Effect of various transition metal ions on mordanting stage of yak wool bleaching process

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Abstract

Yak wool is a smooth, warm, and durable natural protein-structured fiber that could compete with cashmere and other high-end protein-structured fibers on the market. However, it suffers from drawing consumers' attention due to the lack of color due to the shortfall of the yak wool bleaching technology. Herein, we studied the applicability of various transition metals, i.e., copper (II), cobalt (II), iron (II), and nickel (II) salts, as a mordanting reagent based on their effect on the hydrogen peroxide decomposition reaction and the morphological and mechanical properties of the bleached yak wool with the presence of these transition metal. Our study suggested that the iron (II) ion was the most efficient reagent for the mordant bleaching since it provided less fiber damage, relatively high strength, and elongation to the bleached yak wool with good whiteness, while the Cu (II) was the least favorable agent for the yak wool bleaching process.

Keywords: yak wool, transition metal ions, mordanting, bleaching.

Introduction

Yak wool-made products are very convenient in cold and damp weather due to their smooth, warm, and moisture absorption nature [1]. Indeed, yak wool owns the properties of better shrinkage, elasticity, and durability because of higher sulfur and cysteine contents as compared to the other protein-structured high-class material like cashmere. Still, it costs a quarter of cashmere's price. These remarkable properties of yak wool are influenced directly by the climate that yaks are needed to adapt to live in extremely cold weather down to -50°C. Due to the critical climate influence on the formation of such unique properties of yak wool [2], Mongolia is the second biggest yak wool provider to the world market and one of the few countries that manufacture yak wool fabrics. However, yak wool-made products suffer from drawing less attention among customers because of their lack of choices in colors and designs, although it has shown great potential in marketing in terms of qualities and prices.

Taking account of being about 69% of collected yak wool is dark, 17% is brown, 8% is blue, and only 6% is white-colored; currently, most yak wool-made products are manufactured with natural, dark-colors owing to the fact that no suitable technological condition for bleaching has developed specifically considering the yak wool properties [3]. Yak wool fibers are relatively short compared to other protein-structured fibers because yak wools are collected by the shearing technique [4]. Therefore, short fibers tend to be damaged easily during technological treatment, such as bleaching and dyeing, compared to longer fibers like cashmere. Although occasionally, the cashmere bleaching condition is attempted to be used for yak wool, the quality of the products deteriorates due to the damages caused by the harsh treatment conditions. For this reason, insight into yak wool bleaching technology is crucial to broaden the yak wool mass production to the market in the future.

The dark color of the protein-structured fibers is a result of a natural pigment, so-called melanin [2, 5]. Therefore, the purpose of the bleaching process is to remove the melanin pigments from the surface and in-depths of the fibers, as well. Practically, hydrogen peroxide is employed to prompt the defragmentation process in textile factories due to its convenience to handling, ease of operation, simplicity of batch design, inexpensiveness, and environmental friendliness [6]. However, the hydrogen peroxide-based techniques require a particular catalyst to enhance the effectiveness of the bleaching process for promoting the decomposition reaction of hydrogen peroxide during the bleaching process [7]. The suitable catalysts should be added to the dark-colored wool-containing batch as a preparation for the bleaching by hydrogen peroxide, known as a mordanting stage. For this reason, this technique, so-called mordant bleaching, is needed to be covered by three sequential stages, such as mordanting, rinsing, and bleaching. Any of these three processes could cause damage to the wool since harsh chemical treatments at high temperatures are applied. However, a careful mordanting agent choice is crucial to maintain the intrinsic quality of yak wool after the whole bleaching process is conducted through adjusting the bleaching condition.

Transition metal salts are applied to assist in bleaching wool as the mordanting agents because metal ions are likely to stick with the melanin rather than keratin due to its' higher electron density resulting from having more hydroxyl, carboxyl, and amine groups [8]. According to the previous studies, although iron (II) [9-12], copper (II) [5, 9, 13-15], and calcium ions [13] were employed and studied as the mordanting agent for various protein-structured fiber, only a few attempts using iron (II) ion for bleaching yak wool were made [16, 17]. Therefore, there is still plenty of room for exploring a suitable mordanting reagent for yak wool bleaching and its impacts on the wool properties. In this study, we studied the effect of various transition metals, i.e., copper (II), cobalt (II), iron (II), and nickel (II) on yak wool properties such as whiteness, mechanical properties, and surface morphology after bleaching and demonstrated the relationship between the yak wool properties and mordanting agents for the first time.

Experimental

Materials

Brown-colored yak wool yarns (breaking strength>280.21 cN (centinewton), breaking elongation >10.60%, whiteness >28.66%) from Mongolia which is pre-treated in the primary factory "Uguuj Shim Co., Ltd" and knitted in the spinning factory "Caprodoro Co., Ltd" was sampled in this study. Iron (II) sulfate ($FeSO_4{\cdot}7H_2O$), copper (II) sulfate ($CuSO_4{\cdot}5H_2O$), cobalt (II) sulfate ($CoSO_4{\cdot}7H_2O$), nickel (II) sulfate ($NiSO_4{\cdot}6H_2O$), and iron (III) sulfate ($Fe_2(SO_4)_3$) were chosen as the mordanting reagent, and a pH of the solution was adjusted by citric acid ($C_6H_8O_6$) in the mordanting stage. A solution of 30% (w/w) hydrogen peroxide (H_2O_2) as the bleaching reagent and tetrasodium pyrophosphate ($Na_4P_2O_7{\cdot}10H_2O$) as a stabilizing reagent was used in the bleaching stage. All chemicals were analytical reagent grade.

Methods

Hydrogen peroxide (H_2O_2) decomposition reactions were carried out in a batch system with 0.065 mol·L^{-1} of H_2O_2 and 1·10^{-4} mol·L^{-1} transition metal salts at 50°C for 180 min to examine the effect of transition metal ions on the decomposition rate. The solution pH was adjusted at 8.5 using sodium pyrophosphate solution with a concentration of 0.1 mol·L^{-1}. The remained concentration of H_2O_2 was monitored using the titration method with potassium permanganate solution (0.01 mol·L^{-1}) in an acidic condition. For choosing the suitable mordanting agent for the yak wool, the yak wool was mordanted with the concentration of $1 \cdot 10^{-4}$ mol·L^{-1} of transition metal salts with the concentration of 6 g·L^{-1} of citric acid, which was used as an auxiliary reagent at 50°C for 25 min. Following that, the bleaching stage was carried out by adapting the same bleaching condition previously reported [18].

Characterization

The breaking load or strength and elongation properties of yak wool knit samples were measured with an electromechanical testing machine (MTS Insight 2, MTS, USA). Vertical test spaces and test speeds were adjusted to 500 mm and 500 mm·min^{-1}, respectively. The whiteness index was spectrophotometrically obtained by Datacolor SF 600 (Datacolor Inc., USA) apparatus at standard illuminant D65 and observer 10° combination. The surface characteristics of yak wool samples were analyzed from scanning electron microscopy (SEM) (TM-1000, Hitachi, Japan) using an accelerating voltage of 10 kV and magnification ranging from 1500-fold.

Results and Discussions

The effect of transition metals on the decomposition of hydrogen peroxide in vitro condition

Mainly transition metal salts are utilized in the mordanting stage to conduct the decomposition reaction with a desirable rate because the decomposition rate of hydrogen peroxide is crucial in the fiber bleaching process [19]. In this study, we chose the transition metal salts of cobalt (II), nickel (II), copper (II), and iron (II) ions as a mordanting reagent by considering their electron configuration, first ionization energy, and atomic radius [20] in order to investigate the most suitable reagent for mordanting the yak wool. First, we conducted a hydrogen peroxide decomposition reaction with the presence of the various transition metals in vitro conditions without yak wool in order to reveal their catalytic activity for solely the hydrogen peroxide decomposition reaction. We depicted the experimental results of the hydrogen peroxide decomposition with the chosen catalysts in Fig. 1 and summarized the reaction rate constant and activation energy values from the relationship between the reaction rate constant and temperature in Table 1. Fig. 1 displayed that these transition metals exhibited catalytic effects on the decomposition of hydrogen peroxide at different rates, and all decomposition reactions obeyed the first-order rate law. According to previous studies which have studied the decoloring mechanisms of melanin by hydrogen peroxide with the presence of transition metal, the rate-determining step of the bleaching process obeyed the first-order law, as well [21, 22], which supported our results. From the rate constant and activation energy values (Table 1), the rate constant values decreased to 2.6×10^{-3}, 3.4×10^{-3}, 4.0×10^{-4}, 7.0×10^{-5} min^{-1}, and the activation energy values escalated to 63.9, 76.2, 82.9, 107.3 kJ mol^{-1} with the order of Cu (II), Co (II), Fe (II), and Ni (II). These results revealed that the decomposition rate was decreased with the order of Cu (II) > Co (II) > Fe (II)> Ni (II) due to the increased activation energy of the decomposition reaction.

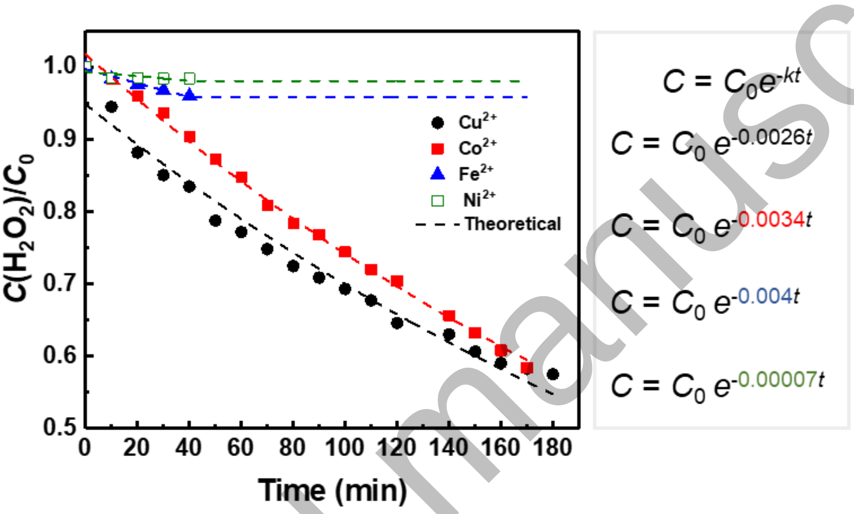

Fig. 1. The effect of different transition metal ions on hydrogen peroxide decomposition.

Table 1. The rate constants of hydrogen peroxide decomposition with different transition metal ions at different temperatures and activation energies

Transition metal ions	The rate constant, min^{-1}	Activation energy, kJ mol^{-1}
Copper (II) (Cu^{2+})	$2.6\cdot10^{-3}$	63.9
Cobalt (II) (Co^{2+})	$3.4\cdot10^{-3}$	76.2
Iron (II) (Fe^{2+})	$4.0\cdot10^{-4}$	82.9
Nickel (II) (Ni^{2+})	$7.0\cdot10^{-5}$	107.3

The effect of transition metals on bleaching effectiveness for the yak wool

Considering the results from the previous section, we utilized these transition metal salts as a mordanting agent for the yak wool bleaching process to investigate their applicability for the yak wool bleaching process since these transition metals showed catalytic effects on the hydrogen peroxide decomposition. The photos of yak wool after the bleaching, which were treated with the different transition metals as a mordanting agent, are shown in Fig. 2. From the photos, it was seen that the bleaching efficiencies vary depending on the mordanting agents. Cu (II) resulted in the highest bleaching efficiency as compared to that of the other metal ions, while Ni (II) showed the poorest bleaching efficiency. Not only bleaching efficiency but also maintaining the initial mechanical and morphological properties after bleaching is essential to obtain light-colored high-quality yak wool; the morphologies of the fibers with different mordanting agents were analyzed through SEM, and the obtained images of the bleached yak wool fiber are shown in Fig. 3 in comparison to that of the natural yak wool. The SEM images revealed that the yak wool fiber treated with Cu (II) ion had the highest cuticle damage as compared with the other fibers, while the fibers treated with Fe (II), Co (II), and Ni (II) were shown nearly the same morphology as compared with the natural yak wool fiber. This morphological study disclosed that the high degree of whiteness achieved with the aid of Cu (II) was a result of severe yak wool morphology damage caused by a detrimental effect of Cu (II) ions. For further investigation, the mechanical properties of the yak wool knit, such as strength, elongation, and whiteness, were measured after the bleaching process when, as stated above, transition metals were used as a mordanting agent (Fig. 4). Due to the serious damage to the yak wool that was treated with Cu (II), these mechanical properties were not able to obtain in the case of Cu (II). As in Fig. 4a, Co (II), Fe (II), and Ni (II) were used as a mordanting agents, and the strength values were 202.7, 269.5, and 261.3 cN with the elongation values of 9.3, 9.9, and 8.1 %, respectively, while the strength value of 274.8 cN and the elongation value of 10.6 % were referenced as initial values for the natural yak wool. In terms of whiteness (Fig. 4b), the highest value was 57.00% when Fe (II) was used as the mordanting agent, while only the whiteness of 35.87% and 32.40% were achieved when Co (II) and Ni (II) were used as the mordanting agent, respectively (The initial whiteness was 28.66%). The photographic images in Fig. 2 supported these whiteness results. When the Fe (II) was used as the mordanting agent, the mechanical properties were maximally maintained while obtaining sufficient whiteness. In the case of Co (II) and Ni (II), poor whiteness efficiency, as well as a loss of mechanical properties, were obtained. Taking into account the mechanical properties and whiteness results, it suggested that too fast or slow rate of the hydrogen decomposition reaction is not desirable. Therefore, for achieving high-quality yak wool after the bleaching process, the decomposition rate is needed to be balanced. Besides, our results confirmed that Fe (II) exhibited the property of a selective mordanting agent among these transition metals by considering the yak wool properties after the bleaching.

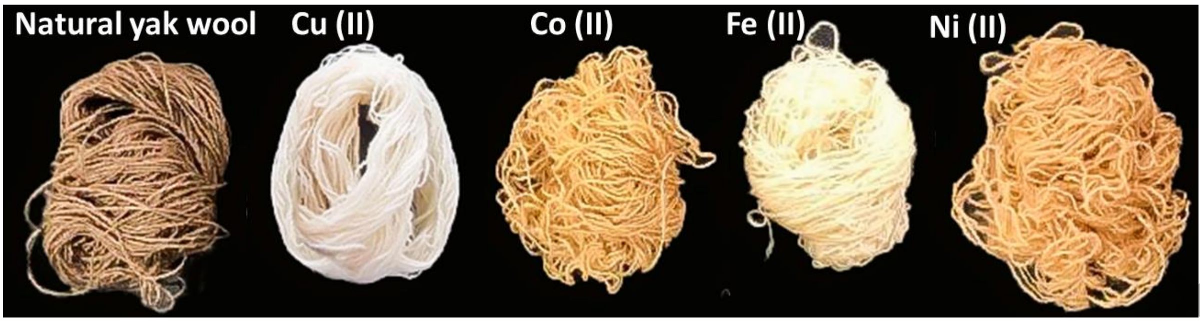

Fig. 2. Photo images of bleached yak wool mordanting with different transition metal ions.

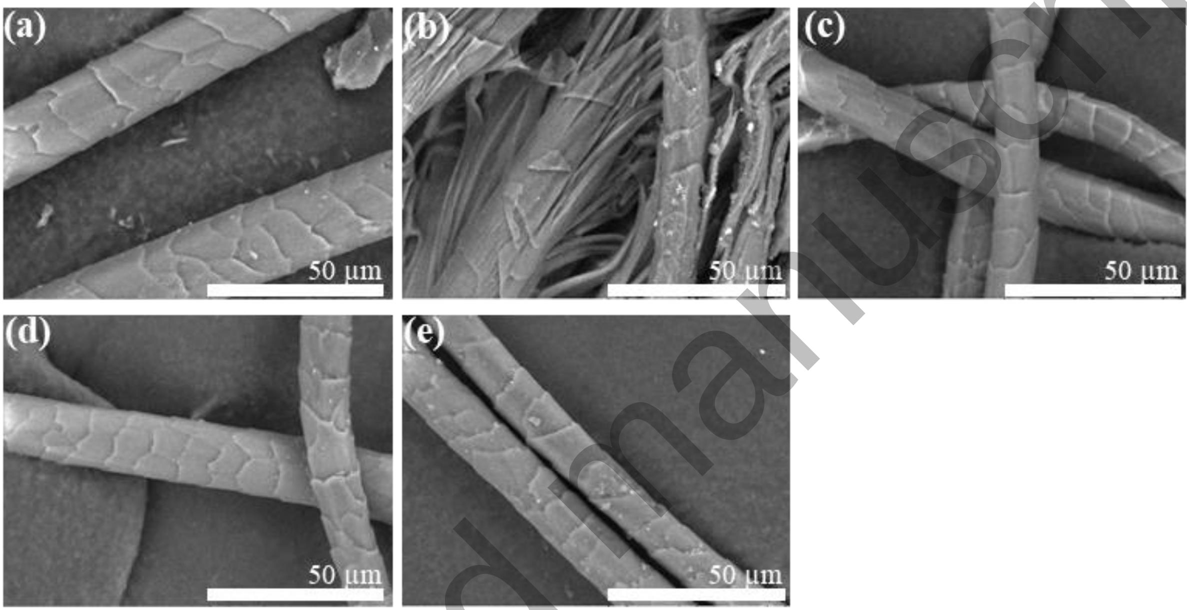

Fig. 3. SEM images of the bleached yak wool mordanting with different transition metal ions (A) natural yak wool, (B) Cu (II), (C) Co (II), (D) Fe (II), (E) Ni (II) ion.

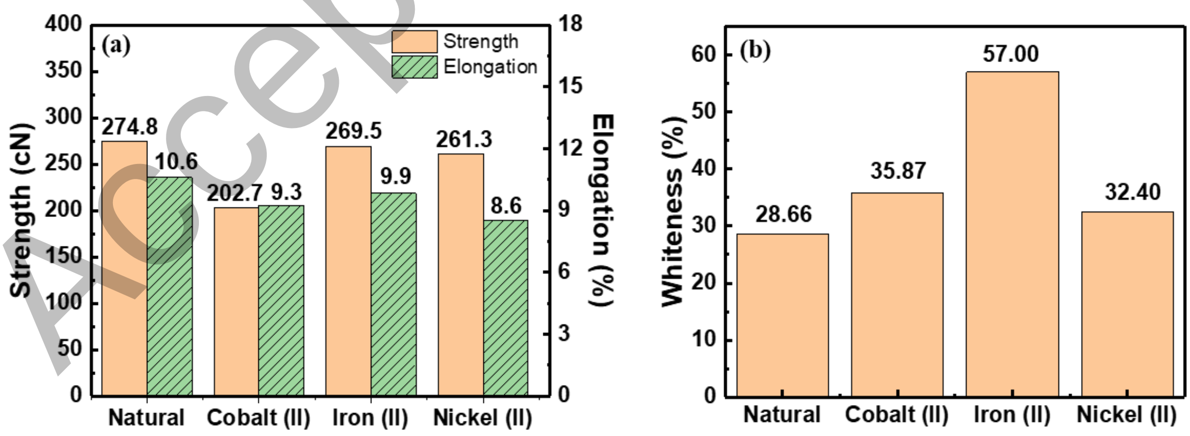

Fig. 4. (A) The strength (cN) and elongation (%) and (B) whiteness (%) of yak wool using Co (II), Fe (II), and Ni (II) ions as a mordanting agent.

Last, the unusual detrimental effect of Cu (II) on the yak wool during the bleaching process was investigated. Since the bleaching process takes place through a redox reaction of hydrogen peroxide, it is necessary to consider the redox species in the bleaching media. In the alkaline condition where the bleaching process is conducted, the hydrogen peroxide oxidation reaction takes place forming oxygen, which has a reduction potential ($E°(H_2O_2/O_2)$) of 0.146 V [23]. When there are any oxidizing species which has a higher reduction potential than the $E°(H_2O_2/O_2)$ that could gain electrons and be reduced, any redox reaction is thermodynamically favorable in this reaction environment. Unlike Co (II), Fe (II), and Ni (II) ions, Cu (II) owns a dissimilarity of being reduced from Cu (II) to Cu (I) ($E°(Cu^{2+}/Cu^{+}) = 0.153$ V) with the presence of reducing agent while the other transition metals are not able to be reduced spontaneously during the bleaching process. Thus, there is a high probability that Cu (I) ion is formed in this reaction media through the galvanic effect. According to the Hard-Soft Acid-Base Theory (HSAB), Cu (II), Co (II), Fe (II), and Ni (II) ions are categorized as the borderline acid, while Cu (I) is categorized as the soft acid which makes Cu (I) being distinctive of the other ions [24]. Therefore, it is known that hard acids tend to bind to hard bases and soft acids tend to bind to soft bases; Cu (I) presumably is more likely to form coordination bonds with functional groups containing sulfur atoms in the protein of yak wool, thereby causing a dissolution of the proteins from the yak wool into the bleaching solution and/or breaking the protein structure of the yak wool surface. In order to support this assumption for revealing the notorious impact of the soft acid of Cu (I), we arranged a completely opposite case with the bleaching process adding Fe (III) ion as the mordanting agent because the hard acid of Fe (III) only reduces to the borderline acid of Fe (II) and doesn't form any soft acid species in contrast to Cu (II). The photo and SEM images of yak wool fibers before and after the bleaching process with Fe (III) and Cu (II) in comparison to natural yak wool are shown in Figure 5. As we expected, the fiber damage was severe, and the cuticle layers were completely polished when the Cu (II) was the mordanting agent, while only mere damage to the fibers was seen when Fe (III) was used as a mordanting agent. This result supported the idea of having detrimental effects of soft acids as a mordanting agent on yak wool.

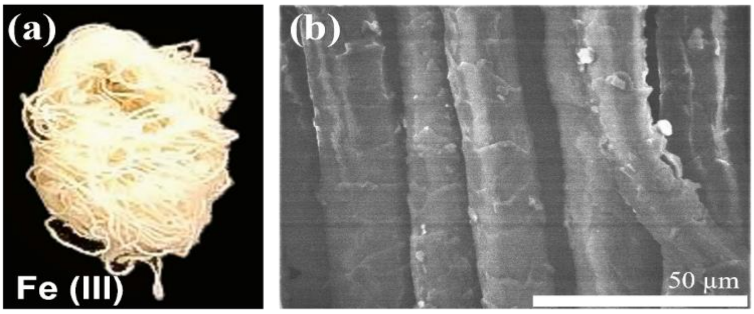

Fig. 5. (A) Photo images of bleached yak wool with Fe (III) as a mordanting agent and (B) SEM image of the bleached yak wool with a mordanting agent as Fe (III).

Conclusion

In this study, we demonstrated the unique and selective property of Fe (II) ion as a mordanting agent in the yak wool bleaching process based on the analysis of morphological and mechanical properties of bleached yak wools with the mordanting agents of Cu (II), Co (II), Fe (II), Ni (II) ion. Among the transition metal ions, Cu (II) was found to be the least favorable mordanting agent for the yak wool bleaching by causing the dissolution of the protein in the yak wool and/or breaking the protein structure of the yak wool surface due to the formation of Cu (I) ion during the bleaching process. Therefore, we suggested the HSAB theory to explain the notorious effect of Cu (II) ion on the yak wool properties. Moreover, we find that the wool properties critically affected the active site formation rate of the hydrogen peroxide decomposition during the bleaching process. We believe that these findings will be a potential reference to suggest a suitable mordanting agent for not only yak wool but also different protein-structured fibers and help to improve the qualities of woolen products in the future.

Disclosure statement

No potential conflict of interest was reported by the authors.

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