

DETERMINATION OF CHROMIUM IN THE WASTEWATER BY FLAME ATOMIC ABSORPTION SPECTROMETRY AND UV- VISIBLE SPECTROPHOTOMETRY

Aboma Roro

Abstract

Different kinds of methods have been designed and used to determine the level of concentration of chromium in the wastewater and many techniques have been designed, recommended and used to reduce the concentration level of chromium in the tannery effluents. The chromium through tannery effluents has become a global concern. Tanneries must thoroughly check and monitor their waste stream regularly to obey regulatory standards set out. This work is likely a take part to this global concern; by this work, the level of chromium concentration of Bahir Dar tannery was determined by using FAAS and UV-visible spectrophotometric methods; the methods have been compared for their precisions, and the efficiency of the wastewater treatment mechanism of the tannery under discussion has been evaluated. The concentration of Cr of the wastewater in the final outlet was found to be 7.461 ppm for Cr (III) and 4.33 ppm for Cr (VI). The total Cr concentration determined by the two methods were comparable, the methods were equally precise at 95% level. The treatment system was 98.8% efficient with regard to Cr (III) but the system has aggravated the concentration of Cr (VI).

Key words: Chromium, Tannery wastewater, FAAS and UV-visible Spectrophotometry

1. Introduction

Several analytical methods such as: Flame Atomic Absorption (FAAS), Electro thermal Atomic Absorption Spectrometry (ET AAS), Spectrophotometry using different reagents especially 1,5-Diphenylcarbazide, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES), Inductively Coupled Plasma Mass Spectrometry (ICP MS), X-ray Fluorescence Spectroscopy (XFS), Capillary Electrophoreses (CE), Neutron Activation Analysis (NAA) and the others can be used for Chromium determination in wastewater [5, 8, 10, 13]. Some of these methods are valence-specific and some others are valence-non-specific.

Atomic absorption spectrometry is a method of detecting and measuring chemical elements, particularly metallic elements [5, 6]. FAAS is the most widely used technique for analysis of trace metals in contaminated water, soil and industrial wastewater [7]. The introduction of FAAS has produced a rapid and relatively inexpensive method for the quantitative determination of metals at trace (0.1 – 100 ppm) in a wide variety of samples, e.g. soil, sediment, sludge and industrial effluent. This technique is based on the vaporization of the analyte sample by aspirator of the solution into a flame. The compounds to be investigated have to be broken into their atoms. This is done by aspirating the sample solution into a hot flame. Before it enters the flame the solution is dispersed into a mist of very fine droplets, which evaporates in the flame to give first the dry salt, then the vapour of the salt. At least a part of the vaporized molecules must dissociate into atoms of the element to be measured [7].

Light of certain wavelengths, produced by a special kind of lamp, is passed through the long axis of a flat flame and into a spectrometer. The atoms, dispersed in the flame, absorb some of the radiation. They do not absorb all the lines emitted by the lamp, since nearly all the atoms are in their ground state. Therefore, only those emission lines that correspond to transitions from the ground state will be absorbed. Consequently, the beam of radiation coming out of the sample misses the radiation in the corresponding wavelength which is a measure of the characteristics of the sample. FAAS is therefore valence-non-specific method which enables only the determination of total chromium [10, 14].

The UV-visible spectrophotometric method using 1,5-Diphenylcarbazide complexing reagent was used for this study. This technique is a valence-specific technique, which enables the direct measurement of Cr (VI) in the presence of Cr (III). The total Chromium concentration can also be determined using this method by oxidising Cr (III) to Cr (VI) and complexing it with Diphenylcarbazide[7, 13]. Thus it is advantageous over the other techniques due to the possibility of the speciation study, and it doesn't require separation by means of extraction as well [12].

The possibility of determination of chromium in wastewater by spectrophotometric method is due to the special property of Cr (VI) to form a stable complex with 1,5-Diphenylcarbazide, the complex which absorbs light in the UV-visible region with molar absorptivity being about $40,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 540 nm in acidic medium [7]. There are two proposed possible structures for this complex. The first one is the one in which Cr (VI) will form octahedral complexes with ligands. By constructing a molecular model of the ligand (1,5-Diphenylcarbazide) and positioning it around a suitable six branched element the structure indicated as in Figure 6 can be obtained. The second structure has also been proposed as

shown in Figure 7 with the Cr (VI) being ‘sandwiched’ between the delocalized rings. It is proposed as a result of the use of x-ray diffraction. The apparent conflicts between the two theories for the structure are due to one version being borne out of complexation models (as in Figure 6) while the second one is as a result of the use of x-ray diffraction techniques [13].

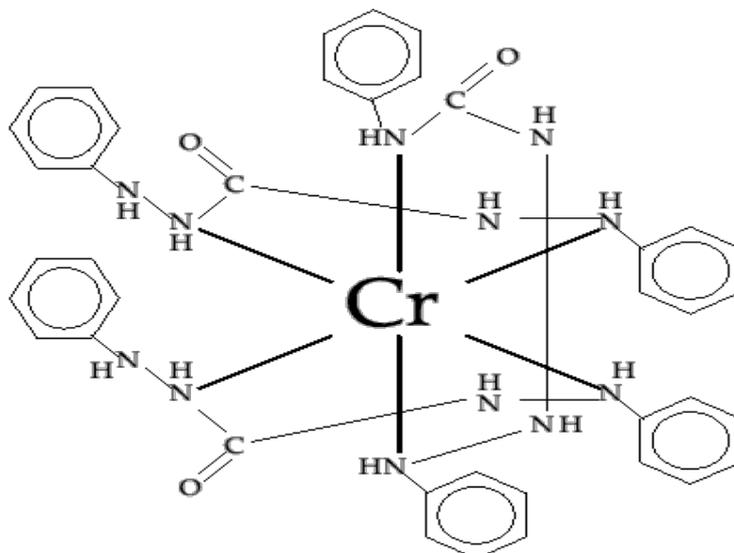


Figure 1: Complexation Model of DPC-Cr (VI) Complex [14]

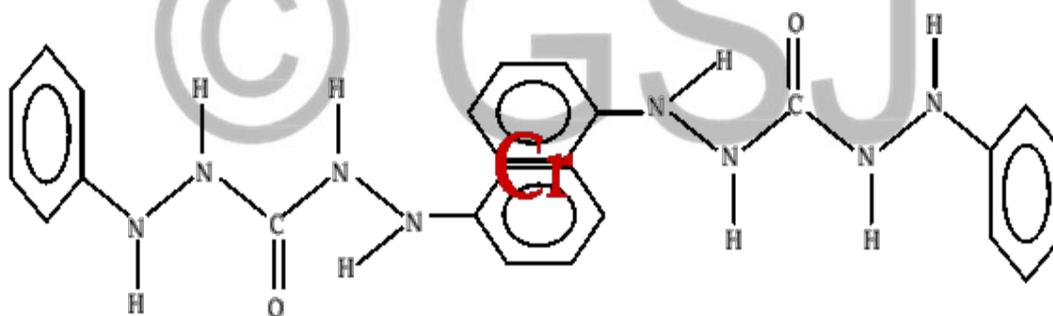


Figure 2: X-ray Diffraction of DPC-Cr (VI) Complex [14]

The colour of the compound is as a result of electron transfer, rather than the d-orbital shifts. Since Cr has the outer electron configuration of $3d^54s^1$, Cr (VI) will have the d^0 configuration; without anything in the d-orbital to shift hence the colour has to be due to electron transfer.

2. Objectives and Significances of the Study

2.1 Objectives

The objectives of this study are:

- To determine the concentration of chromium released to the environment through the wastewater of Bahir Dar tannery industry.
- To compare the two methods i.e., the UV-Visible spectrophotometry and FAAS method for determination of total chromium concentration in tannery wastewater.
- To suggest on the efficiency of wastewater treatment system of Bahir Dar tannery to reduce risk of chromium discharge to the environment

2.2 Significances

According to the World Health Organization (WHO), chromium is one of the metals of most immediate concern [2, 10]. It has been considered as one the top 16th toxic pollutants, and believed to be the second common inorganic contaminant after lead [4, 10]. The tannery wastewater is one of the main sources of chromium discharge to the environment; all tanneries must thoroughly check their waste stream regularly [3, 9]. Therefore, this study is significant in checking the level of concentration of chromium discharge to the environment through tannery wastewater of Bahir Dar Tannery. Secondly this study compares the two methods namely, the flame atomic absorption spectrometry (FAAS) with that of UV-visible spectrophotometer for better way of determination of chromium in wastewater. More over, the study will give suggestion on the treatment efficiency of the treatment mechanism used for treating the tannery wastewater of Bahir Dar Tannery to avoid the risk of environmental pollution problem.

3. Materials and Methods

3.1 Instrumentation

3.1.1 Instrumentation of FAAS

The FAAS used for this study was buck scientific, model 210VGP Atomic Absorption Spectrometer. It was equipped with deuterium arc back ground corrector, nebulizer and hollow cathode lamp corresponding to chromium metal. The flame used was air -acetylene. The following operating conditions were used during the operation

- The wave length (λ) = 357.9nm
- The detection limit (DL) = 0.5mg/L
- The slit width (SW) = 0.7nm
- The lamp energy = 3.7ev

3.1.2 Instrumentation of UV-visible Spectrophotometry

The UV-visible spectrophotometer used was SANYO, SP65 UV/Visible Spectrophotometer with the following instrument parameters

- Wave length range 190 – 800 nm
- Absorbance limit 0.001
- Deuterium lamp and 10mm quartz cuvette

3.2 Apparatus and Chemicals

3.2.1 Apparatus

Volumetric flasks, conical flasks, XE-50A electrical balance, measuring cylinders, pipettes, polypropylene bottles, beakers, 1203 hotplate electrical heater, pH meter, thermometer

3.2.2 Reagents and Chemicals

0.25g 1,5-Diphenylcarbazide (Batch No. 7321), 0.36g potassium dichromate (analytical grade), concentrated sulphuric acid, concentrated nitric acid, 0.2M sulphuric acid, 50% v/v sulphuric acid, (1:1) sulphuric and nitric acids, ammonium hydroxide (ammonia solution), sodium azide, potassium permanganate, hydrated chromium chloride ($\text{CrCl}_3 \cdot \text{H}_2\text{O}$), acetone, methyl orange and distilled water

3.3 Sample Collection

Samples were collected from tannery effluents of Bahir Dar Tannery. The samples were collected from two sites i.e., from pre-treatment site and post-treatment site as one of the objectives of this study was to suggest on the treatment efficiency of the wastewater treating mechanism used by the tannery with respect to the chromium content. So one sample was the sample collected from the discharge point of the tanning process as the effluents were eliminated from the tanning drum before it gets diluted as it mixes with the effluents of other processing units. This effluent has a characteristic of dark-green colour (which is probably, an indication that the effluent contains chromium). Since the tanning process is 'batch' type, the wastewater eliminated from the tanning drum seems homogeneous; hence a 500 ml grab sample was collected in a 1 liter bottle.

The other sample was collected at the outlet of the wastewater from the series of the treatment tanks. This site of sample could be called as post-treatment site. Figure 8 is the photograph captured during the collection of sample from this site. This post-treatment site sample of wastewater was collected in a systematic way throughout 12 hours in regular intervals of time. The sample was a composite type since the grab samples collected the

whole day were taken into the same bottle. The colour of the sample was completely different from the pre-treatment site sample i.e., its colour was not dark-green; its colour like a colour of water mixed with mud or dust. Its odour was bad (sulphide smell) even after days or weeks as it was being kept in the laboratory.



Figure 3: The final outlet point of the wastewater from systems of treatment

The pHs of the two samples were different; the pH of the pre-treatment site sample was 4 and that of the post-treatment site one was about 7.5; by adding nitric acid solution the pHs of both samples were reduced to about 1. The type of bottle used for sample collection was a plastic (polypropylene) bottle. The samples kept in the plastic bottles were put in a plastic bag filled with ice to keep the temperature below 4 C° and transported to the laboratory for analysis. Figure 9 shows the samples in the bottles in the laboratory with necessary information written on each bottle.



Figure 4: Samples brought to the laboratory - the left side is sample from pre-treatment site where as the one on the right side is the sample from the post-treatment site

3.4 Preparation of Standard Solutions for FAAS

Before the determination of chromium in the real sample, first four series of standard chromium solutions in different concentrations were prepared by diluting the stock solution of chromium with distilled water. A blank (distilled water) and the standards were run with FAAS and four points of calibration curve was established.

Stock solutions of Cr (III) and Cr (VI) at a concentration of 1000 mg/L were prepared by dissolving of 5.1240 g analytically pure $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.3725 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 L volumetric flask and diluted to the mark with distilled water. 10 mL of the stock solution was taken into 100 mL volumetric flask and diluted to the mark. Further working solutions (0.5, 1, 2, and 4 ppm) were prepared by appropriate dilutions of the secondary stock solution. Figure 10 shows series of standard solutions including the prepared primary and secondary stock solutions.



Figure 5: The prepared standards-prepared stock solutions and the working solutions

3.5 Preparation of Standard Solutions for UV-visible Spectrophotometric Analysis

Before preparation of standards, solution of 1,5-Diphenylcarbazide, the main complexing agent, was prepared. Solution of 1, 5-Diphenylcarbazide was prepared by taking 0.25g 1, 5-Diphenylcarbazide powder into a 100 ml volumetric flask and dissolving it with acetone; after it was completely dissolved in acetone, the flask was filled to the mark with distilled water. Figure 6 is the solution of 1, 5-Diphenylcarbazide prepared in this way.



Figure 6: Solution of 1, 5-Diphenylcarbazide, 0.25g 1, 5-Diphenylcarbazide in distilled water after it completely dissolved in acetone

Analytical grade 0.360 g of $K_2Cr_2O_7$ was taken and dissolved with deionized water and was diluted to 1 L. Then 10 mL of the standard was taken and further diluted to 100 mL. This was a standard from which a series of ten standard solutions of different concentrations were prepared. A series of ten standards containing 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5, 2.0, 2.5 and 3 mL were taken into 100 mL flasks and acidified with 0.4 M of 5 mL of sulphuric acid. Then a

freshly prepared 1 mL of 1,5-Diphenyl-carbazide was added to each standard. Pink colour was developed immediately and each flask was filled to the mark. Figure 7 shows series of standard solutions ready for colour comparisons in the analysis using colour comparison and for calibration curve construction in the analysis of the analyte by UV-visible spectrophotometer. A graph of absorbance versus concentration of the standards (calibration curve) is shown under the section of results and discussion.

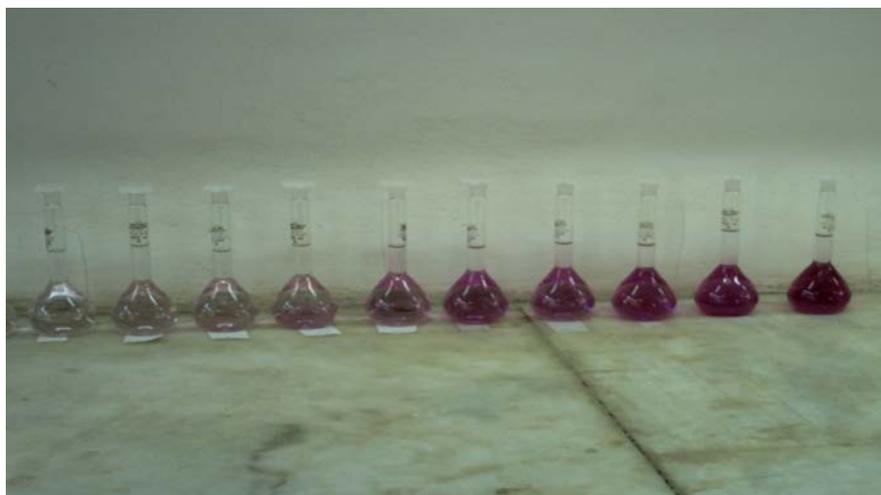


Figure 7: Series of standards (working solutions), red violet colour being intensified with increase of concentration

3.6 Sample Preparation for FAAS Analysis

50 mL of sample was taken into 250 mL conical flask; 5 mL concentrated HNO_3 was added to it. The mixture was boiled for 45 min on hot plate after adding boiling chips. 5 mL of concentrated HNO_3 was added for the second time after cooling the solution. The solution was then heated and boiled for 15 min, the liquid part was almost evaporated and the solution started to change into solid ash. It was then cooled and diluted to 100 mL with distilled water, and put for analysis. Figure 8 shows the samples prepared for analysis.



Figure 8: Samples prepared for analysis – the left one is sample of post-treatment site and the right one is the sample of the pre-treatment site

3.7 Sample Preparation for UV-visible Spectrophotometric Analysis

In the determination of the concentration of total chromium, 10 mL of sample was taken and added into 50 mL conical flask. A few drops of a methyl orange was added as an indicator, followed by addition of a few drops of concentrated NH_4OH (ammonia solution) for pH increase to basic values. Afterwards, 1:1 (50% v/v) H_2SO_4 solution was drop-wised into the solution until it was acidic; 1 mL was added in excess. The sample volume was adjusted to about 40 mL by adding distilled water, boiling chips were added and it was heated on hot plate to the boiling point for 30 min. After boiling, 3 drops of KMnO_4 were added to the solution, dark red colour was produced, corresponding to the oxidation of Cr (III) to Cr (VI). The boiling continued for 2 min, and then 1 mL of Na_3N was added to remove the excess KMnO_4 . The solution continued to boil gently, 1 min longer, after the colour had faded. After cooling, it was acidified by adding 0.2 M sulphuric acid solution and a pH meter were used to adjust the solution to $\text{pH } 1.0 \pm 0.3$. The solution was transferred to a 100 ml volumetric flask, and diluted to 100 ml, and mixed. 2 mL 1,5-diphenyl-carbazide solution was added, mixed and let stand for 5 to 10 min for full colour development. After colour development it was taken for colour comparison against the prepared series of standards as shown under the section of results and discussion. The same procedures were followed for both samples of pre-treatment and post-treatment sites; the preparations were made simultaneously in different conical flasks.

In the case of selective determination Chromium (VI); 5 mL of a sample of pre-treatment site and 5 mL of a sample of post-treatment were taken into a separate 100 mL volumetric flasks.

1 mL 0.4M H₂SO₄ and 2 mL 1, 5-diphenylcarbazide solutions were added to each flask and diluted to the mark by distilled water. The solutions were let stand for 5 min for colour development. After colour development it was taken for colour comparisons against the standards and spectrophotometric measurement and analysis.

4. Results and Discussion

Using both FAAS and UV-visible spectrophotometric methods the results were obtained by computing of the data recorded during the analysis. By FAAS the total chromium concentration was determined for both samples of pre-treatment and post-treatment sites. By UV-visible spectrophotometric method both total chromium and chromium (VI) concentrations were determined for samples of effluents collected from post-treatment site and post-treatment site. Concentration of chromium (III) was calculated by taking the difference between the concentrations of the total chromium and Cr (VI). The average of the concentrations total chromium determined by the two methods was taken to find the difference between concentrations of total chromium and chromium (VI). The results are given in Table 3. Details of the results are discussed under the sub-sections of this unit.

Table 1: The concentration of total chromium, chromium (III) and chromium (VI) for both samples of effluents of pre-treatment and post-treatment sites (Concentration ± SD in ppm)

| Before/After | Total Chromium Concentration in ppm | | Concentration of Cr (VI) in ppm | Concentration of Cr (III) in ppm |
|------------------|-------------------------------------|------------------------------|---------------------------------|----------------------------------|
| | By FAAS | By UV- Vis Spectrophotometry | | |
| Before Treatment | 661.800 ± 39.800 | 634.250 ± 16.250 | 2.13 ± 0.000 | 645.985 ± 21.490 |
| After Treatment | 12.072 ± 0.842 | 11.510 ± 0.560 | 4.330 ± 0.240 | 7.461 ± 0.560 |

4.1 Results of Determination by FAAS

In principle FAAS is a non-valence specific technique as a result it was used in the determination of the total chromium concentration. Series of four standard solutions with concentrations 0.5, 1, 2, and 4ppm were prepared and a calibration curve was constructed as given in Figure 14. When the curve was analysed, it has had a linear regression, R = 0.99961 and a linear equation $y = -0.00622 + 0.04278x$

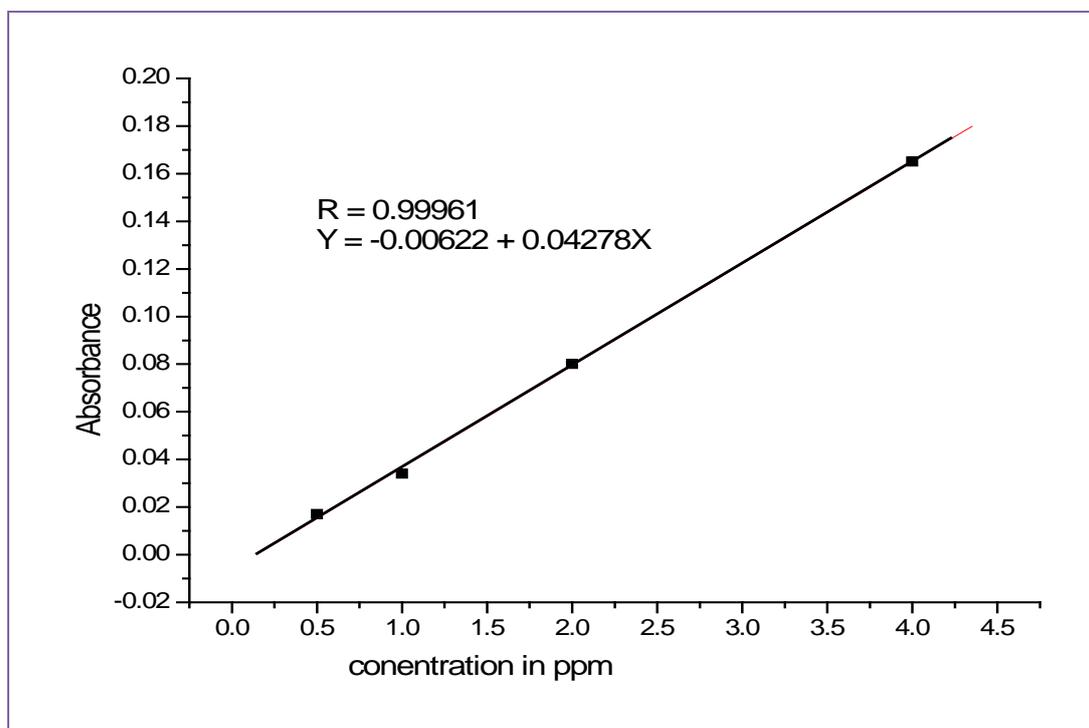


Figure 7: Calibration curve obtained by running of the four working solutions by FAAS

After the construction of the calibration curve, the absorbances of the prepared samples were measured by FAAS and compared against the calibration to obtain the corresponding concentrations. The means of the concentrations, calculated after replicate measurements were 3.309 ± 0.199 and 1.509 ± 0.105 ppm for pre-treatment post-treatment sample sites respectively. After this the dilution factors were considered, and the obtained results were multiplied by their respective dilution factors because the samples have been diluted to bring their absorbances in the range of the absorbances of the standards. The pre-treatment sample has been diluted by factor of 200, first by factor of 2 in which 50 mL of a sample was diluted to 100 mL after digestion, secondly by factor of 100 in which 1 mL of the prepared sample was taken and diluted to 100 mL. The post treatment sample has been diluted by factor of 8 (first by 2 and then by 4). Thus the concentrations of total chromium as determined by FAAS and multiplied by factors of dilution were 661.800 ± 39.800 and 12.072 ± 0.842 ppm for representative samples of pre-treatment and post-treatment sites of effluents respectively as given in Table 3. The confidence intervals at 95% confidence level have been calculated and given as follows

- 95% CI for pre-treatment sample = 661.800 ± 98.808 ppm
- 95% CI for post-treatment sample = 12.093 ± 2.090 ppm

So it is only 5% probable that the concentration level could be beyond 562.992 – 760.608 ppm and 10.003 – 14.183 ppm for pre-treatment and post-treatment sites effluents respectively.

4.2 Results of Determination by UV-visible Spectrophotometric Method

Both total Cr and Cr (VI) concentrations were determined by UV-visible spectrophotometric method using 1,5-Diphenylcarbazide complexing reagent. Series of ten standard solutions with concentrations 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ppm were prepared. The standard solutions developed a red-violet colour when treated with sulphuric acid and 1,5-Diphenylcarbazide with increase of the intensity of the colour with increasing concentration of standards as seen in Figure 7. Like wise when the prepared samples were treated with sulphuric acid and 1,5-Diphenylcarbazide similar colour with that of the standards was developed. So before taking the UV-Visible absorbance reading, the colours developed by the prepared samples as treated with sulphuric acid and 1,5-Diphenylcarbazide were compared with standards colour intensity, simply to estimate the chromium concentration in the sample. Those samples which were prepared for the determination of the concentration of Cr (VI) had shown colour resemblance with standards of less concentration (0.2 – 0.5 ppm) except they were diluted by factor of ten during preparation. The sample from the post-treatment site when prepared for the determination of total chromium and treated with sulphuric acid and 1,5-Diphenylcarbazide, has developed a colour which has similar intensity to the standard of 1 ppm but it was diluted by a factor of 10 during preparation. The post-treatment site sample that was prepared for total chromium concentration determination when treated with sulphuric acid and 1,5-Diphenylcarbazide didn't show any colour resemblance with any of the standards i.e. the colour developed became out side of the range of the colours of the standards but with further dilution, the matching colour intensity with some of the standards has been developed; in other words with further dilution its concentration was found to fall in the range of the concentrations of the standards as shown in Figure 15. Figure 16 shows the further dilution series for determination of total chromium in the sample of effluents before treatment site. It has had a colour correspondence with standards in the range of concentration 2.0 – 3.0 ppm after two successive dilutions, of course, with different factors; the total dilution factor was 250.

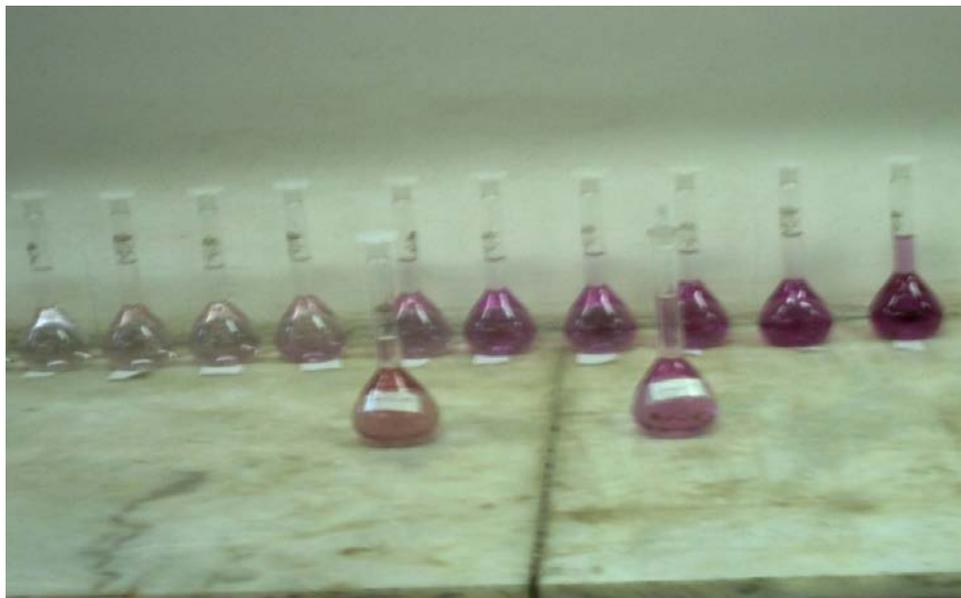


Figure 8: Comparison of colour intensities the samples after appropriate dilution, acidification and treatment with 1, 5-Diphenylcarbazine with the series of standards



Figure 9: Samples prepared for determination of total chromium from samples of effluents of pre-treatment site; the 1st one from right is the first prepared sample in which 10 mL of the sample was taken and diluted to 100 mL after oxidation process, the 2nd one was obtained by taking 10 mL of the 1st and diluting to 100 mL, and the 3rd one is 40mL of the 2nd being diluted to the mark

After the colour comparison, the standards and the prepared samples were taken for UV-visible spectrophotometric absorbance reading. Absorbances of the standards were recorded and the calibration curve was established as shown in Figure 17 with linear regression, $R = 0.99865$ and linear equation $Y = 2.75728 \times 10^{-4} + 4.089 \times 10^{-4}X$. Absorbance readings of the samples were recorded and compared against the standard calibration curve to obtain the corresponding concentrations. The averages of the replicate measurements were taken and multiplied by dilution factors to obtain the concentrations in the representative samples as

given in Table 2. The confidence intervals were also calculated at the 95% confidence level as given below

- 95% CI for total Cr in the pre-treatment sample = 634.250 ± 40.34 ppm
- 95% CI for total Cr in the post-treatment sample = 11.510 ± 1.390 ppm
- 95% CI for Cr (VI) in the pre-treatment sample = 2.13 ± 0.000 ppm
- 95% CI for Cr (VI) in the post-treatment sample = 4.330 ± 0.596 ppm

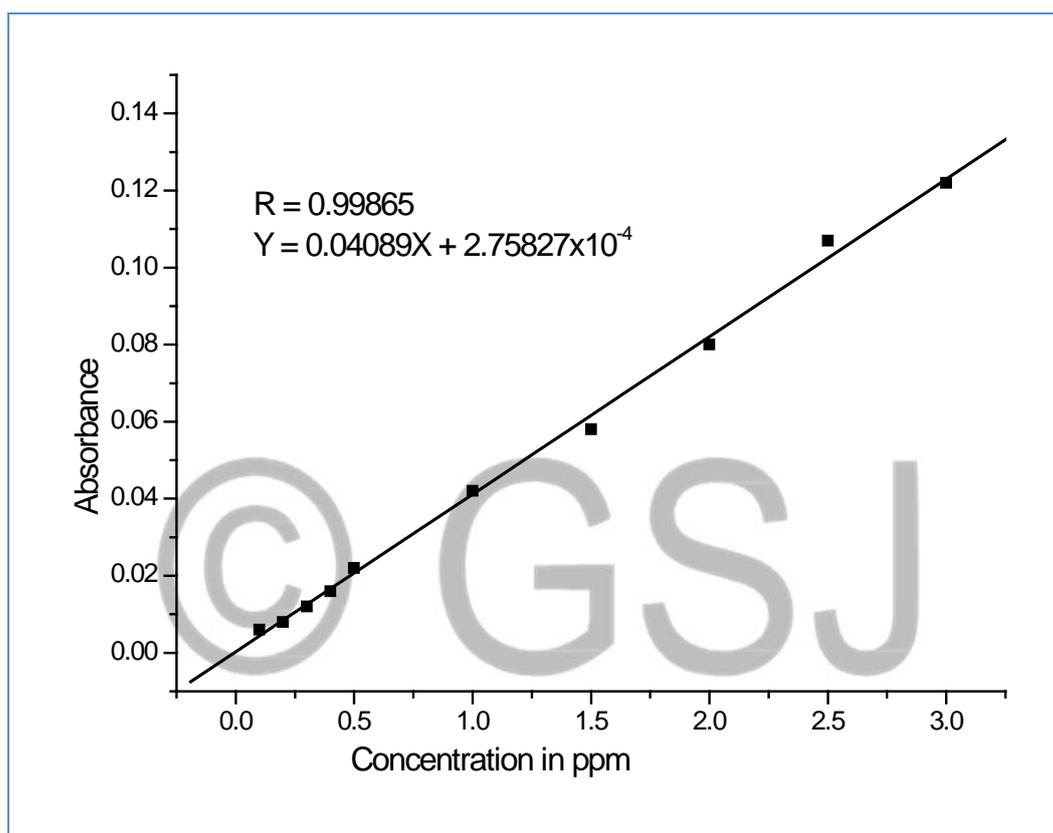


Figure 10: Calibration curve established after taking the absorbencies of all the ten standard solutions by UV-visible spectrophotometry

4.3 Comparison of the Precisions of the Two Methods Used for the Total Cr Concentration Determination

The total chromium concentrations were determined both by FAAS and spectrophotometric methods. As it can be seen from Table 3, the magnitudes are comparable. The bar graph was also used to compare the concentrations determined by the two methods as shown in Figure 18. However, comparing simply by looking at the magnitudes of concentrations is not enough

to suggest whether the two methods are equally important for the total chromium concentration determination or not. Consequently, the test statistic F, was used to compare the precisions of the two methods. The F values were calculated in the following way and compared with the critical value of F at the 95% confidence level (95% $F_{crit} = 19$).

$$F_1 = S_1^2 / S_2^2 = (39.8)^2 / (16.25)^2 = \mathbf{5.999}$$

$$F_2 = S_3^2 / S_4^2 = (0.842)^2 / (0.56)^2 = \mathbf{2.261}$$

Where:

F_1 – stands for F value for samples of pre-treatment site

F_2 – stands for F value for samples of post-treatment site

S_1^2 – stands for variance of total Cr concentration value determined by FAAS in the sample of pre-treatment site

S_2^2 – stands for variance of total Cr concentration value determined by spectrophotometric method in the sample of pre-treatment site

S_3^2 – stands for variance of total Cr concentration value determined by FAAS in the sample of post-treatment site

S_4^2 – stands for variance of total Cr concentration value determined by spectrophotometric in the sample of post-treatment site

The values of F calculated (F_1 and F_2) were by far less than the value of F_{crit} at 95% confidence level because $F_{crit} = 19$ at the 95% level for degrees of freedom of both numerator and denominator is 2. As a result good agreement between the results were obtained, using the two methods, by the F test at 95% level, the difference in the means of the sets of data was not real but only the result of random errors.

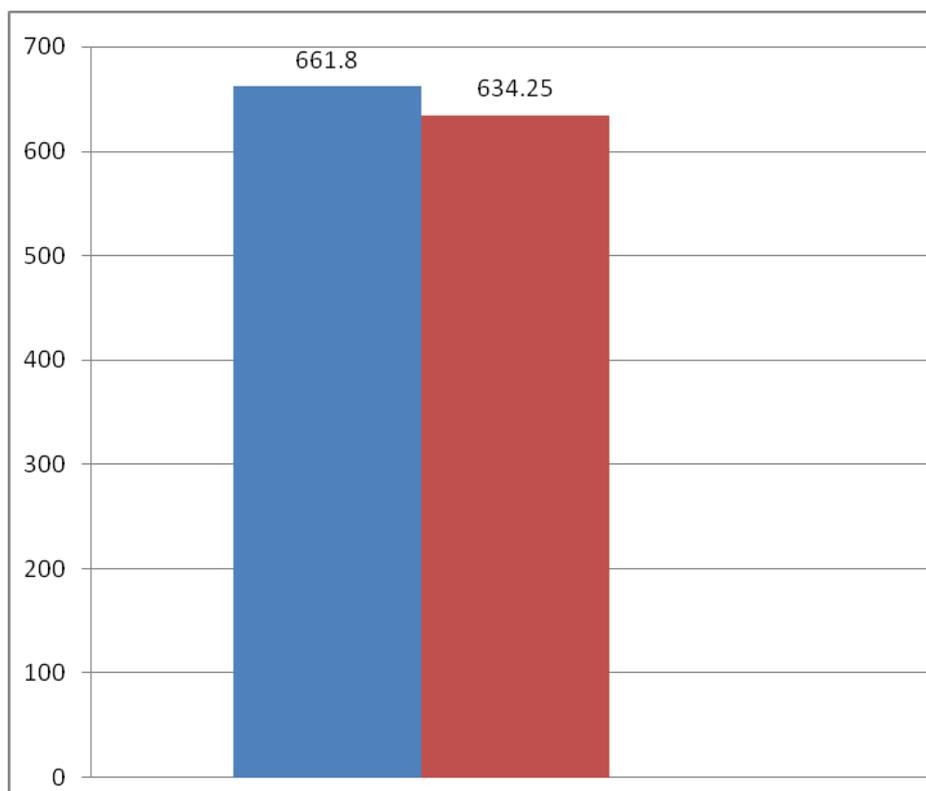


Figure 11: A bar graph for comparison of the total chromium concentration determined by the two methods in ppm (661.8 was the concentration level determined by FAAS and 634.25 was that of the spectrophotometric one)

4. 4 Correlation of the Chromium Concentration per Species, and Sites of Sampling

Here is a section where the difference in concentrations of Cr (III) and Cr (VI) of both sampling sites were compared and explained. The efficiency of the treating mechanism of the wastewater for removal of chromium of the tannery industry can be suggested from this comparisons and explanations.

The Cr (III) concentrations were found to be greater than concentrations of Cr (VI) from both sampling sites i.e., in the samples both of pre-treatment and post-treatment sites. However, the concentration of Cr (III) was reduced by wastewater treatment mechanism employed by the tannery industry. The treatment mechanism involved dilution and sedimentation (passage effluents through sand filled tanks). About 98.8% of Cr (III) was found to be removed as it was computed from the recorded data of chromium concentration of this study. To the contrary, the concentration of Chromium (VI) was increased as the effluent traverse through the treatment system. It was found to be more than double in the sample of post-treatment site than it was in the pre-treatment one. This means, there could conditions favouring the oxidation of Cr (III) to Cr (VI) in the treatment system. These conditions have to be assessed and identified in order to stop this unfortunate happening. Figure 20 and 21 are the bar graphs used to compare physically, the concentration levels of the chromium (III) and

chromium (VI) respectively between the two sampling sites. A simple F test has also been used to see whether these differences are real or the result of random errors.

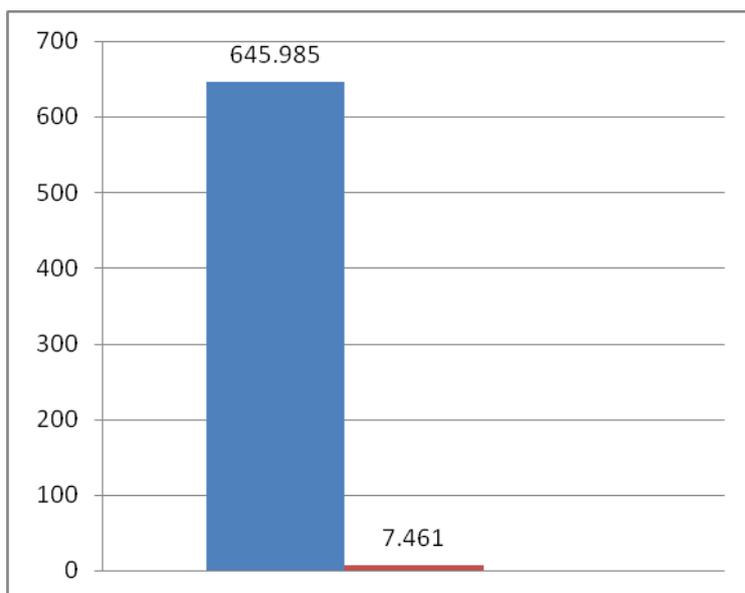


Figure 12: Comparison of concentration chromium (III) calculated from the two sampling sites in ppm, '645.985' is the concentration of chromium (III) of pre-treatment site and '7.461' is for the post-treatment one

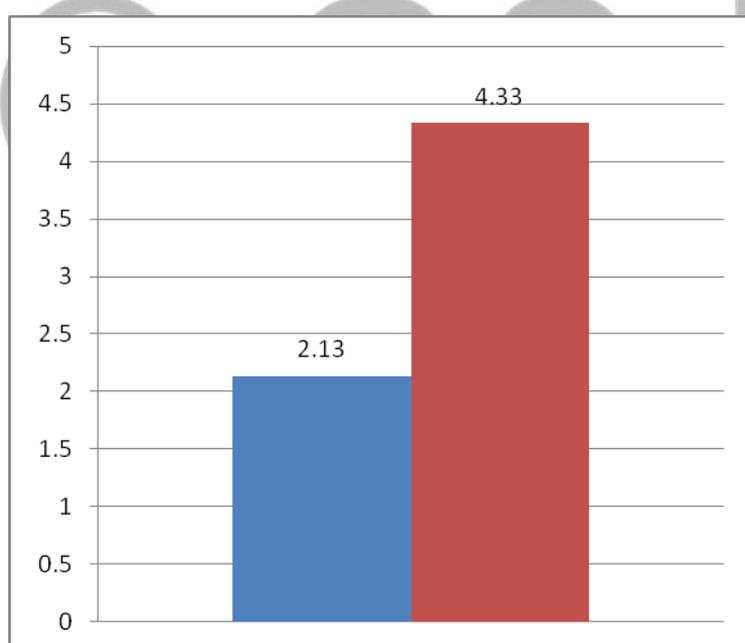


Figure 13: Graphical comparison of the level of concentration of chromium (VI) of the two sampling sites, '2.13' is the concentration of chromium (VI) of the pre-treatment site and '4.33' is that of the Post-treatment one (ppm)

The test statistical F, was given in Table 2, compares the calculated values of F with the critical value of F at 95% confidence level from which we can decide whether the difference in concentrations of each species at different sampling sites i.e., before and after treatment was real or the result of random error.

Table 2: Comparison of F Values of Each Species of Chromium Concentrations from the two sampling sites with critical value of F at 95% confidence level

| | F | F_{crit} | Comparison |
|-----------------|----------|-------------------------|-------------------|
| Cr (III) | 1472.640 | 19 | $F > F_{crit}$ |
| Cr (VI) | infinity | 19 | $F > F_{crit}$ |

As it can be seen from Table 4, the values of F are greater than the value of critical F in both cases, this dictates that the concentrations of Cr (III) of the two sites of the effluent were potentially different and the difference in means was a real difference and was not because of the input of random errors; the same was true for chromium (VI).

5. Conclusions and Recommendations

The concentrations of total chromium, Cr (III) and that of Cr (VI) of the wastewater of Bahir Dar tannery have been determined. FAAS and UV-visible spectrophotometric methods have been employed for the determination. The determination was made for two sampling sites, the first site was the pre-treatment site i.e., before the treatment of the wastewater by treatment system (dilution and passage of effluents through sand filled tanks) and the second site was the post-treatment site i.e., after the chromium rich effluent has been diluted by mixing with other effluents and passed through the sand filled tanks, just at the point of its exit to the environment. The results were given in Table 3. At its final outlet (as it passes out of the treatment system), the effluent was found to contain 7.461ppm Cr (III) and 4.33 ppm Cr (VI). The concentrations determined for both species are greater than the maximum level permitted by different parts of the world and different international organizations. For example, according to WHO, the maximum permissible level is 0.5 and 0.05 ppm in drinking water respectively [1, 8] and according to U. S. Environmental Agency, the recommended limit is 0.1 ppm for Cr (III) and 0.05 ppm for Cr (VI) with regard to drinking water [1, 11].

The two methods, the FAAS and the UV-vis spectrophotometric, have been compared for their precisions in the determination of total Cr concentration. Though the means determined by the methods were not exactly alike, they were comparable as shown using a bar graph (figure 13). The precisions of the results obtained by the methods have been compared using the test statistic F, in which $F < F_{crit}$ at 95% confidence level. So for the determination of total Cr in the wastewater of tannery industry one can either use FAAS or UV-visible spectrophotometric method and can obtain comparable mean values with similar precisions

regardless of the difference in simplicity or difficulty of sample and standard preparation, and difference in availability of main reagents required for each method.

Due to the fact that the concentrations of both Cr (III) and Cr (VI) were determined both before and after treatment systems, the efficiency of the treatment system of the tannery has been evaluated. Accordingly, the treatment mechanism was 98.8% efficient in avoiding or removing of Cr (III) from the effluent discharged to the surrounding. However, unfortunately the treatment system was not efficient to reduce the concentration of the toxic form of Cr that is Cr (VI). The treatment system has aggravated the concentrations of Cr (VI) rather. It was found to increase by more than 2 factors (i.e. from 2.13 – 4.33 ppm). The value is, by large greater than the standard permissible level of different world organization and different parts of the world. Here is the point of a big concern; the concentration level should come below the permissible level to obey ecological regulations, to make the effluent friendly with the environment.

Here are some points of considerations as probable recommendations: conditions favouring the oxidation of Cr (III) to Cr (VI) must have been created as the effluent traverses through the treatment system. These conditions need to be investigated; especially the pH and Eh influencing factors have to be assessed, and the pH and Eh values of the system have to be controlled to the levels that they can help to reverse the happening situations. On the top of that, a number of different mechanisms have been designed, recommended and practiced by different researchers and tanneries to tackle such problems, as listed under the section of 1.5, to make the effluents free of chromium and even to recover chromium from tannery effluents. Of those methods, one that is likely recommendable for this tannery industry could be – “Direct reuse of wastewater, and adsorption of Cr (VI) from aqueous solution by wheat bran in combination” because, 1) the wastewater in pre-treatment site is potentially rich in Cr (III), hence direct reuse of it could be cost effective, 2) Cr (VI) was specially larger in concentration beyond the limit in the post-treatment site, it needs to be avoided from the effluent. This could be done by constructing one tank next to final tank filled with sand and allowing the effluent to pass through after filling with wheat bran. Instead of wheat bran other agricultural wastes such as sunflowers stalks, maize bran, coconut shell, waste tea, rice straw and tree leaves can be used.

6. References

- [1] Chromium - wikipedia, the free encyclopaedia
<http://en.wikipedia.org/wiki/chromium>, received on September19, 2009

- [2] Committee on Biologic Effects of Environmental Pollutants, Chromium, Natural Academy of Sciences, Washington, D.C., 1974
- [3] W. Weixiao, H. Jing, L. Zhaoyang L. Kui, G. Lchang; 113014pe, vol:11, No.3, pp.14 – 19, March1, 2009 <http://www.chemistrymag.orgcji/2009/113014pe.htm> , March 2009
- [4] T. C. Voice, M. L. Davis, G. B. Johnson and L. L. Sturgess; *Hazardous Waste and Hazardous Materials*; Volume 5, Number 4, 1988, PP. 343-350
- [5] Skoog/ West/ Holler/ Crouch, *Fundamentals of Analytical Chemistry* 8th edition
- [6] F. Rouessac and A. Rouessac; *Chemical Analysis, Modern Instrumental Methods and Technique*; 4th edition, pp.189 – 171, 4th edition, pp.189 – 171
- [7] D. Harvey, *Modern Analytical Chemistry*, 1st edition, pp. 368 – 422
- [8] T. P. Dhungana and P. N. Yadav, J. Nepal Chem. Soc., vol. 23, 2008/2009, pp. 93 – 101
- [9] Iva Reizic and Michaela Zeiner; Montshette for cheme/chemical Monthly Journal; volume 140, Number 3, March 2009
- [10] A. Bedemo; *Removal of Chromium from Wastewater Using Locally Available*
- [11] A.Bobrowski, J. Molak, J. Dominik, H. Pereira, B. Bas and W. Knap; Acta Chim. Slov. 2004, 51, 77 - 93
- [12] B. Jankiewicz, B. Ptaszynski; Journal of Environmental Studies Volomue 14, Issue 6, 2005, pp. 869 – 875
- [13] V.Gomez, A. Pasamontes, M. P. Callao; Microchemical Journal, Volume 83, Issue 2, July 2006, pp. 98 – 104
- [14] <http://www.acornuser.org/education/HNC-web/Theory>, November 2009