Thermodynamic Investigations on Chrome and Aluminum Tanning

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Abstract

Chromium(III) and aluminum(III) have some history of use in the leather industry, and the leathers tanned by them are greatly different in hydrothermal stability. However, the direct measure of thermodynamic characteristics of the tanning process is difficult due to the binary fibers/solution system. In this paper, the thermodynamics of chrome/aluminum tanning reaction was obtained by means of adsorption thermodynamics. The hide powder was used to investigate the adsorption behavior of both Cr(III) and Al(III), and the surface electrochemical property of hide powder was characterized by Zeta potential analyzer. The results showed that the adsorption isotherm of both Cr(III) and Al(III) could be well described by the Langmuir equation, and the quantity of Cr(III) absorbed at pH 4 is similar to that of Al(III) at pH 3.5 using the dimension of mol/g collagen fibers. Then the dimensionless equilibrium constants of such binary fibers/solution systems were obtained. The data of Gibbs free energy change (ΔG) indicate that the interaction between Cr(III) and collagen is slightly stronger (about 1.8 $kJ \cdot mol^{-1}$) than Al(III), which is insufficient to assume the large difference in stability of chrome-tanned and alum-tanned leathers. However, ΔS of the adsorption process is positive for Cr(III) and negative for Al(III), and the addition of Cr(III) results in bigger conformational change of collagen than Al(III) indicated by both the CD spectra and SEM images, which suggest that the big differences in conformation of collagen induced by Cr(III) and Al(III) may be the foundation of difference in stability.

Introduction

Tanning operation converts raw hides and skins into leather which represents a stable collagen fiber structure to prevent being putrefied by bacteria.[1] The chrome tanned leather has high hydrothermal stability, top organoleptic property and versatile applicability, whereas other tanning methods cannot confer the same properties as chrome hitherto.[2] However, due to its alleged environmental impact, the recent study on chrome tanning has been centered on cleaner tanning processes, such as improving chrome exhaustion by developing novel auxiliary agents, modifying collagen fiber by adding carboxyl group content or integrating tanning process.[3-6] In the meantime, attention is also turned to find non-chrome tanning metal, and aluminum is considered as a potential alternative although the use of Al(III) salts is still very limited now. Unfortunately, questions regarding the exact reason of the difference between Cr(III) and Al(III) in tanning have still not been satisfactorily answered, although the real understanding of the questions may let us find the solution for better use of Al(III).

The considerable difference between Cr(III) and Al(III) in tanning was explained by the more stronger bonding interaction between Cr(III) and skin collagen compared with Al(III) in the past. However, Covington *et al*. proposed that the metal tanning bonds did not break down during heat shrinking of collagen fibers based on ^{27}Al NMR tests.[7] In fact, the literature about the thermodynamic limit of metal tanning reaction can be rarely found. Rao *et al* obtained the experimental equilibrium constants for NCS^- coordinating with Cr(III) species to indicate the relative thermodynamic stability of Cr(III) species-nucleophile complex.[8] The getting of thermodynamic data for tanning reaction is not easy because the determination of binding constants for collagen-metal complexes is very difficult due to the heterogeneous nature of hide and tanning liquor. To the best of our knowledge, no prior work on the simulation calculation of Cr(III)/Al(III) - collagen fiber surface reaction equilibrium constants have been reported. Thus, it is necessary to investigate the equilibrium of their tanning reactions to further understand the real mechanisms, and so as to improve the tanning process.

In the tanning process, Cr(III) or Al(III) ions attach to collagen fibers by means of the creation of covalent complex between carboxyl groups of collagen fiber and the metal ions, which is similar to chemisorption. Then the thermodynamics of

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adsorption could reflect the relative thermodynamic stability of tanning reaction. To minimize impact of the penetration and better understand the metal tanning reactions at interface, the collagen fibers were used to investigate adsorption behavior of Cr(III) and Al(III) in this paper.

Experimental

Materials and Chemicals

Collagen fiber was prepared by using unhaired bovine pelts. The pelt was cleaned, limed, split and delimed according to common leather processing, so that the non-collagen components were removed. Then the pelt was dehydrated by absolute ethyl alcohol, cut into pieces (2 cm × 2 cm) and dried in drying oven at 45°C. The dried pelt pieces were ground into fibers and particles with diameter less than 1 mm using cutting mill (SM 100, Retsch, Germany), then sealed for following determinations.[9-11]

Collagen from pig skin was provided by Guangzhou Huangyao Bio-tech Co., Ltd (Guangzhou, China). $Cr_2(SO_4)_3 \cdot 6H_2O$ solution (50 wt%) was purchased from Tianjin Shentai Chemical Co., Ltd (Tianjin, China). $Al_2(SO_4)_3 \cdot 18H_2O$, NaOH and HCl were purchased form Chengdu Kelong Chemical Co., Ltd (Chengdu, China). All chemicals used for experiment were of analytical grade, and the deionized water was produced by UPK- II-20T water purification system (Ulupure, China).

Experiments

All batch adsorption experiments were carried out in Erlenmeyer flasks, and repeated twice to confirm the results. The data were the mean values of two replicate determinations.

Isoelectric Point (pI) Measurement of Hide Powder

The collagen fiber was characterized by the measurement of isoelectric point (pI). 10g of collagen fiber was dispersed in 400 mL of deionized water to form suspension. Then 0.1mol/L NaOH or 0.1mol/L HCl solution was added to form a pH gradient of the suspension, and then vibrated at 150 rpm in 25°C water bath for 30 min for soaking equilibrium. Then the pI was determined by using Zeta Potential Analyzer (Mütek™ SZP-10, BTG, Germany).[9]

Adsorption Kinetics

Cr(III) adsorption kinetics was studied as functions of pH (3.0, 4.0 and 4.5), contact time (from 0.5 h to 24 h), and temperature (25°C, 35°C and 45°C) in a batch system containing 0.1 g of collagen fibers and 100 mL 1.3 mmol/L of Cr(III) solution (initial concentration, C_0). The initial pH of Cr(III) solution was adjusted using 0.1mol/L NaOH solution or 0.1mol/L HCl solution. The adsorption experiments were performed with constant shaking (120 rpm). The sample solution after adsorption was collected, and Cr(III) concentration (C_t) in the solution was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 8000, PerkinElmer, USA). The fixation capacity (q_t) of collagen fiber to Cr(III) was calculated by the following equation:

$$q_t = \frac{[(C_0 - C_t)V]}{m} \tag{1}$$

where q_t is the fixation capacity of Cr(III) on collagen fiber at time t (mg/g), m is the mass of collagen fiber (g), V is the volume of solution (L), C_0 and C_t are the concentrations of Cr(III) (mg/L) in solution before and after adsorption, respectively.

Al (III) adsorption kinetics was studied as functions of pH (3.0, 3.5 and 4.0), contact time (from 0.5 h to 24 h), and temperature (25°C, 35°C and 45°C) in a batch system containing 0.1 g of collagen fibers and 100 mL of 1.3 mmol/L Al(III) solution . The procedure of adsorption experiments and data determinations were the same as for Cr(III) adsorption.

Adsorption Isotherms

The experiments for adsorption isotherm investigation were performed in the same procedure as for adsorption kinetics determination except that the initial Cr(III) and Al(III) concentrations were changed from 0.44mmol/L to 3.00 mmol/L. The adsorption data were fitted to both the Langmuir and Freundlich isotherm equations. The linearized forms of the Langmuir isotherm (Eq. (2)) and Freundlich isotherm (Eq. (3)) are expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_{\max}} + \frac{C_e}{q_{\max}} \tag{2}$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{3}$$

where q_e (mg/g) and C_e (mg/L) are the amount adsorbed and the bulk concentration at equilibrium, respectively; q_{max} is the maximum adsorption amount (mg/g); K_L is the coefficient related to the binding energy or affinity parameter of the adsorption system; and K_F is the Freundlich constant indicating adsorption capacity; 1/n is an empirical parameter related to the nature and strength of the adsorption process and the distribution of the active sites.

Circular Dichroism Measurements

Collagen -Cr(III)/Al(III) complex solutions were prepared by adding 5 ug/mL Cr(III)/Al(III) to 0.05 mg/mL collagen in 0.2 mol/L acetic acid solution, then reacted under magnetic stirring for 24 h at 25°C after adjusting the pH to 4.0 using 0.1 mol/L NaOH solution. The circular dichroism (CD) measurements in the far-UV region from 190 to 260 nm were carried out on a J-810 CD spectropolarimeter (Jasco, Japan) with a resolution of 0.1 nm. Each sample was scanned 3 times at a speed of 100 nm/min. A reference spectrum containing a matching acetic acid was also recorded as the baseline.

Results and Discussions

Isoelectric Point (pI) of Collagen Fibers

The zeta potentials of hide powder at different pH were determined by Zeta Potential Analyzer, and a graph of zeta potential vs. pH was plotted, as shown in Fig.1. It can be seen from Fig.1 the isoelectric point (pI) of hide powder is 5.14.

The zeta potential of hide powder is consistent with the amino acid composition of collagen type I. Collagen type I contains about 12% carboxy amino acid residues including aspartic acid, asparagine, glutamic acid, and glutamine, whereas the basic amino acid residue content is about 9.6% including lysine, hydroxylysine, arginine and histidine.[12] Only 13.7% Asp and 6% Glu were ionized at pH 3, and the percent of ionization increases rapidly at higher pH. For example, the percent of ionized Asp and Glu attained 34.3% and 16.7% respectively at pH 3.5, and 77.1% and 58.3% at pH 4.5.

The Zeta potential indicates that when the pH of solution is lower than pI, the surface of the collagen fiber is positively charged which increases the electrostatic repulsion between the sorbent surface and metal cationic ions, and thus the metal cationic ions are bound to the collagen fibers mainly by the ways of chemical bonding with ionized carboxyl other than physical deposition. Negatively charged collagen fiber surface is formed only when the pH is higher than pI, where the physical deposition of metal cationic ions could occur.

The Kinetics of Cr(III) and Al(III) Adsorption

Kinetics studies of Cr(III)and Al(III) adsorption by collagen fiber were accomplished to ascertain the time necessary to reach the equilibrium. Results from the batch adsorption experiments are presented in Fig.2.

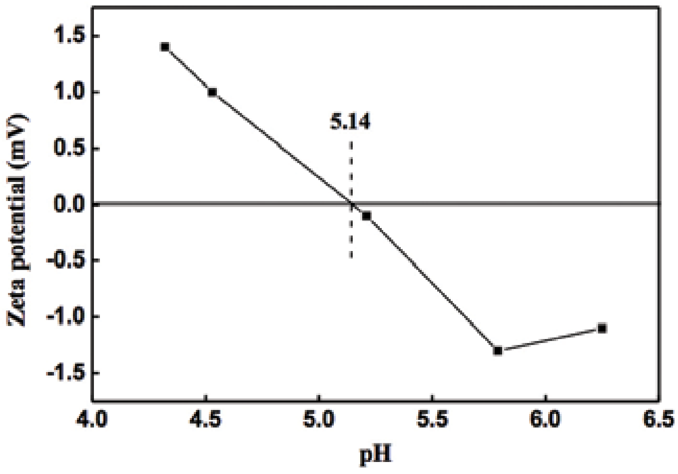

Figure 1. Zeta potential measurement of 2.5% hide powder suspension.

It can be seen from Fig.2 (a) that the adsorption rate of Cr(III) can be divided into three stages. In initial stage (≤1h), q_t values increase rapidly with time. In this stage, the unoccupied binding sites of collagen fibers and large initial metal ion concentration make the metal ions have great possibility to get in contact with carboxyl groups of collagen fibers, so that the reaction speed is fast. In second stage between 1h to 12h, q_t values increase slowly with time. In this stage, collagen fibers have lesser active sites to bond with Cr (III) and the metal ion concentration decreases, which lead to the retardation of adsorption reaction. Furthermore, the mass effect of reacted metal also results in the decline of reaction rate.[2] In the final stage after 12h, q_t values almost unchanged with time, indicating the arrival of dynamic adsorption equilibrium. With the increase of temperature and pH, the q_t values increase gradually. It was observed that the Cr(III) adsorption rates at pH=3 under 45°C are similar to those at pH=4 under 25°C, indicating both temperature and pH considerably affect the adsorption.

Fig.2 (b) shows that the adsorption rates of Al(III) can be divided into two stages. In initial stage (≤0.5h), q_t values increase rapidly

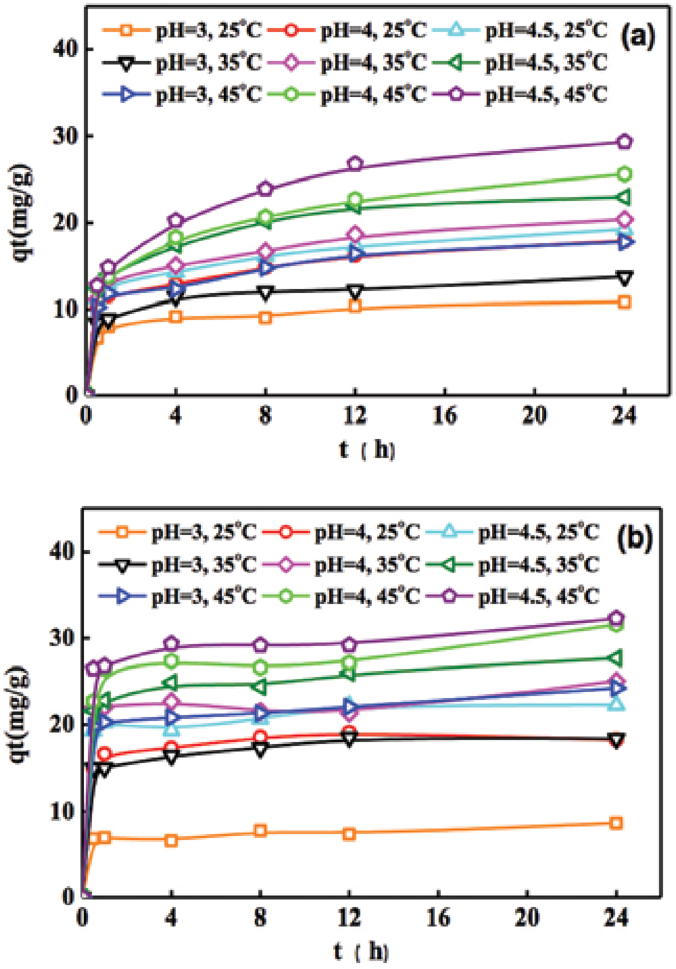

Figure 2. Reaction equilibrium curves between collagen fibers and Cr(III) (a), Al(III)(b) (collagen fibers 1 g/L, initial concentration of Cr(III) & Al(III) 1.3 mmol/L).

with time. In second stage between 0.5h to 24h, q_t values almost unchanged with time, implying that the dynamic adsorption equilibrium of Al(III) was arrived in shorter time in comparison with Cr(III). This should be due to the fact that there are about 30% negative charged ions i.e. $Al(SO_4)_2(H_2O)_2^-$ in the pH range of tanning (pH3.0-4.5) in Al(III) solution and the electrostatic attraction between negatively charged Al(III) and positively charged surface of collagen fiber speed up the deposition of Al(III) on the surface.[13] In the meantime, Cr(III) form inner-orbital coordination compound with carboxyls of collagen side chain, whereas Al(III) form outer-orbital coordination compound , which result in the higher reactivity of Al(III).

The Adsorption Isotherm and Thermodynamics

The adsorption isotherm constants from Langmuir and Frundlich isotherm for Cr(III) and Al(III) sorption onto collagen fiber and their corresponding R^2 were calculated. Langmuir isotherm showed a better fitting with higher value of R^2 for Cr(III), whereas both Langmuir and Frundlich isotherms can well fit the adsorption of Al(III) with similar R^2 (the data from Frundlich isotherm were omitted). Then we believe that the equilibrium data of metal tanning system can be better described by Langmuir model as listed in Table I.

The quantity of metal fixed under 318K is almost doubled for Cr(III) and three times more for Al(III) compared with those under 298K at each pH, whereas the effect of pH on the quantity is complicated. The quantity almost remains the same with the increase of pH from 3.0 to 4.0 for Cr(III) and pH 3 to 3.5 for Al(III) at each temperature, showing that metal fixation is mainly dominated by temperature during lower pH range. However, the further elevation of pH about 0.5 promoted the fixation of both Cr(III) and Al(III), and the quantity increases more than 40% at each temperature. The increased temperature and pH speed up both polymerization of metal ions and ionization of collagen carboxyls, and facilitate adsorption on collagen fiber. The quantity of Cr(III) absorbed is similar to that of Al(III) in consideration of the dimension of mol/g collagen fiber. For example, at 308K, the quantity of Cr(III) absorbed is 0.44 mol/g at pH 4 and that of Al(III) is 0.39 mol/g at pH 3.5, whereas at 318K, the quantity absorbed is 0.67 mol/g and 0.73 mol/g respectively. Obviously the quantity absorbed seems not to be responsible for the stability difference of leather tanned by chrome and alum. This is very different from the statements of Casaburi that the quantity of aluminum salts absorbed is insufficient to produce a commercial leather.[14] In fact, in spite of less multinuclear metal species in Al(III) tanning liquor than in Cr(III) tanning liquor, there are large amount of negative specie $Al(SO_4)_2(H_2O)_2^-$ in $Al_2(SO_4)_3$ solution (about 30% in the range of pH 2.5~4.5),[13] which could interact electrostatically with the positively charged surface of collagen fibers, so as to increase the fixed quantity.

The Langmuir constant could be described as $K_L=k_a/k_d$, where k_a is the rate constant of adsorption and k_d is the rate constant of desorption.[15] K_L is considered as the equilibrium constant for the

Table I

Isotherm constants obtained by Langmuir model for Cr(III), Al(III) sorption onto collagen fiber.

T (K)	Cr(III)				Al(III)			
	pH	q_{max} (mg/g)	$K_L \times 10^{-2}$ L/mg	R^2	pH	q_{max} (mg/g)	$K_L \times 10^{-2}$ (L/mg)	R^2
298	3.0	18.05	1.15	0.9812	3.0	5.47	1.73	0.9774
308	3.0	24.98	0.87	0.9897	3.0	7.77	1.31	0.9997
318	3.0	39.22	0.65	0.9945	3.0	19.05	1.09	0.9641
298	4.0	17.59	3.97	0.9504	3.5	5.50	4.16	0.9966
308	4.0	23.07	3.03	0.9926	3.5	10.49	3.53	0.9926
318	4.0	35.06	2.5	0.9790	3.5	19.66	2.14	0.9933
298	4.5	25.95	2.45	0.9976	4.0	10.75	1.79	0.9948
308	4.5	32.47	1.96	0.9970	4.0	15.01	1.46	0.9641
318	4.5	51.39	1.65	0.9780	4.0	30.42	1.09	0.9613

adsorption reaction, and usually used to obtain thermodynamics parameter of the process based on equation:

$$\Delta G = -RT \ln K_L \tag{4}$$

where T is solution temperature (K), and R is the gas constant, 8.314 J·mol^{-1}·K^{-1}.[16] However, it should be noticed that K_L has a dimension of inverse concentration (L/mg) just as listed in Table 1. But, based on fundamental thermodynamics, the above thermodynamic equation is meaningful only when the equilibrium constant K_L is a dimensionless quantity.[17-18] From the linear Langmuir equation, the Langmuir constant K_L could be transformed into dimensionless quantity as follow:

$$\frac{C_e/C^\theta}{q_e} = \frac{1}{K_L^\theta \cdot q_{max}} + \frac{C_e/C^\theta}{q_{max}} \tag{5}$$

where C^θ=1 mol/L, K_L^θ is thermodynamic equilibrium constant and obtained from the intercept and slope of adsorption isotherms at different conditions. Then the thermodynamic data were evaluated from Langmuir isotherms using following equations:

$$\Delta G = -RT \ln K_L^\theta \tag{12}$$

$$\log K_L^\theta = \frac{-\Delta H}{2.303RT} + \text{Constant} \tag{13}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{14}$$

Evaluated thermodynamic parameters, change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) are presented in Table II.

As well known, a viable reaction should have energetic driving force, which may be a decrease in enthalpy, an increase in entropy, or a combination of the both. From Table 2, the negative values of ΔG indicate the spontaneity of adsorption for both Cr(III) and Al(III) onto collagen fiber in the pH range of 3 to 4.5 from 25°C to 40°C, and the lower values relate to stronger binding energy of the adsorption system. Then based on the value of ΔG, collagen fiber showed the strongest affinity for Cr(III) at 318K with pH 4.0 (-18.96 kJ/mol), and for Al(III) at 308K with pH 3.5 (-17.15 kJ/mol) respectively, consistent with the results of tanning experiments. Though the thermal stability of chrome tanning leather is much higher than that of leather tanned by alum, the difference in ΔG is not so obvious. For example, under the conditions of the corresponding best fixation pH and temperature, ΔG of adsorption Cr(III) only about 1.8 kJ·mol^{-1} more negative than that of adsorption Al(III). Based on the Gibbs-Helmholtz equation, the isosteric enthalpy changes (ΔH) of adsorption process were calculated (Table II). The negative values indicate a decrease in enthalpy driving the adsorption during all the adsorption processes considered.

It is interesting to note that the changes of ΔS of Cr(III) and Al(III) adsorption process are very different. For Cr(III) the

Table II

Thermodynamic parameters for adsorption of Cr(III) and Al(III) on collagen fibers.

T (K)	Cr(III)					Al(III)				
	pH	K_L^θ (x 10^2)	ΔG (kJ.mol^{-1})	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})	pH	K_L^θ (x 10^2)	ΔG (kJ.mol^{-1})	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
298	3.0	5.96	-15.83	-22.20	-21.36	3.0	3.98	-14.83	-19.44	-11.70
308	3.0	4.51	-15.65		-21.24	3.0	3.00	-14.61		-12.05
318	3.0	3.39	-15.40		-21.36	3.0	2.50	-14.60		-11.70
298	4.0	19.33	-18.75	-15.64	10.42	3.5	9.56	-17.00	-26.05	-30.37
308	4.0	15.76	-18.85		10.42	3.5	8.11	-17.15		-28.90
318	4.0	13.00	-18.96		10.42	3.5	4.92	-16.39		-30.40
298	4.5	12.74	-17.71	-15.48	7.48	4.0	4.12	-14.92	-18.32	-15.17
308	4.5	10.17	-17.73		7.29	4.0	3.36	-14.89		-14.77
318	4.5	8.60	-17.86		7.48	4.0	2.52	-14.61		-15.18

values of ΔS changes from negative to positive value with the increase of pH, whereas, as for Al(III) the value of ΔS remains negative during the considered pH range. This implies that though Al(III) resembles Cr(III) in interacting with collagen carboxyls, the behavior of ΔS of the process is very different. A positive value of ΔS reflects the increased randomness in the solid-liquid interface and more favourable condition for the occurrence of the adsorption process. However, a negative ΔS implicates a lesser active interface of the solid-liquid system causing a reduction in adsorption. When Cr(III) and Al(III) are fixed on collagen fiber, the translational freedom of the metal species is reduced. At the same time, the conformation of collagen is also changed by the fixation of metal species. Then circular dichroism spectra were obtained to characterize the change of collagen conformation induced by Cr(III) and Al(III), see Fig.3. The parameter R_{pn} is calculated by the intensity ratio of positive peak over negative peak to denote the conformation of collagen. The R_{pn} ratio for collagen solution was found to be 0.110, while it was changed to 0.090 and 0.105 after the addition of Cr(III) and Al(III), respectively, suggesting the bigger conformation change induced by Cr(III) than by Al(III).[19]

In addition, the voids between collagen fibers are more or less enlarged by the addition of Cr(III) and Al(III) with the isolation of fibrils and fibres, just as shown in the scanning electron microscopic images (Fig.4). It is clear that Cr(III) showed a better effect on separating fibres than Al(III). These results showed that the good affinity of Cr(III) towards the collagen fibers is driven by the combination of both the decrease in enthalpy and the increase in entropy, whereas the affinity of Al(III) towards the collagen fibers is driven only by the decrease in enthalpy. This might be the main reason for better tanning effect of chrome.

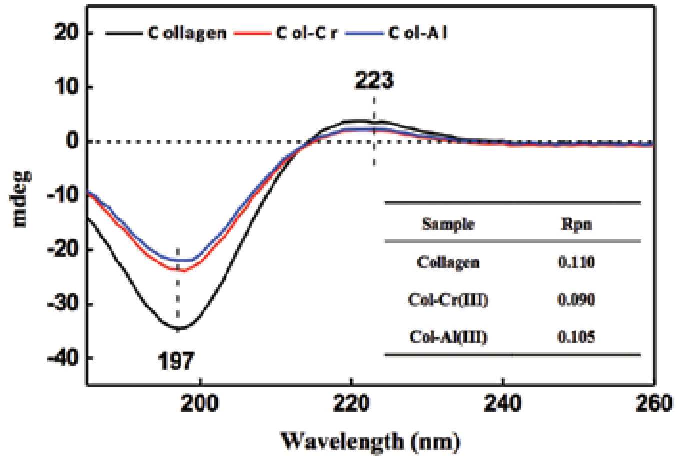

Figure 3. CD spectra of collagen, collagen-Cr(III) and collagen-Al(III) complex solution.

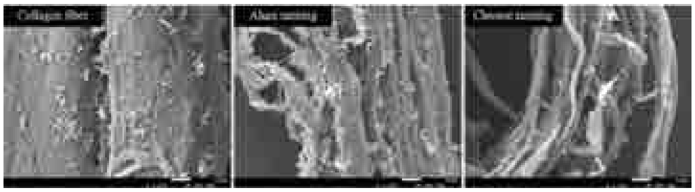

Figure 4. SEM images (×1000) of collagen fiber, alum tanning fiber and chrome tanning fiber (35°C, pH 4.0, 24 h, concentration of alum/chrome 150 mg/L).

Conclusion

The study on the adsorption isotherm of Cr(III) and Al(III) by collagen fiber leads to the following conclusions. Both elevating temperature and increasing pH improve the quantity of Cr(III) and Al(III) fixed with collagen. Equilibrium parameters, such as the maximum adsorption amount and Langmuir constant, have been deduced from binary fibres/solution systems. By means of these parameters, binary equilibria have been predicted. The adsorption process is exothermic for both Cr(III) and Al(III). Cr(III) and Al(III) fixation occurs best at about pH 4 and pH 3.5 respectively, and Δ*G* of the process of Cr(III) adsorption is more negative than that of Al(III) under the corresponding best fixation pH and temperature. Though the translational freedom of the metal species is reduced when it is absorbed by collagen fiber, ΔS of the adsorption process is positive for Cr(III) and negative for Al(III), and both the CD spectra and SEM images indicate that the bigger conformation change of collagen was induced by the addition of Cr(III) than Al(III). This might be the main reason for better tanning effect of chrome.

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