Poll Res. 41 (1) : 42-46 (2022)

ISSN 0257–8050
DOI No.: http://doi.org/10.53350/PR.2022.v41i01.005

AN APPROACH FOR CR+3 IONS RECYCLE FROM THE INDUSTRIAL WASTEWATER BY THE CHEMICAL PRECIPITATION METHODS

DR HUSAM ELDIN SADIG[1] AND MOHAMMED TABIDI[2]

[1]*Dhofar University (DU) Department of Mathematics & Sciences, College of Arts and Applied Sciences*
[2]*Dhofar University (DU) Department of Mathematics & Sciences, College of Arts and Applied Sciences, School of Chemistry University of Sciences Malaysia (USM), Malaysia*

(Received 1 June, 2021; Accepted 17 July, 2021)

ABSTRACT

The global concern about leather industries is increasing as the leather industries expand each year. These industries face very challenging tasks with an increase in stringent pollution control regulations enforced by various bodies due to environmental concerns and human risks. Chromium salts comprise the most widely employed chemical for the tanning process in leather industries. Approximately 35% of chromium utilized in the tanning process remains as metal and is discharged to wastewater streams. The removal and recovery of this quantity of wasted chromium are necessary for environmental pollution control and economic policymaking. This paper highlights chromium recovery and reuse systems of chromium salts in tanning wastewater by using NaOH as an effective chemical precipitation method to regenerate chromium solutions, adapt chrome recovery plants and technically and economically evaluate the systems.

KEY WORDS : Chromium, Precipitation, Tanning, Leather industries, Wastewater, Sodium hydroxide

INTRODUCTION

The leather industry is an old and fast-growing industry due to the increasing demand for different types of leather finished products, which has caused the growth of the tanning industries in many countries. To improve the quality of leather, the leather cleaning and treatment process involves the following steps: soaking, liming, deliming, pickling, vegetable tanning and chrome tanning (Richard Daniels, 2017). These processes in leather industries involve a high quantity of chemicals, such as sodium chloride (NaCl), sodium sulphate (Na_2SO_4) (Avudainayagam *et al.* (2003)., chromium and ammonium salt (NH_4Cl). These chemicals are discharged as industrial waste effluent, which means that the leather industry is one of the heavy polluting industries due to the use of heavy metals (Fenglian Fu and Qi Wang, 2010), such as chromium, copper, nickel, and lead, with high concentrations exceeding the discharge limit, which are not easily removed by normal treatment. Chromium is a common pollutant in tannery industries introduced to natural water from the discharge of tannery effluent to wastewater (Esmaeili *et al.,* 2005).

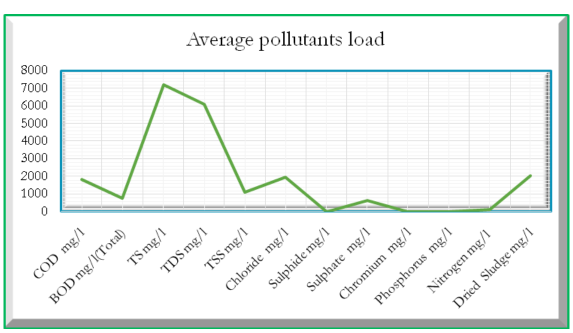
Chromium is one of the heavy metals found in Earth's crust. Chromium exists in two oxidation states (trivalent state and hexavalent state) (Karale *et al.*, 2007) chromium is generally found in the trivalent state. Chromium is discharged to wastewater during tanning operations (Karale *et al.*, 2007). Approximately 30 to 40% of the chromium used for the chrome tanning process is discharged to wastewater; hence, it becomes necessary to remove chromium from wastewater due to environmental concerns and human risks (Khan, 2001).

MATERIALS AND METHODS

Many specialized methods and advanced treatments have been utilized to remove total chromium and hexavalent chromium from waste streams, e.g., ion exchange, membrane filtration, reverse osmosis, coagulation – flocculation, adsorption, electrocoagulation, and flotation. A combination of biological removal by using the actinomycetes method (Bopp and Ehrlich, 1988). and chemical precipitation reactions, which has become the most important method to remove heavy metals, has been reported (Baltpurvins *et al.*, 1997). The literature showed that the percent of chromium removed from wastewater by using MgO is 99%, which is a more effective chemical precipitation method. However, MgO is too expensive to be economical. The precipitation reaction method of recovery and reuse of chromium occurs in the form of chromium hydroxide by using various agents, such as magnesium oxide, calcium oxide, lime, sodium carbonate and sodium hydroxide (Panswad *et al.*, 2001). This paper highlights NaOH as a superior chemical precipitation method that is used to recover and reuse chromium from wastewater. Sodium hydroxide is a promising alternative for overcoming a precipitation reaction method for the recovery and reuse of chromium.

Chromium is recovered by the addition of sodium hydroxide as chromium hydroxide. Chromium hydroxide is dissolved by using sulphuric acid, and the recovered chromium is used as a tanning liquor (Baltpurvins *et al.*, 1997). This method is a more effective and cleaner solution that cannot affect the quality of the leather.

Parameters	Average Pollutants Load
COD mg/l	1850
COD mg/l (soluble)	1300 mg/l
BOD mg/l (total)	780
BOD mg/l (soluble)	555
TS mg/l	7220
TDS mg/l	6100
TSS mg/l	1120
Chloride mg/l	1975
Sulphide mg/l	25
Sulphate mg/l	630
Chromium mg/l	25
Phosphorus mg/l	4.5
Nitrogen mg/l	150
Dried sludge mg/l	2050



Technology Adopted for Chrome Recovery and Reuse System

The list of equipments installed in a chrome recovery plant includes stainless steel screens fixed before the collection tank pump; effluent collection equipped with a reactor and stirrer; a sodium hydroxide tank with a stirrer; a chromium regeneration tank with a mixer; a dosing tank with a dosing pump filled with sulphuric acid and a chromium liquor storage tank with a pump for regenerated chrome liquor. Figure 1-2 shows the process flow diagram for the chrome recovery plant.

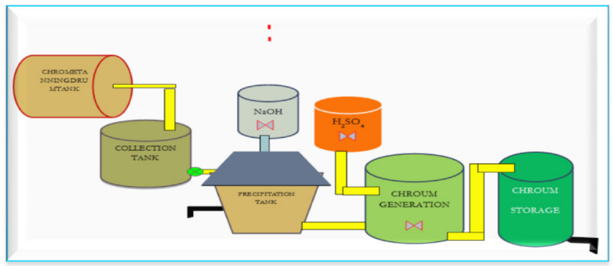


Fig. 1-2. Process flow diagram for chrome recovery

Chrome Recovery Operation Procedures

The chrome tanning drums discharge solution into a chromium drain channel, and tanning solution is filtered with a stainless steel screen fixed at the inlet point of the chrome liquor's collection tank to remove large impurities. From this point, the sample was collected and utilized for all the tests in this study, such as Cr^{+3}, Cr^{+6}, biochemical oxygen demand (BOD) chemical oxygen demand (COD), pH, total solids, and suspended solids (SS). The spent tanning solution is pumped by the submersible pump from the collection tank into the separation tank. The solution is then stirred with the mechanical mixer in the separation tank (Korekt Pierc and Thomas c. Thokstensen). The solution is basified to a pH vale of 11 by the addition of caustic soda and a known quantity of calcium carbonate added to the solution with continuous stirring for a period of one hour. Next, stirring is stopped to allow the liquor to settle for 5 hrs. Two layers of supernatant and precipitate layers are formed and will be separated. The precipitate layer, which contained chromium trivalent, was separated from the salt, transferred to a chromium regeneration tank and stirred by a mechanical stirrer connected to a chromium regeneration tank. During stirring, sulphuric acid is added from the sulphuric acid dosing tank to the acidified solution. The pH range is adjusted to 2-3 in the regeneration tank. Theoretically, Cr^{3+} removal depends on the solution pH and temperature. The treated chromium is transferred to the chromium liquor storage tank.

Fundamental Method of Precipitation

Chemical Precipitation

The chemistry of chromium is usually described clearly, particularly in the reaction of hexaaquachromium(III) ion $\{Cr(H_2O)_6\}^3$ complex ions with ligands of water.(Dargo H., Ayalew A.)

To achieve stabilization, the stability of the free hexaaquachromium(III) ions $\{Cr(H_2O)_6\}^3$ coordinated with anions containing free pairs of electrons depends on the concentration of chromium metal and ligand, the number and orientation of the ligand of water as donor groups, the formed number and size of the chelate ring and the pH of the solution (Zheng and Bai, 2001).

The reaction of free hexaaquachromium(III) ion $\{Cr(H_2O)_6\}^3$ with NaOH removed hydrogen ions from the water ligand in the hexaaquachromium(III) ion; the hydrogen removed from the three water molecules attached to hexaaquachromium(III) ion $\{Cr(H_2O)_6\}^3$; the chromium complex became insoluble in water without charge (neutral complex) and precipitated in the solution.

Hydroxide precipitation

Liquor solutions containing violet octahedral chromium(III) ion complexes react with hydroxides to form precipitates of $\{Cr(OH)_3(H_2O)_3\}_{(s)}$

Reactions of hexaaquachromium ions with sodium hydroxide

Step-1 Adding hydroxide ions to 2+ hexaaquachromium ions

$\{Cr\ (H_2O)_6\}^{3+}\ (aq) + 3OH^-(aq) \rightarrow \{Cr(OH)_3(H_2O)_3\}_{(s)} + 3H_2O_{(l)}$

Violet solution green solid.

Hydroxide ions are added until a new complex is formed. This formed complex is a neutral compound that is insoluble in water and precipitates in solution (https://www.chemguide.co.uk/inorganic/complexions/aquaoh.htm)

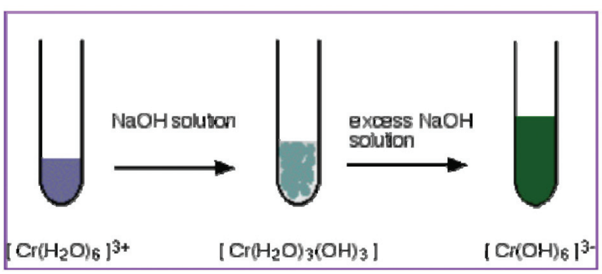
Step – 2 Adding acid to hexahydroxochromate(III) ions

Chromium (III) hydroxide $[Cr(OH)_6]^{3-}$ is known as an amphoteric hydroxide. Chromium (III) hydroxides are amphoteric compounds that may react with bases (hydroxide ions) to give $[Cr(OH)_6]^{3-}$ and with acids such as sulphuric acid (hydrogen ions) to give $[Cr(H_2O)_6]^{3+}$. When sulphuric acid was added, decreasing the pH caused an increase in the H^+/H_3O^+ concentration and protonated the chromium (III) complexe as the hydrogen H+ is obtained (Alguacil *et al.* (2004).

RESULTS AND DISCUSSION

The characteristic of tanning wastewater (Basu and Paul *et al.*, 1999). The tanning liquor was acidified, and treated wastewater contained concentrated Cr^{3+} and BOD refer to Table 1.

Measurements of the inlet streams of the



$\{Cr\ (H_2O)_6\ \}^{2+}_{(aq)}$ ↓

OH^-

In each step, one proton is removed from each complex (from 3^+ to 3)

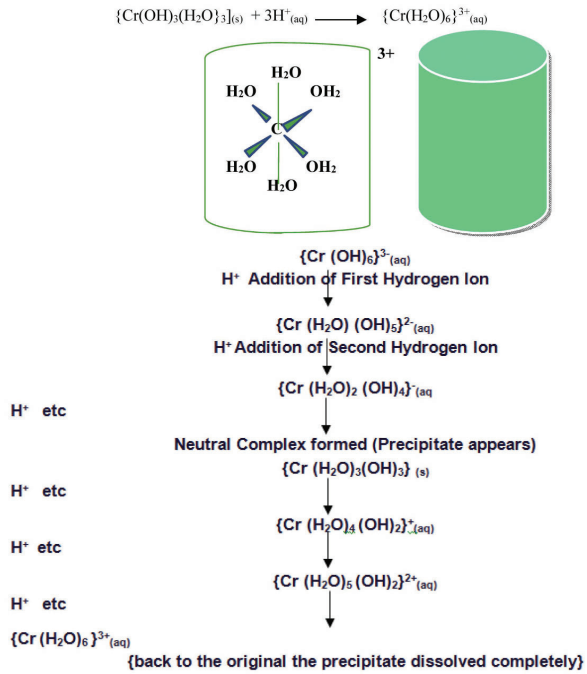
$\{Cr\ (H_2O)_5\ OH^-\}^+_{(aq)}$ ↓

OH^-

$\{Cr\ (H_2O)_4\ (OH)_2\}+_{(S)}$

{with the addition of more hydroxide, complex ions of chromium (hydroxide III) ionsare neutralized and precipitated by ligand displacement OR replacement reactions as $[Cr\ (H_2O)_6]^{3+}$}

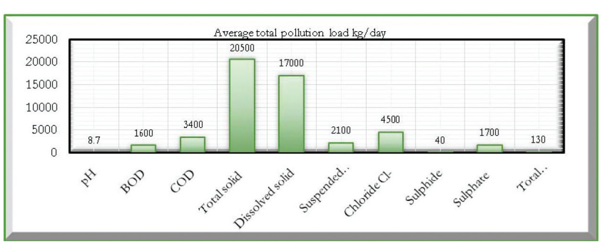
Not including the water ligands, the formed chromium hydroxide precipitate is written as $Cr(OH)_2$.



Parameters	Value	Average total pollution load kg/day
pH	9 – 7	-
BOD	1000 – 3000	1600
COD	2500 – 8000	3400
Total solid	15,000 – 25,000	20,500
Dissolved solid	13,000 – 21,000	17,000
Suspended solid	2000 – 4000	2100
Chloride Cl-	6000 – 9500	4500
Sulphide	30 – 50	40
Sulphate	1400 – 2000	1700
Total chromium	100 – 250	130

treatment pilot plant and chromium recovery plant

All values accepting pH are in mg/l; sources of Al Omania data for the tannery and leather industries.



Emission factors for chrome tanning in AL Omania for the tannery and leather industries.

Cost-benefit analysis

The cost-benefit analysis is limited by the investment, performance, maintenance costs, and

Parameter	Chrome tanning
BOD	1.5
COD	2.2
Total solids	70
Dissolved solids	60
Suspended solids	2.5
Chloride	30
Total chromium	3.8

supply of chemicals. The recovery of chromium is profitable. Each year, the price of new chromium salt increases, which introduces additional benefits. According to Table 4, the total capital investment in the chromium recovery system is \$52,000, and the annual consumption of BCS is 240 tons per year.The waste is approximately 80 tons. The efficiency of the chrome recovery system is greater than 99%. We can collect 90% of the fluid from the chrome exhaust host andchrome drum. Therefore, 70% of the chromium salts can be recycled and reused from a cost-benefit analysis. The total cost recovered from chromium is approximately 400 US/T, while the cost of the new chromium salt can exceed \$800/t. The recovery period for the maintenance of the vineyard is less than three years. In addition to the direct economic benefits, the costs to operators and the maintenance of waste management facilities are low.

CONCLUSION

Recovery of chromium(III) salts discharged through spent tanning solution from tannery effluent by using the chemical precipitation reaction to precipitate chromium as chromic hydroxide ($Cr(HO)_3.nH_2O$, $Cr(OH)_3$ or CrH_6O_3) is performed. This design shows the effect of sodium hydroxide as the best precipitant coagulant, which yields a voluminous chromium sludge. Therefore,the chromium sludge is separated by decanting the supernatant liquor, and chrome slurry is dissolved in sulphuric acid and chromium sulphate $\{Cr_2(SO_4)_3\}$, which formed again as reusable liquor. The system is more than 99% efficient in recovering

Total processing capacity	3000 tons
Use of chromium salt (BCS)	240tons/year
Capital cost of the central chrome recovery system	52,000US$
Annual operating cost	Cost in US dollars
Maintenance	1,500
Labour	1,000
Chemicals	9,000
Electricity	500
Miscellaneous	2,000
Total annual operating cost	14,000
Financial cost	7,800
Depreciation	7,800
Total annual cost	29,600
Benefits	-
Value of chromium recovery @ approximately US$800 per ton for 70 tons	$56,000
Net profit/year	$26,000

(UNIDO) Regional workshop on the design, operation and maintenance of effluent treatment plants
13 – 24 October 1997 – Chennai, India (Ludvík and Buljan, 2000)

chrome from the chrome tanning drum. The level of chromium in wastewater decreases from 100 – 150 mg/l to 10 – 20 mg/l, and the system reuses water, which results in an increased financial benefit to prevent the disbursement of chromium pollution in the environment.

REFERENCES

Esmaeili, A., Mesdaghinia, A. and Vazirinejad, R. 2000. Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process. *American Journal of Applied Sciences*. 2(10): 1471-1473.

Alguacil, 2004 #6; Avudainayagam, 2003#1; Avudainayagam, 2003 #2; Kowalik-Klimczak, 2017 #4Liu, 2001 #8; Pietrelli, 2004 #7; Religa, 2015 #5; Selvaraj, 2018 #3

Alguacil, F. J. 2004. Chromium (III) recovery from waste acid solution by ion exchange processing using Amberlite IR-120 resin: batch and continuous ion exchangemodelling. *Chemosphere.* 57(8): 789-793.

Khan, A.G. 2001. Relationships between chromium biomagnifications ratio, accumulation factor, and mycorrhizae in plants growing on tannery effluent-polluted soil. *Environ. Int.* 26 : 417-423.

Avudainayagam, S. 2003. Chemistry of chromium in soils with emphasis on tannery waste sites. *Rev Environ Contam Toxicol.* 178 : 53-91.

Basu, M. and Paul, A.K. 1999. Chromium resistant soil actinomycetes: their tolerance to other metals and antibiotics. *Acta Microbiol. Immunol. Hungarica*. 46: 25-32.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., Stuart, A.D. 1997. Effect of electrolyte composition on zinc hydroxide precipitation by lime. *Water Res.* 31 : 973-980.

Bopp, L.H. and Ehrlich, H.L. 1988. Chromate resistance and reduction in Pseudomonas fluorescens

Dargo, H. and Ayalew, A. 2014. Tannery Waste Water Treatment: A Review. *Int. J. Emerg. Tren. Sci. & Tech.* 1 (9) : 1488-1494,

Fenglian, Fu. and Wang, Qi, 2010. Removal of heavy metal ions from wastewaters. *Journal of Environmental Management.* 92 : 407-418.

Ludvík, J. and Buljan, J. 2000. United nations industrial development organization regional programme for pollution control in the tanning industry in south east Asia

Multilateral Investment Guarantee Agency November 10, 2017. Environmental Guidelines for Tanning and Leather Finishing, P.499-503.[https://www.miga.org/documents/Tanning and Leather Finishing.pdf

Panswad, T., Techovanich, A. and Anotai, J. 2001. A bench-scale study on chromium recovery from tanning wastewater. *Water Science Technol.* 31(9) : 73-81.

Richard Daniels, 2017. World Leather Magazine A radical new approach within liming and chrome tanning technologies.

Karale, R.S., Nangare, P.B. and Wadkar, D.V. 2007. Removal and Recovery of Hexavalent Chromium from Industrial Wastewater by Precipitation with Due Consideration to Cost Optimization. *Journal of Environmental Research and Develeopment.* 2(2) : 209-216.

Zheng, Y. and Bai, D. 2001. Physio-chemical-biological treatment of tannery wastewater. *Industrial Water and Wastewater.* 32(5) : 52-4.