



Chromium recovery from tannery sludge with saponin and oxidative remediation

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ABSTRACT

Two new methods for treatment of tannery sludge were studied to achieve cost-effective and environmentally acceptable remediation solutions for high chromium containing tannery sludge. Quillaja bark saponin, a plant derived biosurfactant, was applied to dewatered tannery sludge for chromium recovery and a comparative assessment with H₂O₂ oxidative treatment method is presented. Tannery sludge samples were treated on a laboratory scale with saponin in the pH range 2–3. The effects of various factors like time, concentration of saponin, pH, and temperature on the extraction of chromium were studied. The treatment with saponin extracted 24% of Cr from tannery sludge at a pH around 2, performing multiple wash of 6 h, at 33 °C. On the other hand, the H₂O₂ treatment, which include Cr(III) oxidation to Cr(VI) and extraction with sulfuric acid solution at pH 2, enabled to extract 70% of chromium within less than 4 h at room temperature (21 °C). The results indicate that the extraction efficiency of saponin was strongly dependent on the organic matter content of the sample, which affects chromium mobility by its high adsorption capacity. On the other hand hydrogen peroxide treatment is effective and the duration of the process is short and requires cheap chemicals and moderate conditions.

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1. Introduction

In leather tanning industry, chromium(III) salts are the most widely used tanning agent. Cr(III) is one of the most important source of environmental contamination due to discharge of large quantities of tannery wastewater [1,2] and disposal of chromium contaminated sludge that is produced as a byproduct of tannery wastewater treatment [3]. The contamination of soil and water by chromium and the disposal of tannery sludge is of great environmental concern. Cr(III) is less toxic and soluble according to Cr(VI) compounds that are both acutely and chronically toxic [4]; however under certain circumstances Cr(III) may be oxidized to Cr(VI) [5]. Hexavalent chromium formed due to oxidation of Cr(III) compounds may percolate down into the soil during the rainy season and pollute the underground water [6]. Apte et al., determined considerable amounts of Cr(VI) in sludge, soil and leachate samples collected from a chromium-contaminated tannery waste dumping site [7]. High levels of Cr supply can inhibit seed germination and subsequent seedling growth [8] and plants growing in higher concentration of chromium take up more chromium, that accumulates in the plant tissues and through plants enter in the food chain [9].

The chromium level in the tannery sludge is sufficiently high and landfilling of these wastes is loss of potential resource in the form of chromium. Recovery of chromium from tannery sludge would minimize the prospective health risks during land application of sludge, reduce the volume of waste and from an economic point of view prevent the loss of valuable raw material.

A number of articles have been reported regarding removal of Cr from various types of samples in the light of its severe hazardous impact upon environment.

Chromium recovery from tannery chrome shavings was investigated by Erdem [10]. In the study organic substances of tannery chrome shavings were removed by incinerating at 850 °C prior to chromium recovery in the form of chromate and obtained 99.45% of chrome removal by using Na₂O₂ as an oxidation agent.

Shen et al. [11], have employed mineral acids to tannery sludge samples for extraction of Cr. Macchi et al. have investigated separation of Cr(III) with sulfuric acid and recovery by oxidation to Cr(VI) [3]. Chuan and Liu [12] investigated the effect of pH on leaching behavior of chromium from tannery sludge. According to other report, de Souza e Silva et al. were able to extract 92% of chromium from electroplating sludge using 30% hydrogen peroxide at 60 °C [13]. In an another study following the oxidation of Cr(III) to Cr(VI) chromium was extracted using a solvent [14].

Other workers used microemulsion system and have treated the dried, grounded and sieved tannery sludge by a solid-liquid extrac-

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tion process [15]. Generally these methods have good extraction yields, however application of chemical extraction methods are limited and expensive due to operational difficulties, high chemical consumption and requirement of long processing time.

Zhou et al. [16] have employed a more environmentally acceptable bioleaching method, to tannery sludge using the mixture of ingenious iron- and sulfur-oxidizing bacteria. However bioleaching method requires strict monitoring of process conditions and has applicability to only low sludge solids concentration [17].

In the last decade the increasing environmental concern and the regulatory rules imposed by governments have forced industry to search for environmentally friendly bioremediation approaches to polluted soil and has become one of the key research activities in environmental science and technology. In the light of these developments *microbial biosurfactants* that are produced extracellular or as a part of the cell membrane by bacteria and *plant derived biosurfactants* have particular interest in environmental applications and promising non-toxic washing agents [18] due to their low toxicity, biodegradable nature, enhancing biodegradation, easy production and possibility of reuse; moreover they do not cause secondary pollution even if they are leaked and discharged to the ecosystem.

The feasibility of using biodegradable biosurfactants to remove heavy metals from an oil-contaminated soil [19] and heavy metal contaminated sediments [20] was recently demonstrated by batch washes with microbial originated surfactin, a rhamnolipid and a sophorolipid. High chromium removal rates have been obtained by rhamnolipid from heavy metal spiked soil [21]. Massara et al. [22] reported that the rhamnolipids have the capability of extracting 25% portion of the stable form of chromium from contaminated kaolinite and could be beneficial for long-term conversion of Cr(VI) to Cr(III).

Plant-derived biosurfactant aescin [23] and saponin have been used in aqueous solutions for remediation of heavy metal contaminated soil [24], kaolin [25] and incinerator fly ash. The treatment with saponins extracted 45% of Cr from fly ashes [26].

A review of the current literature indicates that most of the previous laboratory studies done were mostly limited to experiments conducted by artificially introducing heavy metal contaminants on commercially available clay minerals, such as kaolinite. Compared with artificially spiked soils, tannery sludge possesses greater acid buffering capacity, higher concentrations of organic compounds and Cr(III). To our knowledge up to date there has been no reported research on the application of naturally occurring saponins for recovery of chromium from tannery sludge.

The aims of the present study are to ascertain, if the bioremediation with biosurfactant soil washing technology developed for artificially contaminated soils and the oxidative remediation method used for Cr recovery from chrome shavings can be applied into tannery sludge. The environmental and economic benefits make the investigation of both methods interesting when compared with the previous methods described in the literature.

2. Experimental

2.1. Reagents and samples

The dewatered tannery sludge was obtained from Igualadina de Depuració i Recuperació (IDR) wastewater treatment plant located in Catalunya, which is the region with the highest tanning activity in Spain. The sludge was collected in polypropylene bottles and stored at 4 °C until further use. In all experiments sludge samples were used without performing any pretreatment such as drying, sieving or digesting.

Hydrogen peroxide H₂O₂ (50%) used for the oxidative dechroming process was purchased from FMC Foret (Barcelona,

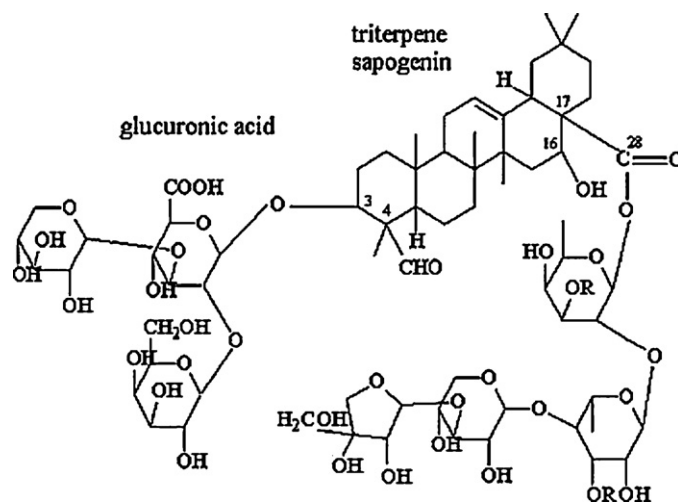


Fig. 1. Chemical structure of Quillaja saponin [25] according to Higuchi formula [30].

Spain). HCl (37%, $M = 37.46$), HNO₃ (65%, $M = 63.01$) were of analytical grade and were purchased from Panreac Quimica (Barcelona, Spain). The standard solutions for ICP spectrometry calibration were purchased from Scharlau Chemie. Solution of Fe₂O₃ 40% was prepared using technical grade Fe₂O₃ (p.m. 159.70) powder that is purchased from Probys Química.

2.2. Saponin

Quillaja saponaria Molina is a tree endemic to Chile and has been used for over 100 years for the production of triterpenoid saponin-rich extracts. Quillaja bark is the preferred raw material for saponin production owing to its high content of saponin, 5% and ease of transportation [27].

Quillaja saponins have been used as a surfactant in the production of photosensitized film, as a foaming agent in beverages and shampoos, a natural emulsifier in foods and similar uses. They have a wide range of industrial applications [28]. Saponins as biosurfactants have advantages of easy production, sustainability of supply, availability on market, lower price and possibility of reuse [29]. Therefore the use of saponins is considered to be cost-effective process as compared to other microbial and plant derived biosurfactants.

Quillaja bark saponins consist of triterpene glycoside and contained β-D-glucuronic acid with carboxyl group of sugar moiety in hydrophilic fraction (Fig. 1). According to the elemental analysis of saponin, the percentage compositions of each element were 51% for oxygen, 44% for carbon, and 6% for hydrogen. Saponin shows weakly acidic nature (pH 4.6) due to the hydrolysis of glycosides [29]. Saponin from Quillaja bark 26% used in the experiments was obtained from Sigma Chemical Co. (St. Louis, MO) and used without further purification.

2.3. Characterization of tannery sludge

Sludge samples were analyzed for moisture, organic matter, metal content, nitrogen, phosphorus and pH to determine its composition; the results are presented in Table 1. Ultrapure water quality (18.2 mΩ), obtained by a Milli-Q system from Millipore was used in all the analyses carried out. In order to determine moisture content, a weighed sample of sludge was dried in an oven at 102 ± 2 °C for 6 h. The pH values were measured using 1:5 water extraction mechanically agitated shake for 6 h and subsequent determination with Crison GLP22 pH meter. Electrical conductiv-

Table 1
Analytical results for tannery sludge.

Parameters		Tannery sludge
Moisture	% Weight on dry basis	75
pH		7.25
Electrical conductivity	dS/m	2.54
Organic matter	% d.m.b.	76.4
Kjeldahl Nitrogen	% d.m.b.	5.51
N ammoniacal	% d.m.b.	1.07
P	% d.m.b.	1.04
K	% d.m.b.	0.14
Ca	% d.m.b.	5.89
Na	% d.m.b.	0.59
Mg	% d.m.b.	0.38
Fe	% d.m.b.	1.32
Zn	% d.m.b.	0.13
Al	% d.m.b.	0.22
Cr	mg/kg d.m.b.	8041
Pb	mg/kg d.m.b.	98.5
Cd	mg/kg d.m.b.	18.5
Ni	mg/kg d.m.b.	34.5
Cu	mg/kg d.m.b.	174
Hg	mg/kg d.m.b.	0.07
C/N ratio		6.3

d.m.b.: dry matter basis.

ity was measured also in a 1:5 water extract of the sludge at 25 °C. Total and ammonia Nitrogen values were determined according to Kjeldahl method, with and without selenium catalyzed digestion of the sample, respectively.

Organic matter was determined by oxidation with potassium dichromate at 100 °C and the excess dichromate titrated with ferrous ammonium sulfate.

In order to analyze total metal content, 1–1.2 g of sludge sample was weighed and digested at 130–140 °C with 5 ml HNO₃ and 15 ml HCl until the supernatant became clear and a brownish colored fume no longer generated. The solution obtained after sludge digestion was diluted to 500 ml using water and filtered through Whatman No.: 1 filter paper. Each metal concentration was calculated as an average of the two samples.

Concentrations of Ca, Mg, Fe, Cr, Pb, Cd, Ni, Na, Al, Zn, Hg and Cu were measured by Perkin-Elmer Optical Emission Spectrometer Optima 2100 DV using standards solutions of 0.04 ppm, 0.5 ppm and 2.5 ppm.

Potassium determination was performed using a Philips PU9200 atomic absorption spectrophotometer. Standards of 1.00 mg/L and 5.00 mg/L were prepared for the calibration and absorbance values of samples were read.

Total phosphorus was determined by the spectrophotometric method based on the formation of molybdenum blue.

2.4. Experimental design of saponin remediation

Saponin remediation was performed in a batch procedure. Considering the previous studies conducted with saponin [29]. Three percentage saponin concentration was selected to determine the effects of contact time on heavy metal removal efficiency. Two grams of tannery sludge was mixed with 3.75% of saponin solution. After adjusting the pH of the sludge-saponin solution to 2 using 3 M HCl, the volume is made up to 25 ml with deionized water, by this way the final saponin concentration was 3%. The saponin remediation procedure is presented in Fig. 2.

In order to determine the Cr removal efficiency as a function of time, the variables like pH, temperature and the concentration of saponin were kept constant. The saponin-sludge solution was placed on an orbital shaker at 210 rpm for 6 h, 24 h, 48 h and 72 h at room temperature (21 °C). After determining the reasonable contact time all the batch sludge washing studies were carried out by

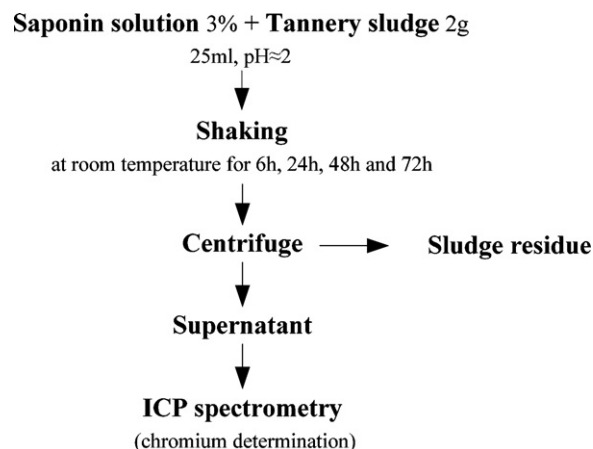


Fig. 2. Flow diagram of the biosurfactant remediation procedure.

varying the operating conditions such as time, saponin concentration, temperature and pH values.

After each experiment the washing solutions were centrifuged using P. Selecta centrifuge at 4000 rpm for 10 min to separate the two phases, liquid and solid.

To investigate the effect of double washing stage, the washing procedures performed at room temperature (21 °C) and at 33 °C were repeated a second time by adding fresh saponin solution to sludge sample after the removal of supernatant.

The aqueous supernatant obtained from washing procedures was analyzed for chromium concentration using ICP spectrometry. When the supernatants are basified with NaOH, heavy metals can be recovered and used saponin obtained through precipitation process can be recycled for the subsequent treatment [24]. Control samples were prepared by adding 2 g of sludge sample to deionized water in comply with the same procedure and compared with the results of saponin remediation process. The experiments were performed in duplicate and mean values were taken into account.

2.5. Experimental design of oxidative remediation

We have applied the dechroming process, developed to isolate collagenic material with “zero” chrome containing by Cot and Aramon [31] to tannery sludge. With this method chromium containing sludge is oxidized to chrome (VI) under basic conditions through the use of hydrogen peroxide at room temperature. We have slightly modified the dechroming method in order to decrease the amount of chemicals used and the volume of wastewater produced.

Process diagram is presented in Fig. 3. The amount of tannery sludge used for the experiments was 36 g. The percentages of all chemicals used in the process are related to the total volume bath which is 225% of sludge weight.

In order to recover chromium in the form of CrO₄²⁻ solution, commercial hydrogen peroxide H₂O₂ (50%) solution was selected due to its low price, simplicity and hazardous-free final products of reaction [32]. Application of hydrogen peroxide avoids any risk of toxic chlorinated organic compound formation because the reaction product is water, as shown in the following reaction [33]:



The oxidation takes place in alkali medium. The medium should have enough [OH]⁻ concentration for all Cr(III) to be oxidized to Cr(VI); therefore pH > 10 was reached by using sodium carbonate.

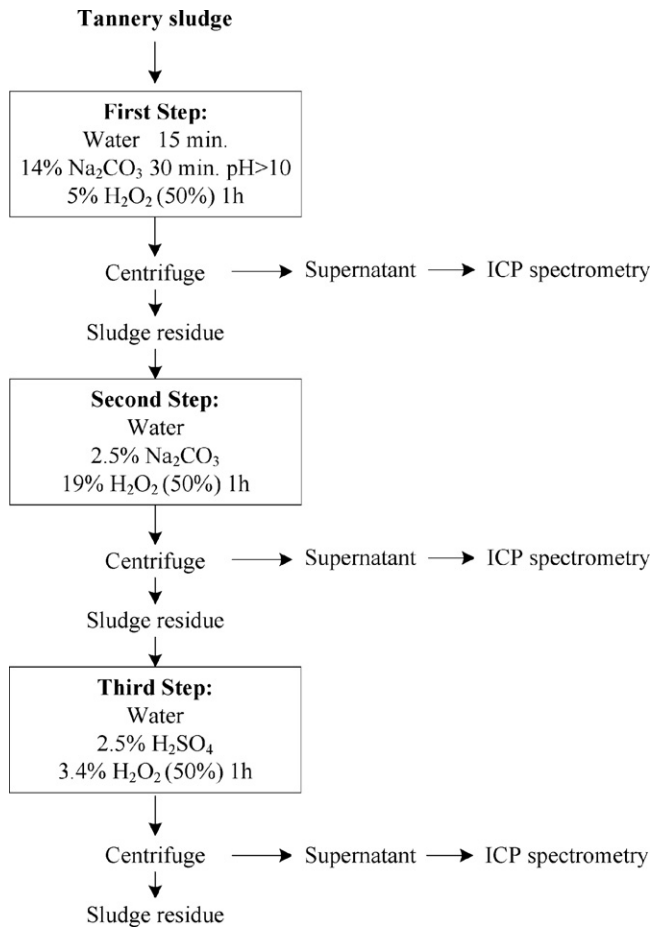


Fig. 3. Flow diagram of the oxidative remediation procedure.

Chromium loses its complexing capacity by means of oxidation; therefore all types of ligands are liberated into the bath.

Following the oxidation process another washing process is performed with sodium carbonate and hydrogen peroxide. The following step is in situ reduction of Cr(VI) to Cr(III) using sulfuric acid which produce a concentrated and pure solution of chrome (III). The reuse of the chromium recovered from tannery sludge in the form of chromate is suitable for using in tanning when reduced with Na₂SO₃ and basified by adding a basification agent like sodium hydrogen carbonate [10]. At the end of the reduction process, solution is centrifuged and the supernatant was analyzed for the chromium content using ICP spectrometry.

Following the chromium determination, the supernatants obtained from the first and the second washing processes were mixed at a ratio of 1:1 and analyzed for Chemical Oxygen Demand (COD) and TKN values in order to determine the nitrogen amount that dissolved during the oxidation process. TKN values of the last washing solutions were also determined.

COD value was determined with colorimetric method in accordance with UNE-EN 1484:1998 (DIN EN 1484). In order to eliminate the residual hydrogen peroxide in the final washing solution the pH of the mixture of first and second washing solutions was arranged to 5–5.2 using 1 M H₂SO₄. The decomposition of hydrogen peroxide catalyzed by iron oxide [34] was performed by adding Fe₂O₃ (40%) to the solution to provide the 100 ppm concentration in the final solution:

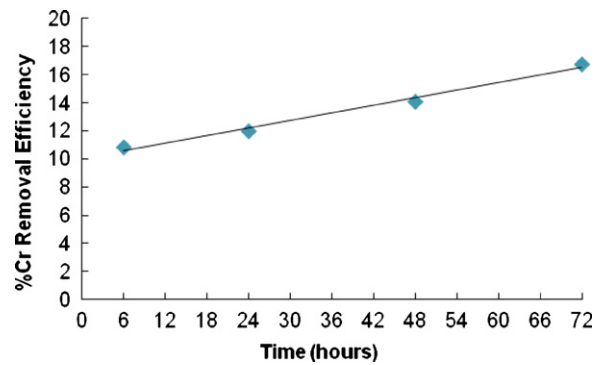
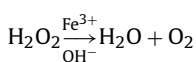


Fig. 4. Cr concentration in the 3% saponin washing solutions as a function of time at pH 2.

The solution was stirred for 4 h at room temperature (21 °C) and then the COD of the final solution was measured. The experiments were performed in triplicate and the results are presented by the mean values.

3. Results and discussion

3.1. Saponin remediation

The effect of contact time between sludge samples and 3% of saponin solution at pH 2 was determined within 6 h, 24 h, 48 h, and 72 h. Results are presented in Fig. 4. The amount of chromium removed with saponin solution increased in a low rate with longer contact time. After 72 h of washing process saponin removed 16.8% of chromium when compared with 10.8% removal obtained by 6 h of washing.

However with the aim of reducing the experimentation to an acceptable and practical level, 6 h period of contact time was considered reasonable, since longer periods of time did not result in an extensive additional removal of chromium and the further experiments carried out for 6 h.

The effect of pH on removal of chromium from tannery sludge was investigated by using 3% saponin solutions at pH of 2, 2.5, 3 and 4 which gave the highest removal efficiency at pH 2. The results are shown in Fig. 5.

The effect of saponin concentration on chromium removal efficiency was investigated using 0%, 3% and 5% saponin solutions at pH 2, 2.5 and 3 (Fig. 6).

In the absence of saponin, deionized water removed 3.4% of chromium from the sludge at pH 2. Saponin was more effective than that of deionized water at pH < 3. The maximum amount of

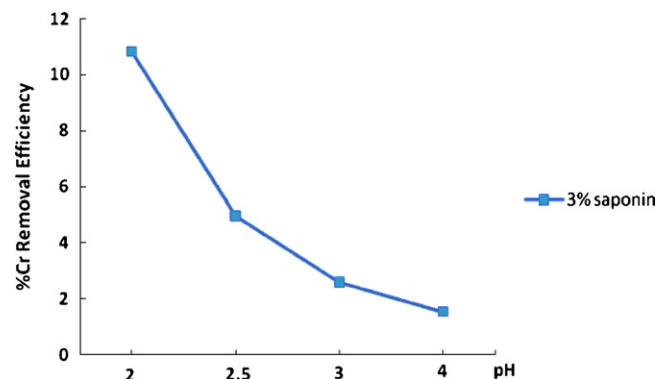


Fig. 5. Effect of pH and on Cr removal efficiency of 3% saponin solutions with a contact time of 6 h.

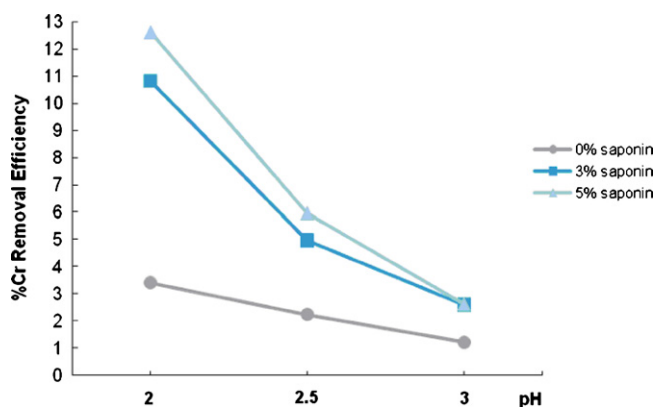


Fig. 6. Effect of concentration on Cr removal efficiency of 0%, 3% and 5% saponin solutions at pH 2, 2.5 and 3 with a contact time of 6 h.

Cr removed by saponin was nearly 4-fold of the deionized water at pH 2.

The percentage extraction of Cr with the saponin treatment was pH dependent and increased with decreasing pH attaining 12.6% extraction with 5% saponin solution at pH 2. In the range higher than pH 2.5 saponin was not effective in removing chromium. Only 2.6% of chromium was removed at pH 3.

Previous studies showed that performing series of washing with biosurfactants, significantly increased the metal removal from contaminated soil [19]. Taking into consideration the energy consumption and feasible washing conditions only double stage washings were performed in order to investigate the effect on chromium removal from tannery sludge. The cumulative metal removals after two washings are shown in Fig. 7. Saponin solutions removed higher percentages of Cr than single stage and control washings from tannery sludge.

Owing to the fact that washing with 5% saponin solution gave the higher removal rates than 3%, further experiments were carried out using 5% saponin solution.

In order to enhance the kinetic rates of washing and improve the Cr removal temperature of washing process was increased. Considering the practical application and energy efficiency of the process, washings were performed only at 33 °C. The Cr removal rates were increased by increasing temperature. Treatment with deionized water at pH 2 had removed 2.8 times more Cr at 33 °C than washings performed at room temperature (21 °C).

The removal of Cr increased from 12.6% to 18.5% when washing with 5% saponin solution was performed at 33 °C.

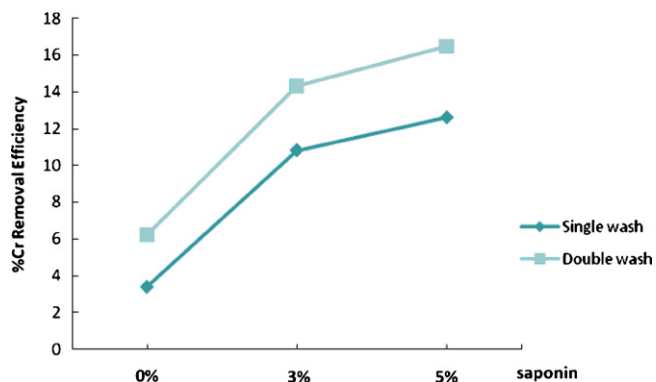


Fig. 7. Effect of single and double washing stages on Cr removal efficiency of 0%, 3% and 5% saponin solutions with a contact time of 6 h at pH 2.

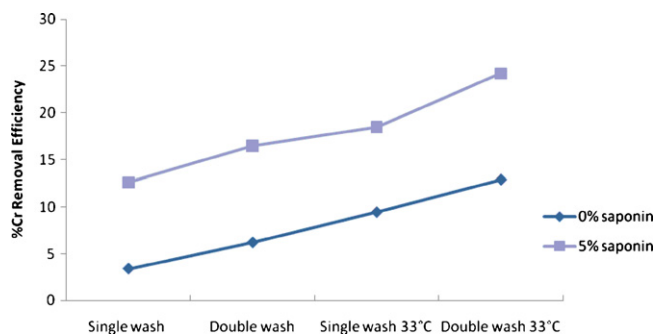


Fig. 8. Effect of washing at 33 °C by integrating with double stage washings on Cr removal efficiency of 0% and 5% saponin solutions with a contact time of 6 h at pH 2.

Another experiment was performed to make use of the positive effects of washing at 33 °C by integrating with double stage washings (Fig. 8). The maximum Cr removal rate 24.2% was obtained by performing double washing process with 5% saponin at 33 °C.

On the contrary to previous studies performed by Juwarkar et al. [35] and Hong et al. [26] the removal of chromium from tannery sludge using biosurfactant is significantly low thus preventing it from being an economical feasible process. Juwarkar et al. found that rhamnolipid biosurfactant selectively favors 92% overall removal of Cr from artificially spiked soil and Hong et al. attained 45% extraction of Cr from fly ashes. The spiked soil and fly ash used in these studies have very low content of organic material such as 7.2%, 11.3% and 0.07%. However tannery sludge has nearly 76% of organic content and chromium in tannery sludge tightly bound to colloidal particles and organic matter.

Early work done by Hong et al. on heavy metal removal with saponins showed that Cr was strongly bound to the residual fraction in soils. The percentage of each fraction of Cr decrease after the saponin treatment but the residual fraction of Cr is still abundant. Moreover, the chromium concentration of the studied samples varies between 60 and 120 ppm, when compared with the 8041 ppm initial concentration of Cr in tannery sludge they have much more lower concentration of chromium than tannery sludge.

The extraction mechanism of heavy metals by saponin was described to be the formation of soluble complexes with heavy metal ions [29]. The complexation reaction was described as a function of pH and saponin concentration. Heavy metals studied were: Cd, Cu, Pb and Zn. Recovery of heavy metals and recycling of used saponin were possible after alkali treatment (pH 10) to decompose the soluble complexes. In the case of Cr in tannery sludge, according to the results obtained, the Cr was probably tightly bound to the organic matter hindering the formation of the saponin–Cr soluble complexes. More detailed studies on the mechanisms in the case of Cr need to be done.

3.2. Oxidative remediation

The dechroming process based on the oxidation of Cr(III) to Cr(VI) with hydrogen peroxide and followed by two washes removed 70.2% of chromium from tannery sludge. Table 2 presents

Table 2
Cr content of sludge samples before and after treatment.

Experiment no.	Before treatment Initial Cr (mg)	After treatment Residual Cr (mg)	Cr removal (%)
1	72.13	23.38	67.59
2	72.17	21.88	69.69
3	72.21	19.34	73.21

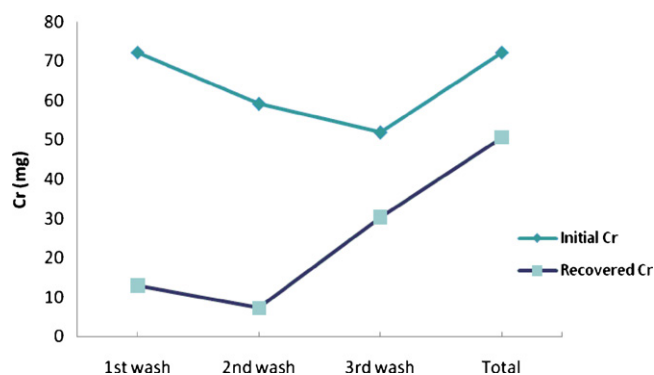


Fig. 9. Cr content of sludge samples before and after washing processes. Experimental conditions being: First wash: water, 15 min, 14% Na_2CO_3 , 30 min ($\text{pH} > 10$), 5% H_2O_2 , 1 h. Second wash: water, 2.5% Na_2CO_3 , 19% H_2O_2 , 1 h. Third wash: water, 2.5% H_2SO_4 , 3.4% H_2O_2 , 1 h.

the chromium amounts of tannery sludge samples before and after each experiment.

The washing solution of first and second step had lower chromium removal percentages and they possessed dark brown color indicating that some of the organic material existing in sludge was decomposed and passed into the solution. On the contrary the washing solution of third step had a transparent light green color owing to high Cr(III) concentration. As it can be seen in Fig. 9 the highest chromium amount was removed within third washing step (42% of initial chromium).

COD analysis result for the mixture of resulted washing solutions is significantly high 32264 mgO_2/L due to the hydrogen peroxide residues. After the COD reduction treatment using Fe_2O_3 the COD value was determined as 15178 mgO_2/L . By this way 47% reduction of final COD value was obtained.

Total Kjeldahl Nitrogen value was determined as 3.36% for sludge samples and 1278.8 mg/L for the mixture of first and second filtrates. Nitrogen present in the washing filtrates can be recovered with precipitation of proteins at isoelectric pH using a method that is potentially applicable to the leather industry and may find use as fertilizer, solid fertilizer for soils and protein retanning agents for tanneries [36,37]. Or, on the other hand, this wastewater might be treated in the same WWTP, as all waste water coming from tannery processes, to reduce the COD before discharge to river.

In previous studies performed by Cot and Aramon[31] and Erdem [10] chrome shavings were used for recovery of chromium by oxidative treatment and higher yield of chromium was recovered. This may be due to differences in composition and chromium content of these two tannery wastes. Because tannery sludge contains various pollutants such as hair, hair degradation products, synthetic tannins, nitrogen species and several toxic substances originated from various leather tanning stages.

Cot et al. subjected chrome shavings to repetitive treatments in the dechroming reactors in order to obtain a material with zero chrome content. In our case repeating the washing cycles would produce large volumes of wastewater and obtaining tannery sludge with zero content is not required.

4. Conclusions

This research focused on the investigation of chromium recovery from tannery sludge. For this aim applicability of biosurfactants used for heavy metal recovery from soils and hydrogen peroxide used for Cr recovery from chrome shavings were investigated and following conclusions have been drawn.

The saponin treatment was more effective at $\text{pH} < 3$ when compared to that of deionized water treatment. The percentage

extraction of Cr with the saponin treatment was pH dependent. In the pH range higher than 2.5 saponin was not effective in removing chromium. The maximum Cr removal rate 24.2% was obtained by performing double stage wash at 33 °C with 5% saponin solutions at pH 2. Unlike the previous studies performed with artificially spiked soils the removal of chromium from tannery sludge using saponin as a biosurfactant was lower due to the fact that tannery sludge acts as aged contaminated soil and chromium in tannery sludge tightly bound to colloidal particles and organic matter.

Oxidative remediation process was carried out using H_2O_2 . Cr(III) in tannery sludge oxidized to Cr(VI) and extracted with sulfuric acid solution at pH 2. It was determined that it is possible to recover 70% of chromium within less than 4 h and this chromium can be reused in tanning.

In this respect, although saponin is an environmentally friendly product and enables recovery of both Cr and saponin, the study showed that the presence of high organic content and high chromium concentration like in the case of tannery sludge affects chromium mobility primarily by its high sorptive capacity and represents a major constraint to its removal by plant derived saponin. On the other hand oxidative recovery is effective, the duration of the process is short and requires cheap chemicals and moderate conditions. Application of oxidative treatment to tannery sludge will provide economical benefit and environmental protection as it enables high percentage of chromium recovery.

In case of saponin treatment the removal of organic material in tannery sludge may lead to an improvement in chromium recovery. Investigations are in progress to improve the efficiency of saponin recovery process.

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