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Application of persimmon (*Diospyros kaki* L.) peel extract in indigo dyeing as an eco-friendly alternative reductant

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Abstract

The aim of this study is to investigate the efficacy of persimmon (*Diospyros kaki* L.) peel extract as a reductant for indigo dyeing. Dried persimmon peel was water extracted and its sugar contents and functionalities were determined. Its reducing power was studied in terms of redox potential of the indigo bath and color strength (K/S value) of the ramie fabrics dyed in the indigo reduction bath. Total sugar content of the extract was 74.3%. Antioxidant capacity reached up to 86.0% at 3.5 µg/mL of the extract concentration. The persimmon peel extract had an effect on indigo reduction and the maximum color strength was obtained within one or two day. At 2–3% of the extract concentration, the redox potential of the indigo bath was maintained in the range of – 550 ~ – 600 mV for 10 days. With increase in the extract concentration, reduction state lasted for longer time and higher color strength was obtained. The persimmon peel extract can be used for indigo reduction dyeing as a sustainable, nontoxic, biodegradable alternative to sodium dithionite.

Keywords: Persimmon peel, Reductant, Indigo dyeing, Redox potential, Reducing power, Color strength, Antioxidant capacity

Introduction

Persimmons are the edible fruits of a number of species of trees in the genus *Diospyros* in the family *Ebenaceae*. Persimmons are eaten fresh, dried, raw, or cooked. Commercially and in general, there are two types of persimmon fruit: astringent and non-astringent. Astringent varieties of persimmons also can be prepared for commercial purposes by peeling and drying to produce dried persimmon, Gotgam. The non-astringent persimmon called by Dangam is one of popular fruits in South Korea. Dangam (*Diospyros kaki* L.) is consumed when still very firm and eaten raw, after peeling. In 2018, 0.3 million of tonnes of persimmon were produced in South Korea and its consumption tends to increase. A significant amount of waste is generated during the peeling process for commercial products. Recently, the exploitation of biomass wastes or by-products from food, agriculture, and forest industries has been drawn interests to recover potentially valuable components and reuse to convert to value-added products (Jha et al. 2019; Hong 2018; Peschel et al. 2006; Piccirillo et al. 2010; Rodríguez Couto et al. 2004; Vareed

et al. 2006). The reuse of biomass wastes would contribute to the sustainable development by maximum utilization of limited resources and to waste handling problems. New application of persimmon waste is of significant interest especially due to the increase in persimmon consumption in South Korea.

To date, sodium hydrosulphite is mainly used as a reducing agent in industrial indigo dyeing process. It causes environmental pollution by generating detrimental toxic by-products. There has been several studies to replace sodium dithionite to greener reducing agents such as glucose, fructose, lactose, galactose and maltose (Blackburn and Harvey 2004; Choi et al. 2006; Meksi et al. 2012). These reducing sugars are presented in many fruits and persimmon peel has high concentration of carotenoids, sugars, and polyphenols (George and Redpath 2008; Jimenez-Sanchez et al. 2015; Ku and Mun 2008; Lee et al. 2007; Wang et al. 2008). Keeping concern on this point, we carried out several studies for developing greener indigo dyeing process with organic reducing agents from food by-products (Shin et al. 2013, 2014).

In this study, the efficacy of persimmon peel extract as a reducing agent in indigo dyeing was investigated. Persimmon peel extract was water extracted and characterized by estimating total sugar content, antioxidant capacity, and antibacterial activity. Reducing power of the persimmon peel extract was assessed in terms of the color strength (K/S value) of dyed ramie fabrics and redox potential of the indigo bath.

Methods

Materials

Persimmon peels were obtained from non-astringent persimmon, Dan Gam, purchased at a local market. The peels were dried at room temperature, crushed and stored in a refrigerator. All the chemicals and reagents were of analytical grade. Synthetic indigo (Sigma) and 100% ramie fabric (density: $60 \times 46/\text{in}^2$, weight: 118 g/m^2 , thickness: 0.32 mm) were purchased commercially. All the chemicals and reagents were of analytical grade.

Preparation of persimmon peel extract

Dried persimmon peels (50 g) were extracted in the distilled water by refluxing at 100°C for 60 min. After filtering, the extract was concentrated in a rotary evaporator and shock frozen at -80°C followed by freeze drying at -50°C to get the extract powder.

Characterization of persimmon peel extract

Phenol–sulfuric acid method was followed to determine total sugar content (Masukoa et al. 2005; Saha and Brewer 1994) using glucose as a standard sugar. Absorbance was measured by UV–Vis spectrophotometer (Agilent 8453, Agilent Technologies, Waldbronn, Germany) at 490 nm.

DPPH (1,1-diphenyl-2-picryl-hydrazyl) radical scavenging activity of the extract solution was assessed by Blois method (Blois 1958). The absorbance of extract solution was measured by UV–Vis spectrophotometer at 517 nm and DPPH scavenging activity was calculated from the equation

$$\text{Radical scavenging activity (\%)} = (A_c - A_s)/A_c$$

where A_c is the absorbance of control sample and A_s is the absorbance of extract solution sample.

The antimicrobial activity of the extract was checked by the disc diffusion technique against *Staphylococcus aureus*. Bacterial suspension, controlled with optical density ($OD = 1.0$) at 600 nm, were spread to form microbial lawns on the surfaces of agar plate. The Persimmon peel extract assay discs were prepared by pipetted the extract onto sterile paper disc (8 mm in diameter, Advantec, Japan). The assay discs were placed on the surface of the inoculated agar plate and then incubated for 24 h at 38 °C (Maidment et al. 2006). Control assay discs impregnated with water as a negative control as well as tetracycline (10 µg) as a positive control were also tested against the same bacteria. The size of clear zone was measured as an indicator of inhibition of bacterial growth.

Reducing power evaluation of persimmon peel extract

The indigo reduction bath (150 mL) consisted of synthetic indigo (0.5 g), calcium hydroxide (5 g), and persimmon peel extract powder. Reduction reaction was done by raising the bath temperature to 80 °C. Redox potential of the bath was measured at 60 °C with a Bioanalytical Systems CV-27 Voltammograph (BAS, USA) consisting of a platinum band electrode and an Ag–AgCl reference electrode.

Ramie fabric samples were dyed in the indigo reduction bath to evaluate reducing ability of persimmon peel extract. Fabric samples were dyed in the reduction bath at 60 °C for 20 min, followed by exposed in air, rinsed, neutralized, rinsed, dried and measured color strength of dyed fabrics. The color strength (K/S value) was calculated from the Kubelka–Munk equation

$$K/S = (1 - R)^2/2R$$

where R is the reflection of the dyed sample.

The reflectance of the dyed sample was measured at the maximum adsorption wavelength on a Macbeth Coloreye 3100 spectrophotometer. Absorbance of the extract solution was measured using a UV–Vis spectrophotometer (Agilent 8453, Agilent Technologies, Waldbronn, Germany).

Results and discussion

Characterization of persimmon peel extract

Extraction yield was 41.0% on the weight of dried persimmon peel. Total sugar content of the extract was 74.3%. Namely, more than 30 g of total sugar can be extracted from 100 g of dried persimmon peel waste. The sugars are one of main compounds in the fresh persimmon and they are fructose, glucose, and sucrose (Jimenez-Sanchez et al. 2015; Veberic et al. 2010). These sugars have been applied to reduce indigo and sulfur dyes as greener reductants (Blackburn and Harvey 2004; Meksi et al. 2012). Their reducing effect is associated with an electron-rich intermediate (Vuorema et al. 2009). Employment of food by-products as a source of reducing sugars for indigo dyeing has effects of waste disposal minimization and cleaner environment.

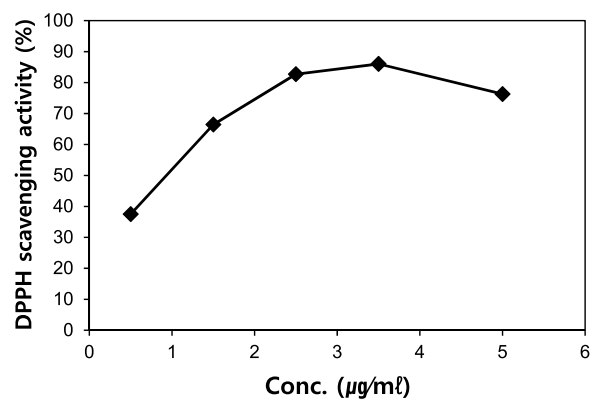


Fig. 1 DPPH radical scavenging activity of the persimmon extract

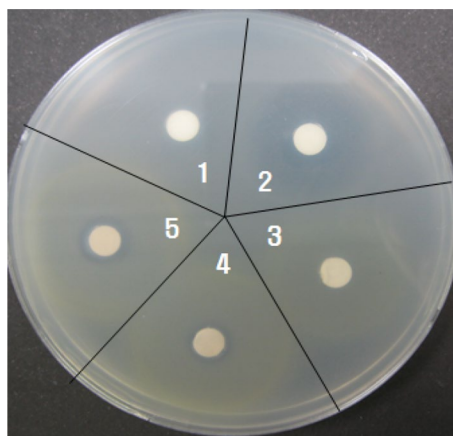


Fig. 2 Antibacterial rates of persimmon peel extract: (1) control (H_2O), (2) tetracycline 10 µg, (3) 2 mg/disc, (4) 5 mg/disc, (5) 10 mg/disc

DPPH radical scavenging activity indicates the ability of inhibiting oxidation and it is widely used to characterize antioxidant capacity of plant material (Arnao 2000; Fu et al. 2011; Yoon et al. 2003). The DPPH radical scavenging activity of persimmon peel extract was concentration-dependent, as shown in Fig. 1. The DPPH radical scavenging activity reached up to 86.0% at 3.5 µg/mL of the extract concentration. Antioxidant activity of persimmon reported to be highly correlated to phenolic contents (Fu et al. 2011). High antioxidant activity of the extract would have a positive influence on indigo reduction process by inhibiting the oxidation of leuco-indigo and stabilizing reduction reaction.

The antimicrobial activity of extract was tested using the disc diffusion technique against *Staphylococcus aureus*. Tetracycline was used as a positive control to assess test validity and also to increase the reliability of the results. Tetracycline is known to possess some level of bacteriostatic activity against almost all bacterial genera including *Staphylococcus aureus* with a few exceptions, such as *Pseudomonas aeruginosa*. The size of clear zone indicates inhibition area, as seen in Fig. 2. With persimmon peel extract, inhibition zones were formed 2 mm at 5 mg/disc and 4 mm at 10 mg/disc. This result

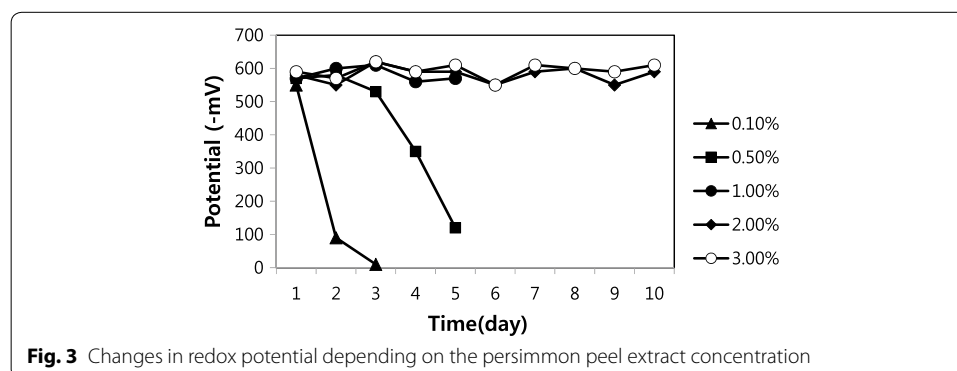
indicates that the extracts have respectable antimicrobial activity. It may help to keep the reduction bath from spoiling or degenerating. Tetracycline showed large clear zone confirming a high level of antimicrobial activity and water showed no antimicrobial activity, as expected. It was reported that plant polyphenols show antimicrobial activity against Gram-positive bacteria such as *Staphylococcus aureus* (Álvarez-Martínez et al. 2020).

Reducing power of persimmon peel extract

Redox potential, also known as reduction–oxidation potential, is known as a measure of the tendency of chemical molecules to gain electrons or lose electrons and thereby be reduced or oxidised, respectively. Therefore, more negative redox potential could indicate higher reducing power which converts indigo to leuco-indigo. The reducing sugars in the persimmon peel extract are oxidized and provides electrons to indigo, and indigo is reduced to leuco-indigo by accepting electrons (Meksi et al. 2012).

Figure 3 shows the redox potential of indigo reduction bath depending on the persimmon peel extract. It is evident that an increase in the concentration of extract caused more negative redox potential of the reduction bath. Indigo reduced quickly and generated redox potential was in the range of $-500 \sim -600$ mV in all of the bath irrespective of extract concentration. This redox potential value is slightly higher compared to the redox potential (-700 mV) when using banana peel extract (Shin et al. 2013). Redox potential could be varied according to reduction conditions including pH and temperature of dye bath. The redox potential was stably maintained for longer time at higher concentration of the extract. At 0.1% of the extract, reduction was maintained for only one day as indicated by the change in redox potential from -560 mV to -90 mV. At 3.0% of the extract concentration, redox potential in the range of $-550 \sim -620$ mV was lasted for longer than 10 days. This indicates that the indigo reduction bath can be used repeatedly at higher concentration as long as reducing power of the reduction bath lasted. It was reported that redox potential should be evolved at least $-550 \sim -600$ mV for occurring reduction reaction and attaining color yield on the fabric (Blackburn et al. 2009; Bozic and Kokol 2008). If so, the persimmon peel extract can be used as an alternative reductant to sodium dithionite in indigo dyeing.

Since the direct measurement of leuco-indigo concentration in the bath was difficult due to the rapid oxidation of leuco-indigo into indigo, ramie fabric samples were



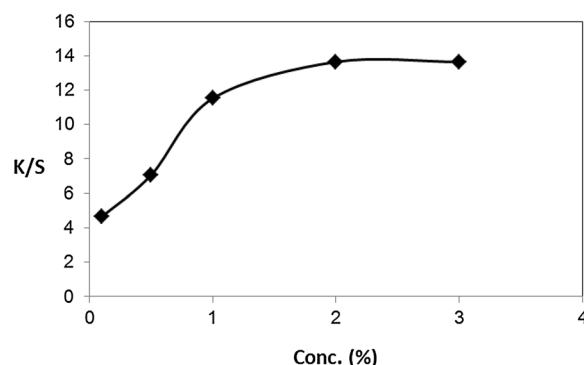


Fig. 4 Color strength depending on the concentration of persimmon peel extract

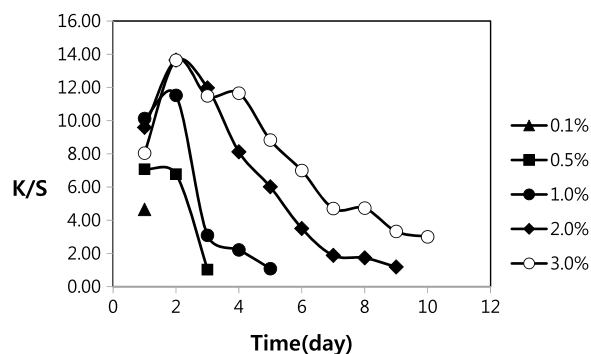


Fig. 5 Time-based changes in K/S values depending on the extract concentration

died in the reduction bath. The color strength of dyed fabric samples would be correlated to leuco-indigo concentration, indicating the reducing power of persimmon peel extract. Figure 4 shows color strength depending on the concentration of persimmon peel extract. Color strength increased with increasing the extract concentration up to 2% and further increase of the extract concentration was not effective under the experimental conditions of this study. This result agreed with changes in redox potential depending on extract concentration as in Fig. 3, showing similar level of redox potential at 2% and 3% of extract concentration. The reduction state was maintained for some period of time depending on the extract concentration. Thus, time based change in color strength was monitored and the results are presented in Fig. 5. Except the case of 0.1%, K/S increased to maximum color strength and thereafter decreased. The higher the extract concentration, higher color strength and longer reduction time maintained. It is expected that the reduction baths can be used repeatedly by supplementing the extract powder.

The results of redox potential and color strength measurements verified that the persimmon peel extract have reducing power towards indigo and can be a sustainable, nontoxic, and biodegradable alternative to sodium dithionite. Reducing power of the persimmon peel extract was compared with conventional sodium dithionite, as shown in Table 1. Redox potentials of the indigo bath with persimmon peel

Table 1 Comparison of reducing power of persimmon peel extract and sodium dithionite

Reducing agent	Redox potential (mV)	K/S	H V/C
Persimmon peel extract			
0.75 g	− 570	7.07	3.6 PB 3.9/5.1
1.50 g	− 600	11.52	3.8 PB 3.3/4.7
3.00 g	− 620	13.64	4.2 PB 3.0/4.4
Sodium dithionite			
0.45 g	− 550	20.47	5.3 PB 1.9/2.7
1.00 g	− 600	22.48	6.0 PB 1.7/1.9

Table 2 Scale-up dyeing using persimmon peel extract (6L, 1.5yd of ramie fabric)

Indigo	Extract	Ca(OH) ₂	Redox potential (mV)	K/S	H V/C
20 g	120 g	200 g	− 690	9.89	3.3 PB 3.2/3.7
20 g	180 g	200 g	− 690	15.37	4.1 PB 2.5/3.5

extract were comparable to those generated in the reduction bath with sodium dithionite. Although the reduction bath with sodium dithionite rendered higher color strength on the ramie fabrics, reduction state was maintained for shorter period of time, 2–3 days, compared with the persimmon peel extract maintained for more than 10 days.

Scale-up reduction

Scale up reduction was carried out for practical use of persimmon peel extract as an alternative reductant for indigo dyeing. Ramie fabric (1.5 yds) was dyed in a larger volume (6 L) of dyebath at different conditions for 30 min. The recipe and the results are shown in Table 2. The redox potential was stabilized at − 690 mV, which is more negative than obtained in lab scale experiments.

Conclusion

It was confirmed that the persimmon peel extract had an effect on indigo reduction as indicated by the generated redox potential of indigo bath and color strength(K/S value) on the ramie fabrics dyed with indigo reduction medium. The reduction of indigo was occurred with the persimmon peel extract rapidly at 80 °C and the maximum color yield was reached in one or two days. The redox potential of the extract was stabilized at about − 550 ~ − 600 mV at 2–3% of extract concentration. With increase of the extract concentration, higher color strength was obtained and reduction was maintained for longer time. In scale-up reduction, the redox potential was stabilized at 690 mV and the dyeing bath could be reused several times. The persimmon peel extract can be used in indigo reduction dyeing as a sustainable, nontoxic, biodegradable alternative to conventional sodium dithionite.

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Authors' contributions

Both of YS and DIY carried out the experiments and analysis of data. Both authors drafted the manuscript. Both authors read and approved the final manuscript.

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Availability of data and materials

The data sets used and analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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