TREATMENT OF HIDE LIMING WASTEWATER BY CARBON DIOXIDE

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Results of the investigation of hide liming process wastewater treatment by carbon dioxide are presented in a paper. Comparison of the wastewater characteristics before and after the treatment by carbon dioxide was carried out. It was attempted to regenerate sodium sulphide using three different solutions: 10% solution of sodium carbonate and 5% or 10% solution of sodium hydroxide. The kinetic of sodium sulphide concentration, general alkalinity and pH was established. The solutions with the regenerated sodium sulphide were explored for unhairing of hide. The solution of 10% sodium hydroxide with regenerated sulphides was the mostly suitable for this aim. The properties of unhaird pelt were determined and assessed.

Keywords: leather, liming, carbon dioxide, sodium sulphide, regeneration.

INTRODUCTION

The leather industry is one of the most environmentally polluting branches of industry, especially due to its wastewaters. Huge amounts of lime sludge and total solids formation are the main drawbacks of lime (Thanikaivelan *et al.*, 2001). Herewith, the cleaning of unhairing solutions, polluted with lime, sulphides and the products of protein degradation, remains very difficult and expensive (Sirvaityte *et al.*, 2016).

Despite the fact that numerous unhairing methods were developed trying to avoid the use of lime (Thanikaivelan *et al.*, 2001; Munz and Sonnleitner, 2005; Valeika *et al.*, 2000). or even both lime and sulphide (Andrioli and Gutterres, 2014; Khandelwal *et al.*, 2014), the use of the lime-sulphide process remains the most commonly applied method of unhairing and opening up of the derma in the leather industry (Sirvaityte *et al.*, 2016).

The attempts were done to use the liming solution repeatedly. Faki *et al.* (2018), report that recycling of the spent unhairing-liming liquor can safely be applied in tanneries without affecting the quality of produced leathers. Nazer *et al.* (2006) developed method which allowed for four times reuse of the unhairing-liming liquor without visibly affecting the quality of the final product of leather. Unfortunately, the repeated use of liming solutions is not adapted in practise.

Other way of utilization of the used liming solution is just to process it before cleaning getting chemicals, which can be reused for various purposes as well as in leather industry. The study of Venkatakrishnan *et al.* (2019) depicts an innovative approach to reduce pollutant and recover calcite (CaCO_3) from the liming process waste by carbon dioxide (CO_2) fixation. The results indicated over >95% of calcite (CaCO_3) recovery from synthetic lime wastewater followed by 85-90% from lime sludge product and relime sludge product under optimized conditions.

Unfortunately, the used liming solution is a complicated system containing not only calcium hydroxide but sodium sulphide/hydrosulphide, hair and hide-skin proteins degradation products as well. Accordingly, the interaction of CO_2 with the used liming solution containing conventional ingredients should not be as simple as with pure calcium hydroxide solution.

The presented research had aim to investigate the treatment of the used liming solution with gaseous CO_2 and assess the possibilities to reuse the regenerated sulphides for leather processing.

EXPERIMENTAL

Materials

All chemical materials used for experiments were of analytical grade.

The hide liming-unhairing wastewater (HLW) used for experiments was obtained after unhairing according to the method: H_2O 40%, temperature $20\text{--}22^\circ\text{C}$, $\text{Ca}(\text{OH})_2$ 2.3%, $\text{Na}_2\text{S}(100\%)$ 1.2%, 1 h run continuously, $\text{Ca}(\text{OH})_2$ 2.3%, 1 h run continuously, H_2O 100%, 2 h run continuously, later 5 min. every 3 h, total duration 24 hours. A sample of soaked cattle hide was used in the liming-unhairing process.

Equipment

The equipment (Fig.1) used for the experiments consisted of balloon (1) with gaseous CO_2 , gas flow meter (2) and three Drechsel's bottles with 100 ml of HLW (3) and with solutions for catching of hydrogen sulphide: 100 ml of sodium hydroxide solution (4 and 5) or sodium carbonate solution (in such case also 4 and 5).

The rate of CO_2 flow was 60 g per hour.

Figure 1. Equipment for treatment of unhairing-liming solution with gaseous CO_2

Analysis Methods

The concentrations of calcium hydroxide, sodium sulphide and total amount of nitrogen in solutions were determined according to methods described in literature (Golovteeva *et al.*, 1982).

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Total alkalinity was determined by titration of solutions with hydrochloric acid using methyl orange as indicator.

The amounts of soluble and insoluble materials in solutions were established by gravimetric method weighing sediments after filtration (insoluble materials) or dry residue after drying of filtrate.

The amount of collagen proteins removed was estimated from the amount of hydroxyproline in the treatment solution. The amount of hydroxyproline was determined using a photo colorimetric method (Zaides *et al.*, 1964).

RESULTS AND DISCUSSION

The first step was to evaluate the amount of CO₂ necessary for complete removal of sulphides from HLW. Accordingly, the CO₂ had been blown (60 g per h) through the HLW and the blowing was continued till all sulphides were completely removed from the HLW. It was reached during 7 hours, hence, 420 g of CO₂ were absorbed. The characteristics of the treated HLW are presented in Table 1.

Table 1. Characteristics of hide liming-unhairing wastewater before and after treatment with gaseous CO₂

Characteristic	Values of characteristics' of hide liming-unhairing wastewater	
	before treatment	after treatment
pH	12.6	6.7
Na ₂ S, g/l	5.75	0
Ca(OH) ₂ , g/l	12.8	0
Total nitrogen in filtrated solution, g/l	1.47	1.08
Soluble materials, g/l	28.4	25.7
Insoluble materials, g/l	16.3	26.5

The possible chemical reactions between CO₂ and components of the HLW can be as follows:

The HLW have become acidic during the treatment, and, probably, calcium bicarbonate is formed because it predominates within the pH range 6.36–10.25 (Wikipedia, 2020). Sodium sulphide converts into hydrogen sulphide, which is blown out from the HLW. Later, the formed sodium carbonate converts into sodium bicarbonate.

Therefore, CO₂ can be applied for the neutralization of HLW but the formed poisonous hydrogen sulphide can not be released into environment in such form.

Afterwards, the conversion of hydrogen sulphide into sodium sulphide using solutions of 10% sodium carbonate and 5% or 10% sodium hydroxide has been explored. After formation of hydrogen sulphide in Drechsel bottle (3) with HLW, the mixture of H₂S and CO₂ is pushed firstly through Drechsel bottle (4) and secondly, may be, through Drechsel bottle (5) (see Fig. 1).

During such process the pH of first catching solution decreases significantly (Fig. 2): down to 7.8-7.9 for 10% sodium carbonate and 5% sodium hydroxide solutions and

down to 8.9 for 10% sodium hydroxide solution. The possible reactions should be as follows:

Figure 2. pH of solution for catching of hydrogen sulphide dependence on blown CO_2 amount (solution and Drechsel bottle number: 1 – 10% NaOH, 5; 2 – 5% NaOH, 5; 3 – 10% NaOH, 4; 4 – 10% Na_2CO_3 , 5; 5 – 5% NaOH, 4; 6 – 10% Na_2CO_3 , 4)

The changes of regenerated Na_2S in catching solutions are presented in Fig. 3.

Figure 3. Na_2S concentration in solution for catching of hydrogen sulphide dependence on blown CO_2 amount (solution and Drechsel bottle number: 1 – 10% NaOH, 4; 2 – 10% Na_2CO_3 , 4; 3 – 5% NaOH, 4; 4 – 5% NaOH, 5; 5 – 10% NaOH, 5; 6 – 10% Na_2CO_3 , 5)

Therefore, the situation is very complicated: due to the decrease of pH of catching solutions (Fig. 2), the formed Na_2S begins again to convert into H_2S . In the case of Na_2CO_3 , additional CO_2 releases, mixes with new formed H_2S and runs into second bottle with the same catching solution and process continues. The similar situation we have in the bottles with sodium hydroxide, just the excess of CO_2 forms again H_2S and begins to push it through second bottle containing the same NaOH solution. Theoretically, such a process can be infinite if blown CO_2 for a very long time using many solutions for the conversion of H_2S to Na_2S .

The former 10% NaOH solution (solution A) with regenerated Na_2S was taken after CO_2 blowing during 3 hours, when the concentration of Na_2S was highest (about 2 g/l) and used for lime free unhairing of soaked cattle hide sample.

Parameters of unhairing-derma structure opening up are presented in Table 2. After process, the obtained pelt and unhairing-derma opening solution were analysed (Table 3).

Table 2. Parameters of hide unhairing-opening up of derma structure

Control	Methods of hide unhairing-derma opening up process		
	1 st experimental	2 nd experimental	3 rd experimental
H_2O 100 %;	H_2O 74 %;	H_2O 87 %;	H_2O 93.5 %;
NaOH 2 %;	Solution A 26 %;	Solution A 13 %;	A tirpalas 6.5 %;
Na_2S 12g/l;	Na_2S adjusted to 12 g/l;	NaOH 1 %;	NaOH 1.5 %;
NaCl 5 %.	NaCl 5 %.	Na_2S adjusted to 12 g/l;	Na_2S adjusted to 12 g/l;
		NaCl – 5 %.	NaCl 5 %.

Notes: 1) Temperature 20–22°C, 4 hours run continuously, later 5 min. every 3 hours, total duration 24 hours. 2) % are based on hide weight.

Table 3. Characteristics of pelt and unhairing-opening up of derma structure solution after process carried out adding NaOH solution with regenerated sulphides

Index	Methods of hide unhairing-derma opening up process			
	Control	1 st experimental	2 nd experimental	3 rd experimental
Swelling of hide, %	149	105	136	142
Na_2S concentration, g/l	3.5	2.9	3.5	3.9
pH of solution	12.9	9.8	12.4	12.7
Total alkalinity of solution, g/l	15.4	17.2	16.0	17.4
Amount of removed collagenous proteins, g from 1 g of hide	0.68	0.15	0.34	0.49
Quality of unhairing	Very good	Bad	Good	Good

The mostly qualitative pelt is obtained when unhairing according to control process parameters. The least effect on pelt and worst unhairing-opening up of derma structure was obtained replacing all necessary NaOH by 26 % of Solution A. Relatively good results were reached using 2nd and 3rd experimental methods.

It can be assumed that despite the fact that the total alkalinity is high in all cases, the addition of a larger amount of the former NaOH solution with regenerated sulphides at the same time leads to a higher amount of NaHCO_3 (which forms parallel with Na_2S) entering the unhairing solution. Accordingly, the NaHCO_3 as weak base stops the degradation of hair and opening up of derma structure.

CONCLUSIONS

It was found that when blowing CO₂ at a flow rate (60 g/h) through 100 ml of liming-unhairing wastewater containing 5.75 g/l sulphides and 12.88 g/l calcium hydroxide, no sulphides and calcium hydroxide remained after 7 hours.

Regeneration of sodium sulphide has been found to take place best in a 10% sodium hydroxide solution into which hydrogen sulphide enters at a flow of 60 g/h CO₂ through liming-unhairing wastewater. The concentration of regenerated Na₂S was highest after 3 h. when reached about 2 g/l and the total alkalinity remained high.

The worst regeneration of sodium sulphide is on in 10% sodium carbonate solution. Maximum sulphide concentration was not higher than 1.6 g/l and the pH of this solution decreases rapidly as sodium carbonate is converted to sodium bicarbonate.

In any case, the neutralization of the liming-unhairing wastewater and the regeneration of sulphides is a very complex process in which a wide variety of chemical reactions take place. In addition, such a process takes a long time and requires a relatively large amount of CO₂.

Unhairing-opening up of derma structure was best performed using a 10% sodium hydroxide solution with regenerated sulphides to replace some of the sodium hydroxide.

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