A Circular Economic Mode and its Approach to Ecological Production of Leather Tanning

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Abstract: Based on the properties and the principles of recycling economics, a CE model was built up to simplify the circular economic process with different levels of complexity. Additionally, the quantities of both the material saved and pollutant discharge reduced can be expressed in the formula with empirical factors. According to this invention, ecological aspects of leather production were analyzed, especially of beamhouse; it is attained markedly reduction of pollution load in leather manufacture field. And it is also a new approach to clean ecology of leather production.

Key words: recycling economy; ecology; leather manufacture; beam house

Introduction

In recent twenties years, China has had a rapid development in leather industry, and now has become the biggest center in the world both of the leather manufacture and trade of leather articles. Statistics shows that export exchange of Chinese leather manufacture has kept on increment in past several years, and holden the No.1 position in 6 successive years among the light industries which are 19.5, 23.2, 27.34 and 32.71 billion USD from 2002 to 2005 respectively[1]. Leather manufacture has made a great economic benefit, whereas it at the same time led to tremendous environment pollution, biological destructiveness and the huge wastage of energy and resource. For the reason, leather manufacture has become one of the most serious environmental industries today. The pollution is not only due to the characteristic of leather manufacture itself, but due to the old-style industrialization featuring as “high input, high consumption and high pollution”.

With the implementation of global sustainable development and concern to the environment protection, the National Development Reform Commission (NDRC) brought forwards the “Developing Recycling Economy, Building up An Economization Society”. There are series policies issued in recent years relating to the leather industries. Further the REACH (Registration, Evaluation and Authorization of Chemicals) will limit the usage of traditional leather chemicals. It seems more that the environment policies will become stricter in China as in the other developed countries.

However, from the globe point of view, leather manufacture will never disappear, but develop at a rather stable rate. Though more legislations make the ecology more prominent, abundant raw hides come to new pollution if they were changed into leather. According to the statistical figures of GLiPHA, the global livestock production has no big change in the last twenty years [2] and in medium term in the future, global production of hides and skins is expected to continue growing at a slow rate. While level of prices, income and consumer preferences for other product attributes mainly determines the consumption of leather products, the leather production depends more on factors related to the meat market that are exogenous to the hides and skins and leather markets. It was estimated that consumption of leather products is expected to remain the same level or just a little increase, expressed in raw equivalent [3]. It was also estimated that compliance with environmental requirements could continue to lead to a shift in tanneries from developed to developing countries where regulations are still less stringent and labor costs are lower.
To withhold the contribution of the leather to the national economy, the conflicts between its development and pollution must be solved. Hence, it is essential with ecological concerns to reevaluate the traditional leather operations, to choice the eco-friendly chemicals, to conduct the production and to treat with the waste stuff. In this article, a hypothetical mode was provided with usage guidance base on the theories of recycling economics, meanwhile, the author applied this model in analysis of the leather processes, and provides the prospective about the ecology to Chinese leather industry.

1. Circular Economy (CE)

Circular economy is a economic growth and development system to integrate the economy resource and environment factors based on the material metabolism mode, which has the mechanism of efficient use and waste stream feedback. It is a revolution on linear economy and viewed as a new inter-discipline.

In 1965, Kenneth E. Boulding suggested at the first time in his Spaceship Earth that the earth has become a single spaceship, without unlimited reservoirs of anything, either for extraction or for pollution, and in which, therefore, many must find his place in a cyclical ecological system which is capable of continuous reproduction of material form even though it cannot escape having inputs of energy [4-9].

In 1990, Pearce, D.W. and Turner, R.K. in the first used the item as Circular Economy (CE) and provides two basic principal rulers: the exploitation rate of the renewable resources should not be greater than the nature regeneration rate; waste flows to the environment should always be kept at or below the assimilative capacity of the environment, meanwhile, the reduction of exhaustible resource should be recompensed by the increase of the nature regeneration. After achievement of certain living level, the exhaustible resource should be reduced or the reservoir of resource regeneration should be built up [3].

To level up the resource-use efficiency and attain the sustainable development, China has issued the law on promoting the cleaner production and initiated CE activities by the revaluation of the experience accumulated at deferent scales such as from the industries sides, regions(provinces, cities); industrial parks, enterprises, etc.. The Chinese CE characteristic can be generalized by the management of the material and energy flow during the production and consumption activities, that is, the material and energy flow management by CE legislation and policies under the guidance of 3R( Reduce, Reuse and recycle). The target is to resolve the contradiction between the rapid development and ecosystem led by the industrialization, urbanization and to fundamentally change the traditional growth pattern of "mass production, mass consumption, the large number of abundance". Many economists in China have explained, researched and developed CE. Wu jisong has put forward the 5R principles, that is, Rethink Reduce, Reuse, Recycle and Repair. Some others argue that the new development strategy, new economic development pattern, aiming at maximizing resource efficiency as well as minimizing waste discharge, and realizing sustainable economic and social development.

1.1 CE connotation

CE theory is based on an assumed static or close metabolism system, within which all the human activities was guided by the ecological rules and this system should be compatible with the whole ecosystem. It is also called eco-economy.

This recycle includes natural recycle and industrial recycle. Natural recycle should be exploited and maintained instead of broken by human activities, whereas, industrial recycle can be changed or innovated by the new developed technology to get more efficiency and reduce the environment pressure of waste discharge. Hence, CE is characterized with high efficiency of nature resource and ecology.
4R can more generally describe CE regarding human activities in whole EC process \cite{6}, that is, Reduce (reduce the amount of the resource and energy and reduce the waste discharge to environment), Reuse (reuse the waste resource directly or the waste resource simply modified), Recycle (recycle the waste as the feed of its or the other production), Recover (recover the waste with technical treatment for new value).

If Reduce viewed as the control at the beginning of the production and consumption process, the rest Reuse, Recycle and Recover can be regarded as that of terminal with gradually increased complexity of re-treatments. From the same point of view to the above definition, Reuse, Recycle and Recover can have intersections. Considered the scopes of more processes or whole system, Recycle and Recover is aimed to Reuse, and Reuse to Reduce. Therefore, there is no need to strictly discriminate which process belongs to each of them, which all reduce the discharge to ecosystem.

It is noted that Replace also represents in the some articles of CE. While the new replacement occurs, the material or energy flow and the whole system has fundamentally changed, which deviate the originality of CE. However, Replace has an extremely positive effect to the ecology in case that the harmful substance cannot be technically reduced to the settled limitation while the new replacement is eco friendly.

1.2 EC mode Assumption

The assumption is demonstrated in Figure 1, where process refers to all activities of resource/energy productions and consumptions. The process can also be understood as a certain process or certain processes.

The span of these two processes is determined by the scope of CE. The arrangement of these two processes is flexible to the scopes and their intrinsic properties. The process 2 can strictly follow the procedure 1, or completely not, or even previous to process 1. During the implementation of this mode, the following issues should be taken into account: (1) the application of the recycle, i.e. in which process the recycled material or energy can be more efficiently used; (2) the facility of Reuse, Recycle and Recover in certain circumstances. Whichever is simpler, is conducted with higher priority. Normally, process 2 differ to process 1. In case, process 2 is the same as process 1, this mode can be transferred to Figure 2.

![Figure 1: The recycling economic mode](image1)

![Figure 2: The special circular economic mode](image2)

In three steps can any economic activity be analyzed with assumed CE mode. Firstly, Reduce analysis. The impact is valued during the Reduction. In case this impaction is little or can be accepted, Reduce is prior to others. Second, analysis of own process. The new technology applied in the process may increase efficiency of the output. In the case that the impact of the first step cannot be ignores, the study to the process is essential. Third, Recycle. Recycle is the last step to be focused, which includes Reuse, Recycle and Recovery supplying a process with complement of material or energy. In mode 2, it works directly to this process and in mode 1, it does partly or
wholly to other processes (Here the assumed mode is viewed stable, in which the same result or effect is expected under the same condition.).

The system is close when the recycled can be full reused; the system is open, some of recycled releases outside of this system. Provided that the release is discharged to the environment directly, the nature can absorb some of them in metabolism, and the other offering pressure to the ecosystem is regarded as pollution when the nature balance is broken.

In the mode 2, the following are defined: Re is exhaustion rate of the material or energy; Er is the reuse rate of recycled material or energy; in this material or energy flow, the other is viewed as waste. After n times of Recycle, the side effect can not be ignored, the new Recycle is necessary to be relaunched. Under this condition without Reduce action, if we name the Efficiency of the saved material or energy as Es (i.e. the ratio of the saved with n times Recycles to the total demand of the material or energy), the reduction of this material pollution as Rp, the formula 1 and formula 2 can be inferred. Inside it noted that Er is the key measurement of the pollution.

\[
\begin{align*}
Es &= n(1-Re)Er/(n+1) \\
Rp &= Er/(n+1)
\end{align*}
\]  

\textbf{Formula 1}  
\textbf{Formula 2}

\textbf{2. Pollution in the leather production}

Leather manufacture needs abundant water and chemicals. Normally when 1 tone of raw hides is transferred into approximate 25 kg leather, the processes generate 15-50 tones waste water and 450-730 solid waste. Mostly part of the waste was released from Beamhouse, whose material flow is shown in Figure 3. The waste analysis is given below according to Beamhouse process.

Water demand varies to the deferent articles and deferent process, for example, beamhouse needs 57% of the water and retanning does 18% of the whole water consumption from raw hide till final articles. Normally 1 tone raw hides consumes 15-120 tons water, even with updated technology, the level still maintains at 15-50 tons water. This waste liquid will be transferred to 500 kg sludge with 40% dry matter through the water treatment plant. Simultaneously, this 1 ton raw hide to leather manufacturing process generates circa 240kg COD, 100kg BOD (waste water of beamhouse and retanning contain 80% and 17% respectively of the total COD), 150kg suspended solids, 170 kg common salt, 80 kg sulfate, 5 kg chromate and 10 kg sulfide. Statistically the leather industry emits 0.1 billion tons waste effluence in China, which obviously leads to heavy water pollution [7].

In mechanical operation, such as fleshing, shaving, trimming and buffing, 1 tone raw hides generates again 70-350 kg fleshings, 225kg shavings, 150kg trimmings and 2kg buffing dust.

The typical salt pollution is the sodium chloride. In that the normal preserving raw hides is salted and 1 tone fresh hides need 300-400 kg salt. 70% salt pollution in the tannery comes out from the raw hides [8]. Related research reveals that the growth rate of the active sludge decreases while the salt concentration of the sludge increases and the duration of low speed growth is prolonged. High concentrated salt reduces the bio-degradation and the grade of the degradation, hence, the rate of organic compound degradation and removal decreases [9-10].

Certain amount of sulfide and lime are applied in the liming process, and 40% of the sulfide is not absorbed by the pelts and then discharged in the waste water. Hydrogen sulfide starts to release while the pH is lower than 8.5. A limited study suggests that long-term, low-level exposure to H2S may be associated with reduced lung function. Loss of sensory neurons in the nasal cavity was observed in male rats exposed to 30 or 80 ppm for 10 weeks. High content of sulfide in the waste water can make the river become dark and the vegetable root dark and rotten [11]. Lime slightly resolves in water and belongs to strong alkaline. Mass of the waste lime changes the trace element take of the vegetable root.
Broken hair and epidermis in the liming and non structural protein in the soaking and liming augments the COD and BOD content in the water, which leads to water pollution and propagates microorganism for supernutrition. The result is the fish death due to low oxygen content in the water led by microorganism propagation.

Nitrogen- amine may come out from the liming, deliming, bating and retanning. Nitrogen is the key factor for the nutrition of waste water plants. It stimulates the growth of algae which leads to development of a toxic anaerobic system that kills the bacteria of the waste water plant. The existence of NH$_3$-N is toxic to human and fish. The dosage of 2.6×10$^2$mg/L can already make fishes die$^{[12]}$. Besides, due to its nutrition, high content of NH$_3$-N make the water dark and odoriferous, which presents in polluted oceans, lakes and rivers with moss$^{[13]}$. It is reported that Tai Lake and Su Yang river recently has this phenomenon of moss which was suspected due to this reason. To protect the limited water resource, during the execution of “the Eleventh Five-year” plan, cleaner production program and subprogram in sector, Chinese government invests more than 700 billion RMB to waste water treatment.

In the traditional recipe, the chrome exhaust rate is only 70%. The direct release of the high contented chrome liquid causes pollution. Chromium(III) is essential trace element except sensitizing effect or allergies to part group persons, while Chromium(VI) oxidized from Chromium(III) is high toxic with mutagenic and cancerogenic effect.

Alkyl phenol ethoxylates(APEs), in particular the use of nonyl phenol ethoxylates(NPEs) are nonionic surfactant which can be components of leather chemicals of a wide range such as emulsifying agents, dispersing agents and fat liquors. APEO mainly refers to NPEO, OPOE, DPEO and DNPEO, which have a low biodegradable rate reported as 0-9% per year. The European Union has implemented sales and use restrictions on certain applications because of their alleged toxicity, persistence, and the liability to bioaccumulate. Studies done on laboratory rats have shown that when exposed to certain types of alklyphenols, the rats developed mammary gland cancer. The more eco friendly method would be the water based fatty alcohol ethoxylates(FAEs). BASF has launched this type of new generation of surfactants such as Eusapon OD and Eusapon OC.

To sum up, focusing on the beamhouse may be a feasible way to reduce the leather pollution which provides more waste than other process$^{[14]}$.
Figure 3 the material flow chart in beamhouse

3 Application of CE mode in beamhouse

3.1 Reduce the discharge of waste water

Firstly, with the guidance of Reduce, the recipe with less water is recommended to maximize the efficacy of the water. Specially can the washing effect in the washing process be achieved with less water by proper mechanical action which relates to the load, the drum speed and float ratio instead of with more fresh water and times of washing. 1 ton of fresh water saved not only means less water cost, but less money spent on the waste effluent treatment.

Second, by the control of the recipe, with less water, better removal of non structural protein, dirty stuff and salt is possible with cleaner pelts in the processes before pickling and better exhaustion rate can be achieved with tighter and fuller leather in chrome tanning. Better chrome exhaustion is feasible to waste water treatment and less difficulty of recycle followed.

Finally, Recycle is considered. As figure 3 shows, different processes generate different waste effluent. The first principle of Recycle is separate gather and separate treatment. Waste water gathering system fixed on the paddle or drum and pits are necessary to get better management and treatment. The cost of system becomes rather less as time being because the recycled effluent may do not need complex treatment any more by separate treatment.
Further, the leather manufacture processes are investigated to demonstrate how to reduce the discharge of waste water with EC mode.

The liming can be arranged after soaking directly without changing the float, specially to well preserved hides with less grease and salt. In conventional processing soaking salt-preserved hides, the amount of soaking effluent discharged is 7 m³/t raw hide. The typical pollution load of soaking effluents is presented in Table 2.

<table>
<thead>
<tr>
<th>Discharged float</th>
<th>Salt</th>
<th>Suspended solids</th>
<th>COD</th>
<th>BOD</th>
<th>Total nitrogen</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kg/T raw hide</td>
<td>85-113</td>
<td>11-17</td>
<td>22-33</td>
<td>7-11</td>
<td>1-2</td>
<td>1-2</td>
</tr>
</tbody>
</table>

The washing float of liming and reliming can be recycled for liming or reliming. The liming float can be reused for liming. The amount of effluent in typical liming is 5 up to 7 m³/t raw hides (including the washing process). Table 3 shows the pollution load of liming. It can also be calculated from the table that more than 40% of sodium sulfide in the effluent with empirical dosage of sodium sulfide; COD is high due to broken non structural protein, hair and epidermis; there is also high percentage of lime. This float can reused directly for liming after the simple filtration of the solids and deposition of lime.

<table>
<thead>
<tr>
<th>Discharged float</th>
<th>sulfide</th>
<th>Suspended solids</th>
<th>COD</th>
<th>BOD</th>
<th>Total nitrogen</th>
<th>Neutral salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kg/T raw hide</td>
<td>3.8-8.7</td>
<td>53-97</td>
<td>79-122</td>
<td>28-45</td>
<td>6-8</td>
<td>6-17</td>
</tr>
</tbody>
</table>

Applied the recycled float in the CE demonstrated above, assumed that gathering rate of liming liquid is 90% and Er of this liquid is 70%, that Re of sulfide and lime are 60% and 30% respectively, the Es of water, sulfide and lime are 57.3%, 25.5%, 44.6% accordingly, the Rp of effluent, sulfide and lime are all 63.6% after 10 times recycling.

In the practice of the recycling spent float, the additional chemical dosage is strictly controlled by the measurement of reused float before the processing, because this system in practice is not completely close due to evaporation of hydrogen sulfide and deposition of lime. To get better effect such as cleanness and swelling, the process can be adjusted slightly, for example, after times recycling, the spent float has masking effect to alkaline, therefore, it is necessary to reduce the dosage of liming auxiliary and add soda or caustic soda to balance the swelling. After 10 or 20 liming float cycles, the masking effect is too strong to continue, a new recycling is restarted. Mair made success of up to 27 cycles of liming spent float without impact to the final leather properties. Rao J.R etc. recycled more than 10 times of the liming spent float saving more than 50% water. It is prominent that recycling of the liming effluent can save water and can reduce the pollution tremendously.

Theoretically part of the recycled liming liquid or its washing liquid can be added the late stage of the soaking, because the alkaline inside can accelerate the soaking speed.
The predeliming float can be also used for liming and reliming for very low content of waste. Here the volume of float is big, there is no need of times recycles and of recipe adjustment.

The effluent of main deliming and bating contains ammonium salt, calcium salt, enzyme, hydrolyzed protein and epidermis. If it is used for soaking or liming, enzyme and calcium impacts the quality of the pelts, whereas, they impacts less if used for predeliming, deliming and bating, specially the second or third washing float of bating contains very less enzyme and calcium. Anyhow, when this method is applied, the dosage of enzyme can be slightly reduced or kept as the same.

Effluent from the tanning can be used for pickling and tanning, which normally has common salt, sulfate, chrome, fat and suspended solids. A separate pit is essential to filtration of solid and skimming off fat. Xu Leng etc. [18] analyzed and compared this traditional effluent and pickled float. The data shows in Table 4 similar components in both. Hence, after the simple treatment of adding sulfuric acid or formic acid to reduce the pH (the final pH of tanning float is 4.0) and fixing tendency with leather fibers, the effluent can be added directly in pickling after the pelt and salt running 10 minutes in drum (or with additional masking with formic acid to make sure its penetration).

<table>
<thead>
<tr>
<th></th>
<th>C12O7%/</th>
<th>Neutral salt /%</th>
<th>pH</th>
<th>Density /kgL-1</th>
<th>Solid /%</th>
<th>Temperature /°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanning spent float</td>
<td>0.4-1</td>
<td>6-10</td>
<td>2.5-4</td>
<td>1.06</td>
<td>0.02-0.2</td>
<td>37-40</td>
</tr>
<tr>
<td>Pickling spent float</td>
<td>0</td>
<td>6-10</td>
<td>1.8-2.5</td>
<td>1.06</td>
<td>0</td>
<td>20-22</td>
</tr>
</tbody>
</table>

This effluent can be heated up to be added at the late stage of tanning. As it has masking effect, the final pH and Temperature can be a little higher than the traditional to have better chrome fixation. This effluent can be used in retanning to partly replace of chrome powder. The most efficient and practical way in the tannery is to use this effluent in split tanning, since there is less chrome required and the exhaustion is much better.

The key point of reduce the leather manufacture pollution is rational Reuse the waste water, specially the waste water from beamhouse [19]. The above methods can be inferred according to the CE mode, and tannery should balance the own processes and choose the best way to reduce the consumption and waste water as its individual condition. For complexity of the chemical reaction in the leather processes, attention should be paid to the overlap of certain materials such as salt, ammonium and sulfate which can be balanced by the reduction at the previous stage. In one word, the CE mode can help comprehensive ecological analysis in leather manufacture.

### 3.2 Reduce solid waste

One ton raw hide generates at least half solid waste in the processes, hence, there is visionary value to reuse this waste. Recently, researchers in China have initiated comprehensive works, for example, the fleshing is reused to get grease and feedstuff, the hair is used to make brushes, etc. With wide scope, more instances can be built up as CE mode. The dehydrated sludge can be use as fertilizer; the waste liming pelt scraps as pet chews after treatment; shaving dust as raw material of retanning agents [20] and finishing agents [21-22]. Çolak etc. [23] prepared biodiesel with fleshing. These examples provide less solid pollution and considerable economic benefit.
3.3 Reduce sulfide and COD

When the waste water discharged is reduced as demonstrated in 3.1, the sulfide and COD are also reduced. The analysis of Reduce and the process itself is given below on how reduce the discharge of sulfide and COD.

In traditional liming process, the amount of sulfide is overdosage to make sure the complete removal of hair and epidermis. With the CE mode, the dosage of sulfide can be less to 1.3% with very clean pelts. Besides, the enzyme and liming auxiliary help the depilation as well.

More and more new methods are applied in the industrial scale with less sulfide and COD. Painting is traditional hair saving method for calf, sheep or long haired goat skin. The skins are painted on the flesh side with a paste consisting of sodium sulphide, lime or china clay or organic thickeners and water. Another typical method is the hair saving system initiated in 1990s, most of which consist of immunization, depilation and additional liming with recycling system drum, which has filtration function. Hair-saving system not only is more ecological but increases leather properties and yield. The Sirolime method \(^{24,26}\) was developed in 1981 by CSIRO (Commonwealth Scientific and Industrial Research Organization) Leather Research Centre, Australia. Sodium hydrosulfide was at the beginning of the dehairing to impregnating the hair root. At rather low pH 9–11 here ensures that the hydrosulphide has an immunization effect, yet does not attack the hair. The hydrosulfide associated with the external part of the hair is later oxidized with calcium hypochlorite. The remaining hydrosulfide will be activated by lime and loosen the hair. The float is afterward recirculated through the filter to separate the loose hair. The pelts are relimed after the unhairing is finished. For the reason that there is the release risk of hydrogen sulfide, this method is modified. Reductive and liming is added at beginning with lime to immunization. Sodium hydrosulfide is used as dehauling agent, and the unhaired pelts are relimed after 3 hours filtration. This method is flexible because the process can be delayed between individual steps, is advantageous or necessary and is with low cost because there no proprietary products are used. The disadvantage is risk of insufficient unhairing in patches with large batches of hides.

The Blair Hair method \(^{26}\) was developed in 1985 by Rohm and Haas Co. in cooperation with Eagle Ottawa Leather Co. The recipe is as following: after immunization with lime, sodium hydrosulfide is added and the hairs gradually loosen. When hair loosening is complete, the liquor is pumped out and filtered. The subsequent reliming is carried out by the means of lime, hydrosulfide and an auxiliary. A strict control of the process is necessary as the temperature and times are critical. Not all hair is entirely removed for possible over-immunization. Washing with running water leads to excessive water consumption, however, there is no need of recirculation system. The research from BASF reveals that the hair saving process is more ecological, more helpful to reduce the amount of sulfide, lime and COD. The detail is shown in Table 5.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Hair destroying</th>
<th>Hair saving</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD mgO₂/l</td>
<td>50–60.000</td>
<td>20–25.000</td>
<td>59%</td>
</tr>
<tr>
<td>BOD mgO₂/l</td>
<td>~30.000</td>
<td>10–12.000</td>
<td>63%</td>
</tr>
<tr>
<td>H₂S mg/l</td>
<td>~4.000</td>
<td>~2.000</td>
<td>50%</td>
</tr>
<tr>
<td>TKN mg/l</td>
<td>~5.500</td>
<td>~3.500</td>
<td>36%</td>
</tr>
</tbody>
</table>
3.4 Reduce ammonium salt

The amount of deliming and bating effluents, including washing waters, fluctuates between 7 and 11 m³/t raw hide. A typical pollution load is shown in Table 6. Ammonium free deliming is the definite trend in future for high content of ammonium sulfate in typical effluent[27].

Table 6 components of the typical effluent including the followed washing

<table>
<thead>
<tr>
<th>Load kg/t raw hide</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfide</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>COD</td>
<td>13-20</td>
</tr>
<tr>
<td>BOD</td>
<td>5-9</td>
</tr>
<tr>
<td>Sulfate</td>
<td>10-26</td>
</tr>
<tr>
<td>TKN</td>
<td>3-5</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>2.6-3.9</td>
</tr>
</tbody>
</table>

Ammonium free deliming agents are usually based on various organic and inorganic acids, ester of carboxylic acids, non-swelling aromatic acids etc. From table 7, it is obviously that ammonium free deliming and bating can tremendously reduces NH₃-N pollution. Besides, carbon dioxide works in the same way, however, a small amount of ammonium salt has to be added to make sure the penetration due to poor penetration of carbon dioxide. In practice, pure carbon dioxide deliming is limited on thin pelt or liming split hide. The working place should be well ventilated to avoid workers’ suffocation of less oxygen. Normally the special drum is required, hence, few tanneries adopt this method[28].

Table 7 NH₃-N Comparison of ammonium deliming against ammonium free deliming

<table>
<thead>
<tr>
<th>NH₃-N mg/l</th>
<th>kg/t raw hide</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonium deliming</td>
<td>2170</td>
</tr>
<tr>
<td>ammonium free deliming</td>
<td>85</td>
</tr>
</tbody>
</table>

It can be concluded that when CE mode is applied in deliming and bating, Reduce is still the first guidance to reduce pollution load. The span of ammonium deliming to ammonium free deliming can also be regarded as the gradual process of Reduce.

On the recycling, recently the spent deliming and bating effluent was used as farmland irrigation after strict dilution.

3.5 Reduce salt

The salt pollution mainly comes from soaking and pickling process. The traditional soaking has 85-113 Kg/t raw hide, which is not easily eliminated when waste water undergoes physical, chemical and biological treatment[27]. Tanneries in China ever shake the dry salt from the raw hide with special drum. Although the salt sometime is too dirty to use, this method can decrease 8-10% of the salt pollution. New preservation of raw hides is more efficient way to reduce the salt pollution by adding less salt with biodegradable biocide. The raw hide prefleshed in the slaughter is cured by brine by which less salt needs. Approach to no salt or less salt in pickling system is either based on no swelling organic acid or based on pretannage before tanning.

3.6 Reduce Chrome

There is approximate 2-5 Kg /t raw hide in the chrome tanning effluent. While the CE mode is used on reduction of chrome pollution load, the first step is reducing the offer of the chrome
tanning agents through which not only the pollution load is reduced, but the rate of the chrome fixation increases, also through which wet blue has better yield with acceptable fullness. The second step is change the recipe to get better fixation by the modification of the tanning influencing factors such as the float ratio, fixing time, temperature and the final pH, or by using high exhaustion chrome and masking agent. The last step is adoption of recycling system which has been explained in 3.1.

The CE mode can be utilized as both close system and open system. One example for chrome recycling system is the chrome liquid recovery from the chrome tanning effluent by precipitation with alkaline and then dissolved by sulfuric acid. Although this method is simple, the cost is relative higher for more alkaline needed. Wang Zhongjun prepared ceramics with common clay, chrome sludge and alkaline sinter from steel factory. This method can be considered as open system. It is an economic way digesting solid pollution [30].

4. Conclusion

Leather manufacture will never wither away which closely relates to the human living and economy. However, the pollution at present is the key issue of its sustainable development. In this article, circular economy (CE) is applied on leather pollution reduction with consideration of cost-efficiency. The author believes that more solutions can come out based on CE mode.

References

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