Studies on System Engineering of Fur Processing Wastewater Recycling

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Abstract： The process of fur production has the characteristic of larger volume wastewater, big difference of wastewater, large fluctuation of water quality and so on. The wastewater treatment effect by using the integrated process of wastewater treatment was bad. As the characteristic of fur industry wastewater and the problem in wastewater treatment, study on using systems engineering method to treat and utilize the wastewater of each process separately in this paper. The processes including 1) Recycling grease from the degreasing wastewater, after that the water could be recycled in fleshing machine. 2) The wastewater of pickling process could be recycled in the self-process after treated with flocculation and sedimentation. The method could achieve recycling neutral salt, acid, and water. 3) The wastewater of chrome tanning and chrome retanning could recycle the chrome tanning agent and water by treating with flocculation and sedimentation. 4) The color dyeing wastewater could be reused to other process after decolorization treatment. The method would recycle water and heat energy. 5) The recycling of fat-liquoring wastewater. In conclusion, the wastewater recycling system could save water more than 50%, salt 60% and chrome tanning agents 60% and so on, which had great significant in economy and environment.

Key words: fur processing wastewater; recycling; Systems Engineering

1 Introduction

As the raw skins and products were various, the volume of water consumption in the process was large. So the process of fur has the characteristic of larger volume wastewater, big difference of wastewater, large fluctuation of water quality and so on. The wastewater treatment effect by using the integrated process of wastewater treatment was bad. Using systems engineering method to treat and utilize the wastewater separately and then utilizing integrated treatment maybe a better choice. It was not only saving water and chemical materials, and reducing pollution and the treatment cost of wastewater, but also promotes the realization of cleaner production and sustainable development of fur processing enterprises. In this paper, taking the great recycling value process containing degreasing, pickling, tanning, retanning, dyeing, fat-liquoring as the point of entry, the treatment of different process wastewater using systems engineering of recycling was studied based on the characteristics of waste water.

2 Experimental

2.1 Materials

The paddle was supplied by Tongxiang Xinnuo Fur & Leather Co., Ltd., Tu-1810 UV-Vis Spectrophotometer was supplied by Beijing Purkinje General Instrument Co., Ltd., DJ-Q2020A electrolysis

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ozone generator was supplied by the Jinhua Jianqiao Development of Environment Protection Science and Technology Co., Ltd., SHB-666 multi-using recycling water pump was supplied by Zhengzhou Great Wall Industry and Trade Co., Ltd., PHS-3C acidity meter, the soxhlet extractor and FA1004 electronic balance were supplied by Shanghai Zhiguang Instruments and Measuring Appliance Co., Ltd., The coagulation testing device was suppied by Jiangsu Gaoyou Motian Electronic Instruments Co., Ltd., The potassium dichromate, the ferrous ammonium sulfate, the silver nitrate, the chromium potassium, the alizarin red S, the polyacrylamide, the series Fatliquor, the sodium hydroxide and the sulfuric acidother drugs were supplied by Shanghai Wshine Chemical Industy Co., Ltd., the wastewater of fur process was supplied by Tongxiang Zhonghui Fur & Leather Co., Ltd..

2.2 Determination of the water quality index

The index of wastewater coming from degreasing, pickling, tanning, retanning, dyeing, fat-liquoring was determined. The COD_{cr} was determined by potassium dichromate method. The suspended substance of wastewater was determined by gravimetric method. The chloride was determined by titration with silver nitrate. The chrome content was determined by colorimetry with sodium Chromate.The sulfate content was determined by alizarin red S method. The colority was determined by dilution multiple method. The content of fat-liquor was determined by Soxhlet extraction method.

2.3 Recycling grease from the degreasing wastewater

It put the degreasing liquid to acidification with sulfuric acid, then extracted the degreasing wastewater with petroleum ether and cyclohexane respectively, eventually recovered the extractant with distilling. Then the testing conditions of extraction was optimized.

2.4 Coagulation treatment and recycling of pickling wastewater

To recycling the pickling process wastewater without treatment, the COD_{cr} contents was determined after the end of each recycling. The relations were studied between the number of recycling and the COD_{cr} contents. The coagulation treatment of pickling wastewater with mixed using flocculant of polymer Aluminum and organic flocculant of polyacrylamide. And the coagulation conditions were optimized which contained the flocculant type, the using dosage, the compatibility relations, the coagulation conditions and so on.

2.5 Coagulation treatment and recycling of tanning wastewater

To recycle the tanning process wastewater without treatment, the COD_{cr} contents was determined after the end of each recycling. The relations were studied between the number of recycling and the COD_{cr} contents. The coagulation treatment of tanning wastewater with mixed using flocculant of polymer Aluminum and organic flocculant of polyacrylamide. And the coagulation conditions were optimized which contained the flocculant type, the using dosage, the compatibility relations, the coagulation conditions and so on.

2.6 Studying the COD_{cr} contents of chrome retanning operating fluid related to recycling times

To recycle the retanning process wastewater without treatment, the COD_{cr} contents was determined after the end of each recycling. And the feasibility of its reusing was studied.

2.7 Treatment and recycling of dyeing wastewater

The treatment of ozone oxygenation and coagulation sedimentation was taken on the dyeing wastewater, after that recycled it. And the effect of ozone oxygenation and coagulation sedimentation was investigated. At the same time, the dosage of ozone, the type of flocculant and the coagulation conditions were optimized.

2.8 Recycling of fat-liquoring wastewater

To determining the contents of fat-liquoring agents in the process of after and before the fat-liquoring

with the soxhlet extraction method, and on the basis of that calculating the absorption rate of fat-liquoring agents. The determination results provided a premium dosage of fat-liquoring agents for recycling.

3 Results and discussion

3.1 The system of recycling fur processing wastewater

According to the wastewater treatment processes and combined with the purpose of recycling, the wastewater recycling systems was shown in Fig.1.

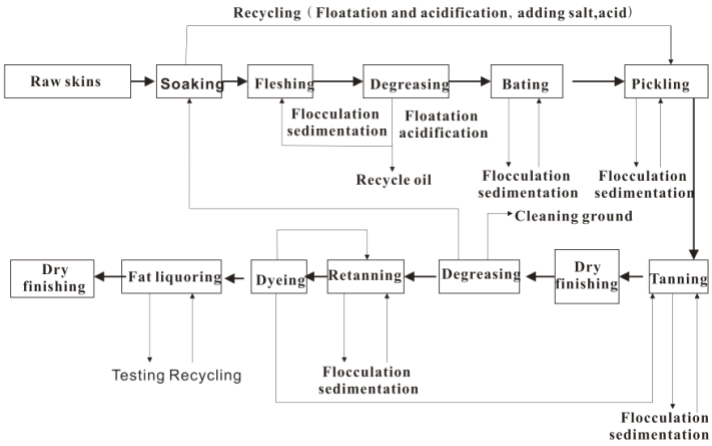

Fig.1 The fur wastewater recycling system

3.2 The index of degreasing wastewater and recycling grease

The COD_{cr} of degreasing wastewater was 18000 mg/L. Tab.1 was the removal rate of COD_{cr} and the volume of recovered oil after extraction with petroleum ether.

Tab.1 The effect of extraction with petroleum ether

The volume ratio of wastewater and extractant	1 : 1	2 : 1	3 : 1	4 : 1
The volume of extracted oil (g/L)	3	2.5	1.2	0.8
The removal rate of COD_{cr}(%)	56	53	48	20

We can see from Tab.1, when the volume ratio of wastewater and extractant was 1: 1, could the most amount of grease be accessd, and the removal rate of COD_{cr} was the highest. If extracting in three times at the same proportion, it could extracted 4g grease from per liter wastewater. And then the COD_{cr} of degreasing wastewater can be reduced to 6870 mg / L, the removal rate of COD_{cr} is about 60%.

When the volume ratio of wastewater and extractant was 1: 1 with using cyclohexane as extractant, it could extracted 3g grease from per liter wastewater, the removal rate of COD_{cr} is also about 60%.

To sum up, the treated wastewater can be used in the fleshing machine.

3.3 The recycling of pickling wastewater

Tab.2 was the relevance between the COD_{cr} contents and cycle times of the Sheepskin Shoe-upper double face pickling liquids without treatment.

Tab.2 the relevance between the COD_{cr} contents and cycle times

Cycle times	0	1	2	3
COD_{cr}(mg/L)	5500	7400	9200	11200

The pickling solution may dissolve a large number of proteins and their degradation products and oils or fats, as well as the floating hair and the dirt that were desquamated from the pelage and so on. If the wastewater were recycled without treatment, the waste such as proteins, oils and fats will be accumulated with the increasing of the number of cycle. And the liquid COD_{cr} was also increasing significantly, and the liquid color was suspended with yellow creamy. And then, if using continually, it would affect the quality of products badly. The liquid pickling must be discharged with two times recycling when using the sheep skin which contained fat as high as raw skins. In addition, the pickling liquid contained the salt about 50-60g/L and the formic acid about 4-6g/L, If discharged without treatment, it would pollute environment and the chemical material was also wasted.

The experiment showed that the pH of pickling wastewater was adjusted to 3.5, and poly-aluminum chloride (PAC) and VN730H were added at the ratio of 160.0+2.5mg/L, the turbidimetric of wastewater can be get rid of up to 90%, the COD_{Cr} can be get rid of up to 60%. After the treatment, the water was limpid and met the requirement of pickling process. So the wastewater can be recycled to manufacture furs.

3.4 The recycling of tannling wastewater

Tab.3 was the relevance among the COD_{cr} contents, the sodium sulfate contents and cycle times of the Sheepskin Shoe-upper double face ptanning liquids without treatment.

Tab.3 the relevance among **the CODcr contents, the sodium sulfate contents and cycle times**

Cycle times	0	1	2	3	4	5
The contents of COD_{cr}(mg/L)	4000	7000	7500	8500	9800	14500
The contents of sodium sulfate(g/L)	20	32	36	40	45	50

If the wastewater were recycled without treatment, the COD_{cr} of operation solution showed evident rising trend with the increase of reuse times. A part of the COD_{cr} comes from the chemical used, the other part comes from the dissolution protein and oils and fats in leather. so if the tanning liquid could not be dealt with before reusing, the reuse times should be restricted.

PAC and VN730H were added to tanning wastewater at the ratio of 130+2mg/L, the COD_{cr} was get rid of up to 65%, but it couldn't get rid of chrome tanning agents, it could only benefit recycling chrome tanning agents from 5% to 8%.

3.5 The recycling of retanling wastewater

Tab.4 was the relevance between the COD_{cr} contents and cycle times of the rabbit skins cover retanning liquids without treatment.

Tab.4 The relevance between the COD_{cr} contents and cycle times of the retanning liquids

Cycle times	0	1	2	3	4	5	6
The contents of COD_{cr}(mg/L)	2750	3200	3300	3600	3800	4000	4000
The contents of sodium sulfate(g/L)	13	18	19	19	22	23	25

With the increasing of cycling times, the COD_{cr} of operation liquid showed an evident increasing

trend. But this trend and the COD_{cr} content were much less than that of in the disposal of tanning liquids. And the content of sulfate was increased gradually, but it was not in large amount. So the retanning liquids could be reused 8-10 times with filtering treatment at least.

3.6 The reusing of dyeing wastewater

Tab.5 was the quality index of dyeing wastewater.

Tab.5 The quality index of dyeing wastewater

The quality index	COD_{cr} (mg/L)	Colority (times)	pH
number	1119.19	700	3.14

The method of ozone oxygenation and coagulation sedimentation was used in disposing the dyeing wastewater. It showed that when the dosage of ozone was 2666.7mg/L and the dosage of PAC was 1588mg/L, the removal rate of COD_{cr} was 44.69%, the removal rate of $colority_r$ was 86.01%, the colority of treated wastewater was 30 times. And when using PAM, the dosage of PAM was 200mg/L, the removal rate of COD_{cr} was 40.41%, the removal rate of colority was 81.51%, the colority of treated wastewater was 30 times. According to the results, the effect of using PAC was better, but the dosage of PAC was much more than using PAM. The effect of treatment was in Tab.6.

Tab.6 The effect of treating dyeing wastewater with ozone oxygenation and coagulation sedimentation

Content	The removal rate of COD_{cr} (%)	The removal rate of colority(%)	The colority of treated(times)
Ozone oxygenation	22.93	61.12	100
Ozone oxygenation and coagulating(PAC)	44.69	86.01	30
Ozone oxygenation and coagulating(PAM)	40.41	81.51	30

3.7 The recycling of fat-liquoring wastewater

The absorption rate of fat-liquoring agents was about 55% with conventional fat-liquoring process. When cycling the wastewater from fat-liquoring process, the amount of the original fat-liquor of 60% could be added And the fat-liquoring liquids can be reused more than three times.

4 Conclusions

The wastewater recycling system could save water more than 70%, salt 60% , chrome tanning agents 60% and fat-liquoring agents 50% and so on. These are very important for clear environment. These approaches significantly increase the economic benefits and are beneficial to environmental protection.

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