Effect of Precipitating Efficiencies of Magnesium Oxide, Alum and PAC-18 in the Treatment of Chrome Tan Liquor

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Abstract

The efficiencies of chemical precipitating agents for the removal of chromium from spent chrome Tan liquor was compared and studied. The advantages of a selected precipitating agent over others with respect to sludge formation, dosage, pH, minimum turbidity have been studied for MgO, Alum and PAC-18. It was observed that PAC-18 proved to be a better coagulant than alum, as lower turbidity and organic matter content were observed in samples treated by PAC-18, than in samples treated by alum. Furthermore, it was deduced that higher removal capacities were obtained at a high pH value, 8.0.

Keywords: Chromium, Precipitation, Turbidity, Tan Liquor

Introduction

Tanning is the most important step in the production of leather and it is carried out in an aqueous environment with water in rotating drums. Its objective is to process the skins which arrive from the abattoirs in a dried, salted state, to a condition which will facilitate the chemical operation of tanning. During this operation, collagen, the principal protein of the skin, will fix the tanning agent to its reactive sites, thus stopping the putrefaction phenomenon. Trivalent chromium salts are the most widely used tanning agent in the world for the transformation of hides and skins into leather. The leather manufacturing process generates liquid and solid wastes containing chromium (III). This manufacturing activity and the resulting by-products prompt questions concerning their impact upon the environment and mankind.

To obtain good quality leather, it is necessary to use a quantity of chromium salts representing 2 to 2.5 % (calculated as Cr_2O_3) of the mass of skins to be tanned. This implies the use of 8 to 10 % of commercial product containing on average 25 % of Cr_2O_3.This procedure has thus replaced all the techniques based upon the use of chromium (VI) which, in the past, necessitated the reduction to a valency of (III) in the tannery, before tanning. After tanning, the leather is stored for several days which allow the consolidation of the chromium/collagen bonds. The resulting product can resist temperatures as high as 120°C whilst collagen is denatured at 50°C.In order to be transformed into a commercial product, the leather needs to be split and shaved to an even thickness, then superficially re-tanned with low quantities of tanning agents such as chromium, aluminium salts or vegetable/synthetic tannins, dyed with colouring agents, then fat liquored with natural or synthetic fats in order to render the product flexible. After drying, it is embellished with a film of more or less pigmented products on its outer surface in order to attain the appearance and degree of protection required for its final use. The last stages are called leather finishing.

Chromium tanning is preferred because the process is quick, simple, reproducible and is very cost effective. It yields a material with a high mechanical and thermal resistance and a pronounced capacity for dyeing, so that a wide range of colours, rich or pastel shades are possible. The collagen chromium bond is actually the strongest known today amongst the various alternatives, including vegetable and synthetic tannins.

Study was undertaken to investigate the removal of total chromium (Both Hexavalent and Trivalent) from synthetic and industrial effluents by chemical means in order to achieve the 100% removal efficiency (Ramakrishnaiah, C.R., Prathima B.,2012).

Extensive chemical analysis was done to detoxify Cr (VI) by reducing it to Cr (III) by using reducing agents such as ferrous sulphate and sodium metabisulphite, and the precipitation of chromium hydroxide by addition of base (Karale, R.S., Wadkar. D.V., P.B. Nangare, P.B. (2007). A design curve for reduction process was established which can act as a tool for treatment of waste samples from chrome tanning and electroplating industries, when precipitated at pH of 12 gave 100% efficiency at a settling time of 30 minutes and confined that chemical means of reduction and precipitation is a feasible and viable solution for treating chromium wastes from industries (Baig M.A., Mir, M., Murtaza, S., Bhatti, Z.I. (2003).The comparative studies are carried out for chromium removal under different experimental conditions viz. doses of precipitating agents, pH and settling time. The trivalent chromium removal efficiency using Calcium Hydroxide was found to be approximately 76% and that using Sodium Hydroxide was found to be approximately 90%.(Baijnath, LakhanLal, VineetaGautam, Vijay LaxmiYadav.(2014).The separation of the chromium(III) dissolved in a tanning wastewater was studied by means of precipitation with calcium carbonate, reverse osmosis with polyamide membrane and adsorption on activated carbon(Hintermeyer, B.H., Lacour, N.A., Perez Padilla. A E. L. Tavani, E.L.(2008).Chromium was precipitated by the addition of magnesium oxide which also aid as a neutralizer for the acidic effluent. The laboratory treatment was carried out to find the optimum conditions (Mahmood M. Barbooti,(2010).Hexavalent chromium is removed by reduction and precipitation reaction, by using Ferrous sulphate and Sodium metabisulphite as reducing agents to convert Cr(VI) to Cr(III) and Calcium hydroxide , Sodium hydroxide and combination of Calcium hydroxide, Sodium hydroxide are used as precipitating agents to precipitate Cr(III) as hydroxides (Sowmya, T.P., Mahadevraju,(2013).

Leather tanning is an oldest and fastest growing industry in India and there are about 2161 tanneries excluding cottage industries, which process 500,000 tonnes of hides and 314kg of skins annually with overall annual discharge of 9,420,000m^3 wastewater (Mohan, D. (2006). Chromium containing wastes are generated by industries such as leather tanning, electroplating, paint and pigment manufacturing, metal plating and other applications, is responsible for environment pollution. Chromium is not biodegradable and tends to accumulate in living organisms, causing serious diseases and disorders (Barrera, H. (2006). In this process about 60%-70% of chromium reacts with the hides and 30-40% of chromium remains in the solid and liquid wastes and is discharged to open fields, cultivable land, river streams and water bodies causing large scale pollution of soil and water posing eco toxicological risks. Tanning process using chromium compounds is one of the most common Chromium recovery and detoxification are practiced in modern units, but still many of the older and smaller units resort to conventional effluent treatment (Alexander, K.T.W. (1992), Covington, A.D., Alexander, K.T.W. (1993). The precipitation, oxidation/reduction, lime neutralization have traditionally been the most commonly used (Boddu, V.M. (2003). Biosorption appears to be an economically feasible means for the removal and/or recovery of heavy metals from industrial wastewaters (Volesky, B. (1994). The low cost of biosorbents is a tangible advantage over other technologies, such as ion exchange and reverse osmosis. Extensive efforts have been made to explore new types of biosorbent materials capable of effectively sequestering heavy metals (Bailey SE. (1998),Ozer, A., Ozer, D. (2003), Jalali, R. (2002), Ahluwalia, S.S.,Goyal,D. (2007).

Tannery effluent is one of the most industrial wastes and the problem of treatment and disposal of this waste requires considerable attention. Tanning of animal hides to convert them into leather is an important industrial activity. But the pollution from tanneries has a long-term negative impact on the environmental resources. The liquid waste from tanneries is a dangerous pollutant because it contains organic matter and inorganic pollutants in the solution, in suspension as well as in colloidal dispersion. Hence, there is a need to remove these pollutants before they are released to render them harmless. Arumugam has reported on the recovery of chromium from spent chrome tan liquor by chemical precipitation using lime (Arumugam V, (1976) . Pathe et al. have studied the properties of chromium sludge from chrome tan liquor and related the sludge volume, sludge settling rate, surface loading rate etc. (Pathe P P et al.,(1996). ArchanaShukla and Shukla have studied the treatment of tannery and electroplating effluents by using lime, NaOH and their mixture in the temperature range of 25 to 100^0C(ArchanaShukla and N P Shukla.(1994). Rao and Bhola studied on the adsorption technique and the high uptake of hexavalent chromium was observed with PAC at pH 2.0, and for the other adsorbents at pH 6.0 (Rao M, BholaAG(2000).

Materials and Methods

The process was optimized by studying the effect of temperature, alkali dose, and initial chromium concentration on chromium removal efficiency. About 100 mL of the chrome tan liquor was taken in 8 beakers and adjusted to different pH values by the addition of MgO in different doses from 2 to 5.5 g. The pH was noted after each dose addition of the precipitating agent. The sludge was filtered and the filtrate was analysed for its Chromium content. For the determination of total chromium about 10 mL of sample were added into a 50 mL conical flask. A few drops of methyl orange were added as an indicator, followed by the addition of few drops of concentrated NH_4OH solution for pH increase to basic values. Afterwards, 1:1 H_2SO_4 was added drop-wise into the solution until it became acidic; 1 mL was added in excess. The sample volume was adjusted to about 40 mL by deionised water and it was heated to the boiling point for 30 minutes. After boiling, 2 drops of $KMnO_4$ were added to the solution, in order to receive a dark red color, corresponding to the oxidation of Cr(III) into Cr(VI). The boiling continued for 2 minutes, and then 1 mL of NaN_3 was added to the solution, followed by cooling to a temperature of 15-20°C. Finally, 0.25 mL (5 drops) of H_3PO_4 and 1 mL 1,5-diphenylcarbazide were added until the solution turned to a violet color. Total chromium concentration was measured at 543 nm by a spectrophotometer.

For the determination of hexavalent chromium, about 10 mL of sample, 1 M H_2SO_4 and 1 mL 1,5-diphenylcarbazide were added into a 25 mL conical flask and chromium concentration was measured at 543 nm. The concentration of trivalent chromium was estimated by the difference between the concentration of total Cr and hexavalent Cr. Turbidity and absorbance at 254 nm were also measured in the samples in order to have an indication of solids and organic matter content, according to standard methods of analysis. The efficiency of coagulation-sedimentation for the removal of chromium was assessed by the performance of specific jar test experiments, according to the following procedure:

Four 1 L beakers containing 500 mL of tannery wastewater samples were placed in the jar test equipment. Precipitation agents (such as coagulant reagents PAC-18, alum and $Al_2(SO_4)_3 18\ H_2O$ were added to each sample in various dosages, followed by mixing of each solution. The mixing process consisted of three phases namely, phase-I where the solution was agitated at 160 rpm for three minutes, phase-II where solution was agitated at 45 rpm for 30 min, and phase-III, where the solution was left for settling for 1 hour. At the end of the settling period, samples were withdrawn from the supernatant solution, filtered, and analyzed for the determination of chromium content.

Results and Discussion

Effect of MgO

Samples were subjected to chemical analysis and the corresponding results are given in Table 1. The chrome liquor is a concentrated, acidic with a pH of 3.5, Chromium content 1600 mg/L, chlorides and other toxic substances which need to be treated before being discharged. General characteristics of the spent chrome tan liquor was shown in table 1.The chromium was removed as chromium hydroxide using MgO and a maximum removal of 99% was obtained at a pH of 8.9 with a dose of 4.4 g of MgO. The decrease in the percentage removal beyond the optimum pH was observed which might be due to the redissolution of the substance under such experimental conditions. It was further observed that as the pH increases, the floc formed appeared to carry the suspended particles resulting in the reduction of other dissolved organic matter as well.

High concentrations of total chromium were observed in wastewaters samples indicate that the values were higher than the maximum allowable values that have been set in order to introduce industrial wastewaters to the existing municipal wastewater sewage system. In addition, high concentrations of hexavalent chromium were measured, varied from 1 mg/L to 24 mg/L. However, no specific trends were observed in the hexavalent chromium contribution to the total chromium. As a result, a specific treatment process was required, aiming to the reduction of chromium content in the tannery effluents.

Effect of Alum and PAC-18

The effect of coagulant type on the removal of pollutants from the tannery effluent sample was indicated in table 3. Three sets of jar-tests experiments were examined, the appropriate coagulant type was determined in the first set of experiments; the optimum coagulation conditions, as well as, the concentration of coagulant and pH values were determined in the second set; the third set of experiments included the implementation of the determined optimum conditions by using a commercial coagulant, already used in several tanneries in the area.

Jar test experiment carried out using two coagulants, PAC-18 and alum, at a dosage of about 300 mg/L, under various pH ranges, from 6 to 8, and the corresponding results for pollutants removal are given in Table 3. As shown in this table, PAC-18 proved to be a better coagulant than alum, as lower turbidity and organic matter content were observed in samples treated by PAC-18, than in samples treated by alum. Furthermore, it was deduced that higher removal capacities were obtained at a high pH value, 8. As a result, PAC-18 was used in further experiments, in order to determine the required coagulant dosage for the highest chromium removal. Thus, jar test experiments carried out, using PAC-18, ranging from 100 up to 300 mg/L, at a pH adjusted to 8, and the corresponding results are shown in Table 4.

According to the data presented in Table 3, pollutants removal depended upon the coagulant dosage: organic matter content corresponding to UV_{254} values ranged from 1.186 to 1.278 cm-1; total and hexavalent chromium concentration in the treated effluents varied from 0.45 to 1.38 and from 0.09 to 0.12 mg/L respectively. The highest removal capacity was observed at a 100 mg/L coagulant dosage. However, at this dosage poor settleability of suspended solids was observed resulting in high turbidity values.

Additional work carried out in order to examine the effect of a commercial coagulant, $Al_2(SO_4)_3.18\ H_2O$, in the pollutants removal. This coagulant is commonly used for the treatment of tanneries effluent. Preliminary coagulation experiments showed that the best pH range for the particular coagulant was 7.0. This value was used in the bench scale jar experiments, taking into account that the effluents from the particular unit had a pH of about 6.5; pH increase to values higher than 7.0 was not recommended, due to the high cost associated to a high consumption of chemicals required for pH adjustment. Jar test experiments were conducted using various dosages of the coagulant, ranging from 100 to 300 mg/L, and the corresponding results are given in Table 4. As shown in this table, the highest removal capacity was measured at a high coagulant dosage: at 300 mg/L, the lowest concentration of chromium was measured, together with low organic matter content and a low turbidity. However, the corresponding samples were of lower quality that the samples treated by PAC-18. The latter coagulant appeared to have a higher chromium removal capacity at a lower dosage; this is associated to a lower produced sludge volume, resulting in lower sludge handling costs.

Conclusion

1. The use of MgO as a chemical precipitating agent resulted in about 99% removal of Chromium with lesser sludge formation.
2. The chromium was removed as chromium hydroxide using MgO and a maximum removal of 99% was obtained at a pH of 8.9 with a dose of 4.4 g of MgO
3. PAC-18 proved to be a better coagulant than alum, as lower turbidity and organic matter content were observed in samples treated by PAC-18, than in samples treated by alum.
4. The highest removal capacity was measured at a high coagulant dosage: at 300 mg/L, the lowest concentration of chromium was measured, together with a low organic matter content and a low turbidity.

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Table 1: General Characteristics of Chrome Tan Liquor

Parameter	Value
pH	3.5
Acidity	3800
Total solids	32400
Total dissolved solids	30040
Total suspended solids	2360
Volatile suspended solids	810
Chlorides	7600
Sulphates	4840
BOD	250
COD	480
Chromium	1600

All Values except pH are expressed in mg/L.

Table 2: Effect of Lime on Chromium Precipitation

Weight ofMgO added(g/L)	pH	Chromium in filtrate (mg/L)
2.0	8.1	3.64
2.5	8.3	2.89
3.0	8.5	2.66
3.5	8.6	2.00
4.0	8.8	1.64
4.2	8.8	0.90
4.4	8.9	0.40
4.6	9.1	0.54
5.0	9.4	0.66
5.5	9.9	0.68

Table 3: The Effect of Coagulant Type on the Removal of Pollutants from the Tannery Effluent Sample

Coagulant	pH	Turbidity ,NTU	UV_{254} cm^{-1}
Alum	6.0	123	2.84
PAC-18	6.0	47.5	1.63
Alum	7.0	20.5	1.65
PAC-18	7.0	21	1.55
Alum	8.0	11.1	1.51
PAC-1	8.0	24.1	1.32

Table 4: The Effect of Coagulant Dosage on Pollutants Removal from the Tannery Effluent

Coagulant dosage,mg/L	Hexavalent Chromium,mg/L	Turbidity, NTU	UV_{254} cm^{-1}	Total chromium, mg/L
100	0.09	15.5	1.186	0.45
200	0.12	13.2	1.278	0.62
300	0.09	9.8	1.242	1.38

Table 5: The Effect of a Commercial Coagulant on the Pollutants Removal Capacity from the Tannery Effluent

Coagulant dosage,mg/L	Hexavalent Chromium,mg/L	Turbidity, NTU	UV_{254} cm^{-1}	Total chromium, mg/L
100	3.8	635	2.68	12
200	3.1	284	2.785	9.5
300	3.2	165	2.6	4.1