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Recovery of Chromium from the waste water of Leather Industry

***Moghira Badar*[*], *M.K. Qamar*[*] *and M. Saleem Akhtar*[**]**
[*]*Department of Environmental Management,*
National College of Business Administration and Economics, Lahore, PAKISTAN
[**]*Department of Chemistry, University of Sargodha, Lahore Campus, PAKISTAN*

(Corresponding author: Moghira Badar, moghirab@yahoo.com)
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ABSTRACT: The Recovery of chromium from tannery wastewater is attractive not only environmentally but also economically. Chromium III containing wastewaters were oxidized independently in alkaline conditions with three aqueous oxidants *i.e.* Magnesium Oxide, Sodium Hypochlorite and Calcium Hypochlorite to soluble chromate. Magnesium Oxide was potentially a suitable oxidant as it could oxidize a suspension of $Cr(OH)_3$ to chromate to 98.5% (synthetic solution) and 88.3% (waste water). The percentage recoveries by the hypochlorites were lower than those by Magnesium Oxide. For all three oxidants complete recovery could not be achieved despite different experimental conditions (temperatures and oxidation time). The amount of chromate recovered was determined by spectrophotometry. The results clearly indicate that Magnesium Oxide is the most efficient among the three oxidants.

INTRODUCTION

Leather tanning is one of the main sectors in Pakistan's leather industry (consisting of tannery, shoemaking, furs, and leather products). About 90% of its products are exported in finished form. There are some 600 tanneries in the formal sector and an equally large number of tanneries in the informal sector (Badar *et al.*, 2016).

Leather tanneries in Pakistan produce all three categories of waste: wastewater, solid waste and air emissions. However, wastewater is by far the most important environmental challenge being faced by Pakistan's tanneries. Although the exact quantity varies widely between tanneries, a normal requirement of around 50-60 litres of water per kilogram of hide is suggested. Tannery wastewater is highly polluted in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, settleable solids, total kjeldhal nitrogen, conductivity, sulphate, sulphide and chromium. The values of these parameters are very high as compared to the values mentioned in the National Environmental Quality Standards (NEQS) set by the Government of Pakistan (Moghira *et al.*, 2016).

About 80% of the cases untreated tannery effluent is discharged directly into recipient water bodies or onto open land and only 115 is discharged into municipal sewers that also drain into natural water bodies without any treatment. Traditionally 60 – 70% chrome applied in the form of BCS (Basic Chromium Sulphate) are absorbed by the hides and skins during process and the remaining is discharged as waste. Under certain environmental conditions, Cr III may be oxidized to Cr VI compounds and carcinogenic compounds. Such compounds become threat to the environment. The recovery of chromium could help in overcoming environmental deterioration (Reed S, 2010)

Oxidation of the chromium containing wastewater under basic conditions is considered to be suitable for the recovery of chromium as chromate. In this work three different oxidizing agents i.e. Magnesium Oxide(MGO), Sodium Hypochlorite (NaOCl) and Calcium Hypochlorite $\{Ca(OCl)_2\}$ would be used to recover chromium in the form of CrO_4^{2-} solution. The optimum dosage of selected reagents used would determine cost of the process (Russell RL *et al*., 2009).

In the present study we develop the process for recovery of chromium from tannery wastewater of leather industry.

MATERIAL AND METHODS

The actual tanning effluents (1 & 2) were collected in plastic containers (from tanning drums and discharge pipes) from tanneries on Sambrial road, Sialkot. The samples were analyzed for COD, BOD, total solids, and metals (Mn, Cd, Cr, Zn, Ni, Cu, Pb, Co, Fe, Na and K) using standard methods including Atomic Absorption spectrophotometer, Varian.

Two effluents containing relatively higher chromium concentration were selected for the recovery purpose. Since, we were interested in recovering chromium (Cr III) as chromate (CrO_4^{2-}) and determining its concentration spectrophotometerically, we first determined its maximum wavelength (λ_{max}) on SPECTROSONICR GENEYSISTM 5 spectrophotometer and the value obtained was 372nm.

The original Merck hydrogen peroxide, sodium and calcium hypochlorites solution were used for the recovery. Exact concentrations of the three oxidants were determined by standardizing them against a 0.1N sodium thiosulphate solution.

A standard solution (synthetic) of $CrCl_3$ of the concentration 100-mg/L was prepared. Then with the help of balanced equations (Stoichiometeric) the amount of MGO and NaOH required were calculated. A 100mL of synthetic Cr III solution was taken in a 250mL Erlenmeyer flask and the calculated amount of NaOH was added to bring its pH>9. Cr III produced thick green precipitates of $Cr(OH)_3$. MGO solution was then added and the flask contents were heated for 5 minutes at 100^{o}C. The solution was then left for 5 minutes to complete reaction. The concentration of chromate (produced) was found from a calibration curve prepared by standard solutions of sodium chromate on SPECTROSONICR GENEYSISTM-5 spectrophotometer (Kim DS *et al.,* 1995).

The total chromium concentrations of the two tanning samples were 2877mg/L and 220mg/L. These were diluted to 100mg/L. 100mL of both the samples were taken 250mL Erlenmeyer flasks and oxidized with MGO as described for synthetic solution. The same steps were repeated at two more temperatures, 24 and 50°C with longer oxidation duration i.e. 90 and 1440 minutes.

The above procedural steps are applied first on the synthetic Cr III and then on the two tanning samples while treating them independently with (i). NaOH plus sodium hypochlorite and (ii). CaO plus calcium hypochlorite.

RESULTS AND DISCUSSION

Table 1 represents the overall picture obtained from the analysis of the two actual tanning effluents. The most alarming values are for TDS, COD and chromium and are a real threat to the environment. These effluents also contained sodium sulphide, sodium chloride, lime, formic acid, sulphuric acid, sodium formate etc. like a typical tannery waste water. Addition of a base (NaOH or CaO) to the Cr III solutions (both synthetic and actual effluents) produced thick green precipitates of $Cr(OH)_3$.

Table 1: Parameters obtained from the analysis of actual tanning effluents.

S. No	Parameter	Effluent 1	Effluent 2
1	pH	3.4	4.8
2	Conductivity	43.7 mS/cm	7.5mS/cm
3	COD	3413 mg/l	609 mg/l
4	Sulphate	4221.6 mg/l	1846mg/l
6	TDS	91972	6456
7	TSS	294	70
8	Manganese	0.821	0.411
9	Cadmium	0.262	0.296
10	Chromium	2877	220

The pH of the samples was raised automatically to around 9.5 during this addition. The pH, however got lower by 1–2 units when the oxidant was added, such decrease was also observed (Fatima *et al.,* 2016).

It is essential that the oxidizing agents added should react completely with $Cr(OH)_3$ precipitates. In order to determine the time required for complete oxidation, the process was carried out at three different temperatures. The oxidation capabilities of the three oxidants at different temperatures and oxidation durations are given in Table 2.

It was observed that the maximum recovery was achieved at higher temperature or even at lower temperature for longer period. In summer, the temperature in Sialkot (study area) is around 40^{o}C. If the reaction time is increased to 30 hours the best results could be achieved.

The effect of pH on the recovery was also studied in this work. As already mentioned, pH of the samples automatically rises when an alkali is added. The pH was then adjusted to 6.5 by adding 1:1 HCl solution but at this pH precipitates [$Cr(OH)_3$] got dissolved; hence the recovery was not possible. pH was also adjusted around 8 but at this occasion less denser precipitates of $Cr(OH)_3$ were formed and hence the recovery was lower. The maximum recovery was only achieved when pH of the samples was around 9.5.

It was observed that the maximum recovery was obtained utilizing Magnesium Oxideas oxidizing agent. It caused least interference in the oxidation process because it do not contain either metallic cation or chlorine (as hypochlorites did). The recovered CrO_4^{2-} was in the form of yellow solution and its concentration was determined spectrophotometrically (Peters TB *et al.,* 2010).

In any sample 100 per cent recovery could not be obtained because the treatment of Cr III with NaOH or CaO formed very minute hydrolytic polymers Cr-O-Cr and Cr-OH-Cr along with bulk $Cr(OH)_3$.

These hydrolytic polymers are not oxidizable and were present in the form of green precipitates.

Table 2: Oxidation at different temperatures and oxidation durations.

Oxidant	Sample (Initial Conc. 200mg/L)	Temperature (Treatment)	Duration (min)	%age Recovery
Magnesium Oxide	Synthetic Cr III	100 ºC	10	98.5
		50 ºC	90	96
		25 ºC	1440	95
	Effluent 1	100 ºC	10	88.3
		50 ºC	90	62
		25 ºC	1440	58
	Effluent 2	100 ºC	10	84
		50 ºC	90	63
		25 ºC	1440	60
Sodium Hypochlorite	Synthetic Cr III	100 ºC	10	94
		50 ºC	90	91
		25 ºC	1440	90
	Effluent 1	100 ºC	10	67
		50 ºC	90	41
		25 ºC	1440	39
	Effluent 2	100 ºC	10	65
		50 ºC	90	44
		25 ºC	1440	41
Calcium Hypochlorite	Synthetic Cr III	100 ºC	10	90
		50 ºC	90	87
		25 ºC	1440	85
	Effluent 1	100 ºC	10	49
		50 ºC	90	23
		25 ºC	1440	17
	Effluent 2	100 ºC	10	49
		50 ºC	90	27
		25 ºC	1440	21

Other reasons for not achieving 100% recovery could be:

a) The presence of some other metals (in low concentrations) in the effluents along with chromium. Added MGO might had also been consumed in their oxidation.

b) The Sulfides present in access would also oxidized to Sulfates.

c) Formation of certain insoluble precipitates such as $CaCrO_4$, $NiCrO_4$, $Fe_2(CrO_4)_3$, $PbCrO_4$, $CuCrO_4$, $ZnCrO_4$ etc.

d) The presence of other interfering substances such as formic acid.

For all the samples treated with sodium hypochlorite, the percentage recovery was lower than that with hydrogen peroxide. For calcium hypochlorite the recovery was even lower than that by sodium hypochlorite (Dunn K., 2010). The main reasons for this were the same as discussed above.

In the case of calcium hypochlorite a small portion of recovered chromate was converted into insoluble $CaCrO_4$. Unrecovered chromium existed as insoluble salts. Such insoluble precipitates were also observed (Daniel RC *et al.*, 2011).

These insoluble precipitates can be easily separated and if at all, they are released would settle down in drain and would not be problematic as they are insoluble precipitates.

The advantages associated with the use of MgO are:

a) The percentage recovery is higher than other two oxidants.

b) Only hydrolytic polymers exist as non-recoverable matter, the remaining is converted to chromate whereas in case of $Ca(OCl)_2$ insoluble $CaCrO_4$ is formed resulting in the loss of chromate.

c) The MgO present in excess has no adverse effect on recovery and it eliminates itself with the passage of time whereas hypochlorites leave toxic OCl-, Cl_2, HCl and halogenated hydrocarbons in the effluents.

d) MgO is cheaper and easily available in the market.

e) Reaction time is less than the other two oxidants.

CONCLUSION

The recovery using Magnesium Oxide (MgO) is economical, environment friendly and simple. The cost expended on the recovery of chromate from a 1L 100mg/L Cr III synthetic solution showed that the value for MgO is 19 times lower than that for NaOCl and 8 times lower than that for $Ca(OCl)_2$.

In tanneries the concentration of chromium (tanning drum) after chrome tanning may range from 3000-6000 mg/L depending on the size of the drum. The drum normally used in small and medium size tanneries are of 8 feet diameter and 8 feet in length. Therefore, we can estimate the amount of water in a drum and in turn the amount oxidant plus alkali required for the recovery.

The recovered chromate can be reused in the in the tanning process in various proportions. Besides the recovered chromate can be converted to other useful products such as lead and barium chromates, dichromate, chromic oxide, chromium sulphate, etc.

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