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Recovery of Spent Liming Liquor Case study: Afrotan Tannery, Sudan

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Abstract: Spent liming liquor is produced from unhairing and liming processes. This study was carried out in Afrotan Tannery, by using the existing liming recovery unit in the tannery. The aim of the study is to determine and to evaluate the efficiency of the method of treatment applied in liming liquor recovery unit. The results showed that the value of pH was 12 and the values of TSS, Cl, NH4 and COD in liming liquor before treatment were 10623, 8511, 498 and 37396 mg/l, respectively. The value of pH is 11.5 and the values of TSS, Cl, NH_4, COD and sulphide in liming liquor after treatment were 4321, 7796, 407, 21985 and1602mg/l, respectively. The liming liquor recovery unit receives 300 m3/day of spent liming liquor. 140 m^3/day of the quantity is floated and precipitated as sludge. 60 m3/day of this sludge does not enter sludge treatment unit and directly is filled in land contaminating the soil with sulphide. 160 m3/day of the quantity is the treated spent liming liquor which is mixed with fresh makeup basic sodium sulfide and ammonium sulphate and recycled in unhairing and liming processes. The study concludes that it is important to conduct further studies to decrease COD in clear liming liquor and to send all sludge to sludge treatment unit.

Keywords*: Spent liming liquor; treated liming liquor; liming recovery unit; Afrotan Tannery*

1. INTRODUCTION

The amount and kind of tannery effluents is variable and depends on several factors such as breed, slaughtering procedure, conservation of hides, and the technology used for hair removal and tanning [1]. Animal skins are converted to leather in several steps. Liming process is one of these steps [2]. The aim of liming process is to remove the hair, flesh, fat (partially), inter-fibrillary protein and to open-up the fibrous structure for osmotic swelling [2].

In liming process most of the proteins such as hair and the non-structural hide proteins are being removed from the hide to provide a well opened-up hide with a clean grain [3]. The process of liming is classified into unhairing and re-liming [2]. In unhairing process; the animal skins are steeped in an alkali solution like sodium or calcium hydroxide and sodium sulfide to remove hair [4]. In liming process; the hairless skin is immersed in a solution of alkali and sulfide usually using calcium hydroxide to open up fibrous structure. The pH of the skin being processed will rise to 12- 12.5 [5]. The process of liming and unhairing carried out by using drums, paddles and mixers [6]. Spent liming liquor contains high amount of chemical oxygen demand [7]. Also spent liming liquor contains SS, hydrogen sulfide gas, hair, sulfide and lime [3].

Sulfur in spent liming liquor generated from hair (organic matter) and from alkali (sodium sulfide). Sulfur is found in effluents in the form of sulfates and sulfides. The impact of hydrogen sulfide gas formation during effluent treatment poses a serious environmental problem. To avoid generation of hydrogen sulfide gas in effluent, the sulfide should be oxidized, which requires an additional step in wastewater treatment. The unhairing process can be performed using bacteria or chemicals such as hydrogen peroxide and sodium hypochlorite to oxidize substances. The unhairing process also can be performed by using enzyme and meta silicate [8].

Bhavan et al. [9] studied the technical and economic feasibility of a co enzymatic hair removal process, in which the lime/sulfide system in drums was replaced by the dip and pile method with enzymes and sodium meta silicate. A comparison between the conventional (lime/ sulfides) and co enzymatic process showed a significant reduction in chemical oxygen demand (COD) and total solid (TS) loads by 55% and 25%, respectively.

Saravanabhavan et al. [10] suggested a green solution for hair removal by using enzymatic unhairing. Valeika et al. [11] proposed utilization of enzymes in unhairing step at low pH to avoid the usage of lime that causes a strongly alkaline pH. Lime/sulfide is widely used in hair removal because it is

more efficient and cheaper than other currently available technologies [1]. 80 – 90% of pollution loads in tanneries done by using lime and sulfide in unhairing process [12].

Treatment of tannery effluent is difficult and not economic and represents a serious environmental and technological problem due to presence of various hazardous chemicals. These chemicals have low biodegradability. Several studies and researches have been carried out for the treatment of tannery waste water through coagulation and flocculation process [13]. The best available techniques applied in liming process is to use hair-save technology, the thigh cost can be an issue for existing plants when re-use of the saved hair is not possible. For reducing sulphide consumption by using the enzyme, it is not suitable for sheep skins. For recycling spent liquors only when processing sheepskins are dowelled by painting [7]. Reduction the loss of chemicals, water and raw materials is the concept of cleaner production has been applied in the tanneries [14].

2. MATERIALS AND METHODS

This study was carried out in Afrotan Tannery in liming recovery unit. Afrotan Tannery is a big tannery in Sudan, located in Elgazira State, Giad Industrial Area in Al-bageer City, Sudan. Equipment in liming liquor recovery unit is presented in Table (1).

Process description in liming liquor recovery unit:

The waste liming liquor from liming tanks is conveyed to the sumps, then to floating tank to remove sludge, to screw sedimentation tank to remove sludge and finally to recycling tank.

Measurements and analysis in liming liquor recovery unit:

Parameters like pH (pH by using pH meter device), chemical oxygen demand (COD), total suspended solids (TSS), sulphide, chlorides and ammonia were measured by using spectrophotometer (spectroquart- pharo 100, merck kGaA, 6471 Darmstadt, Germany), the samples were taken before and after the treatment processes where averages of readings were taken. The quantity of waste liming liquor before treatment and the quantity of clean liming liquor and the quantity of sludge resulted from the unit were measured by pumps flow rates gauges.

Table1. Equipment in liming liquor recovery unit

Equipment	Functions
Floating tank	To remove the sludge by settling and floating it
Sedimentation tank	To separate liming liquor from sludge
Recycling tank	To store the cleaned liming liquor for recycling

3. RESULTS AND DISCUSSION

The liming liquor recovery unit receives 300 m^3/day of spent liming liquor. The flow diagram of liming liquor recovery unit and the amounts in cubic meter per day of sludge and cleaned liming liquor are showed in Fig. 1.

Fig. 1 showed that the value of pH is 11.5 and this means that the pH value is good when recycling this treated liquor in the liming process while Fig. 3 showed that the value of the total suspended solids in spent liming liquor before and after treatment processes were 10623 and 4321 mg/l respectively.

The amount of total suspended solids is decreased and that means high hair removal. Fig. 4 showed that the rate of ammonia removal in spent liming liquor after treatment processes is very low because the treatment method applied in the unit is a physical method. The ammonia is generated from the nitrogen contained in protein aceous materials in liming/unhairing processes [15].

Fig. 5 showed that the values of chemical oxygen demand (COD) before treatment was 37396 mg/l and this high amount of COD results from hair (organic matter) [8]. Fig. 6 showed that the value of sulfide in recycled spent liming liquor after treatment processes was 1602 mg/l. The sulfur present in the liming liquor generates from hair (organic matter) and from sodium sulfide [8]. This high amount of sulphide in the treated liming liquor can decrease the consumption of sulfides when recycling this treated liquor in unhairing processes. Fig. 7 shows the amount of sludge generated from the unit is about 46.7% that come from hair.

Table 2. Inlet versus outlet in liming recovery unit

Parameters	Unit	Value
Amount of spent liming solution before treatment	m^3/day	300
Amount of clean spent liming solution after treatment process	m^3/day	160
Amount of clean liming liquor recycled in production line	%	100
Amount of clean spent liming solution un recycled in process		Nil
Amount of sludge resulted from floating tank not entering sludge dewatering system	m^3/day	40
Amount of sludge results from top of sedimentation tank and skimmed manually (not interring dewatering system)	m^3/day	20
Total amount of sludge not entering dewatering system	m^3/day	60
Amount of sludge resulted from bottom of sedimentation tank and sent to (sludge dewatering system)	m^3/day	80

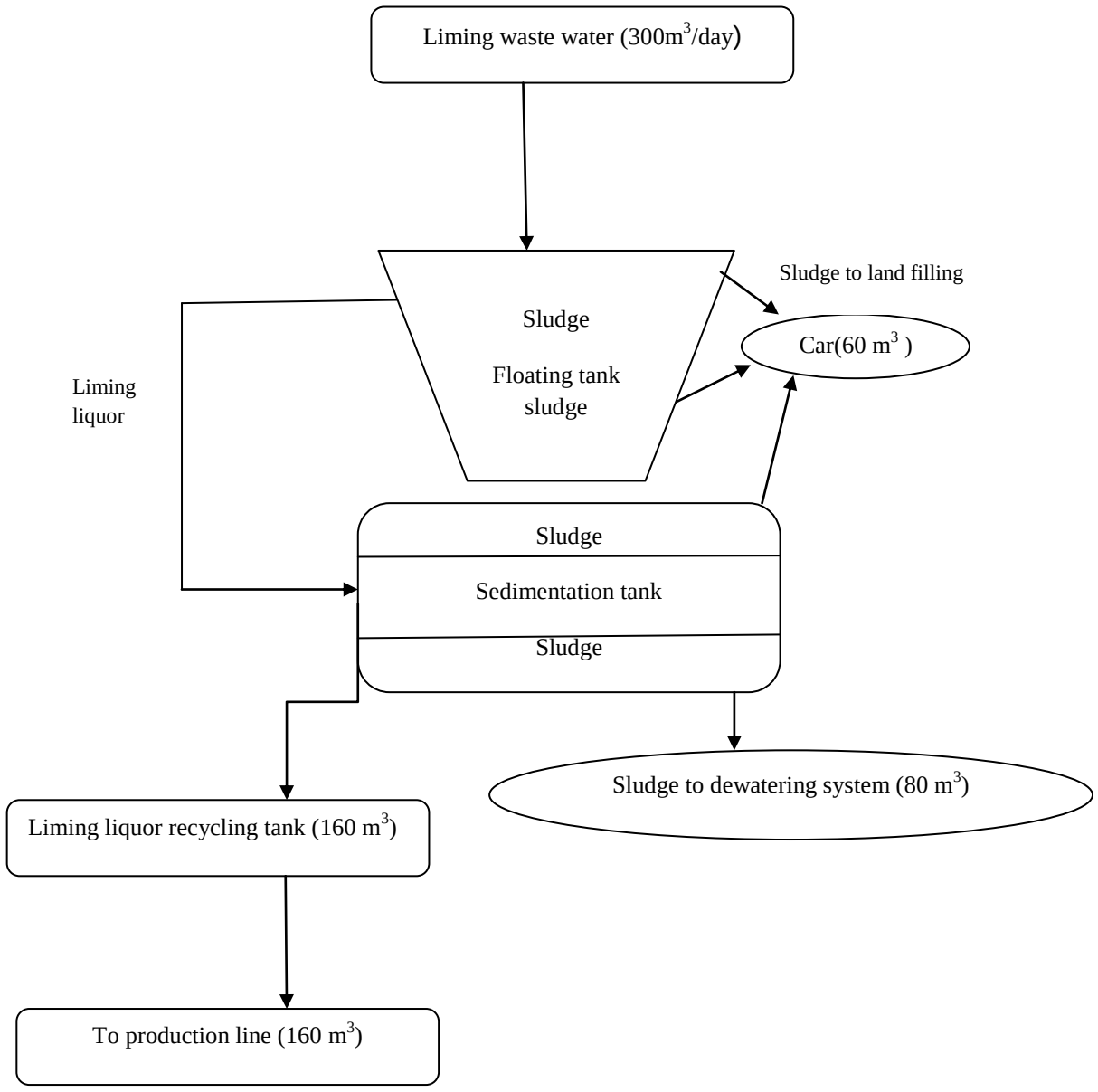

Fig. 1. Flow diagram of liming liquor recovery unit (inputs vs. outputs m^3 per day)

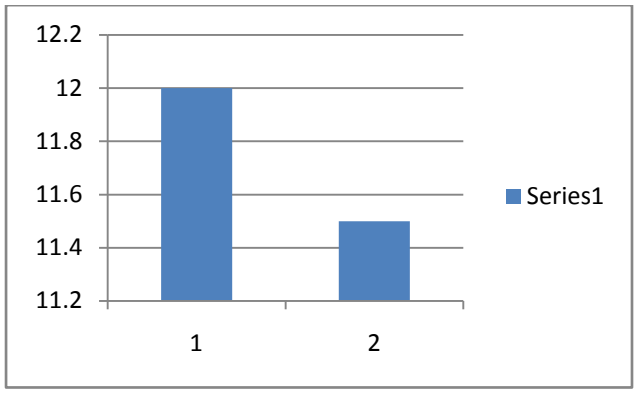

Fig. 2. pH of liming liquor before (1) and after (2) treatment

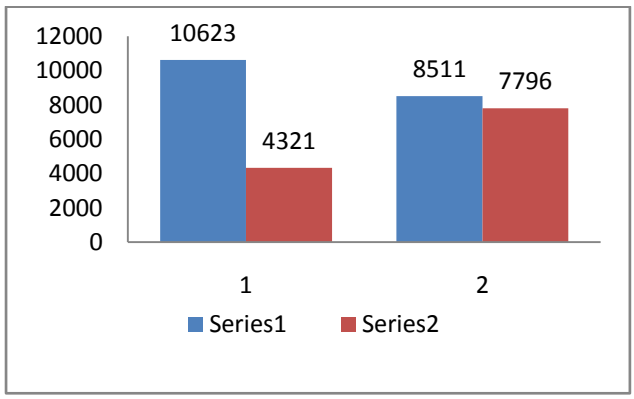

Fig. 3. Concentration of TSS (1), Cl (2) in mg/l in liming liquor before (series 1) and after (series 2) treatment

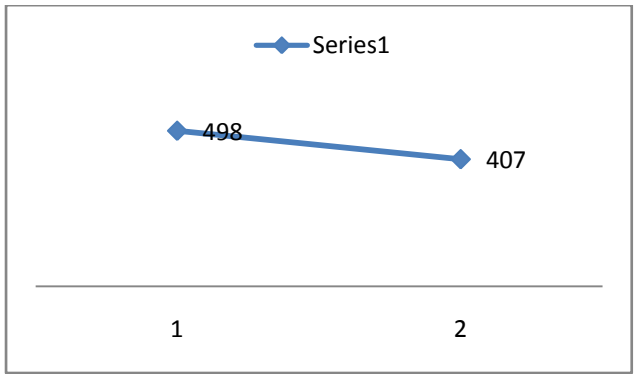

Fig. 4. Concentration of NH_4 in mg/l in liming liquor before (1) and after (2) treatment

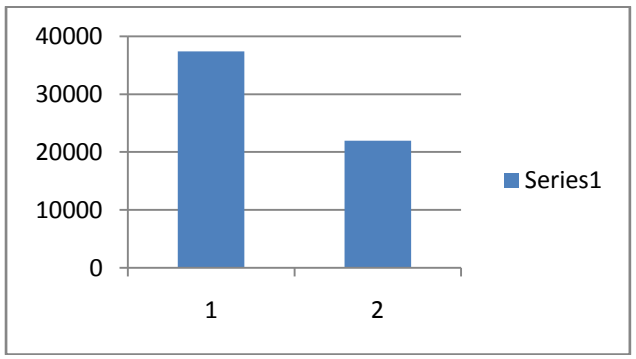

Fig. 5. Concentration of COD in mg/l in liming liquor before (1) and after (2) treatment

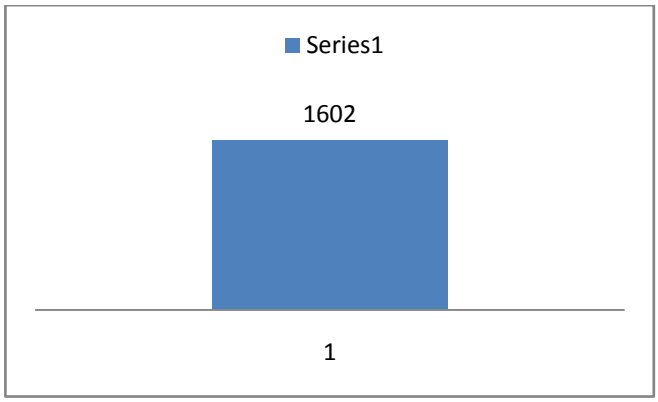

Fig. 6. Concentration of sulfides in mg/l in liming liquor after treatment (series 1)

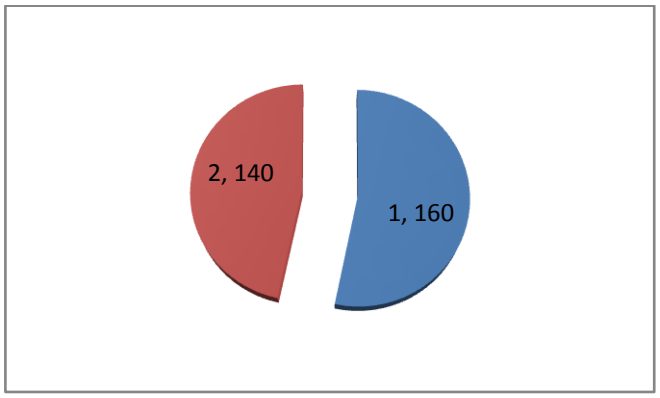

Fig. 7. Amount of treated liming liquor and sludge in liming liquor recovery unit in m^3/day

4. CONCLUSIONS

Liming liquor recovery unit receives 300 m^3/day of liming spent liquor. 140 m^3/day of the quantity is floated and precipitated as sludge. 160 m^3/day of the quantity is the clear liming liquor which is mixed with fresh makeup basic sodium sulfide and ammonium sulphate in ratio 1:4 (treated spent liming liquor: fresh liming solution) and recycled in unhairing and liming processes, this suggests that the unit has economic and environmental advantages.

The decreasing rates of chemical oxygen demand (COD) and ammonia are not significant because the treatment method applied in the unit is a physical method and there are no biological or chemical treatment steps.

The study recommended furthers studies to remove or to decrease the organic matters. Skimming and removal of sludge automatically is one of the important recommendations make by study.

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