

## Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process

<sup>1</sup>Abass Esmaeili, <sup>2</sup>Alireza Mesdaghi nia and <sup>1</sup>Reza Vazirinejad

<sup>1</sup>Department of Social Medicine, Rafsanjan University of Medical Sciences, Rafsanjan, Iran

<sup>2</sup>Department of Environmental Health Engineering, Tehran University of Medical Sciences, Tehran, Iran

**Abstract:** Chromium (III) salts are the most widely used chemicals for tanning processes, but 60-70% of total chromium salts reacts with the hides. In the other word, about 30-40% of the chromium amount remains in the solids and liquid wastes (especially spent tanning solutions). Therefore, the removal and recovery of the chromium content of these wastewaters are necessary for environmental protection and economic reasons. Removal and recovery of chromium were carried out by using precipitation process. For this purpose, three precipitating agents calcium hydroxide, sodium hydroxide and magnesium oxide were used. The effects of pH, stirring time, settling rate and sludge volume were studied in batch experiments. Results show that the optimum pH is 8-9 and the good sludge with high settling rate and lower volume obtain by the MgO precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tanning wastewater.

**Key words:** Chromium, removal, recovery, precipitation, tannery wastewater

### INTRODUCTION

Chromium solutions are widely used in many industrial processes such as chrome plating, wood preserving, textile dyeing, pigmenting, Cr chemical production, pulp and paper industrial and tanning. The wastewater resulting from these processes contains high amount of chromium metal which is harmful for the environment and human health<sup>[1,2]</sup>.

Tanning process using chromium compounds is one of the most common methods for processing of hides<sup>[3]</sup>. In this process about 60% - 70% of chromium reacts with the hides. In the other word, about 30%-40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions). Hence, the wastewater of the tanning process is an important source adding Cr pollutant to the environment. In addition, the cost of the chromium metal is also important and it is possible to be recovered from the wastewater<sup>[4-6]</sup>. Hafez *et al.*<sup>[7]</sup> and Chaudry *et al.*<sup>[8]</sup> reported that the Cr ion concentration in the tanning wastewater varies from 2500 to 8000 ppm and 1300 to 2500 ppm, respectively<sup>[7,8]</sup>.

Several methods have been used for removing toxic metal ions from aqueous solutions. These include chemical precipitation, ion exchange, reverse osmosis, membrane processes, evaporation, solvent extraction, and adsorption<sup>[1,4,5]</sup>. Of these, chemical precipitation is the usual way for this purpose. Many factors affect the process of chemical precipitation including the type of precipitation agent, pH, velocity of precipitation, sludge volume, time of mixing and complexing agents<sup>[1,6,9]</sup>.

The purpose of this research was to compare pH, velocity of precipitation, sludge volume, time of mixing and complexing agent when using the three precipitation agents (lime, sodium hydroxide and magnesium oxide) in the precipitation process of the tannery waste water chromium.

### MATERIALS AND METHODS

The chemicals used in this research were raw wastewater from tanning process; solutions of lime, sodium hydroxide 15% and magnesium oxide 10%. All chemicals used are of analytical reagent grade.

Since the process of tanning is batch, after finishing the process (12 h), spot samples were collected and transported to the laboratory for the determination of the most important parameters as quick as possible. These parameters include chromium concentration, pH, total solids, dissolved solids, suspended solids, color, sulfate and chlorine concentration<sup>[10]</sup>.

The jar test method has been used to determine the effect of each parameter, (six baker has been used for each stage) and 500 ml of wastewater was added to each beaker. Precipitation agents were added to each sample separately and pH was controlled between 6 to 12 using nitric acid. In order to mixed solution, a sample was taken to the jar machine and samples were mixed for one minute in 90 RPM as the first step. In the next step samples were mixed for 20 min with the speed of 30 RPM. After this 20 min. Samples were taken out from the jar machine. In the last stage, after 4 h settling time, a sample was taken from the supernatant. Supernatant solution was then filtered and chromium concentration was determined.

**Corresponding Author:** A. Esmaeili, Rafsanjan University of Medical Sciences, Social Medicine Department. Rafsanjan, Iran, Tel: + 98 391 5234003-5, Fax: +98 391 5225209

Table 1: Chemical analysis of tannery wastewater

Parameter	Variation range	Average	Parameter	Variation range	Average
COD (mg L <sup>-1</sup> )	1850-2900	2275	color	Black green	-
T.S (mg L <sup>-1</sup> )	76530-65440	88650	pH	3.23.7	3.5
T.D (mg L <sup>-1</sup> )	73050-94210	86500	Total Cr (mg L <sup>-1</sup> )	3250-5300	3950
T.S.S (mg L <sup>-1</sup> )	-	2150	Sulfate (mg L <sup>-1</sup> )	2115-4250	3525
-	-	-	Chloride (mg L <sup>-1</sup> )	18600-26700	22070

The effect of each factor on the three precipitation agents was measured by fixing the effect of the other variables. For instance settling rate, sludge volume and the shape of the precipitation for all precipitation agents were measured when pH was fixed at the optimum level. In order to determine the settling rate and sludge volumes, the samples were poured into scaled cylinders and after 5 h the height of supernatant or sludge volume was read. Atomic Absorption Spectroscopy method (Varian 975) was used for measuring chromium concentration in wastewater before and after settling process<sup>[10]</sup>.

### RESULTS AND DISCUSSION

The characteristics of the wastewaters are shown in Table 1. The average of chromium concentration in the raw wastewater of tannery process was 3950 ppm. The results of this study showed that the wastewater of tannery process is one the most important sources of environmental pollutants as the concentration of chromium and other harmful material in the wastewater is extremely high. This is also confirmed by many other studies<sup>[11,12]</sup>.

The optimum pH for removing chromium from the tannery wastewater by sodium hydroxide and calcium hydroxide is shown in Fig. 1.

Figure 1 shows the minimum solution of chromium is presented at pH 8.5 when using sodium hydroxide as the precipitating agent. In case of using calcium hydroxide as the precipitating agent, chromium concentration of settled wastewater decreased as pH increased. Increasing pH resulted in decreasing the chromium concentration in the supernatant. Although the optimum pH for NaOH was 8.5-9.5, the results showed when using CA (OH)<sub>2</sub> as precipitation agent, increasing pH decreased the chromium concentration. This discrepancy can be due to the difference between the ability of the two precipitating agents for dissolving in water. This ability for NaOH is 100%. Resulting chromium hydroxide from using NaOH has the most stability at the pH of 8.5-9.5. However adding more NaOH increases pH and this results in peptizing. In this situation, the chromium redissolve and therefore, the concentration of chromium in supernatant increases. In contrast, since the solubility of CA (OH)<sub>2</sub> is low, once a CA (OH)<sub>2</sub> is added to the wastewater pH increases and increasing pH results in peptizing. However, adsorption causes chromium ions take apart from the supernatant. Panswad *et al.* Reported that the optimum pH for MgO is 7-8<sup>[13]</sup>.

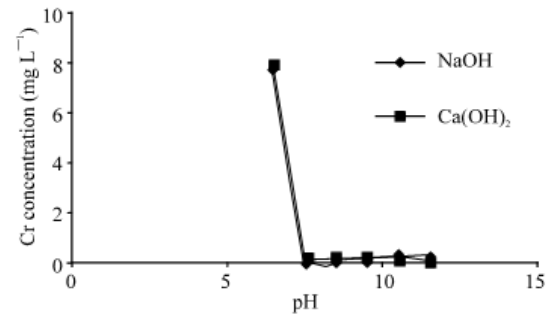


Fig. 1: Chromium concentration in supernatant solution vs pH for sodium hydroxide and lime (after 4 h)

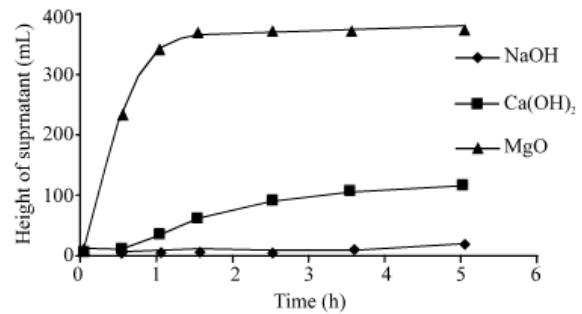


Fig. 2: Precipitation settling rate for three precipitation agents

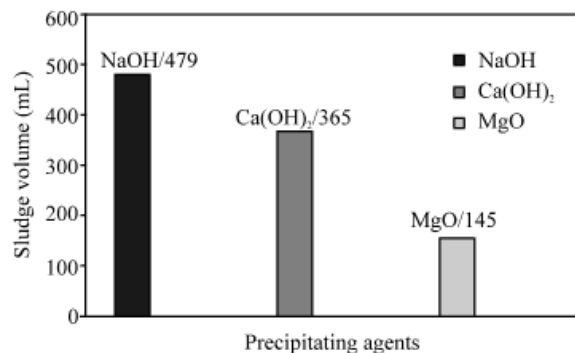


Fig. 3: Sludge volume for the three precipitation agents (settling time 5 h)

The settling rate for the three precipitating agents is shown in Fig. 2. The settling rate of the process for magnesium oxide is much more than this rate for the other two agents. Furthermore, a grainy, dense, easily settleable precipitate can also be formed when MgO is used as the precipitate.

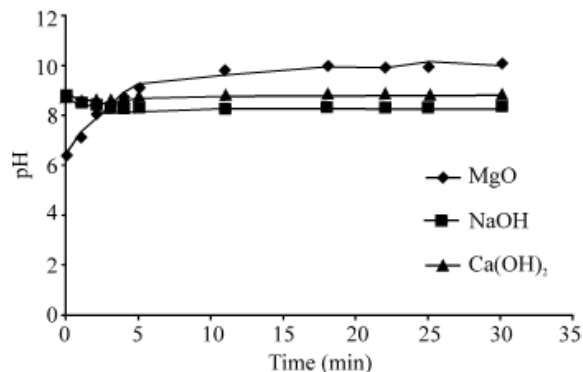


Fig. 4: Variation of pH vs mixing time for the three precipitating agents (velocity of mixing 90 RPM)

Whereas, precipitate forming from NaOH was very gelatinous and the settling rate was low. Sludges forming from  $\text{Ca}(\text{OH})_2$  was not also desirable. The results of the present study showed that high quality sludge, high settling rate and low volume of sludge was obtained by MgO. Whereas, sludge forming from NaOH and  $\text{Ca}(\text{OH})_2$  are very gelatinous. Furthermore, the settling rate for NaOH and  $\text{Ca}(\text{OH})_2$  is low and dewatering sludge is difficult. Similar to the results obtained by Panswad *et al.* and Hemming *et al.*<sup>[13,14]</sup>, our results showed that MgO is a suitable precipitating agent for removing and recovering chromium from tanning wastewater.

Figure 3 shows the sludge volume produced by the three precipitation agents. Sludge volume by MgO is much less than the sludge volume produced by  $\text{Ca}(\text{OH})_2$  and NaOH. The ratio of sludge is:

$$V_{\text{MgO}} : V_{\text{Ca}(\text{OH})_2} : V_{\text{NaOH}} : 1 : 2.5 : 3.3$$

As Fig. 3 shows the sludge volume of chromium hydroxide resulted from the MgO is also much smaller than this volume when using NaOH and  $\text{Ca}(\text{OH})_2$ . This is important because not only helps to reduce the volume of the treatment plants, but also recovering chromium from such sludges is much easier than sludges with huge volume. The results of Panswad *et al.* confirm these results<sup>[13]</sup>.

An optimum time of rapid mixing for the three precipitation agents is shown in Fig. 4. The time needed for rapid mixing of MgO was longer than the other two precipitation agents.

## CONCLUSION

It is concluded from our results that the optimum pH for the precipitating chromium from tannery wastewater is 8-9 and the good sludge with high settling rate and lower volume was obtained when using MgO as the precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tanning wastewater. It is also concluded that magnesium oxide is much more

desirable than lime and sodium hydroxide for removing and recovering chromium from tannery wastewater.

## ACKNOWLEDGEMENT

The authors would like to thank Mr. Ghoshooni and Mr. Minasian for their cooperation.

## REFERENCES

- Patterson, J.W., 1985. Industrial wastewater treatment technology: Butter Worths: Boston.
- Zayed, A.M. and N. Terry, 2003. Chromium in environment: Factors affecting biological remediation. *Plant and Soil*, 249: 139-156.
- Sreeram, K.J. and T. Ramasami, 2003. Sustaining tanning process through conservation, recovery and better utilization of chromium. *Resources, Conservation and Recycling*, 81: 185-212.
- Fabiani, C., F. Ruscio, M. Spadoni and M. Pizzichini, 1997. Chromium (III) salts recovery process from tannery wastewaters. *Desalination*, 10: 183-191.
- Ludvik, J., 2000. Chrome balance in leather processing. United Nation Industrial Development Organization.
- Kocaoba, S. and G. Akin, 2002. Removal and recovery of chromium and chromium speciation with MINTEQA2. *Talanta*, 57: 23-30.
- Hafez, A.I., M.S. El-Manharawy and M.A. Khedr, 2002. RO membrane removal of unreacted chromium from spending tanning effluent. A pilot-scale study, part 2. *Desalination*, 14: 237-242.
- Ashraf Chaudry, M., S. Ahmad and M.T. Malik, 1998. Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Manag.*, 17: 211-218.
- Tsugita, R.A. and R.H. Ellis, 1981. Pretreatment of industrial wastes manual of practice. WPCF No ED-3.
- American Public Health Association, 1992. Standard Methods for the Examination of Water and Wastewater. 18th Ed. APHA, Washington DC.
- Song, Z., C.J. Williams and R.G.J. Edyvean, 2000. Sedimentation of tannery wastewater. *Water Res.*, 34: 2171-2176.
- Ro, M. and A. Ganter, 1998. Possibilities of reduction of recipient loading of tannery wastewater in Slovenia. *Water Sci. Technol.*, 3: 145-152.
- Panswad, T., O. Chavalparit, Y. Suchariththam and S. Charoenwisedsin, 1995. A bench-scale study on chromium recovery from tanning wastewater. *Water Sci. Technol.*, 3: 73-81.
- Hemming, D., R.E. Hahn, J.R. Robinson and W. John, 1978. Recovery of chromium values from waste streams by the use of alkaline magnesium compounds. U.S. Patent 4108596.