

# Speciation of Metallic Elements in Tannery Waste Water Case Study: Mohammedia Tannery Morocco

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**Abstract:** *Tanneries discharge wastes without any treatment on the vast areas. Untreated effluents contain toxic materials like heavy metals which accumulate in soils and cause many hazards health. The tannery wastewaters samples were collected from tannery in Mohammedia Morocco. The metallic speciation is referred to physical fractionation (particulate, colloidal, dissolved). This study describes the physical speciation of Cr, Cd, Pb, Zn, Cu, Fe, Ni and Hg in tannery wastewaters. Five important steps of process were selected for sampling process wastes and seven hourly samples from collection basin were collected in order to evaluate total metallic pollution along the process. After Mineralization of Samples, this one was analyzed by ICP-AES. The results indicate that most of the metals have high abundance in particulate forms. Hence, small amounts of Cr, Cu, Pb, Hg and Ni were found in dissolved form: (Cr: 0.05 – 8% ; Cu: 7.1 - 47.2%; Pb: 4.4 - 50%; Hg: 2 – 11%, Ni: 0 – 14% ). While high quantities of Cd were present in dissolved forms (60 –100%).The average of presence in particulate forms for the metals giving the following order: Cr> Ni > Hg > Cu > Fe > Pb >Zn > Cd.*

**Keywords:** Tannery Wastewaters, Heavy Metals, Speciation, Particulate Fraction, Dissolved Fraction

## 1. Introduction

Metal wastewater pollution is one of the most important environmental problems in industrial areas. Heavy metal pollution, especially chromium pollution in the wastewater sources from tannery has affected the life on earth. This pollution can affect on all ecosystems and human health directly or by food chain. Tannery industry in Morocco is the significant contributor to the economy and provides large scale employment opportunity for people of economically weaker part of the society.

Treatment of various wastewaters is become more important due to diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste stream [1]. Tanning process involves a complex combination of mechanical and chemical processes.

The preservation and processing of raw hides and skins for tanning process causes severe pollution problem towards environment. Two types of tanning operations based on tanning agents are chrome and vegetable tanning [2].

Heavy metals are important for proper functioning of biological systems but their deficiency or excess could lead to a number of disorders [3]. Industrial effluents which discharged from tannery contains a higher amount of metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped in to the surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living beings because they cannot be completely degraded [4].

There are two types of heavy metal sources namely natural and man-made [5]. The major sources of these heavy metals in the environmental samples are man-made such as soils and

dusts from traffic, industry and weathered materials. Trace metals are useful indicators of contamination in surface soil environments by man-made emission sources [6,7,8]. Among heavy metal pollutants, chromium plays a major role in polluting environment. Investigation on chromium contamination is also an important part of analytical chemistry, due to importance of the chromium species on the human health [9].

The chemical speciation of trace elements in samples is very important because of the effects of trace heavy metals on ecological and environmental systems are generally influenced by their chemical forms [10, 11].

In the aquatic environment, trace metals are distributed in different phases (particulate, colloidal and dissolved) and the relationships between these phases influence the fate of metals, and therefore, the impact of these on the environment. For example, the slow exchange of metals between dissolved and particulate fractions can occur by aggregation of colloids [12]. In addition, the metals associated with low molecular weight ligands of the dissolved phase have a high residence time in the water and can be transported over long distances compared to metals associated with very small particles such as colloids [13]. The combination of metal colloids can decrease their bioavailability to aquatic organisms [14,15,16]. Metals associated with colloids and must be considered separately from those that are permeable (truly dissolved). This last fraction should be of particular interest to achieve a better ecotoxicological assessment of rejection [17,18,19,20,21].

The main objective of the present study is to carry out the analysis and speciation of metallic elements in tannery wastewater.

2. Material and Methods

2.1. Sampling

The wastewaters are pre-treated by primary, secondary and tertiary decantation. The figure 2 shows the different steps of the pre-treatment station in a tannery located at Mohamedia city in Morocco.

Water samples were collected manually over 3 day’s period from:

- The collection basin B3 (figure 1) that release directly to the sewerage system, at hourly interval, numbered from 1 to 7;
- The end of five important stage of the process during a cycle of production.

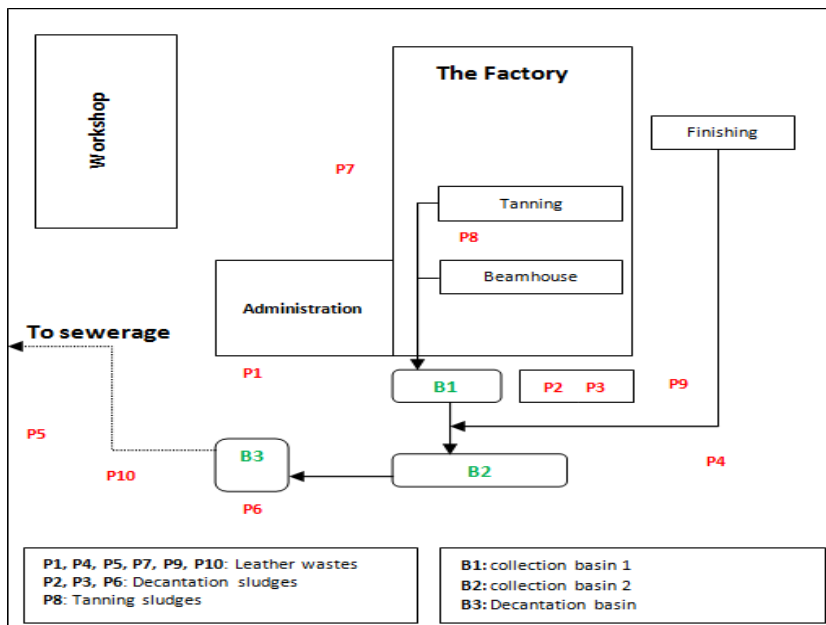


Figure 1: Schematic description of the sampling points

Sampling bottles were rinsed in the laboratory with distilled water and rinsed again with sampled water just before collection.

production and discharges at the outlet of the collection basin.

2.2. Analytical Methods

In order to determine the fractional speciation of heavy metals (Chromium, Cadmium, mercury, lead, Copper, Nickel, Zinc and Iron) in dissolved phases, water samples were filtered on Teflon membrane of 0.45 µm pore (diameter 47 mm, Millipore™ Type FH) for separating the dissolved and particulate phases before mineralization.

Table 1: Characterization of tannery wastewaters (Process waters)

	pH	Cond. (ms/cm)	Turb. (NTU)	SS (mg/l)	CO D (g/l)	BOD5 (mg/l)	sulfate (mg/l)	sulfide (mg/l)	BOD5 / COD
Soaking	6.8	27	3,050	3,000	8.28	0	2,825.6	13.43	0
Unhairing/ Scudding	10	22	4,500	14,200	44.16	2,800	3,005.1	22.04	0.07
Delimiting/ Bating	8.6	10.9	2,664	1,000	7.36	0	8,979.5	22.04	0
Pickling	3.4	45.6	733	100	2.76	2,000	11,748.7	29.05	0.73
Tanning	3.6	52.6	220	100	4.6	0	28,748.7	2.5	0

Mineralization wastewater [22]: 10.5 ml of concentrated hydraulic acid and 3.5 ml concentrated nitric acid were added to 50 ml of the wastes. The samples were left for 16 hours and, next, heated for 2 hours up to the appearance of white fumes. After cooling, the solution was placed in measuring flasks of 50 ml capacity and made up to the mark with distilled water.

ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) has been used for the determination of trace elements in various samples due to its high detection power, multi-element analysis, minor matrix effects, minor memory effects, high analysis speed, and tolerance to high salt concentrations.

Tables 1 and 2 show the physico-chemical characterization of effluents from the tannery to the output of each stage of

**Table 2:** Characterization of tannery wastewaters (wastewaters from collection basin)

Time	pH	Cond. (ms/cm)	Turb. NTU	SS (mg/l)	COD (g/l)	BOD5 (mg/l)	sulfate (mg/l)	sulfide (mg/l)	BOD <sub>5</sub> / COD
T1	6.9	3.95	705	2 600	5.52	-	876.9	37.17	-
T2	4.7	15.5	1,150	1,600	4.6	125	6,825.6	38.97	0.03
T3	4.9	19.8	3,100	1,600	5.52	100	6,876.9	39.57	0
T4	5.4	13.5	3,750	9,400	27.6	100	4,646.2	38.27	0
T5	9.1	17.5	3,800	1,500	11.96	850	3,620.5	31.66	0.07
T6	9.6	9.4	2,450	500	11.96	750	1,800.0	39.37	0.06
T7	8.3	6.0	1,150	2,000	5.52	200	2,646.2	26.55	0.04

**3. Results**

The results obtained for this study to examine the status of metals in tannery effluents and their contamination. Among various industries, tannery industry is major producer of metals like Chromium, iron, cadmium, copper, lead, nickel and zinc.

The data of metal concentration in dissolved phase of tannery effluents along the steps of the process and effluents taken from collection basin (B3) are given in Table 3 and Table 4 respectively.

**Table 3:** Concentration of metallic elements in tannery wastewaters (Process waters)

	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Soaking	0.0 04	0.202	0.1 2	8.2 7	0.0 1	0.0 07	0.7 3	1.8 5
Unhairing/ Scudding	0.0 04	0.38	0.2 04	7.8 6	0.1 5	0.0 6	0.3 5	2.0 2
Delimiting/ Bating	0.0 03	0.83	0.0 67	2.7 17	0.3 17	0.0 06	0.2 4	0.7 3
Pickling	0.0 04	3.20	0.0 61	1.8 0	0.0 12	0.0 05	0.2 4	1.6 3
Tanning	0.0 05	4325.75	0.0 08	1.9 6	0.6 49	0.0 32	0.1 4	0.6 6

All values are in mg/l of wastewater

**Table 4:** Concentration of metallic elements in tannery wastewaters: Collection basin

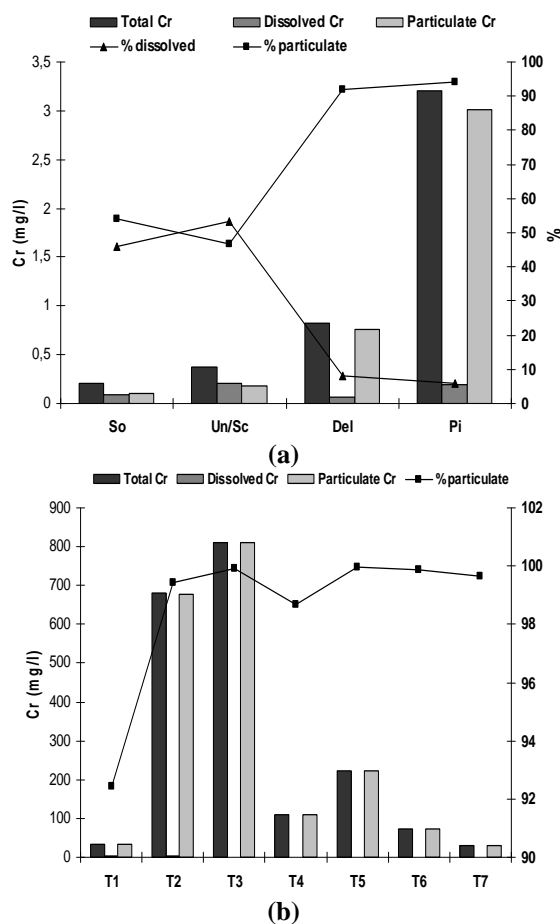
	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
T1	0.004	34.20	0.04	2.34	0.09	0.014	0.14	0.35
T2	0.005	682.08	0.02	2.004	0.12	0.01	0.13	0.32
T3	0.005	811.41	0.07	3.020	0.72	0.02	0.11	0.57
T4	0.003	110.1	0.07	5.96	0.45	0.07	0.085	0.86
T5	0.004	223.73	0.1	4.17	0.17	0.04	0.06	0.94
T6	0.005	74.35	0.07	8.09	0.17	0.03	0.14	0.92
T7	0.003	29.215	0.04	1.64	0.01	0.007	0.76	2.4

All values are in mg/l of wastewater

The production unit generate wastewater quality variable over time, the effluent of a sample varies to another. This variation is due to the changing composition of waste collected along different process steps.

Analytical results (Table 4) revealed that the average concentration of chromium were recorded ranged from 29.2 to 811.41 mg/l at, respectively, T7 and T3 (time of releasing tanning waters with a concentration of 4325.75 mg/l). However, low values of cadmium and nickel range from 0.003 to 0.005 mg/l and 0.007 to 0.02 mg/l, respectively, was reported.

In this study speciation refers to physical fractionation (particulate, colloidal, dissolved). The results for particulate and dissolved chromium, cadmium, lead and mercury speciation in effluents prior to discharge are shown in Figures (2, 3, 4, 5), (a) for process wastewaters samples, and (b) for the hourly samples collected from the basin.



**Figure 2:** (a) Chromium speciation in process wastewaters, (b)- Chromium speciation in basin effluents

In tanning effluents the particulate fraction of chromium reaches 98.96% (4280.6mg/l).

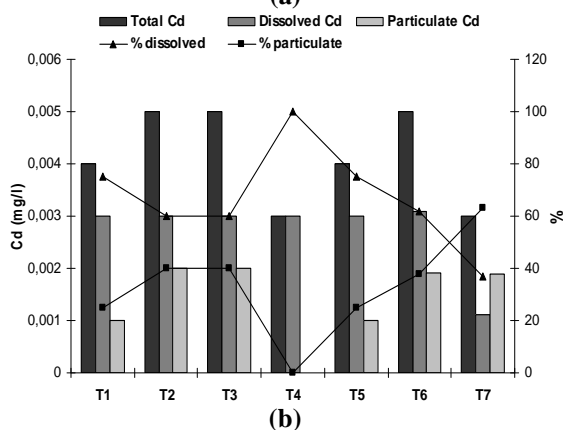
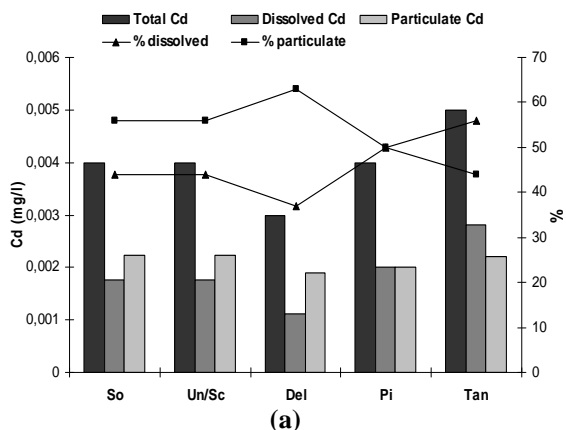


Figure 3: (a)- Cadmium speciation in process wastewaters, (b)- Cadmium speciation in basin effluents

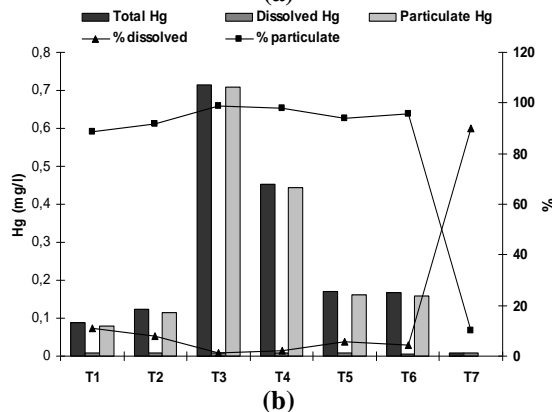
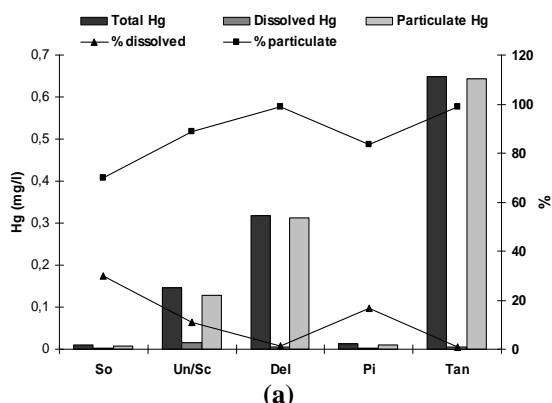


Figure 5: (a)- Mercury speciation in process wastewaters, (b)- Mercury speciation in basin effluents of all the metals analyzed four are illustrated in Figure (2, 3, 4 and 5) the other metals are grouped in (Table 5,6)

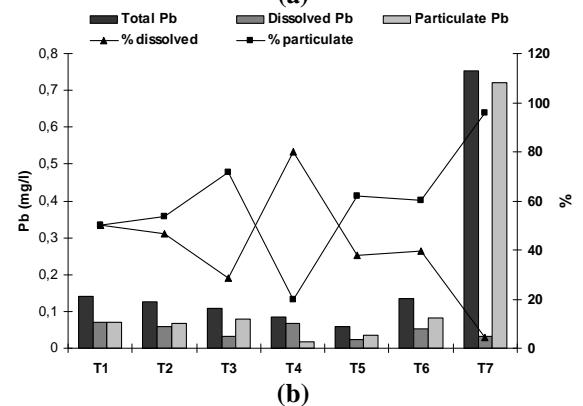
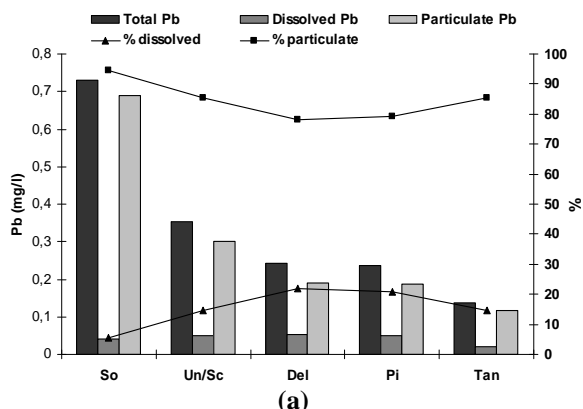


Figure 4: (a)- Lead speciation in process wastewaters, (b)- Lead speciation in basin effluents

Table 5: Metals speciation in waters from basin B3

	Cu		Fe		Ni		Zn	
	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate
T1	47.2	52.8	46.7	53.3	64.3	35.7	80.8	19.2
T2	27.3	72.7	33.6	66.4	10.0	90.0	87.7	12.3
T3	7.1	92.9	13.2	86.8	0.0	100.0	54.6	45.4
T4	15.5	84.5	31.3	68.7	0.0	100.0	37.0	63.0
T5	9.3	90.7	58.1	41.9	7.9	92.1	34.7	65.3
T6	12.1	87.9	3.8	96.2	11.1	88.9	29.4	70.6
T7	12.2	87.8	29.2	70.8	14.3	85.7	1.1	98.9

**Table 6:** Metals speciation in process waters

	Cu		Fe		Ni		Zn	
	Dis solv ed	Part icul ate	Dis solv ed	Part icul ate	Dis solv ed	Part icul ate	Dis solv ed	Part icul ate
Soaking /Unhair ing	11. 67	88.3 3	8.9 8	91.0 2	14. 29	85.7 1	11. 22	88.7 8
Scuddin g /Delimi ng	11. 76	88.2 4	8.9 8	91.0 2	20. 69	79.3 1	6.4 8	93.5 2
Bating	7.4 6	92.5 4	57. 34	42.6 6	50. 00	50.0 0	0.1 4	99.8 6
Pickling	14. 75	85.2 5	36. 96	63.0 4	40. 00	60.0 0	17. 04	82.9 6
Tanning	37. 50	62.5 0	40. 85	59.1 5	21. 88	78.1 3	24. 40	75.6 0

In spite of the limited database and the different definition of the dissolved fraction ( $<0.45\mu\text{m}$ ) the results show that particulate phase is important for almost all heavy metals in the samples, except cadmium.

#### 1. Chromium:

Several health problems are related to chromium consumption such as chronic ulceration and perforation of the nasal septum and allergic skin reactions [23]. Particulate chromium levels in the studied waters range from 52.8 % (T1) to 92.9% (T3).

Chromium has low acute and chronic toxicity to humans at high doses and his toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical forms of exposure. Cr (VI) compounds are much more soluble than Cr (III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans. The excess of Cr (III) is proven to be a potential soil, surface water, ground water and air contaminant under specific condition [2].

#### 2. Lead:

Lead is number two (after arsenic) on the top 20 list of the most poisoning heavy metals. Its target organs are the bones, brain, blood, kidneys, reproductive and cardiovascular systems, and thyroid gland [24,25]. The measured concentrations of particulate Pb in our samples were in the range of 50 % (T1) to 95.62% (T3).

#### 3. Mercury:

Mercury is generally considered to be one of the most toxic metals found in the environment. Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in humans and animals. Mercury also brings about genetic defects causing chromosome breaking and interference in cell division, resulting in abnormal distribution of chromosome. Mercury causes impairment of pulmonary function and kidney, chest pain and dyspnoea [26,27]. In this study, we found that particulate mercury is in the range of 10 – 98.88% with the highest value at T3 and the lowest at T7.

#### 4. Cadmium:

Cadmium and some of its compounds are considered carcinogenic and may cause damage to all types of body cells. The main target organs for Cd are the kidneys and liver. Cadmium is becoming an element of concern due to its presence in waste products, primarily sewage sludge, that are disposed in land and its content in surface soils and sediments is strongly influenced by man's activity [28]. In this study, the concentrations of dissolved Cd were within the range of 60 – 100% with the lowest at T2, T3 and the highest at T4.

#### 5. Zinc:

Zinc is a common metal in the human environment. Little is known about its toxic effects toward human beings [24]. High levels of Zn may cause Pancreatitis, anemia, muscle pain, acute renal failure, and death [28]. The range of particulate Zn in the studied waters was 12.3 – 98.9% with the lowest value T2 and the highest at T7.

#### 6. Iron:

Iron toxicity is due to its rapid absorption by the body. Drinking water, iron pipes, cookware, and preparations are the main sources of iron and its target organs are the liver, cardiovascular system, and kidneys [28]. In this study, we found that particulate iron is in the range of 41.9 – 96.2% with the highest value at T6 and the lowest at T6.

#### 7. Nickel:

Nickel is a carcinogenic metal and any overexposure to it can cause a decreased body weight, heart and liver damage and skin irritation [24]. The range of particulate Ni found in this study was 35.7 – 100%, the highest concentration was found at T3, T4 and the lowest at T1.

#### 8. Copper:

Copper is an essential element in mammalian nutrition as a component of metallo-enzymes in which it acts as an electron donor or acceptor. Conversely, exposure to high levels of copper can result in a number of adverse health effects [29]. The measured concentrations of particulate Pb in our samples were in the range of 52.8 % (T1) to 92.9% (T3).

### 4. Discussion

Environmental contamination with toxic heavy metal ions in the industrial wastes is a matter of concerns to developing countries.

Heavy metals are highly persistent in the environment and are known to alter soil ecosystem diversity structure and function. Chromium undergoes a rapid sorption in the environment and consequently, the concentration of soluble chromium is low compared to sorbed chromium [30]. The toxicity, mobility and bioavailability of Cr depend fundamentally on its chemical form. Chromium in the environment might be present mainly as  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$ .

$\text{Cr}^{6+}$  is highly soluble and about 300 times more toxic than  $\text{Cr}^{3+}$ . On the other hand,  $\text{Cr}^{3+}$  precipitates at the average pH of natural waters. Tannery wastewaters contain mainly  $\text{Cr}^{3+}$ . The nature behaviour of Cr in wastewaters depends on the physico-chemical conditions of the effluents [31].

Cr III salts are efficiently used as tanning agents in the leather industry. When the waste is disposed off on sewerage or on soil, the risk of potential oxidation of some Cr III species to the hazardous hexavalent state exists in the presence of manganese IV oxide. Recovery of chromium is one of the options to make leather industry environmental friendly.

In addition, knowledge of the total metal concentration is often insufficient to evaluate the risk due to its presence in the effluents. Heavy metals may present some mobility along the ground and regain water tables [32, 33]. Chromium in general and chromium (VI) in particular can migrate up deep horizons of the soil [34]. Chemical speciation of metal traces gives information on their probable behavior in the environment.

In this study, the particulate fraction is dominant for all the heavy metals, except Cd. The dissolved fraction of metal is defined as the dissolved concentration (in percent) of the total concentration. Waters samples collected from B3 and filtered through a  $0.45\mu\text{m}$  filter were analyzed. As illustrated in Figure 2 and Figure 5, the fractions of Cr and Hg bound to particles, which mean that the free metal ions constitute less than 10% of the total metal concentration. Whereas for Pb, dissolved and particulate fractions are approximately the same. The Cd showed higher fraction of dissolved species than the other metals, especially at time T4.

The wastewater as results of tanning process is an important source adding Cr pollutant to the environment which causes many health hazards to all sort of life. The pressure by the environment protection agencies is so that becomes a common occurrence that the tanneries are forced to close down not only in developed countries but also in developing countries. Chromium III salts are most widely used chemicals for tanning processes, but only 60% - 70% of total chromium salts react with the hides. In the other words, about 30%-40% of the chromium amount remains in the solids and liquid wastes (especially spent tanning solutions).

Toxicological studies have indicated that the degree of toxicity of metals including chromium (Cr) depends on the chemical form in which the element is present [35].

Cr may appear in solution in the form of Cr (III) and Cr (VI). Chromium species exist primarily depending on the pH Cr (VI) as  $\text{CrO}_2^{-4}$  and Cr (III) as  $\text{Cr}(\text{OH})^{2+}$  [36,37]. Cr (VI) is toxic due to its highly oxidizing effect and the ease with which it penetrates biological membranes, and is thus considered to be a carcinogenic agent, while Cr (III) is essential for the maintenance of the metabolism of lipids, glucose and proteins. Although Cr is a biologically important metal, in concentrations greater than 0.05 mg/l it is a very hazardous metal for living organisms, especially

humans [38]. So, the pollution must be considered and industrial fabric, especially tannery waste taken control because aquatic organisms, especially fish, accumulate heavy metals such as Cr in their tissues and organs in higher quantities than those found in the ambient water [39,40]. So, this pollution causes various serious negative effects on some organisms such as fish and these are carried over to the human body by means of the web food. Therefore, there is a need for investigation of accumulation of Cr, especially  $\text{Cr}^{+6}$ , in view of human health.

Traditional methods used to separate dissolved and particulate phases through a filter pore size of  $0.45\mu\text{m}$ , colloids ( $<0.45\text{ mm}$  and  $> 10\text{ kDa}$ ) are included in the dissolved fraction itself. This absence of separation between the colloidal fraction and the fraction permeable may have certain consequences in studies on the fate and behavior of contaminants in the aquatic environment. Thus, we recognize more the importance of the distinction between permeable and colloidal phases on become of the biogeochemical trace metals in the aquatic environment [16, 17].

## 5. Conclusion

In this study, the concentrations of total heavy metals, especially total Cr in tannery wastewater samples, were determined successfully by ICP-AES technique. The found excessively total metals concentrations indicated that studied area was so much polluted in view of the total concentration. This pollution causes various serious high negative effects on environment, and these are carried over to the human body by means of the web food.

The observed changes in physical speciation of trace metals point out the importance of distinguishing permeable phase (truly dissolved) of all dissolved species to better assess environmental discharges.

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