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In-situ fabric coloration with indigo synthesized in flow

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Abstract

Indigo (C.I. Vat Blue 1) is a water-insoluble pigment exhibiting no affinity for fibres, and must be chemically reduced in basic solution to form the water-soluble, alkaline leucoindigo (C.I. Reduced Vat Blue 1), in order exhibit substantivity for fibres. Typical vat dyeing processes are time and resource intensive, and hazardous by-products are formed, primarily through the use of reducing agents. We describe a method for synthesizing indigo in a flow reactor that allows for application of dye precursors to fibres moments before the reaction completes. The soluble precursors soak into the cotton fabric just prior to the precipitation of the insoluble indigo, effectively providing in-situ coloration, without the need for a traditional redox dyebath. The reaction may be coupled with a propellant, an adaptation that allows for a "sprayable" form of indigo. In-situ coloration with Tyrian purple (6,6′-dibromoindigo; C.I. Natural Violet 1) was also demonstrated using the flow chemistry method. The research provides compelling proof-of-concept, but we acknowledge that the process is in its infancy and needs further development to get it to a stage where it can compete commercially with current technology.

Keywords

Vat dyes, flow chemistry, microfluidics, cotton, green chemistry.

1. Introduction

Indigo (C.I. Vat Blue 1; **1**) is among one of the oldest known textile dyes, and has been used to dye cellulose textiles, especially cotton, for over 4000 years [1,2]. Historically, indigo was obtained from the leaves of Isatis tinctoria in Northern Europe and from Indigofera tinctoria in Asia using a fermentation process [3]. As the process modernized, Isatis tinctoria, the woad plant, was dissolved

in wooden vats by a natural fermentation process in a method that became known as "vatting" [4]. The first synthetic indigo was available in 1897, and beginning in about 1970, it became one of the most important dyes in use today through its use in denim dyeing. Currently, well over 99% of indigo used in textiles is synthetic. Each year, 2 billion pairs of blue jeans are manufactured, employing a minimum of 3 grams of indigo for each [5].

Currently, the vat dyeing industry is a multimillion dollar industry that produces and uses over 80,000 tonnes of vat dyes each year [6]. Indigo is a deep blue solid, and can be prepared by the combination of 2-nitrobenzaldehyde and acetone in basic solution using the Baeyer-Drewson aldol condensation reaction (Figure 1) [7]. From an industrial perspective this method was displaced by routes from aniline [8].
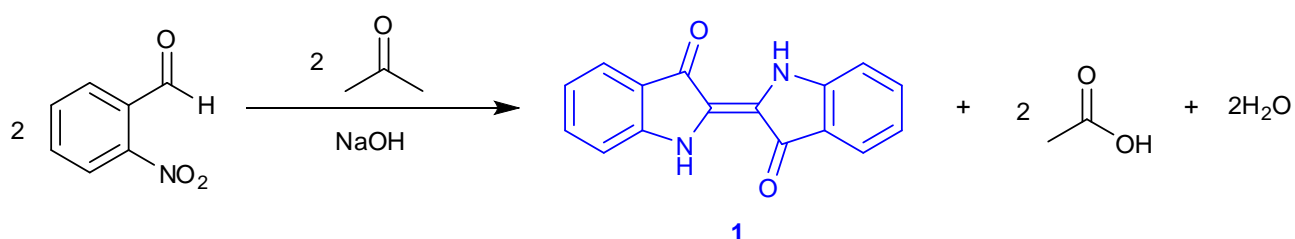

Figure 1. Baeyer-Drewson indigo synthesis (1882).

Once formed, indigo is a water-insoluble pigment exhibiting no affinity for fibres. Thus, the compound must be reduced in basic solution to form a water-soluble form called alkaline leucoindigo (C.I. Reduced Vat Blue 1; **2**), in order to exhibit substantivity for cellulosic fibres. The reduction of indigo, and other similar vat dyes, is done primarily through the use of sodium dithionite (sodium hydrosulfite), $Na_2S_2O_4$. The reduction process changes the chromophore of the molecule, such that acid leucoindigo is an off-white solid and alkaline leucoindigo a pale yellow solution. Once the yellow, aqueous solution has intercalated into the fibres, the leucoindigo is subsequently air oxidized back to the original insoluble indigo, physically trapping the blue dye in the fibre (Figure 2). Commercial dyeing of denim with indigo is primarily done via the sequential wetting of cotton rope in a series of basic leucoindigo baths, followed by air-oxidation (with O_2) to convert the leucoindigo back into the insoluble blue pigment form. The formation of the insoluble indigo within the fibre secures a wash-fast dyeing by virtue of the fact that the dye is mechanically trapped within the fibre structure.
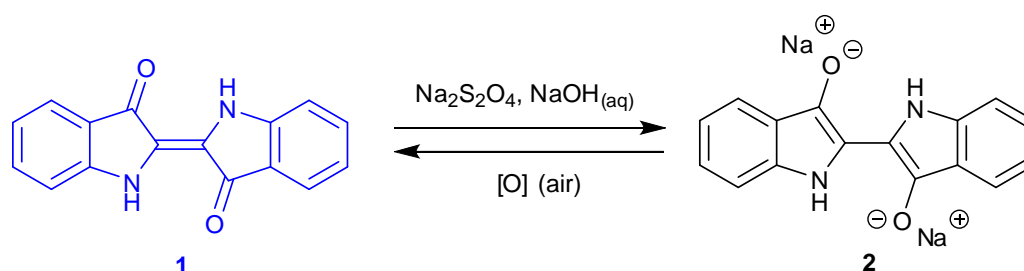
Figure 2. Indigo reduction upon addition of sodium dithionite and oxidation upon air oxidation.

There are a number of issues associated with the vat dyeing process. Sodium dithionite is easily oxidized into sulfates (SO_4^{2-}), sulfites (SO_3^{2-}) and thiosulfates ($S_2O_3^{2-}$), which are environmental toxins, and their corrosive properties can threaten concrete waste pipes [9]. In addition, these anions can form toxic by-products such as hydrogen sulfide ions, by means of anaerobic degradation. More recently, newer methods such as catalytic hydrogenation, bacterial-driven reduction, and electrochemical reduction processes are promising alternatives for the preparation of leucoindigo and reduced indigo [10]. Regardless of which method is employed, the need to use reducing agents to create dye baths costs time, infrastructure, and large quantities of water, all of which creates chemical waste, and adds to the overall cost of the process. Ideally, the elimination of the vat dyeing step would represent a significant advancement in the production of indigo.

Recently, syntheses performed using microfluidic devices have been the subject of intense interest. Besides minimizing air contact, flow reactors offer controlled mixing, increased surface-to-reactor-volume, and controlled use of highly reactive and toxic materials with reliable reproducibility [11,12]. Flow production also offers a reduction in hazardous waste materials as well as safer synthesis processes. Micro- or meso-fluidic flow devices can be easily scaled for large-scale production which can offer advantages in economics, safety, time, and space [13,14]. The flow synthesis of insoluble indigo was reported in 2006, demonstrating that precipitate-forming reactions could proceed in a microreactor without clogging the reaction channel [15].

Herein, we propose a modified version of this flow reaction to allow for the combined reagent mixture to be directly applied to fibres moments before the reaction completes. This allows for the soluble precursors to soak into the fibre just prior to the precipitation of the insoluble indigo, effectively dyeing the fibre without the use of a traditional alkaline leucoindigo bath. Here, we report conditions for the direct dyeing of textiles with indigo, synthesized in flow.

2. Experimental

2.1. Materials

The flow device was comprised of a Harvard Apparatus PhD 2000 Infusion syringe pump equipped with two 50 mL Norm-ject polypropylene syringes, attached to 1.59 mm diameter PVC tubing via an Upchurch Scientific PEEK tubing Y-adapter, all available from VWR Scientific. 2-nitrobenzaldehyde, 4-bromo-2-nitrobenzaldehyde, sodium hydroxide, and acetone were purchased from VWR or Aldrich and used without further purification. Plain weave cotton fabric was obtained from Lily Cotton Company. For wash fastness comparison, commercial denim was obtained from the Centre for Test materials B.V. and cut into 100 x 40 mm strips. Multifibre strips were obtained from James Heal and cut into 100 x 40 mm strips.

2.2. In-flow synthesis of indigo in microfluidic device

Synthetic indigo was synthesized in-flow using the Baeyer-Drewson method via the combination of a 2-nitrobenzaldehyde solution in acetone and aqueous base in flow using a set-up shown in Figure 3. The microfluidic device was assembled from a syringe pump, tubing (PVC tubing, 1.59 mm in diameter), and plastic syringes. The continuous phase, aqueous sodium hydroxide (2 M) was loaded into one syringe. The second syringe contained a solution of 2-nitrobenzaldehyde (1.0 g) in acetone (20 mL). The syringes were each equipped with approximately 10-15 cm of PVC tubing (1.59 mm in diameter), and were joined via a Y-junction and linked into a single continuous tube. The colourless sodium hydroxide solution and the pale yellow 2-nitrobenzaldehyde solution were loaded onto a syringe pump injected at a flow rate of 0.5 mL min^{-1}. Upon meeting at the Y-junction, the colour of the solution immediately changed and grew darker as the solution moved through the reactor. Downstream, the soluble indigo precursor was expelled, allowing the isotropic solution to penetrate the dry fibre prior to the precipitation of insoluble indigo pigment. Within a minute or two, the formation of indigo completed and, after subsequent washing, the characteristic blue of indigo was observed. Alternatively, the reaction output tube can be attached to the input of an aerosolised spray can, allowing the user to spray the indigo precursor onto fibres (Figure 4). The fabric was dry prior to application and only sprayed once.
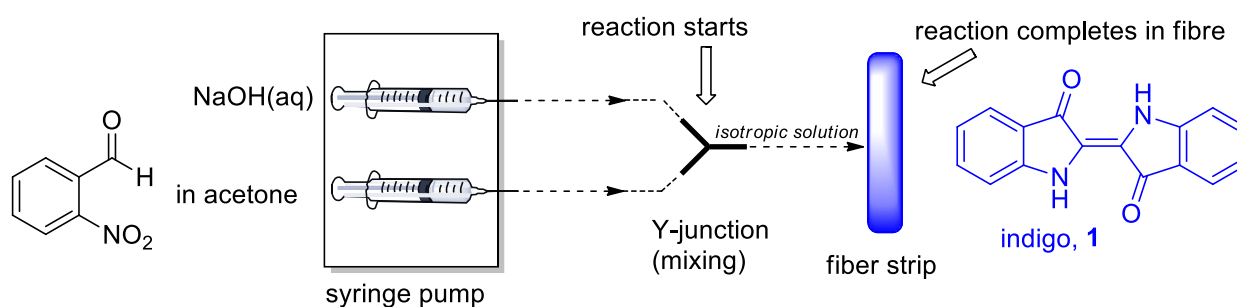

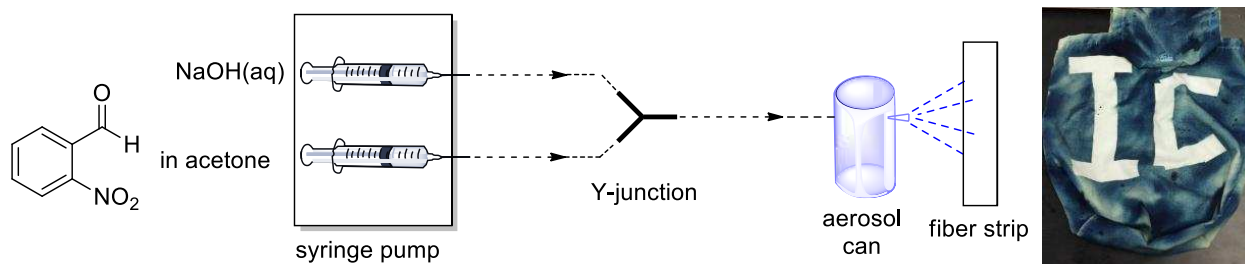**Figure 3.** Synthesis of indigo in flow using Baeyer-Drewson reaction.

Figure 4. Synthesis of indigo in flow into an aerosol can for subsequent application. A cotton sample sprayed with indigo prepared in our flow reaction is shown.

2.3. Infrared spectroscopy

Infrared (IR) spectra were recorded using a Nicolet iS50 FT-IR instrument. Vibrational frequencies are reported in wavenumbers (cm^{-1}).

2.4. Colour measurement

Spectral reflectance factors (taken between 400 and 700 nm wavelengths in 20-nm increments) of the samples were measured using a Datacolor Spectraflash SF600 reflectance spectrophotometer (Datacolor International Ltd, UK) interfaced to a computer. Three different areas of each sample were measured and the average colour value was automatically calculated and saved by the computer. CIELAB values (under illuminant D65 using the 10° standard observer) were automatically calculated. From reflectance values (R) at a specified wavelength (λ) of the dyeings, the colour strength (K/S) of the sample was calculated using the Kubelka-Munk equation (Equation 1) [16].

$$\frac{K}{S} = \frac{(1-R_\lambda)^2}{2R_\lambda} \tag{1}$$

2.5. Wash fastness testing

Samples were subjected to the ISO 105:C06/A2S wash test (40 °C) using multifibre fabric as adjacent [17]. K/S values after washing were measured. Any staining of adjacent fibre that occurred as a result of washing was evaluated using the ΔE2000 colour difference (ΔE^*_{00}) was calculated from CIELAB coordinates L*C*h* using equation 2 [18]:

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)} \tag{2}$$

How the $L*C*h*$ values are transformed into L', C' and H' has been explained in detail [19]. The ΔE2000 formula has five corrections to CIELab: A lightness weighting function ($k_L S_L$), a chroma weighting function ($k_C S_C$), a hue weighting function ($k_H S_H$), an interactive term between chroma and hue differences for improving the performance for blue colours and a factor (R_T) for rescaling the CIELab a*-axis for improving performance for grey colours.

3. Results and Discussion

Synthesis of indigo using the microfluidic device (Figure 3) was successful and formation of indigo and, after subsequent washing, the characteristic blue of indigo is observed. An infrared spectrum of solid collected and filtered from the output of the flow reactor (Figure 5) closely matches the spectrum of authentic indigo [20]. The FT-IR spectrum shows a peak at 3270 cm^{-1} that is attributed to the N–

H stretching in secondary amines, a peak at 1620 cm^{-1} may be attributed to C=O stretching coupled with C=C stretching. Further, weak bands in the range of 1300-1000 cm^{-1} have contributions from C–N stretching of the amine group. The peak around 750 cm^{-1} may be assigned to C–H out of the plane bending in aromatic group.
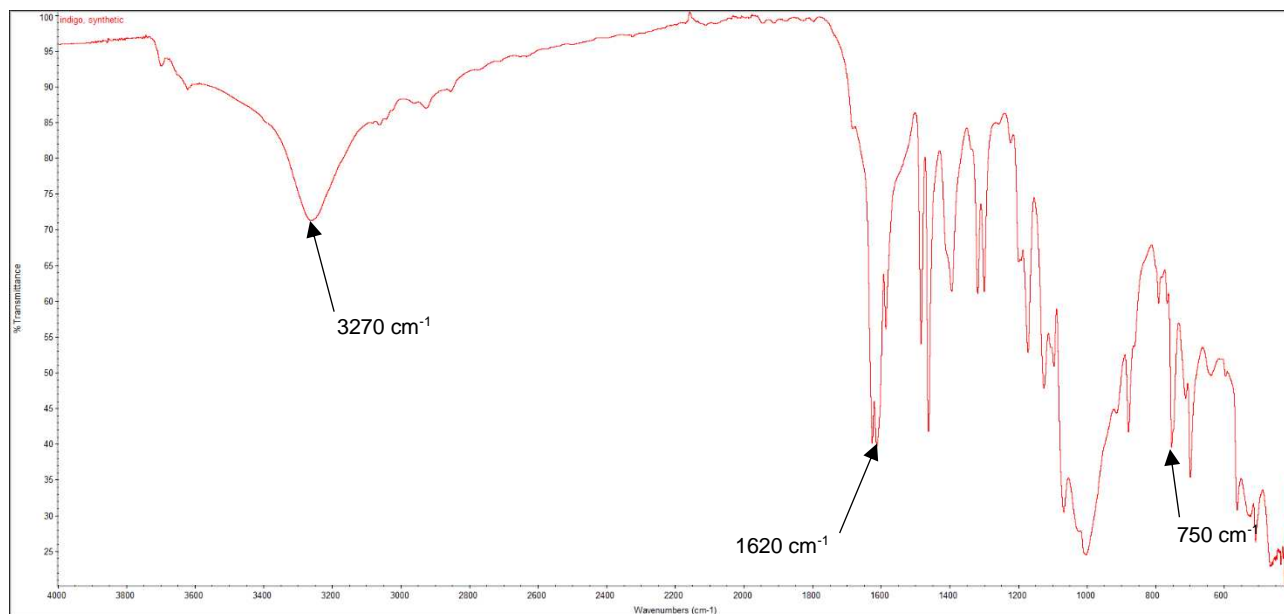

Figure 5. Infrared spectrum of indigo synthesized in flow reactor

Whether the fabric is dyed directly from the tubing output or sprayed with the aerosol propellant (Figure 4), the dye appeared to remain in the fabric samples well, with minimal bleeding, after the samples are rinsed and allowed to dry. Furthermore, the scope of this method is not limited to dyeing with indigo, and structurally related molecules can also be made in flow. For example, Tyrian purple (6,6′-dibromoindigo; C.I. Natural Violet 1; **3**) can be made simply by using 4-bromo-2-nitrobenzaldehye in the flow reactor, and fabrics can be dyed directly in a similar fashion. Presumably, this reaction method would allow the use of a variety of substituted benzaldehydes to form a variety of different coloured dyes.
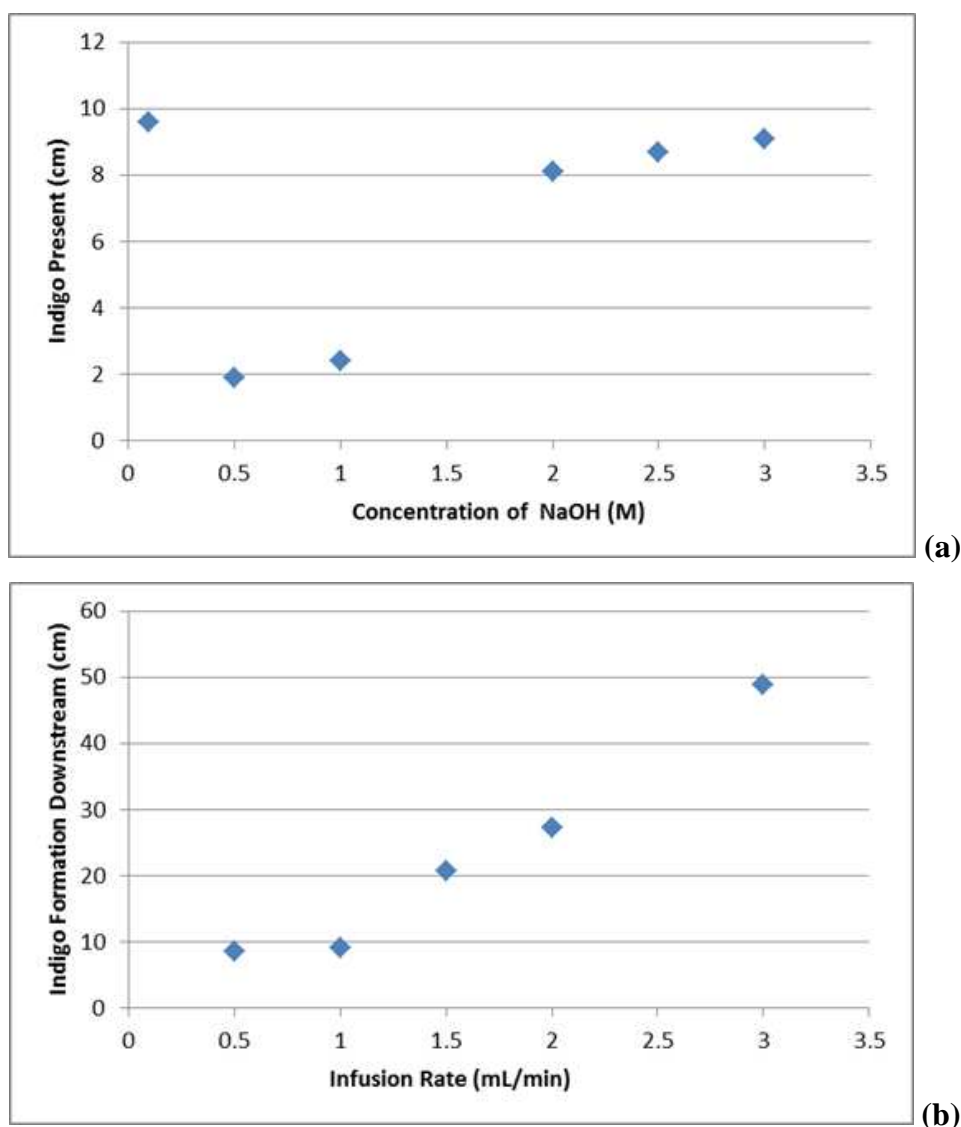

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(a)

(b)
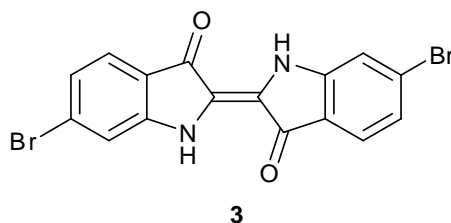
Figure 6. Results of varying **(a)** NaOH concentration and **(b)** infusion rate and the effect on indigo formation downstream from the mixing point (distance in cm).

To determine the optimal NaOH concentration for indigo formation, various concentrations were tested at a constant reaction flow rate of 0.5 mL min^{-1} (**Figure 6a**). Using 0.5 M NaOH solution, indigo began precipitating at about 10 cm downstream from the mixing point, but the reaction was too sluggish to dye fabrics effectively. At concentrations of 0.5 M and 1.0 M, indigo formed much more quickly, at approximately 2 cm from the point of mixing at the Y-joint, which was too fast for the system to handle without clogging. Interestingly, when 2.0 M sodium hydroxide was used, indigo formed downstream at 8 cm, a convenient distance for the dyeing experiment. A slower apparent reaction rate with higher NaOH concentrations is somewhat counterintuitive, though the reason for this is most likely due to the increased viscosity of the more concentrated solution, resulting in sluggish mixing [21,22]. Adjusting the concentrations of the NaOH solutions above 2 M had minimal

effect on the reaction rate, so the 2 M NaOH solution concentration was selected for further experiments. The flow rates of the reaction also affected the rate of indigo formation (**Figure 6b**); generally, faster flow times resulted in product formation further downstream from the mixing point at the Y-joint. Coincidentally, a flow rate of 0.5 mL min^{-1} was ideal as it afforded product far enough downstream to prevent clogging, but not so far that we needed to use excessive tubing. Thus, the best initial conditions were determined to be 2 M sodium hydroxide with an infusion rate of 0.5 mL min^{-1}.

Colour measurements on cotton fabric dyed with indigo and Tyrian purple using the flow reactor indicates that the dyes exhibit modest colour strength and fastness relative to commercial samples. Figure 7 shows that significant K/S values can be achieved from the flow coloration method for Tyrian purple and indigo. These are not as high as the commercial denim comparison, but this was not the intention; the λ_{max} of the commercial denim dyed with indigo and the cotton coloured with indigo using the flow method is the same (620 nm). After washing, a significant decrease in K/S values is observed, and the colour loss from the commercial denim dyed with indigo (5%) is significantly lower than from the and the cotton coloured with indigo using the flow method (54%), however, significant colour is retained. Similarly, staining the adjacent components of the attached multifibre (Figure 8) is higher for the cotton coloured with indigo using the flow method in comparison with the commercial denim dyed with indigo. Interestingly, staining from the cotton coloured with Tyrian purple using the flow method is lower than both indigo-dyed substrates. The explanation for the lower wash fastness of the flow coloration process is most likely a result of the rudimentary nature of the coloration process and the fact that the dye is unable to penetrate significantly within the yarn interior, this is an area worthy of further investigation in process design. This system is not currently optimised and these initial results offer encouragement that the properties of the coloured fibres can be improved; with optimisation, evaluation of other properties, such as rub fastness, will be essential to determining if the system has realistic commercial potential.
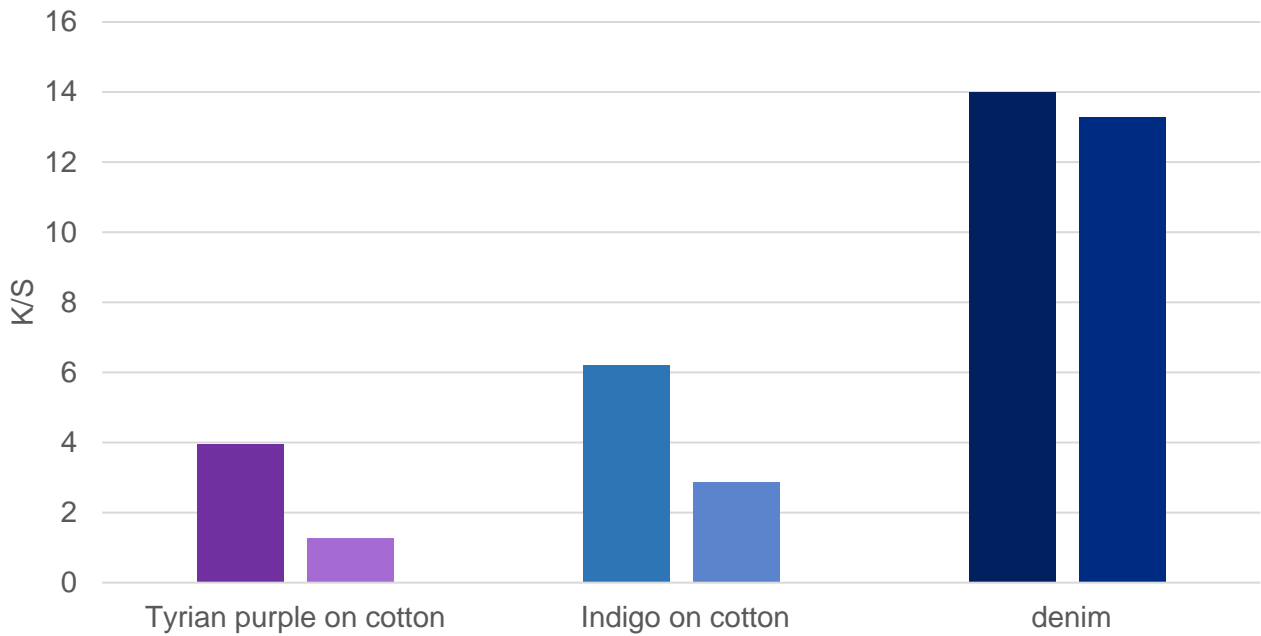
Figure 7. Colour strength (K/S) values of Tyrian purple and indigo dyeings on cotton using the flow process and commercial denim test fabric. Columns shown are before washing (left) and after washing (right).
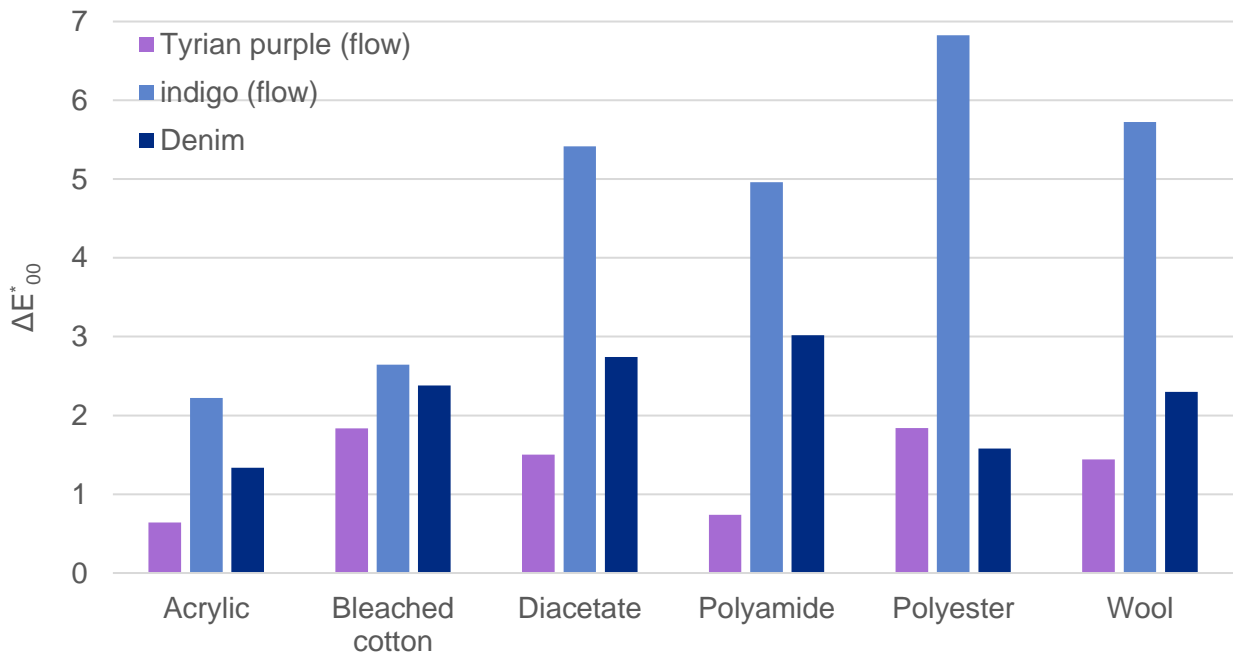

Figure 8. Staining of SDC multifibre adjacent after washing Tyrian purple and indigo dyeings (flow process) and commercial denim test fabric. Staining quantified using ΔE^*_{00} values of material components of multifibre.

4. Conclusions

We have developed a method that allows for the synthesis of indigo and its structural relatives in flow using a simple microfluidic device. This method, in the spirit of controlled "flash chemistry" processes [23], allows for the rapid capture of ephemeral, soluble precursors in fibers moments before the formation of the insoluble colorant forms. Thus, it allows one to circumvent the vat-dyeing process, resulting in a more efficient in situ dyeing process. The reaction may also be coupled with a propellant, an adaptation that allows for a "sprayable" form of indigo.

The research provides compelling proof-of-concept, but we acknowledge that the process is in its infancy and needs further development to get it to a stage where it can compete commercially with current technology. Typical wash fastness for indigo dyed goods is more related to the wash-down effect, which relies on depth of shade (layers of indigo) as well as controlled ring dyeing. Further research to evaluate the effect of pre-wetting and multiple sprays to build up layers of dye are planned.

Flow reactions may be run in parallel and thus, after optimization, this method could be scaled for industrial use to create an indigo dyeing process that is potentially faster, cheaper, less wasteful, and less hazardous, as no reducing agent is required to make soluble dye precursors. Eliminating the need for a reduction with sodium dithionite could conservatively save two US cents per kilogram of indigo produced, which translates to annual costs savings in the hundreds of thousands of US dollars. Further, less water would be required to complete the dyeing process and problematic waste products would be dramatically reduced, hence an optimised system could be a significantly 'greener' chemistry process. Ultimately, this straightforward method eliminates the need for the traditional vat dye, and thus could provide savings in cost, time, and resources.

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