UTILIZATION OF SLUDGE FROM LEATHER TANNING RESIDUAL BATHS AS ADDITIVE IN MORTARS

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In tanneries, one of the environmental issues is the removal of trivalent Chromium from residual leather tanning floats. In this paper we have experimented separation of floats from leather tanning process and the precipitation of trivalent Chromium by flocculation with synthetic polymers. The method presents the following advantages: on one hand the trivalent Chromium can be extracted from sludge and re-use in tanning process; on the other hand, the sludge containing trivalent Chromium and synthetic polymers (polyacrylamide) can be used in the construction industry, as a binder with cement to obtain mortars. The freeze-thaw resistance of the mortar containing “polymer-sludge” addition, compared to the control subjected to 15-25 freeze-thaw cycles was greatly improved.

Keywords: tanning floats, sludge, polymers, mortar

INTRODUCTION

Wastewaters from tanneries are highly polluted with chemicals such as: sodium chloride (preservative), lime, sodium sulphide, protein hydrolysates, vegetable and synthetic tanning agents, mineral tanning agents, dyes, surfactants, grease, solvents (Zăinescu *et al.*, 2005).

There are a large number of studies concerning the elimination, through precipitation of chromium salts from tannery's wastewaters; due to the incomplete exhaustion of the chromium salts was proposed its utilization after a concentration in Cr₂O₃. After each utilization, wastewaters are enriched in neutral salts so, they couldn't be used for more times in tanning process; for this reason, was proposed chromium recovery from these waters. Usually, after tanning process results exhausted tanning solutions with variable concentration of chromium salts, in the range of 3...9 g Cr₂O₃/l; also, washing waters before the neutralization contain 2...3 g Cr₂O₃/l (Panagiotakis *et al.*, 2015).

In scientific papers there were presented some methods used for chrome recovery from exhausted baths, specially using the chrome precipitation as chromium hydroxide that is then transformed in basic salt of chromium sulfate or sodium bichromate (Vollpracht *et al.*, 2016). For the chrome precipitation as chromium hydroxide there are using alkaline substances like: sodium hydroxide, sodium carbonate, ammonium hydroxide, calcium hydroxide, magnesium oxide, etc. The use of hydroxide sodium or soda salt may create some problems due to the sodium sulphate (Bulijan and Kral, 2018). It is known that sodium sulphate as well as sodium chlorides couldn't be removed from the wastewaters by the traditional treatment methods and that is why, it is recommended to avoid their introduction into the treatment floats.

Nowadays, the using of synthetic polyelectrolytes presents some advantages as: the reducing quantity of inorganic coagulants, the increasing of treatment efficiency and

rate sedimentation of wastewaters, reducing in the same time the dimensions of equipments and treatment costs, also.

In this work it was proposed a precipitation system using lime (calcium hydroxide), flocculation system with polyelectrolytes and filtration system of chrome hydroxide on a rotary filter, on blankness. Through this method, the basis chrome solution is treated with calcium hydroxide and, after the reaction, results a precipitate composed by chrome hydroxide and lime sulphate (Zainescu *et al.*, 2008). The pH value of 8.2... 8.5 allows a complete precipitation of chrome without the risk of formatting the chromite ($\text{pH} > 9.5$).

The chemical physical analysis, have shown that in the wastewater samples from the hide tannage process, with an initial content of Cr_2O_3 of 5,2...5,5 g/l, had finally resulted a content of Cr_2O_3 between 10...25mg/l, after the treatment through the precipitation system, using the system calcium hydroxide polyelectrolyte.

There are two possibilities for utilization of “polymer-sludge” obtained by this method:

- a) The precipitate is treated with sulphuric acid of high concentration with the aim to convert the chrome hydroxide into the chrome sulphate (the idea is to be used again at the hides tannage). In order to increase the reaction speed, it could be added the sulphuric acid in excess. It results chromium sulphate which pass into solution, the sulphuric acid which did not participate in the reaction and lime sulphate a precipitate.

Scheme 1. Installation for obtaining polymer-sludge from tannery wastewater

- b) The “polymer-sludge” containing calcium hydroxide combined with synthetic polymers and Cr^{3+} can be used in obtaining construction materials.

In this paper is proposed a method for valorization of “polymer-sludge” as construction materials, e.g. mortars or concrete, that are suitable for use in various frost-thaw phenomena.

EXPERIMENTAL

Materials and Methods

Obtaining of “Polymer-Sludge”

The experiments using synthetic polymers have been realized within two bovine hides tanneries, with a water consumption of 63 m³/hide tons, respectively of 37 m³/hide tons. The wastewaters resulted from the tanning stage, are collected in a tank first, where are homogenized. In that tank, it is introduced lime milk for neutralization at pH 8,3...8,5, where all the heavy metals in the water are quantitatively precipitated as hydroxides. The modified polyelectrolyte to this treated effluent is added, while stirring. By this way, it is produced the flocculation and coagulation phenomenon, decantation taking place in the secondary basin the purified waters go to the sewage.

Obtaining of Mortars Containing Polymer-Sludge

The sludge containing trivalent chromium and synthetic polymers (polyacrylamide) was used in the construction industry. The sludge was tested as binder with cement to obtain mortars.

The composition for mortars or concrete, based on cement as binder, natural aggregates of maximum 3 mm and water, is characterized by the fact that the binder consists of a compound from cement and dry or wet sludge with calcium and chromium content resulting from the treatment of wastewater from leather tanning.

The mortar composition was made in two variants: N₁ (containing 9% dry sludge from the total binder) and N₂ (containing wet sludge in a proportion of 9% of the total binder), which comprises a cement compound and dry or wet sludge with calcium and chromium content as a binder. These compositions were compared to a sludge-free composition (M).

To make mortars, natural aggregates of (0 ÷ 3) mm and two CEM II/B-M (21...35)% composite Portland cements were used. Assays for aggregate and cement characterization were performed according to STAS 4606-1980 “Heavy natural aggregates for concrete and mortar with mineral binders. Test methods”, and SR EN 196-1: 1995 “Test methods for cements. Determination of mechanical strengths”, respectively.

RESULTS AND DISCUSSION

The study of dry and wet sludge mortar characteristics resulting from treatment of waste water from tanning process has included laboratory tests on mortars prepared with the two types of sludge and characterization of their behavior for up to 30 days.

Compressive Strength of Mortars

The compressive strength of the mortars was determined by tests after 7 and 28 days. The results of mortars resistance are presented in comparison with the resistance values of the control mortars containing only cement. The mortar series N₁, The compressive strengths of the N₁ mortar series are superior to those of control sludge-free mortar M: after 7 days they are +60% higher and after 28 days +66% higher. The increase in compression strength of N1 mortar over time is +46% from 7 to 28 days.

The compressive strength of the N₂ mortar series is higher than that of the control mortar M: after 7 days +31% higher, after 28 days +43% higher.

Frost-Thaw Behavior of Mortars

The compressive strengths of the N₂ mortar series have an increase of +53% from 7 to 28 days. The freeze-thaw resistance is expressed by the loss of compressive strength of sludge mortars subjected to 15 and 25 freeze-thaw cycles compared to the sludge-free mortar specimens having the same compositions but which have been kept in water between 28 days and the age of the compression resistance test of mortar specimens subjected to freeze-thaw. The loss of compressive strength of sludge mortars subjected to 15 and 25 freeze-thaw cycles is presented compared to the loss of compressive strength of sludge-free mortars subjected to the same number of freeze-thaw cycles.

The loss of compressive strength of the N₁ mortar series after 15 freeze-thaw cycles is 2%. After 25 freeze-thaw cycles the loss of compressive strength is 3.56%.

The loss of compressive strength of the M mortar series after 15 freeze-thaw cycles is 3.01%. After 25 freeze-thaw cycles the loss of compressive strength is 10.07%.

The experiments show that the compressive strength of mortars with sludge is much higher than the strength of control samples (7%).

CONCLUSIONS

It has been proposed a process which allows the Cr³⁺ precipitation, by using as additives the polyelectrolytes. This process presents the following economic and environmental advantages:

a) tannery waste waters decontamination from leather tanning process and the obtaining of chromium (III) solution being able to be recycled for leather tanning or for use in other industries, for ex. additives in footwear adhesives. By this method, the final sludge can be used in agriculture as fertilizer, because do not content chromium.

b) the “polymer-sludge” resulting by precipitation with polyelectrolytes has been experienced in mortars’ compositions for construction industry; the freeze-thaw resistance of the mortar with “polymer-sludge” addition compared to the control subjected to 15-25 freeze-thaw cycles was greatly improved.

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