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RESEARCH ARTICLE

REMOVAL OF CHROMIUM FROM TANNERY WASTEWATER BY TANNERY LIME LIQUOR; A VERY COST EFFECTIVE METHOD

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ABSTRACT

Tanning industries produces large quantities of waste water which on direct discharge causes severe environmental pollution. Basic chromium sulphate used in the tanning process is not consumed fully and about 30-40% of it is washed away to the environment and thus creates severe environmental problem especially to the aquatic system. Here a simple method is developed to remove the chromium content of the tannery waste water. Waste water discharged from tannery has different character (pH) at different stages of the tanning process. The chrome liquor (discharged during chrome tanning process) has pH of about 3.5 to 4.0 while the lime liquor (discharged during lime tanning process) has pH of about 11 to 13. Neutralization of these liquors through mixing with each other results precipitation of chromium which was removed by simple filtration. Neutralized liquor was found to have chromium content 2 ppm while the original chrome liquor had 3600 ppm.

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INTRODUCTION

In the last few decades, concerning the environmental pollution, leather industry has been attracted a considerable attention. Tanning industry is one of the oldest industries in the world. They are the user of the by-product of the meat industries and in this sense leather industries should have been considered as green industries. Unfortunately, this is not the case and in fact, it is considered as one of the most polluting industries having potential threat to our environment. Basic chromium sulphate is one of the main chemicals used in the tanning process after which the spent tanning solution is discharged with a high concentration of chromium, causing harmful effects to the environment. About 60-70% of total chromium salts reacts with the hides and rest 40-30% of chromium remains in the solid and liquid wastes specially in spent tanning solution (Adeel *et al*., 2012). Leather industry consumes more than 50 m^3 of water for processing 1 ton of raw hides (Esmaeili *et al*., 2005 and Cot, 2004). In addition, the cost of the chromium compound is also an important issue and it is possible to be recover from the wastewater (Fabiani *et al*. 1997, Ludvik, 2000, Kocaoba and Akin, 2002). Cr ion concentration in the tannery wastewater were found to be 2500-8000 ppm (Hafez *et al*., 2002) and 2000-5000 ppm (Chandra *et al*., 1997). Direct discharge of these effluents from industries has become a severe environmental problem. It would cause the alteration of physical, chemical and biological properties of aquatic environment. Chromium compounds in wastewater have an unfavorable effect on the life and growth of aquatic organism (FAO, 1999). Hexavalent chromium is carcinogenic at very low level and more toxic to aquatic environment (Wang, 1986). Prolonged contact with certain chromium compounds may cause allergic reactions, diarrhea, heart burning, respiratory tract infection, loss of eye sight, dermatitis in individual and acute tubular necrosis of the kidney (Adeel *et al*., 2012). Lung cancer, high blood pressure and kidney failure were reported in many cases (Kolomaznik *et al*., 2000). The permissible limits of total chromium discharge in effluents are in the range 0.5 -10 mg/L directly into water body and 1-50 mg/L on indirect discharges into sewage systems (Bosnc, 1988). Another way, Liming involves the use of alkaline medium (e.g. lime) to condition raw hides and skins and Na_2S is added to facilitate de-hairing. The aim is to remove the hair, flesh and splitting up

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of the fibre bundles by chemical and physical means. Unused calcium hydroxide, sodium sulfide and sodium bi sulfide remain in lime liquor that discharges directly from tanning industries without treatment and causes harm for aquatic system. So treatment of the tannery wastewater is a major issue for pollution control in leather processing countries. Many research have been done for the future sustainability of the tannery industry in respect of environmental pollution; the industry must aim to reduce the consumption of chemicals, water and energy resources and to minimize the production of solid and liquid waste to maintain a safe environment for both aquatic life and human health (Sepehr *et al*., 2005, Mottalib *et al*., 2014, Barbooti *et al*., 2010, Buljan and Kral, 2011, HRW, 2012). The removal of chromium from wastewater may be accomplished by precipitation using the addition of lime and caustic soda (Barbooti *et al.* 2011). In order to reduce chromium from tannery effluents, many researchers used different chemicals and materials like bacillus subtilis (Adeel *et al.* 2012), magnesium oxide (Barbooti *et al*. 2010), three precipitation agents calcium hydroxide, sodium hydroxide and magnesium hydroxide (Esmaeili *et al.*, 2005), aspergillus oryzae (Sepehr *et al.*, 2005), alge, fungi and bacteria (Beleza *et al.*, 2001), reverse osmosis membrane (Hafez *et al.*, 2002) employed and amberliet IR 120 resin (Meshrem *et al.* 2012).

Several studies considering the chromium removal by ion exchange resins have been reported in the literature. Agrawal *et al.* (2006) have recently reviewed the remediation options for the treatment of chromium containing wastewater and summarized the possibilities of using different methods including ion exchange. Another research group have developed a process for removal, recovery and reuse of chromium from tannery wastewater. About 99% chromium can be removed from tanning effluents by this process (Petruzzelli *et al.*, 1995). Kocaoba and Akcin have reported the removal of chromium and cadmium from aqueous solution using a strong cation exchange resin (Kocaoba and Akcin, 2005). Most of the above mentioned methods are good to excellent to remove chromium from tannery effluents, but all of them involve additional chemicals or agents that increase the costing of effluents treatment.

In this paper a simple but efficient and cost effective method for removal of chromium from tanning effluent will be described. No additional chemicals were used in this method so no additional cost involved. It was noticed that waste water discharged from tannery has different character (pH) at different stages of the tanning process. The chrome liquor (discharged during chrome tanning process) has pH of about 3.5 to 4.0 while the lime liquor (discharged during lime tanning process) has pH of about 11 to 13. It was expected that neutralization of acidic chrome liquor by basic lime liquors would precipitate out chromium which could be removed by simple filtration. And it works very nicely – it reduces chromium content from 3600 ppm to 2 ppm.

MATERIALS AND METHODS

Wastewater - fresh lime liquor and chrome liquor were collected from tannery in Hazaribagh, Bangladesh and transferred to the laboratory for the determination of pH and chromium contents as soon as possible. Whitman no. 42 filter paper was used for filtration.

Determination of total water soluble chromium in wastewater

Reagents: No additional chemicals were added.

Formation of precipitation: In order to form precipitation, chrome liquor was treated with lime liquor. According to the simple acid-base reaction, precipitation of $Cr(OH)_3$ was formed. 40 mL of chrome liquor were taken in four different conical flasks, then 10, 20, 30 and 40 mL of lime liquor was added so that the ratios of chrome liquor and lime liquor were 40:10; 40:20; 40:30 and 40: 40 v/v respectively. The mixtures were stirred for overnight at room temperature and left for a few hours for sedimentation. The whole procedure is shown in scheme 1. The chromium precipitates were in the form of compact sludge and was filtered through Whatman no. 42 filter paper. The filtrates were analyzed for the determination of pH and chromium content. Chromium content was measured by Atomic Absorption Spectrophotometer (AAS). Chromium (wavelength 357.9 nm) hollow cathode lamp was used to analyze the samples. Samples were aspirated through nebulizer and the absorbance was measured with a blank as reference.

RESULTS AND DISCUSSION

The pH of chrome liquor was acidic with pH 3.5 while the pH of lime liquor was alkaline with pH 12.50. Huge amount of chromium remain in the wastewater after completion of tanning process. The average of chromium concentration in chrome tanned wastewater was 3600 ppm. Thus the wastewater of tanning process is one of the most important sources of environmental pollutants as the concentration of chromium and other harmful material in the wastewater is extremely high. When this wastewater is directly discharged on soil or in water, the risk of potential oxidation of some Cr(III) species to the more hazardous hexavalent state exists in the presence of manganese (IV) oxide . Mixing of lime liquor with chrome liquor at different ratios changes the pH value of the mixture; the pH of the mixture trends to increase with the increase of the volume of lime liquor as shown in Table 1.

Table 1 shows chromium concentration decreases with the increases of pH of the mixture. The optimum pH for removing chromium content from tannery wastewater by lime liquor is near to neutral solution. The pH and the chromium concentration in chrome tanned waste liquor was 3.5 and 3600 ppm respectively. With the increase of pH, the amount of chromium in the mixture reduces. In the first mixture, the ratio of chrome and lime liquor was 40:10, the pH value did not increased much (pH, 5.4) but the chromium content was significantly reduced and the value was found to be 1057 ppm. Further increase in pH caused in further reduction of chromium concentration in the solution. About 95% chromium was reduced for chrome and lime liquors ratio 40:20 where pH was near to neutral, 6.4. Very good to excellent results were obtained for chrome and lime liquor ratios 40:30 and 40:40 respectively.

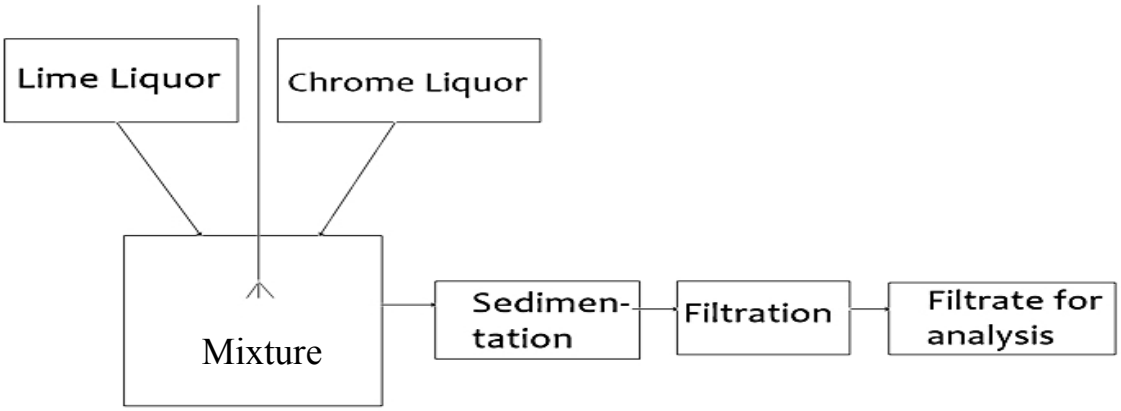

Table 1. The pH value and chromium content at different ratios of chrome and lime liquor

Sample	Mixture		Ratio	pH	Chromium concentration ppm	% of reduction
	volume of chrome liquor (ml)	Volume of lime liquor (ml)				
1	40	-	4:0	3.25	3600	-
2	40	10	4:1	5.40	1057	71%
3	40	20	4:2	6.40	180	95%
4	40	30	4:3	7.60	19	99%
5	40	40	4:4	8.40	2.0	>99%

The pH values of these ratios were 7.6 and 8.4 and the chrome content were found 19 and 2 ppm respectively. The result shows that the pH of the reaction mixture have a vital role to reduce chrome content from the waste liquor and maximum amount of chromium reduced, over 99% (99.99%), at pH 8.4. Permissible limits of total chrome discharge in effluents are in the range 0.5 to 10 ppm directly into water bodies and 1-50 ppm on indirect discharges into sewage system (Bosnc, 1988). Thus the present procedure reduces the chromium content of tannery waste water within the safe limit to discharge directly to the water bodies after treatment. Physical appearance of the filtrate water was colourless and the COD, BOD and TS values of the treated tannery wastewater are reduced significantly (Mottalib *et al*., 2014).

The chemical process involved in the procedure is a simple acid – base neutralization reaction of chrome liquor and lime liquor to form $Cr(OH)_3$ which is insoluble in water and remain in sludge. Thus, the pH of the solution has an important role to form precipitation of $Cr(OH)_3$. Increasing the pH value results more formation/precipitation of $Cr(OH)_3$ and thus chromium concentration decrease in the superentent liquor. The pH of the solution is a major parameter in determining the composition of the products formed. At the pH values of 8.0 to 9.9, $Cr(OH)_3$ is virtually insoluble (Eckenfelder, 1966).

A similar result was obtained when $Ca(OH)_2$, NaOH and MgO were used as precipitating agents (Esmaeili *et al.*, 2005). Al-Bassam *et al.*, 2002, obtained similar results (6 ppm) by using bentonite an porcilinite. Activation of the clay minerals with acid was necessary to improve the efficiency of extraction in the high chromium concentration (>5000 ppm). This is in agreement of the reported documents on the utilization of MgO for chromium recovery. The water remaining after separation of the precipitation contains less than 5 ppm chromium which is in agreement with some reported results (Barbooti *et al.*, 2010).

Conclusion

Since both the chrome liquor and lime liquor generate from tanning industry and their direct discharge causes harmful for land and aquatic system, therefore, it is necessary to treat both the wastewater before discharging to the water body. This paper demonstrates a simple but very efficient and economic procedure for removal of chromium content from tannery waste water. Although many research groups worked for removing chromium content from tannery waste liquor, as far we know, all the methods used additional chemicals or precipitating agents. In present method, no additional chemicals were required to remove chromium from wastewater – here just waste liquors from two different stages of tanning process were treated with each other. The optimum pH for the precipitation of chromium from tannery wastewater is 8.4 and the ratio of chrome liquor and lime liquor was 1:1. And under these conditions more than 99% reduction of chromium was achieved. So this method can be regarded as very efficient, cost effective and environmental friendly process for chromium removing from tanning wastewater especially for developing countries. Furthermore, in liming steps of tanning process uses about double amount of water compared to the chrome tanning steps. Thus the waste liquor generated from liming step is always higher than the waste liquor generated from the chrome tanning steps. Hence the tannery effluent of a particular tannery industry can easily be treated completely by this simple noble method. Further investigation for speciation of chromium and finding the way to recovery of chromium is in progress and will be communicated soon.

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