

REMOVAL OF CHROMIUM AND SULPHIDE FROM TANNERY EFFLUENTS

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ABSTRACT. The treatment of tannery effluents in specific liquors is studied. The chromium removal efficiency of conventional chrome precipitating agents (CPA) such as magnesium oxide and lime are compared with that of Magadi soda (97% Na_2CO_3) which is abundantly available in Kenya. Optimum conditions for chrome recovery are specified. The results of studies on recycling of chrome using CPAs are reported. The reduction of sulphide levels in unhairing liquors by aerating with oxygen and with air using different flow rates is recorded. Co^{2+} and Ni^{2+} are found to be the most effective catalysts for the aerial oxidation of sulphides.

INTRODUCTION

Environmental pollution has become a major concern in developing countries in the last few decades. Consequently, there is an increasing awareness to minimise the levels of pollutants discharged into the environment through various human activities. Among the various pollution problems the quality of water is of major concern. Major sources of water pollution are the untreated or partially treated industrial effluents. Tanning industry is one of the industries which contributes to water pollution (1). This is particularly true in developing countries, which export partially or completely tanned skins and hides. The quality of discharged waters from tanneries in general are far from the desired level for acceptance into waterways (2). The major concerns are to monitor the high level of BOD, COD, sulphide and chromium in the tannery effluents. Current practices require that tannery effluent is diverted at the source into three main categories to allow more practical and economic treatment: (i) unhairing liquors - containing high levels of sulphides; (ii) chrome liquors - containing high levels of chromium; and (iii) other liquors (3). All the three liquors contain varied amounts of suspended and dissolved forms of different organic matter.

Although adequate modern technology for tertiary treatment is available, costs involved make it less attractive resulting in poor quality discharges into waterways (4). In the present studies, an attempt is made to improve the existing low cost methods for treatment of chrome liquors containing chromium and unhairing liquors containing sulphides. Investigations are carried out to evaluate the utility of conventionally used chrome precipitating agents with particular emphasis on locally available raw materials in Kenya. Investigations are also carried out to evaluate the catalytic efficiencies of several metal ions for the aerial oxidation of sulphides in unhairing liquors.

EXPERIMENTAL

For all the experiments, the mixed raw effluent, the untreated chrome liquor

and the unhairing liquor were collected from a local tannery which discharges untreated effluents into city sewerage systems.

The quality parameters of water samples, namely BOD, COD, total non-filtrable residue and total filtrable residue were determined employing standard procedures (5, 6). Sulphide levels were determined using sulphide ion selective electrode, a commercial Ag/AgS electrode (Orion 94-16 A) consisting of a silver sulphide membrane bonded into an epoxy body. For the analysis of heavy metals in raw mixed effluent, X-ray fluorescence spectrometer consisting of Ortec Si(Li) detector (HFW-200 eV at 5.9 K eV) and Canberra Multi Channel analyser (MCA-40) linked to a Professional 350 Computer were used. The excitation source was ^{109}Cd of energy 22.1 eV and half life of 453 days (7). For the studies on chrome precipitation using different precipitating agents, AAS was used for the analyses of chromium in samples (6).

Precipitation of chromium. Preliminary experiments were done adding different amounts of a CPA to fixed volumes of raw chrome liquor. After thorough mixing the pH of the mixtures were measured and the solutions kept overnight (14 hr) for precipitates to settle. The clear supernatant solutions were decanted and filtered. The total chromium content in the filtrates were determined using AAS (6). The precipitates obtained under the optimum conditions were dried in an oven at 105°C for 4 hr and the masses of the dry cakes in each case calculated.

Redissolution of chrome. The dry cakes were finally ground and 1 g each of the fine powder was mixed with 10 ml of different strengths of sulphuric acid (0.8 M to 2.0 M) in duplicate at 20°C and 70°C . The mixtures were allowed to stand for 10 minutes. For high temperature experiments mixtures were put into hot water bath at 70°C for 5 minutes and then allowed to cool. The cooled solutions were filtered, washed with small volumes of cold distilled water, and diluted to 1 l. The total chromium content of the resulting solutions was analysed with AAS.

Oxidation of sulphide. Experiments were conducted by bubbling compressed oxygen or air at different flow rates through 100 ml unhairing liquor samples taken into 250 ml fabricated impingers with 0.5 cm bubbler diameter. Flow rates were adjusted manually with a valve arrangement and were monitored by measuring the flow rate of a soap bubble in a graduated tube. Preliminary experiments were done using various flow rates of oxygen 50 to 600 ml/min per 100 ml of liquor. Aliquots of samples were removed at fixed intervals and analysed for residual sulphide levels using sulphide ion selective electrode. The same aeration procedure was repeated with different cations as catalysts.

Determination of sulphide. Sulphide anti-oxidant buffer (SAOB) was added to the unhairing liquor to prevent the sulphide ion from oxidation, to free it from hydrogen ion and to adjust the ionic strength. The SAOB was prepared by adding 200 ml of 10 M NaOH, 600 ml deionized water, 35 g ascorbic acid and 67 g disodium EDTA into a 1 l volumetric flask and diluting to the mark. The concentrations of sulphide ion were calculated from the corresponding potentials using calibration curves.

RESULTS AND DISCUSSION

Mixed raw effluents collected on different days prior to discharge into the municipal sewage system were analysed for characterization of the discharged effluents. The quality parameters monitored for a typical sample of raw mixed effluent (Table 1) shows that the effluents discharged are very acidic, with high total sulphide levels and considerable amount of chromium. The effluent has a large organic load as evidenced by the high COD and BOD values. In the

acidic pH range the effluent could generate hydrogen sulphide gas. The high total chromium levels pose serious difficulties in the biological treatment stage of the sewage effluents unless they are effectively diluted.

Table 1. Characteristic parameters of typical tannery mixed effluent sample.

Temperature	31°C
pH	3.5
Total sulphides	1600 mg/l
BOI ₅ (20°C)	450 mg/l
COD	3450 mg/l
Total non-filtrable residue	460 mg/l
Total filtrable residue	84820 mg/l
Chromium	348 ± 37 mg/l
Iron	3.9 ± 0.5 mg/l
Copper	0.4 ± 0.3 mg/l
Zinc	0.9 ± 0.3 mg/l
Lead	0.2 ± 0.1 mg/l

Table 2. Precipitation of chrome under optimum conditions.

Quantity measured	Magnesium Lime		Magadi
	Oxide	Soda	
Mass of CPA, g	5.0	7.3	15.8
pH	9.3	9.4	8.2
Total chromium in filtrate, ppm	1.30	1.60	2.60
Mass of dry precipitate, g	19.35	25.52	17.74
Chromium in dry cake, mg/g	169.5	130.3	188.4
Chromium precipitated, %	99.96	99.95	99.92

Total chromium content of raw liquor = 3280 ± 130 ppm; pH = 3.7 ± 0.1
 Values are the average of duplicate experiments with variation of about 5% deviation.

Precipitation of chromium. Conventionally, sodium hydroxide, magnesium oxide and lime are used as chrome precipitating agents (CPA) from waste chrome liquors (8). Sodium hydroxide and magnesium oxide are imported into Kenya as well as into many developing countries. Lime (52.2% CaO) is abundant in different parts of Kenya. Furthermore Magadi soda (about 97% Na₂CO₃) extracted from lake Magadi is cheap, abundant and is exported by Kenya as raw material. Hence, magnesium oxide and lime and the non-conventional CPA, Magadi soda were studied to evaluate their relative efficiencies.

The results obtained show that increasing amounts of magnesium oxide raised the pH and enhanced the precipitation of chromium from the raw chrome liquor. At pH 9.3, a 99.9% precipitation of chromium from the effluent was achieved with 4 g of MgO per l of chrome liquor. Further increase in MgO did not result in complete removal of chromium showing a limiting condition.

The results with lime and Magadi soda as CPAs show that maximum removal of chromium (99.9%) is possible in the pH range 9.3 to 9.7 and 8.1 to 8.4 with about 7.6 g of lime and 16 g of Magadi soda, per l of chrome liquor respectively. At higher pH chromium concentration in the filtrates was found to increase possibly due to the redissolution of chromium hydroxide (9).

Table 2 summarises the results obtained under optimum conditions. From the table it is clear that the highest amount of chromium that could be extracted

was from the precipitate with Magadi soda as CPA. The chromium concentration determined in the filtrates obtained using the three CAPs show that magnesium oxide is relatively more efficient, though the difference is within the experimental accuracy of 5% deviation. These results show that the three CPAs are of the same efficiency. Hence the use of Magadi Soda or lime will be more economical since they are locally available.

Recycling of chrome. Through out the world there are two main systems of recycling of chrome liquors that are practised in tanneries. One system involves direct recycling of chrome liquor floats after filtering through a mesh to remove solids and then supplementing with some chrome, sulphuric acid, formic acid and salts. The other system involves recycling of chrome following precipitation and then resolubilizing. The latter system has greater flexibility in choice of tanning compared to the direct recycling process.

In the present studies, investigations were done to look into the redissolution of chrome from the dry cakes obtained using the three CPAs. Experiments were done at 20°C and at 70°C. The results (Table 3) show that dissolution of chromium increases with increase in strength of acid and temperature. This is because at lower pH and at higher temperatures digestion of organic matter, whose matrix holds chromium by adsorption increases thereby releasing more chromium into solution (9). Although harsher conditions such as longer digestion at 70°C could have improved chromium recovery, they were not considered. Chrome recovery is comparable using all the three CPAs, about 30-33% in cold

Table 3. Effect of sulphuric acid concentration on the dissolution of chrome cake.

Total chromium in cake		with magnesium oxide	with lime	with Magadi Soda		
mg/g		169.5	130.3	188.4		
Extracted chromium mg/l*						
H ₂ SO ₄ (M)	with MgO	%	with lime	%	with Magadi soda	%
At 20°C						
0.8	44	26	27	21	36	19
1.0	49	29	36	28	43	23
1.5	56	33	41	32	55	29
2.0	61	36	43	33	61	32
At 70°C						
0.8	83	49	72	55	88	47
1.0	91	54	79	61	97	52
1.5	96	57	83	64	111	59
2.0	99	59	88	68	114	61

*Values are average of duplicate experiments with variation of about 4%.

Table 4. Effect of catalysts on depletion of sulphide by aeration with oxygen.

Time (hr)	None	Mn ²⁺	Fe ²⁺	Cu ²⁺	Co ²⁺	Ni ²⁺
Sulphide concentration (mg.l ⁻¹)*						
0	1580	1580	1580	1580	1580	1580
15	604	405	386	215	155	125
17	424	305	289	105	65	49
19	306	248	235	45	33	27
21	270	216	205	23	19	15
23	250	197	190	12	11	8

Catalyst concentration = 1.0 x 10⁻³ M

*Average values of duplicate experiments with about 4% deviation.

solution and about 60-68% in hot solution with 2 M acid.

In chrome tanning about 5% sulphuric acid (1.0 M) solutions are used. Hence the acid solution can be adjusted to the required acidity and be recycled into tanning process. During the recycling, the concentration of neutral salts may significantly change, and may therefore be necessary to supplement the liquor with adequate levels of sulphate in order to maintain the required quality of tanning (10).

Let us consider the cost economics of chrome recovery for a tannery which processes 25,000 kg of hides using 550 kg of chrome per day. Since only 2/3 of the chrome will be absorbed by the leather, the remaining 183 kg (i.e. 1/3) will remain in the float (10). A 60% recovery would amount to 110 kg of chrome per day. For a 220-day-working year 24,200 kg of chrome would be recovered annually, which will be a 20% saving on the cost of chrome. In addition, this would result in a considerable reduction in the levels of chrome discharged by the tannery. Thus Magadi soda stands a good chance as a CPA having most of the characteristics of other CPAs. It is not only locally abundant and cheap, but also gives higher chromium content per g of dry cake, which further reduces energy costs.

Oxidation of sulphides. High levels of sulphide is a problem associated with a number of industries such as paper mills, tanneries, sodium thiosulphate and allied chemical manufacturing facilities and can be identified by the stinking odours of hydrogen sulphide. The kinetics and mechanism of oxidation of sulphides have been studied by various workers under different reaction conditions (10). Factors that affect the rate of oxidation include temperature, pH, sulphide ion concentration, oxygen flow rate, neutral salts, bacterial action, organic species and catalysts. The oxidation rate constant has been reported to depend upon the presence of metallic impurities (11,12). The present studies were limited to looking into the effect of aeration with oxygen or air on the real sulphide samples from tanneries at room temperature ($19 \pm 1^\circ\text{C}$).

Monitoring experiments during the first 8 hr with 60 ml/min oxygen flow rate per 100 ml liquor (600 ml/min per l) showed that sulphide levels were depleted from initial 1540 mg/l to 650 mg/l. For convenience sulphide liquors were aerated with oxygen (60 ml/min) overnight and aliquots analysed after the first 15 hr at two hour intervals. Table 4 compares the uncatalysed reaction results with the efficiencies of conventionally used catalysts and other cations used as catalysts. The results in Table 4 show that the efficiency of the catalysts in accelerating the oxidation process by oxygen is in the order $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$. Zn^{2+} , Al^{3+} and Ce^{4+} were found to have negligible effect on the sulphide depletion reaction even at 10^{-3} M.

Aeration with air. Considering the economic advantages of using air instead of pure oxygen, specially on a large scale, aeration experiments were done with compressed air. Aliquots were analysed after 15 hr and onwards at 2 hr intervals. Table 5 summarises the effect of air flow rate on the sulphide depletion in the absence of any added catalyst. The results show that increase in flow rate of air enhances the reduction of sulphide levels. At 600 ml/min per 100 ml of liquor (6 l of air/min per l) sulphide levels were reduced from initial 1580 mg/l to 84 mg/l in 23 hr. Employing flow rate of 6 l of air per min per l of sample, the effect of the presence of two potential catalysts Ni^{2+} and Co^{2+} were studied (Table 6). The results show that the efficiencies of the two catalysts are comparable. With an aeration rate of 6 l/min per l (sample) i.e. 6 m^3 of air/min per m^3 of unhairing liquor, the sulphide levels could be reduced from 1580 mg/l to less than 20 mg/l in 23 hr employing 1.0×10^{-5} M of the catalyst Ni^{2+} or Co^{2+} . The same results could be achieved with 15 hr aeration by increasing the catalyst concentration to 1.0×10^{-4} M. The desired level of sulphide below 29 mg/l in the discharges could also be achieved with much lower catalyst concentrations, but employing much higher flow rates. Experiments

Table 5. Effect of air flow rates on oxidation of sulphide ion in unhairing liquours.

Flow rate Time, hr	Sulphide concentration (mg/l)*		
	150 ml/min	300 ml/min	600 ml/min
0	1590	1590	1590
15	510	336	224
17	404	250	163
19	324	205	123
21	284	165	97
23	245	142	84

*Values are average of duplicate experiments with about 5% deviation.

Table 6. Effect of Co^{2+} and Ni^{2+} concentrations on aerial oxidation of sulphide[§]

Time (hr)	Co^{2+} M	Sulphide level (mg/l)*			
		1.0×10^{-6}	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}
15		97	84	24	16
17		74	53	17	11
19		56	30	14	8
21		44	21	10	7
23		35	14	8	5
	Ni^{2+} M	1.0×10^{-6}	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}
15		94	76	24	16
17		73	51	12	10
19		51	25	12	8
21		33	19	9	6
23		26	12	6	5

* Values are average of duplicate experiments with deviation of about 5%. [§]Initial concentration of sulphide in the liquor = 1580 ± 80 mg/l; volume of sample = 100 ml; air flow rate = 600 ml/min per 100 ml.

were done on unhairing liquors collected from two different tanneries and found that initial sulphide levels 1700 mg/l and 1850 mg/l could be reduced below 20 mg/l in 23 hr with an aeration rate of 6 m^3 of air/min per m^3 of liquor using 1.0×10^{-5} M Ni^{2+} as catalyst. This confirms the reliability of the method for reducing sulphide levels effectively before discharging into waterways.

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