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Improving the dyeability of cotton with tannin-rich natural dye through pretreatment with whey protein isolate

P. Pisitsak[a,*], J. Hutakamol[a], R. Thongcharoen[b], P. Phokaew[a], K. Kanjanawan[a], N. Saksaeng[a]

[a] Department of Textile Science and Technology, Faculty of Science and Technology, Thammasat University, Pathum Thani 12121, Thailand
[b] Thailand Textile Institute, Bangkok 10110, Thailand

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ABSTRACT

Cotton fabrics were pretreated with whey protein isolate (WPI) to improve their dyeability toward a tannin-rich natural dye obtained from *Xylocarpus granatum* bark. Comprehensive studies were conducted on these fabrics assessing their dyeability, color fastness, physical characteristics, and ultraviolet protection level. All dyed samples were reddish-brown with a significant enhancement in the sample color strength (*K*/*S*) being observed for the pretreated samples. This is due to insoluble complex formation between WPI and tannin, stabilized through hydrogen bonding and hydrophobic interactions. Dyeing at elevated temperatures and with longer times resulted in higher color strength values. Acidic pH values favor dye absorption with pH 5 yielding the highest color strength, probably due to tannin forming complexes with proteins most efficiently near the protein isoelectric point. Padding cotton with WPI at only 0.35% solid content afforded dyed fabrics having an approximately 50% increase in the *K*/*S* value in comparison to untreated fabrics. The color strength of the WPI-treated cotton was enhanced relative to that treated with soy protein isolate (SPI), under the same dyeing conditions. For protein-treated cotton fabrics, except for color fastness to light and crocking, all other fastness properties (washing, water, sea water, perspiration and hot pressing) were rated as good to excellent. After protein pretreatment, the tensile strength and tearing strength of fabrics were slightly reduced whereas a small increase in fabric stiffness was obtained. Measurements of the ultraviolet protection factor (UPF) indicated better fabric shielding against ultraviolet radiation on treatment with either natural dye or WPI.

1. Introduction

Cotton is the most important natural textile fiber. Its structure consists of cellulose, a polymer constructed of monomeric glucose units. Since cellulose is susceptible to hydrolysis when heated in acidic medium, dyeing of cotton must be achieved at pH values above 4 (Broadbent, 2001). The pendant hydroxymethyl groups in the cellulose chains are partially oxidized to carboxyl groups during plant growth, and subsequent processing. These carboxyl groups confer a negative charge to the surface of cotton upon immersion during the dyeing process. At higher pH values (>8), side chain hydroxyl groups can be ionized, thus increasing the negative surface charge significantly (Rattee, 1995). Therefore, cotton generally shows poor affinity toward anionic dyes due to charge repulsion, leading to low uptake of such dyes (Janhom et al., 2006; Rattanaphani et al., 2007). To improve the dyeability of cotton with anionic dyes, pretreatment with synthetic cationic fixing agents in the form of secondary, tertiary and quaternary amine compounds has been proposed (Burkinshaw et al., 1989; Lewis and Lei, 1991; Eorn et al., 2001; Janhom et al., 2004; Ticha et al., 2013). More environmentally friendly approaches using biopolymers appended with amino groups e.g., chitosan (Rattanaphani et al., 2007) and proteins derived from natural sources (soybean, egg albumin, milk casein, and wheat gluten) (Kashino et al., 1988) to attach to cotton have also been reported as these compounds contain cationic sites at acidic pH which show affinity for anionic dyes.

To date, the use of whey protein isolate (WPI) to improve dye uptake of cellulose fibers has not been reported. Whey protein is a by-product from the dairy industry and consists of a mixture of globular proteins isolated from whey, the liquid fraction remaining after milk clotting and casein removal, during cheese production. The major whey proteins are β-lactoglobulin (β-Lg), α-lactalbumin (α-La) and bovine serum albumin (BSA) (Wijayanti et al., 2014). Whey was once considered a major pollutant arising from the dairy

* Corresponding author. Fax: +66 25644440x2600.
E-mail address: penwisa@tu.ac.th (P. Pisitsak).

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industry but this perception has now changed due to the discovery of its functional and bioactive properties (Brandelli et al., 2015). Having desirable gelling, foaming and emulsifying properties, whey proteins are widely used in the food industry, (Lam and Nickerson, 2013) however, the potential use of WPI in the textile industry has yet to be explored.

In this work, a natural colorant extracted from *Xylocarpus granatum* is employed as a dye material to realize completely eco-friendly textiles. Natural dyeing of textiles has now been revived due to environmental and safety concerns. Dyes derived from natural sources are perceived as an alternative to potentially harmful synthetic dyes. (Selvi et al., 2013; Haddar et al., 2014; Tchinda et al., 2014). *X. granatum*, also known as the cannonball mangrove, is widely distributed in East Africa, tropical Australia and Southeast Asia (Wangensteen et al., 2013). It is a small to medium-sized tree with branched ribbon-like surface roots and a thin, scaly bark. The bark of mature trees is tannin rich (20–34% on dry matter basis) and can be used for tanning leather and textile dyeing, affording a reddish-brown color. Even after removal of its bark, *X. granatum* can still propagate well; therefore, the use of the bark of *X. granatum* for dyeing can be considered eco-friendly. Tannins are secondary plant metabolites derived from phenolic compounds that have great structural diversity. There are two major categories of tannins: hydrolysable tannins and condensed tannins. Condensed tannins are polyphenols with high molecular weights (500–20,000 kDa) based on monomeric units of flavan-3-ols, such as catechin and epicatechin (see Fig. 1). This class of tannins is a major constituent of the colorants found in mangrove barks (Punrattanasin et al., 2013). Tannin has an ability to form insoluble complexes with proteins, which are stabilized mainly through hydrophobic and hydrogen bonding interactions. Maximum binding affinities occur at pH values near the isoelectric point of the protein (Kadam et al., 1990). When tannin-rich dyes are used in conjunction with proteins to dye fabric, apart from reducing the amount of negative surface charge the protein may provide further improvements in dyeability through tannin–protein complexation (Rattanaphani et al., 2007). It should be noted that the protein itself binds to the cotton surface through hydrogen bonding, and van der Waals forces (McLean et al., 2000; Zhang et al., 2011).

The aim of this work is to carry out a systematic study of cotton dyeing with natural dye extract from *X. granatum*, and to improve the dyeability of cotton by means of pretreatment with whey protein isolate. The dyeing properties of such fabrics, as well as other physical and functional properties relevant to textile applications are reported herein.

2. Materials and methods

2.1. Materials

Plain weave cotton fabric (mass per unit area of 155 g/m^2 as measured after scouring and bleaching; warp and weft yarn counts of Ne 28 and Ne 34, respectively; threads per unit length of 131 ends/cm and 69 picks/cm) was purchased from a local store in Thailand. *X. granatum* bark was obtained from Samut Sakorn province, Thailand. The amount of tannin in the bark extract was 74.0% (based on the spray-dried powder) as determined by a gravimetric method (Makkar et al., 1993). The whey protein isolate

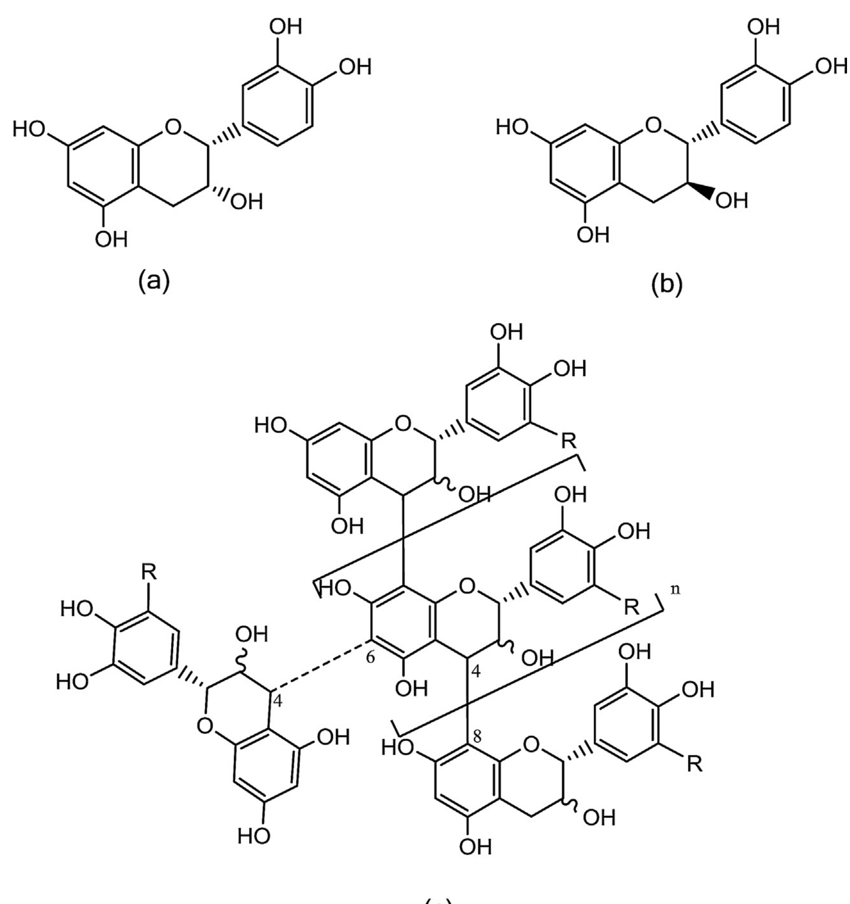

Fig. 1. Schematic representation of the base units (a) epicatechin; and (b) catechin of tannins, and (c) the condensed tannin molecule showing linear (attachment through 4,8-positions) and branched (attachment through 4,6-positions) structural features (Hrckova and Velebny, 2013).