Industrial Crops and Products 64 (2015) 224–232

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Simultaneous dyeing and functionalization of silk with three natural yellow dyes

Yuyang Zhou[a], Jue Zhang[a], Ren-Cheng Tang[a,*], Jun Zhang[b]

[a] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou 215123, China
[b] Suzhou Institute of Trade and Commerce, 287 Xuefu Road, Suzhou 215009, China

ARTICLE INFO

Article history:
Received 10 June 2014
Received in revised form
17 September 2014
Accepted 21 September 2014
Available online 13 October 2014

Keywords:
Rheum emodi
Gardenia yellow
Curcumin
Silk
Antioxidant activity
Antibacterial activity.

ABSTRACT

Three natural yellow dyes, namely *Rheum emodi*, *Gardenia* yellow and curcumin, were applied to the simultaneous dyeing and functionalization of silk. Their dyeing properties and functionalities as well as the effects of post-mordanting on the hue, color fastness and functionalities of dyeings were compared, and the correlations between the chemical structures and application characteristics of dyes were revealed. The three dyes exhibited large variations in dyeing and mordanting properties, and functionalities. Curcumin displayed the greatest coloring power. The uptake of *Gardenia* yellow was most sensitive to the pH of dyebath. *Gardenia* yellow and curcumin had much higher building-up ability than *R. emodi* with anthraquinone structures. *Gardenia* yellow possessed the highest fastness ratings, while curcumin and *R. emodi* showed poor wet rub fastness and wash fastness for staining. Curcumin imparted the highest antioxidant activity to silk because of its high adsorption and two phenolic hydroxyl groups in its structure and also gave the highest UV protection ability. Curcumin and *R. emodi* provided higher antibacterial activities than *Gardenia* yellow. The post-mordanting with ferrous and ferric salts exerted great influence on the color parameters, color fastness and UV protection ability of dyeings. This study points out that the common dyeing process of three natural yellow dyes can impart the color and functional properties to silk.

1. Introduction

Silk fiber has been historically referred to as the "queen of textiles", and used as a natural source of textile materials for thousands of years owing to its excellent performance such as softness, smoothness, luster, comfortableness, breath ability, hygroscopicity and so on. Silk has also found a wide range of applications as a biomaterial in the medical field for sutures and scaffolds due to its remarkable mechanical performance, biocompatibility, and controlled degradability (Li et al., 2012). With all its advantages, silk fiber is by no means without its limitations. Silk suffers from some shortcomings such as wrinkling, photooxidation, deterioration, yellowing, poor UV protection capability, poor antioxidant and antimicrobial activities, etc. (Baltova and Vassileva, 1998; Jiang et al., 2009; Li et al., 2011, 2012). These defects inevitably restrict the application of silk fiber; hence some measures must be taken to overcome the disadvantages and enhance the functionalities of silk. In particular, if silk fabric is used for the purposes of medical and healthy clothing, and bioactive dressings, its biological activities such as antimicrobial and antioxidant activities should be upgraded.

Antioxidant activity is one of the most important properties of bioactive textiles, and the radical scavenging textiles can deactivate highly reactive and harmful species such as active oxygen radicals. However, up to now, much less attention has been paid to the antioxidant activity of silk textiles. The adsorption treatment with oleuropein and rutin extracted from olive leaf extract was found to enhance the antioxidant capacity of silk fibroin powder (Bayçin et al., 2007). The simultaneous coloration and functionalization of the tyrosinase-catalyzed oxidation products of caffeic acid was able to significantly increase the antioxidant activity of silk fabric (Sun et al., 2013).

Silk fiber allows microbial growth and multiplication by providing good environments such as nutrient (protein), moisture, etc. Microbial growth and proliferation on silk fiber lead to generation of foul odors, discoloration, mildew formation, fiber degradation, dermal infection, allergic responses and other related diseases (Shahid et al., 2013). In recent years, a lot of reports have focused on the antimicrobial functionalization of silk by the treatment with quaternary ammonium compounds (Koller et al., 2007), quaternary

* Corresponding author. Tel.: +86 512 6716 4993; fax: +86 512 6724 6786.
E-mail address: tangrencheng@suda.edu.cn (R.-C. Tang).

http://dx.doi.org/10.1016/j.indcrop.2014.09.041
0926-6690/

ammonium organosilanes (Higgins et al., 2010), chlorinated compounds (Dickerson et al., 2012), inorganic materials (Jiang et al., 2009; Li et al., 2011; Tang et al., 2014), chitosan (Periolatto et al., 2012), antimicrobial peptides (Bai et al., 2008) and bactericidal enzyme lysozyme (Dickerson et al., 2011). In addition, some synthetic dyes, e.g., metallic dyes (Tsukada et al., 2002) and quinazolinone-based monoazo reactive dyes (Patel and Patel, 2011), were able to show good antimicrobial properties when applied to the dyeing of silk fiber, suggesting that the dyeing and antimicrobial finishing of silk are simultaneously accomplished. The one-step dyeing and finishing achieved by choosing specific dyes possesses the potential to save time and energy, reduce cost, increase production and efficiency, and reduce effluent load. In this regard, natural dyes as naturally derived colorants and antimicrobial agents have more advantages over synthetic dyes in that they exhibit good biodegradability and compatibility with the environment (Shahid et al., 2013), and most of them possess a wide range of functional properties such as antimicrobial activity (Ghoreishian et al., 2013; Han and Yang, 2005; Hong et al., 2012; Khan et al., 2012; Koh and Hong, 2014; Mirjalili and Karimi, 2013; Shahid et al., 2013; Silva et al., 2011; Singh et al., 2005; Sousa et al., 2009) and antioxidant activity (Hong et al., 2012; Koh and Hong, 2014; Liu et al., 2013; Silva et al., 2011; Sousa et al., 2009).

Natural dyes are obtained mainly from plants, producing different colors like yellow, red, blue, brown, black and a combination of these colors. The sources for yellow dyes are enormous (Bechtold and Mussak, 2009), and the plants which yield yellow dyes outnumber those yielding other colors. The chromophores of natural yellow dyes include flavonoids, carotenoids, hydroxylanthraquinones, and bis-α,β-unsaturated diketone polyphenols (Bechtold and Mussak, 2009; Ferreira et al., 2004). *Rheum emodi*, *Curcuma longa* L., and *Gardenia jasminoides* Ellis are the vital sources of natural yellow dyes. *R. emodi* or Rhubarb is a valuable medicinal herb and distributed in the temperate and sub-tropical regions of Asian countries. A large number of anthraquinone derivatives are present in the roots of the plant and also used in the coloring of food stuffs and textiles (Khan et al., 2012). Curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione) is extracted from the ground roots of *C. longa* L., a plant growing abundantly in the East Indies and China, and well known both in traditional and in modern medicine due to its antioxidant, anti-inflammatory, antifungal, and anticancer properties (Barzegar, 2012). Curcumin is often used as spice, cosmetic ingredient, natural medicine, food preservative, food colorant, and textile colorant. The yellow colorant extracted from gardenia fruits, *G. jasminoides* Ellis, is well known as *Gardenia* yellow in China. *Gardenia* yellow is a typical plant carotenoid, and its major constituents are crocins and crocetin. It is utilized as herb medicine and food colorant on account of its water solubility (Chen et al., 2008). The structures shown in Fig. 1 reflect the chemical components present in these dyes (Chen et al., 2008; Han and Yang, 2005; Khan et al., 2012).

R. emodi has been used to the dyeing of wool, silk, and cotton fibers with and without the treatment of metal mordants (Das et al., 2008; Khan et al., 2012; Vankar et al., 2007), and the good antimicrobial activity of dyed wool was found (Khan et al., 2012). Curcumin has been successfully utilized to the antibacterial dyeing of wool, silk, nylon fibers (Ghoreishian et al., 2013; Han and Yang, 2005; Mirjalili and Karimi, 2013), and applied to the dyeing of polyester and modified acrylic fibers (El-Shishtawy et al., 2009; Kerkeni et al., 2012). *Gardenia* yellow widely used as a dye in middle China in ancient times is being investigated for its application in the dyeing of various fibers (Liu and Tang, 2013; Shen et al., 2014), and it was found that the chitosan fiber dyed with it had the good antioxidant and deodorant properties (Liu and Tang, 2013). In spite of the above investigations, the comparison of the dyeing properties of *R. emodi*, *Gardenia* yellow and curcumin for silk has not been reported, and little attention has been paid to the antibacterial and antioxidant activities of silk dyed with these dyes. In this study, the important dyeing properties of *R. emodi*, *Gardenia* yellow, and curcumin applied to silk fabric were compared in terms of pH dependence, building-up capability, color fastness, and post-mordanting properties; and what is more, the antibacterial, antioxidant, and UV protection properties of the dyed silk without and with post-mordanting were evaluated. This research is expected to provide the basis for developing healthy and hygienic silk textiles and materials, and the assistance for better understanding the relationships between the chemical structures and functionalities of natural yellow dyes.

2. Materials and methods

2.1. Materials

The scoured silk fabric of crepe de Chine fabric was supplied by Wujiang Zhiyuan Textile Co. Ltd., China. *R. emodi* dye with a purity of 95% was purchased from Xi'an Qing Yue Biotechnology Co. Ltd., China; *Gardenia* yellow with a color value of 550, and curcumin with a purity of 90% were obtained from Yunnan Tonghai Yang Natural Products Co. Ltd., China. 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS) was bought from Sigma-Aldrich (Shanghai) Trading Co. Ltd. Citric acid, disodium hydrogen phosphate, potassium dihydrogen phosphate, potassium persulfate, ethanol, aluminum sulfate, ferrous sulfate, and ferric sulfate were of analytical reagent grade. Nutrient agar and nutrient broth were obtained from Sinopharm Chemical Reagent Co. Ltd., China, and Shanghai Sincere Biotech Co. Ltd., China, respectively.

2.2. Dyeing experiments

All the experiments were carried out in the sealed and conical flasks housed in a XW–ZDR low-noise oscillated dyeing machine (Jingjiang Xinwang Dyeing and Finishing Machinery Factory, China). The liquor ratio was 50:1. The dyeing temperature was started at 30 °C, and raised to 90 °C at a rate of 2 °C/min with a holding time of 60 min. At the end of dyeing, the fabrics were washed in tap water and then dried in the open air.

To assess the dependence of the uptake of natural yellow dyes on the pH value of dyebath, the silk fabrics were dyed with 3% owf (on the weight of fabric) dyes at the pH values approximately ranging from 2.3 to 7.4; McIlvaine buffers (citric acid and disodium hydrogen phosphate mixture) were added to adjust pH. To estimate the building-up properties of natural yellow dyes on silk, the dye concentration of 0.5–8% owf were used; the pH values of *R. emodi*, *Gardenia* yellow, and curcumin solutions were adjusted by McIlvaine buffers to 5.18, 2.75, and 2.32, respectively.

2.3. Post-mordanting treatment

The fabrics dyed with 3% owf dyes were mordanted using three metallic salts (aluminum sulfate, ferrous sulfate, and ferric sulfate). The concentrations of the mordants ranged from 2 to 8% owf. The dyed fabrics were immersed in the mordant solutions at 70 °C for 30 min. After post-mordanting, the fabrics were rinsed thoroughly in tap water and allowed to dry in the open air.

2.4. Measurements

2.4.1. Uptake of dyes by silk

The absorption spectra and absorbance of the solutions were measured using a Shimadzu UV-1800 UV–Vis spectrophotometer. Because *R. emodi* and curcumin have poor solubility in water, the