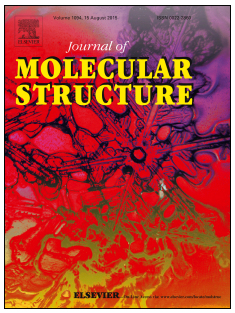

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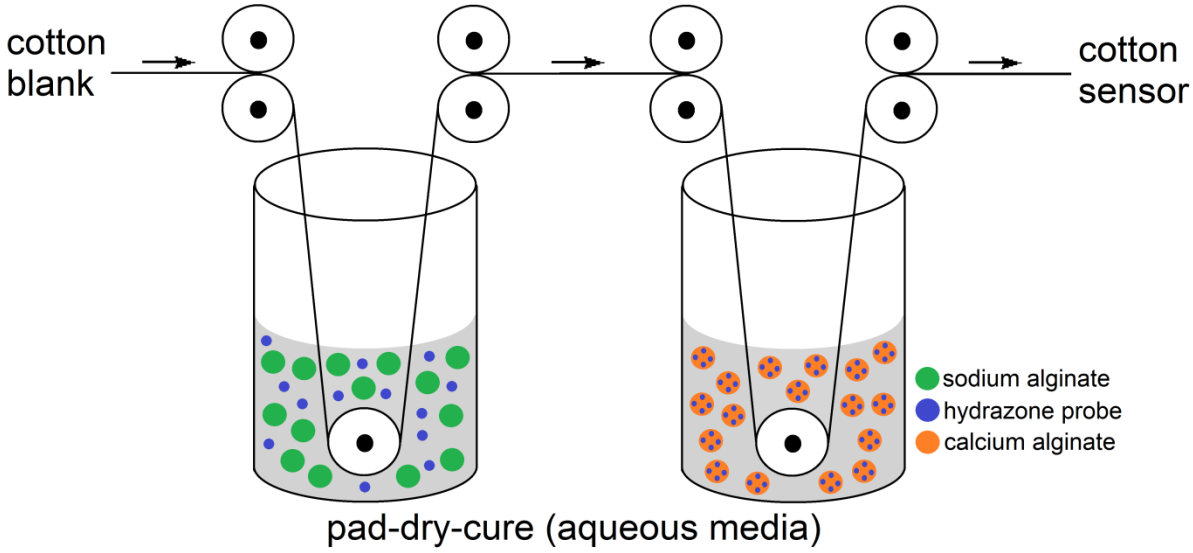
Credit Author Statement

Meram S. Abdelrahman: Preparation of tricyanofuran and measuring melting points. **Moustafa M. G. Fouda:** Preparation of tricyanofuran-hydrazone and study NMR spectra. **Jamaan S. Ajarem:** Studying elemental analysis, mass spectra, colorimetry and colorfastness measurements. **Saleh N. Maodaa:** Incorporation of microcapsules onto cotton substrates. **Ahmed A. Allam:** Cotton sensor testing and studying IR spectra. **Tawfik A. Khattab:** Studying SEM, EDX, writing, reviewing and editing.

Graphical abstract



Development of colorimetric cotton swab using molecular switching hydrazone probe in calcium alginate

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Abstract

Smart cotton fabric was developed to function as a swab for sweat pH monitoring in real-time toward a potential application for drug testing and monitoring human healthcare. A wearable, flexible and disposable microencapsulated chemical barcode was incorporated onto the highly absorptive cotton fabric to monitor sweat biochemical variations. A pH-responsive tricyanofuran hydrazone molecular switch encapsulated inside calcium alginate (Ca-alginate) microcapsule was loaded onto a cotton fabric matrix to keep an eye on sweat pH variations. Calcium alginate sensor microcapsules were prepared using tricyanofuran-hydrazone receptor sites as the core material and cross-linked calcium alginate biopolymer as the wall-former. The cotton fabric was dyed *in-situ* with a microencapsulated tricyanofuran-hydrazone in calcium alginate using the pad-dry-cure technique at room temperature. The chromogenic activity of the cotton detection tool depended mainly on the halochromic performance of the tricyanofuran hydrazone spectroscopic probe, which demonstrated color shift from light yellow to darker yellow, orange and purple due to protonation/deprotonation reversible mechanism of the tricyanofuran hydrazone chromophore. The visible color shift was monitored by CIELAB coordinates. The surface morphology, distribution and composition of fabrics were explored employing scanning electron microscopic (SEM) images, energy dispersive X-ray (EDX) spectra, and mapping analytical techniques. Microencapsulated

tricyanofuran-hydrazone sensor probe on fabrics was characterized in terms of their air-permeability, stiffness and colorfastness.

Keywords: Smart Swab; Hydrazone; Alginate; Microcapsules; Colorimetric; Sweat Monitoring.

1. Introduction

Smart technical textile materials are generally defined as clothing materials that are able to detect or response to external stimuli, such as temperature, chemicals or gases, light, magnetic or electric field, pH, pressure, and solvent polarity [1-6]. For instance, smart garments can release medication onto human skin to help regulating muscular vibrations during physical or sport activities. Smart cloths that produce sufficient responsiveness due to an external stimulus, such as heat, high voltage electric field, hazardous chemicals and irradiation, are prone to improve their protective function [7-9]. Sensing materials can be incorporated into clothing to determine the biochemical variations in fluids of human body, such as sweat, tears, saliva and urine [10-12]. Sweat is mainly composed of water as well as small quantities of other biological substances, such as amino acids, potassium and sodium ions, urea, lactate, and pyruvate [13, 14]. Sweat is naturally excreted by skin with a pH value from 4 to 6.8. Increasing pH value of sweat fluid higher than 6.8 is usually an indication of an abnormal performance of the human body. Therefore, its contents can be monitored to introduce important diagnosis about the individual physiological case. A sweat sample can be analyzed to monitor pathological disorders, dehydration, hyponatremia, which is significant to optimize the reasons of rehydration and remineralization [15, 16]. In case of drug abuse, sweat fluid might hold drug opiates, amphetamines, cocaine buprenorphine, and cannabinoids, which usually correlate sweat pH to person health [17-19]. Thus, monitoring human sweat fluid is beneficial for personal healthcare; however, the sweat fluid sample collection is a difficult issue as the useful examination must be made in real-time [20]. The use of illegal drugs leads to a huge number of related threats to public health particularly in road traffic [21, 22]. The action of law against drunken drivers led to a decrease in alcohol associated accidents. The breathing alcohol test can be simply performed on-site; however, the case is different for drug-messed drivers as particular signs are less noticeable and can be complicated to detect without the support of examining biological samples [23, 24]. Recently, police authorities took a high concern in the recognition of an impaired driver by using roadside screen examination and called upon the forensic employee to present non-invasive

sampling methods and appropriate screen approaches for *on-site* drug exams. However, such techniques require complicated instrumentations, difficult operation, hard processing and trained personnel, in addition to their failure to introduce real-time detection results [23-27]. Thus, monitoring sweat changes *on-site* in real-time can afford a preliminary beneficial physiological evaluation. Colorimetric sensors are characterized by their simple fabrication and operation, as well as their ability for naked-eye recognition making them particularly attractive. Thus, colorimetric probes have been acknowledged as one of the most easy-to-use, low-cost and effective analytical methods to monitor primary hazards or changes in the surrounding environmental pollution [28-31]. Using colorimetric approach for sweat examination is a helpful diagnostic tool due to the benefit of being non-invasive and simply reachable. Additionally, colorimetric detection tools are characterized by their ability to introduce real-time detection results, no need for complicated instrumentations or trained personnel, simple operation and easy processing [32-37]. Herein, we developed a novel, simple, robust and flexible halochromic cotton-based sensor with the ability to real-time follow up the performance of biochemical changes in human body sweat fluid. Such cotton sensor matrix is characterized by their being flexible, comfortable, high porosity and potential high surface area that can be treated [38]. The current microencapsulated cotton swab sensor device proved to function as a real-time detection tool for the variations in sweat without the requirement of any electronic components, trained personnel, power source or complicated instrumentation as it can be directly function by direct touch with human skin to guarantee instant response to sweat contents.

2. Experimental

2.1. Materials and reagents

Plain weave cotton (100%) substrate, micronaire 3.88 μg/inch, thickness 0.4 mm, weft 30 yarn/cm, warp 36 yarn/cm, 150 g m^{-2} were used. The cotton substrates, supplied from Spinning and Weaving Misr Mehalla of Egypt, were desized, scoured, and bleached employing previous literature procedures [7]. Calcium chloride ($CaCl_2$) and sodium alginate (Na-alginate) were obtained from Sigma-Aldrich. Tricyanofuran and tricyanofuran-hydrazone were prepared according to previous synthetic procedures [39, 40], in which tricyanofuran and tricyanofuran-hydrazone were recrystallized and obtained in high purity using flash column chromatography and reactions were visually monitored by TLC (PF254) under ultraviolet lamp (365nm). Organic solvents were purchased from Aldrich, while

malononitrile, 3-hydroxy-3-methylbutan-2-one and 4-nitroaniline were purchased from Sigma Aldrich.

2.2. Methods and instrumentation

Melting points were obtained uncorrected (^{o}C) on Stuart/SMP30. FTIR spectrum of the prepared tricyanofuran-hydrazone was recorded on Nexus-670 (Nicolet, United States). NMR spectra were explored by BRUKER/AVANCE/400 spectrometer at 400 MHz. Elemental analysis was carried out on PerkinElmer/2400 (Norwalk, USA). Mass spectrum was measured on Shimadzu GCMS-QP-1000-EX spectrometer. Scanning electron microscope (SEM) was applied to investigate both morphological properties and elemental content using Quanta FEG250 (Czech Republic) coupled to energy-dispersive X-ray (TEAM-EDXA). The calcium alginate microparticle diameter was measured by Image J software.

2.3. Preparation of tricyanofuran [39]

Sodium metal (6.5 mmol) was dissolved in 15 mL of absolute ethyl alcohol in a water bath at room temperature to introduce sodium ethoxide solution, followed by adding 3-hydroxy-3-methylbutan-2-one (45 mmol) and malononitrile (90 mmol) with stirring. After stirring for one hour at room temperature, an additional 20 mL of absolute ethyl alcohol was added. The mixture was refluxed for another two hours. After cooling in a refrigerator, the resultant precipitate was filtered under vacuum, subjected to washing with a minimal quantity of cold ethyl alcohol, and air-dried to give an off-white crystalline product. The filtrate was then concentrated, cooled and filtered off to give a second crop (total yield 59%). mp 202ºC–204ºC. ^{1}H NMR (400 MHz, $CDCl_3$): ppm 2.36 (s, 3H), 1.64 (s, 6H).

2.4. Preparation of tricyanofuran-hydrazone [40]

Tricyanofuran-hydrazone was prepared by stirring 4-nitroaniline (2 mmol) and hydrochloric acid (15 mL) on a magnetic stirrer at 0-5ºC. An aqueous solution of $NaNO_2$ (2 mmol) in was then added slowly to afford the corresponding diazonium salt, which was added slowly to a solution of tricyanofuran (2 mmol) and sodium acetate (3 g) in acetone (15 mL) at 0-5ºC with vigorous stirring. The precipitate was filtered, subjected to washing with distilled water, crystallized from a mixture of ethyl alcohol/chloroform (2:1) to give a dark orange powder (yield 81%); mp 225-226°C; ^{1}H NMR (400 MHz, DMSO-d_6): ppm 12.79 (singlet broad, 1 H, NH), 8.26 (doublet, 2 H, *J*= 9.2 Hz), 7.99 (singlet, 1 H, =C-H), 7.38 (doublet, 2 H, *J*= 8.8 Hz), 1.81 (singlet, 6 H); ^{13}C NMR (400 MHz, DMSO-d_6): ppm 177.38, 171.91, 147.82, 142.86, 129.19, 126.53, 115.19, 113.14, 112.38, 110.87, 99.44, 99.30, 26.36; IR (neat, ν/cm^{-1}) 3275 (for secondary amine group), 2224 (for cyanide group), 1577 (for C=N group), 1511 and 1309 (for nitro group); MS *m/z* (%): 347 [*M*-H]$^{+}$; Elemental analysis for tricyanofuran-

hydrazone ($C_{17}H_{12}N_6O_3$; 348.10): *calculated* C 58.62, H 3.47, N 24.13; *established* C 58.51, H 3.62, N 24.03.

2.5. *In-situ* preparation of microcapsules on cotton substrates

Sodium alginate (0.5wt % to water volume) and hydrazone probe (0.1 (H_1), 0.5 (H_2), 1 (H_3), 1.5 (H_4) and 2 (H_5) wt% to the weight of sodium alginate) dissolved in 1-3mL acetone were added to distilled water (100 mL). The mixture was stirred on a mechanical stirrer for 1 hour to ensure a homogenous mixture. Cotton fabrics were subjected to padding in the prepared solutions for 15 minutes, and then padded in a calcium chloride aqueous solution (500 mM) for 15 minutes. The treated cotton fabrics were then washed with distilled water to get rid of any remained depositions of NaCl or $CaCl_2$, and air-dried. The *In-situ* preparation of microcapsules onto cotton fabrics is displayed in **Figure 1.**

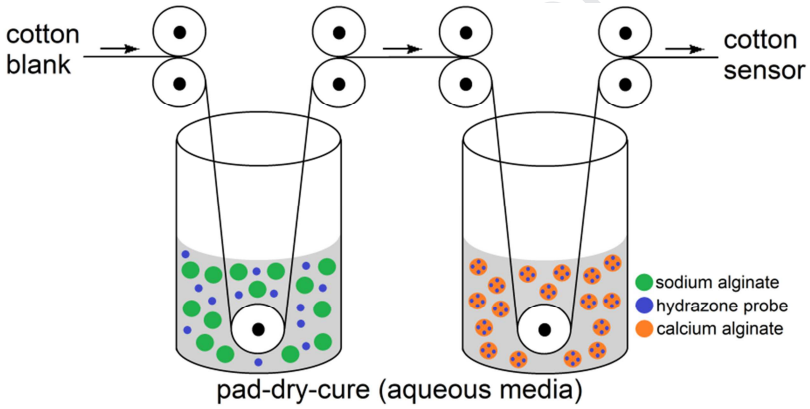

Figure 1: *In-situ* preparation of microcapsules immobilized onto cotton fibers.

2.6. Colorimetric and colorfastness measurements

The color changes were reported on a Texflash ACS/Datacolor 600 spectrophotometer. The color data were explored by CIE **(**L^*, a^*, and b^*) coordinates and color strength. The colorfastness properties against rubbing, light, washing and perspiration were examined according to ISO standards; ISO105-X12(1987), ISO/105-B02 (1988), ISO/105-C02 (1989) and ISO/105-E04 (1989), respectively.

2.7. Cotton sensor test

Sweat mimic solution was assembled depending on ISO/105/E04:1989 standard test. L-α-Amino-β-(4-imidazolyl)propionic acid monohydrochloride (0.25 $g \cdot L^{-1}$), sodium chloride (NaCl; 10 g/L), and sodium dihydrogen phosphate (NaH_2PO_4; 1 g L^{-1}) were added to distilled water (1 L). The pH was tuned between 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 and 8 using aqueous solutions of acetic acid (0.1 N) and NaOH (0.1 N) to reduce and to raise the pH value,

respectively. The designed nine sweat mimic solutions with different pH values was sprayed on the cotton fabrics to show an instant color shifting from light yellow to darker yellow, orange and purple relying on the pH of the medium. The pH values of sweat mimic solutions were monitored by BECKMAN-COULTER pHI340.

The reversibility of dyed cotton sensor (1 wt %) was tested by exposing the cotton fabric to sweat fluid (pH 7.5) to demonstrate purple color. The fabric was then washed with an aqueous solution of acetic acid (pH 6) in distilled water to remove the effect of the sweat fluid and finally air-dried. The absorption wavelength was recorded on Texflash ACS Datacolor. The same procedure was repeated several cycles.

3. Results and discussion

3.1. Preparation of microcapsules immobilized onto cotton fabric

There are a diversity of materials, such as cellulose acetate [41], mesoporous silica [42] and silicate sol-gel [43] that have been employed as supporting carrier substrates to fabricate sensor tools. However, most of those materials comprise several drawbacks, such as ageing, poor sensitivity and reversibility, expensive, difficult processing, as well as long-time sensing. Alginate is a polysaccharide, naturally occurred in brown algae, that has been applied for several purposes, such as nontoxic wound dressing, foodstuff, thickener, stabilizer and gelator, and other medical substrates. Alginate-based microencapsulated devices can be assembled by the crosslinking process of Na-alginate polymer chains. This is carried out by the replacement of monovalent Na(I) with divalent Ca (II) to function in an aqueous medium at mild conditions [44, 45]. Immobilization of one or more active detection sites into calcium alginate (Ca-alginate) microcapsules can be accomplished by co-precipitating those active sites within Ca-alginate capsules.

Tricyanofuran hydrazones are pH-stimuli responsive dyes characterized by excellent ability to create pH-responsive colorimetric sensor devices due to their excellent color changes at different values, reversibility, and thermal and photochemical stability. Tricyanofuran-hydrazone sensor dyes have been known as multi-stimuli responsive dyes to pH and temperature. They have been used as solution probes and as solid state sensors in polymer matrices for the production halochromic tools, and determination of ammonia and amines. The tricyanofuran (**1**) starting material bearing an active-methyl was simply prepared depending previous literature procedure [40, 41]. The tricyanofuran-hydrazone sensor probe (**2**) was prepared via azo-coupling of heterocyclic compound **1** and diazonium salt of 4-nitroaniline **(Figure 2)**.

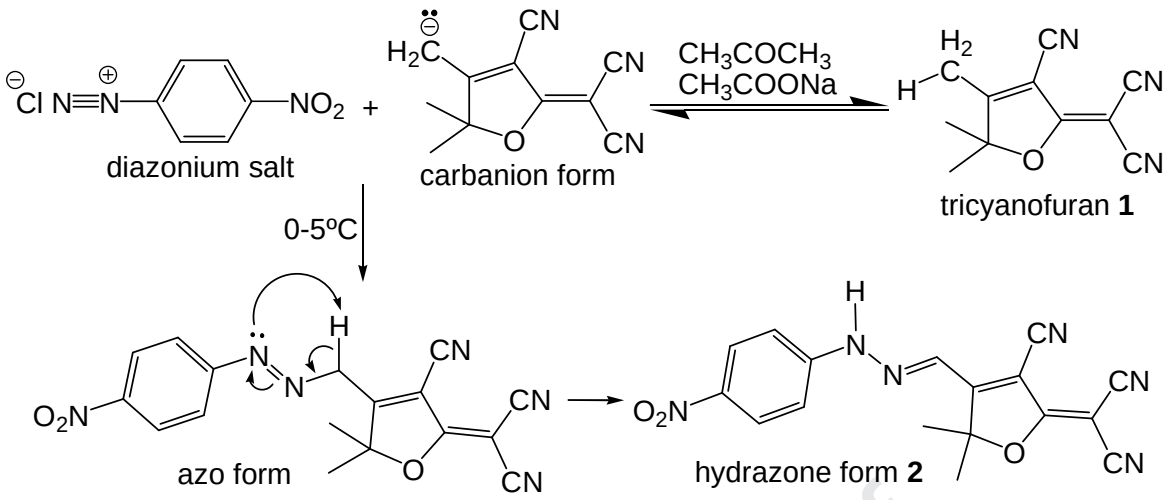

Figure 2: Preparation of tricyanofuran-hydrazone probe

Illegal drugs and other health problems can be easily reflected spectroscopically by apparent shifts in the pH value of human sweat, which diffuses through the porous film of alginate microcapsules on cotton fabric into the tricyanofuran-hydrazone detection active sites to change their color between light yellow and purple. Mechanism of perspiration solution sensing depended mainly on the protonation-deprotonation reversible process of tricyanofuran-hydrazone which was integrated within Ca-alginate microcapsules on cotton substrates. The strong electron-withdrawing nitro group at *para* position of the phenylhydrazone moiety led to deprotonating NH hydrzone introducing the corresponding hydrazone anion bearing negative charges as a result of the increased acidity of this NH hydrazone proton. Consequently, the hydrazone anion form functions as an electron-donor fragment conjugated with the electron-withdrawing tricyanofuran heterocycle in a push-pull extended conjugation molecular structure **(Figure 3)**.

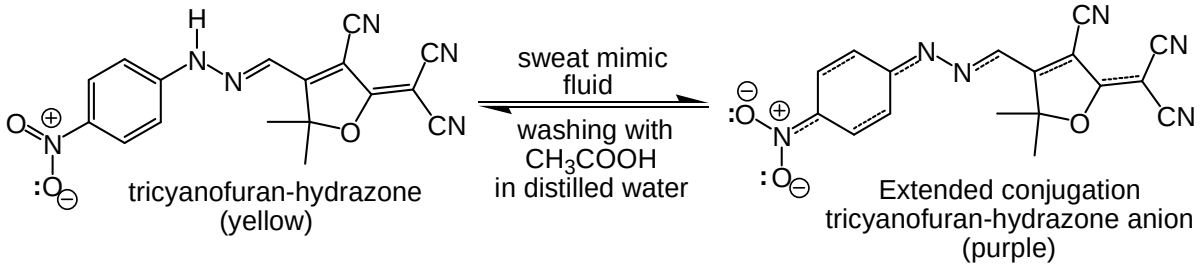

Figure 3: Mechanism of tricyanofuran-hydrazone protonation-deprotonation reversible process

The sensor microcapsules were assembled by concurrent co-precipitation of Na-alginate and tricyanofuran-hydrazone into cross-linked Ca-alginate enclosing tricyanofuran-hydrazone dispersed active sites through the alginate polymer matrix. Cotton samples were immersed in an aqueous Na-alginate and tricyanofuran-hydrazone, and air-dried followed by immersion in an aqueous $CaCl_2$ to commence the cross-linking operation. In the alginate polymer strains, Upon adding Na-alginate into an aqueous solution of $CaCl_2$, the divalent Ca^{++} replaced the monovalent Na^{+}. Each Ca^{++} can be cross-linked to two polymer strains. Alginate is a polysaccharide that has been applied in foodstuffs, pharmaceutical and dental purposes, thickeners, stabilizing and gelling agents, and wound dressings. Five different solutions were prepared depending on tricyanofuran-hydrazone concentration in solution (0.1 (H_1), 0.5 (H_2), 1 (H_3), 1.5 (H_4) and 2 (H_5) wt %).

3.2. Characterization and morphological properties

Cotton fabric conventionally dyed with tricyanofuran-hydrazone probe did not demonstrate color change to the sweat mimic solution, which could be attributed to the steric hindrance that tricyanofuran-hydrazone molecules experience in the fibrous matrix of cotton fabric, where both the active tricyanofuran-hydrazone probe and cotton fibers are not in the nano/microscale and accordingly cannot be stimulated easily by the targeted molecules to be monitored. In comparison to large diameter particles, microcapsules are distinguished by their high surface area, outstanding mechanical features and high surface functionality [46-50]. For instance, the solid powder of tricyanofuran-hydrazone probe did not demonstrate any sensing performance as was already demonstrated by the same material probe in solution phase. This is because the guest molecules cannot diffuse easily through the solid powder of the tricyanofuran-hydrazone probe. On the other hand, microcapsules possess higher surface area compared to the corresponding solid powder of the same material, which enabled diffusion of the targeted molecules to be detected through the sensing device matrix. The current pH-responsive tricyanofuran hydrazone molecular switch can be classified as a disperse dye because it is water-insoluble and characterized with small molecular structure. Thus, this tricyanofuran hydrazone disperse dye has absolutely no affinity to dyeing cotton fibers and it can only be attached to cotton fibers via encapsulation within the calcium alginate cross-linked mediator [46, 51-54]. Compared to previously report blank cotton fibers [7], scanning electron microscope images of treated samples proved the formation of calcium alginate microcapsules incorporated on the surface of cotton fabric, which resulted in a higher surface area with porous structure to allow better diffusion of sweat fluid into the tricyanofuran-hydrazone active sites. The morphological properties and elemental

composition of the treated cotton substrate surface dip-coated with Ca-alginate microcapsules molecularly imprinted by tricyanofuran-hydrazone were explored **(Figure 4)**. The scanning electron microscopic images of pad-dry-cured cotton demonstrated successful dip-coating of cotton surface with clusters of Ca-alginate microcapsules displaying nano/microstructures of irregular shapes. The alginate microcapsules diameter distribution was measured on software program employing SEM images. The size distribution of the obtained nano/microstructured Ca-alginate microcapsules on cotton fabric surface was in the range from ~550nm to ~5μm. The main size average of the Ca-alginate microcapsules was about ~2μm. Such nano/microstructural Ca-alginate microcapsules tended to agglomerate, and accordingly dispersed slightly heterogeneous onto the pad-dry-cured cotton fabric, which could be attributed to the sort of chemical and physical interactions of Ca-alginate macromolecules with the cotton fabric. Moreover, SEM images demonstrated no physical variations happened to the surface of pad-dry-cured cotton fabric.

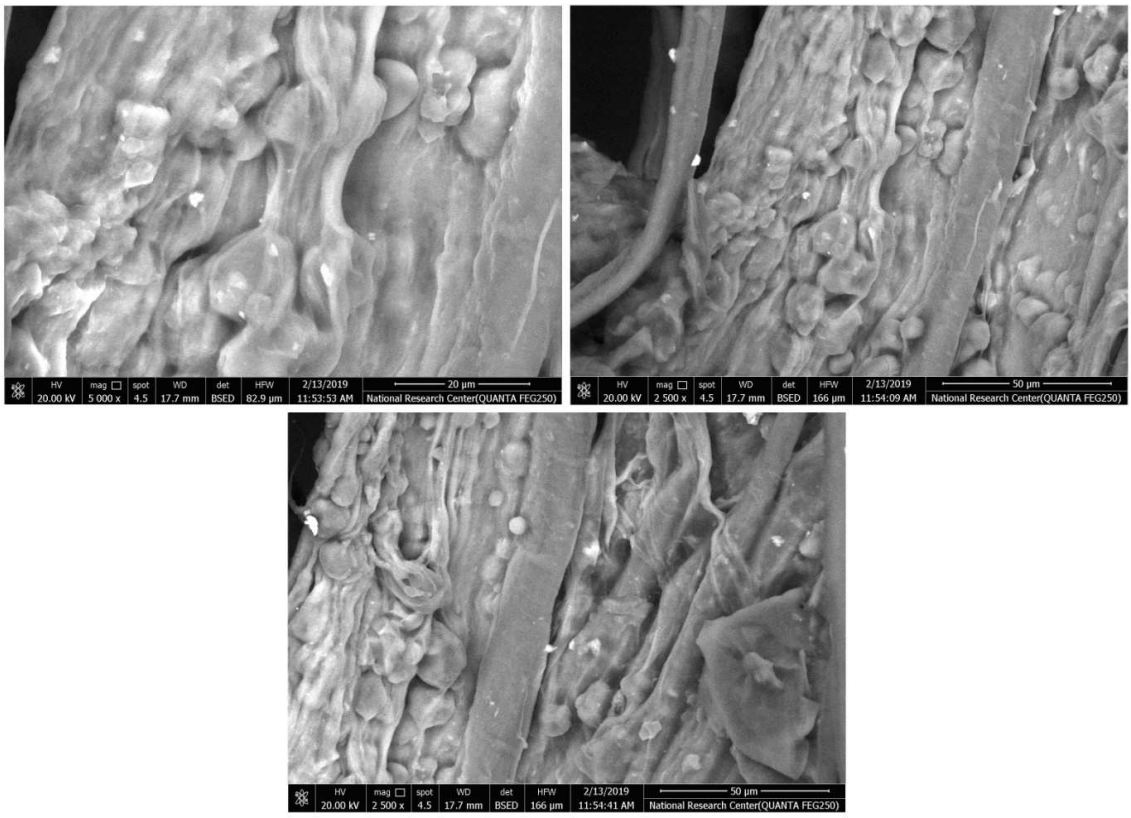

Figure 4: Scanning electron microscope images of dip-coated (pad-dry-cured at room temperature) cotton fabric (Sample H_3)

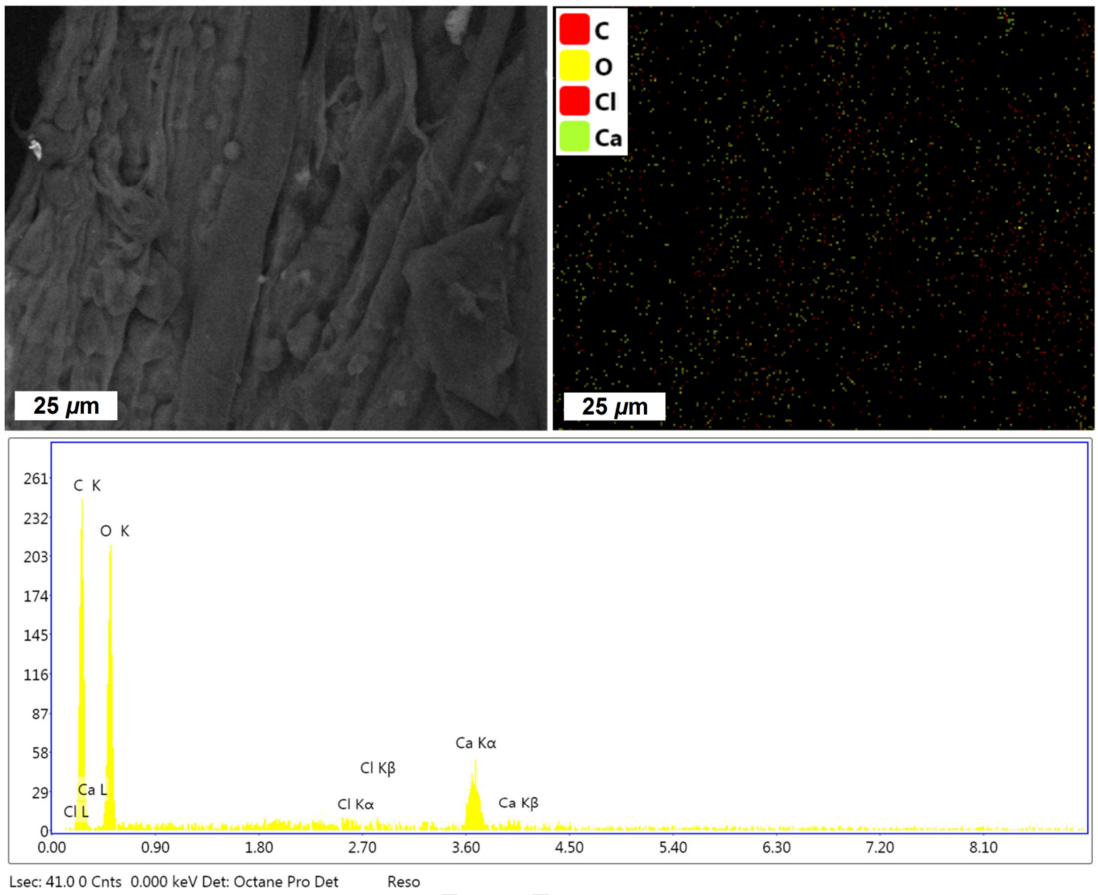

Figure 5: Elemental mapping image (*top*) and energy dispersive X-ray analysis spectrum (*bottom*) of dip-coated (pad-dry-cured at room temperature) cotton fabric (Sample H_3)

The elemental composition of the dip-coated (pad-dry-cured) cotton was also explored by EDAX spectroscopic analysis via measuring the elemental weight percent at three different spots on the surface of the pad-dry-cured fabric as shown in **Figure 5**. The elemental composition selected at these three spots was closely similar. This proved the homogenous incorporation of Ca-alginate microcapsules on cotton surface. The mapping diagram of the major elements confirmed the consistent distribution of Ca-alginate microcapsules on the surface of the pad-dry-cured cotton. The Ca-alginate microcapsules were immobilized onto cotton fabric to establish porous three-dimensional architecture bearing highly porous surface area. Thus, solid state cotton sensor showed high sensitivity toward sweat fluid due to the high surface to volume ratio and large porous structural design, which facilitated the diffusion of the guest sweat fluid within the Ca-alginate microcapsules integrated within cotton matrix. Fourier transform infrared (FTIR) spectra were employed to investigate the key characteristic peaks of the dyed cotton including both hydroxyl and CH aliphatic groups. In general, there are no considerable shifts were detected. Slight reduction was monitored in the absorbance

band at 3305 cm^{-1} for OH groups, which could be attributed to H-bond formation among the hydroxyl groups on the cellulose polymer strains of the cotton fabric and the carboxylate anion comprised from the alginate biopolymer. Also, slight increments in the absorbance peaks were monitored at 2965 and 1013 cm^{-1} for both aliphatic C-H stretching and bending, respectively. This could be assigned to the extra aliphatic C-H from the alginate layer.

3.3. Colorimetric measurements toward sweat monitoring

Solid-state detection tools are more practical than liquid probes because they are characterized by portability, reversibility and simplicity leading to fast online detection at low cost. Thus, it is very interesting and also challenging, to assemble solid state sensing devices for real time detection of a trace material. Solid state devices could potentially be applied as detection devices for general laboratory assays and household purposes as commercial sensors [55-59]. Hence, the research for an environmentally friendly simple solid sensor is of high importance. Cotton is originally natural solid cellulosic material with a fibrous-like porous structure characterized by low density, high porosity and high surface area. The calcium alginate biopolymer-based microcapsules were immobilized into cotton fabric to present porous three-dimensional architecture characterized by highly porous scaffolds with large surface area. The colorimetric cotton sensor has the ability to function directly as a swab on human skin. To inspect the solid state cotton fabric detector, we designed a sweat mimic solution to be sprayed, which is similar to swabbing human skin, onto the surface of the dip-coated cotton to display an immediate color shift from light yellow to darker yellow, orange and purple relying on the medium pH of the sweat mimic system as demonstrated in **Figure 6** and **Table 1**. Changes in *K/S* and CIE color space values were explored to evaluate the cotton fabric sensing ability of sweat biochemical changes. The coloration data of the dip-coated cotton fabrics at different concentration values of tricyanofuran-hydrazone probe before and after exposing to sweat solution are demonstrated in **Table 2**. For both situations, before and after exposing to sweat solution, a significant increase in *K/S* was detected due to variation to better *K/S* upon increasing the concentration values of tricyanofuran hydrazone within the range of 0.1-1.0 wt %. A slight change was observed in *K/S* upon increasing the concentration values of tricyanofuran hydrazone within the range of 1.0-2.0 wt %. This is because the uptake of Ca-alginate/tricyanofuran hydrazone from the solution bath into the cotton fabric under treatment was increased between 0.1-1.0 wt%, while the uptake of Ca-alginate/tricyanofuran hydrazone reached equilibrium within the range of 1.0-2.0 wt%. Therefore, Ca-alginate/tricyanofuran hydrazone content on the fabric was at highest saturation at 1.0 wt%. The fabric at this equilibrium stage paused absorption of Ca-

alginate/tricyanofuran hydrazone during the padding process. Thus, the best coloration values of the cotton fabric were monitored at 1 wt%. The exposure of cotton fabric to sweat solutions resulted in an increase in the absorption maxima of the fabric from 455 (pH 4) to 515 nm (pH 8). The cotton fabric sensor was integrated with tricyanofuran-hydrazone immobilized within Ca-alginate microcapsules. The instantaneous color change was visually recognized from light yellow to darker yellow, orange and purple relying on the biochemical variations of the sweat fluid. The three dimensional color parameters (L^*, a^*, b^*) of the pad-dry-cured fabrics treated at different concentration values of tricyanofuran hydrazone before and after exposure to sweat fluid were displayed in **Table 2.** The lightness/darkness range was denoted by the symbol L^*, green/red range was denoted by the symbol a^*, and blue/yellow range was denoted by the symbol b^*. The dip-coated cotton fabrics possessed yellow color, while the blank untreated cotton possessed white color (L^*= 95.83, a^*= 0.02, b^*= -1.05). The color coordinates of the Ca-alginate microcapsules incorporated on cotton fabrics were measured before and after exposing to the sweat solution. Depending on the concentration of tricyanofuran-hydrazone, all treated cotton fabrics, before and after exposing to perspiration solution, showed significantly dissimilar L^*, a^* and b^* magnitudes comparative to blank cotton. For both conditions, before and after exposing to perspiration solution, L^* was comparatively decreased with increasing tricyanofuran-hydrazone total content within the range of 0.1-2.0 %. However, a significant increase was monitored in L^*, mostly for the tricyanofuran-hydrazone concentration at 1.0 wt %, after exposing to perspiration solution to signify darker color. Before exposing to perspiration solution, the decreased b^* and increased a^* positive values indicated yellow color of all pad-dry-cured cotton fabrics at all tricyanofuran-hydrazone concentrations. After subjecting to perspiration solution, the increased positive a^* and negative b^* values indicated purple color of all pad-dry-cured cotton fabrics. For all samples, after exposure to perspiration solution, a^* positive magnitudes were increased to designate more red, while positive b^* magnitudes were shifted to negative to designate more blue.

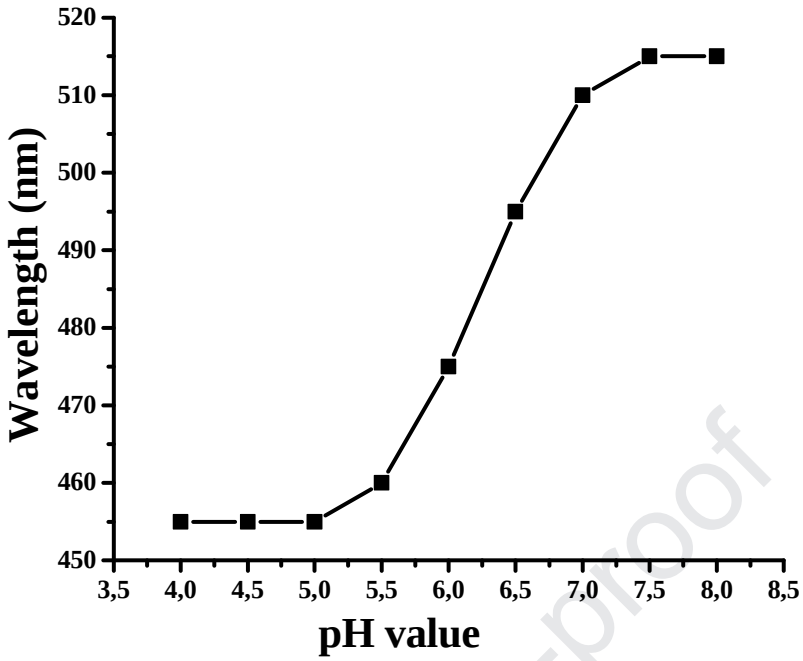

Figure 6: Relationship between maximum absorption wavelength and different pH values of sweat fluid

Table 1: Changes in color and absorption wavelength according to changes in pH values of sweat fluid

pH value	λ_{max}	Color of fabric
4	**455**	**Light yellow**
4.5	**455**	**Light yellow**
5	**455**	**Light yellow**
5.5	**460**	**Light yellow**
6	**475**	**Yellow**
6.5	**495**	**Orange**
7	**510**	**Orange**
7.5	**515**	**Purple**
8	**515**	**Purple**

Table 2: Color coordinates of Ca-alginate microcapsules incorporated on cotton fabrics with different contents of tricyanofuran-hydrazone, and before (B) and after (A) exposure to the perspiration mimic mixture.

Probe	L*		a*		b*		*K/S*	
wt%	B	A	B	A	B	A	B	A
H_1	72.67	48.26	3.09	4.21	18.25	- 6.14	3.23	5.00
H_2	68.92	47.08	6.78	7.89	14.47	- 8.33	4.19	5.87
H_3	67.01	37.85	8.55	10.32	11.71	- 11.59	5.07	7.23
H_4	65.83	36.36	8.34	11.29	8.56	- 13.90	5.72	7.85
H_5	65.12	36.58	8.15	12.13	5.82	- 17.05	6.10	8.12

3.4. Durability and comfort measurements

The main reason of applying the pad-dry-curing technique is to establish a smooth fabric surface with low film thickness and low roughness, while maintaining the cotton substrate's flexibility and air-permeability. Shirley Stiffness Testing Machine was employed to measure the bending length of the pad-dry-cured cotton fabrics **(Table 3)**. Mainly, the pad-dry-curing procedure did not affect on air-permeability, but a slight decrease in flexibility of the pad-dry-cured cotton fabrics was detected in warp/weft with raising the concentration of tricyanofuran-hydrazone probe. The pad-dry-cured film possessed a surface free energy (35 mN/m) as demonstrated by a tensiometer (KRÜSS/DSA30S). This proved that the pad-dry-cured cotton fabric surface had a high wettability. The durable performance of the pad-dry-cured cotton to light, perspiration, washing and rubbing was explored. No changes were detected for the pad-dry-cured cotton after wash. The pad-dry-cured cotton fabrics showed softness to touch. The colorfastness and photostability were satisfactory for all concentrations of tricyanofuran-hydrazone as shown in **Table 4**. However, a little decrease in the colorfastness and photostability was monitored upon increasing tricyanofuran-hydrazone concentration.

Table 3: Bending length and air-permeability properties of the pad-dry-cured fabrics

Probe wt%	Bend length (cm)		Air-permeability ($cm^3/cm^2/s^1$)
	weft	*wrap*	
Blank	**2.50**	**2.91**	**52.58**
H_1	**2.87**	**3.25**	**48.91**
H_2	**3.10**	**3.43**	**47.08**
H_3	**3.38**	**3.47**	**47.28**
H_4	**3.53**	**3.68**	**47.39**
H_5	**3.61**	**3.75**	**47.24**

Table 4: Colorfastness properties of the pad-dry-cured fabrics

Probe wt%	Wash		Perspiration				Rubbing		Light
	Alt.*	St.*	Acidic		Basic		Dry	Wet	
			Alt.*	St.*	Alt.*	St.*			
H_1	**4-5**	**4-5**	**4**	**4-5**	**4-5**	**4-5**	**4**	**4**	**6**
H_2	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4**	**4**	**6**
H_3	**4**	**4**	**4**	**4**	**4**	**4**	**3-4**	**3-4**	**6**
H_4	**4**	**4**	**3-4**	**4**	**4**	**3-4**	**3-4**	**3-4**	**5-6**
H_5	**3-4**	**4**	**4**	**4**	**3-4**	**3-4**	**3-4**	**3**	**5-6**

**Alt. = color alteration; St. = cotton staining.*

The reversibility of treated cotton (H_3) was explored after perspiration monitoring by exposing the cotton fabric to sweat fluid (pH 7.5) to demonstrate purple color, the maximum absorbance wavelength were repeated back-and-forth as the fabric exhibited purple (515 nm) color after exposure to perspiration solution and yellow color (475 nm) after washing with an aqueous solution of acetic acid (pH 6) in distilled water and air-drying to remove the effect of the perspiration solution. The absorbance wavelength was reported on Texflash ACS

Datacolor. This cycle of exposure to perspiration solution followed by washing was repeated **(Figure 7)** to indicate high stability.

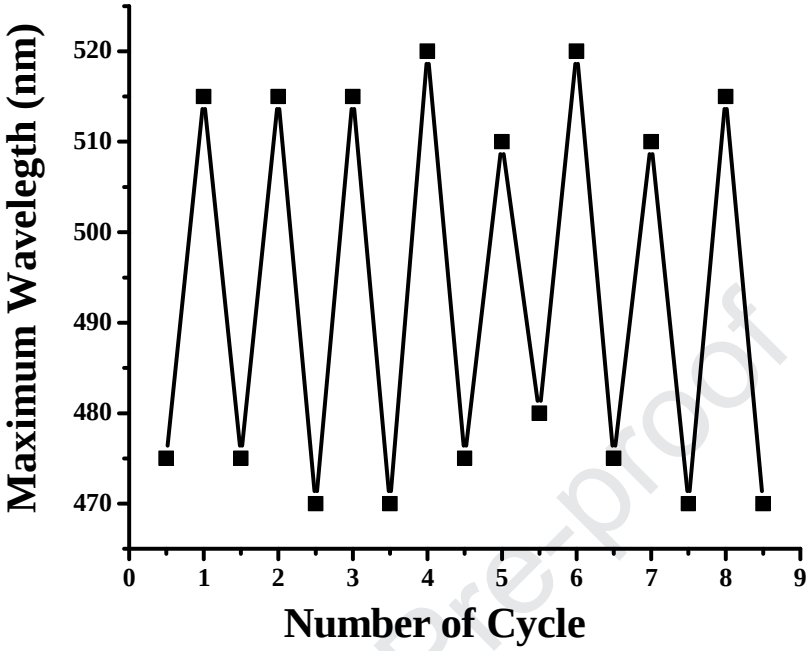

Figure 7: Changes in the absorbance wavelength (475nm for yellow and 515nm for purple) of dip-coated (pad-dry-cured at room temperature) cotton fabric (Sample H_3)

4. Conclusions

We prepared, characterized and assessed the activity of a simple solid state pH responsive cotton fabric for potential monitoring sweat biochemical variations. The microcapsules were prepared by cross-linkable coupling of Ca^{+2} with the aqueous gel of Na-alginate. Microcapsules were assembled from a cross-linked Ca-alginate capsule shell integrated with tricyanofuran-hydrazone capsule core. Those microcapsules were loaded on smart cotton fabric to be applied for naked-eye sweat pH monitoring depending on the color change of the deprotonated-protonated tricyanofuran-hydrazone from light yellow to darker yellow, orange and purple associated with the medium pH from acidic to alkaline. The detector performance was demonstrated by colorimetric measurements. The results were confirmed by exploring surface morphological properties and composition of pad-dry-cured fabric employing scanning electron microscopy, energy dispersive X-ray spectra, and mapping of elements. The comfort properties of the pad-dry-cured cotton fabrics were evaluated to show acceptable results of colorfastness, stability to wash and light, bend-length and air-permeability. This method can be potentially employed for identification of sweat fluid status, such as *on-site*

real time drug test device and monitoring sporting activities. Compared to earlier identification techniques which require sophisticated instrumentation, electric power, trained personnel and electronic parts, the environmentally friendly cotton/alginate colorimetric detector is an easy-to-fabricate and easy-to-apply with high response time technique for *on-site* real-time sweat status identification.

Compliance with ethical standards: All procedures by this study were in accordance with international ethical standards. The research involved no human participants.

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Highlights

- Simple colorimetric cotton fabric for sweat monitoring was introduced.
- Probe encapsulated within calcium alginate was immobilized *in-situ* onto cotton.
- Potential chromogenic sensor to be applied as a drug test by direct swab of skin.
- Cotton displayed color change from yellow to purple upon exposure to sweat mimic.

Declaration of interests

√ The 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Signature (on behalf of all co-authors)

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