TEST Engineering & Management

January - February 2020
ISSN: 0193 - 4120 Page No. 7675 - 7680

Studies Of Chemical Precipitating Agents Magnesium, Sodium And Calcium Oxide In Removal Of Chromium From Chrome Tan Liquor

Sathish Thangamuthu[1], Shanmugam Palanisamy[2], Subramanian Nallasamy[3], Gowri Shankar Velusamy[4]
[1,2,3] *School of Chemical and Food Science, Kongu Engineering College, Erode-638 060*
[4] *Assistant Professor,Department of EEE,Kongu Engineering College,Erode-638 060*
**Corresponding author-Email: sathish.chem@kongu.ac.in , Tel: +91 9790065522*

Article Info
Volume 82
Page Number: 7675 - 7680
Publication Issue:
January-February 2020

Article History
Article Received*: 18 May 2019*
Revised*: 14 July 2019*
Accepted*: 22 December 2019*
Publication*: 04 February 2020*

Abstract:
In this present study, chromium removed from chrome tan liquor using chemical precipitating agents such as MgO, CaO and Na2O. The potential evaluation of sludge from precipitation was investiged by varying temperature, pH, stirring speed and ratio of liqour to agents on synthetic and industrial effluents. The result shows that MgO and CaO have faster rate in precipitation and sludge formation, and higher dosage of CaO enabled in higher Cr removal efficiency. Higher in temperature and acidic pH have major impact in dissociation of precipitate from Cr removal, which reduce the eficiency below 75% when pH<6 and temperature >50oC.

Keywords: synthetic, industrial effluents, acidic Ph.

I. Introduction

Even though water scarcity is a major threads in all over the world, the developing countries like India, required huge volume of fresh water to suppy for both domestic and industrial need. Particularly, the production sector required fresh water in cleaning, neutralizing, washing, as a coolent, seperation and other processes. During operation of production, the water discharged from various outlet get contaminated and contains different pollutants like heavy metals, volatile organic compounds, inorganic salts, suspended and dissolved solids.

This contaminated water are directly or indirectly mixed with fresh waters such as river, lakes, ponds and canals. So, Industrial sector are focused in restriciting the waste water contamination with fresh water and with adoptive technology, waste water should reduce, reuse and recycle within the constrainted geographical boundry of industries.

In particular, the leather industries utilize water at various process like soaking, pickling, tanning, coloring and to have a better quality of leather chrome tanning is unavoidable process, obviously the effluent is highly contaminated with chromium. Removing the contamination from the effluent, One of the conventional method is using suitable precipitating agent such as magnesium oxide, calcium hydroxide, sodium hydroxide, etc. The removal efficiency depends on the pH, temperature, mass of precipitating agent, period of stirring, speed of stirring. Chromium removal efficiency were stuided with MgO, Alum and PAC-18 has higher efficiency at a pH of 8. Overall reduction in chromium 98.5%, COD 61.5% and colour 99% is carried in batch process with calcium hydroxide at a neutral pH. Chromium salts not only affect the human health, it kills the growth of microorganisms utilized in sewage treatment and also settled as sludge and build-up of chromium, which is undesirable waste

January - February 2020
ISSN: 0193 - 4120 Page No. 01 - 11

cannot be used as a fertilizer. Aluminum sulphate and ferric chloride were used as a coagulant in the process. The influence of pH and coagulant dosages on the coagulation process was studied and found to be optimum at neutral pH ad increasing the dosage. The research carried on the chromium removal in tanning effluent using chemical precipitation and electro-coagulation. Chromium is separated as insoluble precipitate in both process, Chemical precipitation has 99.74% chromium removal efficiency and has efficiency of 97.76%, 69.91% and 90.27% with aluminum, copper and iron electrodes respectively in electro-coagulation method. Recent investigation has carried to precipitate chromium (VI) using lead sulfate as a precipitation agent, observed that reduction of chromium from 0.2 mol/L to 0.08 mg/L at a higher pH 13.90 and the ratio of $PbSO_4$ to K_2CrO_4 is 4, along with these no changes can be made by altering reaction temperature and reaction time. Due to the usage of lead sulphate no secondary pollutant has been carried because of insoluble nature. The present study focused in removal of chromium using chemical precipitation such as calcium oxide, sodium oxide and magnesium oxide by varying pH, precipitating dosage, stirring speed. stirring time and temperature in the solution.

II. Material and mathods

The study used pure chromium, potassium dichromate, HCl, H_2SO_4 and 1,5-diphenylcarbazide from Sigma-aldrich. All the reagents were used without prior treatment in analytical grade. Flame Atomic Absorption Spectrometer (S-series Thermo Scientific) equiped with deuterium quadline background correction and 6 lamp auto-aligning lamp turret using air-acetylene flame is used to determine the chromium. Five series of 1 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L known 1000 mg/L chromium standard were prepared in 50 mL volumetric flasks with diluting deionized water. The five point linear calibration curves were established by running known standard concentration in flame atomic absorption spectrometer. The chromium determinations are identified by run of blanks and chromium solution directly in spectrometer. The difference in amount of blanks and chromium precipitate in deionized water gives the reading of chromium.

Double beam UV-Vis spectrophotometer (Elico SL244) contains pre aligned deuterium lamp (D_2) and tungsten (W) halogen lamp used to determine the hexavalent Cr content in the solution measurement point at 543 nm. The concentration of the Cr can be identified by preparing blank and standard Cr solution with above mentioned procedure. Reference tan Cr solution is prepared by taking 100 gm of potassium dichromate (based on 100% purity) in 750 mL of distilled water (1:7.5) in 1 L beaker to obtain 133.33 ppm concentration. Later, the pH was adjusted by adding HCl in the prepared solution to obtain acidic medium. Hexavalent Cr can be determined by 50 mL of sample prepared by 1 M H_2SO_4 and 5mL of 1,5-diphenylcarbazide were added into a 100 mL conical flask and measured in spectrophotometer at 543 nm. Difference between the concentration of Cr(IV) and total Cr can give the concentration of Cr(III) present in the solution.

Chrome tan liquor collected from leather processing, Erode,India, in 5 L plastic bottle. The tan samples collected in spot of batch tanning process, had transported to laboratory quickly to determine the parameters. The collected tan samples were allowed into parameter invesigation such as Suspended solids, Cr concentration, pH, total solids, BOD, COD and colour. To determine the effect of these parameters, different precipitating agents are taken in each beaker with capacity of 500 ml each after get sieve screening. Each samples with precipitating agents (CaO, Na_2O and MgO), Conc. HCl can be added to maintain the pH between 6 and 8. Stagewise mixing of agents with waste water were carried out with 50 rpm for 1 h, 90 rpm for 20 min and

January - February 2020
ISSN: 0193 - 4120 Page No. 01 - 11

150 to 600 rpm for 30 min in hot plate with varying temperature using magnetic stirrer. Settling of precipitate was carried out for 5 h. The investigation on addition of the precipitating agents were measured by the effects of temperature, pH, stirring speed, and precipitating agents to sample ratio. The samples are taken directly from each process before and after settling to measure Cr concentration in waste water by spectrophotometer. After addition of precipitating agents, the required pH was controlled using concentrated HCl by 5, 10, 15, 20, 25 mL to 500 mL of tan liquor and the parameters are measured as Conductivity with conductivity meter and pH with pH meter. Adding conc. HCl drop by drop in the waste water carried out with stirriering speed of 150 rpm for 30 and 60 min, settled for 4 h, filtered, washed and diluted in deionized water and stored in refrigerator until Cr analysis. Chromium hydroxide or Chromium carbonate was calculated as the ratio of [Cr concentration initially present in before treatment (Ci) – Cr concentration finally present after the treatment(Cf)] to Cr concentration initially present in before treatment (Ci). Sludge volume on wet basis were measured in this removal efficiency. Also, Wet sludge was dried in hot air oven at 110^{o}C for 6, 12, 18, 24 and 30 h and diluted 5 mg sludge in deionized water of 500 mL for spectrophotometer analysis.

III. Result and Discussion

Effect of stirrering speed

As per the previous investigation the chromium removal is higher at increasing dosage and neutral pH irrespective of precipitating agent. 10 g of precipitating agent, pH and temperatute of the effulent are maintained at 7- 8 and 30-35^{o}C thoughout the experiment respectively. By keeping the stirring time 30 and 60 min as costant and varied the stirrering speed as 50, 90, 150, 200 300 & 600 rpm. The removal of chromium was analyzed before and after treatment. We observed that chromiun removal increase with raising the speed, as on amplify the speed chromium removal efficiency differences was mininum above 150 rpm at 60 min, obiviously the sludge volume raise initially and after no change in sludge volume. So, the stirring speed maintained at 150 rpm in this investigation.

IV. Effect of Stirring time

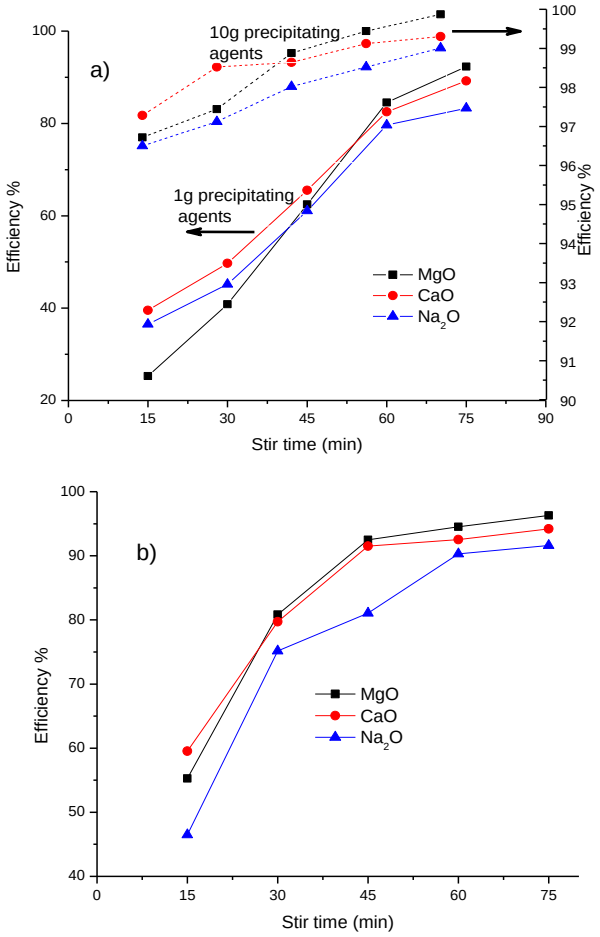


fig 1(a & b) - Effect of stirring time

Figure 1 (a & b) - Effect of stirring time for various precipitating agent of potassium dichromate solutio and tan liquor

The investigation was carried for the varriation of stirring speed between from 15 and 75 min. For the higher mixing time the removal efficiency also higher for CaO, Mgo & Na_2O . The oservation from fig 1 for 1 g and 10 g of CaO the removal efficiency was around 35% and 76% respectively at 15 min, later for stirring time of 30 min the removal efficiency werw 42% and 80% , then extreme change in removal from 42 to 80%

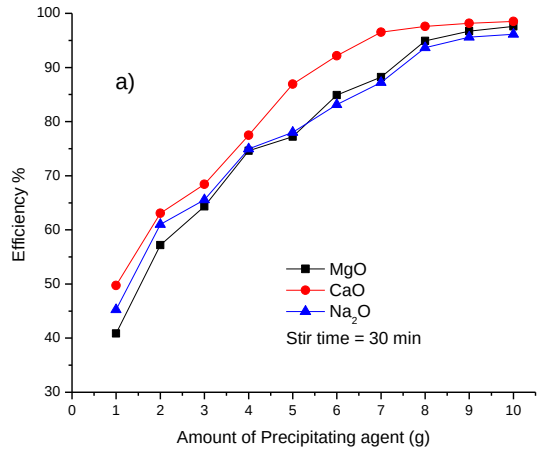
TEST Engineering & Management

January - February 2020
ISSN: 0193 - 4120 Page No. 01 - 11

between 30 min and 60 min for 1 g but using 10g gradual increment of removal efficiency were 84%, 87% and 91 % for 45, 60 and 75 min respectively . The efficiency difference found to be 2% at 75 min for 1 g. So, the stirring time maintained at 30 and 60 min in this investigation.

V. Effect of Dosage

The effect of precipitating agent dosage had been carried under 30 and 60 min stirring time for CaO, MgO and Na_2O starting from 1 g to 10 g. In the figure observed that the chrome removal efficiency of synthetic effluent were raised from 50% and 82.5 % to 97 and 98 %. at 30 and 60 min stirring time for the dosage of CaO 1g to 10 g. As the same for tannery effluent raised from 83% and 89 % to 97% and 97%. So for the CaO the efficiency increased as the dosage raised.



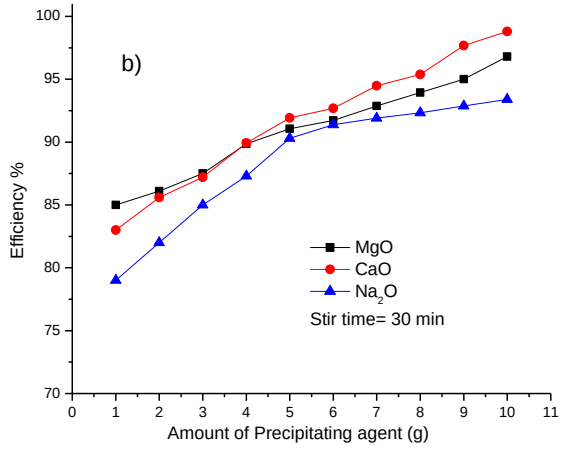
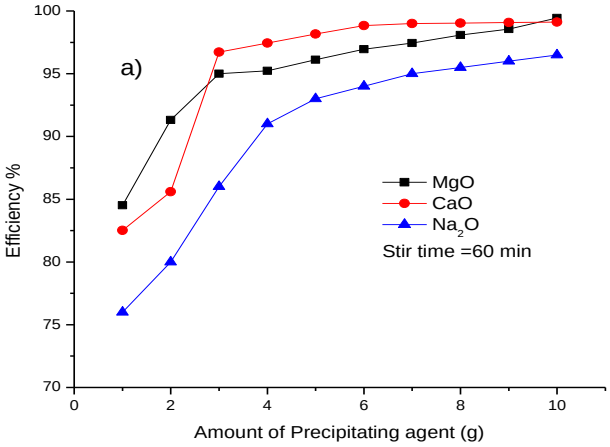


Fig 2(a & b)

Figure 2 (a & b) - Effect of amount of various precipitating agent of potassium dichromate solutio and tan liquor for stirring time 30 min.



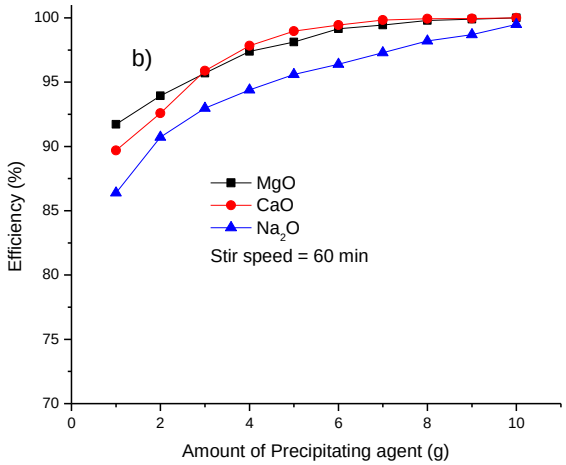


fig 3 (a & b)

Figure 3 (a & b) - Effect of amount of various precipitating agent of potassium dichromate solutio and tan liquor for stirring time 60 min

Effect of pH

Sample No	pH	Vol. of Conc. HCl (mL)	Conductivity (mS/cm)	Appearances	Supernatant Cr concentration (ppm)	Sludge volume (mL)	Removal efficiency (%)
1	4.25	25	4.32	Cloudy	95	72	28.75
2	5.66	20	7.85	Cloudy	35	91	73.75
3	6.51	15	9.01	Transition	12	138	91.00
4	7.48	10	14.54	Clear	3.8	151	97.15
5	8.53	5	16.36	Clear	2.99	152	97.76
6	9.85	0	18.82	Clear	3.67	149	97.24

January - February 2020
ISSN: 0193 - 4120 Page No. 01 - 11

Table 1. Effect of pH in Sludge volume collection using 10 g of CaO added in 500 mL sample of potassium dichromate at stir time of 60 min and settling period of 4 h.

The pH of the sample was maintained using HCl. The study was carried for 10 g of CaO with the stirring time of 60 min at 150 stirring speed. As the pH increased from 4.75 to 5.66, the appearance of the sample still cloudy. There was transition region between the pH 6 and 7, start looking clearly above pH 7. The chromium removal efficiency and the sludge volume formation were 97.76 % and 152 mL for 500mL of sample at 8.53 pH.

Effect of Temperature

Sample No	Temperature (^oC)	Appearances	Supernatant Cr concentration (ppm)	Sludge volume (mL)	Removal efficiency (%)
1	30	Clear	2.99	152	97.76
2	40	Clear	4.4	151	96.70
3	50	Cloudy	32	112	76.00
4	60	Cloudy	46	98	65.50
5	70	Cloudy	59	85	55.75

Table 2. Effect of Temperature using 10 g of CaO added in 500 mL sample with potassium dichromate at stir time of 60 min, pH=8.5 and settling period of 4 h.

Effect of temperature for chromium removal was studied using 10 g of $CaCO_3$ added in 500 mL sample with potassium dichromate at stir time of 60 min, pH=8.5 and settling period of 4 h. At the lower temperature of 25 ^oC the sample was very clear. As the temperature increase solution become unclear, slowly moved to cloudy at temperature 70 ^oC. The chromium removal efficiency and the sludge volume formation were 97.76 % and 152 mL for 500mL of sample at 25 ^oC

VI. Conclusion

The chromium removal efficiecy difference low afoe above 150 rpm. For MgO and CaO have higher precipitation and sludge formation, and higher dosage of CaO enabled in higher Cr removal efficiency. Higher in temperature and acidic pH have major impact in dissociation of precipitate from Cr removal, which reduce the eficiency below 75% when pH<6 and temperature >50^oC.

VII. References

[1] Fenta Minas, Bhagwan Singh Chandravanshi and Seyoum Leta, " Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia" Chemistry International 3(4) (2017), 291

[2] Prakash NanjanBellie, Vimala Sockan & Syed Ikmal Murtaza, " Effect of Precipitating Efficiencies of Magnesium Oxide, Alum and PAC-18 in the Treatment of Chrome Tan Liquor" International Journal of Applied Science and Technology Vol. 4, No. 6; November 2014.

[3] Hao Peng, Jing Guo, Bing Li, Zuohua Liu, Changyuan Tao, " High-efficient recovery of chromium (VI) with lead sulfate", Journal of the Taiwan Instituteof Chemical Engineers 85 (2018), 149–154.

[4] Bianca Mella, Ana Cláudia C. Glanert, Mariliz Gutterres, " Removal of Chromium from Tanning Wastewater by Chemical Precipitation and Electrocoagulation" XXXII. Congress of IULTCS May 29th–31th 2013 Istanbul/TURKEY

[5] Z. Song, C. J. Williams, and R. G. J. Edyvean 'Treatment of Tannery Wastewater by Chemical Coagulation' (2003)

January - February 2020
ISSN: 0193 - 4120 Page No. 01 - 11

[6] Mwinyihija. M 'Main Pollutants and Environmental Impacts of the Tanning Industry' Ecotoxicological Diagnosis in the TanningIindustr ISBN: 978-1-4419-6265-2 (2010)
[7] Bianca Mella, Ana Claudia Glanert, Mariliz Gutterres 'Removal of Chromium from Tanning Wastewater and its Reuse' (2015)
[8] Rathinam Aravindhan, Balaraman Madhan, Jonnalagadda Raghava Rao, Balachandran Unni Nair and Thirumalachari Ramasani 'Bioaccumulation of chromium from tannery wastewater: An approach for chrome recovery and reuse'(2004)
[9] N. F. Fahim, B. N. Barsoum, A. E. Eid and M. S. Khalil 'Removal of Chromium (III) from Tannery Wastewater using Activated Carbon from Sugar Industrial Waste' (2005)
[10] Hongrui Ma, Jianjun Zhou, Li Hua, Fengxia Cheng, Lixiang Zhou and Xianrong Qiao 'Chromium Recovery from Tannery Sludge by Bioleaching and its Reuse in Tanning Process' (2016)
[11] K. M. S. Sumathi, S.Mahimairaja, R.Naidu 'Use of Low cost Biological Wastes and Vermiculite for Removal of Chromium from Tannery Effluent' (2004)
[12] Mahmood M.Brbooti, Balasim A.Abid, and Najah M. Al-ShuwaikI 'Removal of Heavy Metals Using Chemicals Precipitation' (2010)
[13] Kefa K. Onchoke and Salomey A.Sasu 'Determination of Hexavalent Chromium (CR(VI)) concentrations Via Ion Chratography and UV-Vis Spectrophotometry in Samples Collected from Nacogdoches Wastewater Treatment Plant, East Taxas(USA)' (2016)
[14] K. Suvardhan, S. Ramanaiah and K.Suresh Kumar 'Spectrophotometric Determination of Chromium in Water and Pharmaceutical Samples Using 1- Naphtho' (2005)
[15] D. Sivakumar 'Hexavalent chromium removal in a tannery industry wastewater using rice husk silica' Global J. Environ. Sci. Manage, ISSN 2383-3572, (2014)
[16] M. Bosnic, J. Buljan and R. P. Daniels'Polluntants in Tannery Effluents' US/RAS/92/120 (2004)
[17] Eylem Kilic, Joaquim Font , Rita Puig , Selime ¸ Colak, Deniz Celika 'Chromium recovery from tannery sludge with saponin and oxidative remediation' (2010)
[18] Azza Hafez , Samir E1-Manharawy 'Design and performance of the two-stage/two-pass RO membrane system for chromium removal from tannery wastewater' (2004)
[19] V. Vinodhini, Nilanjana Das 'Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust' (2010)
[20] Dinesh Mohan , Kunwar P. Singh, Vinod K. Singh 'Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth' Journal of Hazardous Materials B135 (2006) 280–295