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A number balance approach for estimation of microcapsules surface affinity for fabrics: Implications towards sustainable use of microcapsules in consumer care and specialty chemicals

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ABSTRACT

This study proposes a novel number balance approach for evaluating the affinity of microcapsules for a target substrate (e.g., cotton and polyester fabric). Using single particle optical sizing (SPOS) technique, the affinity of polyurea and silica microcapsules was studied by quantifying the capsules present in the dispersions before and after exposure to the fabric. Silica and polyurea microcapsules with encapsulated silicone oil were successfully synthesized and used as model capsules for affinity studies. Accuracy and reproducibility of the data generated from the SPOS were evaluated by relative standard deviation. Results of the affinity experiments revealed that, under the test conditions, not more than one-third of the capsules was deposited on the fabrics with silica capsules showing the highest affinity of 34.4% towards the polyester fabric. The observed affinity trends were explained by surface charge and the structural pattern of the fabrics, with capsules having a greater affinity for oppositely charged fabrics. We also found that the polyester fabric, which inherently contains bigger pores and higher exposed surface area, deposited more capsules than the cotton fabric. We demonstrated that while the microscopic techniques, such as scanning electron microscopy, can only confirm the deposition of capsules on the fabrics, alternative techniques such as SPOS provides an accurate measure of number of capsules, thereby determining the surface affinity of the capsules for the fabric.

1. Introduction

Protection of active agents and ensuring their efficient targeted delivery have become increasingly important in numerous industries for providing pharmaceutical, cosmetic, food and nutrition, agrochemical, and personal and home care formulations (Ye and Chi, 2018; Liu et al., 2022; Sridhar et al., 2022; An et al., 2022; Ogilvie-Battersby et al., 2022; Mehta et al., 2022). Most of these applications use micro or nano encapsulation technologies where sustainability concerns have peaked in recent years (Martins et al., 2023; Prasad et al., 2017; Calamak et al., 2021; Trajkovska Petkoska et al., 2021). One challenging area where capsules are used is in protecting volatile compounds in laundry and personal care applications (Bruyninckx and Dusselier, 2019; Chen et al., 2020, 2021). Detergent formulations incorporate water-insoluble microcapsules filled with perfumes or oils. These microcapsules are designed to release their contents when needed, making them a crucial method for delivering fragrance and softness in the fabric care industry (McCoy, 2018). Since the eventual fate of these capsules is environmental contamination in land and water bodies, biodegradability (non-persistence in the environment) is considered to be a key requirement for their use (Parente et al., 2022). Therefore, regulatory authorities are imposing limitations on the use of non-biodegradable capsules in these applications. Consequently, manufacturers are actively seeking high-performance biodegradable capsules derived from renewable sources as viable alternatives (Boh Podgornik et al., 2021). The active ingredients in these capsules are usually costly and increasing the surface affinity will reduce the loss of capsules to the environment as well as minimize the use of costly ingredients in the formulations. In this

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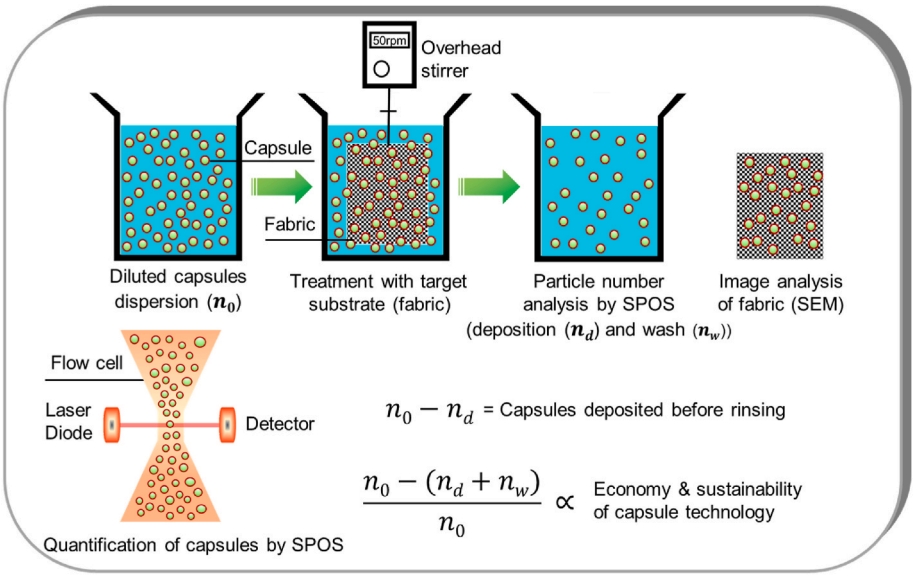
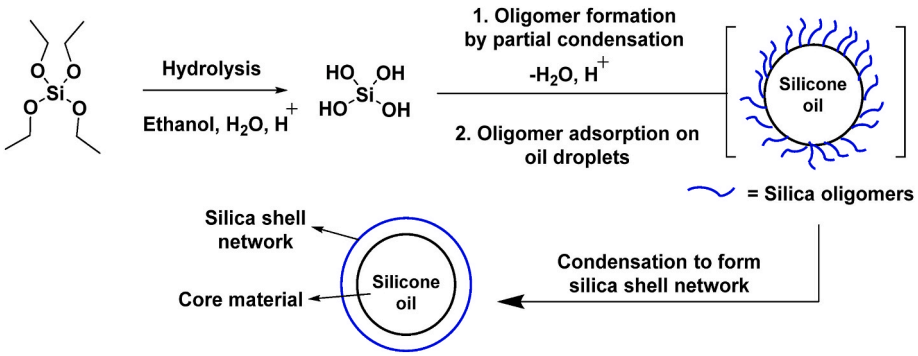


Scheme 1. Proposed number balance approach for evaluating efficiency of capsules deposition.

regard, all aspects of the microcapsule life cycle must be optimized to ensure that new generation capsules have high affinity for the target surface. This is particularly significant in the laundry applications as there have been no studies on how many capsules used in the washing liquid are wasted during the rinse cycle and the affinity of the capsules for the fabric. In this regard, the industry-standard method of assessing active release using GC-MS (Zhao et al., 2019a), followed by performance evaluation by a sensory panel, does not comprehensively tackle sustainability concerns within the capsule technology. Therefore, there is a pressing need for a method to quantify the wastage of capsules during the development of capsule applications. This would hasten the discovery of the next generation high performing environment-friendly capsules by preventing wastage by estimating the deposition of capsules on a target substrate and thereby understanding their affinity.

Quantifying capsules to evaluate their performance has been a challenge so far and mostly limited to microscopic analysis of the application substrate and the use of indirect methods of analyzing active concentration (Mercadé et al., 2012; Cheng et al., 2000; Yan et al., 2016). The deposition and retention of micro and nanoparticles under aqueous conditions onto textiles has been investigated and the rate of deposition was found to be dependent on the features such as particle size, morphology and surface characteristics, and the type of textile (Manga et al., 2022; Wang et al., 2019). Owing to their larger surface area-to-volume ratio and high surface energies compared to micro capsules, nanoparticles have been reported to have a high affinity for textile surfaces (Khanjani et al., 2013). Nanoparticles are also able to penetrate the interstices of fibers and fill the pore spaces. Moreover, textile characteristics such as hydrophilicity (as in the case of cotton which can swell in water and shrink when dry) can enhance particle retention (Racz and Borsa, 1997). Nanoparticles like zinc oxide, titania, silica, and alumina that impart UV-blocking (Xin et al., 2004; Yang et al., 2004; Marsh et al., 2009), anti-bacterial (Saito, 1993; Soo et al., 2020) and wrinkle-resistant (Wang and Chen, 2005; Gao et al., 2020) properties to the fabric and can be deposited and retained on the fabric over repeated wash cycles (Xin et al., 2004; Daoud and Xin, 2004). However, retention of micron-sized spherical particles is generally very low, as has been demonstrated for commercial microcapsules carrying fragrance oils (Teixeira et al., 2012). For example, Teixeira et al. used a combination of mass balance, SEM and headspace-GC analysis and showed that 46% of the encapsulated limonene oil was lost from the microcapsules impregnated on the textile substrates in a single wash and as much as 97% of the oil was lost after 20 wash cycles (Teixeira et al., 2012). Although this approach works by quantifying the active compound present as a measure of capsule deposition, it may not present a real picture of the surface retention of intact microcapsules.

Jing et al. investigated microstructures of the fragrance loaded nanoparticles on the fabric by FT-IR and evaluated fragrance concentration based on the determination of the components in the headspace of the washing completed cotton fabrics (Jing et al., 2014). Similar approaches were used wherein the main principle of measurement was based on GC-MS which does not address the capsule itself and only the contents of the capsule were analyzed. Using image-based techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) or optical microscopy methods substantially challenges the accuracy of capsule quantification since most fabrics have a complicated structure of weavings and fibers. Fabric substrates with smooth surface have been previously used as a model to facilitate counting of deposited capsules as well as excluding filtration effect (capsules getting stuck in the framework structure of the fabric due to comparable pore size as capsules and roughness) which might not give a clear understanding of the capsule affinity (Liu, 2019). SEM, TEM and optical microscopy methods can partially reveal specific locations or fiber types in the fabric where capsules adhere and provide a qualitative understanding of the capsules deposition on the substrate. For example, Mercadé-Prieto et al. have recently proposed a methodology for quantifying microcapsules deposited on fabrics (Mercadé et al., 2012). They deposited fluorescent-doped melamine-formaldehyde (MF) microcapsules on a cotton fabric by submerging it in the capsules dispersion. The capsules deposited on the fabric were quantified using a fluorescent microscope. Mercadé-Prieto et al. then studied the impact of abrasive forces on the retention of deposited capsules by using a micromanipulation rig to simulate abrasion in the fabric and counting the microcapsules insitu using a fluorescent microscope (Mercadé et al., 2012). They have found that while the number of capsules retained on the fabric decreases with the number of abrasion passes, more small capsules survived compared to the larger microcapsules. Manga et al. have used a combination of mass balance approach and image analysis for capsule quantification and showed that retention level increased up to 3 times when the capsule surface is rough (Manga et al., 2022). While these existing methods successfully quantified the capsules deposited on the fabric, they still have limitations which curtail its wide applicability for real fabrics with fibers and complex weavings. For example, it is not possible to capture information on the capsules overlapped by the nonfluorescent fabric fibers that results in underestimating the capsule



Scheme 2. Reaction scheme to make silica microcapsules using interfacial hydrolysis condensation mechanism.

number and size. In addition, since the deposition of microcapsules on the fabrics is not uniform, the overall reliability and accuracy of the quantification depends on the number of images analyzed and area of the fabric focused for imaging. Therefore, these approaches will provide only a qualitative measure of the affinity especially for real fabrics.

The current study explores the use of single particle optical sizing (SPOS) (Pelssers et al., 1990) as a simple method for providing a comparative evaluation of the adsorption of industrially used polyurea (PU) or MF capsules (Bruyninckx and Dusselier, 2019; Wu et al., 2021) with that of emerging sustainable capsules based on silica-based shells (Athinarayanan et al., 2020; Ryu et al., 2018; Yeom et al., 2022). We synthesized PU and silica capsules, and a new methodology was developed for evaluating efficiency of capsules deposition (Scheme 1). Even though PU capsules are widely used in laundry delivery technologies and is an industry benchmark for fragrance delivery (Bruyninckx and Dusselier, 2019), they are considered as micro-plastics and hence comparison with capsules made of a more sustainable material like silica will be important for the development of future alternatives to MF and PU capsules. To understand how industrially important capsule wall materials (PU) and silica affects the affinity towards a given substrate, we used an inert material like silicon oil (Aziz et al., 2019; Barca et al., 2014) as the content of the microcapsule and evaluated different fabric materials as our substrate.

2. Experimental

2.1. Materials

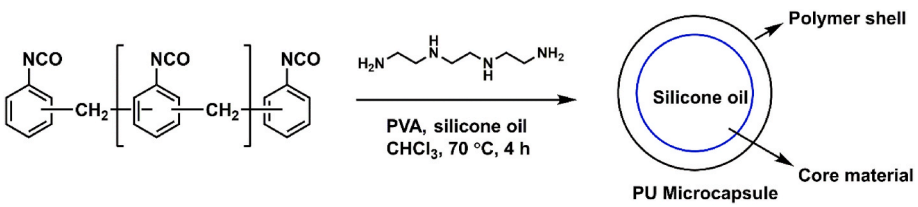
Tetraethoxysilane (TEOS), hexadecane, Triton X-100 (a nonionic surfactant), sodium chloride (NaCl), potassium chloride (KCl), poly [(phenyl isocyanate)-co-formaldehyde] (Mn ~340), triethylenetetramine (60%, TETA), and a polyvinylalcohol (PVA); Mowiol® 8–88 (Mw ~67,000) were purchased from Sigma-Aldrich, Singapore and used as received. Silicone oil (Xiameter PMX-200) was purchased from Ellsworth Adhesives (Singapore) Pte. Ltd. Analytical grade solvents were used for synthesis of capsules. Woven 100% cotton and polyester fabrics used for affinity studies were sourced from RVC International Pte Ltd. The ultrapure water was obtained from Millipore Milli-Q system.

2.2. Synthesis of silica microcapsules

Silica microcapsules were prepared by our patented technology (Scheme 2) (Thoniyot and Herk, 2020). In a typical experiment, NaCl (0.70 g, 15 mmol) and Triton X (11.4 mL, 18.9 mmol) were dissolved in 800 mL of ethanol/water solvent mixture (26/74 v/v). After which, silicone oil (114 mL, 14.3 vol%) was added to the mixture and stirred with ultra-turrax IKA T25 (4000 rpm) for approximately 2 min to obtain a coarse pre-emulsion with size ranging from 50 to 200 μm. Subsequently, the pre-emulsion was subjected to high-pressure homogenization (500 bar, 3 cycles, EmulsiFlex-05) to obtain a uniform emulsion with mono-modal particle size distribution. The particle size was monitored by optical microscope. The mixture was then transferred to a 1L reactor fitted with overhead stirrer and stirred at 600 rpm under ambient conditions for 5 min. After that, TEOS (69 mL, 8.62 vol%) was added via syringe pump over a period of 30 min. The reaction mixture was stirred for another 4 days under ambient conditions, yielding 119 g of the encapsulated material (92% based on solid content) as a white slurry.

2.3. Synthesis of PU microcapsules

Microcapsules with PU shell were prepared by interfacial polymerization of an aromatic isocyanate (poly [(phenyl isocyanate)-co-formaldehyde]) and an aliphatic tetramine, TETA, at the oil droplet interface in oil-in-water (O/W) emulsions (Scheme 3) (Kwon et al., 2019). The oil phase was prepared by dissolving isocyanate (1.0 g) in chloroform (7 mL) followed by the addition of silicone oil (7.0 g). The oil phase was stirred with a magnetic stir bar for 10 min before dropwise addition to the PVA aqueous solution (25.0 g, 1.2 wt%) in a 50 mL glass beaker while homogenizing with a high shear mixer (ultra-turrax IKA T25) at 12,000 rpm agitation speed at 5 °C for 2 min. Then an aqueous TETA solution (1.05 g in 3.0 g of deionized (DI) water, 35 wt%) was added dropwise to the resulting emulsion and homogenized for a further 1 min at the same agitation speed and temperature. The combined reaction mixture was transferred to a 3-neck 250 mL glass reactor which was connected to an overhead stirrer and then submerged in a preheated oil bath at 50 °C. The reaction was carried out for 4 h. The reaction mixture was cooled to room temperature and transferred to a 50 mL centrifuging Falcon tube before purification. The pure PU microcapsules



Scheme 3. Reaction scheme to make PU microcapsules from interfacial polymerization of the corresponding isocyanate and tetramine.

were obtained by centrifuging the capsules at 5000 rpm for 5 min. The supernatant was removed and pellet containing solid capsules was added to 30 mL of DI water and vortexed to disperse the capsules again. The purification process by centrifugation was repeated 3–4 times to remove the PVA stabilizer. The pure capsules were stored in DI water as a dispersion at room temperature for downstream characterization and application.

2.4. Thermal analysis

Solid content in the silica microcapsule dispersion was estimated using thermogravimetric analysis (TGA). The experiments were performed on a TA Instruments SDT Q600 thermogravimetric analyzer. Approximately 15 mg of the sample was added to an alumina crucible. The samples were heated over the temperature range of 25–700 °C at a constant heating rate of 10 °C min^{-1}. The samples were purged with a stream of flowing nitrogen throughout the experiment at 100 mL min^{-1}.

2.5. Scanning electron microscopy (SEM)

The morphology of the silica and PU microcapsules was analyzed with a scanning electron microscope (JEOL, JSM-7610F, Tokyo, Japan) operating at 1.5 kV. The samples were prepared by drop-casting the diluted dispersions on silicon wafers and were coated with a thin layer of gold prior to analysis.

2.6. Particle analysis

The size and particle size distribution of the silica and PU capsules were measured using laser diffraction technique (Mastersizer 3000 with a HydroMV setup module, Malvern Instruments, MS 3000, MAL1114945). Dilutions were done with ultrapure water during measurements. The particle detection was based on the refractive indices of silica (1.54) and the dispersant, ultrapure water (1.33). All the measurements were done in triplicate and averaged values were reported. Mean size of the capsules was also calculated from ImageJ analysis (Schneider et al., 2012) of the micrographs obtained from SEM. Diameter of a total of 200 capsules was manually measured and used for computation of the mean size. In addition to the particle concentration, SPOS also provides information pertaining to particle size, hence, the data obtained from SPOS are compared with the data obtained from other analyses.

2.7. Zeta-potential measurements

Surface charge on the silica capsules was measured using Zetasizer (Malvern Instruments, Worcester, U.K.). Zeta potential measurements were conducted in 1 mM KCl solution to keep the ionic strength of the continuous phase fixed so that the measured value reflects mainly the charge of the capsules (Lu et al., 2022). In the case of fabrics, they were cut to the length of approximately 1 mm and stirred in 1 mM KCl solution with a magnetic stirrer for 10 min. Then the zeta potential was measured. The zeta potential measurements were an average of 3 individual measurements.

2.8. Estimation of particle number

Concentration of the silica capsules from affinity studies was quantified using SPOS (AccuSizer® A9000 FX Nano AD System, Entegris®, Billerica, MA 01821, USA) tool (White, 2003). In a typical experiment, a predefined sampling volume of the sample dispersion was diluted with 50 mL of ultrapure water and injected into the SPOS system using sample loop automatic fill mode (loop volume 11.02 mL). LE400 sensor was used for detecting the capsules in the size range of 1.5–20 μm and the coincidence limit was set at 4000 particles mL^{-1}. The FX nano system provides automatic dilution such that the samples were diluted within the system to meet the coincidence limit. However, all the samples were sufficiently diluted prior to analysis to avoid long dilution times so that no particles were missed out during the auto-dilution. A pre-dilution factor corresponding to the dilution used for sample preparation was included as one of the experimental parameters. This allows the software to calculate the original concentration of sampled dispersion from the affinity experiment. Each sample was analyzed four times and data repeatability was judged based on relative standard deviation (RSD or coefficient of variation). A set of data with an RSD of not more than 5% was considered to have good repeatability. The LE400 sensor was calibrated using the polystyrene latex standard particles following the protocol recommended by Entegris®.

2.9. Methodology for estimation of capsule number balance

We used a number balance approach as a simple and practical alternative to the mass balance approach for estimating the number of capsules in the dispersion. In the mass balance approach, variables such as fabric hygroscopicity, humidity, and loss in fabric weight due to shedding of fibers are expected to make a substantial impact on the concentration estimates (Manga et al., 2022). The number balance approach by contrast focuses on only the particles introduced into the system and particle counting techniques such as SPOS are expected to accurately measure particle concentration. We hypothesize that when the capsules are dispersed in a medium and then exposed to a surface (e.g., a fabric), a fraction may adsorb to the surface. Quantification of the capsules in the dispersion before and after exposure to the surface provides a direct measure of capsules affinity for the target substrate. Using this approach, deposition of capsules from a slurry of a known particle concentration (number of particles per unit volume) under ambient conditions for a given time can be estimated by equation I. This can be considered proportional to the number of capsules that loads onto the fabric during an actual washing step, even though the current approach does not reproduce washing conditions of a laundry machine or hand wash. Subsequently, the same fabric which has capsules deposited on it can be subjected to a rinsing step with fresh water and by quantifying the capsules in the rinsed water, the number of capsules retained on the fabric can be estimated. We define the affinity of the capsules as the percentage of capsules deposited and retained on the fabric during washing or rinsing process (equation II).

$$\text{Capsules deposited before rinsing } (\%) = \frac{n_0 - n_d}{n_0} \times 100 \quad \text{(I)}$$

$$\text{Affinity of capsules } (\%) = \frac{n_0 - (n_d + n_w)}{n_0} \times 100 \quad \text{(II)}$$

Where n_0 denotes the concentration of the capsules in the initial dispersion while n_d denotes that do not deposit on the substrate and n_w is the concentration of the capsules washed-off from the substrate during the rinsing.

Using the proposed approach, keeping all the other experimental parameters constant (e.g., concentration, temperature, apparatus, sampling, quantification method) and varying the capsule concentration or the type of capsules, variation in the number of capsules deposited on the surface can be calculated and deposition for different capsules on varying substrates can be compared. Prior to testing our hypothesis, we conducted measurements in SPOS to test the reproducibility of the data produced. These include a control experiment to measure the change in concentration of the capsules over time, data reproducibility by analyzing the RSD of a set of data, and comparison of the particle size measured in SPOS with the data generated from other complementary techniques, e.g., laser diffraction and image analysis (*vide supra*).

2.10. Experimental setup for affinity studies

White 100% woven cotton and spun polyester fabrics of the size 6

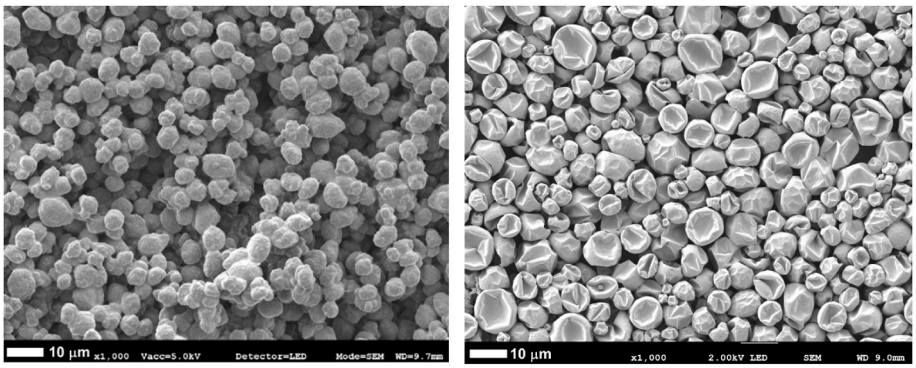


Fig. 1. SEM images of silicone oil loaded silica (left) and PU (right) microcapsules at a magnification of 1000×.

cm × 6 cm were used as model fabrics for affinity studies (Scheme 1). Prior to the affinity experiments, dust particles on the fabric were removed by cleaning with ultrapure water. The fabric was first attached to an overhead stirrer and submerged in a beaker of 250 mL of ultrapure water. The optimum time to get rid of the dust particles was determined by a series of cleaning experiments. The fabric was left stirring at 100 rpm in ultrapure water and the particle count in water was tested at regular intervals using SPOS. The time at which the particle count was the highest was determined and used for the subsequent washing of the fabric. Upon washing, the fabric was removed from the water and left in the air until no water was dripping from the fabric. Affinity of capsules for a target substrate is a function of initial concentration of the capsules and temperature and therefore these parameters are kept constant. All the experiments were conducted at ambient temperature and the initial concentration of the dispersions was kept constant by the following procedure. A 1.2 mL of the as prepared capsules dispersion was added into 1000 g of ultrapure water and mixed with an overhead stirrer for 10 min at a speed of 100 rpm. Subsequently, the dispersion was split into four equal parts into 250 mL beakers and used for four independent deposition experiments (n = 4). A 0.2 mL from each of these beakers was diluted into 50 mL of ultrapure water. Quantification of the capsules concentration by SPOS resulted in similar values. An average of these values was used as the initial capsules concentration (n_0). The concentration values obtained from deposition (n_d) and wash (n_w) experiments were normalized against the initial dispersion concentration and reported in percentage. For deposition of capsules on the fabric, a prewashed fabric was hung to an overhead stirrer using a clip (Scheme 1) and submerged in the 250 mL of the preprepared capsules dispersion. Four such experiments were conducted parallelly using the preprepared dispersions of similar concentration (n = 4). In each experiment, the fabric was rotated at a speed of 50 rpm to facilitate uniform distribution of the capsules. A 0.2 mL of the dispersion was sampled after 1 h and diluted using 50 mL of ultrapure water for quantification of the capsules concentration (n_d). Subsequently, the fabrics from three of the four experiments were removed from the capsules dispersion and the excess water was allowed to drip before being transferred and stirred at 50 rpm for washing in 250 mL of fresh ultrapure water (n = 3). The water that now contains the capsules detached from the fabric was sampled after 1 h and the capsules concentration (n_w) was quantified. The fabric from the fourth deposition experiment as well as the fabric from the wash experiments were dried for 24 h under ambient condition. A small portion of the fabric was cut and used for SEM analysis of the capsules retained on the fabric.

3. Results and discussion

Capsules for textile applications should be robust enough to withstand the physical forces applied during the washing process (Nelson, 2002). Furthermore, the ever-growing need for sustainable alternatives to meet regulatory legislations have prompted the search for

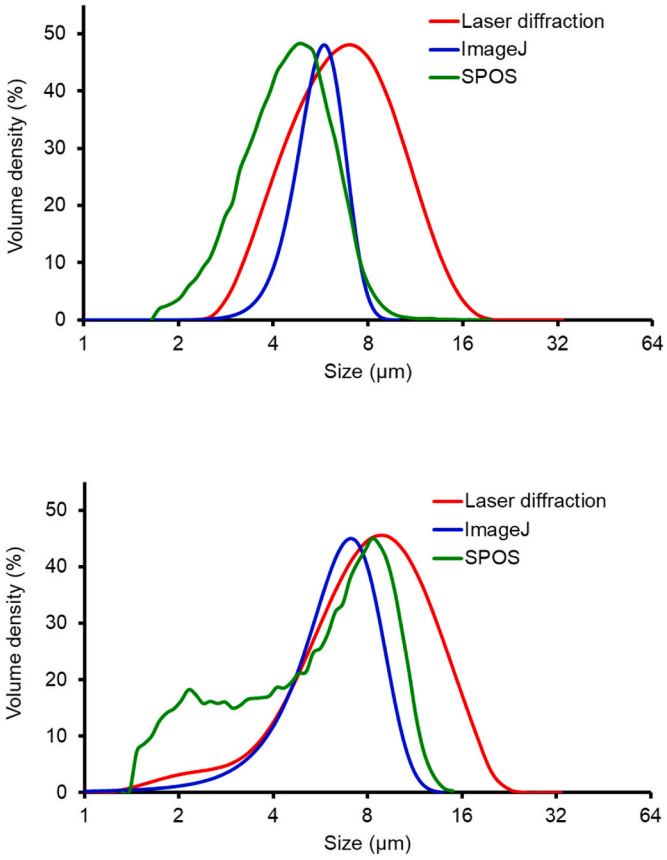


Fig. 2. Particle size distribution of silica (top) and PU (bottom) microcapsules as determined by laser diffraction, SPOS and ImageJ analysis of the SEM images.

biodegradable polymeric shell materials (Sedlak, 2017). In this regard, we chose two different microcapsules which have proven to be versatile in their applications, namely silica and PU-based capsules. Over the past two decades, silica capsules have been widely used owing to their biodegradability and cost-effectiveness of raw materials (Zhang et al., 2015; Cao et al., 2015; Deng et al., 2011). However, silica capsules developed by conventional methods suffer from easy breakage or rupture, causing unwanted leakage of the core materials. In addition, conventional synthesis of silica capsules requires multiple synthetic steps, expensive reagents and suffer from low scalability and reproducibility. We have recently devised an emulsion polymerization method for the synthesis of silica capsules that addresses the aforementioned problems (Thoniyot and Herk, 2020). The method is easy to scale up and is reproducible at an industrial scale. On the other hand, the

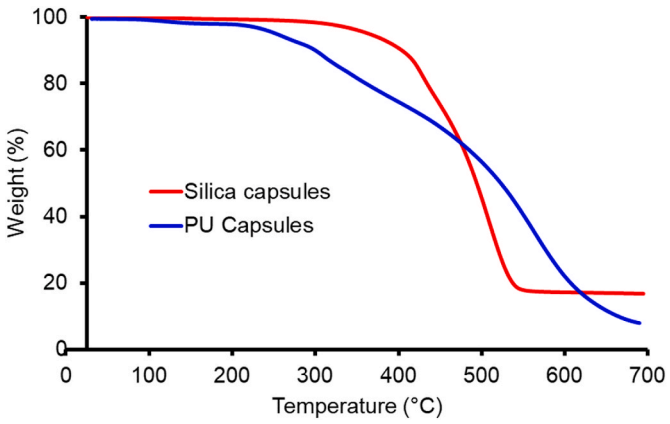


Fig. 3. Thermogravimetric curves of silicone oil-loaded silica and PU microcapsules showing the stability of the capsules until 200 °C and the release of silicone oil thereafter.

robustness of PU microcapsules and their diverse applications have been widely reported and reviewed (Bruyninckx and Dusselier, 2019; Luo et al., 2022; Santana et al., 2021). They are used in many commercial personal care and laundry formulations which make them the ideal capsules for testing our hypothesis.

3.1. *Characteristics of microcapsules*

The silica and PU microcapsules have a spherical morphology (Fig. 1) with the latter having a collapsed or dented surface. An optical microscopic analysis of the capsules has also confirmed the dented surface morphology of the PU capsules (Fig. S1, Supporting Information). This unique surface morphology might be due to the presence of chloroform in the oil phase which was added to solubilize the amine precursor. Upon capsule formation and subsequent purification, the chloroform is expected to evaporate from the capsule by diffusion through the shell wall leading to the collapsed morphology. Similar spherical but dented morphology of the PU capsules has been previously reported (Yin et al., 2018). We conducted a particle size analysis of the silica and PU capsules using laser diffraction, SPOS, and SEM image analysis by Image J (Fig. 2). The particle size distribution plots obtained from the laser diffraction data suggest that both the silica and PU capsules have a unimodal distribution with mean particle diameter Dx (50) of 7 and 8 μm, respectively. Furthermore, the particle size of these capsules varied in the range of 2–23 μm for silica capsules and 1–29 μm for PU capsules (Fig. 2). For the PU capsules, there is a small proportion of smaller-sized capsules (~2 μm), likely due to high shear homogenization during the emulsification of the oil and aqueous phases. However, the average size distribution can be compared with those of silica capsules. A comparison of the particle size distribution curves obtained from the image analysis and laser diffraction methods (Fig. 2) showed distinct differences, with the particle size distributions from the laser diffraction centered at much higher particle sizes compared to that obtained from SPOS and image analysis. A similar observation has been recently made (Grubbs et al., 2021) which highlighted the fact that the laser diffraction is influenced greatly by particle morphology and any deviation from the spherical morphology results in different diffraction angle and hence particle size (Islam et al., 2022). Satellites attached to particles or agglomerates and particles of irregular morphology are expected to influence the diffraction angle when passing through the path of the laser beam, resulting in an overestimation of their particle size. In contrast, individual particles are visually observed in the image analysis and measured for their absolute size (Vippola et al., 2016). The accuracy of SPOS is expected to be higher than those for light scattering sizing techniques due to the fact that the SPOS involves counting and sizing one particle at a time, eliminating particle coincidence (Entegris, 2019a). Other studies have shown SPOS's particle size accuracy is to be ~5% and particle count accuracy to be ~10%, making it a reliable technique for counting as well as sizing of the particles in a dispersion (Entegris, 2019b). As SPOS represents an optical projection of particles, it produces values closer to the more realistic SEM values. Silica and PU capsules displayed no stability issues for as long as 4 weeks in the dispersion. Thermogravimetric analysis was used to gauge the thermal stability and endurance limits of the microcapsules. This additionally allowed us to determine the percentage of oil present in these core-shell capsules. Upon heating the capsules, the observed weight loss due to the release of silicone oil from the capsules was ~85% in the case of silica microcapsules, compared to 80% in PU capsules (Fig. 3). The TGA analysis thus confirmed that the silica and PU capsules are stable at high temperatures (>200 °C) and are suitable for textile applications.

3.2. *Quantification of capsules' concentration and single particle optical sizing (SPOS)*

With increasing interest in capsule technology for consumer and industrial applications, quantifying particle concentration is increasingly important for understanding the performance of a dispersed system. From a sustainability point of view, this information aids in the assessment of capsules' performance and development of novel methods for their sustainable use to minimize wastage. Similar to methods for quantification of microparticles/capsules (Mercadé et al., 2012; Morrison, 2009; Rodrigues et al., 2008; Zhao et al., 2019b), the quantification of nanoparticles/capsules has also been studied by many and innovative analytical methods have been developed (Hassellö et al., 2008; Paunescu et al., 2015; Claudia et al., 2017a). Early developments in this field focused on the data obtained from dynamic light scattering (DLS) for size determination and Brunauer, Emmett and Teller (BET) method for surface area estimation (Hassellö et al., 2008). However, these methods can only provide an estimate of particle size and concentration. Particle counting using images obtained from electron microscopy has been a standard approach for quantifying unimodal particles and has been extensively used in the past (Mercadé et al., 2012; Cheng et al., 2000; Yan et al., 2016; Zhang et al., 2009). However, such a manual approach is time-consuming and tedious in nature and thorough quantification is only possible for smooth model surfaces (Liu, 2019). With the recent technological advancements, the past two decades have witnessed the use of several alternative methods for quantification of nanoparticles (Claudia et al., 2017b; Stelzl et al., 2022; Makra et al., 2015; Cui et al., 2018; Poncelet et al., 2015). Interestingly, most of these methods were used in biomedical assays to measure single particle masses and using such information to count specific cells in a manner similar to flow cytometry. Recently, digital particle polymerase chain reaction, which has previously been used for detection of nucleic acids, has been used for precise detection of DNA loaded silica nanoparticles (Paunescu et al., 2015). In a similar vein, the flow imaging method, which uses a single instrument that combines a flow cytometer and a microscope, has been recently used for estimation of size and number of protein particles, analysis of biopharmaceuticals and parenteral drugs (Gross-Rother et al., 2020). This method involves examining a fluid under a microscope and taking a series of images of magnified particles in the fluid. These images are then used to capture particle characteristics such as diameter, aspect ratio, and volume, and morphology measurements like circularity, elongation, and perimeter. The output data provides the user multiple options to sort, filter, characterize and count the particles based on their specific characteristics. Most of the methods described above are manual approaches and sensitive to many external factors such as refractive index of the sample or dispensing medium and suffer from both limited accuracy and poor resolution. This warrants an alternative tool suitable for quantification of particles independent of particle type and able to analyze the particles of a wider size range.

Over the past few years, SPOS has become a promising alternative tool for determining concentration and size of the particles in a liquid

Table 1
Concentration of the silica capsules as measured over time in a control experiment.

Time (min)	Run 1	Run 2	Run 3	Average	%[a]	RSD (%)
0	4.52E+06	4.54E+06	4.49E+06	4.52E+06	100.0	0.56
20	4.50E+06	4.48E+06	4.52E+06	4.50E+06	99.6	0.44
40	4.43E+06	4.48E+06	4.42E+06	4.44E+06	98.4	0.72
60	4.48E+06	4.53E+06	4.53E+06	4.51E+06	99.9	0.64

[a] Concentration in percentage with respect to the initial concentration at time 0 min.

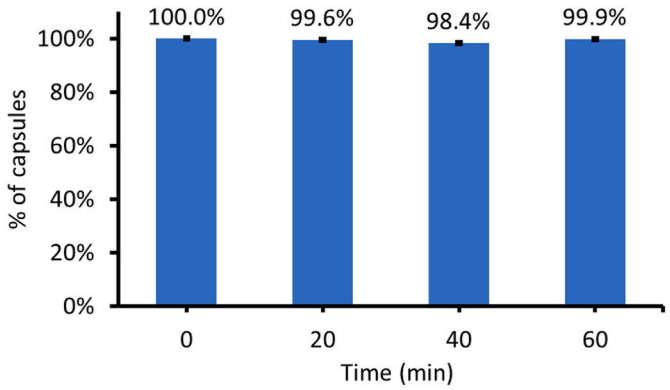


Fig. 4. Percentage of silica capsules as observed in a control experiment at different time points.

suspension (Pelssers et al., 1990; White, 2003). The method has been applied to estimate the particles in the size range of 0.2 μm–400 μm with a greater accuracy and repeatability than the traditional laser diffraction-based techniques. The SPOS works on a main principle that when particles in a liquid dispersion are passed through a photozone, light is absorbed/refracted due to the physical presence of the particle or scattered at some oblique angle (vs). The magnitude of these effects allow particle size and concentration to be determined through the use of a pulse height analyzer and a calibration curve developed from a series of standard homogeneous particles of known diameters. The system uses a light extinction (LE) + light scattering (LS) dual detection system, which facilitates sizing and counting of particles in both submicron and micron range. The SPOS system requires the particle suspension to be sufficiently diluted so that the particles pass through the photozone one at a time, avoiding coincidences. To achieve this, the SPOS is built with an automated dilution process which automatically dilutes the input dispersion to reach a threshold concentration limit before it is analyzed. To the best of our knowledge, our manuscript reports the first use of SPOS for understanding the capsule surface affinity.

3.3. Assessing suitability of SPOS for estimation of capsules' concentration and control experiment

To test the reproducibility of SPOS measurements, we conducted a control experiment using silica microcapsules prepared for this study. In an ideal situation, when capsules of a given concentration are dispersed in a medium, the concentration should remain the same for an extended period. However, factors such as deposition of the capsules on the apparatus used for the experiment (glassware, stirrer bar, etc.) and manual error during sampling are expected to lead to a loss of capsules and a reduction in capsules' actual concentration. Therefore, it is important to investigate the impact of these factors on the concentration of the capsules in a dispersion. In a typical control experiment, a fixed amount of stock dispersion of the silica capsules was first diluted with ultrapure water such that the concentration of the dispersion is within

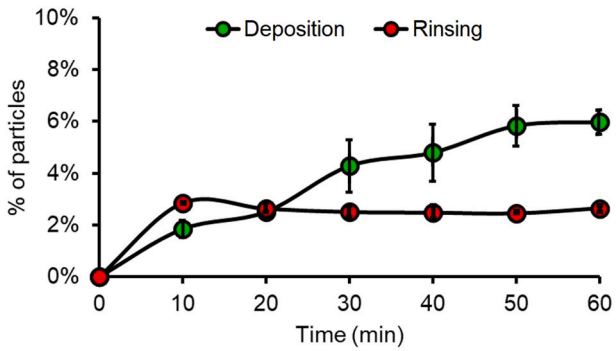


Fig. 5. Percentage of silica capsules deposited and washed-off during a time-dependent experiment. Data represent an average of three independent experiments (n = 3). Note plateau of capsules deposition and detachment after 50 min and 40 min, respectively.

the recommended range of concentration for SPOS analysis. The dispersion was stirred at 50 rpm using an overhead stirrer for uniform distribution of capsules in the dispersion. A predefined volume (0.5 mL) of this dispersion was collected at 20 min intervals for an hour and diluted for quantification of the concentration of the capsules using SPOS (Table 1). The data reproducibility of the SPOS can be determined by the calculated RSD values. The RSD indicates the precision of the mean value derived from individual runs. The higher the RSD, the greater the deviation from the mean. Conversely, a lower RSD indicates greater precision in the measurement of data. A comparison of the data in Table 1 suggests that the SPOS shows an excellent reproducibility with an RSD of concentration values below 1%. Furthermore, the fact that there is little to no change in the concentration of the dispersion over time (Fig. 4) confirms that SPOS is a reliable technique for the quantification of the capsules' concentration and can be used for the proposed affinity studies.

3.4. Capsules' deposition and wash-off

Generally, adsorption and desorption of the capsules is expected to be time-dependent, and it is important to establish how long it takes for the capsules' concentration to reach an equilibrium, both in deposition experiments and in rinsing cycles. Hence, for obtaining reproducible affinity results, the experiment runtime for stable retention of capsules in the deposition and rinsing stages needs to be estimated. To this end, using the cotton fabric, we have conducted a time-dependent experiment to determine appropriate runtime for our proposed experiments. We found that the capsules' concentration reaches equilibrium after 1h in both deposition and rinsing experiments (Fig. 5). As such, all the deposition and rinsing experiments in this study were conducted for 1 h even though for practical high-throughput studies this time can be shorter as more than 50% of the depositable capsules are deposited and almost entire washable capsules are washed-off within 20 min. For this methodology to work, it should be ensured that the capsules should not break during the process and new particulate matter is not coming out from the substrate and capsules (experimental section).

Having tested the reproducibility of concentration measurements by SPOS and established the appropriate experiment runtime, we conducted affinity experiments to quantify the deposition of microcapsules on a fabric substrate. As described in the experimental section, each of these experiments was conducted in quadruplicate and compared to the individual data sets to assess the reproducibility of the data and the reliability of our proposed experimental protocol. Two fabrics of different material were used, cotton and spun polyester. The weaving pattern of both fabrics was kept the same with individual fibers aligned in a woven pattern. The use of two different fabrics allowed us to investigate the effects of surface charge and framework structure of the

Table 2
Zeta potential of microcapsules and fabrics used in the affinity experiments.

	Silica	PU	Cotton	Polyester
Zeta potential (mV)	−7.00 ± 0.68	+3.86 ± 0.21	−19.5 ± 3.3	−1.96 ± 1.95

fabric substrate. In the present case, zeta potential measurements on the fabrics revealed that while the cotton is negatively charged (−19.5 mV), polyester has a near zero (−1.96 mV) zeta potential, which closely matches with the zeta potential values reported previously (Table 2) (Janhom et al., 2006; Gabardo et al., 2021). A SEM analysis of the fabrics revealed larger pores and loose packing of fibers in the polyester fabric; in contrast, the fibers of the cotton fabric are tightly packed with smaller pores leaving minimal gaps between the fibers (Fig. 6).

Fabrics from the affinity experiments were analyzed by SEM before and after one wash cycle to confirm the deposition of the microcapsules and their retention after washing (Figs. 7 and 8). An analysis of the SEM images (Figs. 7 and 8 and Figs. S2–S5 of the Supporting Information) confirmed the deposition of the capsules on the fabric fibers. The particle size of the capsules remained the same after the experiment. However, it was not possible to judge the preferred location and extent of capsules' deposition as no such distinction was made based on the SEM images recorded at several locations of the fabric under investigation. Furthermore, SEM images of the fabric after wash also showed a significant number of capsules on the fabric indicating a higher retention of capsules than is the case through SPOS. Hence, quantifying capsules affinity solely based on microscopic analysis was not conclusive. Therefore, using an alternative quantification tool such as SPOS may provide an accurate measure of capsules' surface affinity. Our concentration measurements using SPOS have provided a numerical measure of the affinity of silica and PU capsules. Results of the affinity experiments were tabulated in Table S1 (Supporting Information) and compared in Figs. 9 and 10. The results suggest that the PU capsules showed 4.4 times higher affinity than the silica capsules (28.6% vs 6.5%) towards cotton fabric. In contrast, when polyester fabric was used for the affinity experiments, the silica capsules showed higher affinity than the PU capsules (34.4% vs 24.9%; Figs. 9 and 10). The marked difference in the percentage of capsules deposited suggests that the affinity of microcapsules is significantly dependent on the type of polymeric material

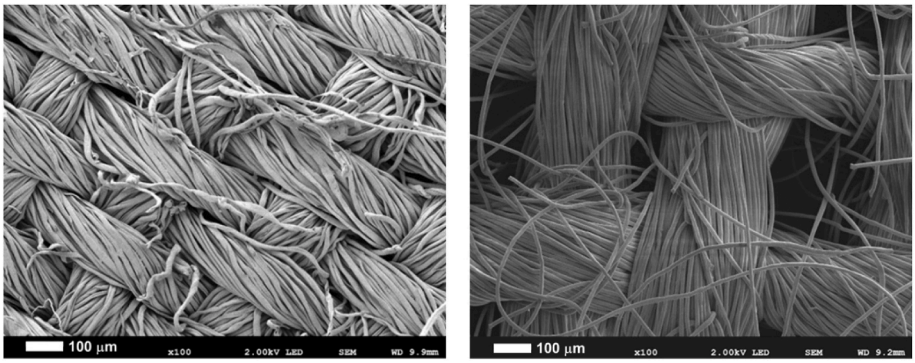


Fig. 6. SEM images of cotton and polyester fabrics at a magnification of 100×. Note the pores of distinct sizes.

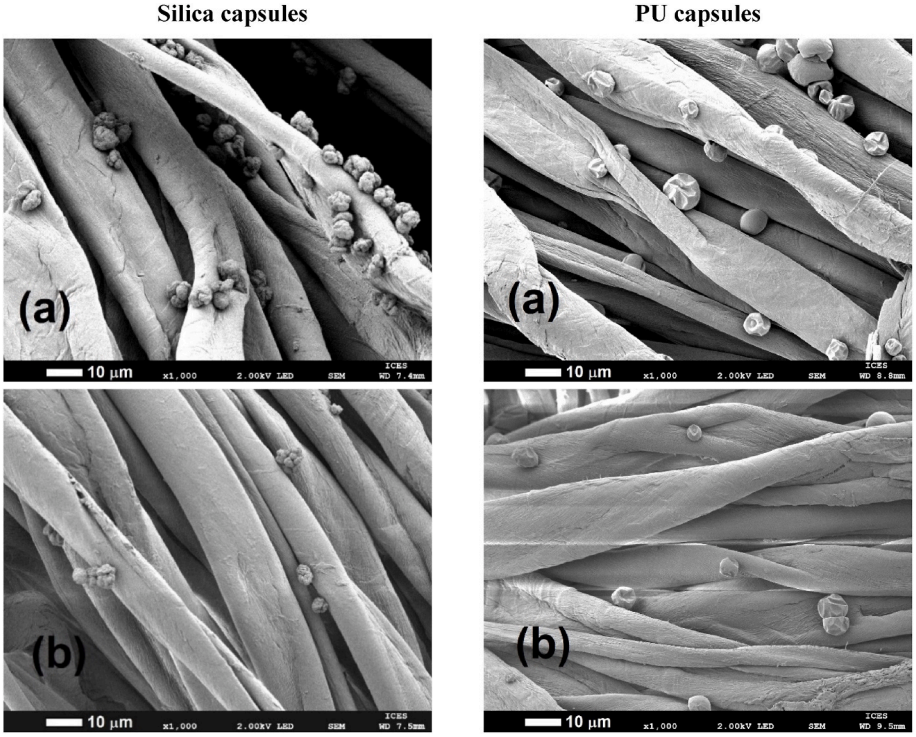


Fig. 7. SEM images of the cotton fabrics with deposited silica and PU microcapsules (a) before and (b) after wash at a magnification of 1000×.

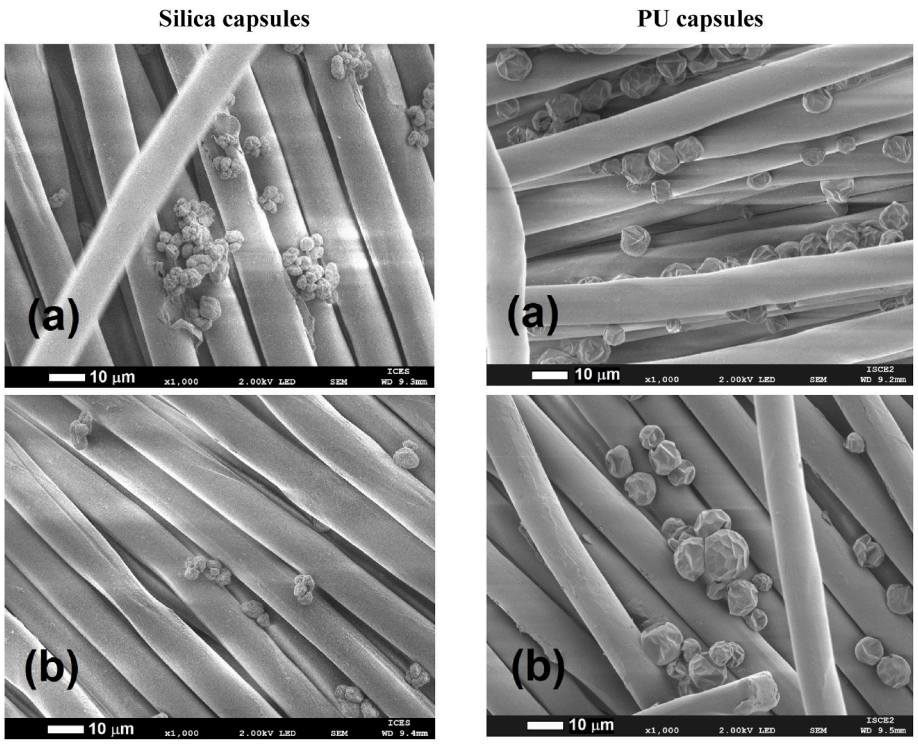


Fig. 8. SEM images of the polyester fabrics with deposited silica and PU microcapsules (a) before and (b) after wash at a magnification of 1000×.

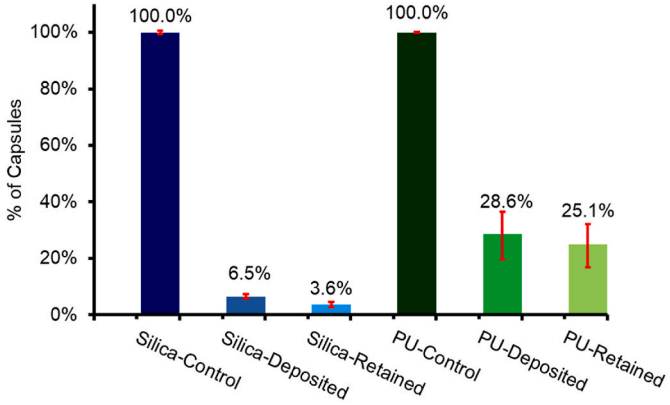


Fig. 9. Percentage of silica and PU capsules deposited and retained on the cotton fabric. Data represent an average of four (n = 4) and three (n = 3) independent experiments for deposition and wash, respectively.

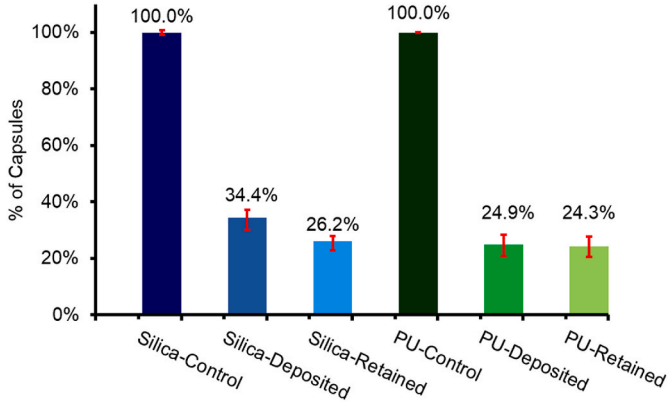


Fig. 10. Percentage of silica and PU capsules deposited and retained on the polyester fabric. Data represent an average of four (n = 4) and three (n = 3) independent experiments for deposition and wash, respectively.

constituting the microcapsule shell.

Affinity is generally regarded as an attractive force between two substances or particles (Button, 1986). In the case of affinity between the microcapsules and fabric fibers, factors such as electrostatic interactions, hydrophilicity, and non-covalent interactions may play a role. We have rationalized the observed trends in the affinity of silica and PU capsules based on zeta potential of the capsules and the fabric. In the case of silica capsules, the presence of many hydroxyl groups imparts a negative zeta potential on silica capsules (−7.00 mV) (Table 2). On the other hand, urea subgroups on the surface confer a positive zeta potential to PU capsules (+3.86 mV). Comparing these zeta potential values with the observed affinity results suggests a strong correlation between them. The capsules prefer to interact with the oppositely charged substrate. The positively charged PU capsules showed a higher affinity for the negatively charged cotton fabric, while the negatively charged silica particles showed a higher affinity for the nearly neutral (less negative) polyester fabric. Similarly, the capsules showed less affinity towards the fabric with the same charge.

Survival or retention of the capsules on the fabrics after washing was quantified by subtracting the percentage of capsules washed-off during rinsing from the percentage of capsules deposited (Table S1, Supporting Information). PU capsules showed a higher retention than silica capsules irrespective of the type of fabric used. Furthermore, both silica and PU capsules showed higher retention in polyester than in cotton fabric. This higher retention can be explained by the surface characteristics and internal structure of the fabric. The polyester fabric contains larger pores than the cotton fabric and is expected to have larger exposed surface area of the fibers for the capsules to interact and be deposited (Fig. 6). In the case of cotton fabric, the positively charged PU capsules have higher affinity towards the negatively charged cotton fabric and are hence expected to have a higher retention. Therefore, both the surface area of the fabric and surface potential of the capsules and fabrics play a

complementary role in determining the affinity of the capsules for a particular fabric.

Factors such as exclusion of capsules through large pores of the fabric, filtration effect due to fabric pores having the same size as capsules, material property (e.g., hydrophobicity) and forces that restrict capsule accessibility to fabric are also expected to impact the deposition and retention of capsules on fabrics. These complex factors, however, not possible to capture effectively using the smooth model surface-based studies and image-based quantification of capsules deposition (Teixeira et al., 2012). In contrast, SPOS-based number balance approach facilitates evaluating capsules' deposition based on the number of capsules in the dispersions before and after exposure to the fabric and provides a direct measure of capsules retained on the fabric either by deposition or as a result of the factors mentioned above. Therefore, our proposed methodology is simple and can be applied to understand the affinity of capsules/particles for any type of substrate.

4. Conclusions

We presented a feasible way for effective quantification of microcapsules deposited on fabrics using a simple single particle optical sizing (SPOS)-based method. We demonstrated that the quantification of capsules in the dispersions before and after exposure to a target substrate (fabric) and a number balance approach facilitate understanding of the capsules affinity for the substrate. Silica capsules, which are regarded as sustainable alternatives to the commercially used polyurea capsules, were synthesized and used as model capsules for affinity studies on two different fabrics, cotton and polyester. Microscopic analysis using scanning electron microscopy (SEM) was unable to distinguish the affinity of the different capsules as no clear differences could be observed in the SEM images of the fabrics with capsules. On the other hand, quantification of capsules using SPOS has provided an accurate measure of the affinity of capsules. Notably, affinity experiments revealed that the silica capsules deposited more on the polyester fabric (34.4% vs 24.9%), while the polyurea capsules showed 4.4 times higher affinity than the silica capsules towards the cotton fabric (28.6% vs 6.5%). The fact that the deposited capsules constitute only one-third of the capsules used indicates a substantial loss of capsules during the laundry process and underscores the importance of understanding the capsule-fabric interaction. In the current study, the observed affinity patterns were explained by considering the fabrics' surface charge and structural characteristics. It was observed that capsules exhibited a stronger attraction to fabrics with opposite charge. Additionally, the polyester fabric, with its larger pores and greater exposed surface area, retained more capsules compared to the cotton fabric.

We believe that our study provides an impetus for further studies to investigate the impact of different factors on the affinity of capsules towards a specific substrate. Further studies would investigate the following questions: (1) does the affinity of capsules depend on their type of material, size, morphology, concentration? (2) do capsules show higher affinity for a particular fabric and what are the formulation and washing parameters that affect microcapsule deposition? The answers to these questions can provide valuable insights into capsules surface affinity and broaden our knowledge for sustainable use of capsules in consumer care and specialty chemicals. Our proposed method is not limited to these areas, but one could also envision biomedical applications for counting controlled drug release capsules with respect to their affinity to tissues, affinity of dust particles to (anti-static) surfaces and any application where particles interact with surfaces and are removed from the surrounding medium.

Credit author statement

Srinivasulu Aitipamula: Experimental design, synthesis of silica capsules and characterization, data analysis, manuscript preparation. **Srinivasa Reddy Mothe**: Synthesis of polyurea capsules, data analysis and manuscript preparation. **Guo Liangfeng**: data analysis and manuscript preparation. **Alexander M. V. Herk**: Conceptualization of the research idea and manuscript preparation. **Praveen Thoniyot**: Development of research idea, data analysis and manuscript preparation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. Two authors of this publication, Praveen Thoniyot and Alex M. van Herk, hold a patent related to the synthesis of model silica capsules used for this study. All other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rsurfi.2023.100149.

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