



Fabrication of wool keratin/polyethylene oxide nano-membrane from wool fabric waste



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ABSTRACT

Wool keratin and wool keratin/poly(ethylene oxide) nanofibrous membranes were prepared through the decoloration of dyes in the wool waste and extraction and electrospinning of regenerated wool keratin. The effect of pH, ironphthalocyanine and H₂O₂ concentration on catalytic oxidation were also studied. Under the support of ironphthalocyanine with better structure stability compared with other metal-phthalocyanines, most azo groups of dyes could be broken into colorless products under the catalytic oxidation of ironphthalocyanine and H₂O₂ at pH = 10, and the decolorization percentage was about 94.2% in 210 min. To improve the spinnability of the extracted wool keratin, poly(ethylene oxide) was introduced into the keratin electrospinning and with the increased loading ratio of poly(ethylene oxide), the diameter of the nanofibers thickened with a value of 546 ± 312 nm for the 70/30 wool keratin-poly(ethyleneoxide) nanofibrous membranes. Decolorizing dyes and extracting wool keratin for the preparation of keratin-based nanomembranes was benefit to recycles of wool waste and decreases the environmental pressure.

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1. Introduction

The fast development of the textile dyeing industry has resulted in a significant amount of waste fabrics in the environment. Traditional methods of treating waste fabrics (including burning and landfills) squander resources and pollute the soil. Considering increasing environmental requirements and energy savings, textile industrial waste recycling is a major concern today and carries a great deal of importance for environmental protection and the efficient use of resources.

One of the major causes of textile industrial waste recycling is

decolorizing textile dyes. Different treatments to decolorize and degrade dyes have been attracting increasing interest, and a wide range of methods have been developed: flocculation, activated carbon adsorption, biotreatment, advanced oxidation processes, and so on (Vandevivere et al., 1998; Chen et al., 2007). Among all these dye decolorizing methods, advanced oxidation processes (AOPs) have been developed in recent years due to their high degradation rates and non-toxicity. Some methods based on H₂O₂ and catalysts have been employed to realize the AOPs for decolorizing wool waste. A highly efficient phase-transfer AOPs system, cobalt tetra (2,4-dichloro-1,3,5-triazine) aminophthalocyanine immobilized on cellulosic fibers (Co-TDTAPc-F) and hydrogen peroxide (H₂O₂), was first reported to decolorize dyes by Chen's group (Chen et al., 2007). Compared to traditional AOPs for dye treatment, Co-TDTAPc-F and H₂O₂ was more effective. In 60 min, more than 98% of acid red 1 was eliminated at an initial pH 2.

Wool waste, which belongs to proteinous biomaterials, can degrade into keratins under reduction, oxidation, sulfitolysis or

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oxidative sulfitolysis (Cardamone, 2010) treatment. Keratin extracted from wool can be fabricated into different shapes (microsized particles (Li et al., 2009a,b), films (Yang et al., 2009), scaffolds (Li et al., 2009a,b), nanofibers (Aluigi et al., 2008, 2011, 2014; Li et al., 2009a,b)) and have the biofunctional applications for tissue reconstruction, drug delivery, water remediation, biogas production, packing materials, cosmetics, and feed additives due to their biocompatibility, absorptivity, and biodegradability (Kabir et al., 2013). By electrospinning keratin polymers with a large number of hydrophilic amino acids that can bind specific toxic adsorbents, it is possible to prepare nanofibrous membranes for water depuration, which offers both adsorption and filtration. Owing to their high specific surface area and high porosity, the nanostructured membranes demonstrated excellent dye removal efficiency also at relatively low adsorbent dosages (Aluigi et al., 2014).

In our work, we employed a simple and effective method to decolorize the dyes and recycle the wool waste. First, iron-phthalocyanine (FePc) was employed for its better structural stability and immobilized on cellulosic fibers to increase the catalytic activity of metallophthalocyanine and benefit recycling. Afterward, keratin was extracted from the decolorized wool fabrics and the keratin-poly(ethylene oxide) nanofibrous membranes were fabricated by electrospinning the keratin and poly(ethylene oxide) (PEO). The dye decolorizing was evaluated by the pH, FePc, and H₂O₂ concentration function. In addition, the surface morphology of the nanofibrous membranes was also characterized.

2. Experimental section

2.1. Materials

Dyed wool fabrics and FePc were kindly provided by Suzhou Shuishan Textiles Co., Ltd and Reading Chemical Technology (Shanghai) Co., Ltd, respectively. The sodium sulfide, H₂O₂ (30%), sodium hydroxide and PEO were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. FePc immobilized on cellulosic fibers (FePc-C), similar to previous works (Chen et al., 2007).

Before wool fabric dye decolorizing, 1 g of wool yarn was cut into slices and immersed into a 0.02 g/mL sodium sulfide solutions (400 mL). After stirring at 80 °C for 2 h, the mixture was used to study the wool fabric decolorization.

2.2. Dye decolorization

The effect of pH (the pH of the solution was adjusted to 7, 9 and 10), FePc concentration (0 mg/mL, 1 mg/mL, 2 mg/mL and 3 mg/mL) and H₂O₂ volume (0 mmol/L, 5 mmol/L and 15 mmol/L) on the dye decolorization was investigated. The mixture was tested at 30 °C, and the data were recorded every 15 min.

2.3. Fabrication and spinning of wool keratin

Wool keratin was fabricated after the filtration, dialysis (4 days) and freeze-drying (3 days) of the discolored mixture. For the preparation of wool keratin spinning solutions, 6 g of wool keratin was dissolved in 100 mL of 88% formic acid and stirred for 2 h until complete dissolution. After that, PEO was added and stirred continuously for an additional 6 h, preparing the spinning solutions.

The wool keratin spinning solutions were spun at 20 °C using a voltage of 14 kv, a needle tip-collector distance of 15 cm, and a solution feeding rate of 0.5 mL/h, controlled with a pump rate of 80 r/min. According to the weight ratio of wool keratin and PEO,

different nanofibrous membranes were named as 100/0 WK-PEO, 90/10 WK-PEO, and 70/30 WK-PEO. The preparation of WK-PEO nanofibrous membranes are summarized and shown in Fig. 1.

2.4. Characterization

The different samples were analyzed on a UV–visible spectrometer (UV-2550, SHIMADZU, Japan) and the changes in the absorption spectrum in the wavelength range of 200–800 nm were recorded. The residual dyes in the decolorized solutions prepared in Section 2.2 were calculated with the following equation:

$$\text{Decolorization Percentage} = \left(1 - \frac{C_{\text{after decolorization}}}{C_{\text{before decolorization}}} \right) \times 100\%$$

where C represented molar concentration (mol/L).

The chemical structures of the wool waste, decolorization solutions and wool keratin were characterized by Fourier transform infrared spectroscopy (Thermo Electron, USA) and the spectra were collected in the wavenumber region of 450–4000 cm⁻¹ with a spectral resolution of 2 cm⁻¹ and 64 scans.

The surface morphology of 100/0 WK-PEO, 90/10 WK-PEO and 70/30 WK-PEO were characterized with a scanning electron microscope (SEM, Hitachi S-4800, Japan). Before analyzing the structures, the surfaces of the nanofibrous membranes were coated with a thin layer of gold using a sputter (Hitachi E-1010, Japan).

3. Results and discussion

3.1. Decolorization of wool fabrics waste

Fig. 2 shows that the extent of dye decolorization depended on the pH. As shown in Fig. 2, the % value of decolorization could reach 38.7% within a period of 210 min at pH = 7. With an increase of pH, the decolorization percentage sharply increased, and about 94.2% of the dyes were eliminated in 210 min at pH = 10, indicating that most dyes reacted with the FePc/H₂O₂ to produce breakdown products. Moreover, the decolorization percentage of 27.0% and 84.3% were measured for 105 min at pH = 7 and pH = 10 respectively, and the color of the solutions decolorized in 105 min at pH = 10 changed more compared with the solutions decolorized in 105 min at pH = 7. These results demonstrate that the catalytic reaction is enhanced as the pH is elevated, mainly arising from the release of H⁺ during the catalytic oxidation and enhancement under alkaline conditions. The related mechanism is discussed in Fig. 5.

The effect of FePc concentration on the catalytic oxidation was



Fig. 1. WK-PEO nanofibrous membranes prepared from wool waste.

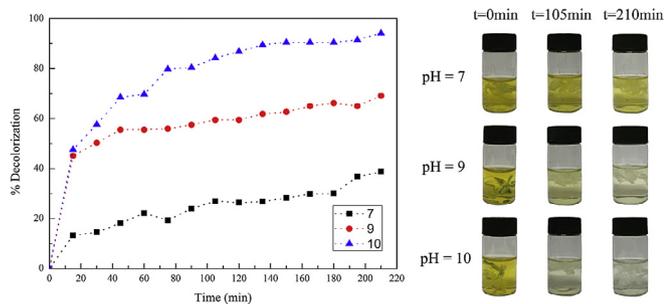


Fig. 2. Concentration and color change of wool dissolutions under different times in the presence of FePc/H₂O₂ (The concentration of acid yellow dyes, FePc and H₂O₂ was 5×10^{-5} mol/L, 3 mg/mL and 15 mmol/L, respectively and the temperature is 30 °C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also studied and the results are shown in Fig. 3. Without the presence of FePc, the decolorization percentage of the decolorizing solutions changed little with time. After the introduction of 1% FePc, a decolorization percentage of 65.2% was observed in 300 min compared with 18.4% without FePc. When the loading ratio of FePc was 2%, the decolorization percentage further increased and the final value was 71.1% in 300 min. With a further increase in the loading ratio of FePc (3%), the decolorization percentage in 300 min showed a value of 69.7%, similar to that of the loading ratio of 2%. However, from 0 min to 200 min, the decolorization percentage of the decolorizing solutions with 3% concentration exhibited a

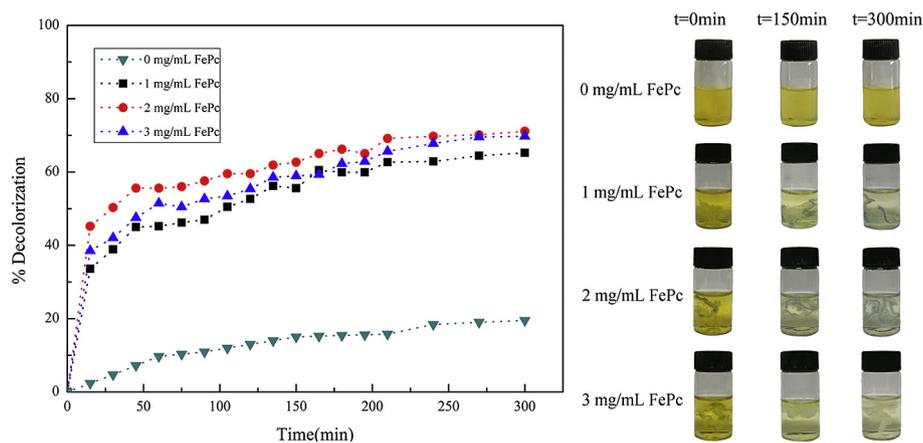


Fig. 3. Effect of FePc concentration on the catalytic oxidation of wool dissolutions under different times (The concentration of acid yellow dyes and H₂O₂ was 5×10^{-5} mol/L and 15 mmol/L, respectively and the temperature is 30 °C, and pH.

was 7).

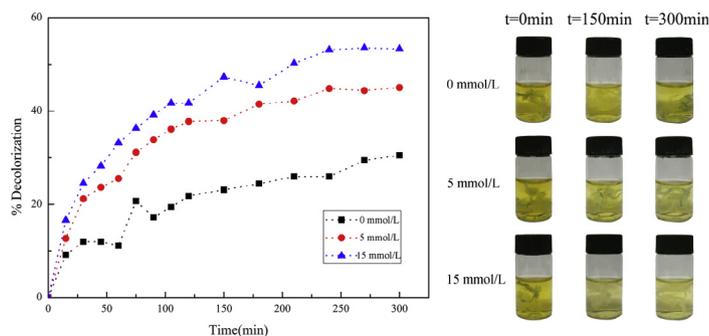


Fig. 4. Change of concentration and color of wool dissolutions under different H₂O₂ concentrations.

decreasing tendency, mainly due to the excessive introduction of red FePc.

Moreover, the dye degradation could be accelerated by an increase of the H₂O₂ concentration. When the loading ratio of H₂O₂ was 150 μ L, the decolorization percentage in 300 min could reach 58.0% (Fig. 4). Comparatively, the effect of H₂O₂ concentration on the decolorization percentage of the decolorizing solutions was smaller than that of the pH and FePc concentration.

Some researchers have demonstrated that under the catalysis of FePc and H₂O₂ with different pH, the azo groups of acid yellow dyes could be broken, resulting in the formation of colorless products. The mechanism is similar to that proposed by C. E. Clarke's group (Clarke et al., 2010). Electron transfer from the hydroxyl groups of pyrazol to the Fe oxide generates a radical which undergoes resonance rearrangement and additional electron transfer to produce a carbocation on the pyrazol ring. A nucleophilic attack by water generates an unstable complex resulting in the cleavage of the C–N bond yielding sodium 4-(4,5-carbonyl-3-methyl-pyrazol-1-yl) benzenesulfonate and phenylazo. Unstable phenylazo derivatives readily oxidize in the presence of oxygen to generate unstable phenyldiazene radicals. In turn, these phenyldiazene radicals lose the azo linkage to yield N₂ and a phenyl compound, take part in coupling reactions with other oxidation products, or undergo further oxidation followed by a nucleophilic attack by water to generate phenol (Fig. 5).

The FTIR results support the proposed mechanism. Fig. 6 shows the FTIR spectra of wool waste before and after decolorizing treatment. The peak at 1184 cm⁻¹ should be assigned to C–N bond

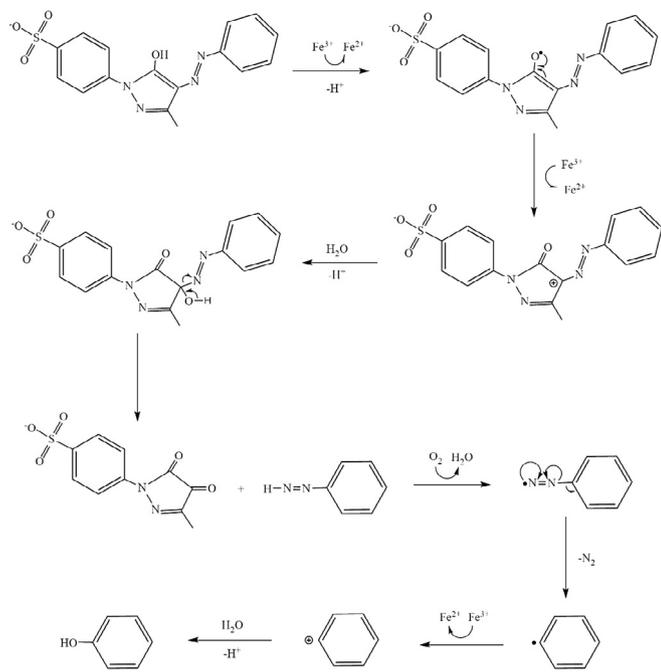


Fig. 5. Proposed mechanism of acid yellow dye oxidation.

stretching, and after the decolorizing treatment, there was no obvious peak in this region, indicating that the C–N dye bond was almost broken down in the process of catalytic degradation. Moreover, the peaks at 3452 cm^{-1} , 1634 cm^{-1} , and 554 cm^{-1} were assigned to the –OH, –NH, and C=O stretching modes of the keratin. These have specific bio-functions and can be used to fabricate block copolymers with potential applications in tissue engineering (Kumar et al., 2012; Cardamone, 2010).

3.2. Spinning of regenerated wool keratin

Fig. 7 shows the SEM images of different nanofibrous membranes. Lots of beads were observed for the 100/0 WK-PEO membranes, indicating that regenerated wool keratin was difficult to spin due to the instability of the jet from the effect of surface

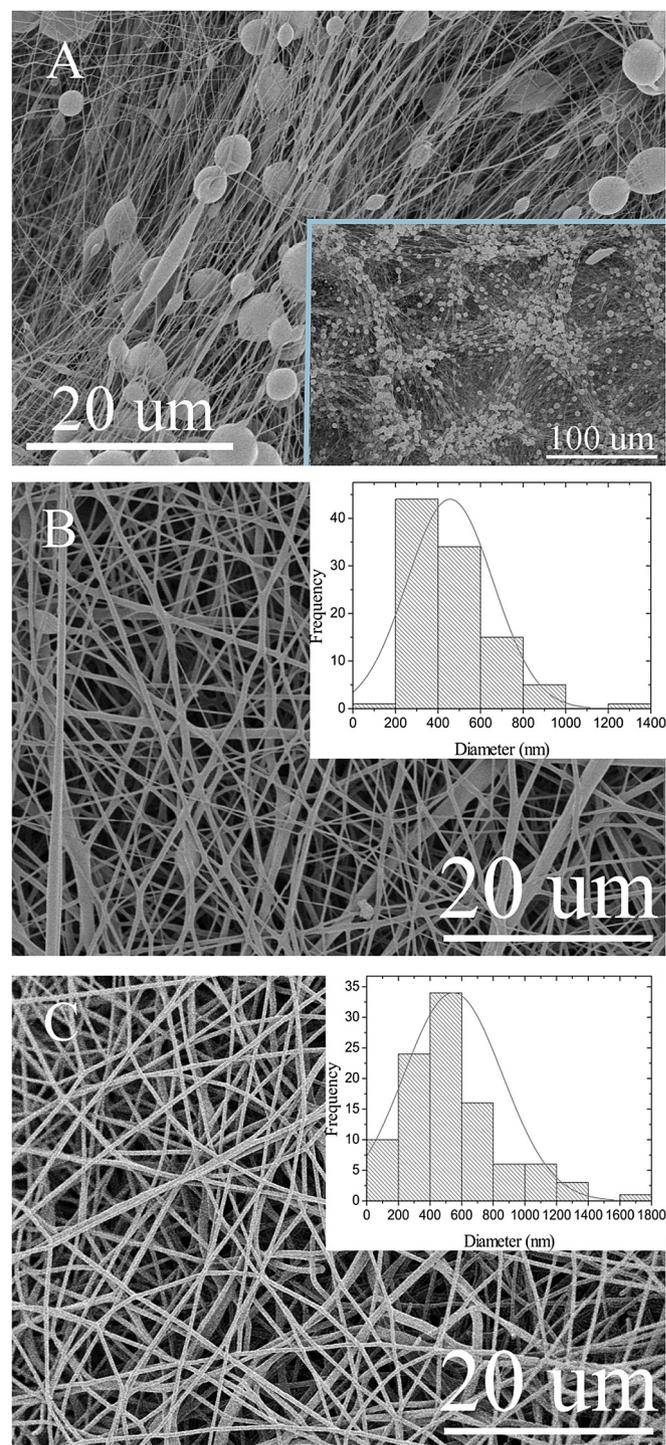


Fig. 7. SEM images of 100/0 WK-PEO, 90/10 WK-PEO, and 70/30 WK-PEO nanofibrous membranes.

tension in the presence of electrical forces. (Zoccola et al., 2008). According to Fig. 7A, the fibers between the beads were very fine, and the average diameter of the beads and fibers were $1.53 \pm 1.07\ \mu\text{m}$, and $226 \pm 112\ \text{nm}$ (calculated by Image J), respectively. With the introduction of PEO, the spinnability of the regenerated wool keratin was improved substantially, and the beads gently disappeared. The average diameter of the nanofibers of 90/10 WK-PEO membranes was about $379 \pm 226\ \text{nm}$. With the further introduction of PEO, the average diameter of the nanofibers of the

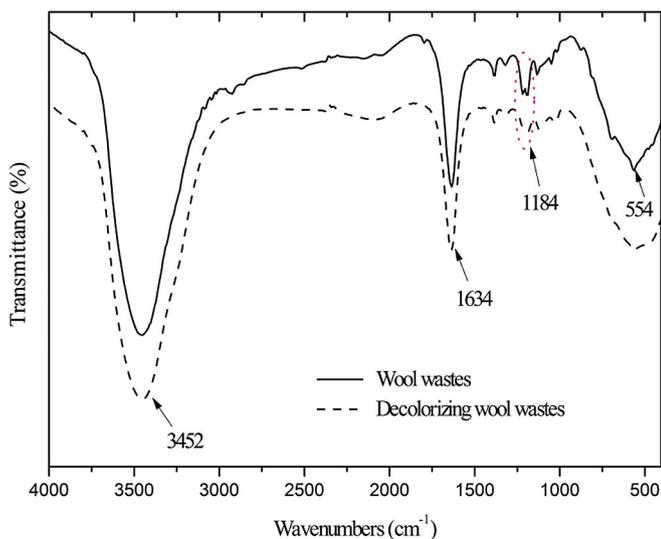


Fig. 6. FTIR spectra of wool waste and decolorized wool waste.

70/30 WK-PEO membranes became 546 ± 312 nm. Compared with the 90/10 WK-PEO membranes, the 70/30 WK-PEO membranes exhibited a thicker diameter, resulting from the increase of the solution viscosity (Wang et al., 2017). The keratin/PEO blend nanofibers proved to can be prepared through electrospinning by A. Aluigi's group (Aluigi et al., 2008). Their studies demonstrated that when the PEO amount is higher than 10 wt.%, there are sufficient molecular chain entanglements to prevent breaking the electrically driven jet.

The limited electrospinnability of pure keratin is the same as other research results because of its low molecular weight (Fan et al., 2016; Ayutthaya et al., 2016; Yuan et al., 2008; Zoccola et al., 2008; Aluigi et al., 2013). Some higher molecular weight polymers, such as polyvinyl alcohol, silk fibroin, and PEO, have been blended with keratin to improve its electrospinnability. With the introduction of higher weight polymers, the viscosity of the related solutions is increased, resulting in the formation of continuous and smooth nanofibers with a thicker diameter.

4. Conclusions

In our work, we prepared different WK-PEO membranes by wool waste decolorization and subsequently spinning the regenerated wool keratin. Under the catalysis of FePc/H₂O₂, the azo groups of dyes could be broken into colorless products. Among the main influencing factors, including pH, FePc, and H₂O₂ concentration, pH proved to provide the strongest accelerating effect for the dye degradation, and the decolorization percentage could reach 94.2% in 210 min at pH = 10. In addition, PEO was introduced to improve the spinnability of the regenerated wool keratin, and the average diameter of the nanofibers of the 70/30 WK-PEO membranes was 546 ± 312 nm. Our results provide a basis for textiles waste recycling and environmental pollution relief.

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References

- Aluigi, A., Corbellini, A., Rombaldoni, F., Zoccola, M., Canetti, M., 2013. Morphological and structural investigation of wool-derived keratin nanofibres cross-linked by thermal treatment. *Int. J. Biol. Macromol.* 57, 30–37.
- Aluigi, A., Rombaldoni, F., Tonetti, C., Jannoke, L., 2014. Study of methylene blue adsorption on keratin nanofibrous membranes. *J. Hazard. Mater.* 268, 156–165.
- Aluigi, A., Tonetti, C., Vineis, C., Tonin, C., Mazzuchetti, G., 2011. Adsorption of copper (II) ions by keratin/PAG blend nanofibers. *Eur. Polym. J.* 47, 1756–1764.
- Aluigi, A., Vineis, C., Varesano, A., Mazzuchetti, G., Ferrero, F., Tonin, C., 2008. Structure and properties of keratin/PEO blend nanofibres. *Eur. Polym. J.* 44, 2465–2475.
- Ayutthaya, S.I.N., Tanpichai, S., Sangkhun, W., Wootthikanokkhan, J., 2016. Effect of clay content on morphology and processability of electrospun keratin/poly(l-lactic acid) nanofiber. *Int. J. Biol. Macromol.* 85, 585–595.
- Cardamone, J.M., 2010. Investigating the microstructure of keratin extracted from wool: peptide sequence (MALDI-TOF/TOF) and protein conformation (FTIR). *J. Mol. Struct.* 969, 97–105.
- Chen, W., Lu, W., Yao, Y., Xu, M., 2007. Highly efficient decomposition of organic dyes by aqueous-fiber phase transfer and in situ catalytic oxidation using fiber-supported cobalt phthalocyanine. *Environ. Sci. Technol.* 41, 6240–6245.
- Clarke, C.E., Kielar, F., Talbot, H.M., Johnson, K.L., 2010. Oxidative decolorization of acid azo dyes by a Mn oxide containing waste. *Environ. Sci. Technol.* 44, 1116–1122.
- Fan, J., Lei, T.D., Li, J., Zhai, P.Y., Wang, Y.H., Cao, F.Y., Liu, Y., 2016. High protein content keratin/poly(ethylene oxide) nanofibers crosslinked in oxygen atmosphere and its cell culture. *Mater. Des.* 104, 60–67.
- Kabir, M.M., Forgács, G., Horváth, I.S., 2013. Enhanced methane production from wool textile residues by thermal and enzymatic pretreatment. *Process. Biochem.* 48, 575–580.
- Kumar, C.G., Mongolla, P., Joseph, J., Sarma, V.U.M., 2012. Decolorization and biodegradation of triphenylmethane dye, brilliant green, by aspergillus sp. isolated from Ladakh, India. *Process. Biochem.* 47, 1388–1394.
- Li, J., Li, Y., Li, L., Mak, A.F.T., Ko, F., Qin, L., 2009a. Fabrication and degradation of poly(L-lactic acid) scaffolds with wool keratin. *Compos. Part. B.* 40, 664–667.
- Li, J., Li, Y., Li, L., Mak, A.F.T., Ko, F., Qin, L., 2009b. Preparation and biodegradation of electrospun PLLA/keratin nonwoven fibrous membrane. *Polym. Degrad. Stabil.* 94, 1800–1807.
- Vandevivere, P.C., Bianchi, R., Verstraete, W., 1998. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *J. Chem. Technol. Biot.* 72, 289–302.
- Wang, J., Hao, S., Luo, T., Zhou, T., Yang, X., Wang, B., 2017. Keratose/poly(vinyl alcohol) blended nanofibers: fabrication and biocompatibility assessment. *Mat. Sci. Eng. C* 72, 212–219.
- Yang, X., Zhang, H., Yuan, X., Cui, S., 2009. Wool keratin: a novel building block for layer-by-layer self-assembly. *J. Colloid. Interf. Sci.* 336, 756–760.
- Yuan, J., Shen, J., Kang, I.K., 2008. Fabrication of protein-doped PLA composite nanofibrous scaffolds for tissue engineering. *Polym. Int.* 57, 1188–1193.
- Zoccola, M., Aluigi, A., Vineis, C., Tonin, C., Ferrero, F., Piacentino, M.G., 2008. Study on cast membranes and electrospun nanofibers made from keratin/fibroin blends. *Biomacromolecules* 9, 2819–2825.