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Coloration Technology

ORIGINAL ARTICLE

A dye–fibre system from food waste: Dyeing casein fibres with anthocyanins

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Abstract

Regenerated protein fibres manufactured from food side-streams offer significant potential as circular and sustainable fibres, but greater knowledge of their dyeing properties is required. In this research, coloration of casein fibres with dyes also extracted from blackcurrant skins left over from juice pressing is explored. Casein fibre was dyed with blackcurrant extract, rich in anthocyanins, from pH 2 to pH 6 and from 40 to 80°C, with and without alum. Casein fibres could be dyed with blackcurrant extract across all conditions tested, and under optimal conditions, dyeing is achieved with medium depths of colour with good wash fastness. Highest sorption of anthocyanins onto casein is observed at pH 4, where anthocyanins are a mixture of 60% neutral purple quinonoidal base form and 40% flavylium cation form; under these conditions dye–fibre interaction is optimal. At pH 2, casein fibre has a highly positively charged surface and anthocyanin is in the flavylium cation form, leading to some dye–fibre repulsion. At pH 6, the slightly negatively charged casein fibre demonstrates lower sorption of the mixture of 40% purple quinonoidal base form and 60% the anionic quinonoidal base form, again leading to some dye–fibre repulsion. Presence of alum in the dyebath enhances sorption of anthocyanins onto fibre at pH 4 due to formation of Al–anthocyanin complexes. Wash fastness of the dyeings is better as pH increases and as temperature increases.

1 | INTRODUCTION

Global annual fibre production in 2021 was over 113 million tonnes (Mt) and is expected to grow to 149 Mt by 2030,[1] with polyester (60.5 Mt) and cotton (24.7 Mt) making up 76% of the total; regenerated cellulosics (e.g., lyocell, viscose; 7.2 Mt), other plant fibres (e.g., linen, hemp; 6.7 Mt), polyamides (5.9 Mt), other synthetics including polypropylene, acrylics, and elastane (5.8 Mt), wool (1.0 Mt), and other animal fibres (0.7 Mt) make up the remainder. Apparel consumption set to rise to 102 Mt by 2030 (a 63% increase from today),[2] and with this increased fibre use comes increased consumption of raw materials, water, energy and chemicals used in their manufacture, and the associated emissions to the environment.

Fibres derived from petrochemical resources receive much media attention for their contribution to the global problem of 'plastics' in the environment. Synthetic microfibres (MFs) account for over a third of all plastic reaching the open ocean[3] and are pervasive in all ecosystems, but natural

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fibres also have a significant impact; recent studies show ~80% of ocean MFs are dyed/finished cellulosic fibres,[4] the impact of which are not yet understood. Wool remains the dominant protein-based fibre for textiles, but recycled wool only contributes 6% of the global total wool market.[1]

There is a clear need to move away from the traditional sources of textile fibres to find options that present more material circularity. In a circular economy, waste and pollution can be reduced and eliminated by increased use of renewable energy, reducing water consumption, ending the use of toxic chemicals, and the design of new materials, products and systems.[5] Utilisation of waste as raw material feedstock is a core concept of circular design. The textile industry has seen in recent years new fibres come into the market that comprise waste as part of the raw materials in their manufacture,[6] such as *Refibra*[7] from pre- and post-consumer cotton waste, *Orange Fibre*[8] from orange peel waste and *Piñayarn*[9] from pineapple leaves. The use of food production waste offers a huge opportunity with benefits to the environment and economy. Up to 2 billion (bn) tonnes per annum (tpa) of all food produced in the world ends up as waste, a carbon footprint of 3.3 bn tonnes carbon dioxide equivalent (CO_2e), which represents about 8% of global greenhouse gas (GHG) emissions.[10,11] Not all food waste is avoidable, and unavoidable by-products from food manufacturing offer an exploitation opportunity for fibres.

But the use of food by-products for making fibres is not a new concept. Regenerated protein fibres (RPFs) have been around for over 100 years, and most of these were manufactured from food side-streams from processing of peanuts, soy, milk and other protein-rich by-products.[6,12] Although these fibres were commercialised as azlons, RPFs were superseded with the advent of synthetic fibres, most notably nylon, due the higher tensile properties, and lower cost.

However, the significant potential for circularity and sustainability of these fibres has reignited interest in their contemporaneous use. One notable example is RPF made from casein extracted from milk waste. According to WRAP (Waste & Resources Action Programme),[13] the UK dairy industry produces ~555,000 tpa of waste from production, which is either incinerated or spread on land; the chief by-product of cheese-making is whey (~228,000 tpa), which contains a significant amount of casein. Furthermore, 82% of milk protein is casein with the remainder being comprised of whey; whey is already utilised in the dietary supplement industry, but the uses for casein are fewer, hence casein from food waste presents an attractive opportunity for valorisation. Recently, the German company QMILK has produced a RPF from casein, which the company claims to be zero-waste and free of hazardous chemicals.[14]

If RPFs are to have a renaissance as textile fibres, then their coloration is of keen interest. There is limited published literature on the sorption of dyes on casein fibre, but it has been demonstrated that the dyeing behaviour of non-metallised and metal complex acid dyes onto the fibre follows similar trends to acid dyes on wool.[15,16]

However, is the use of synthetic acid dyes on casein commensurate with the circularity of the fibre? Alternatively, circularity for RPFs could be partnered with circularity of the colourants applied to dye the fibres. Rose et al[17] demonstrated that anthocyanins extracted from blackcurrant fruit waste gave intense blue-coloured dyeings on human hair. There are many sources of anthocyanins from fruit waste from both the juice pressing and wine manufacturing industries, so this is a potentially untapped raw material for the production of sustainable dyes.

Anthocyanins are the largest group of polyphenolic pigments in the plant kingdom; they are non-toxic, water-soluble, and responsible for pink, red, purple, violet, and blue coloration in fruits, vegetables, and flowers. Their colours are determined by small differences in the chemistry of the different anthocyanins. Anthocyanins take part in acid–base equilibria in aqueous solutions, and a general scheme of reactions (Figure 1) highlights the important equilibrium forms: in aqueous solution of pH < 3, the anthocyanin is red, and the flavan nucleus exists mainly as the very stable flavylium cation ($\mathbf{AH}^+$). Increasing pH leads to kinetic and thermodynamic competition between two reactions. When pH increases, $\mathbf{AH}^+$ undergoes a rapid deprotonation reaction ($pK_{a1} \sim 3.7$) to form the purple quinonoidal base (**A**) as the kinetic product, which leads to formation of the anionic quinonoidal base ($\mathbf{A}^-$) at higher pH ($pK_{a2} \sim 7$) that has a blue colour.[18–21] The alternative thermodynamically favoured colourless hemiketal (**B**) is relatively slowly formed via hydration above pH 2, at position 2 (pK_h 2–3). Ring opening is also slow compared to deprotonation, but typically faster than hydration and can lead to the formation of the yellow *E*-chalcone ($\mathbf{C_E}$), although for many common anthocyanins this is a relatively minor component of the equilibrium. Once formed, $\mathbf{C_E}$ isomerises to give the *Z*-chalcone ($\mathbf{C_Z}$).[22]

Herein, the intention of this research was to use anthocyanins extracted from waste blackcurrant material in the dyeing of casein fibres to produce a potentially sustainable and circular dyeing system. In addition, the optimal dyeing conditions in terms of colour strength and wash fastness was to be determined, and to ascertain if the colour change in anthocyanins observed at different pH values could be used advantageously to produce a range of shades from one dye material. We also include the utilisation of alum as a *meta*-mordant to determine if its inclusion in the dyeing process has any influence on dye sorption, resultant dyeing shade, and subsequent fastness properties; aluminium is a well-known mordant

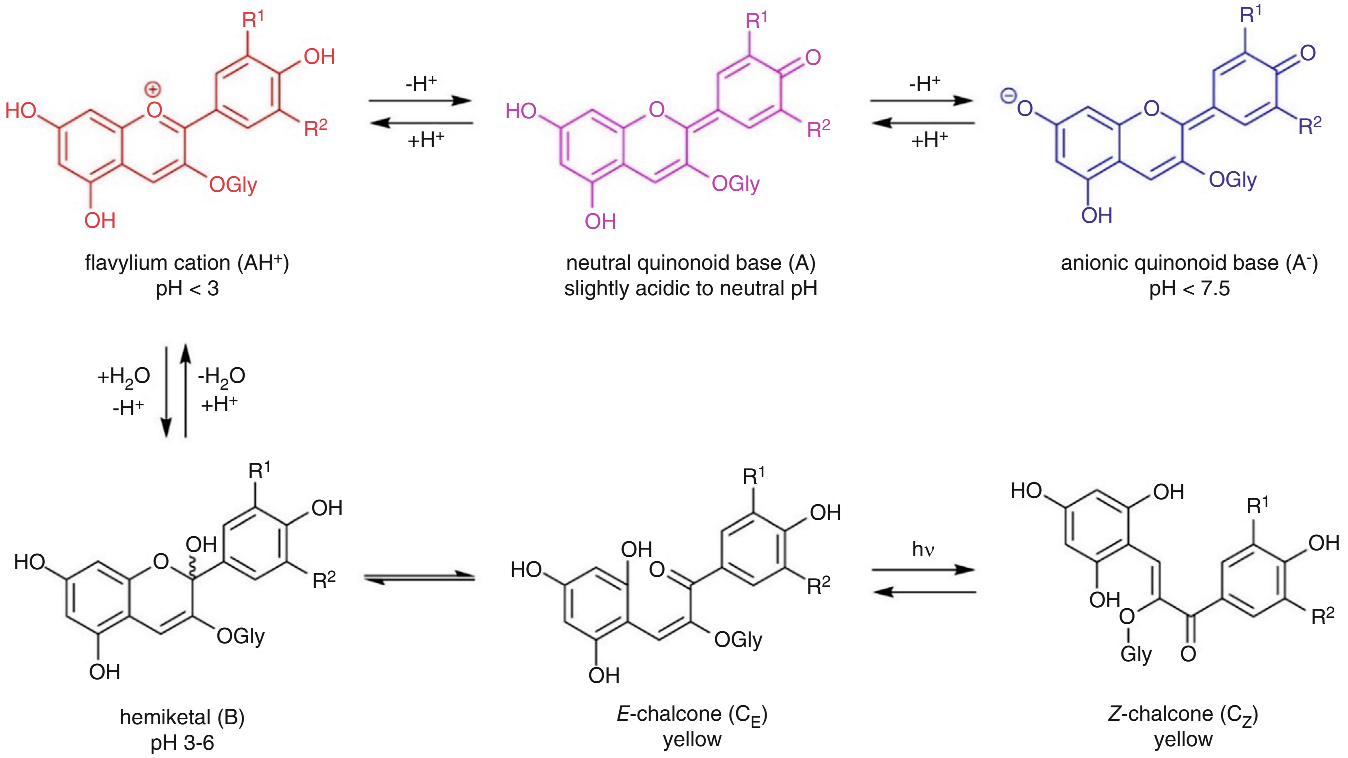


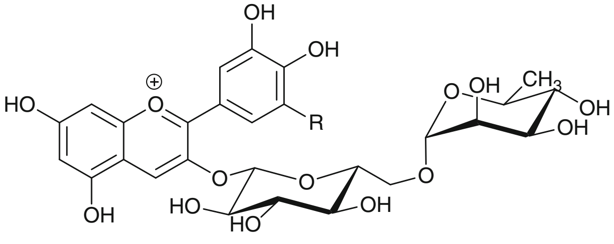
FIGURE 1 Effect of pH on anthocyanin structure and resultant colour.

for natural dyes on natural fibres, but also forms particular structural complexes with anthocyanins that influences colour, as will be discussed later.

2 | MATERIALS AND METHODS

2.1 | Materials

"Milk Protein" (casein) fibre sliver was obtained from George Weil, Guildford, UK. Blackcurrant (*Ribes nigrum* L.) pomace was obtained from A&R House, UK; the raw fruit grown in the UK had been pressed in production of blackcurrant cordial (*Ribena*). The crude waste is referred to as pomace, which comprises the fruit epicarp (*c.* 50 wt%), seeds (*c.* 45 wt%) and extraneous matter (e.g., berry stalks, *c.* 5 wt%). Seeds are separated from this pomace and unwanted stalks removed; the subsequent material received was predominantly dried blackcurrant fruit epicarp. Dried blackcurrant extract dye powder was extracted from the dried blackcurrant fruit epicarp using the method described in Farooque et al[23]; the main dye components in the blackcurrant powder are anthocyanin glycosides, which are present as delphinidin-3-*O*-rutinoside (Dp3rut; **1**; 22.6%), cyanidin-3-*O*-rutinoside (Cy3rut; **2**; 20.4%), delphinidin-3-*O*-glucoside (Dp3glc; **3**; 7.7%), and cyanidin-3-*O*-glucoside (Cy3glc; **4**; 4%), the remaining components are a mixture of polymeric anthocyanins (18%), flavonoids (17%), and hydroxycinnamates (9%). Woolly Wash detergent (anionic surfactants, amphoteric surfactants, lanolin, fragrance and preservative) was obtained from Mitchell's Wool Fat Soap, Bradford, UK. Multifibre DW fabric was obtained from SDC. General purpose chemicals were obtained from Sigma-Aldrich, UK.



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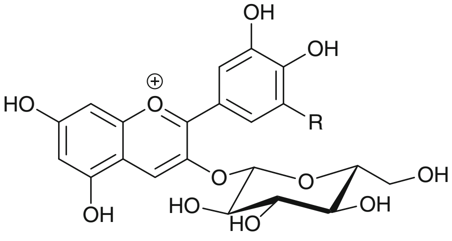
2: R = H



3: R = OH
4: R = H

2.2 | Dyeing process

Casein fibres were dyed in an aqueous solution with 5% owf blackcurrant dye powder, with optional inclusion 1% owf of potassium aluminium sulfate dodecahydrate (alum). Based on the ratio of the anthocyanin glycosides present in the blackcurrant powder, each gram of blackcurrant powder contained 0.55 g anthocyanin, with an average molecular weight of 595 g mol^{-1}, equivalent to 0.92×10^{-3} mol. For every gram of blackcurrant powder, 0.2 g alum was added, equivalent to 0.42×10^{-3} mol of aluminium ion (Al^{3+}). This is approximately equal to a 2:1 ratio of anthocyanin glycoside to Al^{3+} and was intentionally applied to encourage formation of such 2:1 complexes in the fibre.

Dyeing was conducted at varying pH values (pH 2, 4, and 6) using formic acid and sodium hydroxide to modify pH, in an Ugolini Redkrome II dyeing machine, using a liquor–fibre ratio of 20:1. Fibres were introduced to the dyebath at room temperature and temperature increased at the rate of 1°C min^{-1} until the dyeing temperature ($T = 40$, 60, 80 and 98°C) was achieved, and samples held at the dyeing temperature for 30 min. After dyeing, fibre and fabric samples were rinsed in cold water and dried in ambient conditions prior to colour measurement.

2.3 | Wash fastness testing

Samples were subjected to a modified wash fastness test based on ISO 105-C06:2010 protocols using SDC Multifibre DW fabric as adjacent. Briefly, 1 g samples of dyed fibre were washed in individual pots in a James Heal GyroWash Colour Fastness Tester. Pots were filled with 50 cm^3 of an aqueous solution containing 1 g dm^{-3} of Woolly Wash detergent and the fibre/fabric sample and multifibre fabric adjacent added. Samples were washed for 30 min at 30°C. After washing the samples were rinsed, dried, and colour change ascertained from colour measurement before and after washing. The washed samples were also visually assessed using grey scales according to the ISO 105-A03:2019 test protocol to determine the degree of staining. The grey scale ranges from 5 for no stain on the adjacent fibres down to 1 for a severe staining, with half points in between.

2.4 | Colour measurement

Dyed fibre and fabric samples were measured using a Datacolor 500 colour spectrophotometer connected to a personal computer using Datacolor software. From reflectance (R) values 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).

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

Tone of the colour of the dyeings was quantified in terms of L^*, a^* and b^* values within the CIELab system. Colour difference (ΔE) between samples before (L^*_1, a^*_1, b^*_1) and after (L^*_2, a^*_2, b^*_2) washing was quantified by Equation (2):

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \tag{2}$$

The human eye can perceive difference in colour when the ΔE value between two samples is greater than 2 units. Change in lightness values (ΔL) between samples before (L^*_1) and after (L^*_2) washing was quantified by Equation (3):

$$\Delta L = L_2^* - L_1^* \tag{3}$$

3 | RESULTS AND DISCUSSION

Quantitative work was carried out with dyeings using anthocyanin-rich blackcurrant extract across different pH and temperature, with and without alum. From the dyeing results (Figure 2), it is observed that greater colour strength is achieved as temperature increases, which is to be expected as the higher energy affords greater solubility of the dye, greater fibre swelling, and lower viscosity of water, in alignment with general theory of dyeing, which will promote greater sorption and diffusion of the dye within the fibre substrate. In the limited research into dyeing casein fibres, there is evidence that the sorption of non-metallised and metal complex acid dyes onto the fibre follows similar trends to acid dyes on wool, insofar as sorption of acid dyes increases with decreasing pH from pH 7 to pH 2, with a significant increase in sorption from pH 4 to pH 2 in particular.[16] Skinner and Vickerstaff concluded that sorption isotherms of three non-metallised acid dyes on wool and casein fibre at pH < 2 were almost identical.[15] Sorption of anthocyanins onto casein fibre do not follow these trends for acid dyes on casein; highest sorption of anthocyanins is observed at pH 4, which is even higher in the presence of alum.

Protein fibres are amphoteric, meaning that under different conditions they can adsorb acids and bases with equal efficiency. The charge a protein carries at a given pH is relative to the number of side chains that

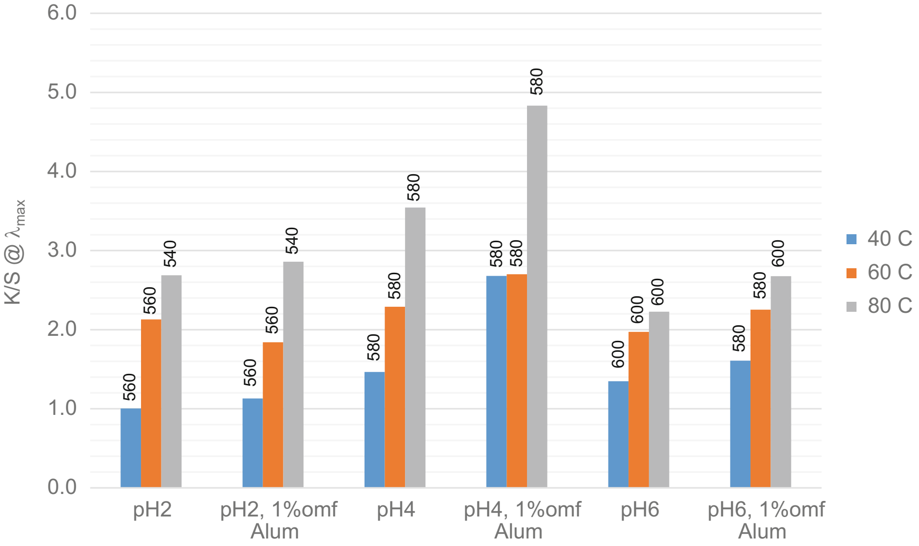


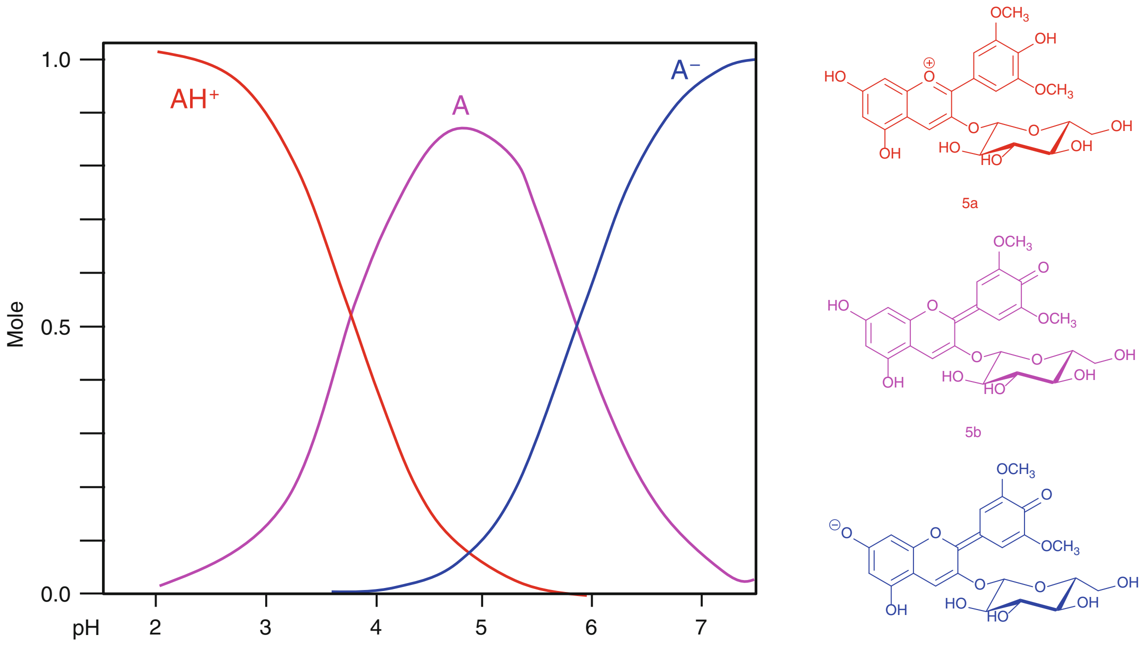
FIGURE 2 Colour strength (K/S) at maximum wavelength (λ_{max}) of dyeings of casein fibre with blackcurrant extract powder with varying, pH, temperature and inclusion of alum. Number on top of column indicates observed λ_{max} of dyeing.

contain –NH_2 and –COOH and the pK_a values of those side chains. This can be illustrated using the model of a theoretical water-soluble protein, as described by Sumner,[24] in which the protein contains 100 aspartic acid residues (pK_a of –COOH groups = 3.86), 30 lysine residues (pK_a of –NH_2 groups = 8.95) and 50 arginine residues (pK_a of –NH_2 groups = 13.2). Using this model, the net charge of the protein is +79 at pH 2, +22 at pH 4, and −18 at pH 6. In casein protein, positively charged side chains are arginine (209 μmol g^{-1}), histidine (179 μmol g^{-1}), and lysine (592 μmol g^{-1}); negatively charged side chains are aspartic acid (606 μmol g^{-1}) and glutamic acid (1651 μmol g^{-1}).[25] By comparison, in virgin merino wool, positively charged side chains are arginine (600 μmol g^{-1}), histidine (82 μmol g^{-1}), and lysine (269 μmol g^{-1}); negatively charged side chains are aspartic acid (560 μmol g^{-1}) and glutamic acid (1049 μmol g^{-1}).[26] As the isoelectric point of casein protein is pH 4.6,[27] this is very close to the Sumner model, so when dyeing at pH 4, where greatest anthocyanin sorption was observed, the casein fibre will have a slightly positive ζ-potential.

The form of the anthocyanin is also critical to dye sorption onto any charged substrate. Work by Nave et al.[28] on the closely related anthocyanin malvidin-3-glucoside (Mv-3-glc) demonstrated that the mole fractions of flavylium cation (**AH**$^+$) form, quinonoidal base (**A**) form and anionic quinonoidal base (**A**$^-$) form vary with pH (Figure 3). It would be expected that at pH 4 the anthocyanins present would be a mixture of *c.* 60% neutral purple quinonoidal base (**A**) form with and 40% flavylium cation (**AH**$^+$) form (Table 1); under these conditions dye–fibre interaction between anthocyanins and casein protein is optimal, as observed through highest dye uptake.

As the overwhelming majority of dyes applied to protein fibres (mainly wool) are anionic, there is little knowledge around the sorption of neutral species onto the substrate. The exception is 1:1 metal complex acid dyes, many of which have an overall net neutral charge. Lemin and Rattee[29] observed when applying C.I. Acid Orange 74 and C.I. Acid Orange 76 (neutral 1:1 chromium complexes) to wool, exhaustion increases significantly as dyebath pH decreased from pH 7 to a maximum around pH 4, which is maintained with further pH reduction to pH 3; however, reduction of dyebath pH to pH 2 caused a decrease in exhaustion. They remarked that the "decrease in exhaustion from the maximum value on further lowering of the dyebath pH is a phenomenon not observed with any other range of dyes used in wool dyeing." Burkinshaw states that the nature of interactions between 1:1 metal complex dyes and wool remains a matter of debate,[30] and no author offers a satisfactory explanation for why sorption of neutral 1:1 metal complex acid dyes is observed to be optimal at pH 4.

It may be that at pH 4 when the ζ-potential of casein is only slightly positive that other non-electrostatic sorption interactions of neutral dyes with the substrate, such as hydrophobic interactions and hydrogen-bonding interactions, are more important to sorption than at other pH values where electrostatic interactions dominate. Hence, at pH 4 where the neutral quinonoidal base (**A**) form of anthocyanins is highest, greatest sorption onto a similarly neutral/slightly positive surface is observed. It is noted that the **A** form of Mv-3-glc is highest at around pH 4.8,[28] which is also close to the casein isoelectric point (pH 4.6). Although the anthocyanins found in blackcurrant are slightly different to Mv-3-glc, it may that with further research an even more optimal pH for sorption of



5a

5b

5c

FIGURE 3 Mole fractions of malvidin-3-glucoside (Mv-3-glc) **AH**$^{+}$ (**5a**), **A** (**5b**) and **A**$^{-}$ (**5c**) forms with varying pH using data from Nave et al.[28]

TABLE 1 Summary of charge of model protein and form of anthocyanin with varying pH values.

pH	Charge on model protein	Mole fraction of anthocyanin AH^{+}	A	A^{-}
2	+79	1.00	0.00	0.00
4	+22	0.39	0.61	0.00
6	−18	0.00	0.42	0.58

blackcurrant anthocyanins onto casein may be found closer to pH 4.8.

Figure 2 also shows the observed maximum wavelength (λ_{max}) of the dyeings obtained at different pH values. At pH 2, anthocyanins in blackcurrant have λ_{max} of approximately 520 nm, then along the deprotonation sequence, λ_{max} typically shifts by 20–30 nm to 540–550 nm (**AH**$^{+}$ → **A**), then by 50–60 nm to around 600 nm (**A** → **A**$^{-}$).[28] However, the observed λ_{max} of the dyeings achieved at pH 4 was 580 nm; if at this pH the primary species adsorbed is the neutral purple quinonoidal base (**A**) form with λ_{max} of 550 nm, why was the colour on substrate observed at a λ_{max} 30 nm higher?

When dyeing human hair with the same anthocyanin extract at pH 5, Rose et al[17] also observed λ_{max} at 580 nm; they attributed this to sorption of the purple quinonoidal base (**A**) form of the dye, but that the hair provided an environment that enabled the anthocyanins to convert to **A**$^{-}$ on adsorption, being stabilised by electrostatic interaction with protonated primary amino functions ($-NH_3^{+}$) in arginine (499 μmol g^{-1}), histidine (64 μmol g^{-1}), and lysine (218 μmol g^{-1}) residues all present in human hair.[31] It may be that the same stabilisation effects were observed herein for casein, despite the levels of those three positively charged side chains being slightly different.

Observations of sorption effects at pH 4 can be compared with dyeings at pH 2, where the casein fibre would have an even higher positive ζ-potential and the anthocyanin would be around 100% the flavylium cation (**AH**$^{+}$) form, which may lead to some dye–fibre repulsion, limiting uptake. It is clear that sorption of dye still occurs, and it is noted that λ_{max} of the dyeings at pH 2 was 540–560 nm, which would be expected from sorption of a mixture of the flavylium cation (**AH**$^{+}$) form and the quinonoidal base (**A**) form of the anthocyanins, which have λ_{max} of *c.* 520 nm and 550 nm, respectively.

At pH 6, the casein fibre would have a negative ζ-potential and the anthocyanin would be a mixture of *c.* 40% the purple quinonoidal base (**A**) form and 60% the anionic quinonoidal base (**A**$^{-}$) form, which again may lead to some dye–fibre repulsion, limiting uptake. Sorption of dye still occurs, and it is noted that λ_{max} of the dyeings at pH 6 was 580–600 nm, which would be expected from sorption of a mixture of a minority of neutral quinonoidal base (**A**) form and majority of anionic quinonoidal base (**A**$^{-}$) form the anthocyanins, which have λ_{max} of *c.* 550 nm and 600 nm, respectively.

Whilst the addition of a *meta* mordant of alum did not make a significant difference to sorption of the dye at pH 2 and pH 6, the presence of alum in the dyebath enhanced the sorption of the anthocyanin onto the fibre at pH 4. Understanding this observation is aided by research into Al–anthocyanin complexes in nature. Petals of *Hydrangea macrophylla* (Thunb.) Ser. change from red through purple to blue, depending on cultivation conditions; in acidic soils (pH < 5.0), the level of water-soluble Al^{3+} in soil is increased and absorbed by the roots, and Al^{3+} forms complexes with anthocyanins resulting in blue petal colour. This colour originates from one single anthocyanin, Dp3glc (**3**) in a 1:1:1 ratio with Al^{3+} and a co-pigment, either 5-*O*-caffeoylquinic acid (**6**) or 5-*O*-*p*-coumaroylquinic acid (**7**). The identified complex was named "hydrangea blue-complex" (Figure 4).[32,33] Other researchers working with Al–anthocyanin complexes have found that in very acidic aqueous conditions the flavylium cation (**AH**$^+$) dominates and no complexation with Al^{3+} takes place. As pH increases, a new species is formed, with a different colour from the quinonoidal base (**A**), and consistent with formation of an Al–anthocyanin complex, which is stable from 3 < pH < 6. In the pH range 6 to 8.5, the anionic quinonoidal base (**A**$^-$) forms, but at this pH the aluminium salt is insoluble and precipitation occurs. For more basic pH values the system is not stable.[34]

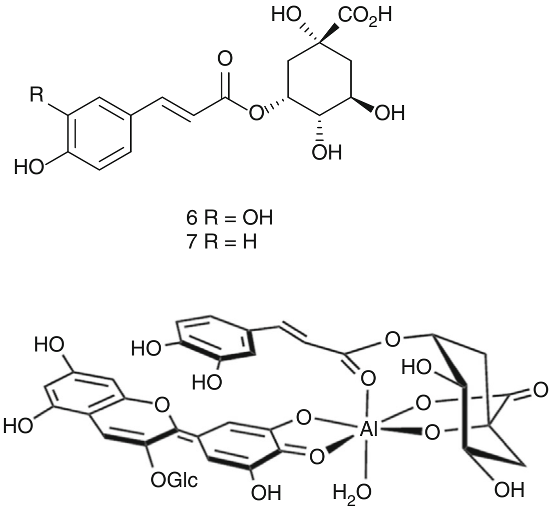


FIGURE 4 Proposed structure of hydrangea blue-complex.

Hence, it is understandable for dyeings herein, where a combination of anthocyanins and alum were applied simultaneously onto casein fibre, that the dyeings at pH 4 with alum are most likely to form Al–anthocyanin complexes, and less likely to form when the same combination was applied at pH 2 and pH 6. Formation of a blue complex with aluminium observed herein is made more likely by the application of a blackcurrant extract that contained other polyphenols in addition to anthocyanins, most notably caffeic acid (3%) and *p*-coumaric acid (5%),[23] which could assist with blue complex formation, as observed for the hydrangea blue-complex. The observed increase in colour strength of the dyeings at pH 4 with alum could be as a result of the ability of the formed Al–anthocyanin complex to have more extensive hydrophobic interactions with the casein substrate due to the overall size of the complex, compared to the single anthocyanins, hence promoting greater dye uptake.

Observations on the wash fastness of the casein dyeings with anthocyanins are summarised in Table 2 for shade change (ΔE) and change in lightness value (ΔL) during washing, and Table 3 for staining to cotton (in general only staining of the cotton component of the adjacent Multifibre DW fabric was observed). It can be seen from Table 2 that wash fastness is better as pH increases and as temperature increases. Overall dyeings at pH 4 and pH 6 at 60 and 80°C all provide very good wash fastness performance. No significant difference in wash fastness performance was observed when alum was used. The higher ΔE values for dyeings at pH 2 are not due to colour loss, as evidenced by the very small ΔL values, but primarily associated with colour change from a purple colour to a blue colour. As shown in Figure 5 for dyeings at pH 2 at 40°C, dyeings before washing have λ_{max} of *c.* 550 nm (associated with the quinonoidal base (**A**) form of the anthocyanins) and dyeings after washing have a λ_{max} of *c.* 580 nm, which is

TABLE 2 Colour change values for casein fibre dyed with blackcurrant extract powder (with varying, pH, temperature and inclusion of alum) following wash fastness testing.

	40°C				**60°C**				**80°C**			
	No alum		**1% owf alum**		**No alum**		**1% owf alum**		**No alum**		**1% owf alum**	
pH	**ΔE**	**ΔL^***	**ΔE**	**ΔL^***	**ΔE**	**ΔL^***	**ΔE**	**ΔL^***	**ΔE**	**ΔL^***	**ΔE**	**ΔL^***
2	7.9	1.8	8.5	3.6	6.8	1.0	7.5	0.7	6.9	1.2	8.4	−1.7
4	9.5	7.1	6.4	3.8	3.1	0.9	3.4	0.3	4.2	3.4	7.9	7.2
6	4.9	1.5	5.3	3.1	2.1	2.0	5.5	1.2	2.0	1.2	2.0	1.6

TABLE 3 Grey scale staining ratings for transfer to cotton portion of Multifibre DW fabric from casein fibre dyed with blackcurrant extract powder (with varying, pH, temperature and inclusion of alum) following wash fastness testing.

	40°C		60°C		80°C	
pH	**No alum**	**1% owf alum**	**No alum**	**1% owf alum**	**No alum**	**1% owf alum**
2	4/5	4/5	4/5	4/5	4/5	4/5
4	3/4	3	4/5	4	5	4/5
6	4/5	3	4/5	5	5	4/5

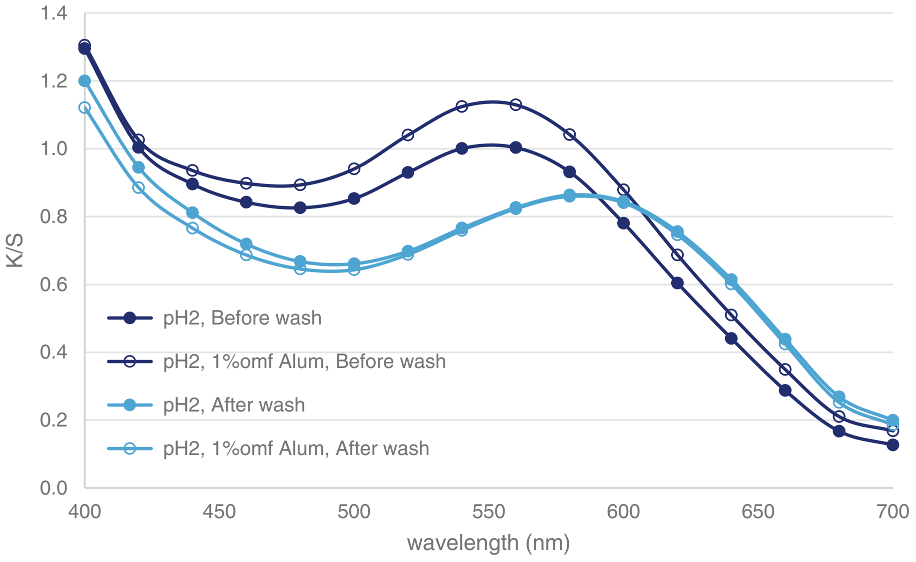


FIGURE 5 Colour strength (K/S) spectra of casein fibres dyed with 5% owf blackcurrant extract at pH 2 at 40°C, with and without alum, before and after wash fastness testing.

most probably a result of a significant proportion of the adsorbed anthocyanins changing in situ to the anionic quinonoidal base (**A**$^-$) form the anthocyanins (λ_{max} *c.* 600 nm). Change in λ_{max} of the dyeings at pH 4 and pH 6 was less significant. The pH of the wash fastness test solution was pH 7, so it is clear from these results that the dyeings at pH 2 were unstable to washing in this environment at a higher pH than their application pH value, causing hue change. However, dyeings at pH 4 are more stable to changes in hue on washing, despite the washing pH still being higher than those of their application conditions; it is possible that the stronger association between dye and fibre at this pH, as discussed earlier, could stabilise the dye in situ and provide some protective effect to change in the form of the adsorbed anthocyanin.

From grey scale staining ratings for transfer of dye to the cotton portion of the Multifibre DW fabric following wash fastness testing, it can be seen that, in general there was minimal staining of the fibre at higher application temperatures. Some staining of the cotton fibre was noted for dyeings at 40°C, and it is suspected that the lower application temperature is associated with lower diffusion of the dye within the fibre structure, hence, the dye is easier to remove from the periphery of the fibre. This is typical of many dye–fibre systems and is unsurprising.

4 | CONCLUSIONS

Casein fibre dyeing using sustainably sourced anthocyanin colourants from food by-products is demonstrated. By optimising dyeing conditions, dyeing is achieved with medium depths of colour with good wash fastness. Highest sorption of anthocyanins is observed at pH 4. At pH 4, anthocyanins in the colourant extract are a mixture of 60% neutral purple quinonoidal base (**A**) form and 40% flavylium cation (**AH**$^+$) form, and under these conditions dye–fibre interaction between anthocyanins and casein protein is optimal, due to sorption of the neutral form of the dye onto a slightly positively charged surface. At pH 2, casein fibre has a highly positively charged surface and anthocyanin is in the flavylium cation (**AH**$^+$) form, leading to some dye–fibre repulsion, limiting uptake. At pH 6, the slightly negatively charged casein fibre demonstrates lower sorption of the mixture of 40% purple quinonoidal base (**A**) form and 60% the anionic quinonoidal base ($\mathbf{A}^-$) form, again leading to some dye–fibre repulsion, limiting uptake.

Presence of alum in the dyebath in an approximate 2:1 ratio of Al–anthocyanin enhances sorption of anthocyanins onto fibre at pH 4; these conditions provide the most likely environment to form Al–anthocyanin complexes, leading to more extensive hydrophobic interactions with the casein substrate, promoting greater dye uptake.

Wash fastness of the dyeings is better as pH increases and as temperature increases. Overall, dyeings at pH 4 and pH 6 at 60°C and 80°C all provide good wash fastness performance. No significant difference in wash fastness performance was observed when alum was used. In general, minimal staining of adjacent fibres was observed at higher application temperatures.

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REFERENCES

1. The Textile Exchange. Preferred Fiber Materials Market Report. 2021. Available online: https://textileexchange.org/app/uploads/2022/10/Textile-Exchange_PFMR_2022.pdf accessed on 01 June 2023.
2. Global Fashion Agenda & Boston Consulting Group. Pulse of the Fashion Industry. 2017. Available online: https://www.greylockglass.com/wp-content/uploads/2021/08/Pulse-of-the-Fashion-Industry_2017.pdf accessed on 01 June 2023.
3. Boucher J, Friot D. *Primary Microplastics in the Oceans: Global Evaluation of Sources*. IUCN; 2017; Available online: https://www.iucn.org/content/primary-microplastics-oceans accessed on 01 June 2023.
4. Sanchez-Vidal A, Thompson RC, Canals M, De Haan WP. The imprint of microfibres in southern European deep seas. *PloS One*. 2018;13:e0207033.
5. Ellen McArthur Foundation. Towards the Circular Economy Volume 1: An Economic and Business Rationale for an Accelerated Transition; Ellen McArthur Foundation: Cowes, UK; 2012. Available online: https://ellenmacarthurfoundation.org/towards-the-circular-economy-vol-1-an-economic-and-business-rationale-for-an (accessed on 01 June 2023)
6. Stenton M, Kapsali V, Blackburn RS, Houghton JA. From clothing rations to fast fashion: Utilising regenerated protein Fibres to alleviate pressures on mass production. *Energies*. 2021;14:5654.
7. https://www.tencel.com/refibra (accessed on 01 June 2023)
8. https://orangefiber.it/ (accessed on 01 June 2023)
9. https://www.ananas-anam.com/pinayarn/ (accessed on 01 June 2023)
10. FAO. 2011. *Global Food Losses and Food Waste – Extent, Causes and Prevention*. https://www.fao.org/3/i2697e/i2697e.pdf
11. FAO. 2013. *Food Wastage Footprint – Impacts on Natural Resources*. https://www.fao.org/3/i3347e/i3347e.pdf
12. Stenton M, Houghton JA, Kapsali V, Blackburn RS. The potential for regenerated protein fibres within a circular economy: lessons from the past can inform sustainable innovation in the textiles industry. *Sustainability*. 2021;13:2328.
13. WRAP. *Quantification of Food Surplus, Waste and Related Materials in the Grocery Supply Chain*. 2016.
14. https://www.qmilkfiber.eu/ (accessed on 01 June 2023)
15. Skinner BG, Vickerstaff T. The absorption of acid dyes by wool, silk, casein fibre and nylon. *J Soc Dyers Colour*. 1945;61:193-201.
16. Choi J-H, Kim M-H. Dyeing characteristics of casein protein fiber with acid dyes and reactive dyes. *Text Color Finish*. 2008;20:14-22.
17. Rose PM, Cantrill V, Benohoud M, Tidder A, Rayner CM, Blackburn RS. Application of Anthocyanins from blackcurrant (Ribes nigrum L.) fruit waste as renewable hair dyes. *J Agric Food Chem*. 2018;66:6790-6798.
18. Wrolstad RE. Anthocyanin pigments – bioactivity and coloring properties. *J Food Sci*. 2004;69:C419-C425.
19. Yoshida K, Mori M, Kondo T. Blue flower color development by anthocyanins: from chemical structure to cell physiology. *Nat Prod Rep*. 2009;26:884-915.
20. Trouillas P, Sancho-García JC, De Freitas V, Gierschner J, Otyepka M, Dangles O. Stabilizing and modulating color by copigmentation: insights from theory and experiment. *Chem Rev*. 2016;116:4937-4982.
21. Maçanita AL, Moreira P, Lima JC, Quina F, Yihwa C, Vautier-Giongo C. Proton transfer in anthocyanins and related flavylium salts. Determination of ground-state rate constants with nanosecond laser flash photolysis. *J Phys Chem A*. 2002;106:1248-1255.
22. Houbiers C, Lima JC, Maçanita AL, Santos H. Color stabilization of malvidin 3-glucoside: self-aggregation of the flavylium cation and copigmentation with the Z-chalcone form. *J Phys Chem B*. 1998;102:3578-3585.
23. Farooque S, Rose PM, Benohoud M, Blackburn RS, Rayner CM. Enhancing the potential exploitation of food waste: extraction, purification, and characterization of renewable specialty chemicals from blackcurrants (*Ribes nigrum* L.). *J Agric Food Chem*. 2018;66:12265-12273.
24. Sumner HH. Thermodynamics of dye sorption. In: Johnson A, ed. *Theory of Coloration of Textiles*. 2nd ed. Society of Dyers and Colourists; 1989.
25. Rasmussen C, Greenwood M, Kalman D, Antonio J. Nutritional supplements for endurance athletes. In: Greenwood M, Kalman D, Antonio J, eds. *Nutritional Supplements in Sports and Exercise*. Humana Press Inc.; 2008.

26. Bradbury JH, Chapman GV, King NLR. The chemical composition of wool. II. Analysis of the major histological components produced by ultrasonic disintegration. *Aust J Biol Sci*. 1965;18:353-364.
27. Sarode AR, Sawale PD, Khedkar CD, Kalyankar SD, Pawshe RD. Casein and caseinate: Methods of manufacture. In: Caballero B, Finglas PM, Toldrá F, eds. *Encyclopedia of Food and Health*. Academic Press; 2016.
28. Nave F, Petrov V, Pina F, Teixeira F, Mateus N, de Freitas V. Thermodynamic and kinetic properties of a red wine pigment: Catechin-(4,8)-malvidin-3-*O*-glucoside. *J Phys Chem B*. 2010;114:13487-13496.
29. Lemin DR, Rattee ID. Some observations on the levelling properties of acid dyes II – Prechromed dyes. *J Soc Dyers Colour*. 1949;65:221-225.
30. Burkinshaw SM. *Physico-Chemical Aspects of Textile Coloration*. John Wiley & Sons; 2016.
31. Robbins CR, Kelly CH. Amino acid composition of human hair. *Text Res J*. 1970;40:891-896.
32. Oyama K-I, YamadaT ID, Kondo T, Yoshida K. Metal-complex pigment involved in the blue sepal color development of hydrangea. *J Agric Food Chem*. 2015;63:7630-7635.
33. Ito T, Oyama K-I, Yoshida K. Direct observation of hydrangea blue-complex composed of 3-*O*-glucosyldelphinidin, Al^{3+} and 5-*O*-acylquinic acid by ESI-mass spectrometry. *Molecules*. 2018;23:1428.
34. Moncada MC, Moura S, Melo MJ, Roque A, Lodeiro C, Pina F. Complexation of aluminum(III) by anthocyanins and synthetic flavylium salts: a source for blue and purple color. *Inorganica Chim Acta*. 2003;356:51-61.

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