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## Extraction of anthocyanins from blackcurrant (*Ribes nigrum* L.) fruit waste and application as renewable textile dyes

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Humans have always been attracted by colour in their day-to-day lives. So much so that the art of dyeing can be traced back to the prehistoric era. Natural dyes are considered to be sustainable as they are obtained from renewable sources and are biodegradable, skin friendly and may also have health benefits. Dyes obtained from natural extracts of plants, insects and minerals were used until the discovery of the first synthetic dye in 1856. Synthetic dyes, due to better application properties replaced natural dyes, however the questions around the sustainability of synthetic dyes could help promote natural dyes back to the forefront of textile dyeing.

Anthocyanins (**1**) are the largest group of polyphenolic pigments in the plant kingdom. They are non-toxic, water-soluble phenolic pigments responsible for the red, purple, blue and orange coloration of fruits, vegetables and flowers. Their colours are determined by the number of hydroxyl groups (and degree of methylation) and the nature, number and position of sugar moieties including associated aliphatic or aromatic acids attached to the sugar.<sup>1</sup> More than 20 different anthocyanidins (aglycons) have been identified in nature, all based on the flavan nucleus, leading to many anthocyanins, due to the diversity of glycosylation;<sup>2</sup> in total more than 600 anthocyanins have been identified in nature.<sup>3</sup> In aqueous solution of pH <3, the anthocyanin is red and the flavan nucleus exists mainly as the very stable flavylium cation (**AH**<sup>+</sup>). Increasing pH leads to kinetic and thermodynamic competition between two reactions. When pH increases, **AH**<sup>+</sup> undergoes a rapid deprotonation reaction to form the purple quinonoidal base (**A**), which leads to formation of the anionic quinonoidal base (**A**<sup>-</sup>) at higher pH that has a blue colour.<sup>4,5,6</sup> The alternative thermodynamically favoured colourless hemiketal is relatively slowly formed via hydration above pH 2, yielding the colourless carbinol pseudobase (**B**). Ring opening is also slow compared to deprotonation and hydration, and can lead to the formation of yellow E-chalcone (**CE**); once formed, **CE** isomerizes to give the Z-chalcone (**CZ**).<sup>7</sup> Co-pigmentation is described as the phenomenon that makes anthocyanins bluer, brighter and helps to stabilize against light induced degradation pathways.<sup>8</sup> A strong complex is formed between the co-pigment and the anthocyanin, is most influenced by intermolecular hydrogen bonding between flavonoid catechol moieties and carbonyl groups of anthocyanin anhydrobases. **Error! Bookmark not defined.** These so-called stacking interactions may also involve self-association (anthocyanin +

anthocyanin), self-association of acylated anthocyanins and the formation metal-anthocyanin complexes.<sup>6</sup>

In our previous research we have developed techniques for extraction of anthocyanins from fruit sources; the purpose of this research was to develop textile colorants. The colorants employed in the proposed system, described herein, are anthocyanin-rich extracts isolated from waste skin from pressing of blackcurrants (*Ribes nigrum* L.) for juice. The skins were extracted using acidified water with a solid-phase purification stage. Anthocyanins colorants were isolated in good yields (2-3% w/w) and characterized by HPLC as a mixture of 3-*O*-glucosides and 3-*O*-rutinosides of cyanidin and delphinidin.

Silk and wool fabrics were dyed using the purified blackcurrant extract. The extract was applied by aqueous exhaust dyeing with and without the addition of metal salts at varying pH. Without the

addition of a metal dyeings generally were a range of pink shades at pH 9 and below, above pH 9 the dye degraded. Dyeing in combination with aluminium sulphate provided deeper colours with a range of purples when applied at pH 2.2 to 7, and blues at pH 9 and 11, attributable to formation of stabilised quinonoidal base-Al<sup>3+</sup> complexes. Dyeing in combination with iron acetate



produced anthocyanin-Fe<sup>3+</sup> complexes that were generally brown and green shades.

After washing, the majority of silk and wool samples were rated grade 5, indicating no difference between washed and unwashed sample. Light-fastness without metal-complex formation was poor. The best results were obtained when silk and wool were dyed with the addition of Fe<sup>3+</sup>, and certain pH combinations with Al<sup>3+</sup> and were rated with grade 4.

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