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Effects of tannin mordanting on coloring and functionalities of wool fabrics dyed with spent coffee grounds

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Abstract

A large amount of functional materials remain in spent coffee grounds and form discards in the coffee beverage industry. Moreover, the extract from these spent coffee grounds contains sufficient amounts of pigments that can be utilized for textile dyeing. Therefore, in this study, the coloring and functional development of textiles by application of spent coffee extracts to wool fabrics was investigated. For preparation of the dyed wool fabrics, spent coffee grounds were dried after collecting them from a local coffee house. They were then subjected to extraction using a manual espresso machine. The spent coffee extract was applied to wool fabrics using an infrared (IR) dyeing machine, and after dyeing, the wool fabrics were post-mordanted in various concentrations of aqueous tannin solutions. The color and surface properties of wool fabrics dyed with spent coffee extract were investigated using spectrophotometry and Fourier-transform IR spectroscopy, respectively. And, their antibacterial and antioxidant capacities were also studied. The dyed wool fabrics were significantly brown in appearance, and their colorfastness to light improved upon mordanting with tannin. In addition, mordanting also improved the antibacterial and antioxidant capacity of the dyed wool fabrics.

Keywords: Spent coffee grounds, Tannins, Wool, Dyeing, Mordanting, Antibacterial ability, Antioxidant ability

Introduction

Coffee is the most widely consumed beverage in the world, with 7.4 million tons of coffee beans produced and distributed annually. It also takes up the second-highest trade volume after petroleum, implying its critical role in the economy (Jo et al. 2017). Coffee consumption by Koreans has been increasing continuously and, according to 2017 statistics, the annual coffee consumption by an average Korean adult has reached approximately 512 cups. According to the Korea Customs Service and the coffee industry, the national coffee market valuation has reached 11 trillion Korean won, which is more than three times larger than that 10 years ago (Yonhap News 2018).

However, with increasing coffee consumption, the amount of spent coffee grounds, a byproduct of coffee consumption, is also increasing accordingly. The Seoul Metropolitan Government estimated that the daily amount of discarded spent coffee grounds in Seoul would reach about 140 tons in 2014 (Maekyung economy news 2016). Unlike the rapid growth rate of the coffee market, a collection and recycling system for spent coffee grounds has not been established, and thus effective strategies to deal with spent coffee grounds need to be implemented. Spent coffee grounds, however, do not represent a simple food waste and could be an environmental pollutant. Spent coffee grounds contain high levels of organic compounds that have various biological effects, including antioxidant, antimicrobial, and other activities (Xu et al. 2015; Rufián-Henares and de la Cueva 2009). Additionally, they release methane gas, which has a 2.5-time higher negative effect than carbon dioxide on global warming (Lee et al. 2017). Therefore, the disposal or incineration of spent coffee grounds into landfills will have detrimental effects on the environment. Therefore, several attempts to utilize the spent coffee grounds have been made on a global scale, and their alternative use as biodiesels or fertilizers have been proposed (Caetano et al. 2012; Preethu et al. 2007).

Previously, we have attempted to apply the extract of spent coffee grounds to wool and cotton fabrics using a pad–dry–cure or dyeing process in order to lend coloring as well as functional effects to the fabrics (Koh and Hong 2017a, b, 2018). Our research findings indicated that the fabrics treated with spent coffee extract had superior antioxidant ability and showed antibacterial ability, particularly to Gram-positive bacteria. Moreover, when fibers containing amide groups, such as wool fibers, were dyed with spent coffee extract, the color and color fastness obtained were of very good quality. In addition, it was recently discovered that the spent coffee extract contains more valuable ingredients when they were extracted with an usual espresso machine than using the methanolic extraction methods proposed by Mussatto et al. (2011). The former type of machine extraction is considered an optimal method in the context of textile finishing and dyeing, compared to the methanolic extraction methods. This is because it does not require the use of methanol, a relatively harmful solvent, and thus we don't need to have the methanol-removing process in order for the extract to be applied to fabrics. Moreover, the optimal dyeing time and temperature conditions were recently derived for this method to apply spent coffee extract to wool dyeing. Therefore, the effects of tannin mordanting were thoroughly investigated in this study. Tannins have been reported to be the most important ingredients which are necessary for dyeing with natural dyes, especially to brown shades of color (Janani et al. 2014). They also have less burdens on the environment compared to the metal mordants. On the other hand, the post-mordanting method was used because it was considered effective for coffee dyeing in terms of coloring effect and color fastness according to Teli and Paul's findings (2006).

Methods

Materials

Scoured wool fabric (ISO 105-F01; plain woven 125 g/m^2) was purchased from Testfabrics Inc. (West Pittston, PA). The spent coffee grounds used in the research were arabica (*Coffee arabica* L.) coffee beans, which were dried in a conventional oven at 60 °C within 24 h after collection of the spent coffee grounds from a coffee house located in Gongju, Chung-nam province. For mordanting, tannic acid (ACS reagent) was purchased from Sigma-Aldrich (St. Louis, MO, USA), and to measure the antioxidant ability, DDPH (1,1-diphenyl-2-picrylhydrazyl) was obtained from Calbiochem (CA, USA).

Preparation method

Obtaining the spent coffee extract

The spent coffee extract was extracted from dried spent coffee grounds collected from the coffee house under a 15-bar pressure using a manual espresso machine (Gaggia Gran Prestige, Milano, Italy). A total of 5 L was extracted and was used as a stock solution for this research.

Dyeing

The wool fabrics were each cut into 30 cm × 30 cm pieces, put into the stock solution, and dyed using an infrared (IR) dyeing machine (Lab IR dyeing machine, Daelim Starlet Co., Ltd; Gyeonggi-do, Korea). The bath ratio was 1:30, and the bath rotational speed was 45 rpm. The dyeing temperature and time were 90 °C and 60 min, which were discovered to be optimal based on preliminary research. After dyeing, the wool fabrics were completely washed with deionized water and dehydrated using a padder to contain a consistent amount of water (100% wet pickup).

Mordanting

After dyeing, dehydrated wool fabrics were placed in containers containing aqueous 0, 0.25, 0.5, 1.0, and 2.0 wt% tannic acid solutions (bath ratio = 1:30). Then, the containers were shaken at 130 rpm for 60 min at 85 °C. After that, the wool fabrics were thoroughly rinsed with deionized water and dried in a convection oven at 60 °C.

Measurement and analysis

In order to identify the changes in the molecular structures in the fabric surfaces after dyeing, the bond structure was analyzed using an infrared spectrometer (Fourier-transform infrared spectroscopy, FTIR). The FTIR spectrum analysis device (100 FTIR spectrum, Perkin-Elmer MA, US) was used with a resolution of 4 cm^{-1}, and attenuated total reflection was used to obtain the results.

The changes in the colors of the dyed samples were investigated using a photoelectric spectrophotometer (CM-2500d, Konica Minolta, Inc., Osaka, Japan) and the values of changes in colors (ΔE) were compared using L*, a*, and b* values. In addition, by using the Kubelka–Munk method, the color strength (K/S) values were derived.

Color fastness to washing (KS K ISO 105 C06:2010, A2S, washing temperature: 40 ± 2 °C, washing time: 30 min, 0.4% ECE standard solution +0.1% natrium used, 10 still balls) and color fastness to light (KS K ISO 105 B02:2010, xenon arc lamp, blue scale) results were obtained on request from the FITI Testing and Research Institute.

The ability of the dyed fabrics to prevent microbial growth and retention were tested using *S. aureus* (ATCC 6538; a Gram-positive bacterium) and *K. pneumoniae* (ATCC 4352; a Gram-negative bacterium) cultures according to an established protocol (KS K 0693).

$$Bacterial\ reduction\ (\%) = \frac{(B - A)}{B} \times 100 \quad (1)$$

In the formula, each of A and B represents the surviving bacterial cells (colony-forming units in mL^{-1}) on the plates inoculated with a bacterial solution derived from the dyed fabric and a control solution derived from untreated fabric, respectively.

For determining the antioxidant ability, the DDPH· method was used. DPPH· can measure radical activity by measuring the reduced speed of chemical response due to radical scavenging after its addition (Alger 1997). The radical scavenging activity was calculated using Eq. (2), and the detailed analysis method is provided in previous literature (Koh and Hong 2017a, 2018).

$$DPPH \cdot scavenging\ activity\,(\%) = \frac{(\mathrm{C} - \mathrm{S})}{\mathrm{C}} \times 100 \qquad (2)$$

Here, C and S refer to the values of absorbance at 517 nm after 1 h of resting in a dark room for the control sample and test sample in DPPH·/methanol solvents.

Results and discussion

Color revelation characteristics of wool fabrics dyed with spent coffee extract

Figures 1, 2, and Table 1 show the results of the color revelation characteristics after dyeing the wool fabrics with spent coffee extract at 90 °C for 60 min and mordanting with tannin. It was discovered that the a* value of the wool fabrics dyed with spent coffee extract increased after tannin mordanting, indicating that the red colors were more visible on tannin mordanting in the dyed wool fabrics. Although no difference was noted on the L* and b* values between before and after mordanting, the value L* somewhat increased and the color change (ΔE) also somewhat decreased as the mordant concentration increased. This suggests that the coffee color pigments not fully integrated into the wool fibers were removed during the mordanting process by being adsorbed by the tannin in aqueous solution. This is because tannins tend to readily bond with proteins, and melanoidins, considered the primary components in coffee that lead to the brownish

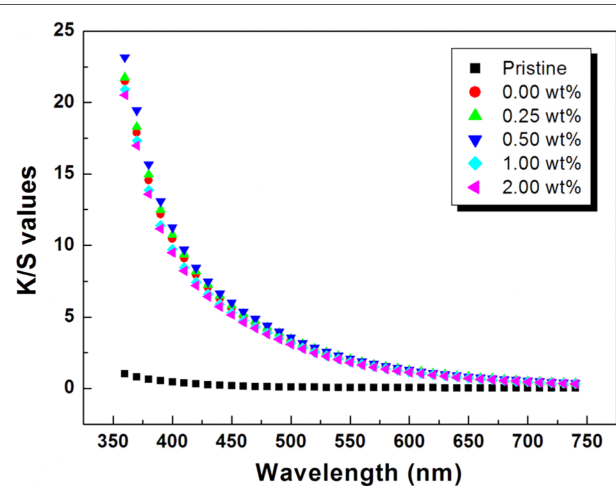

Fig. 1 K/S values of wool fabrics dyed with spent coffee extract as a function of mordanting solution concentration

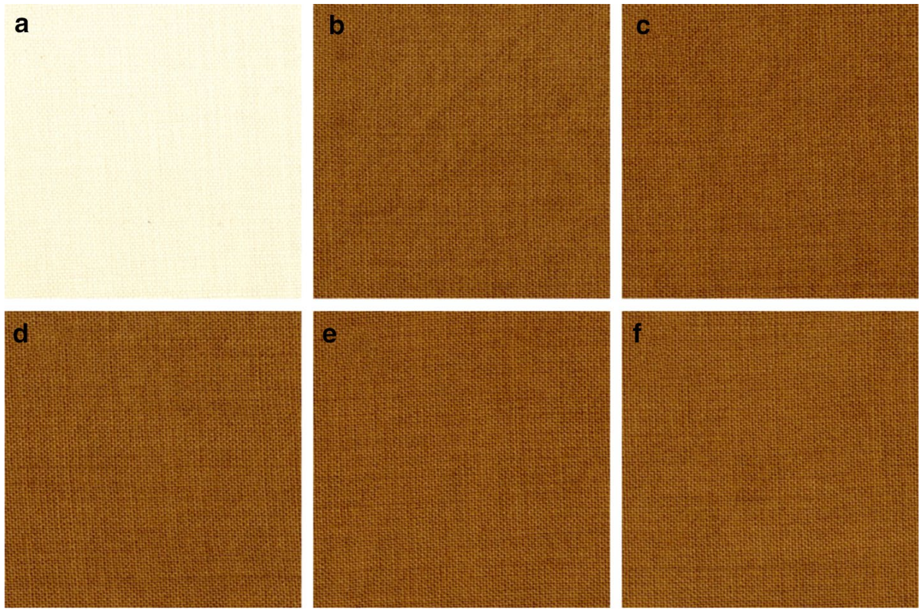

Fig. 2 Color images of wool fabrics dyed with spent coffee extract as a function of mordanting solution concentration: **a** pristine, **b** 0.00 wt%, **c** 0.25 wt%, **d** 0.50 wt%, **e** 1.00 wt%, and **f** 2.00 wt%

Table 1 Color changes of wool fabrics dyed with spent coffee extract

Mordant concentration (wt%)	L*	a*	b*	ΔE
Pristine	86.54	− 0.585	12.68	–
0.00	49.29	9.69	26.82	41.15
0.25	48.77	9.95	26.83	41.68
0.50	48.40	9.93	26.87	42.03
1.00	50.16	9.82	26.92	40.43
2.00	50.50	9.82	26.86	40.10

Table 2 Colorfastness of wool fabrics dyed with spent coffee extract

Mordant concentration (wt%)	Color change to washing (grade)	Color change to light (grade)
0.00	4–5	2–3
0.25	4–5	3
0.50	4–5	3
1.00	4–5	3–4
2.00	4–5	3–4

color, are large molecules containing nitrogen that plausibly display similar characteristics as proteins (Adamczyk et al. 2017).

Table 2 shows the results of the tests for color fastness. The wool fabrics dyed with spent coffee extract showed superior color fastness to washing (4 or 5 grade) even though without mordanting. Meanwhile, the values of color fastness to light, which is a major problem for fabrics dyed with natural colorants, were significantly lower than those obtained for color fastness to washing. However, the level of color fastness to light for the wool fabrics dyed with spent coffee extract was observed to be higher compared to that of other fabrics dyed with other natural colorants (Hong 2015; Koh and Hong 2017b). In particular, the color fastness to light improved significantly with increasing tannin concentration during the mordanting process. Therefore, it was observed that tannin mordanting improved color fastness to light rather than color change of the wool fabrics dyed with spent coffee extract. This result was supported by the previous reports that "tannin mordants and dyes may darken dyed textiles as they age, instead of the color fading due to exposure to washing and light (Cardon 2007; Richards and Tyrl 2005)" (Doty et al. 2016).

Surface characteristics of wool fabrics dyed with spent coffee extract

Figure 3 shows the results obtained by infrared spectroscopy analyses of the wool fabrics dyed with spent coffee extract. Wool is classified as a protein fiber, and so it contains various functional groups such as the carboxyl (–COOH), amino ($-NH_2$), and hydroxyl (–OH) groups (Hsieh et al. 2004). Therefore, in all the spectra seen in Fig. 3, transmittance peaks were observed at the following wavenumbers: 3283 cm^{-1} (N–H and O–H), 2873 cm^{-1} ($-CH_2$), 1634 cm^{-1} (amide I), 1512 cm^{-1} (amide II), 1229 cm^{-1} (amide III). However, in the wool fabrics dyed with spent coffee extract, new transmittance peaks were observed at 1314 and 1038 cm^{-1}, and the strength of the peaks increased as tannin concentration increased during the mordanting process. This is presumed to be driven by the C–O stretching of the ester attributed to tannin existing in the wool fabrics dyed with spent coffee extract. Moreover, as tannin concentration increased during the mordanting process, the peak for the amino group (amide III) moved to lower wavenumbers and grew in width. This could be attributed to the phenolic acid bonding with the wool protein, resulting in the aromatic C=C of the phenolic acid getting closer to the carbonyl group in the wool fiber, delocalizing the π-electrons in the amide groups (Pavia

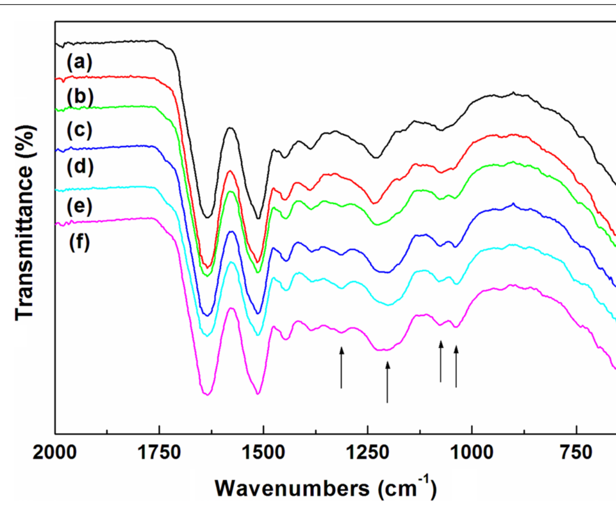

Fig. 3 FTIR-ATR spectra of wool fabrics dyed with spent coffee extract as a function of mordanting solution concentration: **a** Pristine, **b** 0.00 wt%, **c** 0.25 wt%, **d** 0.50 wt%, **e** 1.00 wt%, and **f** 2.00 wt%

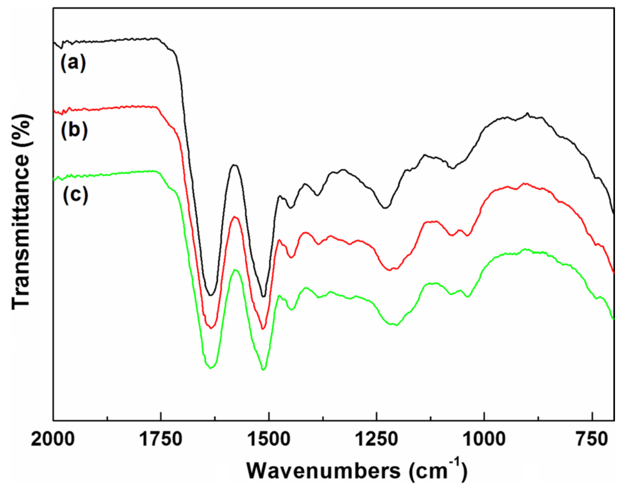

Fig. 4 FTIR-ATR spectra of wool fabrics dyed with spent coffee extract with 1.00% tannin mordanting: **a** pristine, **b** before washing, **c** after 5 cycles of washing

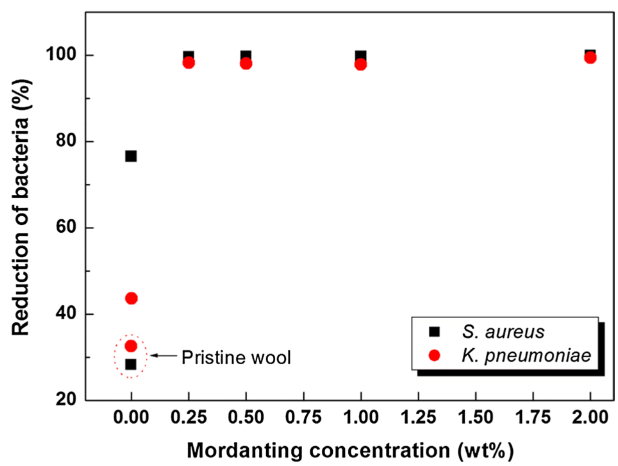

Fig. 5 Antibacterial ability of wool fabrics dyed with spent coffee extract as a function of mordanting solution concentration

et al. 1996). The chemical modification on the wool fabric remained after 5 cycles of washing, as shown in Fig. 4.

Antibacterial ability of wool fabrics dyed with spent coffee extract

Figures 5 and 6 show the antibacterial ability of wool fabrics dyed with spent coffee extract. The wool fabrics dyed with spent coffee extract, but not mordanted, showed 76.5% bacteria reduction rate against the Gram-positive bacteria *S. aureus* and 43.6% reduction rate against the Gram-negative bacteria *K. pneumoniae*. The results indicate some antibacterial ability only against *S. aureus* and no actual antibacterial ability against *K. pneumoniae*. In other words, the antibacterial ability of the fabrics only dyed with spent coffee extract did not qualify them as practical antibacterial products. Therefore, to complement the unimpressive antibacterial performance of the wool fabrics dyed

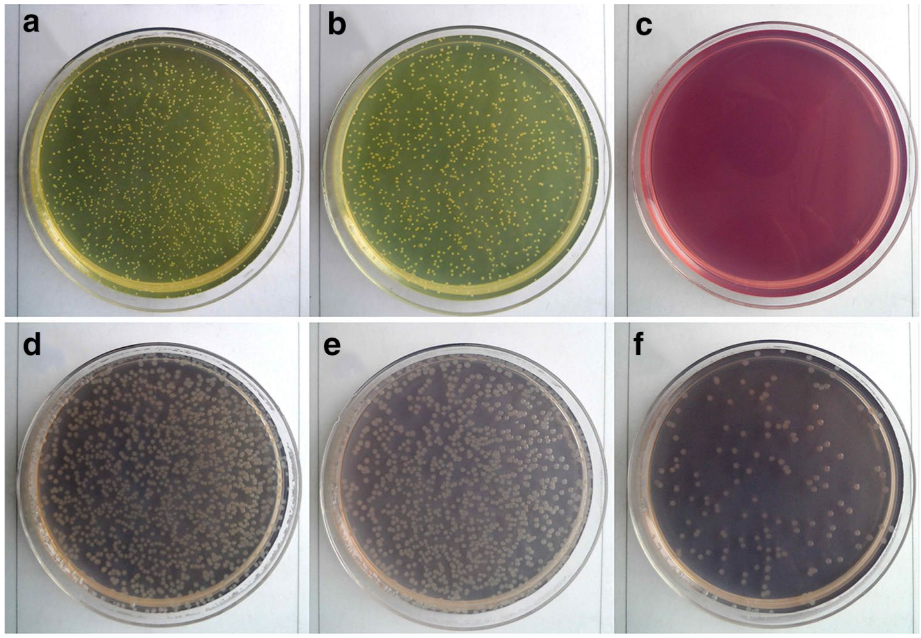

Fig. 6 Antibacterial ability of wool fabrics: **a** *S. aureus*—pristine, **b** *S. aureus*—dyed with spent coffee extract but without mordanting, **c** *S. aureus*—dyed with spent coffee extract and with 1.00% tannin mordanting, **d** *K. pneumonia*—pristine, **e** *K. pneumonia*—dyed with spent coffee extract but without mordanting, **f** *K. pneumonia*—dyed with spent coffee extract and with 1.00% tannin mordanting

with spent coffee grounds, post-mordanting was undertaken with tannins. As the tannin concentration increased, the antibacterial ability was observed to increase. The wool fabrics mordanted with a 0.25 wt% tannin solution showed 99.6% of bacteria reduction rate against *S. aureus* and 98.2% of bacteria reduction rate against *K. pneumoniae*. Even though the difference seems insignificant, the antibacterial ability toward Gram-negative bacteria was still relatively lower than that toward Gram-positive bacteria. Many reports have proposed that coffee extract is more effective against Gram-positive bacteria, and also the antibacterial components in coffee such as melanoidins and caffeine especially work more effectively against Gram-positive bacteria than against Gram-negative bacteria (Fardiaz 1995; Rufián-Henares and de la Cueva 2009; Mohammed and Al-Bayati 2009).

Antioxidant ability of wool fabrics dyed with spent coffee extract

Figure 7 shows the results of the antioxidant ability of wool fabrics dyed with spent coffee extract. All the wool fabrics dyed with spent coffee extract and mordanted with tannin revealed approximately 94% antioxidant capacity. However, the antioxidant ability did not significantly change with the mordant solution concentration. Coffee contains a variety of antioxidant components such as phenolic compounds, caffeine, and melanoidins. They are known for their superior antioxidant functionality by scavenging hydroxyl radical that creates oxidation. However, the wool fabrics dyed with spent coffee extract but not mordanted with tannin showed limited antioxidant abilities of around 60%. Moreover, tannins, used for mordanting in this study, are also well known

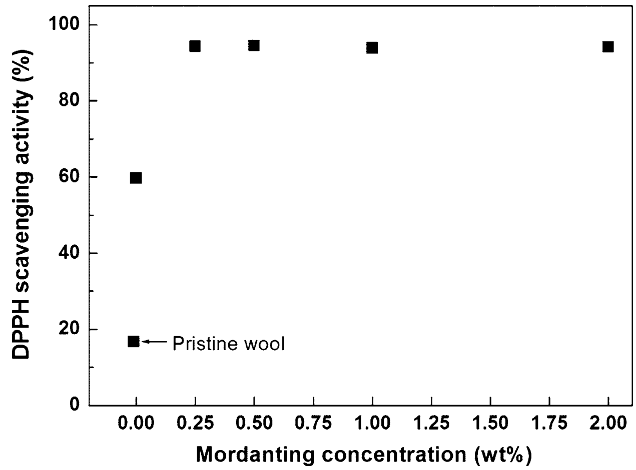

Fig. 7 Antioxidant ability of wool fabrics dyed with spent coffee extract as a function of mordanting solution concentration

for their superior antioxidant ability. When tannins are dissolved in water, they are readily hydrolyzed to various phenolic acids such as gallic acid (Lopes et al. 1999; Akiyama et al. 2001). It was found that tannin mordanting is a crucial process in wool dyeing with spent coffee extract to achieve sufficient antibacterial and antioxidant properties.

Conclusion

Spent coffee grounds, thrown away after extracting coffee drinks, still contain significant amounts of functional ingredients. In addition, the extract obtained from the spent coffee grounds contains sufficient amounts of color to dye fabrics. Therefore, this work attempted to investigate the color and functionalities of wool fabrics by applying spent coffee extract to them. Spent coffee grounds were collected from a local coffee house and dried. Extracts were obtained from the spent coffee grounds using a manual espresso machine. With an infrared ray dyeing machine, the extract was applied to wool fabrics. After dyeing, the dyed fabrics were subjected to mordanting with varying concentrations of aqueous tannin solutions. The wool fabrics dyed with spent coffee extract successfully adsorbed the coffee colorants and were significantly dyed brown. Regarding color revelation, the effect of mordanting was not so much evident. However, wool fabrics dyed with spent coffee extract had limited color fastness to light, which could be considerably improved by tannin mordanting. In addition, the wool fabrics dyed with spent coffee extract showed significant antibacterial and antioxidant ability after tannin mordanting. Therefore, it was found that spent coffee grounds can constitute an effective material for dyeing fabric and lending it additional functionalities. And, it also demonstrated a possible route for recycling spent coffee grounds, which are still recognized as industrial wastes.

Authors' contributions

HKH contributed to the conception of the study, designed the experiment, conducted the work and drafted the manuscript. The author read and approved the final manuscript.

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Competing interests
The author declares no competing interests.

Availability of data and materials
Not applicable.

Ethics approval and consent to participate
Not applicable.

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