MONITORING CHROMIUM CONTENT IN TANNERY

WASTEWATER

Maher Jabari, Fathi Aqra♥, Safa Shahin and Awni Khatib.

Department of Chemistry, Faculty of Science and Technology, Hebron University,

P.O. Box 40, Hebron, West Bank, Palestine.

Abstract

The validity of uv/vis spectrophotometry for the analysis of tannery wastewater containing chromium(III) is investigated. Two peaks were observed in the visible spectra of tannery wastewater and solutions of commercial chromium tanning agents, that were similar to a known visible spectrum of chromium(III), and so indicating the absence of other contaminants. Spectra for freshly prepared solutions of the tanning agents were dependent on time indicating their instability in the first few days. The positions of the two peaks were shifted in wavelengths due to the reaction of chromium(III) with ligands originated from treated hides and dissolved in the tannery wastewater such as amino acids. This shift is increased with increasing the concentration of the amino acid. The chemical residuals which are usually added in tanning and treatment processes had no effect on the chromium spectrum.

Keywords: uv/vis spectrophotometry; chromium; wastewater; tanning; amino acid; adsorption

♥Corresponding author. E-mail: fathiaqra2009@hotmail.com. FAX: 0097022229303

Resumen

Se analiza la validez de la espectrofotometría uv/vis para el análisis de aguas residuales de la curtiembre que contiene chromium(III). Dos máximos fueron observados en el espectro visible para las aguas residuales de la curtiembre y para las soluciones comerciales de agentes de curtido. Estos espectros resultaron ser similares a los del chromium(III), indicando la ausencia de otros contaminantes. Los espectros de soluciones recién preparadas de los agentes de curtido fueron dependientes del tiempo indicando su inestabilidad. Las posiciones de los dos máximos se desplazaron en longitudes de onda debido a la reacción de chromium(III) con ligantes originados en pieles tratadas y disueltos en las aguas residuales tales como diversos aminoácidos. Se observó además que este cambio se incrementó el aumento de la concentración de estos ligantes. Los residuos químicos que generalmente se añaden en el curtido y otros procesos de tratamiento no tuvieron efectos sobre el espectro del cromo.

Palabras clave: espectrofotómetría uv/vis; cromo; aguas residuales; curtido; aminoácidos; adsorción

Introduction

Typical leather manufacturing technology is based on multi-step processes which include liming, pickling, tanning, etc., and involves the use of various chemicals such as lime, ammonium salts, sulfuric acid, and chromium salts. In Palestine, leather manufacturing is one of the traditional industries; where cured raw hides are processed according to such typical technology. The liquid waste from the tanning step is the most polluting waste due to the presence of chromium being a source of contamination due to its toxicity [1].

The two most common valences for chromium in aqueous solutions are 3+ and 6+ [2]. Water soluble hexavalent chromium is extremely irritating and toxic to tissues of human body [3]. When tanning wastewater is disposed without treatment, the infiltration of liquid wastes into ground water resources may cause major pollution problems because Cr(III) would be oxidized to Cr(VI), and hence create high risks to environment and people. On this basis, it was considered worthwhile and essential to monitor and control the chromium content in tanning wastewater. The toxicity, mobility and bioavailability of Cr, a versatile industrial metal and a contaminant, depends on its chemical form, *viz*: Cr(III) and Cr(VI). It may enter humans through plants grown on contaminated soil or irrigated by contaminated water. The chemical form in which Cr(III) is transported by xylem sap was investigated [4].

In tanning industry, the chromium concentration in terms of total chromium in the exhaust chromium liquor, with a volume of 4% to 6% of the total wastewater volume discharged from the tanning process, ranges from 1,500- 5,000 mg/L. The liquor is mixed with other effluent streams from tannery process causing dilution, and thus the concentration of chromium becomes 100-300 mg/L. In most countries, pollution control authorities do not permit the presence of more than 2 mg/L of Cr(III) in treated effluent. Although international standards of wastewater effluents is not more than 0.05 mg/L Cr(VI) and 5.0 mg/L Cr(III) [5]. Treatment methods for chromium wastewater may be performed by various processes such as ion exchange [6, 7], extraction [8, 9] and adsorption [10-14]. The precipitation process is the most common because chromium hydroxide is precipitated followed by recovering of chromium by sulfuric acid.

Chromium wastewater from leather tanning in Palestine is dumped to valleys and into sewage systems. Therefore, it was important to find a simple and useful technique for monitoring the performance of chromium recycling process and for purposes of quality control for the re-use of chromium in the tanning process. There was keen interest to demonstrate uv/vis spectrophotometry for this purpose, and to investigate the effect of various process parameters on the recovery efficiency of chromium.

 Uv/vis spectrophotometry was used for analysis of iron in drinking water, manganese in steel [15] as well as Cr(III) with 2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)

phenol [16]. The method with 1,5-diphenylcarbazide was used for determination of chromium in tannery wastewater [17]. Speciation of chromium in wastewater was studied by various methods such as capillary electrophoresis (CE) [17], graphite furnace atomic absorption spectrometry (GFAAS) [18] and by hydrogen peroxide as an oxidant ion flow injection analysis (FIA) [19].

People are exposed to chromium ions from tanning wastewater. The problem is that Cr ions are extremely toxic and may cause contact allergic dermatitis on the skin and may also be a trigger for many diseases. Huge amounts of chromium ions are released by waste waters to rivers after chromium-tanning processes. The presence of chromium is not only a problem for human health, but also for the environment. For this reason it is extremely important to monitor the presence of chromium. This study aims to present an appropriate analytical method for monitoring Cr ions resulting from tanning. This paper aimed at investigating and confirming the validity of uv/vis spectrophotometry, as a simple and affordable analytical method, for evaluating and investigating the performance of treating tannery wastewater. Although it is of little novelty as there are many methods in the literature with higher performance, it is an interesting study and the method could be adequate for easy monitoring of wastewaters. The stability of Cr(III) spectra and the possible contributions of various possible residuals and contaminants in tannery wastewater on spectra were determined.

Materials and Methods

Wastewater from local tannery, commercial tanning agent (chromitan B (basic chromium sulfate), BASF company, Germany) with 0.015 g/ml concentration, and a model tanning agent: chrome(III)-chloride (Riedel- deHaën AG.D-3016 seelze, Germany) with 0.015 g/ml concentration. A large sample from wastewater was collected from a local leather tanning factory. Tanning agents were obtained in powder form, and stock solutions of this powder were prepared with specific concentrations. Solutions of amino acids were used such as alanine, glycine, arginine, and polypeptide albumine, and the required amount of these solutions were added to chromitan B solution. Also different amounts of alanine (0.36, 0.54, 0.72, 0.90 and 2.7 mmol of 0.9 M solution) were added to 5 ml of 0.015 g/ml chromitan B. The UV/vis spectrophotometric analysis was performed using UV/vis spectrophotometer device (CECIL, CE 2021, 2000 SERIES, Cambridge, England), using type G cell (semi-micro with a volume of 1000μL, and a path length of 10mm). In certain experiments where time was a parameter, fresh solutions were prepared and kept for standing for a while before analysis. Plots of spectra were obtained by computerized spectrophotometer automatically, and were confirmed experimentally to be repeatable and reproducible. It should be noted that using the single wavelength method, the interferential effects of suspension grades and background absorbencies on the absorbance spectra cannot be eliminated. Unfortunately these interferential factors are bound to affect the results. However, we tried to minimize this effect by filtrating and settling wastewater.

Results and Discussion
General Spectrophotometric Behavior

Spectra for solutions of chromium chloride, chromitan B and tannery wastewater were similar (see Figure 1), and each spectrum showed two peaks in the range 390-650 nm. Furthermore, the measured spectra for two solutions of commercial chromitan B prepared from powders obtained from two different local factories with identical content of chromitan B (0.015g/ml), and analyzed by two persons were almost identical and thus confirming the reproducibility of the results.
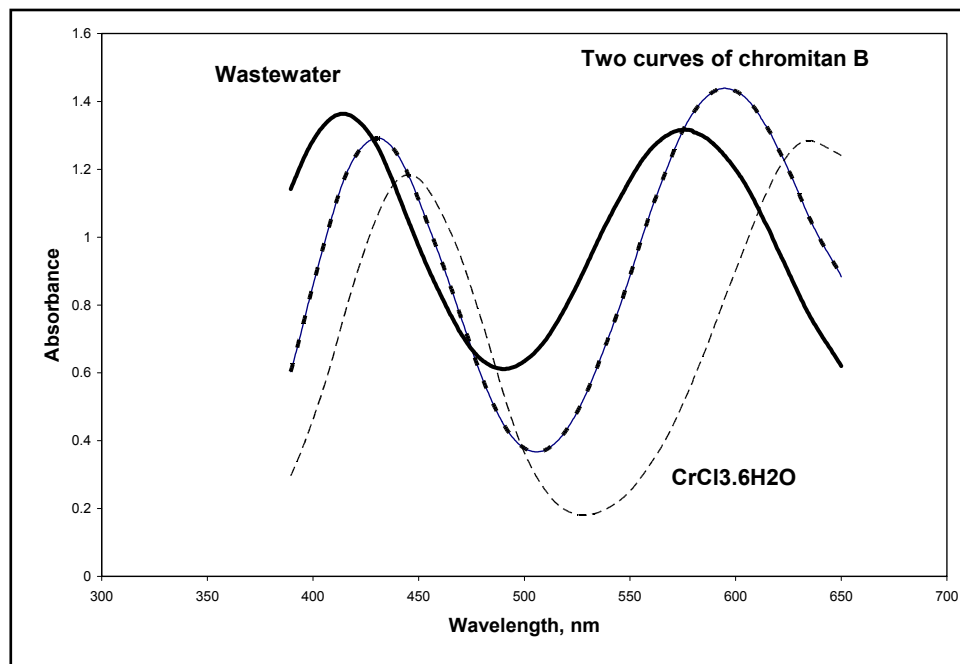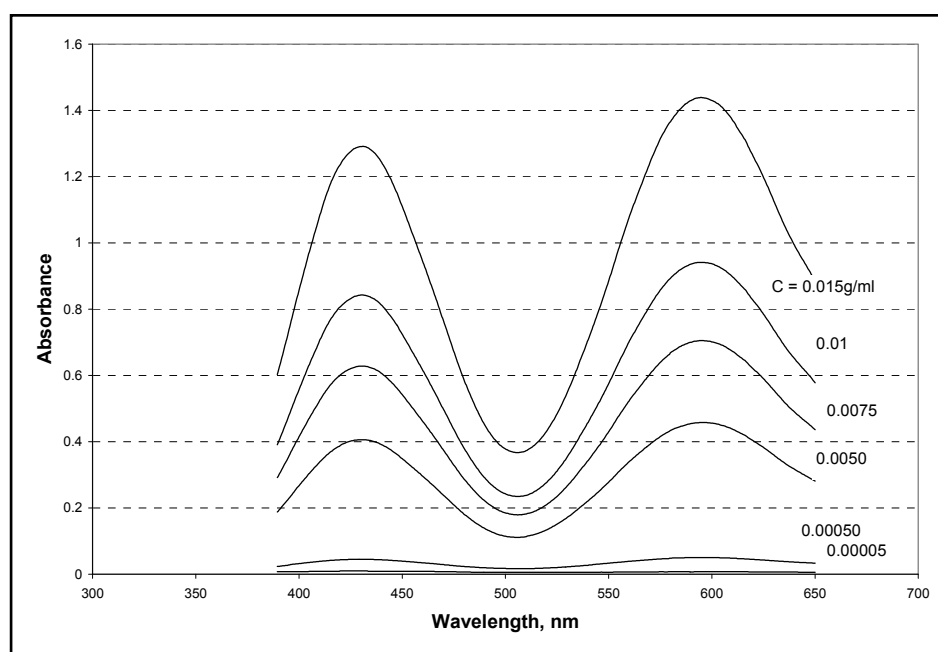
Figure 1. Measured spectra for wastewater, two superimposed plots for chromitan B and chromium chloride. These spectra were measured for freshly prepared solutions.

Three fairly strong absorptions of chromium complex, $[Cr(H_2O)_6]^{3+}$, are known in the visible and near-ultraviolet region, and are assigned to transitions from ground state to the excited states ($^4T_{2g}$, $^4T_{1g}$ (^4F) and $^4T_{1g}$ (^4P)). The spectrum is characteristic of $[Cr(H_2O)_6]^{3+}$ complex in which Cr(III) ion is octahedral, and the water molecules in this complex may be replaced by various ligands present in the wastewater, which is obvious from color change of the solution from green to blue. The values of λ_{max} are consistent with reported ones (Table I) with a standard deviation (SD) between (0.4-2.1). The appearance of these peaks in the visible region is due to ligand field transition. The small variations in the wavelengths are attributed to the fact that Cr(III) reacted with different ligands in each compound. The distance between the two peaks ($\lambda_{max}^2 - \lambda_{max}^1$) was nearly constant for solutions of chromitan B and wastewater, emphasizing that the shift in the spectrum was due to the presence of different ligands. In case of wastewater, organic ligands were generated from processing hides in chromium solutions. The spectra provided quantitative estimation of chromium content. The linear dependence of the spectra of chromitan B on concentration was observed (Figure 2). The absorbance was proportional to the concentration of chromium. The absorbance at each peak was recorded as function of concentration and then fitted to straight line. The fitting parameters provided a regression value (r^2) of 0.9994 for data at λ_{max}^1 and 0.9996 at λ_{max}^2, with (SD) of 0.43 for data at λ_{max}^1 and 0.48 for data at λ_{max}^2. This emphasis the validity of the method for quantifying performance of treatment processes involving various concentrations of chromium.

Table I. The measured wavelengths of the two peaks in spectra of various chromium solutions.

Sample	Observed Wavelength, nm				
	First peak		Second peak		Difference
	λ_{max}^1	SD	λ_{max}^2	SD	$\lambda_{max}^2 - \lambda_{max}^1$
Wastewater	414	0.4	576	0.4	164
Chromitan B	431	1.1	595	1.1	162
Chromium chloride	445	2.1	634	2.1	189
Reported values for Cr(III) as aqua ion (Lee, 1996: 724-32; Cotton and Wilkenson,1980: 730-1).	404		574		170

Figure 2. Spectra of solutions of chromitan B with different concentrations, the spectra were measured for freshly prepared solutions.

Parameters Affecting General Spectrophotometric Behavior

The measured spectra for fresh chromium solutions were dependent on time indicating solution instability (Figure 3); for wastewater (triangle), solution of chromium chloride (square), solution of chromitan B (diamond). The prepared tanning solutions were identical to those used in Figure 1. The plots are compared to the reported value of Cr(III) as aqua ion. The spectra for the prepared solutions (chromitan B and chromium chloride) showed clear dependence on time as the wavelength decreased for both peaks. The peak change in solutions of chromium chloride was more pronounced, since they were associated with structural isomers [20]. The hexaaqua ion complex,

$[Cr (H_2O)_6]^{3+}$, with a regular octahedral shape, usually occurs in aqueous solution and in numerous salts such as the violet hydrate $[Cr(H_2O)_6]Cl_3$. The chloride has two isomers: the usual form dark green trans-$[CrCl_2 (H_2O)_4]Cl.2H_2O$, and pale green $[CrCl (H_2O)_5]Cl_2.H_2O$. The time dependence is attributed to transformation between isomers. On the other hand, the spectra for wastewater showed no obvious dependence on time since samples were obtained from the factory and stored. The peak change of chromitan B may be attributed to oxidation of ligands associated with chromium, however, all solutions stabilize after 4 days.
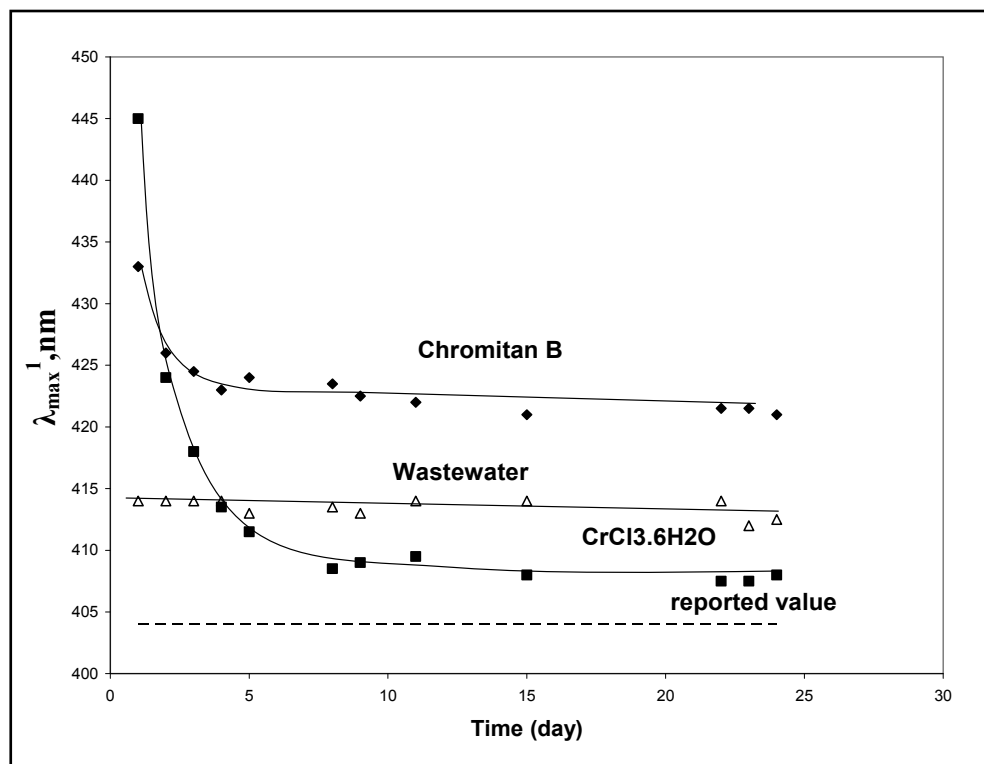

Figure 3. The measured wavelength for the first peak (λ_{max}^1) as functions of time after solutions preparation.

The tanning agent, Chromitan B, is the major contents in tannery wastewater. Thus, it was expected that both chromitan B and wastewater were characterized with the same final values of wavelengths for the two peaks after sufficient times, but the plots show a difference of 10 nm, attributed to the presence of other contaminants in water leading to attachment of ligands to chromium complex ion. The possible contributions of various chemicals and residuals were investigated experimentally.

Theoretically, possible contaminants in tannery wastewater include residual chemicals from previous processing steps such as lime, sulfuric acid, dissolved organics, residues of acids from hides, and salts from tap water (which is used in industry). The effect of the presence of each of the possible chemical contaminants is investigated by adding a representative amount of the contaminant to a known solution of chromitan B (as a pure tanning agent) (Figure 4). In this figure, the thin curves are for solutions of chromitan B (all containing 0.015 g/ml) with different salt contents, thin-dashed curve is for chromitan B dissolved in tap water, thin-dotted curve is for chromitan B dissolved in deionized water, the thin-solid curve is for chromitan B dissolved in

deionized water with the addition of concentrated amount of NaCl salt. While the thick curves compare spectra with and without the addition of lime recorded after 24 hr from solution preparation, where the thick-solid curve is for 0.015 g/ml of chromitan B dissolved in deionized water, and the thick-dashed curve is for 0.015 g/ml of chromitan B dissolved in deionized water with the addition of 0.01g of CaO to 10 ml of 0.015 g/ml chromitan B solution.
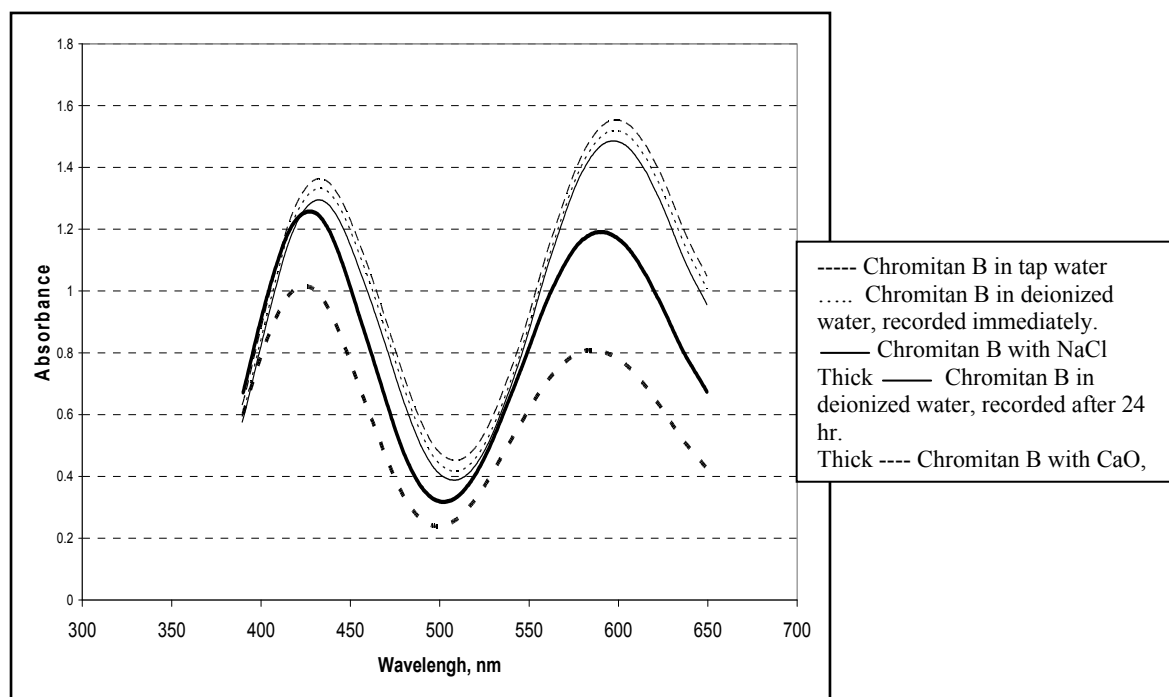

Figure 4. The measured spectra of solutions of chromitan B (0.015 g/ml) with various chemical contaminants described in the text.

The similarity in the spectra of chromitan B prepared in deionized water with chromitan B dissolved in tap water, chromitan B dissolved in deionized water with the addition of NaCl, and chromitan B dissolved in deionized water with sulfuric acid indicates no effect of salts. On the other hand, lime added to solution of chromitan B dissolved in deionized water showed a clear decrease in absorbance due to the precipitation of chromium hydroxide in the resulting alkaline solution. Therefore, lime is used in treating tannery wastewater as a precipitating agent. These results suggest that there is no effect of lime on λ_{max} and this method is valid for quantifying chromium content in wastewater treatment while no qualitative variations in the characteristics of the spectra occurred.

The effect of the presence of various types of amino acids in solutions of chromitan B or chromium chloride were investigated experimentally by adding alanine, glycine, arginine, and polypeptide albumine. The amino acid caused a shift in the spectra (Figure 1) which is attributed to the dissolution of amino acids from hides during tanning processes (in tannery wastewater). Figure 5 shows the obtained wavelengths (λ_{max}^1 and λ_{max}^2) as a function of the amino acid concentration for chromitan B solution. In that figure 162 was added to λ_{max}^2 in order to represent both wavelengths within the same scale. Obviously, as concentration of amino acid in solutions of chromitan B was increased, the wavelength (at each peak) decreased, and became more close to those for wastewater. The effect of alanine behaves as a mono or bidentate ligand that was more pronounced on the

second peak. It may be said that the significant shifts in the peaks in spectra of wastewater and solutions of tanning agents is attributed to the reaction of chromium complex ion with organic ligands from hides such as amino acids present in wastewater, while other possible chemical contaminations provided no effect on the positions of these peaks.
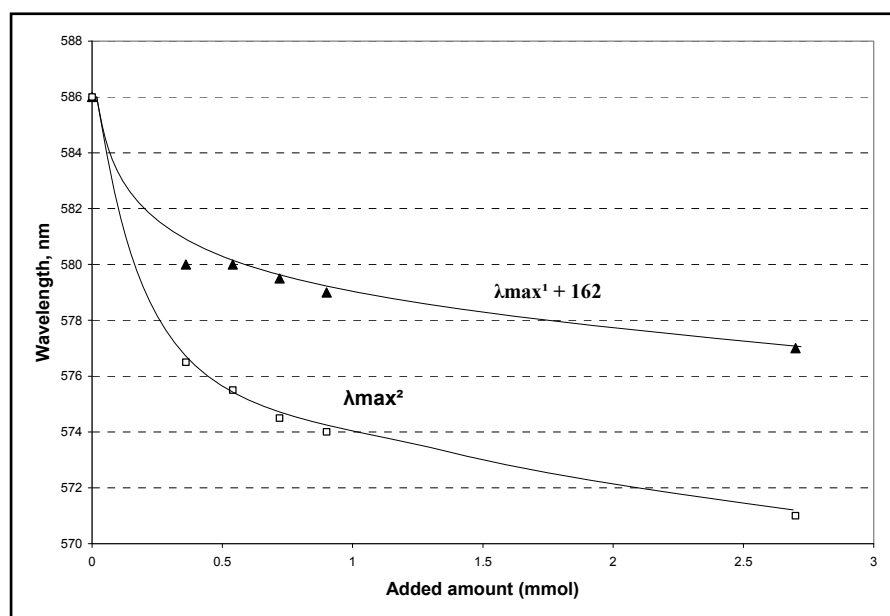

Figure 5. The effect of additions of alanine to solution of chromitan B on (λ_{max}^{1} and λ_{max}^{2}): spectra were recorded after 24 hours from solution preparation.

Tanning various types of hides (e.g. cow, sheep, camel, etc.) would result in dissolving various types of amino acids in the wastewater, as the structure of their hides will be different. Also, variations in practical processing of same hides and wastewater collection may affect the level of dissolved amino acid in waste. However, our samples were collected from local factories which process cow hides. Thus different batches of wastewater collected at different times give the same results.

Method Applicability in Tannery Wastewater Treatments

The spectrophotometric technique was applied to real wastewater samples collected from a local precipitation–regeneration facility recently established for a group of leather manufacturing factories in Palestine. The precipitation was accomplished by adding 2.2- 3 kg of magnesium oxide (MgO) to 1.0 m^3 of wastewater, followed by recovering chromium via addition of 70-80 L of sulfuric acid (H_2SO_4) to 1.0 m^3 of recovered precipitates. Figure 6 compares the obtained spectra for various process streams after dilution: 1ml of each stream was diluted to 10ml by tap water, in order to yield spectra with the linearity range of absorbance (below 2.0). Figure 6 provides an obvious tool for monitoring the process of leather tanning and wastewater treatment, through observing the depth of peaks for each sample (which is proportional to concentration of chromium in solution as illustrated in Figure 2). Quantitative comparisons of these streams are presented in Table II, which lists the measured wavelengths and the absorbance at each wavelength for the

industrial streams. At equivalent wavelengths for chromium, it is clear that the spectrum for treated wastewater had minor absorbance as compared to streams of wastewater, the original and recycled solutions for tanning. Consequently, the method provides qualitative and quantitative tools for monitoring process performance. Relative chromium content of various streams was obtained, and percentages of absorbance ratio at the second wavelengths for the various streams were estimated and compared. Chromium content in the treated wastewater was found to be about 4.7 % of that in wastewater collected from tanneries and fed to the precipitation process, indicating a removal of 95% for chromium. Also, it was 0.7 % of that in the tanning solution, 15.7% of that in the recycled tanning solution. This decrease is a result of the consumption of chromium for tanning hides and dilution of wastewater with other wastewater streams from other tanning steps. This estimation indicates the success of tanning process performance, and the validity of the technique for quality control purposes. Spectrophotometer (e.g. spectronic 21) set at the proper wavelength can be used in quality assurance lab.for monitoring process performance. Obviously, it is a simple and affordable technique for local tanneries. In addition, it is used for investigating the effect of various physicochemical parameters on the efficiency of precipitation tool. For example, Figure 6, indicates that 95% chromium is precipitated as a result of CaO addition, and this percentage removal can be calculated with each parameter. Removal of chromium from tannery wastewater and industrial waste has previously been reported by using various adsorbents [21, 22], and in this study, uv/vis spectrophotometry was a judicious choice to be used for investigating the adsorption of chromium from tannery wastewater on various local adsorbents.
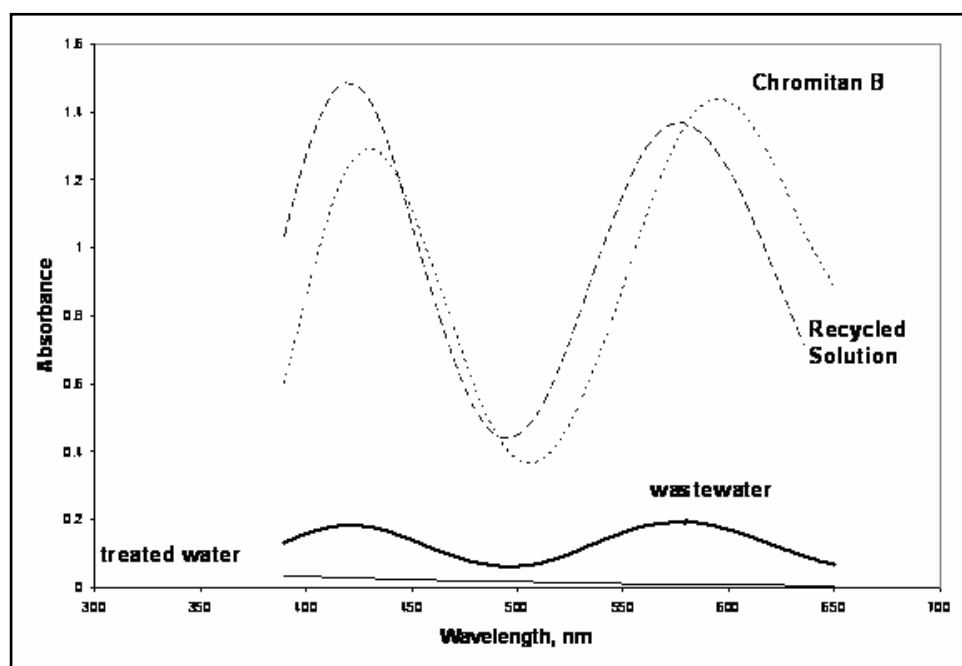

Figure 6. Spectra of tanning and wastewater treatment streams, from the industrial precipitation–regeneration facility.

Table II. The characteristics of different streams collected from the wastewater treatment facility in Hebron

Stream	Wavelengths, nm		Absorbance at		Remarks
	λ_{max}^1	λ_{max}^2	λ_{max}^1	λ_{max}^2	
Chromitan B	431	595	1.292	1.439	Solution was prepared in the lab
Wastewater	420	576	0.203	0.215	Its chromium content is about 15.7% of that in the recycled solution.
Recycled tanning solution	420	576.5	1.523	1.368	Was obtained by adding 70-80 L of (30% H_2SO_4) per 1 m^3 of wastewater.
Treated water	No obvious peaks		0.029	0.01	Its chromium content is about 4.7% of that in wastewater, and about 0.7% of that in the recycled tanning solution.

Conclusions

Chromium is a highly toxic non-essential metal for microorganisms and plants. Due to its widespread industrial use, chromium has become a serious pollutant in diverse environmental settings. The hexavalent form of the metal, Cr(VI), is considered a more toxic species than the relatively innocuous and less mobile Cr(III) form. The presence of Cr in the environment has selected microbial and plant variants able to tolerate high levels of Cr compounds. The diverse Cr-resistance mechanisms displayed by microorganisms, and probably by plants, include biosorption, diminished accumulation, precipitation, reduction of Cr(VI) to Cr(III), and chromate efflux. Some of these systems have been proposed as potential biotechnological tools for the bioremediation of Cr pollution.

Uv/vis spectrophotometric measurements can be used as a quality control technique for monitoring the treatment and the recycling of chromium solution in leather industry. The recorded spectra of tannery wastewater and solutions of tanning agents are similar but the positions of the two peaks are changeable depending on ligands associated to chromium ion. Amino acids (as organic residuals from hides processing) cause noticeable shifts in the positions of these peaks, that increases with increasing concentration. Other possible chemical contaminations resulting from tanning processes such as salts, lime and sulfuric acids are found to have no noticeable effect on the positions of the peaks.

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