









**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 /Unhairi ng	11. 67	88.3 3	8.9 8	91.0 2	14. 29	85.7 1	11. 22	88.7 8
Scuddin g /Delimi	11. 76	88.2 4	8.9 8	91.0 2	20. 69	79.3 1	6.4 8	93.5 2

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



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.

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 Cr<sup>3+</sup> and Cr<sup>6+</sup>.

$\text{Cr}^{6+}$  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 ( $<0.45\mu\text{m}$  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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