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Research Article

Simultaneously Recovering High-Purity Chromium and Removing Organic Pollutants from Tannery Effluent

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Chromium pollution is a serious issue because of carcinogenic toxicities of the pollutants and low recovery rate of chromium because of the presence of organic, such as protein and fat. In this work, high recovery rate and high purity of the chromium ion were successfully prepared by the way of acid enzyme, flocculant, and Fenton oxidation. The experiments were characterized by TG, TOC, UV-VIS, and SEM. In the work, the tannery waste chrome liquor was used as experimental material. The results showed that the percentage of reduction of TOC in the tannery waste chrome liquor by method of Fenton oxidation, acid enzyme, and the flocculant was 71.15%, 65.26%, and 22.05%, respectively. Therefore, the organism content of chrome tanning waste liquid was greatly reduced through the pretreatment. And the application experiment showed that the properties and grain surface and fibers of the tanned leather with commercial chromium powder and chrome tanning agent prepared from the chromium waste liquid treated with Fenton are nearly the same.

1. Introduction

In recent years, the environmental pollution problems involved with the emissions of tannery sludge with chromium are increasing, which bring a huge challenge for society. Chrome tanning is the most popular tanning system in leather industry and the quality of leather is excellently prepared by this method. The tanning process produces leather from the skin and it offers excellent hydrothermal stability, better dyeing characteristics, and softness to the leather [1, 2]. With the development of the economy, the demand for leather products is also increasing significantly. However, only 70–80% of chromium is absorbed by leather during the process of chrome tanning, and the rest is discharged in effluent. There are still excessive amounts of chromium in the biological sludge after the tannery waste treatment, which result in accumulation of the metals in soil [3, 4]. In spite of the fact that trivalent chromium is used to the leather tanning agent and is believed to be good for health frequently, it could be translated into carcinogenic hexavalent chromium and chrome has an effect on the soil fertility. Meanwhile, a great number of organic pollutants such as protein and fat are generated in the tanning industry [5–7]. The chromium ions will coordinate with organics, which can not only decrease the purity of chrome leading to the poor quality of the chrome tanning agent, poor economic returns, and indirect waste of resource but also bring about environmental problems leading to various side effects and carcinogenic nature in water and bodies [8–12].

There are many different methods available to recycle and reuse the chromium, which include chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation, coagulation, and adsorption [13]. Unfortunately, almost all of the solutions proposed have not taken the removal of organic pollutants into account so that the recovered chromium had a poor purity, leading to the poor color of the chrome tanning agent and the poor quality of leather after tanning by recovery chrome powder. The mechanism of chrome tanned proposed by Huttleworth is that appropriate size of chromium complexes could combine with carboxylic ions in collagen side chain after into the bare skin [14]. So, the presence of organic impurities could increase the molecular weight of chrome tanning agent and it would be hard to enter naked skin, leading to the poor effect of tanning. This reaction is expressed as shown in the following equation:

$$\mathrm{P{-}\overset{\overset{O}{\|}}{C}{-}O^-} + \left[\mathrm{Cr(H_2O)_6}\right]_3 \longrightarrow \left[\mathrm{P{-}\overset{\overset{O}{\|}}{C}{-}O{-}Cr(H_2O)_6}\right]^{2+} \quad (1)$$

In the present work, there are three ways to deal with chromium waste liquid: Fenton oxidation, enzymatic degradation, and flocculation. The Fenton oxidation not only allows separating the suspended substances without affecting the form of chrome but also results in partial decomposition of the organic impurities in the chromium waste liquid [15, 16]. Enzymes are typical agents of green technology. Recently, enzymes have been widely used in leather manufacture [17–20]. The flocculants can be used to subside and remove the organic impurity, purifying the chrome liquor [21].

2. Materials and Methods

The waste chrome tanning liquor was collected from the industrial park, Zhanhua, Shandong, without any treatment. The chromium content of chromium waste liquid was 6.8 g/L by method of sodium peroxide. Acid protease (1000 U/g) and acid lipase (2400 U/g) enzymes are all from Novozymes. The organic flocculant (cationic polyacrylamide, 1 g/L) and inorganic flocculent (polyaluminium chloride, 30 g/L) were purchased from Ryan Hunan Chemical Technology Co., Ltd. The amount-of-substance concentration of H_2O_2 (30% w/v) and Fe^{2+} ($FeSO_4{\cdot}7H_2O$) was 7.5 mmol/L and 0.3 mmol/L, respectively [22]. Other drug reagents used in this study were of analytical grade.

A UV-VIS spectrophotometer (UV-2550, Shimadzu) was used to investigate the optical absorption of the chromium ion. Total organic carbon analyzer (TOC-LCPH, Shimadzu) was used to measure TOC of the chrome liquor. The weight of organic matter in chromium sludge sedimentation precipitated by the sodium hydroxide was measured with thermogravimetry (TG). Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700 field-emission scanning electron microscope to compare their differences in the structure of grain surface. The shrinkage temperature of leather after tanning was measured by a MSW-YD4 shrinkage meter according to Chinese Industrial Standard (QB/T 2713-2005). A known weight (ca. 1 g) of the sample was treated by dry digestion and the measurement of the amount of Cr_2O_3 followed Chinese Industrial Standard (QB/T 3812.15-1999). The leathers after tanning were assessed for color, grain tightness, strength, and fullness by hand and visual examination of experienced tanners.

2.1. Fenton Treatment. Firstly, in order to observe the influence of Fenton oxidation on valence of chromium ion, the reactions were carried out by the UV-VIS spectrophotometer (UV-2550) in order to meet the norm (0.5 ppm) specified by China's environmental regulatory agency. Then, preliminary experiments were carried out to determine the amount of Fenton reagent. Moreover, the experiments on optimization of pH (1–6 and control group), optimization of time (0.5–4.5 h and control group), and the optimization of temperature (30–90°C and control group) were carried out. Lastly, the tannery waste chrome liquor was measured by total organic carbon analyzer which was diluted from 5 mL to 50 mL.

Table 1: The combination of two enzyme activities.

The enzyme activity of protease (U)	0	1.8	2.7	3.6	4.5
The enzyme activity of lipase (U)	0	14.4	21.6	28.8	36

Table 2: The dose of combination of two flocculants.

Polyaluminium chloride (mL)	0.7	1.0	0.5	1.2	0.4
Cationic polyacrylamide (mL)	0.7	0.5	1.0	0.4	1.2

2.2. Acid Enzyme Treatment. The reactions were carried out in the same five beakers with the acid protease activity of 0 U, 225 U, 450 U, 675 U, and 1200 U, respectively. The reactions were carried out in the same five beakers with the acid lipase activity of 0 U, 60 U, 96 U, 144 U, and 300 U, respectively. Similarly, combination of two enzymes was carried out in the same five beakers (Table 1). And then the tannery waste chrome liquor was measured by total organic carbon analyzer every two hours at 40°C, which was diluted from 5 mL to 50 mL.

2.3. Flocculant Treatment. When the volume of tannery waste chrome liquor is 50 mL, the reactions were carried out to determine the optimal conditions on polyaluminium chloride treatment with the change of the dose (0–1.6 mL), pH (3.0–5.5), temperature (30–50°C), and the time (30–150 min). Similarly, the optimal conditions were determined on cationic polyacrylamide treatment. Moreover, combination of two flocculants was carried out in the same five beakers with the dose of Table 2. Then, the tannery waste chrome liquor was measured by total organic carbon analyzer which was diluted from 5 mL to 50 mL.

2.4. The Weight of Organic Matter. The chromium sludge precipitated under optimum conditions by the sodium hydroxide in the study and the original chromium sludge precipitated by the sodium hydroxide from leather factory were determined using thermogravimetry (TG) at 550°C for 24 h to observe their weights of organic matter [23].

2.5. Application of Chrome Tanning Agent. The pretreated tannery waste chrome liquor was used to tan goatskin, respectively, with the amount of 47 mL, and the usage amount of chrome tanning agent was 1.84 g in the work [24]. Then, properties and morphologies of grain surface and fibers of the tanned leather were surveyed, respectively.

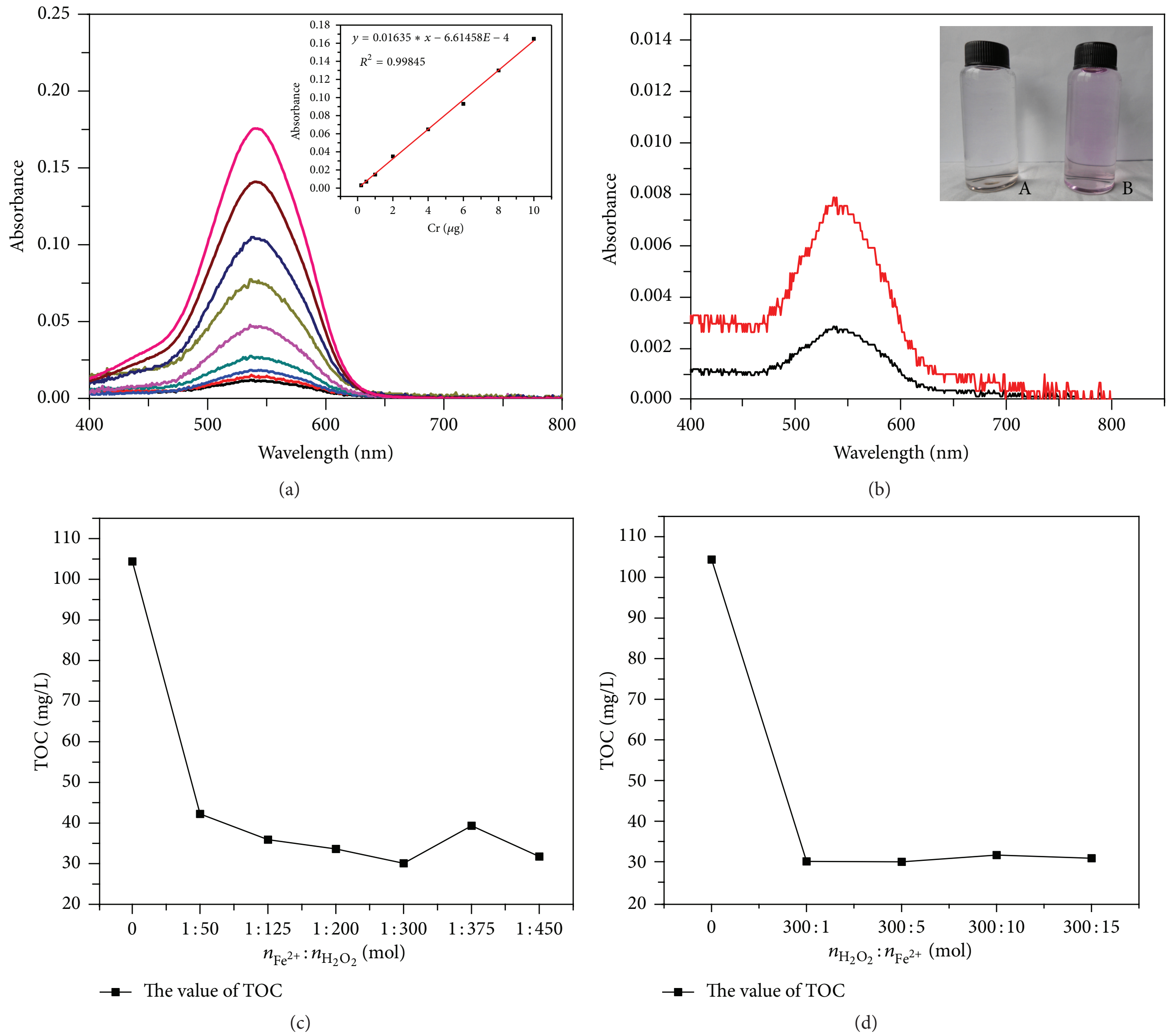


FIGURE 1: The curve of absorbance corresponding to the wavelength and the change of TOC with the amount of Fenton reagent.

3. Results and Discussion

3.1. Fenton Treatment. The test was carried out by the way of GB/T 15555.5-1995. Figure 1(a) depicts the curve by the UV-VIS spectrophotometer (UV-2550) and a standard curve of absorbance corresponding to the chromium content. And Figure 1(b) shows the concentration of hexavalent chromium ion by oxidized and nonoxidized chromium solution. Images (A) and (B) in Figure 1(b) represent the changes of oxidized and nonoxidized chromium solutions. The results showed the concentration of hexavalent chromium ion in oxidized chromium solution complies with emission regulations.

The concentration of ferrous sulphate was a constant value and the concentration of hydrogen peroxide was constantly changing. Figure 1(c) shows the tendency of curve to decrease firstly and then to increase and lastly to decrease again with adding hydrogen peroxide. It was observed that the maximum reduction in the value of TOC was the point of 300 moL (for given $FeSO_4 \cdot 7H_2O$). This reaction is expressed as shown in the following equation: $H_2O_2 \rightarrow HO^{\bullet} + HO^{\bullet}Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^-$. The hydroxyl radicals were translated into hydroxyl lions and the hydroxyl lions could precipitate Fe^{3+} ions. And the concentration of iron is used up in the system resulting in a decrease in the rate of removal of dissolved organics in the tannery waste chrome liquor. On the other hand, the inactivation of Fe^{2+} happened at higher concentrations of H_2O_2, thus weakening the oxidation of Fenton reagent. With increasing the hydrogen peroxide, the curve emerged downward trend. That was because hydrogen peroxide oxidation itself had nothing to do with purpose of the experiment. Therefore, the point of 1 : 300 (for a given ferrous sulphate) was considered to be an optimum dosage.

Similarly, Figure 1(d) depicts the change of TOC with the amount of Fenton reagent (a certain amount of hydrogen

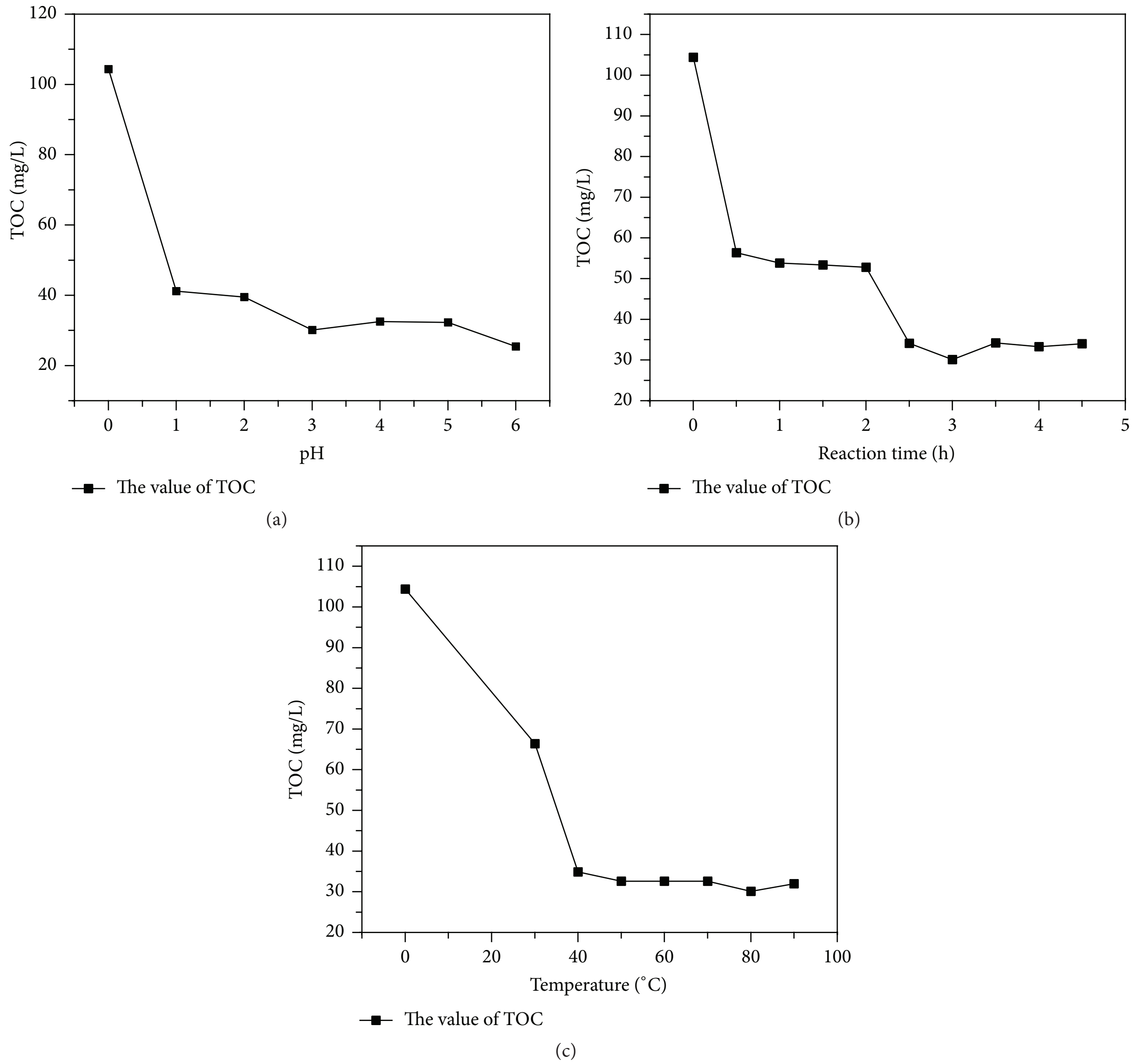


Figure 2: The change of TOC with the amount of reaction conditions (pH, time, and temperature).

peroxide). Figure 1(d) shows the tendency of rising after the first dropping with the addition of Fe^{2+}. Figure 1(d) shows the lowest point is 1 mL (a certain amount of hydrogen peroxide) in the curve. The reason could be the fact that the high dosage of Fe^{2+} enhanced the decomposition of the hydrogen peroxide, which could change into slow rate hydroxyl radicals. Therefore, when beyond this ratio (300 : 1), Fe^{2+} was destroyed and the hydroxyl ion was formed through the reaction: $OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$. The reaction happened at a great speed to form hydroxyl radical from Fe^{2+} and hydrogen peroxide. The formation of hydroxyl radical from Fe^{2+} and hydrogen peroxide could be calculated through the solubility product of ferric hydroxide [25]. Therefore, the optimization of Fenton reagent (a certain amount of hydrogen peroxide) was selected as 300 : 1.

Figure 2(a) showed the change of TOC with the amount of pH. Fenton oxidation is a well-known chemical treatment for environmental renovation and it is very sensitive to pH [26]. The work was carried out at different pH to determine the optimum pH [27, 28]. Figure 2(a) showed that the optimum pH in the study was 3.0 and the tendency of curve was to decrease firstly and then to increase on the whole. The reason could be the fact that the productivity of Fenton's oxidation decreased at high pH and this also could lead to the precipitation of Fe^{3+} by the valid hydroxyl ions. Ferric hydroxide decomposed H_2O_2 into oxygen and water, and the oxidation rate decreased because of low concentration of available hydroxyl radicals. Conversely, the consequence is reversed at low pH, and the surplus hydrogen ions accelerated the reaction which resulted in an increase in

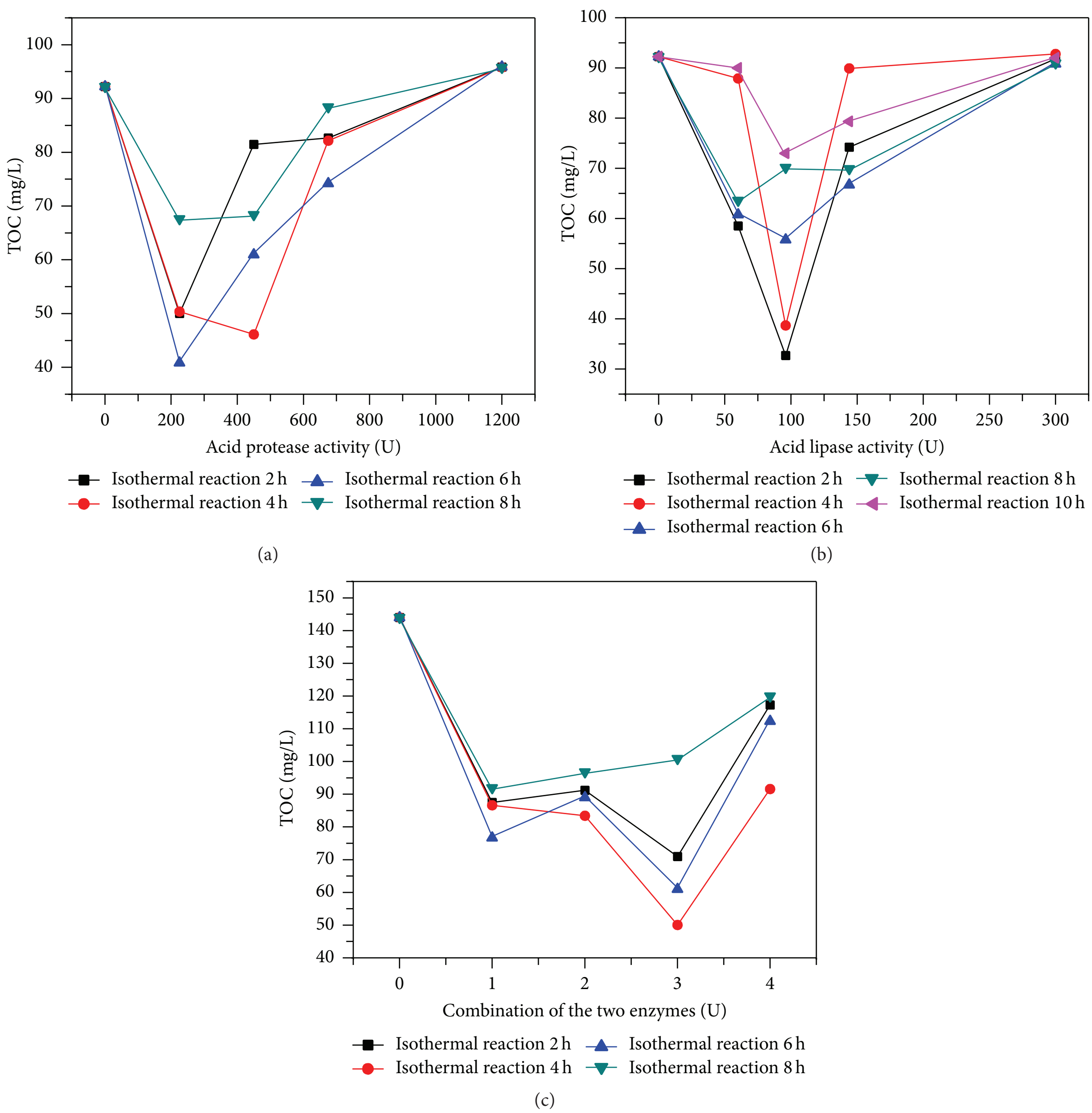


FIGURE 3: The change of TOC with the amount of acid enzyme activities (the combination of acid protease and lipase represented, resp., in (c): (0) control group, (1) 1.8 and 14.4 U, (2) 2.7 and 21.6 U, (3) 3.6 and 28.8 U, and (4) 4.5 and 36 U).

Fe^{3+} concentration [29] with the equations: $Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}OOH^{2+} + H^+$.

Reaction time is a significant factor with regard to Fenton oxidation and it was measured that Fenton reaction had a better transform with an increase in reaction time [30]. Figure 2(b) illustrates the tendency of increasing firstly and then decreasing in degradation organic with change of time. And the optimum reaction time in the study was 3 h. This principle may be the fact that hydroxyl radicals generated could be consumed by the organics in the effluent increasing with the reaction time.

Temperature is one of the important factors influencing any reaction. As seen in Figure 2(c), the temperature has a great influence on the reaction. However, the increase in temperature has two opposite influences on the reaction [31]. Although the producing of hydroxyl radicals increases at the higher temperature, hydrogen peroxide also experienced self-promoting decomposition. This is the reason for the tendency of curve to rise slowly lastly.

3.2. Acid Enzyme Treatment. Enzyme treatment did stimulate the degradation of organic, cleaning the effluent [32]. Figure 3(a) shows that the curve tends to decrease firstly and then to increase on the whole with the adding of acid protease activity. And the lowest point of isothermal reaction time on the curve is 6 hours, which was the optimum

Table 3: Properties of the tanned leather.

Sample	Color	Grain tightness	Strength	Fullness	% Cr_2O_3 in the wet blue (dry basis)	T_s (°C)
(1)	Uneven	Poor	Poor	Poor	2.7	71.4
(2)	Slightly uneven	Slightly poor	Slightly poor	Fair	3.8	89.4
(3)	Good	Good	Good	Fuller	4.3	95.2
(4)	Excellent	Good	Good	Fuller	4.9	104.2

Tanned with chrome tanning agent prepared from the untreated chromium waste liquid (1); tanned with chrome tanning agent prepared with the enzyme in the work (2); tanned with chrome tanning agent prepared with Fenton in the work (3); tanned with commercial chromium powder (4).

reaction time with the acid protease activity of 225 U. In the meanwhile, Figure 3(b) shows the similar tendency of curve to decrease firstly and then to increase on the whole with the adding of acid lipase activity. And we can see the optimum reaction time was 2 hours with the acid lipase activity of 96 U. Moreover, the curve of combination of two acid enzymes still keeps the similar tendency of decreasing firstly and then increasing on the whole. Figure 3(c) expresses that the optimum reaction condition was isothermal 4 hours and the combination of acid protease and acid lipase activity was 3.6 U and 28.8 U, respectively. The reason for this tendency could be the fact that the reactions of acid enzyme and organic were halfway, because only part of acid enzymes worked in the early stages of the reaction. Then more and more enzymes worked with the reaction process, and the reaction was sufficient at the optimum conditions. However, the value of TOC would rise with the increase of enzyme because the enzyme itself belongs to organic matter.

3.3. Flocculant Treatment. The flocculants applied in the study were organic flocculant (cationic polyacrylamide) and inorganic flocculant (polyaluminium chloride) [33]. The result showed in Figure 4(a) that the impact of flocculant treatment could be very clear with the change of dose and the curve tends to decrease firstly and then to increase slightly on the whole. The reason could be that the flocculants and the organic pollutants played an important role in the adsorption bridging action, which brings the pollutants into flocculating setting, and the organic pollutants were dropping. With the increasing of flocculants, the excess flocculants were adsorbed into the same particles. With the losing of adsorption bridging action, the effect of flocculation was reduced. Figure 4(b) showed the impact of flocculant treatment with the change of pH and the tendency of curve was to decrease. The curve changed greatly when the pH was over 5, and it was because high pH caused the precipitation of chrome, which did not agree with the experimental purpose. Figure 4(c) exhibited the impact of flocculant treatment with the change of temperature and the tendency of the curve was to decrease firstly and then to increase. The phenomenon could be due to the fact that the proper temperature was conducive to flocculant treatment. The hydrophobic interaction and hydrated ion group interaction died away and the adsorption bridging action was destroyed with high temperature, which would have an impact on the treatment of flocculant seriously. Figure 4(d) displayed the impact of flocculant treatment with the change of time and the tendency of curve was to decrease firstly and then to increase on the whole. In the adsorption bridge mechanism, the effect of flocculation was related to the reaction time. The effect of flocculation was weakened gradually with time. We can see from Figure 4(e) that the optimal dose of combination of the two flocculants was the fourth group 4 (1.2 and 0.4 mL). However, although in the optimal conditions, the elimination ratio was only 22.05%.

3.4. The Weight of Organic Matter Was Measured by Thermogravimetry (TG). Figure 5 shows the weight of organic matter between the original chromium sludge and the chromium sludge in study. The result shows that the losses of weight of chromium sludge are a big difference in 550°C so that the pretreatment of chrome waste liquid had the obvious effect on removing organics.

3.5. Tanning of Application Experiment. Assessment of organoleptic properties of wet blue leather developed in this study is given in Table 3. The color, strength, grain tightness, and fullness of the commercial chromium powder and chrome tanning agent prepared in the work are seen. The amounts of Cr_2O_3 in the tanned wet blue leathers are, respectively, given in Table 3. Obviously the chromium content in the wet blue tanned with commercial chromium powder and chrome tanning agent prepared from the treated chromium waste liquid is higher than that in the wet blue tanned with chrome tanning agent prepared from the untreated chromium waste liquid, indicating the improved uptake of the chrome due to removing organic impurities. In addition, as can be seen from Table 3, the change of shrinkage temperatures is greatly from 71.4 to 95.2°C. The reason could be the fact that the chrome tanning agent prepared from the untreated chromium waste liquid contains a lot of organic impurities so that a small amount of chromium could combine with collagen.

Scanning electron photomicrographs showing the grain surface at a magnification of 100x and 400x are shown in Figures 6(a), 6(b), 6(c), and 6(d), respectively. The grain surface in Figure 6(a) seems to be flat without any wrinkles compared to that in Figures 6(b), 6(c), and 6(d). The textures are more and more clear in Figures 6(b), 6(c), and 6(d), respectively. The texture in Figure 6(b) seems to be clear compared to that in Figure 6(a) because chrome tanned has convergent

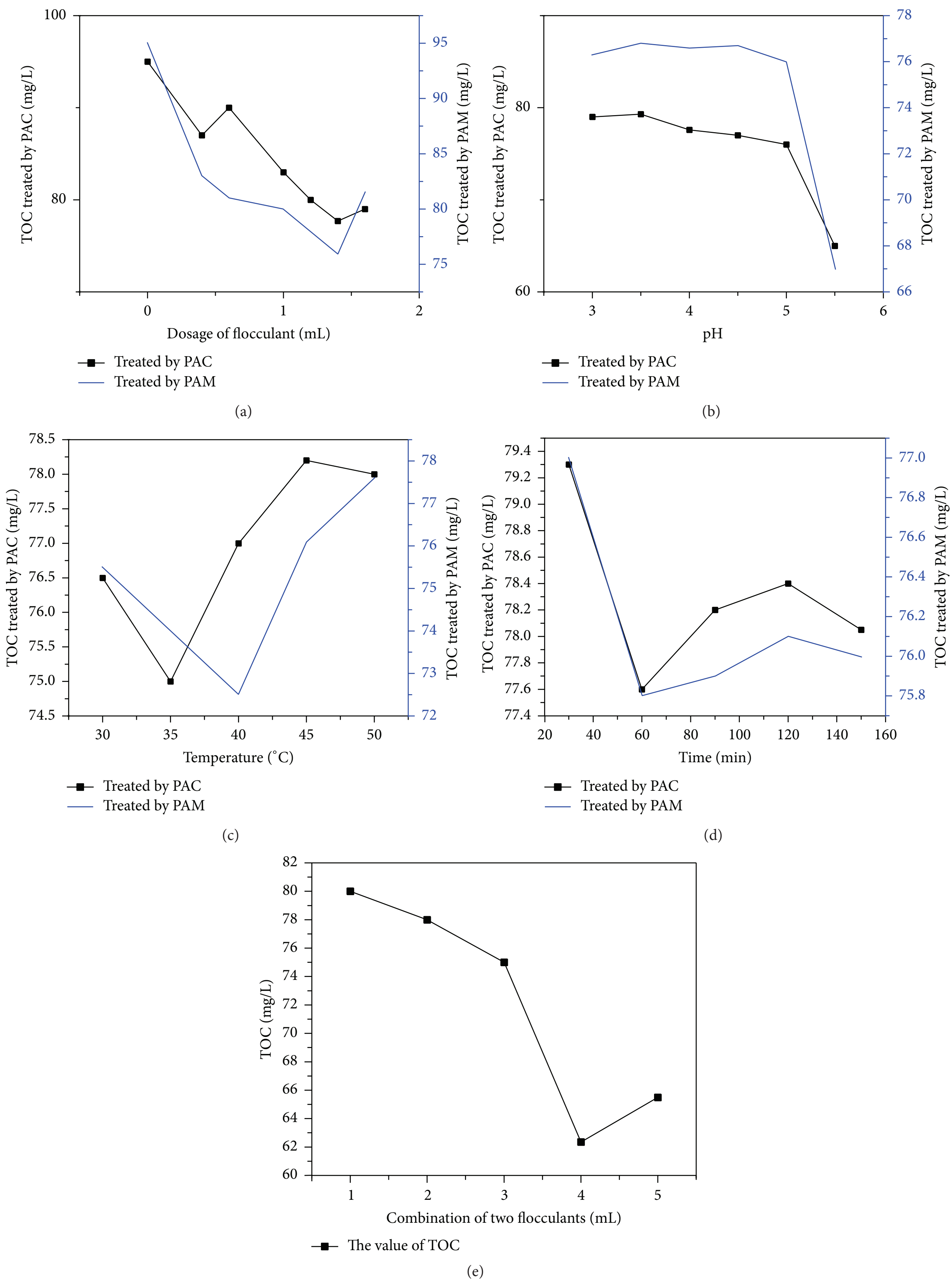


FIGURE 4: The impact on flocculant treatment with the change of reaction conditions (the combination of PAC and PAM represented, resp., in (e): (1) 0.7 and 0.7 mL, (2) 1 and 0.5 mL, (3) 0.5 and 1 mL, (4) 1.2 and 0.4 mL, and (5) 0.4 and 1.2 mL).

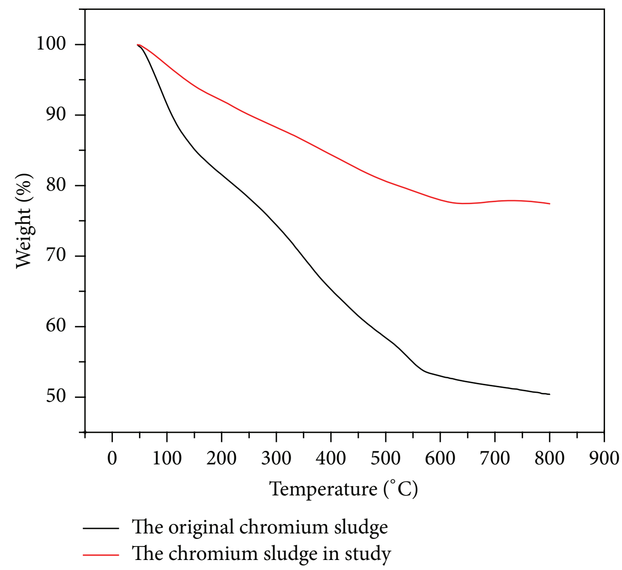
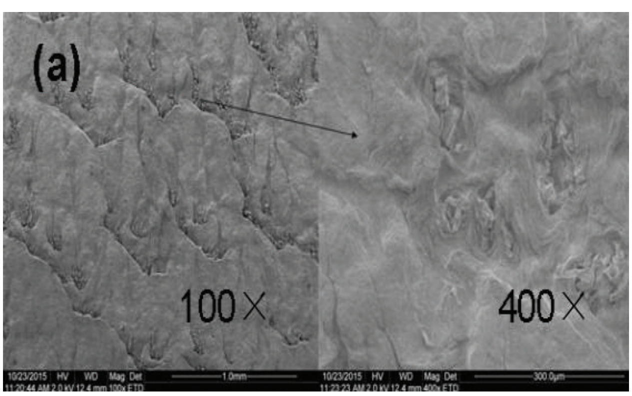
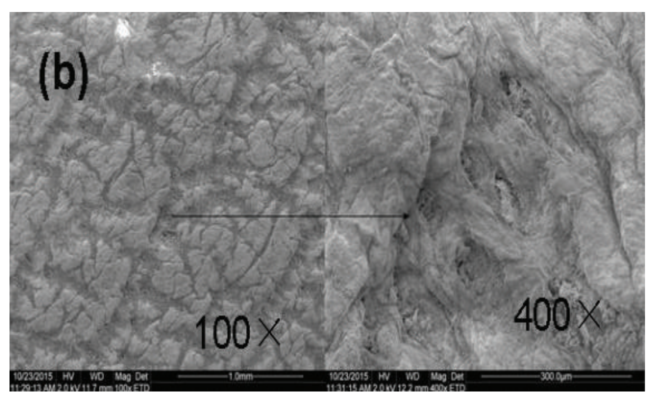


FIGURE 5: The weight of organic matter was measured by thermogravimetry (TG).



(a)



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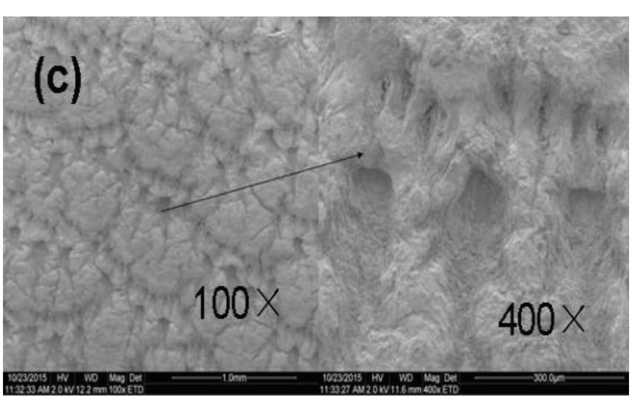

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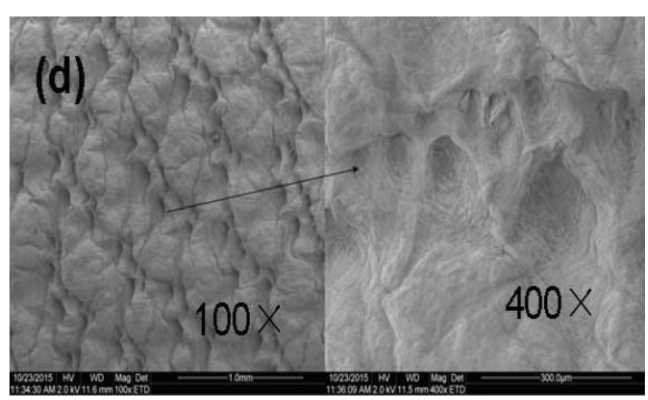
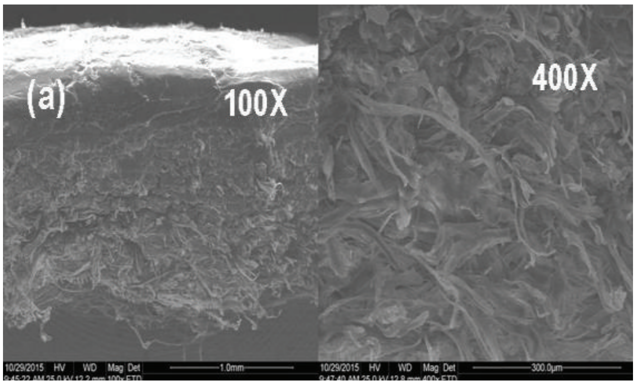
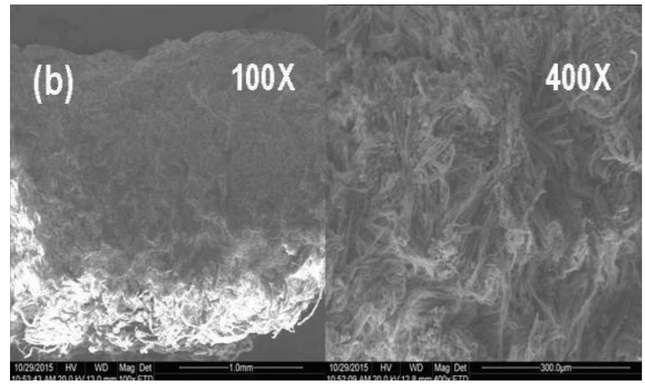


(d)

FIGURE 6: Scanning electron micrographs showing the grain surface (100x and 400x). (a) Tanned with chrome tanning agent prepared from the untreated chromium waste liquid. (b) Tanned with chrome tanning agent prepared from the chromium waste liquid treated with enzyme. (c) Tanned with chrome tanning agent prepared from the chromium waste liquid treated with Fenton. (d) Tanned with commercial chromium powder.



(a)



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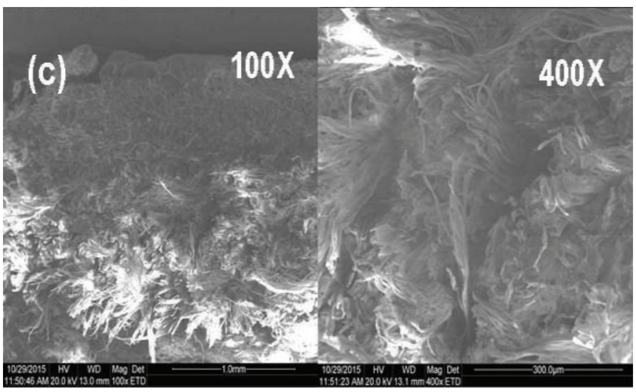
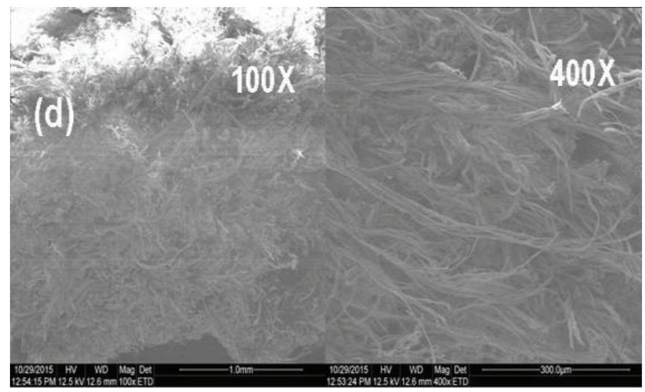


(c)



(d)

Figure 7: Scanning electron micrographs showing the cross section (100x and 400x). (a) Tanned with chrome tanning agent prepared from the untreated chromium waste liquid. (b) Tanned with chrome tanning agent prepared from the chromium waste liquid treated with enzyme. (c) Tanned with chrome tanning agent prepared from the chromium waste liquid treated with Fenton. (d) Tanned with commercial chromium powder.

effect on the grain surface. And the texture in Figure 6(c) seems to be more clear compared to the texture in Figure 6(b). This could be due to a large number of organic impurities influencing the tanning effect in Figure 6(b). Obviously, the texture in Figure 6(d) is the best. However, there is close effect between the chrome tanning agent prepared from chromium waste liquid treated with Fenton in the work and commercial powder. In addition, the three samples exhibit a clearly grained surface, indicating that there is no physical deposition of chromium.

Analogously, the SEM analyses showing cross section in a magnification of 100x and 400x, respectively, are depicted in Figure 7. The fiber bundles seem to be more and more dispersed (separation of fibers) in Figures 7(a), 7(b), 7(c), and 7(d). This is because chrome tanning agent with good tanning effect has a higher binding capacity for chromium (III), which disperses the collagen fibers more effectively. Since the combination tanned sample exhibits better opened up fiber structure, it also shows increased fullness together with softness [22, 23]. The result shows that there is close effect between the chrome tanning agent prepared from chromium waste liquid treated with Fenton in the work and commercial powder.

4. Conclusions

The treatment and recycle of chromium sludge have become key issues in the present global industrial activities. In the work, clean production technology of zero emission will be the most optimal method for sustainable growth in the leather industry [34]. And the main constraint on the recovery of chromium is the organic impurities. What is more, few previous studies specifically surveyed the removal of organic matter. For these reasons, this study was carried out to find the optimized condition to remove the organic matter. And then the results exhibit that the degradation rates of the Fenton oxidation, acid enzyme, and the flocculant are 71.15%, 65.26%, and 22.05%, respectively. Therefore, the organism content of chrome tanning waste liquid was greatly reduced through the pretreatment of Fenton oxidation. The four samples (original chrome waste, commercial chromium powder, and chromium liquid treated by Fenton oxidation and acid enzyme) could be applied to the one-bath tanning process of leather industry. Comparing with these four results of the treatments, the application experiment showed that the properties and grain surface and fibers of the tanned leather with commercial chromium powder and chrome tanning agent prepared from the chromium waste liquid treated with Fenton are nearly the same.

By the way, the threat of the chromium sludge to the environment could be resolved. The organic content will be reduced greatly, and the quality of tanning is improved. Furthermore, the puzzled problem will be solved in the leather industry, which will protect the environment and produce large economic benefit.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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