freshly double distilled and de-ionized; its conductance was 5-10µS. The electrolyte, NaCl (E-Merck, Germany) and mango pulp. All the chemicals used were of analytical grade.

Sample Preparation

Aqueous and Oil Phases

Sodium Chloride (0.3% g/mL) and mango's pulp (0.5% g/mL) were prepared in aqueous phase. Mango's pulp was used as thickening agent, obtained from mango, purchased from the local market. The mango was washed with water. After that a known quantity of this pulp was mixed with de-ionized water and then was filtrated. It was mixed with water to form emulsion. The above mentioned known concentrations of NaCl and mango's pulp were mixed with different contents of water. The oil phase was prepared by adding glyceryl monostearate (0.05% (g/mL) surfactant to soybean oil and then heated to 50 °C until the surfactant was completely dissolved. The oil phase was then cooled to ambient temperature prior to utilization.

Preparation of Emulsion

The samples of W/O emulsions were prepared by emulsifying the known concentration of water into soybean oil at 600 RPM of homogenizer for 13 minutes using Ultra-Turix Homogenizer according to previous procedure [21]. Then the prepared systems were studied as a function of storage time.

Stability of Prepared Emulsions

The prepared emulsions were stored in clean air tight vessels to study the stability as a function of storage time. The samples for analysis were taken from the stored emulsions, using pipette and sucking it slowly so that the shear forces employed in this case should remain at minimum and not to affect the samples. It was also considered that the rest of the stored emulsions should not be disturbed or shaken during the process. The samples were taken at a pre determined time (24 hours) and were investigated as a function of coalescence/ storage time till the both layers were separated from each other.

Characterization of Emulsion

The prepared emulsions were subjected to different techniques, including optical microscopy, turbidity and viscometry to characterize the emulsion and to investigate the coalescence.

Microstructure Analysis

The optical microscopy was used to characterized the W/O emulsions. An optical microscope (C1 Digital Eclipse, Nikon,Tokyo, Japan) with a 60× objective lens was used to capture images of the emulsions. Emulsions were gently stirred to form a homogenous mixture without forming air bubbles. A small aliquot of these emulsions was then transferred to a glass microscope slide covered with a glass cover slip. The cover slip was fixed to the slide using nail polish to avoid evaporation. A small amount of immersion oil (Type A, Nikon, Melville, NY) was placed on top of the cover slip.

Viscosity Measurement

The viscosity of W/O emulsion was measured, using DV_E Viscometer (Brookfield, Germany). A fixed amount of emulsion was taken in adopter and analyzed at 60 shear rate (S^{-1}). The change in viscosity ($cP\%$) was calculated using equation 1.

$$cP\% = \frac{Vi - Vf}{Vi} \times 100 \qquad (1)$$

where

$cP\%$ = Change in viscosity
V_i= Viscosity of fresh emulsion
V_f = Viscosity of stored emulsion

Turbidity Measurements

The turbidity of emulsions was obtained by Turbidity meter model 800 Engineered Systems & Designs, Inc, USA. The instrument was calibrated with de-ionized water to adjust zero, whereas Formozine standard solution of 200 NTU for verification. After standardization, the measurements were made with emulsification and coalescence time. From turbidity measurement the Emulsion Stability Index (ESI) was calculated by following formula:

$$ESI = \frac{T(o) \times t}{T(t) - T(o)} \quad \ldots\ldots\ldots (2)$$

where *T (o)* and *T(t)* are the initial mean turbidity and the turbidity at time t, respectively.

Conclusions

The study investigates the effect of different parameters over the stability as well as the change in viscosity of W/O emulsions. Increase of water contents and addition of salts or mango's pulp encouraged the coalescence and instability of W/O emulsions. Mango's pulp increased the viscosity. Monoglyceride attributed to the increased shelf life as well as the stability of W/O emulsions. The ingredients (mango's pulp/salt/monoglyceride) in W/O emulsion showed high stability of the system. This work could lead the quality as well the stability purposes of W/O emulsions in food, cosmetic and pharmaceutical industries.

Acknowledgments

We thank Professor David Julian McClements, Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01003, USA for his help and useful discussion. One of the authors (Mr. Shahid Iqbal) is thankful to the Higher Education Commission (Pakistan) for financial support under the International Research Support Initiative Program (IRSIP).

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