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Preparation of microcapsules with multi-layers structure stabilized by chitosan and sodium dodecyl sulfate

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ABSTRACT

The microcapsules with oil core and multi-layers shell were developed from poly-cationic chitosan (CS) and anionic SDS in multistep electrostatic layer by layer deposition technique combined with oil in water emulsification process. The net charge of microcapsules determined by zeta potential indicated that microcapsules are highly positive charged because of poly-cationic nature of CS, and charge neutralization of microcapsules occurred after alkali treatment. The granulometry measurement showed increase in average diameter of microcapsules by alkali treatment suggesting swelling or formation of small aggregates. The morphology analysis of microcapsules by optical microscopy corroborated the results of granulometry, and diameter of microcapsules was found to be decreased in multistep process due to tight packing of layers in outer shell of microcapsules. The alkali treatment of microcapsules to solidify outer shell was optimized with 0.02 N NaOH to reduce microcapsules aggregation and gel formation by CS chains as found in optical micrographs.

1. Introduction

Microcapsulation is a technique by which various bioactive materials like drugs (Bouchemal et al., 2004; Pouton & Akhtar, 1996) bioactive proteins (Kwak, Ihm, & Ahn, 2001), pesticides (Scher, Rodson, & Lee, 1998), probiotics, and different active materials used in textile products like phase change materials (Mondal, 2008), antimicrobial fabrics (Saraswathi, Krishnan, & Dilip, 2010), and insect repellents (Specos et al., 2010), long lasting perfume and skin softeners (Rodrigues et al., 2009) are encapsulated into microscopic size materials called microcapsules through the formation of a thin wall around the core materials. The commercially available microcapsules vary in size ranging from less than 1 to 250 μm. The advantages of microcapsulation are described as the controlled release of encapsulated bioactive materials, protection of encapsulated materials from oxidation, and imparting stability to environmental stress (Bansode, Banarjee, Gaikwad, Jadhav, & Thorat, 2010). Microcapsule formation involves different techniques like coacervation, phase separation, interfacial polymerization, and mechanical methods (Obeidat, 2009; Watts, Davies, & Melia, 1990). The effective microcapsule formation through coacervation process depends on several factors such as selection of emulsifier/combination of emulsifiers used in the preparation of oil in water or water in oil emulsions, the polymer/combination of polymers to create the shell materials around the core materials, and the combination of emulsifier and polymer (Ogawa, Decker, & McClements, 2003a).

Conventionally, oil in water emulsion, which consists of small oil droplets dispersed in aqueous medium, is created by homogenizing oil phase and aqueous phase together in presence of emulsifier. An emulsifier is a surface active material that adsorbs to the surface of freshly formed oil droplets in the emulsion during homogenization. The main functions of the emulsifiers are to decrease the average size of oil droplets in the emulsion by reducing interfacial tension between oil and water during homogenization, and prevent droplets from aggregation by developing interfacial protective membranes and generating repulsive force between oil droplets (Mun, Decker, & McClements, 2006). There is a wide variety of natural and synthetic emulsifiers including surfactants, polysaccharides, phospholipids, and proteins, and each emulsifier has its own advantages and disadvantages depending on the stability and size of oil droplets of emulsion (Qian & McClements, 2011). However, some scientific articles reported that surfactant stabilized oil droplets in oil in water emulsion were more protected against oxidation than protein-stabilized interfaces in presence of catalyst

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made of equimolar iron–ethylenediaminetetraacetic acid complex (Berton, Ropers, Viau, & Genot, 2011).

It has been reported in many scientific articles that microcapsules with multilayer shell membranes could be prepared by an electrostatic layer by layer deposition technique (Sukhorukov, Fery, & Möhwald, 2005). The electrostatic layer by layer deposition technique offers microcapsules having very good stability to pH, ionic strength and thermal processing (Ogawa, Decker, & McClements, 2003b). The biodegradable polymers have already been proved to be useful as carriers for different bioactive materials (Park, Ye, & Park, 2005), and especially, microcapsules formed from ionic biopolymer like chitosan (CS) are reported to have novel encapsulating and release properties for various encapsulated bioactive materials (Grenha et al., 2005; Peng, Xiong, Li, Chen, & Zhao, 2010). In this study, CS has been selected as a natural cationic biopolymer to create microcapsules with multilayer structure around the oil droplets by electrostatic layer by layer deposition technique using SDS as an anionic emulsifier. CS is co-biopolymer of glucosamine monomers and small amount of N-acetyl-glucosamine monomers depending on the degree of alkaline deacetylation of chitin, which is the second most abundant biopolymer in the Earth after cellulose. Numerous reports on the applications of CS from food processing (No & Kim, 2006), pharmaceutical and biomedical fields (Ueno, Mori, & Fujinaga, 2001) to wastewater treatment (Crini & Badot, 2008; Guibal, 2004) are available in the literature and most of the cases, CS is found extremely attractive due to its biocompatibility, biodegradability and nontoxicity (Prashanth & Tharanathan, 2007). CS is soluble in dilute acid solutions having $pK_a \approx 6.5$ and it becomes precipitated from the aqueous solution by increasing pH to neutral or alkaline range (Schatz, Viton, Delair, Pichot, & Domard, 2003). The selection of CS as a shell material for microcapsules is advantageous in the view of biodegradable nature of the polymer, and the delayed release of encapsulated materials from microcapsules. In fact, cationic CS could be adsorbed on the surfaces of oil droplets stabilized by anionic sodium dodecyl sulfate (SDS) surfactant molecules by electrostatic interaction (Aoki, Decker, & McClements, 2005). Under certain conditions, the oil in water emulsion having SDS as an emulsifier becomes unstable to creaming with CS addition due to charge neutralization and bridging flocculation, indicating strong electrostatic interactions between negatively charged SDS stabilized oil droplets and positively charged CS molecules (Mun et al., 2006). With further addition of CS in emulsion, the creamy portion disappears and stable emulsion is reformed, suggesting that stable microcapsules are only formed when CS concentration in the emulsion is enough to completely saturate the droplet surfaces and electrical charges of microcapsules completely switch from negative to positive charges (Mun et al., 2006).

In this study, the process of microcapsule formation is carried out in oil in water emulsion by electrostatic layer by layer deposition method using CS as a cationic biopolymer and anionic SDS as an anionic emulsifier in the system. The selection of SDS as an anionic emulsifier in the system is based on the fact that SDS molecules can be rapidly adsorbed on the oil droplets during preparation of oil in water emulsion by homogenization process. The alternative addition of SDS solution and CS solution to the freshly prepared microcapsule suspension is repeated for several cycles to develop multi-layer structure on the microcapsules having increased structural rigidity to environmental stresses for various practical applications. The net charge, average size, and morphology of the microcapsules are monitored by zeta potential and size distribution measurements, as well as optical microscopy, and, the characterizations by zeta potential and size distributions are performed at each step of SDS and CS addition during microcapsules formation in order to develop novel and effective CS based microcapsules as carrier molecules for linseed oil as an active substances.

2. Materials and methods

2.1. Materials

Low molecular weight CS (deacetylation = 75–85% and molecular weight = 50,000–190,000), sodium dodecyl sulfate (SDS), linseed oil and all other analytical grade chemicals such as sodium hydroxide (NaOH), acetic acid, hydrochloric acid (HCl) were purchased from Sigma–Aldrich Co. LLC.

2.2. Solution preparation

3.0 g of CS powder was completely dissolved in 100 ml of 2% (v/v) acetic acid aqueous solution (3%, w/v) at 50 °C in magnetic stirring condition at 1500 rpm. The pH of as prepared CS solution in acetic acid solution was found to be 3.4. The SDS solution was prepared by dissolving 10 g of SDS in 1000 ml of de-ionized water and the pH of SDS solution was found at 5.4.

2.3. Microcapsule formation from oil in water emulsion

2.3.1. Formation of the first layer

The oil in water emulsion was prepared by 80 wt% of aqueous SDS solution (continuous phase), and 20 wt% linseed oil as organic phase under homogenizing condition at 16,000 rpm and 50 °C for 30 min. The oil in water emulsion contains SDS as an anionic emulsifier at a concentration of 8 g/l. The foams developed in oil in water emulsion using SDS as emulsifier by homogenization was removed by allowing to stand it at 50 °C for 3 h under magnetic stirring at 1500 rpm. The microcapsules of CS and SDS were formed through electrostatic layer by layer deposition method with the addition of 35 ml of CS solution (3%, w/v) in 100 ml of oil in water emulsion under homogenization condition at 50 °C and 16,000 rpm for 15 min using homogenizer (Ultra-Turrax, T-25 basic, IKA®WERE, Germany). The as prepared microcapsule suspension contains 15.0 wt% of oil and 0.77% (w/v) of CS, and SDS concentration in the suspension was 5.9 g/l (26.0 mM). The as prepared microcapsule suspension was kept standing for 1 h at 50 °C to reach stability, and the pH of as prepared microcapsule suspension was measured at 4.2.

2.3.2. Formation of the multi-layers

40 ml of 10 g/l SDS solution was added in the as prepared microcapsule suspension followed by the addition of 20 ml 3% (w/v) CS solution at 50 °C and 1500 rpm, and the process of alternative SDS and CS addition to the as prepared microcapsule suspension was continued for 10 cycles to increase the layer numbers of SDS and CS on the multi-layer structure of microcapsules. Here, each cycle of total 10 cycles denotes the alternate addition of 40 ml SDS solution, and then 20 ml CS solution to the as prepared microcapsule suspension under magnetic stirring condition. In this context, the microcapsules are designated as 1 layer, 2 layers and so on, up to 10 layers depending on the number of cycles applied during microcapsule formation, and the microcapsules with 1 layer indicate the microcapsules just obtained after addition of CS solution to oil in water emulsion. The alternative addition of SDS and CS to as prepared suspension was done at 30 min interval. The pH of microcapsule suspension throughout the process with alternative SDS and CS addition was maintained at a constant value ($pH \approx 4.2$) that was obtained for the as prepared microcapsule suspension, and the pH adjustment of as prepared microcapsule suspension after consecutive SDS and CS addition was done by drop wise addition of 0.1 N HCl solution and 0.1 N NaOH solution, respectively. The whole process of microcapsules formation by layer by layer technique is schematized in Fig. 1.

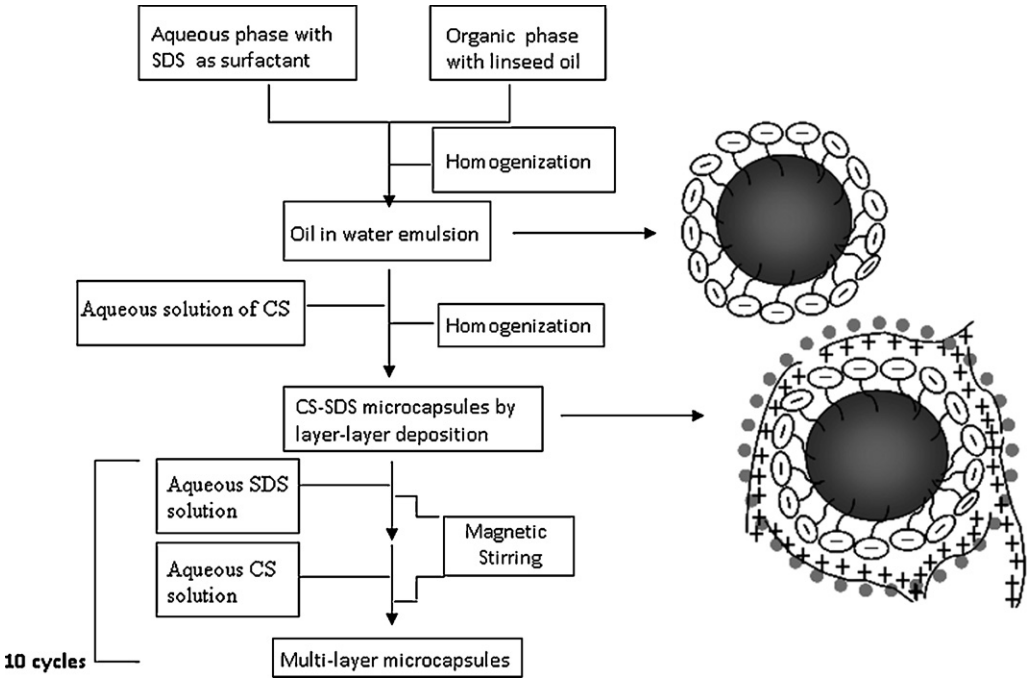

Fig. 1. Schematic diagram of microcapsule formation by electrostatic layer by layer deposition using CS and SDS.

2.3.3. Alkali treatment of microcapsule suspension

The as prepared microcapsule suspension (5 ml) with various layer numbers was dispersed in 20 ml of 0.02 N NaOH solution at 30 °C under stirring condition of 1500 rpm for 10 min, followed by standing at room temperature for 12 h in order to neutralize positive charge of microcapsules as well as for solidification of outer shell on the microcapsules by alkali treatment. The pH of microcapsule suspension after alkali treatment changed from pH 4.2 to 5.4, and with increase in NaOH concentration during alkali treatment up to 1.0 N, pH of the microcapsule suspension could be attained more close to neutral as well as alkaline pH. The precipitation of CS from acetic acid solution by NaOH solution occurs through liquid–liquid phase separation method because NaOH molecules react both with protonated amine groups (NH_2) of CS and acetic acid in CS solution (Lamarque, Lucas, Viton, & Domard, 2005). The alkali treated microcapsules were obtained in the drying state after drying in thermostatic oven at 50 °C for 3 h and kept in desiccators for future use after redispersing in de-ionized water.

2.4. Characterization

The zeta potential of microcapsule suspension was measured using Zetasizer 2000, Malvern instruments Ltd., Malvern, UK, by electrophoresis method after 1000 times dilution of the sample in de-ionized water. The size distribution analysis (granulometry) of microcapsules suspension was performed using Accusizer Particle Sizing Systems (770 Optical Particle Sizer, and 770A Autodiluter), Santa Barbara, CA, USA after diluting the sample by 1000 times in de-ionized water to measure the average size of microcapsules. The optical microscopy was performed using Axioskos Zeiss equipped with a camera (IVC 800 12S) in order to determine the microstructure of the microcapsules. The scanning electron microscopy (SEM) of microcapsules was done using a Leica Cambridge S-360 Microscope with an acceleration voltage of 20 kV.

3. Results and discussion

3.1. Formation of microcapsules in oil in water emulsion by electrostatic layer by layer deposition method

The oil in water emulsion using SDS as anionic emulsifier gave rise to oil droplets surrounded by anionic SDS molecules. The formation of microcapsules started when drops of CS solution were added to the emulsion under homogenizing condition. The oppositely charged SDS and CS come into contact with one another and a shell membrane is formed around oil droplet to give microcapsules. This effect results in shrinkage of oil droplets in the emulsion. Such a network is not only stabilized by electrostatic interaction but also combination of electrostatic, ion-dipole, and hydrophobic interactions (Lapitsky & Kaler, 2004; Thongngam & Julian McClements, 2004). After the first shell membrane layer is formed from CS and SDS interactions, the unbound CS molecules in the emulsion diffuse through the layer for binding with free SDS binding sites attached to oil droplets in emulsion.

The alternative addition of SDS and CS solution in as prepared microcapsule suspension was repeated for ten cycles in order to add more alternate layers of SDS and CS in the shell membrane structure of microcapsules (Fig. 1). The combination of different interactions such as electrostatic, ion-dipole, and hydrophobic could increase the layer numbers on the shell structure of microcapsules. However, SDS and CS molecules in the emulsion are not only supposed to be involved in the microcapsule formation, and there should be some free SDS molecules present in emulsion that adsorb to cationic CS molecules through a strong electrostatic attraction to form complexes (Thongngam & Julian McClements, 2005) under homogenization condition depending on the amount of SDS and CS in the system. The micro-sized complexes of SDS and CS could deposit on the shell membrane structure of microcapsules by coacervation process or remain as microparticles/aggregated form in the emulsion. In this way, alkali treatment of microcapsule suspension gives rise to alkali stabilized microcapsules by charge neutralization, as well

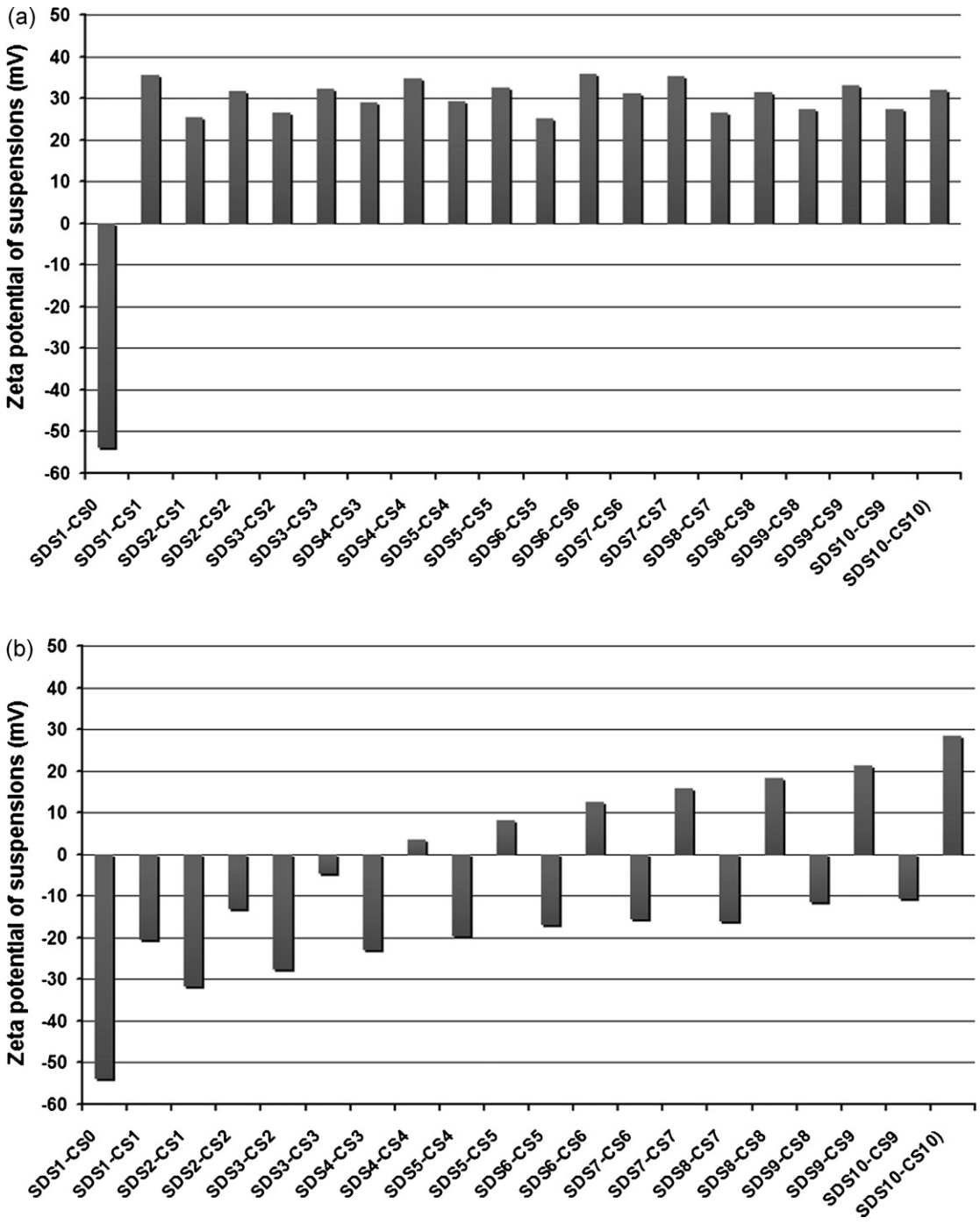

Fig. 2. Zeta potential analysis of microcapsule suspension (a); alkali treated microcapsule suspension (b); after each addition of CS and SDS during layer by layer formation on microcapsules (where SDS_i–CS_j represents the layer number, with the indexes *i* and *j* are SDS and CS number layers, respectively).

as gel materials made of CS and SDS complexes, and only CS molecules.

3.2. Influence of CS and SDS on the microcapsulation process

The microcapsules suspension formed from CS and SDS showed a characteristic white color at the initial stage of microcapsulation process, and it turned into yellow color during multilayer formation. The influence of CS and SDS on the microcapsulation process was monitored using zeta potential, particle size distribution (granulometry) and optical microscopy.

The zeta potential analysis was performed in this study to obtain information of charge density on the surface of microcapsules. As shown in Fig. 2a, the negative zeta potential of oil in water emulsion (−53.8 mV) indicated that SDS as an anionic emulsifier imparted negative charge in the emulsion at a pH of around 5.4. Fig. 2a shows that after addition of 35 ml CS in the emulsion, the electrical charge on the oil droplets changed from negative (−53.8 mV) to positive (+35.6 mV) and net electrical charge of emulsion droplets gradually changed from negative to positive with increase in CS concentration in emulsion (data not shown). This change in net electrical charge of droplets indicates that microcapsules are formed by strong interaction between positively charged

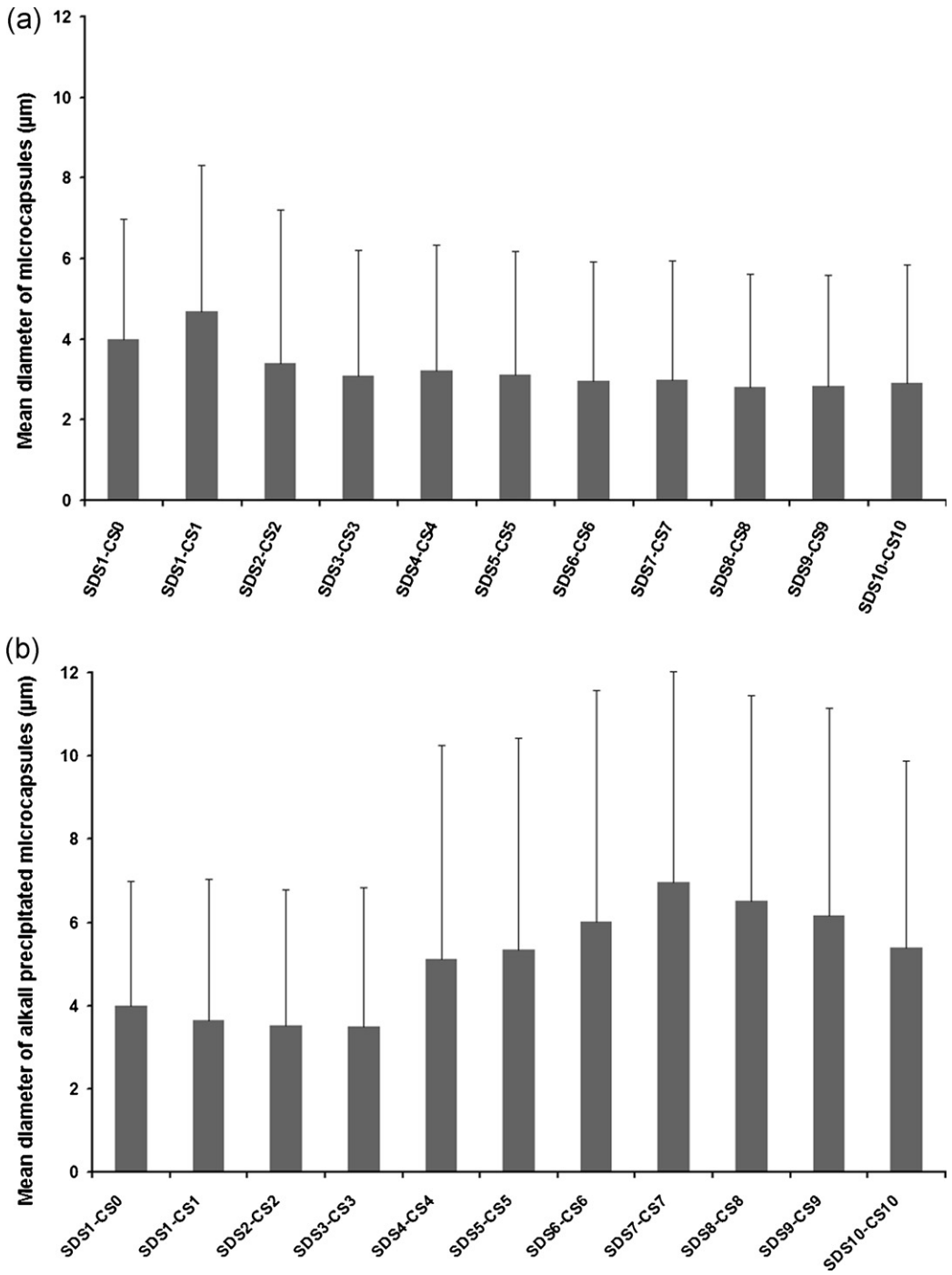

Fig. 3. Average diameter of microcapsule suspension (a); alkali treated microcapsule suspension (b); after each cycle of alternate addition of CS and SDS during layer by layer formation on microcapsules (where SDS_i–CS_j represents the layer number, with the indexes *i* and *j* are SDS and CS number layers, respectively).

CS and anionic SDS molecules around the oil droplets and CS molecules are adsorbed to the surface of SDS coated oil droplets in emulsion. The binding of cationic CS molecules to oppositely charged surface of oil droplets causes reversal of charge to high positive charge of the microcapsules. The high positive charge of microcapsules (overcharging) in the emulsion occurs because only a fraction of positively charged amine groups of CS are required to neutralize oppositely charged group on the surface of emulsion droplets and the remainder of the charged groups on CS could diffuse into aqueous phase or could be in contact with the surface of emulsion droplets having no charges (Dobrynin, 2001). The addition of 40 ml SDS (10 g/l) in as prepared microcapsules suspension for multilayer formation on microcapsules changed electrical charge of the surface of microcapsules from +35.6 mV to +25.3 mV, indicating that a fraction of positively charged amine groups of CS molecules are neutralized by complex formation with SDS. The addition of further 20 ml CS to emulsion increased overcharging of positive charge to +31.6 mV from +25.3 mV. However, the net increase in overcharging during 2 layers formation is found less (+6.3 mV) than that of during formation of 1 layer (+89.4 mV) in the system, indicating that there are still some free negatively charged binding groups of SDS, which are eventually binding with CS molecules during successive layers formation on the membrane structure of microcapsules. The same phenomenon

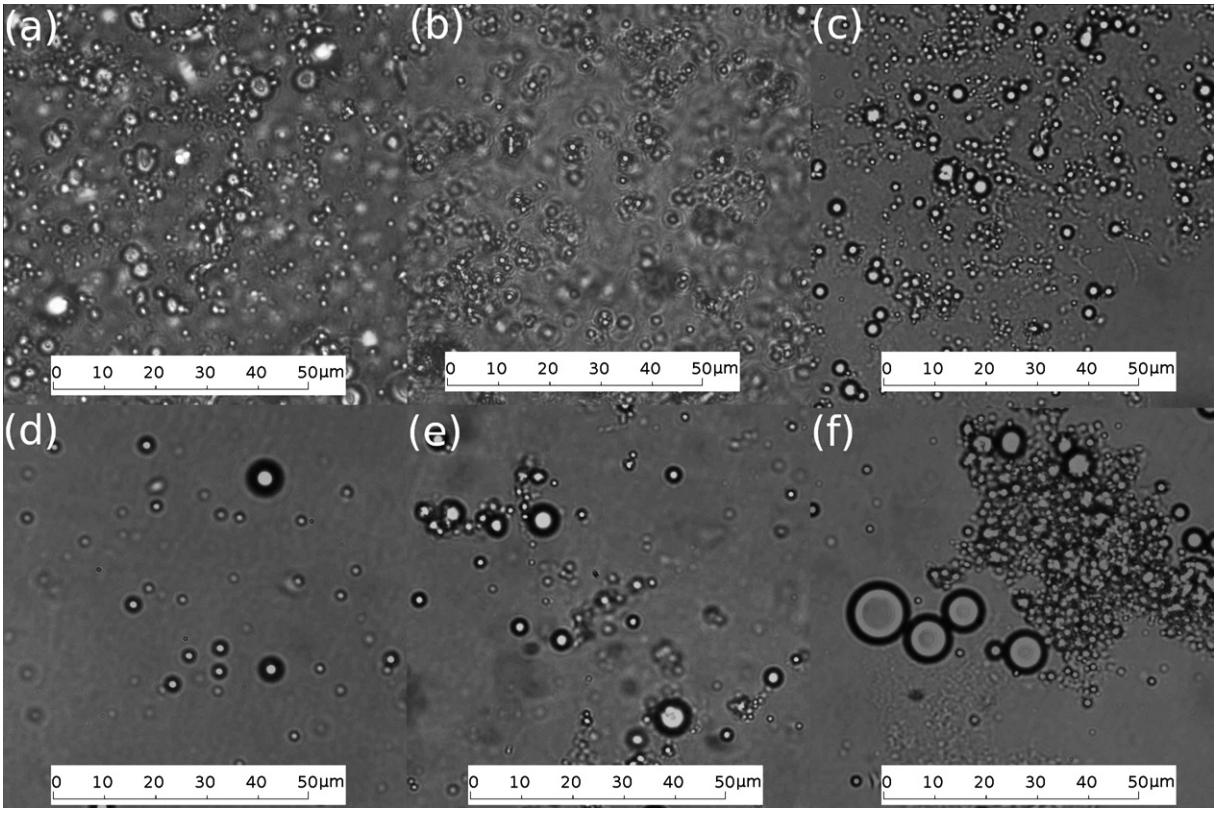

Fig. 4. Optical microscope images for microcapsules at magnification of 40× with 1 layer (a), 4 layers (b), 10 layers (c), and alkali treated microcapsules with 1 layer (d), 4 layers (e), 10 layers (f), with 0.02 N NaOH.

was found to occur during successive layers formation by alternative addition of SDS and CS solutions in as prepared microcapsule suspension up to 10 layers. The pH of microcapsule suspension was maintained throughout the process at a pH of 4.2 that was obtained after the formation of microcapsules in the emulsion after addition of CS in oil in water emulsion at the initial stage (1 layer).

The particle size distribution of microcapsules suspension was performed in this study to determine the average size of the microcapsules, and the measurement of average diameter of microcapsules was made considering diameter range of microcapsules from 0.59 to 20.02 μm. The average diameters and size distribution of oil droplets in the emulsion increased from 4.00 ± 2.98 μm to 4.69 ± 3.62 μm after CS addition in emulsion to form microcapsules by developing shell membranes around the oil droplets as obtained in the particle size distribution analysis. As shown in Fig. 3a, the average diameters and size distribution of microcapsules were found to be decreased from 4.69 ± 3.62 μm (1 layer) to 2.91 ± 2.94 μm (10 layers) with the increasing layer numbers of microcapsules by alternative addition of SDS and CS during electrostatic layer by layer deposition, and this observation suggests that strong electrostatic interaction between SDS and CS on the microcapsules results in tight packing of layers on the microcapsules. Moreover, the decrease in average diameter of the microcapsules with increase in layer numbers indicates the stability of microcapsules to the aggregation due to strong electrostatic repulsion between the microcapsules.

The optical microscope images of microcapsules with 1 layer (Fig. 4a), 4 layers (Fig. 4b), and 10 layers (Fig. 4c) at 40× magnification showed that interactions between oppositely charged SDS (anionic) and CS (cationic) give membrane structure around the emulsion droplets as in the form of microcapsules. The microcapsules are well dispersed in oil in water emulsion, and the measurement of diameter of microcapsules in the optical micrographs indicates that diameters of the microcapsules with 1, 4, and 10 layers are varying in the range of 2.0–5.0 μm. However, microcapsules with 10 layers (Fig. 4c) and 4 layers (Fig. 4b) show less average diameter than microcapsules with 1 layer (Fig. 4a), indicating strong osmotic action of the membrane that leaves only linseed oil as core materials. These results are strongly supported by the size distribution results of microcapsules as described in the study before.

3.3. Influence of alkali treatment on the microcapsulation process

The alkali treated microcapsules suspension exhibited a characteristic yellow color with some visible agglomerates depending on the NaOH amount during alkali treatment as well as amount of uncoated polymer materials. The alkali treated microcapsules showed immediate phase separation after thorough agitation and no visual sign of degradation was observed after storing it for 1 month. The alkali treatment of microcapsules with NaOH solution was performed in order to solidify the outer shell of microcapsules, and the influence of alkali treatment on the microcapsulation process was characterized using zeta potential, particle size distribution (granulometry), optical microscopy and scanning electron microscopy.

The zeta potential measurement of microcapsules after alkali treatment with 0.02 N NaOH indicated that the net electrical charge of microcapsules with 1 layer was −20.4 mV (Fig. 2b), whereas that before alkali treatment was measured to be +35.6 mV (Fig. 2a). This result indicated that neutralization of positive charges of microcapsules from the state of overcharging due to CS is completed by alkali treatment, and the net negative charge on the microcapsules after alkali treatment could be possibly due to negative charge of SDS molecules on the emulsion droplets at pH 5.4 in the system. However, the net negative charge of alkali treated microcapsules

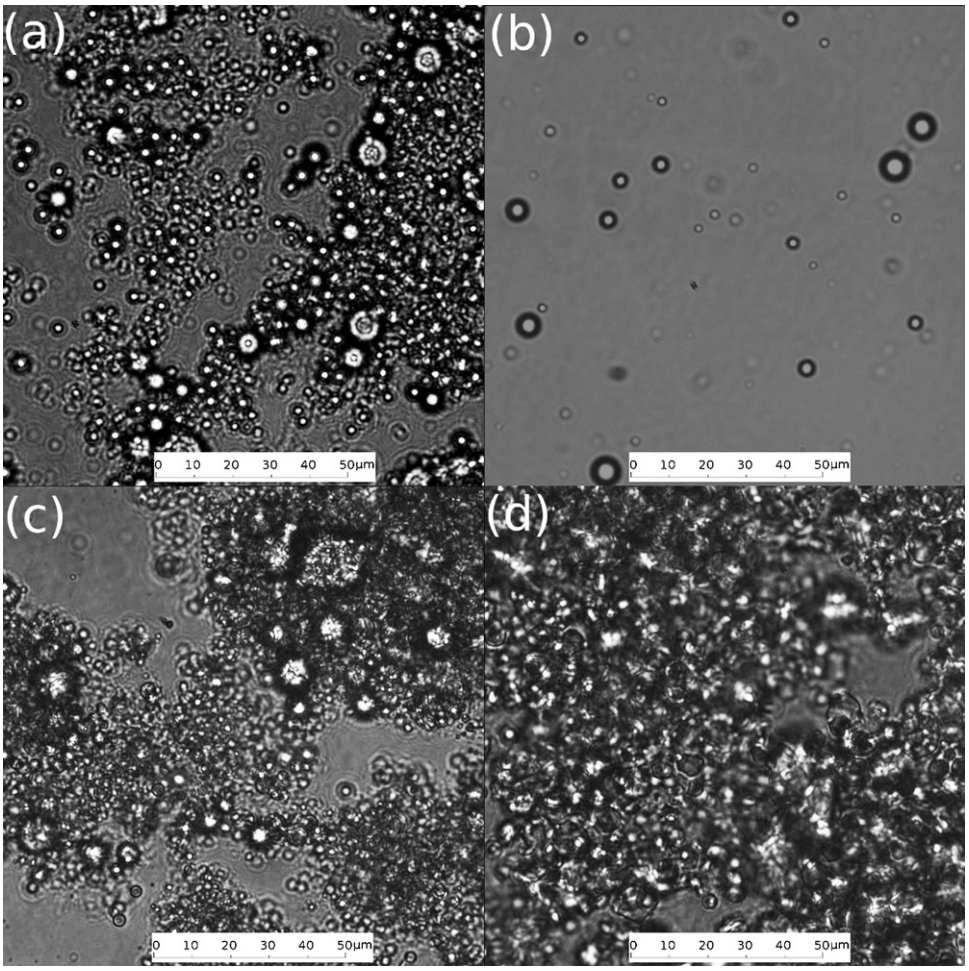

Fig. 5. Optical microscope images of alkali treated microcapsule suspensions (1 layer) at magnification of 40× using alkali treatment of 0.002 N NaOH (a), 0.02 N NaOH (b), 0.2 N NaOH (c), and 1.0 N NaOH (d).

was found to be decreased with the increase in layer numbers. The net charge of the alkali treated microcapsules after CS addition started to be positive from the 4 layers (+3.6 mV) to the maximum at 10 layers (+28.5 mV), indicating that alkali treatment of microcapsules suspension (5 ml) by 20 ml of 0.02 N NaOH is not enough to completely neutralize the positive charge of CS molecules on the microcapsules after 4 layers.

As shown in Fig. 3b, the average diameters of alkali treated microcapsules having 4–10 layer numbers were higher than those of the alkali treated microcapsules with 1–3 layers. The average diameter of alkali treated microcapsules was found to be increased to maximum value at 7 layers ($6.95 \pm 5.08\ \mu m$), suggesting that swelling of polymer shell of microcapsules might occur during alkali treatment of microcapsules with 4–10 layers. Also, alkali treated microcapsules with 4–10 layers could be held together by CS molecules that are adsorbed to more than one microcapsule (Pinotti, Bevilacqua, & Zaritzky, 1999). In this context, it should be taken into account that aggregation of alkali treated

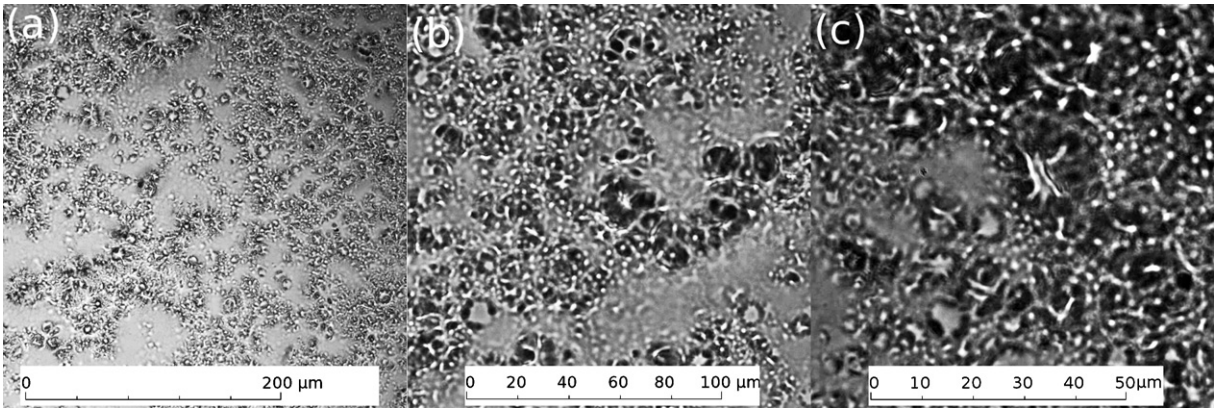

Fig. 6. Optical microscope images of drying phase of alkali treated microcapsules (1 layer) at magnifications of 10× (a), 20× (b) and 40× (c).

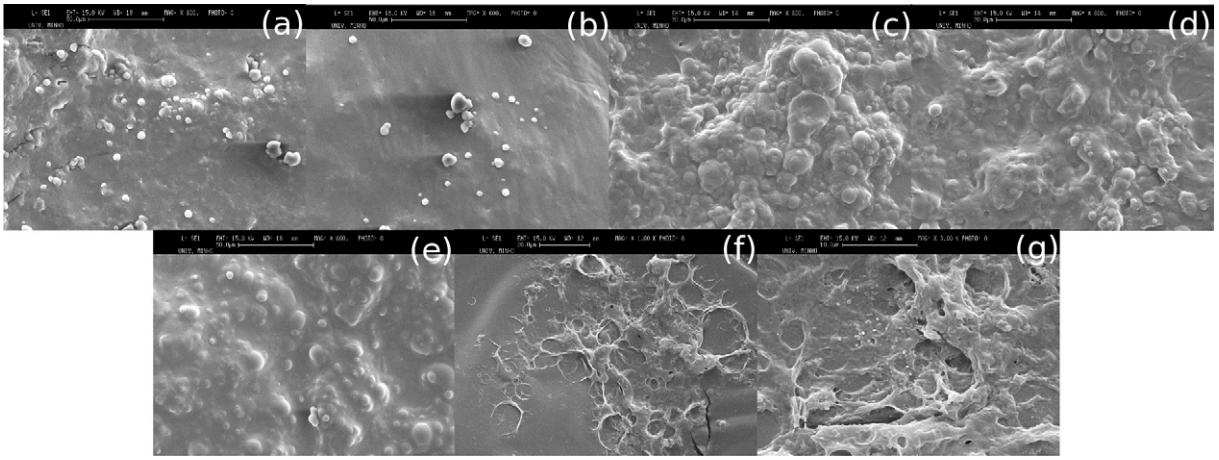

Fig. 7. SEM images of alkali treated microcapsules with 1 layer (a), 2 layers (b), 4 layers (c), 6 layers (d), 10 layers (e), drying at room temperature at 600×; 10 layers at 1000× (f), 3000× (g) after dilution and drying at room temperature.

microcapsules is low because the average diameter of microcapsules with 4–10 layers is increased maximum by 2 times compared to the mean diameter of alkali treated microcapsules with 1 layer ($3.63 \pm 3.40\,\mu m$). As shown in Fig. 3b, the smaller size of microcapsules with 1–3 layers than that of microcapsules with 4–10 layers after alkali treatment suggests that the negative charges on the microcapsules with 1–3 layers after alkali treatment are well enough to prevent aggregation of microcapsules as well as swelling of the polymer shell of microcapsules.

The optical micrographs of the alkali (0.02 N NaOH) treated microcapsules with different layer numbers; 1 layer (Fig. 4d), 4 layers (Fig. 4e), and 10 layers (Fig. 4f) at 40× magnification show that the diameter of the microcapsules after alkali treatment increases with increase in layer numbers. Also, the diameters of alkali treated microcapsules with 4 and 10 layers vary from 2 to 25 μm, while those with 1 layer vary in the small range of 2–10 μm. The diameter values of the microcapsules measured by optical microscopy are confirmed by granulometry (particle size distribution analysis). The average size of alkali treated microcapsules with 1 layer increased from $3.63 \pm 3.40\,\mu m$ to $5.11 \pm 5.14\,\mu m$ for 4 layers, and further increased to $5.39 \pm 4.50\,\mu m$ for 10 layers. Fig. 4f exhibits that some microcapsules are held together by CS molecules which are adsorbed on the surface of more than one microcapsule, and it occurs during alkali neutralization of microcapsules. Also, the swelling of microcapsules is found in Fig. 4f, and this is due to alkali treatment of microcapsules with higher layer numbers (10 layers). As observed in the micrographs of alkali precipitated microcapsule suspension, charge neutralization by alkali process creates some gel particles made of only CS molecules through liquid–liquid phase separation, which are in the aqueous phase as free CS chains before alkali treatment, as well as aggregation of some microcapsules in the suspension. This is the major problem with preparing concentrated microcapsule suspension for different applications.

The optical microscope images of alkali treated microcapsules (1 layer) with different amount of alkali; 0.002 N NaOH (Fig. 5a), 0.02 N NaOH (Fig. 5b), 0.2 N NaOH (Fig. 5c), and 1.0 N NaOH (Fig. 5d) at 40× magnification exhibit that diameters of alkali treated microcapsules vary in the small range of 2–10 μm. As shown in the micrographs, aggregation of microcapsules and gel particles formation by free CS chains are observed higher for alkali treatment of microcapsules with NaOH concentration above 0.02 N, and charge neutralization of the microcapsules with 0.002 N NaOH solution is not effective, resulting in incomplete solidification of outer shell of microcapsules. The microcapsules after alkali treatment with 0.02 N NaOH (Fig. 5b) are well dispersed in the suspension with proper solidification of outer shell of microcapsules, and also, the problem of gelation by free CS chains as well as aggregation of microcapsules are highly overcome by the process.

The optical microscope images of alkali treated microcapsules (1 layer) at 10× (Fig. 6a), 20× (Fig. 6b), and 40× (Fig. 6c) show that the polymer film is formed after drying the samples at 50 °C in a thermostatic oven for 3 h suggesting that the coalescence phenomena occur due to water evaporation and weak thermo-mechanical properties of shell materials. However, the drying phase of alkali treated microcapsules contains microcapsules embedded in the polymer film, and no oil release is found from the core materials of the microcapsules after drying process. Thereby, the observation suggests that the microcapsules could retain its core materials either in solution phase or in drying phase.

The alkali treated microcapsules with 1 layer (Fig. 7a) and 2 layers (Fig. 7b) show some individual microparticles in SEM micrographs at 600× after drying at room temperature, whereas the SEM images of alkali treated microcapsules with 4 layers (Fig. 7c), 6 layers (Fig. 7d), and 10 layers (Fig. 7e) at 600× indicate collapsing and aggregation of materials. However, the SEM images with 4, 6, and 10 layers at 600× reveal microcapsules entrapped in the dense polymer film. Also, SEM images of alkali treated 10 layers at 1000× (Fig. 7f) and 3000× (Fig. 7g) after dilution and drying at room temperature suggests that aggregation could not be inhibited by the dilution process in water.

4. Conclusions

The present study showed the development of microcapsules with an oil core and multilayer shell structure by multistep electrostatic layer by layer deposition technique combined with an emulsification process using chitosan (CS) as a poly-cationic biopolymer and sodium dodecyl sulfate (SDS) as an anionic emulsifier in the oil in water emulsion system. The alkali treatment of microcapsules was performed to solidify the outer shell of microcapsules. The zeta potential analysis of microcapsule suspension indicated that overcharging of microcapsules occurred due to positive charges of CS polymer. The alkali treatment of microcapsules created charge neutralization on the surface of microcapsules. The size distribution analysis of microcapsules indicated that the average diameter of the microcapsules increased after alkali treatment suggesting swelling or small aggregate formation by the microcapsules. The size distribution results were supported by SEM and optical microscopy. However, the gelation of free CS chains and

aggregation of microcapsules during alkali treatment are the major problems with the preparation of concentrated microcapsules. The optimizations for the preparation of concentrated microcapsules suspension are currently being performed to improve the quality and application of microcapsules in different fields especially for textile applications. The optimization process involves the standardization of added CS amount during layer by layer formation with SDS in order to minimize the magnitude of overcharging of microcapsules by positive charges and increase maximum deposition of oppositely charged molecules on the multi-layer structure of microcapsules in the concentrated microcapsules suspension, and also to decrease the amount of free CS chains in the suspension which create gel particles during alkali treatment.

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