Effect of Leather Chemicals on Cr(III) Removal from Post Tanning Wastewater

by

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Abstract

The effect of typical leather chemicals on removal of Cr(III) from tannery post tanning wastewater by PAC coagulation was investigated. It was found that all the leather chemicals investigated could form complexes with Cr(III) through their anionic hydrophilic groups. The determinations of fluorescence quenching titration indicated that the Cr(III)-complexing ability of these anionic hydrophilic groups was in the sequence of phenolic hydroxyl of vegetable tannins and syntans > carboxyl of acrylic resins > sulfonic acid group of fatliquors and dyes. The complexes formed had higher hydrophobicity because a part of anionic hydrophilic groups of leather chemicals were blocked. The Cr(III) complexes with vegetable tannins, syntans and dyes were in the form of hydrophobic colloid or particle due to both the blocking effect of hydrophilic groups and the strong hydrophobicity of benzene ring, which favored the removal of Cr(III) from post tanning wastewater by coagulation (removal extent 82%-99%). But the Cr(III) complexes with acrylic resins existed as water-soluble pieces, probably because a part of free carboxyl group still kept on the polymer chain at reaction equilibrium, and acrylic resins had no structure/group with hydrophobicity as strong as benzene ring. As a result, Cr(III) was difficult to be removed from wastewater when acrylic resins existed (removal extent <60%). That is, the formation of Cr(III)-acrylic resin complexes is the major obstacle in removing Cr(III) effectively from post tanning wastewater.

Introduction

Nowadays, more than 90% of leather goods are made from chrome leather due to its excellent physical properties and comfortable handle.[1] However, the production of chrome leather has been of high concern because it discharges chrome-containing wastewaters from tanning and post tanning procedures, and generates chrome-containing solid wastes during shaving and trimming operations.[2-4] In order to reduce the discharge of the chrome in tannery wastewaters, many technologies, such as alkaline precipitation,[5,6] coagulation,[7] adsorption,[8] membrane separation[9] and electrolytic method[10], have been investigated. Among these technologies, alkaline precipitation and coagulation are preferable because of the simple treatment procedures and low cost. Unfortunately, it was found that alkaline precipitation and coagulation are inefficient in removing Cr(III) from the post tanning wastewater that has an average Cr(III) concentration around 100 mg/L.[11,12] This is due to the fact that the Cr(III) in the post tanning wastewater can form water-soluble negative charged Cr(III)-organics complexes with the residual anionic leather chemicals, which are rather difficult to be alkali-precipitated or to be coagulated.[13-16] This is also the main reason why the concentration of Cr(III) in wastewaters discharged from most of tanneries in China cannot reach the discharge standard (1.5 mg/L at workshop outlet) by using common treatments. Therefore, in order to remove Cr(III) from the post tanning wastewater effectively and economically, it is necessary to fully understand the effects of post tanning chemicals in wastewater on the removal of Cr(III).

In this study, we first investigated the status of Cr(III) complexes with typical post tanning chemicals and its effect on the removal efficiencies of Cr(III) and total organic carbon (TOC) from post tanning wastewaters through coagulation with polyaluminum chloride (PAC). Here, the simulated post tanning wastewaters were prepared by mixing chrome powder with vegetable tannins, phenolic syntans, acrylic resins, acid dye, direct dye and sulfonated fatliquoring agents, respectively. To determine which post tanning chemicals have priority to complex with Cr(III) and dominate the removal efficiency of Cr(III) from post tanning wastewater, the Cr(III)-binding abilities of the post tanning chemicals were detected using a fluorescence quenching titration method. Considering the fact that Cr(III) mainly complex with the anionic hydrophilic groups (e.g., carboxyl, sulfonic acid group and phenolic hydroxyl) of post tanning chemicals, pyrocatechol (PC), poly(acrylic acid) (PAA), sodium

p-styrene sulfonate (SSS) and sodium allylsulfonate (SAS) were chosen as the models of post tanning chemicals to react with Cr(III) under different concentrations. Then, the fluorescence emission spectra of the reaction solutions were analyzed by the Ryan-Weber quenching model to evaluate the Cr(III)-binding abilities of post tanning chemicals.

Experimental

Materials

Chrome powder (25.6% Cr_2O_3, 33.0% basicity) was provided by Brother Enterprises Holding Co., Ltd. Black wattle extract (tannin content 61.2%), valonea extract (tannin content 63.5%), auxiliary syntan (30.0 wt.% in H_2O), replacement syntan (powder), acrylic resins (M_n 40,000, 35 wt.% in H_2O) including poly(acrylic acid) (PAA), poly(acrylic acid-*co*-butyl methacrylate) (P(AA-BMA)) and poly(acrylic acid-*co*-acrylamide) (P(AA-AM)), and sulphated castor oil were provided by Sichuan Tingjiang New Material, Inc. Acid orange II and direct sky blue 5B were purchased from Kelong Chemical Reagent Factory and Tianjin Dyestuff Chemical Factory, respectively. Sulfonated oil was purchased from Zschimmer & Schwarz Chemical (Foshan) Co. Ltd. Polyaluminum chloride (PAC) was purchased from Gongyi Midea Water Purifying Material Co., Ltd. $CrCl_3{\cdot}6H_2O$ of analytical grade was purchased from Kelong Chemical Reagent Factory. Pyrocatechol (PC), sodium p-styrenesulfonate (SSS) and sodium allylsulfonate (SAS) of analytical grade were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Preparation of Simulated Post Tanning Wastewater

A series of Cr(III)-post tanning chemical solutions were prepared by mixing a certain amount of chrome powder and typical post tanning chemicals in distilled water, respectively. Here, the post tanning chemicals were black wattle extract, valonea extract, auxiliary syntan, replacement syntan, PAA, P(AA-BMA), P(AA-AM), acid orange II, direct sky blue 5B, sulphated castor oil and sulfonated oil, respectively. The Cr(III)-post tanning chemical solutions were adjusted to pH 4.0 by using 1.0 mol/L NaOH or 1.0 mol/L HCl, incubated at 40°C for 2 h and then cooled to room temperature. The digital photos of these Cr(III)-post tanning chemical solutions were subsequently taken for observing the status of Cr(III) complexes with typical post tanning chemicals. After filtering by using 400 mesh filter cloth, the filtrates of the Cr(III)-post tanning chemical solutions were collected as simulated post tanning wastewaters. The concentrations of Cr(III) and TOC in the simulated post tanning wastewaters were listed in Table 1. Meanwhile, the aqueous solutions of post tanning chemicals without addition of chrome powder were prepared as the control and observed by digital photo.

Removal of Cr(III) and TOC from the Simulated Post Tanning Wastewater by Coagulation

The pH values of the simulated post tanning wastewaters were adjusted to 5, 6, 7, 8 and 9 by using 0.1 mol/L NaOH or 0.1 mol/L HCl, respectively. Then, PAC was added into the wastewaters to attain an Al concentration of 85.0 mg/L. Here, the dosage of PAC was optimized by our preliminary experiments. The wastewaters were then placed at room temperature for 30 min and centrifuged at 5000 r/min for 5 min. Subsequently, the supernatants were taken for

Table I
Concentrations of Cr(III) and TOC in the simulated post tanning wastewaters.[a]

Simulated post tanning wastewaters	Concentration of Cr(III) (mg/L) [b]	Concentration of TOC (mg/L) [c]
Cr(III)-black wattle extract	27.3	643.2
Cr(III)-valonea extract	37.7	637.0
Cr(III)-auxiliary syntan	41.2	1136.2
Cr(III)-replacement syntan	40.6	1067.7
Cr(III)-PAA	46.4	541.6
Cr(III)-P(AA-BMA)	42.8	513.3
Cr(III)-P(AA-AM)	43.7	620.6
Cr(III)-acid orange II	29.7	1016.6
Cr(III)-direct sky blue 5B	32.8	513.2
Cr(III)-sulphated castor oil	47.6	1713.1
Cr(III)-sulfonated oil	46.5	2525.0

a) More than 95% of Cr(III) in the simulated post tanning wastewaters were negative charged Cr(III) complexes, and little Cr(III) and TOC could be removed by alkaline precipitation in our preliminary experiments.
b) The concentration of Cr(III) was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 8000DV, PerkinElmer, USA) after digesting 3 mL of the simulated wastewater with 10 mL of 65% HNO_3 and 5 mL 30% H_2O_2.
c) The concentration of TOC was measured using a TOC analyzer (TOC, vario, Elementar, Germany).

the measurement of Cr(III) and TOC concentrations (named as residual Cr(III) and TOC concentrations) by ICP-AES and TOC analyzer, respectively. The Cr(III) and TOC concentrations of the simulated post tanning wastewaters before coagulation, as shown in Table 1, were recorded as the initial Cr(III) and TOC concentrations. The removal efficiencies of Cr(III) and TOC from the wastewater by coagulation were calculated as:

$$\% \text{ removal efficiency of Cr(III)} = \frac{\text{initial Cr(III)concentration - residual Cr(III)concentration}}{\text{initial Cr(III)concentration}} \times 100 \quad (1)$$

$$\% \text{ removal efficiency of TOC} = \frac{\text{initial TOC - residual TOC}}{\text{initial TOC}} \times 100 \quad (2)$$

Analysis of Cr(III)-binding Ability of Model Post Tanning Chemicals

The Cr(III)-binding abilities of model post tanning chemicals, viz. PC, PAA, SSS and SAS were analyzed by using the fluorescence quenching titration method.[17-19] CrCl$_3$·6H$_2$O, PC, PAA, SSS and SAS were employed to prepare a series of Cr(III)-PC, Cr(III)-PAA, Cr(III)-SSS and Cr(III)-SAS aqueous solutions. Here, the concentration of Cr(III) in these solutions was 0, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2 and 3.6 mmol/L respectively, while the concentrations of phenolic hydroxyl in Cr(III)-PC solutions, carboxyl in Cr(III)-PAA solutions and sulfonic acid group in Cr(III)-SAS or Cr(III)-SSS solutions were all 83.0 mmol/L. After adjusting pH to 5, all the solutions were kept at room temperature in the dark for 30 min to ensure a primary equilibrium of complexation. Then, the fluorescence emission spectra of the Cr(III)-PC, Cr(III)-PAA, Cr(III)-SSS and Cr(III)-SAS solutions were recorded on a fluorescence spectrophotometer (Cary Eclipse, Varian, USA) with their maximum excitation wavelengths of 290 nm, 320 nm, 320 nm and 260 nm, respectively. Finally, conditional stability constant K_M and binding capacity C_L (total ligand concentration, mmol/L) calculated by fitting the titration results with the Ryan-Weber equation[20,21]:

$$\frac{F}{F_0} = 1 + (\frac{F_{ML}}{F_0} - 1)(\frac{1}{2K_M C_L})[1 + K_M C_L + K_M C_M - \sqrt{(1 + K_M C_L + K_M C_M)^2 - 4K_M^2 C_L C_M}] \quad (3)$$

where F_0 and F are the fluorescence intensities of model post tanning chemical solution without addition of Cr(III) and with addition of Cr(III), respectively, and F_{ML} is the limited fluorescence intensity of model post tanning solution at a Cr(III) concentration of C_M.

Results and Discussion

Effect of Status of Cr(III) Complexes on Removal of Cr(III) from Wastewater

It is known that the existential state of contaminants in wastewater is an important factor influencing their removal from wastewater. The contaminants existing as hydrophobic

colloids or particles are easy to be removed from wastewater, while it is difficult to remove contaminants in the form of soluble status in wastewater.[22,23] Herein, one of our purposes was to investigate the relationship between the status of Cr(III) complexes in post tanning wastewater and the feasibility of removing Cr(III) from the wastewater. At first, a series of solutions of post tanning chemicals and Cr(III)-post tanning chemicals were prepared and observed. As shown in Figure 1(A), all the aqueous solutions of the typical post chemicals were clear except that P(AA-BMA) solution was a stable emulsion. From Figure 1(B), it can be seen that there was some precipitate in the Cr(III)-black wattle extract, Cr(III)-acid orange II and Cr(III)-direct sky blue 5B solutions, and that the solutions of Cr(III)-valonea extract, Cr(III)- auxiliary syntan and Cr(III)-replacement syntan were in the form of suspension liquid. These phenomena were ascribed to the fact that, after reacting with Cr(III), the hydrophilicity of black wattle extract, acid orange II, direct sky blue 5B, valonea extract and syntans was remarkably decreased, which led to the formation of precipitate or hydrophobic colloids. It is interesting to observe that the solutions of Cr(III)-PAA, Cr(III)-P(AA-BMA), Cr(III)-P(AA-AM), Cr(III)-sulphated castor oil and Cr(III)-sulfonated oil were still clear and stable. This implicated that there were still enough free hydrophilic groups in PAA, P(AA-BMA), P(AA-AM), sulphated castor oil and sulfonated oil molecules even they complexed with Cr(III), which gave the complexes good hydrophilicity. These facts also explained why the Cr(III) concentrations in the simulated post tanning wastewaters (the filtrates of the Cr(III)- post tanning chemical solutions) of Cr(III)-black wattle extract, Cr(III)-acid
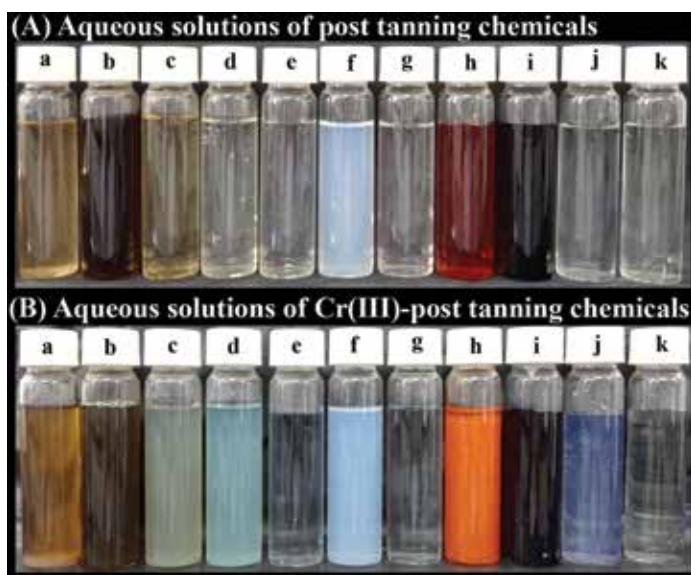

Figure 1. Digital photos of aqueous solutions of post tanning chemicals (A) and Cr(III)-post tanning chemicals (B). The post tanning chemicals were black wattle extract (a), valonea extract (b), auxiliary syntan (c), replacement syntan (d), PAA (e), P(AA-BMA) (f), P(A-AM) (g), acid orange II (h), direct sky blue 5B (i), sulphated castor oil (j) and sulfonated oil (k), respectively.

orange II, Cr(III)-direct sky blue 5B, Cr(III)-valonea extract, Cr(III)-auxiliary syntan and Cr(III)-replacement syntan were lower than those of the simulated wastewaters of Cr(III)-PAA, Cr(III)-P(AA-BMA), Cr(III)-P(AA-AM), Cr(III)-sulphated castor oil and Cr(III)-sulfonated oil (see Table 1).

The removal efficiencies of Cr(III) and TOC from the simulated post tanning wastewaters through PAC coagulation were subsequently determined. As can be seen in Figures 2a, 2b and 2d, the maximum removal efficiencies of Cr(III) from the

simulated post tanning wastewaters of Cr(III)-black wattle extract, Cr(III)-valonea extract, Cr(III)-auxiliary syntan, Cr(III)-replacement syntan, Cr(III)-acid orange II and Cr(III)-direct sky blue 5B reached 98.7%, 95.2%, 99.5%, 82.4%, 98.5% and 99.2%, respectively. The high removal efficiencies of Cr(III) should be due to the fact that hydrophobic colloid or particle was formed when Cr(III) complexed with those chemicals, as observed in Figure 1, which are easy to be removed by coagulation. According to Figures 2c and 2e, the maximum removal efficiencies of Cr(III) from the simulated wastewaters of
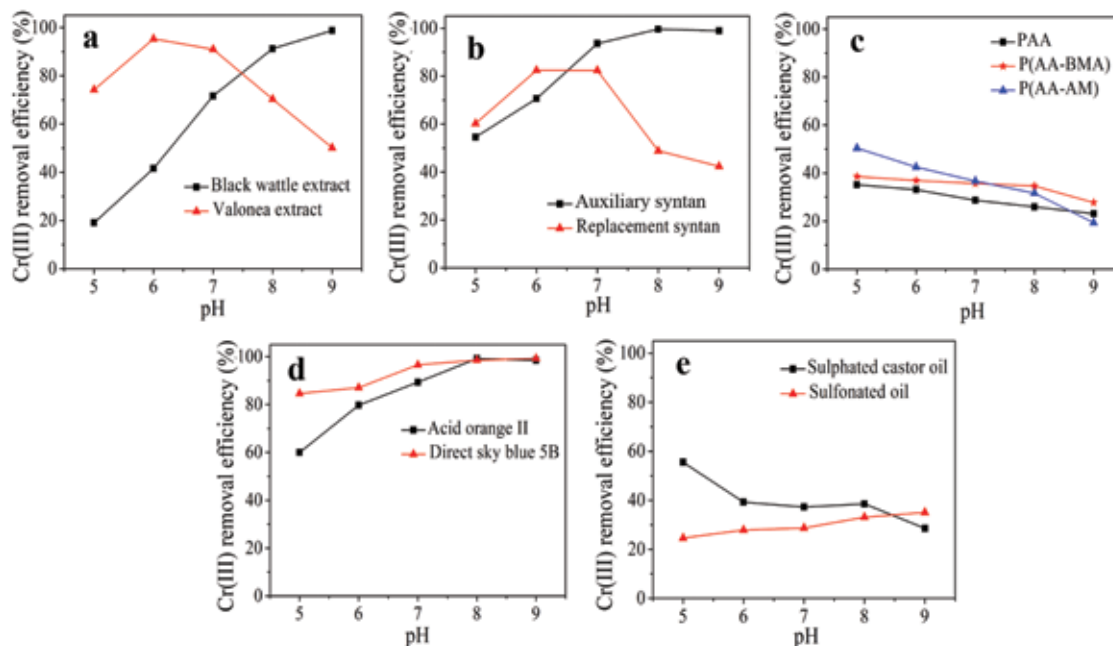

Figure 2. Effect of post tanning chemicals on removal of Cr(III) from simulated post tanning wastewaters.
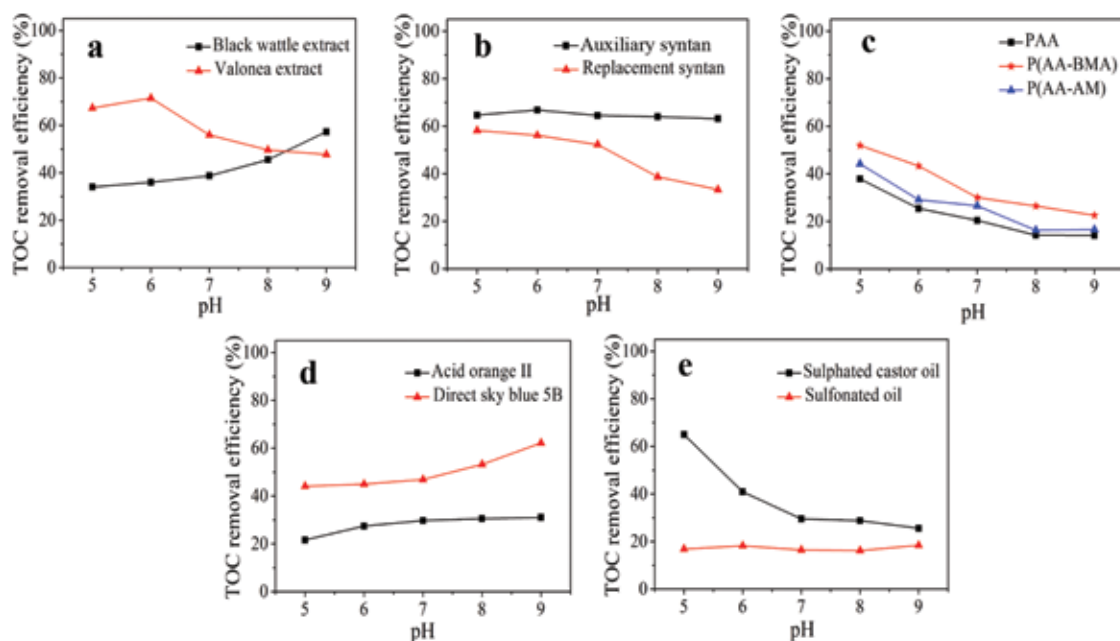

Figure 3. Effect of post tanning chemicals on removal of TOC from simulated post tanning wastewaters.

Cr(III)-PAA, Cr(III)-P(AA-BMA), Cr(III)-P(A-AM), Cr(III)-sulphated castor oil and Cr(III)-sulfonated oil were less than 60%, which was mainly attributed to the solubility/hydrophilicity of complexes formed by Cr(III) and these chemicals. All these results indicated that the status of Cr(III) complexes in post tanning wastewater is closely related to the removal efficiency of Cr(III) from the wastewater. The Cr(III) complexes in the form of hydrophobic colloid or particle can be removed more easily than those with solubility.

Comparing Figures 2 and 3, it was evident that, after PAC coagulation, the removal efficiencies of TOC from the wastewaters of Cr(III)-black wattle extract, Cr(III)-valonea extract, Cr(III)-auxiliary syntan, Cr(III)-replacement syntan, Cr(III)-acid orange II and Cr(III)-direct sky blue 5B were much lower than those of Cr(III). This should be due to the fact that a part of these post tanning chemicals did not complex with Cr(III) and existed as water-soluble matter in wastewater, which are difficult to be removed by coagulation. The removal efficiencies of TOC from the wastewaters of Cr(III)-PAA, Cr(III)-P(AA-BMA), Cr(III)-P(AA-AM), Cr(III)-sulphated castor oil and Cr(III)-sulfonated oil were similar to those of Cr(III), suggesting that these chemicals and their Cr(III) complexes with good hydrophilicity were all difficult to be removed.

Cr(III)-binding Abilities of Model Post Tanning Chemicals
Generally, retanning agents, dyes and fatliquoring agents coexist in actual post tanning wastewater. Most of the anionic hydrophilic groups of post tanning chemicals, such as phenolic hydroxyl, carboxyl and sulfonic acid group, can complex with the Cr(III) released from leather during post tanning processes. In order to evaluate the priority of these hydrophilic groups in complexing with Cr(III) and find the Cr(III) complexes that primarily affects the removal of Cr(III) from post tanning wastewater, PC with phenolic hydroxyl group, PAA with carboxyl on polymer, SSS with sulfonic acid group on benzene ring and SAS with sulfonic acid group on aliphatic chain were chosen as model post tanning chemicals to investigate the Cr(III)-binding abilities of typical hydrophilic groups of post tanning chemicals.

Figure 4 shows the fluorescence emission spectra of PC, PAA, SSS and SAS in the presence of Cr(III) at different concentrations (termed as Cr(III) titration in this determination method).
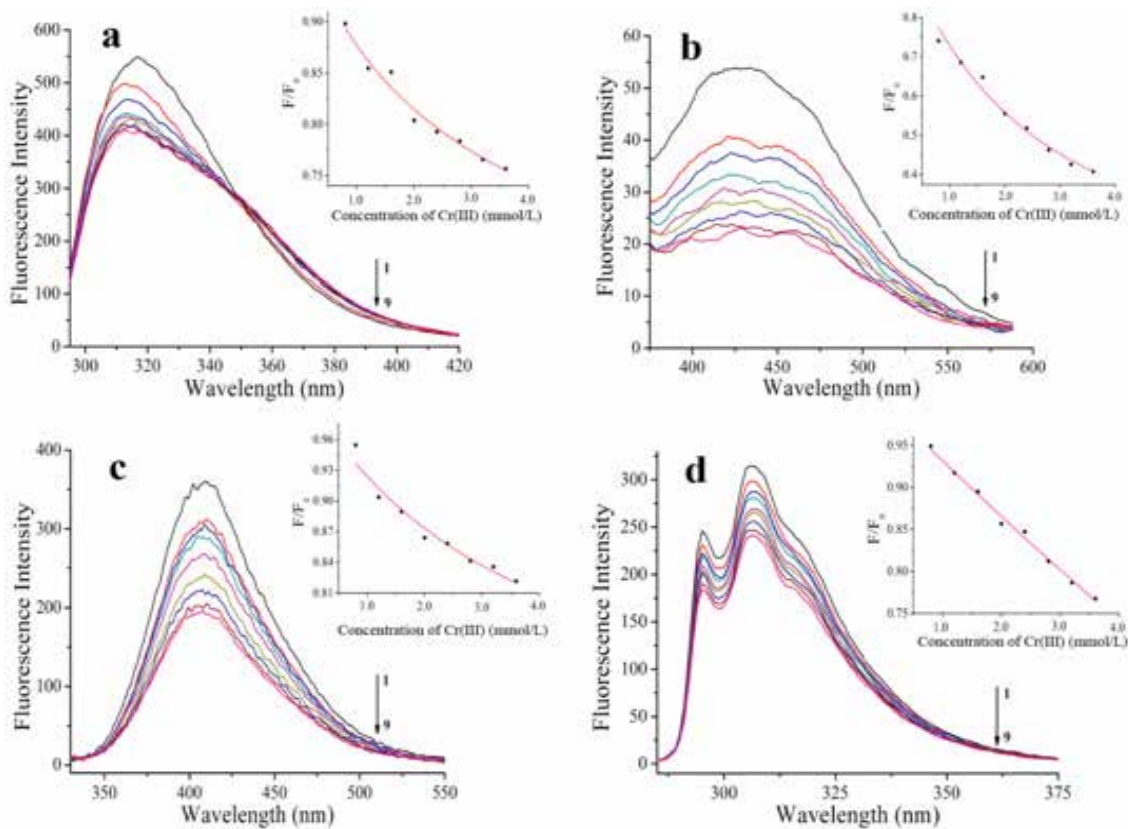

Figure 4. Fluorescence emission spectra of PC (a), PAA (b), SSS (c) and SAS (d) in the presence of Cr(III) (curves 1-9 correspond to Cr(III) concentrations 0, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2 and 3.6 mmol/L, respectively). Concentrations of phenolic hydroxyl group in PC solution, carboxyl in PAA solution, sulfonic acid group in SSS and SAS solutions are all 83.0 mmol/L. Inset: Ryan-Weber model plots of F/F_0 of PC (a), PAA (b), SSS (c) and SAS (d) against Cr(III) concentration.

The fluorescence intensities of PC, PAA, SSS and SAS gradually decreased with increasing concentration of Cr(III), which indicated that the interactions occurred between PC, PAA, SSS and SAS and Cr(III), resulting in the formation of Cr(III)-PC, Cr(III)-PAA, Cr(III)-SSS and Cr(III)-SAS complexes.[24] Based on the Ryan-Weber model, the fitting plots of F/F_0 of PC, PAA, SSS and SAS against Cr(III) concentration are displayed in the insets of Figure 4, and the Cr(III)-binding parameters of PC, PAA, SSS and SAS are detailed in Table 2. It can be seen that the titration results of PC, PAA, SSS and SAS can be well described by Ryan-Weber equation with the correlation coefficients higher than 0.99.

According to the fact that a higher log K_M value means a greater Cr(III)-binding ability, the data in Table 2 indicated that the Cr(III)-binding abilities of phenolic hydroxyl of PC and carboxyl of PAA were greater than those of sulfonic group on aliphatic chain of SAS and sulfonic group on benzene ring of SSS, which is attributed to better electro-donating ability of phenolic hydroxyl and carboxyl.[25,26] These results implied that Cr(III) could preferentially react with phenolic hydroxyls of vegetable tannins and syntans to form Cr(III) complexes. Thus, these kinds of complexes mainly existed in the form of hydrophobic colloid or particle, as presented in Figure 1, due to the blocking effect of the hydrophilic groups of vegetable tannins or syntans through complexing, as well as their hydrophobic benzene ring structure in particular. This explains why Cr(III) is easy to be removed from the simulated post tanning wastewaters of Cr(III)-vegetable tannins and Cr(III)-syntans by coagulation, as observed in the above section. As for dyes acid orange II and direct sky blue 5B, their sulfonic groups have relatively weaker Cr(III)-binding ability. But their complexes with Cr(III) were still in the form of hydrophobic colloid or particle (see Figure 1), and the extents of Cr(III) removal from the simulated post tanning wastewaters of Cr(III)-dye were higher than 98.5% after coagulation (see the above section). This should be mainly due to the hydrophobic benzene ring structure in the dye molecules.

Cr(III) could also react with carboxyl group of acrylic resins easily, although the log K_M value of PAA is a little lower than that of PC. But a part of free carboxyl groups would be still kept on the polymer chain at reaction equilibrium, due to the abundant content of carboxyl group on acrylic resins. Meanwhile, acrylic resins have no structure/group with hydrophobicity as strong as benzene ring. As a result, the Cr(III)-acrylic resin complexes mainly exist as water-soluble pieces and become difficult to be removed from wastewater, as observed in the above section. So, the formation of water-soluble Cr(III)-acrylic resin complexes should be the major obstacle in removing Cr(III) effectively from post tanning wastewater.

Conclusions

The status of Cr(III) complexes in post tanning wastewater is closely related to the removal efficiency of Cr(III) from the wastewater. The Cr(III) complexes existing as hydrophobic colloid or particle, such as Cr(III)-vegelable tannins, Cr(III)-syntans and Cr(III)-dyes complexes, can be effectively removed from wastewater by coagulation. The Cr(III) complexed with acrylic resins was difficult to be removed because of the good solubility of the complexes. Therefore, the future work should focus on the development of an efficient method for removal of Cr(III)-acrylic resin complexes from post tanning wastewater so that the Cr(III) concentration of tannery wastewater could meet the discharge standard.

Acknowledgements

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Table II
Cr(III)-binding parameters of model post tanning chemicals calculated by Ryan-Weber model.

Sample	log K_M	R^2
PC	3.02	0.994
PAA	2.85	0.992
SSS	2.41	0.995
SAS	2.72	0.991

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