Duck Feather/Nonwoven Composite Fabrics for Removing Metals Present In Textile Dyeing Effluents

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ABSTRACT

In this paper, duck feather fiber was treated by alkaline solution first, then its Cu^{2+} sorption capacity was tested, and the sorption mechanism was studied by utilizing infrared spectrum (FTIR) and wide-angle X-ray diffraction (XRD). Moreover, desorption properties of the treated duck feather fiber were investigated in order to exploit it as a recycled industrial effluent treatment material. Finally, the duck feather fiber was air-laid and thermal-bonded into a composite nonwoven fabric by adding bicomponent low melt PE/PP binder fiber.. It was found that the alkaline treated duck feather/bicomponent PE/PP nonwoven fabrics exhibit good mechanical properties and Cu^{2+} and Cr^{6+} sorption capacity is a promising material for textile dyeing effluent treatment.

Keywords: feather, removal, heavy metals, sorption, waste-water

INTRODUCTION

China is one of the largest poultry raising country in the world. About 50 million chickens and ducks are slaughtered each year, and 800 thousand tons of feathers are produced therefrom. Traditionally, 20% of the feathers, commonly known as eiderdown, are further processed into garments and bedding articles. Among the rest, small raw pinaculum (half down feather) can be used by blending with eiderdown. Some feathers are converted into feed additives, and others are further used for fertilizer. However, 80% are treated as waste [1]. Hence, more effective and efficient methods are needed to reuse the feathers.

On the other hand, textiles are the export-oriented industries that contribute greatly to China's economic growth. However, this industry has caused serious environmental pollution in recent years. Heavy metals, particularly, chromium, copper and lead are used widely for the production of color pigments of textile dyes [2]. Trace heavy metals will remain in the waste water discharged from a dyeing factory and be transferred to the environment. A number of techniques aimed at removal of different types of dyes from waste water have been developed [3]. Adsorption, one of the methods, is gaining more and more attention because of its easy operation and versatility [4]. Various potential sorbents have been implemented for the removal of specific metals from water, such as peat, sugar cane bagasse; eucalyptus bark and hen feather [5-7]. Compared to all the other biomass sorbents, feathers do not decay easily in water and can be used for a long time [8]. Hence, feathers are potential sorbents for removing metals from waste water.

Recently, much research has focused on the properties of feathers as sorbents for removal of heavy metals, phenols, and organic dyes from aqueous solutions [9-14]. However, most papers only studied the sorption properties of feathers by immersing them in metal ion solutions. Sayed and Alok et al investigated the sorption properties of chicken feathers and de-oiled soya through fixed-bed columns of adsorbents [15, 16]; however, the glass column is still not a practical method of industrial waste water treatment. To enable feather sorbents to have uniform and reproducible properties and to enable them to be cleaned and reused, feathers need to be formed into a quality mesh shape. It is reported that feather fiber nonwoven fabrics can be made by the air-laid web forming process and bonded by chemical adhesives [17].

In this paper, duck feather fibers are processed into composite nonwoven fabrics by adding bicomponent low melt fibers as a binder. One of the objectives of this paper was to investigate the feasibility of using duck feather fiber/bicomponent PE/PP fiber composite nonwoven fabrics to remove heavy metal ions from textile waste water. In addition, the feather was treated by a NaOH solution and its sorption mechanism was studied by utilizing infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (XRD).

EXPERIMENTAL

Materials

The duck feather fibers without scapus were supplied by Yangzhou Ganquan Down Products Factory.

Bi-component PE/PP sheath/core fibers (9.8dtex×70mm) were supplied by Jiangsu Jiangnan High Polymer Fiber Co., Ltd. The melting temperature of PE and PP are 125°C and 163°C, respectively.

Sample Preparation

Preparation of Duck Feather/ Bicomponent PE/PP Fiber Composite Nonwoven Fabrics

Duck feather fibers and bicomponent PE/PP fibers were blended in the ratio of 80:20, 75:25 and 70:30, respectively. Then the fibers were air-laid into a lofty web by using a Rando-40B air-laid machine. Finally, the lofty web was heated in a 8810A blast oven under 140°C for 20 min. A fabric sample is shown in *Figure 1*.

FIGURE 1. Photo of feather/bicomponent PE/PP fiber nonwoven fabric.

Cu^{2+} sorption measurement

1g duck feather fibers were immersed in 8mmol /l 250ml of $CuSO_4$ solution with pH value 11. The pH value of the solution was regulated with NH_4Cl and $NH_3 \cdot H_2O$ and measured with a PHS-3C pH meter (Shanghai Science Equipment Co. Ltd., China). The temperature was adjusted to 25°C. The solution was stirred for half an hour and then kept for 5 hours. Finally, the solution was filtered and the residual Cu^{2+} concentration of the filtrate was measured by using a VIS-723 spectrophotometer. When NH_4Cl and $NH_3 \cdot H_2O$ are added to $CuSO_4$ solution, the metal ion will precipitate as the light blue hydroxide first. However, addition of excess ammonia (pH=11) will cause the blue hydroxide to dissolve, giving the deep blue solution of tetraammine copper (II).

Alkaline Treatment

Duck feather was pre-treated by 0.1mol/L NaOH and 0.05mol/L H_2SO_4, respectively. It was found that the feather treated by alkaline solution has higher Cu^{2+} sorption capacity. Hence, alkaline solution was used to treat the feather in the following section. 6g duck feather fiber or nine pieces of duck feather/bicomponent PE/PP fiber composite nonwoven fabrics with three duck feather contents were immersed in 0.1mol/L 1000ml NaOH solution under 50°C for 1h, 10h and 20h respectively, and then the treated samples were washed thoroughly with distilled water and air-dried at room temperature for further use.

Desorption Experiment

Duck feather fibers filtered from the above Cu^{2+} sorption measurement were washed thoroughly with distilled water and air-dried at room temperature. Then they were immersed in acid solution with pH value 2.5 for 48h. Finally, the solution was filtered again and the filtered feather fibers was used for the next sorption and desorption cycle.

Cr^{6+} And Cu^{2+} Sorption Measurement of Feather Composite Nonwoven Fabric

A series of Cr^{6+}/Cu^{2+} solutions were prepared by mixing 250mL 8mmol/L $CuSO_4$ solution and 0.1413g, 0.2120g, 0.2827g, 0.3530g and 0.4240g of $K_2Cr_2O_7$ respectively. The pH of the solutions was adjusted to 11 by NH_4Cl and $NH_3 \cdot H_2O$ and the temperature was 25 °C. Three pieces of alkaline treated feather composite nonwoven fabrics with duck feather fibers and bicomponent PE/PP fibers in the ratio of 80:20 (1.5g each) were immersed in each solution and kept for five hours. Finally, the solutions were filtered and the residual Cr^{6+} and Cu^{2+} concentration of the filtrates were tested.

Measurement

Infrared Spectrum Measurement (FTIR)

Duck feather fibers were mixed and grounded with KBr in a quartz crucible and then pressed into pellets by a manual tablet machine. Then they were tested with Nicollet NEXUS670 infrared-Raman spectrometer. The wave number was 500-4000 cm^{-1}, the resolution was 8 cm^{-1} and the scan number is 64.

Wide-Angle X-Ray Diffraction Measurement (XRD)

Duck feather fibers were powdered by hand and then tested with D/max-2550 PC X-ray diffraction tester.

Tensile Testing

The tensile properties of the nonwoven fabrics were measured based on WSP 110.4(2005). Sample strips of 25±1 mm width in the cross direction were prepared and tested at a gauge length of 75±1 mm and at 300±10 mm/min. Five specimens were tested per sample using an Instron 4301 tensile tester. As the samples were made by air-laid and thermal bonding process, its machine direction and cross direction strength were assumed to be similar. Hence only cross direction strength was tested in this paper.

Thickness Testing

Thickness of the duck feather composite nonwoven fabrics was measured based on WSP 120.2(2005). Five specimens of 300×300mm were tested.

Basis Weight Testing

Basis weight of the duck feather composite nonwoven fabrics were measured based on WSP 130.1(2005). Five specimens were tested.

RESULTS AND DISCUSSION

The Influence of Alkaline Treatment on Cu^{2+} Sorption of Duck Feather Fibers

Duck feather fibers were treated by NaOH solution for 1h, 10h and 20h, respectively, and then Cu^{2+} sorption capacity of the treated feather fibers were tested. The results were shown in *Table I* and *Figure 2*.

It can be seen from *Table I* and *Figure 2* that Cu^{2+} sorption capacity of duck feather fibers is increased with the increase of the alkaline treatment time. The concentration of Cu^{2+} in the solution was 6.62 mmol/L, 5.65 mmol/L, 5.11 mmol/L and 4.74 mmol/L, respectively. Hence alkaline treatment is an effective method to improve the Cu^{2+} sorption capacity of feather fibers. In order to uncover the mechanism, the structure of the treated feathers was measured by FTIR and XRD, as shown in *Figure 3* and *Figure 4* respectively.

It is well known that the secondary structures (α helix and β-sheet) of feather have characteristic peaks at 1650 cm^{-1} and 1519 cm^{-1} in FTIR curves, respectively [18-21]. The intensity of the characteristic peak can be used to compare the content of the secondary structures relatively. It can be seen from *Figure 3* that the difference in peak intensity of the two characteristic peaks becomes more noticeable with the increase of treatment time. As we know, the band at 1450 cm^{-1} is the characteristic band of the main chain of feathers and can be used as the benchmark to relatively compare the peak intensity of α helix and β-sheet structure. Hence, the peak intensity of 1450 cm^{-1} is fixed to the same for all the samples, then the peak intensity of α helix is subtracted from the peak intensity of β-sheet, and the differences are listed in *Table II*.

TABLE I. Cu^{2+} sorption capacity of feather fibers alkaline treated for different time.

Treatment time(h)	Cu^{2+} sorption capacity(mg/g)
0	22.1±1.06
1	37.6±1.88
10	46.3±2.40
20	52.2±2.72

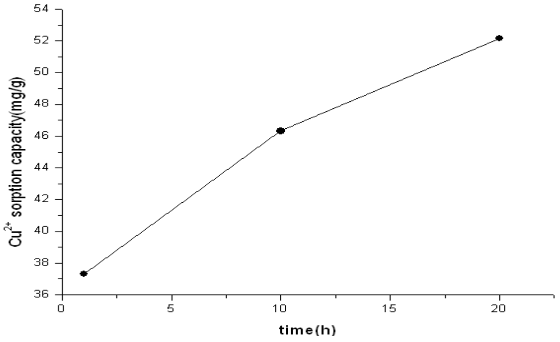
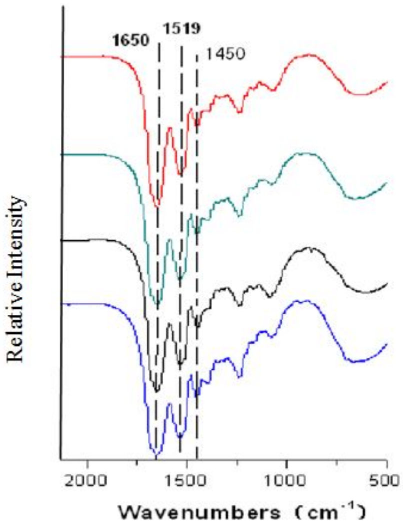


FIGURE 2. Cu^{2+} sorption of feather fibers alkaline treated for different treatment time.

It can be seen from *Table II* that the difference in peak intensity of α helix and *β*-sheet of the treated feather fibers becomes small after treated by NaOH solution for one hour and then becomes big after treated for 10 and 20 hours.



(a) 20 hours (b) 10 hours (c) 1 hour (d) un-treated

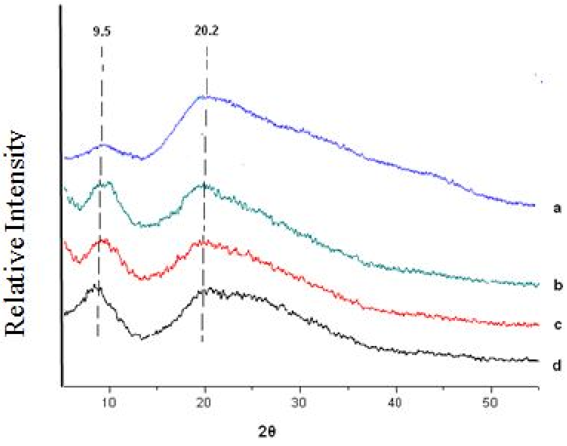
FIGURE 3. FTIR of feather fibers alkaline treated for different time.

TABLE II. Difference in peak intensity of secondary structures of treated feather fibers.

Treated time(h）	Y_α -Y_β
0	10.6
1	8.1
10	10.9
20	12.7

* Y_α and Y_β represent the peak intensity of α helix and β-sheet, respectively.

It is reported that feather fibers have two kinds of crystal structures, namely, *α*-helix and *β*-sheet. Both have characteristic peaks in XRD curves, 2*θ* of about 8.4° (interplanar spacing d = 10*Å* (b)) and 20.48° (d = 4.29 *Å* (b)) for *α*-helix and *β*-sheet, respectively [9]. It can be seen from Figure.4 that the crystal structure of feather fibers changed obviously after alkaline treated for different times. The *α*-helix crystal structure of the feather fiber becomes weak after treated by NaOH solution for one hour, and then it becomes sharp after treated for 10 and 20 hours, respectively. E. Wojciechowska studied the structure of wool treated by NaOH for eight hours and found that *α*-helix and random coil structure of wool increased while *β*-sheet crystal decreased [22]. Based on the result of FTIR and XRD, it can be inferred that there are two kinds of structure changes of feather fibers during NaOH treatment. Part of the un-perfect *α*-helix structure is transferred into a random coil structure first when the feather is treated by NaOH for a short time, while *β*-sheet is mainly transferred into *α*-helix when the feather is treated for a long time. Another explanation is that α helix and *β*-sheet structure of feather fibers exhibit different solubility and more *β*-sheet structure of feather fibers was dissolved and/or etched by NaOH solution, resulting in relatively weak intensity in the XRD spectroscopy. Compared to *β*-sheet, random coil and α helix are a more loose structure of feather proteins, in which more hydrogen bonds were broken during the alkaline treatment. Hence more adsorptive sites are available for Cu^{2+} and the sorption capacity of feather fibers were improved with the increase of the alkali treatment time.



(a) 1 hour (b) 10 hours (c) 20 hours (d) un-treated

FIGURE 4. XRD of feather fibers alkali treated for different time.

Therefore, Cu^{2+} sorption capacity of feather fibers increased with the increase of treated time while *α*-helix structure of the treated feather fibers decreased first and then increased.

Desorption Properties of Alkaline Treated Feather Fibers

In order to find out whether the alkaline treated feather fiber can be used repeatedly as sorbent for removing Cu^{2+} from waste water, duck feather fiber which was first used for Cu^{2+} sorption capacity measurement was desorbed in acid solution. Then its Cu^{2+} sorption capacity was measured by the same method. It is called the first desorption cycle. Similarly, the feather fiber was treated by the second and third desorption cycle sequentially. The Cu^{2+} sorption capacity after each desorption cycle are shown in *Figure 5*.

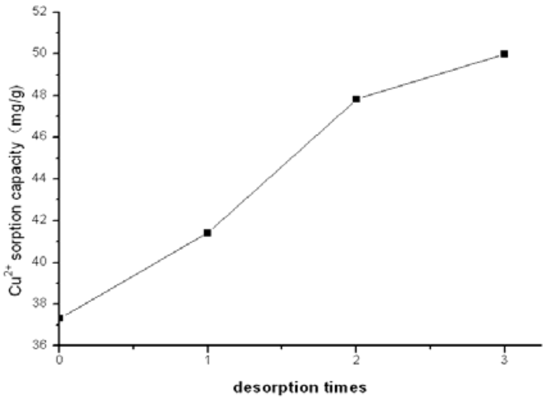
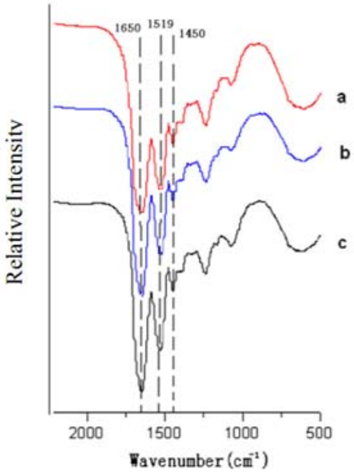


FIGURE 5. Cu^{2+} sorption capacity of feathers treated for different desorption cycles.

It can be seen from *Figure 5* that Cu^{2+} sorption capacity of the alkaline treated feather fibers increased with the increase of the desorption cycles, which means that the alkaline treated feather fibers can be used for Cu^{2+} sorption repeatedly. In order to uncover the reason why Cu^{2+} sorption capacity of the desorbed feather fibers increases after each desorption treatment, their structures were investigated by FTIR and XRD..

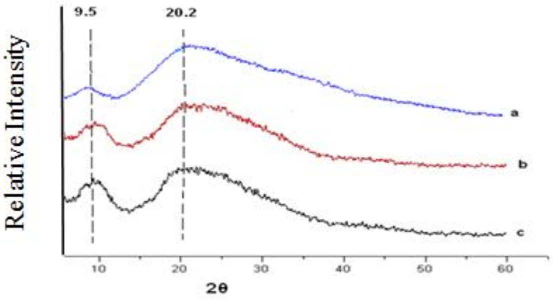
It can be seen from *Figure 6* that the intensity of α helix structure of the alkaline treated feather fibers increase with the increase of the desorption cycles compared with the intensity of β-sheet, which means that more α helix structures of feather fibers appears after it is desorbed in acid solution.

It can be seen from *Figure 7* that the intensity of the characteristic peak of α-helix structure of the treated feather at 2θ of about 8.4° increased with the increase of desorption cycles, which also means that more α-helix structure appears in the treated feathers. Thus the XRD result in *Figure 7* is consistent with the FTIR spectral result in *Figure 6*, which suggests that the increase of α-helix structure causes the increase of Cu^{2+} sorption capacity of the feather fiber.



(a) NaOH treated (b) 2nd desorption (c) 3rd desorption

FIGURE 6. FTIR of feather fibers treated for different desorption cycle.



(a) NaOH treated (b) 2nd desorption (c) 3rd desorption

FIGURE 7. XRD curves of feather treated for different desorption cycle.

Properties of Duck Feather Composite Nonwoven Fabrics for Textile Dyeing Effluent Treatment

Three kinds of duck feather composite nonwoven fabrics with different binder fiber content were made by air-laid web-forming process and air-through thermal-bonding process. Their physical properties were shown in *Table III*. It can be seen from *Table III* that the duck feather/bicomponent PE/PP nonwoven fabric has quite good mechanical strength when the content of PE/PP fiber is higher than 25%. Therefore, air-laid and thermal bonding can be considered to be an excellent method to process duck feather fiber into composite nonwoven fabric. It can keep its shape and be recycled multiple times.

TABLE III. Mechanical properties of feather composite nonwoven fabrics.

	Content of Feather (%)	Basis weight (g/m^2)	Thickness (mm)	Tensile strength (cN)
1	80	226.6±9.0	5.74±0.29	81.2±8.1
2	75	202.0±9.1	5.78±0.30	144±14.4
3	70	197.7±9.5	5.82±0.31	149±13.4

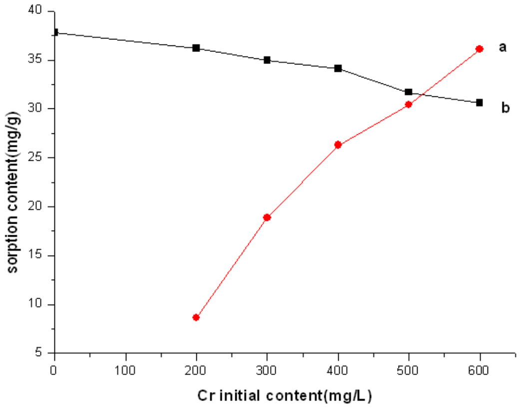
In order to find out whether feather composite nonwoven fabrics have similar Cu^{2+} sorption capacity as feather fibers, the feather composite nonwoven fabrics shown in *Table III* were alkaline treated, and then their Cu^{2+} sorption capacity was tested. Results are shown in *Table IV*.

It can be seen from *Table IV* that the Cu^{2+} sorption capacity of alkaline treated feather composite nonwoven fabrics are similar to feather fibers, which means that the binder fiber does not significantly influence the Cu^{2+} sorption capacity of the feather fiber when the binder fiber is in the range of 20% to 30% studied in this paper.

As we know, there are more than two kinds of heavy metal ions in textile waste water, such as chromium, copper, and lead. In order to investigate whether feather composite nonwoven fabric can be used as a kind of recycled industrial textile effluent treatment materials, the sorption capacity of copper and chromium ions of the feather composite nonwoven fabric were studied. The results were shown in *Figure 8*.

TABLE IV. Cu^{2+} sorption capacity of feather composite nonwoven fabrics.

Sample	Content of Feather (%)	Cu^{2+} sorption capacity(mg/g)
1	80	35.6±1.5
2	75	37.8±1.7
3	70	36.3±1.6



(a) Cr^{6+} (b) Cu^{2+}

FIGURE 8. Cr^{6+} and Cu^{2+} sorption capacity of feather composite nonwoven fabric.

It can be seen from *Figure 8* that the Cr^{6+} sorption capacity of the feather composite nonwoven fabric increased with the increase of the Cr^{6+} concentration in the solution, while the Cu^{2+} sorption capacity decreased with the increase of the Cr^{6+} sorption capacity. Chromium (Cr) occurs in the environment principally in the trivalent and hexavalent oxidation states, Cr(III) and Cr(VI), respectively. Cr(VI) (or Cr^{6+})occurs as $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{-2}$ anions in water, the predominant species depending on the pH and Cr(VI) concentration. It is hard to explain why the Cu^{2+} basic ion sorption capacity of feather fibers decreased with the increase of the Cr^{6+} composite negative ions sorption capacity. Perhaps their sorption capacity is mainly determined by their relative concentration in the solution. In addition, the extrapolation of the Cr^{+6} absorption capacity to the horizontal axis of the graph indicates that in the presence of 8 mmol/L of Cu^{+2}, no absorption of Cr^{+6} occurs until the initial Cr^{+6} concentration exceeds ~125 ppm which is consistent with Sun's findings that NaOH-treated chicken fibers show relatively low sorption capacities for removal of Cr(VI) ions from water in the concentration range of 10-80 ppm [4].

CONCLUSION

The Cu^{2+} sorption capacity of duck feather fiber increases with the increase of the alkaline treated time. Moreover, it still maintains similar Cu^{2+} sorption capacity after 3 times of desorption, which means that alkaline treatment is an effective method to improve the Cu^{2+} sorption capacity of duck feather fiber and the treated fiber can be used for Cu^{2+} sorption repeatedly. According to the FTIR and XRD results of alkaline treated feather fibers, it is inferred that more loose structure of feather proteins appeared after the alkaline treatment, resulting in more adsorptive sites for Cu^{2+} and the sorption capacity of feather fibers were improved with the increase of the alkali treatment time. Finally, the alkaline treated duck feather/bicomponent low melt PE/PP fiber nonwoven fabric shows good mechanical properties and Cu^{2+} and Cr^{6+} sorption capacities in relatively high concentration.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Shanghai Municipal Natural Science Foundation. The project number is 11ZR1400900.

REFERENCE

[1] L. Liu, Z.H. Yu, The study for adsorption of cooper ions from aqueous solutions using feather nonwovens, *Nonwovens* 16(2008) 10-15.

[2] J. Q. Wang, Z. P. Mao, R. Li, Present situation and prospects of energy saving and emission reduction technology in dyeing and finishing industry, *Dyeing & Finishing* (2009) 44-51.

[3] M. Alok, Adsorption kinetics of removal of a toxic dye, Malachite Green, from waste water by using hen feathers, *Journal of Hazardous Materials* (2006) 196–202.

[4] P. Sun, Z.T. Liu, Z. W. Liu, Chemically Modified Chicken Feather as Sorbent for Removing Toxic Chromium(VI) Ions，*Ind. Eng. Chem. Res*. 48(2009) 6882–6889.

[5] M. Alok, M. Arti, K. Dipika Kaur, Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials, *Journal of Hazardous Materials* 148(2007) 229-240.

[6] P. Kar, M Misra, Use of keratin fiber for separation of heavy metals from water, *Journal of Chemical Technology & Biotechnology* 79(2004) 1313-1319.

[7] V. Saucedo-Rivalcoba, A L Martínez-Hernández, G Martínez-Barrera, C Velasco-Santos, J L Rivera-Armenta, V M Castao, Removal of hexavalent chromium from water by polyurethane–keratin hybrid membranes, Water Air Soil Pollution 218(2010), 557-571.

[8] V. T. Evgenia, G. Adriana, N. Georgi, Ecologically safe method for improved feather wastes biodegradation, *International Biodeterioration & Biodegradation* 63(2009) 1008-1012.

[9] P. Sun, Z.T. Liu, Z. W. Liu, Particles from bird feather: A novel application of an ionic liquid and waste resource, *Journal of Hazardous Materials* 170(2009) 786-790.

[10] G. de la Rosa, H. E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodríguez, C. Velasco-Santos, and A. L. Martínez-Hernández, Recycling Poultry Feathers for Pb Removal from Wastewater: Kinetic and Equilibrium Studies, *International Journal of Chemical and Biomolecular Engineering* 1(2008) 185-193.

[11] S. Kyozo, Biosorption of precious metal ions by chicken feather, *Journal Applied Biochemistry and Biotechnology* 57-58(1996) 67－74.

[12] S. Al-Asheh, F. Banat, D. Al-Rousan, Adsorption of copper, zinc and nickel ions from single and binary metal ion mixtures on to chicken feathers, *Adsorption Sci. Technol.* (2002) 849–864.

[13] F. Banat, S. Al-Asheh, Biosorption of phenol by chicken feather, *Environmental Engineering and Policy* (2000) 5–90.

[14] S. Al-Asheh, F. Banat, D. Al-Rousan, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater, *J. Cleaner Prod.* (2003) 321–326.

[15] S. A. Sayed, S M Saleh, E E Hasan, Removal of some polluting metals from industrial water using chicken feathers, *Desalination*, 181 (2005)243-255.

[16] V. K. Gupta, M. Alok, G. Vibha and M. Jyoti, Adsorption of basic fuchsin using waste materials—bottom ash and deoiled soya—as adsorbents, *Journal of Colloid and Interface Science* 319(2008) 30-39.

[17] W. F. Schmidt and S. Jayasundera. "Microcrystalline Keratin Fiber," Wallenberger, F. and Weston, N. (eds.) in Natural Fibers Plastics and Composites Recent Advances, Kluwer Academic Publishers, Norwell, MA. 2003.

[18] J. B. Yao, Y. B. Liu, S. T. Yang, J. Z. Liu, Characterization of Secondary Structure Transformation of Stretched and Slenderized Wool Fibers with FTIR Spectra，*Journal of Engineered Fibers and Fabrics* 3(2008) 22-31.

[19] C. J. Dove, A M Rijke, X Wang, L S Andrews, Infrared analysis of contour feathers: the conservation of body heat radiation in birds, *Journal of Thermal Biology* 32 (2007) 42–46.

[20] A. L. Martínez-Hernández, C Velasco-Santos, M de Icaza, V M Castao, Microstructural characterisation of keratin fibres from chicken feathers, *Int. J. Environment and Pollution* 23(2005) 162-178.

[21] P Yu, J J Mckinnon, C R Christensen, D A Christensen, Using synchrotron-based FTIR microspectroscopy to reveal chemical features of feather protein secondary structure: comparison with other feed protein sources, *J. Agric. Food Chem*., 52(2004) 7353-7361.

[22] E. Wojciechowska, A. Wlochowicz, A Weselucha-Birczyńska, Application of Fourier-transform infrared and Raman spectroscopy to study degradation of the wool fiber keratin, *Journal of Molecular Structure* 511-512(1999) 511-512. 307-318.

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