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Treatment of chromium present in tannery wastewater using chemical & biological techniques

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ABSTRACT

Experimental investigations were carried out to treat tannery wastewater effluent. Various surface-active materials were used to reduce the effect of chromium present in tannery wastewater. This chemical pretreatment was followed by a biological treatment. The aim was to evaluate and optimize the various parameters effecting the chromium removal during the treatment. Different coagulants were used to suggest the efficient surface-active material during chemical pre-treatment phase and thereby the optimum time of contact, dosage and pH were determined. In this present study chemical agents had been used as a pretreatment of tannery effluent to reduce the chromium (VI) whereas the biological treatment ensures rapid reduction in the chromium ions using the bacterial degradation process.

Introduction

Manufacturing of leather, leather goods, leather boards and numerous by-products, solid wastes, high amounts of wastewater contains different loads of pollutants and emits into the air. The uncontrolled release of tannery effluents to natural water bodies increases health risks for human beings and environmental pollution. Effluents from raw hide processing tanneries, which produce wetblue, crust leather or finished leather contain compounds of trivalent chromium (Cr) and sulphides in most cases. Organic and other ingredients are also responsible for high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values and represent an immense pollution load, causing technical problems, sophisticated technologies and high costs in concern with effluent treatment. During the tanning process at least about 300 kg chemicals (lime, salt, etc.) are added per ton of hides.

The different processes by which tannery wastewater produced are:

a) Pretanning (Beamhouse operations):

At the time of cleaning and conditioning of hides and skins, it produce the biggest part of the effluent load. Liming and unhairing also produce the effluent stream with the highest COD value. The unhaired, fleshed and alkaline hides are neutralised with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. This results in the major part of the ammonium load in the effluents.

b) Tanning (Tanyard operations):

Principally, there are two possible processes:

• Chrome tanning:

After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3% by dry weight of Cr (III). Wetblue, i.e. the raw hide after the chrometanning process, has about 40% of dry matter.

c) Wet Finishing (Post-Tanning):

The wet finishing processes are sometimes performed in one single float. Chromium tanned hides or Wetblue are often retanned - during that process the desirable properties of more than one tanning agent are combined - and treated with dye and fat to obtain the proper filling, smoothness and colour. Before actual drying is allowed to take place, the surplus water is removed to make the hides suitable for splitting and shaving. Splitting and shaving is done to obtain the desired thickness of the hide. The composition of pollutants in the wet finishing effluent is complex due to the presence of dyes, fat liquors and combined tanning agents, but the total amounts generated are smaller than in prior steps and often not considered as significant.

d) Finishing

The crust that results after retanning and drying, is subjected to a number of finishing operations. The purpose of these operations is to make the hide softer and to mask small mistakes. The hide is treated with an organic solvent or water based dye and varnish. The finished end product has between 66 and 85% by weight of dry matter. Environmental aspects are mainly related to the finishing chemicals which can also reach effluent water.

Though tannery waste water consists of several constituents, such as Magnesium, Chromium and others heavy metals such as zinc, lead , the present study is based on the study of removal of Chromium (VI) or reduction of Chromium (VI) to its lower form, ie Chromium (III) (Saha et alo., 2007; Saha et al., 2012).

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In this present study the main objective is to establish an unique and cost-effective treatment unit in a combination of chemical and biological treatment so that very less amount of BOD and COD in the finally treated waste water can be achieved and thereby able to show the current treatment efficacy over the traditional process of the said tannery. Moreover the present study aims to evaluate various parameters effecting the BOD and COD level mainly during the treatment so that a clean green belt in and around the leather and tannery premises by maintaining an effective effluent treatment unit can be created.

Materials and Methods

In present study the effluent samples were analyzed using the standard procedure and with the analytical grade instruments. Here the effluent samples were collected from the said tannery industry at the above mentioned sources and were analyzed in the laboratory. Color of the effluents was noted by visual observation. Temperature was measured at the site of collection by using thermometer. pH was recorded immediately at the site of effluent collection with the help of pH meter (APHA 1998).

Treatment Methods

To comply with the stringent environmental regulations of CPCB (India) and to restore safe environment, it was become important to find out the cost effective and easily adaptable wastewater treatment technologies in the tannery premises. Adsorption-based innovative technology developed with low-cost carbonaceous materials showed good potential, more for chromium removal from the wastewater. So based on these approach a simple and economic solution for the existing environmental challenges in the said tannery industry can be examined.

This work was focused on the aerobic treatments of tannery wastewaters that comprise mainly chromium removal using Chemical and Biological agents as described below:

Chemical Treatment

The removal of suspended solids by using surface active chemicals before subsequent biological treatment can be considerably reduce the chromium of the resulting effluent. Fine suspended particles in an effluent may be removed by coagulation and flocculation unit.

In this present study different coagulants was used in a different concentration and also in combination to determine the best surface active agent that could reduce the chromium to a significant level in the chemical treatment phase.

The importance of addition of trivalent Aluminium and iron in waste water treatment can be understood using Schultz theory. The action of coagulation of aluminium ion is due to the hydrolysis leading to the formation of the hydroxide. The intermediate aluminium compounds (hydroxy aluminous complex) provide the charges to neutralize the colloids ions and they also polymerize to form the bridges between colloids and as a result initiate the flocculating process.

Actual effectiveness of the coagulants were evaluated based on the following parameters:

i) Optimum time of contact
ii) Optimum dosage
iii) Optimum pH

The different reactions involved using different coagulants were:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(HCO_3) \rightarrow 3\,CaSO_4 + 2\,Al(OH)_3 + 6\,CO_2 + 18\,H_2O$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(OH)_2 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4 + 18\,H_2O$$

$$2\,FeCl_3 + 3\,Ca(OH)_2 \rightarrow 3\,CaCl_2 + 2\,Fe(OH)_3$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(OH)_2 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4 + 18\,H_2O$$

Biological Treatment of Chemically Treated Effluent:

Since extensive use of Hexavalent Chromium Cr(VI) in various industrial application has caused substantial environmental contamination. Chromium resistant bacteria isolated from soils can be used to remove or reduce Cr(VI) to Cr(III) (a non toxic form). The study was conducted to isolate or culture Chromium resistant bacteria, from soil contaminated with Chromate and examine the effect of some environmental factors such as pH, Time, and presence of other heavy metals.

Chromate reduction activity of whole cells was detected in five Isolates. Most of these isolates belong to the Genes Bascillus as identified by the RNA gene sequencing (Ohtake et al., 1987; Komori et al., 1989; Lovley et al., 1994; Wang et al.,1995; Mabbett et al., 2005; Garbisu et al., 1998).

Bacteria strain, resistant to Cr(vi) were isolated from the contaminated soil (0-15cm depth) from a long term tannery waste disposal site.

The bacteria culture consists of the following steps:

The contaminated soil collected from tannery was diluted into 1:5 ratio. Then the mixture was cold centrifuged for 10 min at 1200 rpm at 10^oC. The clear solution was taken. after that the mixture of clay and cell was cold centrifuged, this solution consisted of the harvested bacterial cells. This cell solution was the diluted in terms of 10^{-1}, 10^{-2}, 10^{-3} & 10^{-4} ratio, in four (4) sterile 100ml conical flasks (Turick et al., 1996). Then from each conical flask 0.1 ml bacterial solution was taken in a previously cleaned and sterile Petri dish, and then 25ml of freshly prepared sterile nutrient agar (NA) solution with 100 mg/L Cr(VI) salt was added. To make this NA solution with Cr(VI)) salt, $K_2Cr_2O_7$ was added in proportion to make a resulting solution of 100 mg/L Cr(VI) strength. The chromium resistant organism was isolated using the pure culture plating method.

Cr(VI) Analysis procedure:

The reduction of hexavalent chromium was determined colorimetrically at 540 nm using the diphenylcarbazide (DPC) method with a detection limit of 5 mgL^{-1}. In a 10mL volumetric flask, 1 mL of sample was mixed with 9 mL of 0.2M H_2SO_4. Then 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added to the volumetric flask. The mixture was then vortexed (Maxi Mix-II Thermolyne) for about 15–30s and let to stand between 10 and 15 min for full colour development. The red-violet to purple colour formed was then measured at OD 540nm using distilled water as reference. Instrument used was calibrated using 0–10 mg/L Cr(VI) prepared from Cr(VI) stock solution (1000 mg/L) (Saha et al., 2012).

The effect of bacteria on the chromium reduction was affected by several factors such as initial concentration of Cr(vi) of the test solution, pH values of the test solution, time of incubation of the test solution and presence of different others heavy metals (such as zinc, lead, manganese, etc) within the test solution. Treatment was performed using bacteria culture on test solution varying the conditions and environment of reduction.

Results and discussion

The characterization of the raw tannery effluent was:

Table 1: The tannery effluent water characetistics:

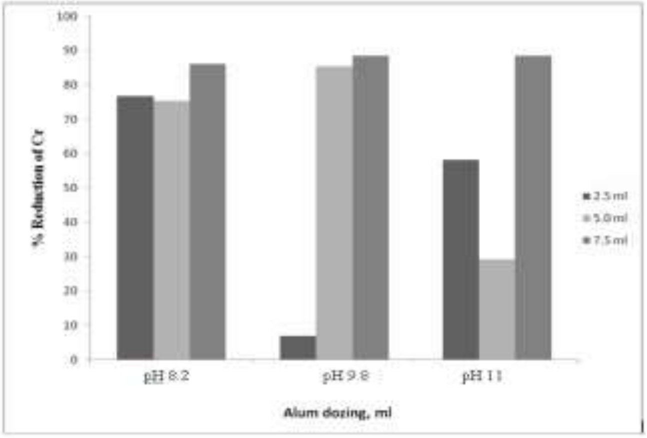
BOD	COD	pH	Ion Concentration	Conductivity	TDS	Resistivity	Cr(VI)
1122 mg/L	2800 mg/L	7.27	32.9 mg/L	2.59 ms/cm	1290 mg/L	438 mho	78 mg/L

It was observed that the Chromium concentration and COD, BOD of the effluent was very high and all the values were higher than the permissible limit of CPCB (India).

Effect of Alum dozing on the removal of Chromium

From Figure1, it was observed that as the alum dozing increases, the % reduction of chromium of the solution increases indicating that at high pH and at high alum dozing, the reduction of chromium from the solution was higher (using 7.5 ml of 10% Alum).

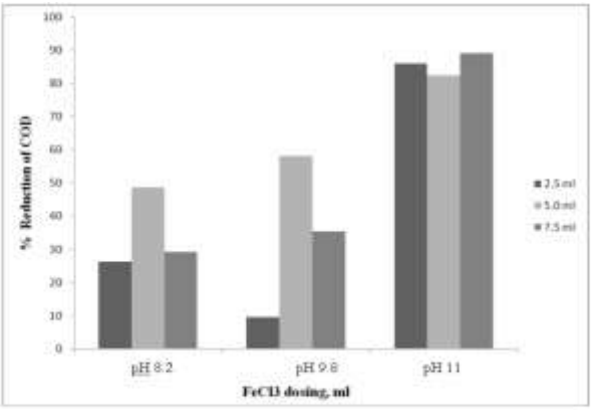
Figure 1: Effect of Alum dozing on chromium removal



Effect of Ferric chloride dozing on chromium removal

From Figure 2, it was observed that as the pH increases, the reduction of chromium increases at different doses and it was observed that at high dozes (7.5 ml of 10% $FeCl_3$ solution), the removal of chromium was higher.

Figure 2: Effect of Ferric chloride dozing on chromium removal

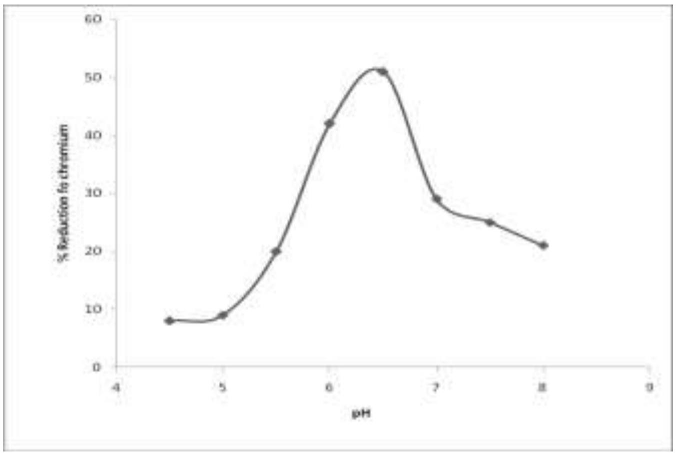


From Figure 1 and Figure 2, it was observed that the alum was more effective among the coagulants as the removal of chromium from the solution was higher in case of alum treatment of the wastewater.

Effect of solution pH on reduction of chromium using isolated bacterial cells

From Figure 3, it was observed that after 10 hrs and at pH 6.5, the reduction of chromium was higher that lower and higher pH. At lower pH bacterial cells may be damaged (due to acidic condition) and as a result the reduction was low. At high pH, the solution was basic in nature and at this pH some organism may not acted and as a result the reduction of chromium in the solution was not so high. So, it can be concluded that at pH 6.5, the bacterial cells better than other pH of the solution.

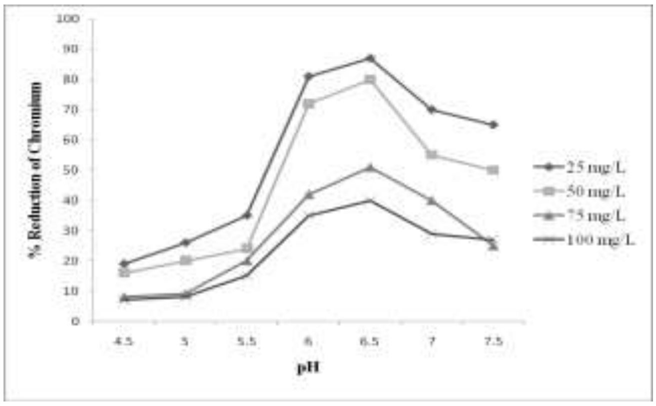
Figure 3: Effect of solution pH on the reduction of chromium from solution



Effect of different concentration on reduction of chromium using isolated bacterial cells

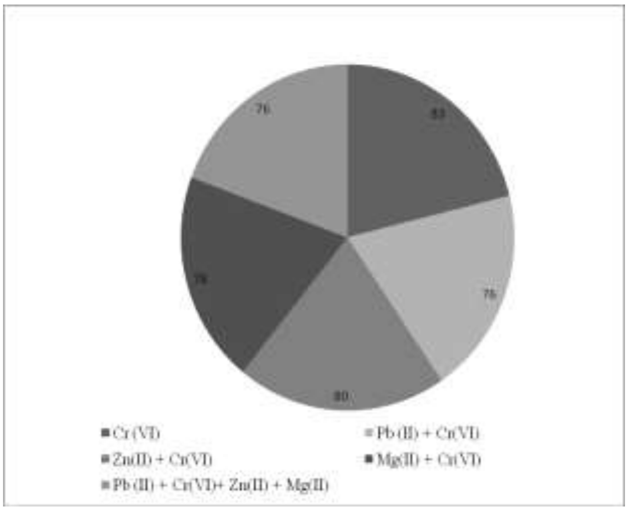
From Figure 4, it was observed that at the optimum pH of 6.5 maximum % chromium removal was achieved for different initial concentration of Cr(VI). Maximum chromium reduction was observed at pH 6.5 and for 25 mg/L of chromium solution (87%).

Figure 4: Effcet of different concentartion on the reduction of chromium



Effect of heavy metals with chromium on reduction of chromium using isolated bacterial cells

The effect of Heavy metals on Cr (VI) reduction by Chromium resistant bacteria was shown in the Figure 5. The concentration of chromium solution was 30 mg/L and the other metals concentration was same (30 mg/L). It was observed that neither the presence of Pb(II), Zn(II), Cd(II) or the mixture of all ,resulted in significant decreased in Cr(VI) reduction. In general the % Cr(VI) reduction ranged from 83 to 76%. However the % Chromium reduction was affected slightly due to the presence of Lead.



Conclusions

Based on these findings experimentations using a lab scale treatment unit comprising of a chemical and biological treatment module was carried out so that reduction of the chromium level of the said tannery industry wastewater in an efficient and cost effective manner could be achieved.

The following important conclusions may be drawn from the experimental results:

i) In the Chemical Treatment phase a reduction of chromium values up to 10% and 88% respectively has been obtained. Moreover this chemical treatment is cost effective and very low amount of dose is required.

iii) 'Biological Treatment' shows a remarkable reduction in the chromium values up to 51% and it shows little inhibitory effects due to the presence of other heavy metals with the chromium effluent.

iv) As per environmental compliance is concern, the bacterial culture after each batch experimentation can be destroyed using acid and heat treatment.

v) The finally treated water can be reused efficiently in the tannery premises

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