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Physico-chemical characterization and pollutant charge of industrial effluents from tanneries under semi-arid climate

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ABSTRACT

This study was conducted to characterize Marrakech City (Morocco) tanneries effluents. The analysis of 5 different tanneries recipes revealed identical temperatures (25°C), acidic pH ranging from 2.69 to 3.65, electrical conductivity ranging from 40.33 ± 1.21 to 90.43 ± 2.40 mS/cm, high chemical oxygen demand (COD: 939.33 ± 26.46 – 7,739.55 ± 297.68 mgO_2/L), biological oxygen demand (BOD: 24–42 mgO_2/L). In addition, there were high quantities of total suspended solids of about 6,400 ± 100 – 15,700 ± 200 mg/L, total dissolved solids (TDS: 22,566.67 ± 57.74 – 50,900 ± 100 mg/L), total solids (TS: 28,966.67 ± 57.74 – 66,600 ± 264.58 mg/L), sulfate (SO_4^{2-}: 1,021.43 ± 61.86 – 2,9 50 ± 35.71 mg/L). High concentrations of total chromium ranging from 200 to 500 mg/L and Cr^{6+} from 117.22 ± 20.19 to 393.37 ± 42.74 mg/L were recorded. Different size and shape of effluents particles and filaments influence the sedimentation speed and scour velocity, as well as the pollutants adsorption. These results indicate that tanneries effluents are polluted, and the physico-chemical characteristics vary from one to another one. This approach could be useful as a decision-making tool for the implementation of a depollution process adapted to the local socio-economic context.

Keywords: Tanning industry; Wastewater; Heavy metal; Chromium; Environmental risks; Leather manufacturing

1. Introduction

For several years, the number of industries in the world is growing steadily. These industries generate many jobs and are much diversified. Having industries that operate in different sectors promotes economic autonomy for some countries. Among these industries, tanning industry is one of the oldest industries in the world [1]. Tanning is the process of treating skins and hides of animals to produce leather. Tannery is also the place where the skins are processed [2]. There are two types of tanning, vegetable tanning and chrome tanning. The oldest and most intricate process is vegetable tanning. It is an organic method relying on vegetable tannins from bark or other plant tissues [3]. Tannins from trees such as oak, chestnut, or mimosa are popular, but hundreds of other tree types and plants are known to have been used. In contrast, Chrome tanning is easy to do and leather has excellent performances, for example higher shrinkage temperature as well as better softness, fullness and endurance [4]. The method of chrome tanning is responsible for 70% to 80% of all leather production worldwide [5]. Indeed, it is due to its properties and product efficiency, making it a low-cost way of preparing leather. Leather tanning process with chromium (Cr) consists of several steps: preservation with salt and storage, pre-soaking, soaking, green fleshing, unhairing, liming, lime fleshing, trimming, lime splitting, deliming, bating, degreasing, pickling, then tanning with Cr salts.

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The stages continue with samming, chrome splitting, shaving, retanning, dyeing, fat liquoring (retanning-neutralizing agents, dyes, fat liquor), samming, drying, buffing, trimming, finishing and finished leather [6–9]. In the process, the collagen matrix is cross-link to prevent putrefaction and hence decomposition. It is done by binding Cr salts to the collagen protein, forming cross-links between the two, thus creating stable structures of Cr-protein complexes. The method uses large rotating drums with Cr salt solutions "washing" the leather [6]. Cr therefore has an important function in leather tanning industry. However, the effluents of leather manufacturing industries are characterized by a very high pollutant load [10]. The toxicity of these effluents is mainly due to Cr and sulfides used in the tanning of animal skins. Much attention is paid to the concentrations of Cr released into the environment [11–13]. On the other hand, Cr is the 21st most abundant element in nature [14] and the 7th most abundant element of the earth's crust [15]. In nature, Cr is not found in a free state but is associated with chemical elements such as oxygen, iron or lead to form oxides such as chromite ($FeCr_2O_4$) and lead chromate ($PbCrO_4$) [16]. Like the other transition metals, there are many Cr compounds (speciation) depending on the oxidation number. Only trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) compounds are detected in the environment in significant quantities [17]. The toxicity of Cr depends on its concentration and oxidation state. Cr^{3+} is of great importance in human physiology. It is an essential trace element for humans. It is involved in carbohydrate and lipid metabolism [18,19]. However, in some cases, it can cause more structural disturbances in erythrocyte membranes [20]. In addition to being relatively inert, Cr^{3+} forms precipitates and can adsorb to solid phases. But, it can also form soluble complexes with organic ligands that may exist in natural waters [21]. Hexavalent Cr is very soluble and mobile in water. In solution, it can be occur as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), depending on both pH and total concentration [22]. However, it has an adverse effect on the environment [23] and is detrimental to human health [24]. It is 100 times more toxic than Cr^{3+} [25–28] and can easily be diffused into cell membranes [29]. Moreover, it has been reported that Cr^{6+} is also 1,000 times more mutagenic than Cr^{3+} [30]. Its toxicity is due to its ability to cross biological membranes causing genotoxicity effects [22]. Inside the cell, Cr^{6+} is rapidly reduced to Cr^{3+} by cellular molecules or reductants such as ascorbate, glutathione and cysteine, leading to its high intracellular accumulation. During the reduction process, Cr^{6+} passes through other chemical species, Cr(V) and Cr(IV), which are suspected to react with and damage DNA [31].

No study had ever been conducted to compare the effluents from Marrakech tanneries. Given the dangerous nature of some toxic chemicals, it is necessary to know the chemical constituents of the tanneries to put in place in the future, methods to control environmental pollution. In addition, most hides produced in the Morocco are chrome tanned. The chrome tanning industries use different recipes to produce leather, but Cr is always the common element. In Marrakech, as in many other Moroccan cities, wastewater from tanneries is discharged directly into the receiving environment (as in the case of the Oued lssil) without any prior treatment. Pollutants will end up in wastewater treatment plants as well as in sewage sludge [32]. This fact could lead to the degradation of soil quality and the contamination of groundwater.

The aim of this study is to carry out physico-chemical characterization and pollutant charge analysis of tannery effluents to identify the main features and constituents. This will help to set up a better environmental clean-up for further works.

2. Material and methods

2.1. Sampling sites

The production of leather follows several stages, the beam house, tanning (in drum), wet finishing and finishing stage (Fig. 1).

Five samples of tannery effluents were collected from two different tannery units.

The first site is in Bab Dbagh, Marrakech–Morocco (31° 37′39″N 07° 58′73″W). In this tannery, workers use four different recipes to produce leather. On September 4th 2020, four different samples in this industry are collected then labelled E1, E2, E3 and E4. Subsequently, the second sample labelled E5 was conducted in a second tannery, used one recipe to produce leather, which, located in the industrial area, Marrakech–Morocco (31° 39′26″N 08° 02′86″W). In this study, grab sampling was carried out according to Aboulhassan et al. [33]. The samples were taken from the drums after chrome tanning. A bottle was dipped inside the drum and effluents were collected, homogenized, and then stored in clean 5 L bottles. The 5 samples were stored at 4°C for subsequent physico-chemical analyses.

2.2. Tannery wastewater characterization

Both physical and chemical parameters of effluents were analyzed. Temperature was evaluated with electrical conductivity (EC)/total dissolved solids (TDS) meter (SELECTA, CD-2005). pH and conductivity (EC) were determined by the electrometric method [34,35]. Assimilable phosphorus was measured with sodium molybdate and hydrazine sulphate [36]. On the other hand, the determination of the chemical oxygen demand (COD) was carried out according to the closed system reflux method followed by an assay by colorimetry with potassium dichromate [37]. The biological oxygen demand in 5 d (BOD) was determined by the manometric method [37]. Sulfate ions (SO_4^{2-}) were determined by the spectrometric method [38].

Total dissolved solids (TDS) were evaluated by using EC/TDS meter (SELECTA, CD-2005). Total suspended solids (TSS), total solids (TS) and total volatile solids (TVS) were determined according to gravimetric method [39,40], by giving the formulas:

TSS is given by the formula [Eq. (1)]:

$$\text{TSS}\left(\text{mg/L}\right) = \frac{\left[\left(A - B\right) \times 1{,}000{,}000\right]}{D} \tag{1}$$

where *A*: weight of filter + solids (g) (after 103°C–105°C); *B*: weight of the blank filter (g) (before 103°C–105°C); *D*: volume of sample used (mL).

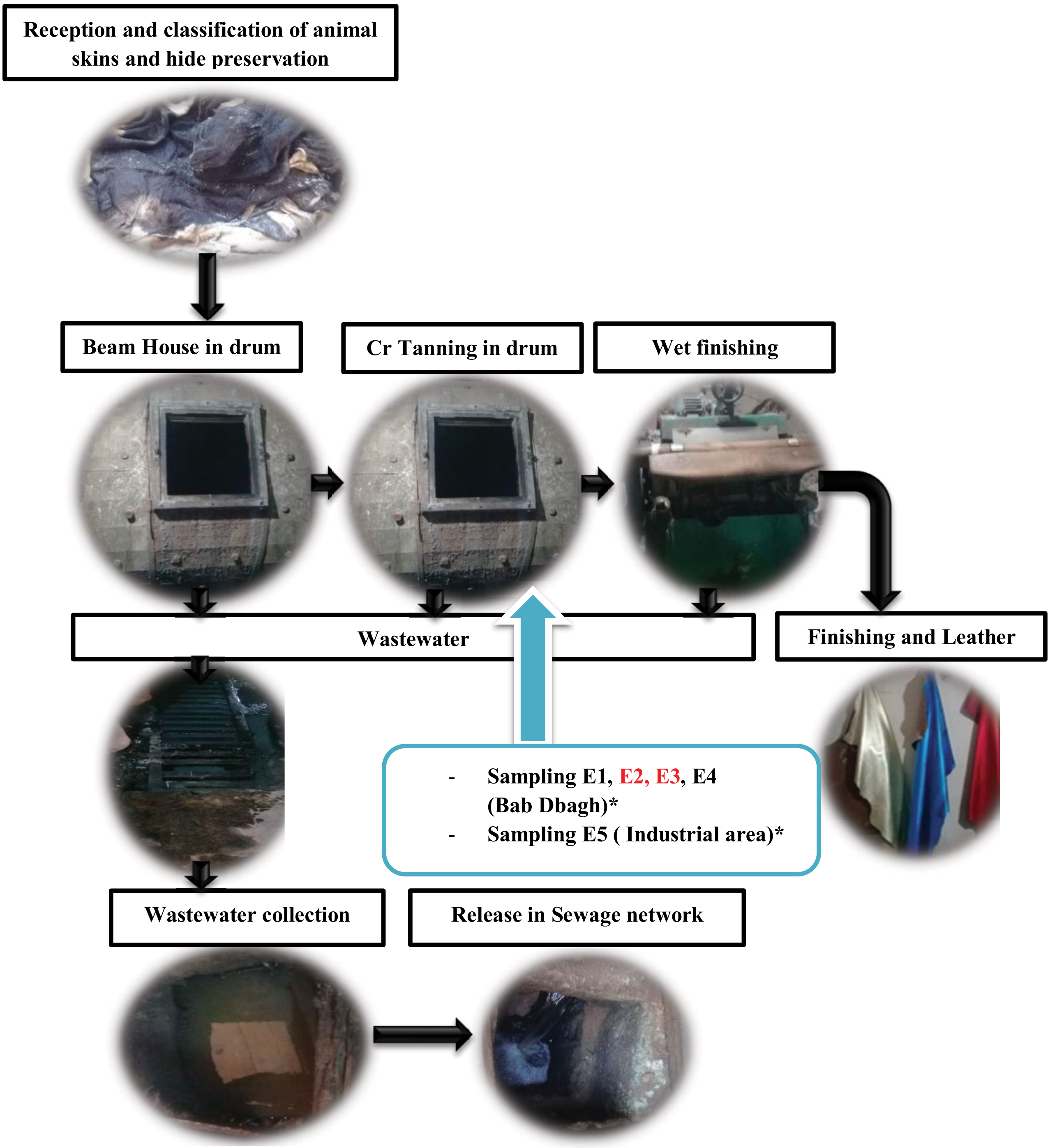


Fig. 1. Tanning process and wastewater discharge from a modern tannery and associated samples. *E1, E2, E3, E4 (Bab Dbagh site) and E5 (industrial area site) represent effluents from different leather production recipes.

TS is given by the equation [Eq. (2)]:

$$\text{TS}\left(\text{mg/L}\right)=\frac{\left[\left(A-B\right)\times 1{,}000\times 1{,}000\right]}{D} \tag{2}$$

where A: weight of capsule + solids (g) (after drying at 103°C–105°C); B: weight of the empty capsule (g); D: Volume of sample used (mL); 1,000: conversion factor between g and mg; 1,000: conversion factor between L and mL.

TS is given by the equation:

$$\text{TVS}\left(\text{mg/L}\right)=\frac{\left[\left(A-E\right)\times 1{,}000\times 1{,}000\right]}{D} \tag{3}$$

where *A*: weight of capsule + solids before calcination (g) (after drying at 103°C–105°C); *E*: weight of capsule + solids after calcination (g) (after calcination at 550°C); *D*: volume of sample used (mL); 1,000: Conversion factor between g and mg; 1,000: conversion factor between L and mL.

The other chemical elements and total Cr were assayed with ICP-MS. Finally, Cr^{6+} was essayed according to colorimetric method adopted by Trifi [41].

The sizes of the particles and filaments contained in the effluents were evaluated using a magnifying glass (G. BOYER) and an optical microscope (REALUX, France).

The sedimentation speed of the particles was calculated and is given by the following formula [42]:

$$S_p = \left[g \times \left(\rho_p - \rho_e\right) \times d^2\right] \times \left[\frac{1}{\left(18 \times h\right)}\right] \tag{4}$$

where S_p: vertical fall speed of the particle (m/s); *g*: acceleration of gravity (9.81 m/s²); ρ_p: real density of the particle (kg/m³); ρ_e: density of water (1,000 kg/m³); *d*: diameter of the particles to be sedimented (m); *h*: dynamic viscosity of water at 4°C (0.0016 Pa·s).

Furthermore, particles are considered settled when they hit the bottom. However, if the tangential velocities are too high, the settled particles can be carried away. This tangential velocity is the scour velocity [42].

This speed is calculated as follows according to Eq. (5):

$$S_v = \left[8 \times k \times \left(s-1\right) \times g \times \left(d / f\right)\right]^{0.5} \tag{5}$$

where S_v: scour velocity; *k*: constant function of the particle (0.04–0.06); *s*: relative density of the particle (T/m³); *g*: gravity acceleration (9.81 m/s²); *d*: diameter of the particles to be sedimented (m); *f*: surface constant (0.02 to 0.03).

2.3. Cr assessment

2.3.1. Total Cr

The samples were mineralized using the method applied by Oumani et al. [43]. After this step, they were diluted and then determined by ICP to obtain total Cr.

2.3.2. Hexavalent Cr

2.3.2.1. Acid solution of diphenylcarbazide

Hexavalent Cr was analyzed using Diphenylcarbazide (DPC) ($C(NH)_4O(C_6H_6)_2$), solution according to method adopted by Trifi [41]. The samples from the tanneries were mineralized. The determination of the concentration of Cr^{6+} was made as follows. 3 mL of the 1,5-DPC solution was added to 50 mL of the sample in a screw tube. The tubes were inverted 3 times and then left to stand for 10 min. the optical density was read at 540 nm with a spectrophotometer (J.P. SELECTA, s.a., VR 2000). In a strongly acidic medium, hexavalent Cr reacts in a complete manner with DPC to form a strongly coloured carbazone violet complex. Cr used in this study was in the commercial form $K_2Cr_2O_7$ (SIGMA-ALDRICH). It was dissolved in distilled water to obtain 10 g/L as a concentration, then sterilized by filtration. It was diluted to perform the calibration ranges.

2.4. Statistical analysis

All experiments were carried out by triplicate. The Statistica soft 7.1 was used for statistical analysis. ANOVA 1 test were performed to identify the differences between the results.

3. Results and discussion

3.1. Physico-chemical characterization

The results of physico-chemical analysis of industrial effluents (E1, E2, E3, E4 and E5) are presented in Table 2 and Figs. 2–5.

3.1.1. Temperature

The temperatures of effluents are illustrated in Fig. 2. All analyzed samples present same temperature value around 25°C. This temperature value of this study is in line with international standards. Both WHO [44] and USEPA [45] recommend 40°C and Moroccan standards is 30°C [46] as a limit value. Chowdhury et al. [47] showed that the effluent temperature varied at different leather manufacturing stages from 25°C to 50°C. The temperature value of E1, E2, E3, E4 and E5 was consistent with that found by Chowdhury et al. [47], the results showed that for two analyzed points the temperature does not exceed 34°C. Amanial [48] showed that the recorded temperatures are of about 26°C and 24°C roughly similar to that of this study. Aboulhassan et al. [33], Aklilu et al. [49] and Amanial [48] obtained the same temperature than that found in this study, that of about 23.4°C, 23.9°C and 24.93°C, respectively. These temperatures of each sample would be due to the climate of the according city or region and the period in which the sampling was carried out.

3.1.2. pH

pH is an important element in the tannery effluents because it influences the other physico-chemical parameters and the availability of metal ion in the tannery wastewater. pH of effluents is illustrated in Fig. 2. Analysis of the samples E1, E2, E3, E4 and E5 revealed acidic pH value. The most acidic sample was E5 with a value of 2.69 ± 0.01. E2 and E3 had similar pH about 3.35 ± 0.04 and 3.31 ± 0.02 respectively. pH of E1 and E4 are significantly identical (3.56 ± 0.01 and 3.65 ± 0.12 respectively). The difference between pH values could be explained by the different amounts of salts used in the manufacture of leather [48]. The pH value for all studied samples ranging from 2.69 ± 0.01 to 3.65 ± 0.12 was below the standard value for industrial effluents discharge into water bodies set by USEPA (pH: 6–9), WHO (pH: 6–9) and Moroccan standards (pH: 5.5–8.5). Several authors Babyshakila [50], Aklilu et al. [49], Amanial [48] showed basic pH values of their analyzed samples. Nevertheless neutral pH were recorded by Chowdhury

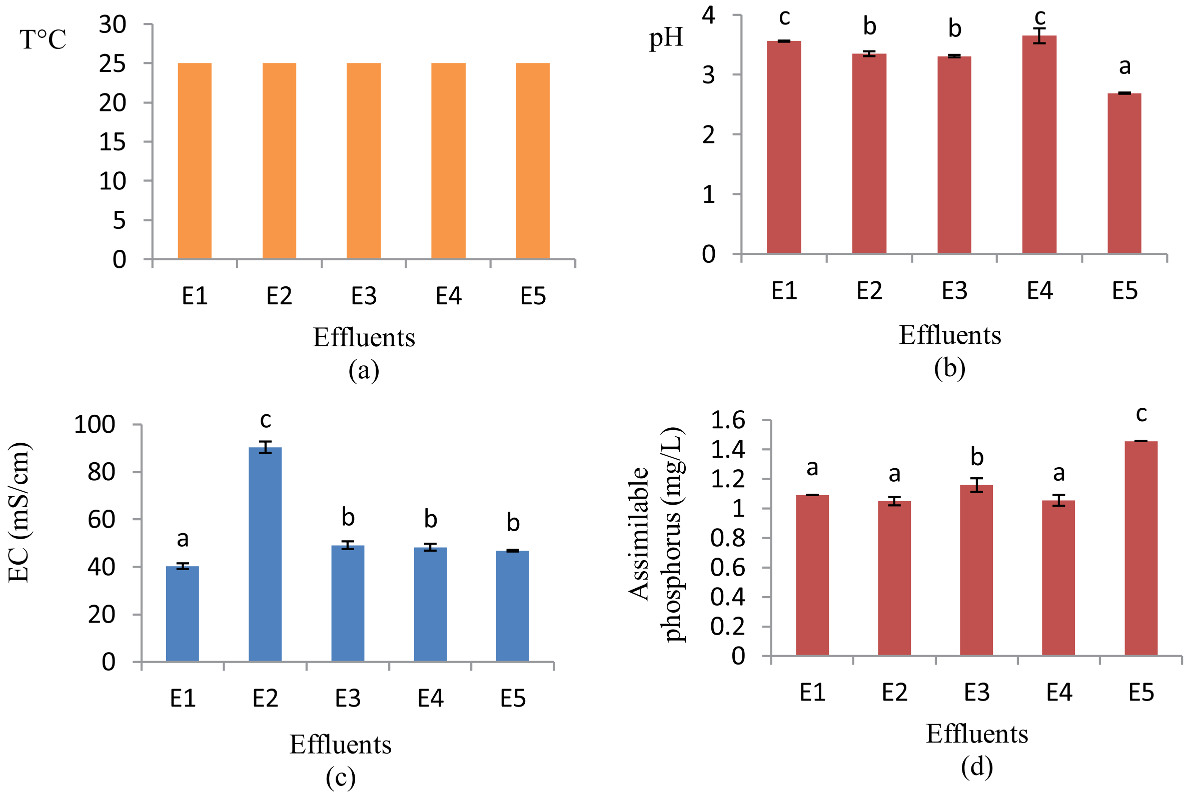


Fig. 2. Physico-chemical characterization T (°C) (a), pH (b), EC (c) and assimilable phosphorus (d) of different effluents from two tanneries Bab Dbagh and industrial area.

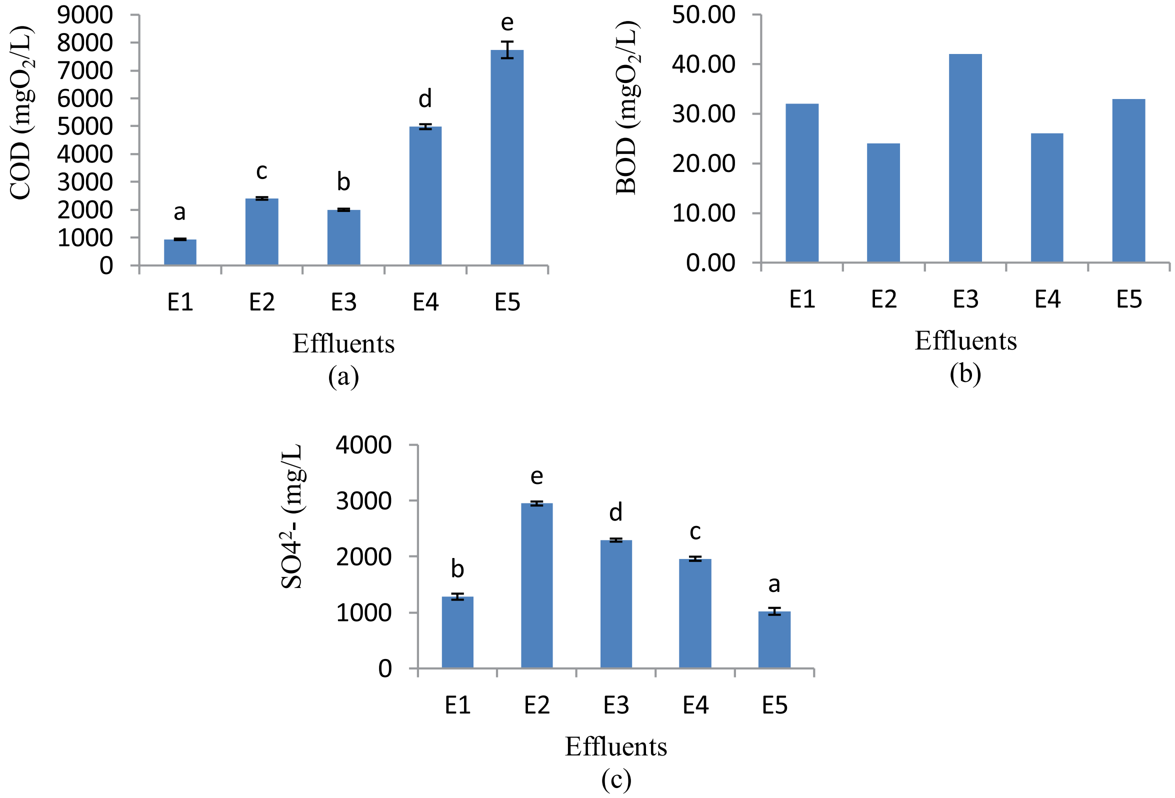


Fig. 3. COD (a), BOD (b), and SO_4^{2-} (c) of various effluents from two tanneries Bab Dbagh and industrial area.

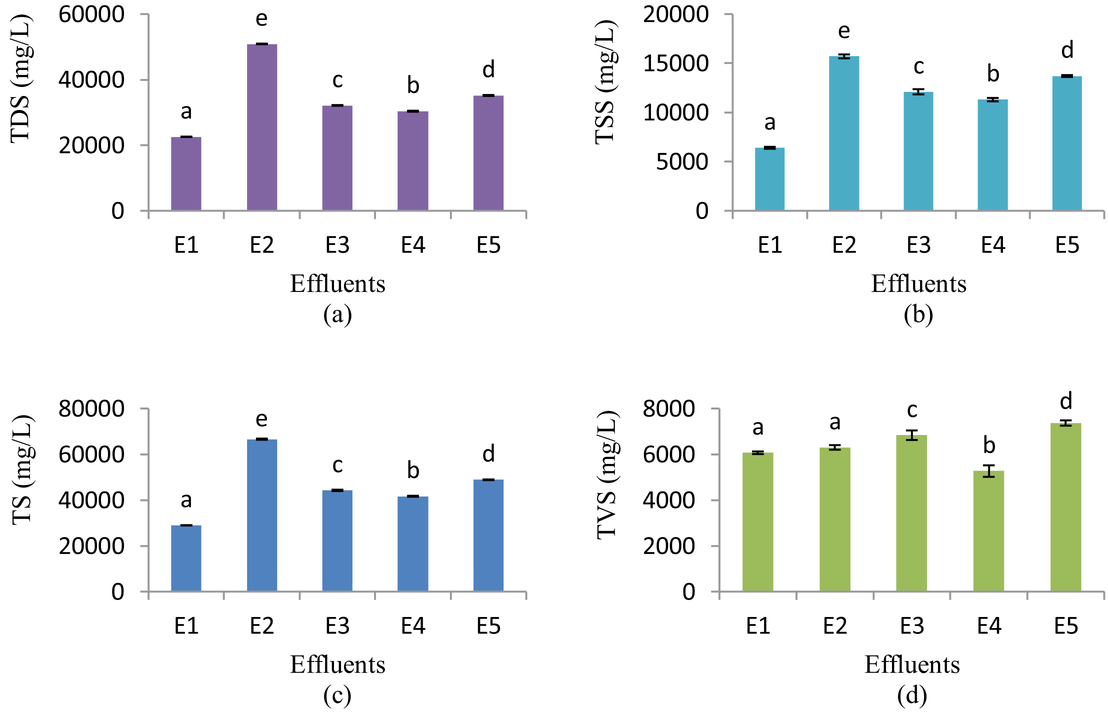


Fig. 4. TDS (a), TSS (b), TS (c) and TVS (d) of various effluents from two tanneries Bab Dbagh and industrial area.

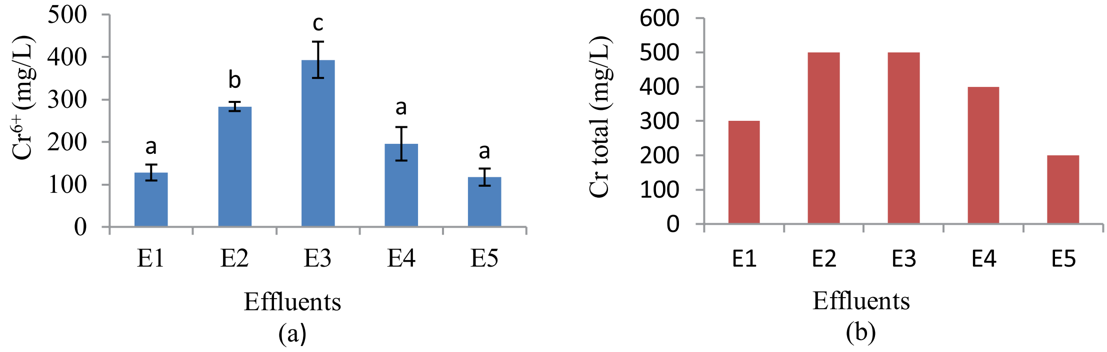


Fig. 5. Cr^{6+} (a) and total Cr (b) of various effluents from two tanneries Bab Dbagh and industrial area.

et al. [47]. This acidity is believed to be due to the salt in the products used in the manufacture of leather.

3.1.3. Electrical conductivity

The EC is a useful measure of the number of ions dissolved in wastewater and water. The EC of effluents is illustrated in Fig. 2. In this study, the EC values were of about 40.33 ± 1.21, 90.43 ± 2.40, 49.17 ± 1.62, 48.33 ± 1.45 and 46.85 ± 0.35 mS/cm for E1, E2, E3, E4 and E5 respectively. There was a significant difference in EC between the value of E1 and E2, but E3, E4 and E5 were statistically identical. These values indicate that the effluents do not have the same amounts of dissolved chemicals. The EC values of the tested samples from E1 to E5 showed higher conductivity, compared to the prescribed standards limits [45]. Amanial [48] found much lower values ranged from 14,496 to 15,670 µS/cm. Chowdhury et al. [47] noted high levels of EC (295–94 mS/cm) in the pickling and chrome-tanning, re-tanning and dyeing and fat-liquoring stages. In contrast, the other stages, soaking, liming and unhairing, deliming and bating, and post-tanning and finishing operational effluents present the following values 19 ± 1, 13 ± 1.2, 12 ± 1.0 and 8.2 ± 1.2, respectively. These high values of EC could be attributed to different dissolved chemicals used in the tanneries industry, that is, organic and inorganic compounds and salts, particularly sodium and chromium salts used in tanning processes. They may have enhanced the electrical conductivity of the effluent samples [48,51]. High EC of collected tanneries effluents could affect the biological properties of receiving water bodies [52].

3.1.4. Assimilable phosphorus

Assimilable phosphorus values of effluents are illustrated in Fig. 2. All samples showed low values of assimilable phosphorus; there is no statistically significant difference between E1, E2 and E4. However, there is a significant difference between E3 and E5. It was of about 1.09 ± 0.00, 1.05 ± 0.03, 1.16 ± 0.05, 1.06 ± 0.04 and 1.46 ± 0.00 for E1, E2, E3, E4 and E5 respectively. However, E3 and E5 showed statistically different values of assimilable phosphorus. That is due to the process and products used in each manufacturing of leather.

3.1.5. Biodegradability degree of tannery wastewater

The degree of pollution by constituents of the tannery effluent was also demonstrated by measuring COD. In the present study, COD of effluents is illustrated in Fig. 3. The effluents had different COD values, 939.33 ± 26.46, 2,407.13 ± 45.90, 1,999.20 ± 39.77, 4,983.30 ± 88.20 and 7,739.55 ± 297.68 mgO_2/L for E1, E2, E3 and E4 respectively. However, E5 presents highest COD value of about 7739.55 ± 297.68 mgO_2/L. All COD values of samples were statistically different. The effluents would contain different proportions of organic matter. These results could be due to total organic content [53]. In a study conducted by Roy et al. [54], in Tamil Nadu (India), the COD was 2,985 mgO_2/L. In another study conducted in Tongxiang (Zhejiang Province, China), a value of 5,900, 6,400 and 4,094 mgO_2/L were found for COD in tanning effluent, Chrome tanning wastewater and retanning effluent respectively [55]. The COD values in our study do not meet the prescribed international standards. In fact, for COD it is recommended to not exceed 500, 250 and 120 mgO_2/L by USEPA [45], WHO [44] and M.S. [46] respectively. High COD value indicate toxic state of the wastewater together with presence of biologically resistant organic substances [48]. It has been revealed that a significant part of chemicals used in the tanning process is not actually absorbed by hide of animal in the process and discharged into the environment [48]. These high levels of COD values recorded in the effluents might be due to high amount of organic matter from hides of animal or organic compound from leather and product used in the process of leather production [48]. El Khalfaouy et al. [56] showed that the high COD values may also be due to hydrolyzed proteins. E5 has the highest COD value and is therefore very rich in total organic content and hydrolyzed proteins. These high COD loads could affect the fauna and flora in receiving soil or water bodies [48].

BOD is an expression to indicate the amount of oxygen that is used for the destruction of decomposable organic matter by biochemical processes. BOD of effluents is illustrated in Fig. 3. The results showed that E3 had the highest value of about 42 mgO_2/L. In contrast, E2 showed the lowest value, which is of 24 mgO_2/L. However, E1, E4 and E5 presented a BOD value of 32, 26 and 33 mgO_2/L respectively. These results indicate the different amount of organic matter containing in each sample. In the raw wastewater of a tannery in Addis-Abeba (Ethiopia), a high recorded value of BOD was about 3,120.6 ± 172 mgO_2/L [57]. In the studies conducted by Roy et al. [54], BOD and COD were 526 and 2,985 mgO_2/L respectively. All these experiment values were above the discharge limit given by international organizations. The high levels of BOD values recorded in the effluent might be due to organic matter [48].

The COD/BOD ratio range from 29.35 to 234.53. The ratios obtained are comparable to those of Chowdhury et al. [47]. The COD/BOD ratio gives a first estimate of the biodegradability of the organic matter of an effluent [58]. For biodegradable organic matter, the COD should be 1.3 to 1.5 times that of the BOD. If the COD is twice or equal to the BOD value, then it can be deduced that the organic matter in the effluent is non-biodegradable. Benkaddour [58] highlighted the biodegradability by the COD/BOD ratio. Thus, when the COD/BOD ratio <2 then the effluent is readily biodegradable. If 2 < COD/BOD < 3 then the effluent is biodegradable and if COD/BOD > 3 then the effluent is not or only slightly biodegradable.

In this experiment, the ratios COD/BOD > 3 indicate that the effluents from these industrial units are not easily biodegradable. The organic matter in these effluents contains recalcitrant refractories, as hydrolyzed proteins derived from animal skins, sulphides and sulphates; besides other compounds with different polarities and high molecular weights. This is in addition to toxic compounds such as metals which could affect the biodegradability of effluents [61]. Biodegradability is the ability of an effluent to be broken down or oxidized by the microorganisms such as *Bacillus* sp. or *Pseudomonas* sp. involved in the biological water treatment process [59,60]. Indeed, tanneries wastewaters contain biorefractory substances and biomass inhibitors [33].

3.1.6. Sulfates variation

Sulfate concentrations of effluents are illustrated in Fig. 3. The values were 1,283.33 ± 54.55, 2,950 ± 35.71, 2,295.24 ± 27.28, 1,961.90 ± 37.17 and 1,021.43 ± 61.86 mg/L for E1, E2, E3, E4 and E5 respectively. E2 showed the highest concentration of sulphate, in contrast, E5 presented the lowest one. All sulfate values of samples were statistically different. In Morocco, the sulphate standard for wastewater discharge is 500 mg/L [46]. This means that the Moroccan standards are not respected.

These results could be explained by the fact that different amounts of sulphate salts are used during leather production. Ilou et al. [62] found various values at different stages of leather production 2,825.6, 3,005.1, 8,979.5, 11,748.7 and 28,748.7 mg/L in soaking, unhairing/scudding, deliming/bating, pickling and tanning stage, respectively. These results demonstrated that the concentration of sulphate varies from one stage to another in the leather manufacturing process. Sawalha et al. [8] explained that these high concentrations of sulphates can be explained by the fact that sulphate salts are used in tanneries in large quantities. For example, ammonium sulphate is used as a deliming agent; it reacts with calcium hydroxide then produces calcium sulphate [63].

3.1.7. Total dissolved solids and suspended solids matter

TDS is one of the indicators of water quality because it directly affects the aesthetic value of the water by increasing turbidity. TDS values are shown in Fig. 4. The recorded TDS were 22,566.67 ± 57.74, 50,900.00 ± 100, 32,133.33 ± 115.47, 30,366.67 ± 152.75 and 35,166.67 ± 152.75 mg/L for E1, E2, E3, E4 and E5 respectively. The results showed that

E2 had the highest TDS while E1 had the lowest value. However, E3, E4 and E5 showed significant different values. The results indicate that the effluents have different amounts of chemicals such as carbonates, bicarbonates, chlorides and potassium [48]. Yadav et al. [64] found 9,700 ± 60 mg/L in untreated tannery effluent of Uttar Pradesh, India. Mekonnen et al. [65] demonstrated that TDS of tannery industry wastewater can reach 7,200 mg/L in Modjo share tannery (Ethiopia). USEPA [45] and WHO [44] accept 500 and 2,100 mg/L of TDS in water. Carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, nitrogen, calcium, sodium, potassium and iron present in effluents could be responsible for these high amounts of TDS. They can alter the osmotic conditions of waters and therefore threaten the life of aquatic animals [48].

TSS of tanneries wastewaters are shown in Fig. 4. E2 showed the highest amount of TSS. However, E1 showed the lowest value. Results revealed 6,400.00 ± 100, 15,700.00 ± 200, 12,100.00 ± 264.58, 11,300.00 ± 173.21 and 13,700.00 ± 100 mg/L for E1, E2, E3, E4 and E5, respectively. All samples showed significantly different TSS values. Looking at these TSS values, it is clear that the effluents are loaded with pollutants. The difference between the TSS values showed that the five effluents did not contain the same amount of leather particles. These high values might be due to the presence of fine leather particles, residues from various chemical discharges and reagents of the tanneries [48]. Scientists have classified the TSS in wastewater as follows, if TSS is less than 100 mg/L, it is weak, greater than 100 mg/L but less than 220 mg/L is medium and greater than 220 mg/L is high-strength wastewater [48]. Babyshakila [50] obtained a much lower value of TSS, which, was 258 mg/L. The chemical compounds such as sulphates, chlorides, calcium, sodium and other used in the manufacture of leather would be a considerable contribution to these high TSS values. The result of this study indicated that wastewater from tanneries could be classified as strong wastewater and should not be discharged without treatment into the stream.

TS which is the sum of TSS and TDS also showed high values. The results are shown in Fig. 4. High values of TS were recorded in this study. E2 showed the highest TS value and E1 the lowest one. All samples presented statistically different amounts of TS. That of about 28,966.67 ± 57.74, 66,600.00 ± 264.58, 44,233.33 ± 305.51, 41,666.67 ± 208.17 and 48,866.67 ± 152.75 mg/L for E1, E2, E3, E4 and E5, respectively. This difference is due to the difference of particles and organic matter as well as chemical compounds samples did not contain the same quantities of polluting substances. A study conducted by Fouda et al. [66] in Cairo (Egypt) showed that the TS of a tannery effluent reached 1,373 mg/L.

3.1.8. Total volatile solids

The TVS of the effluents are shown in Fig. 4. The TVS of the samples exceed 5,000 mg/L. They so contain a high level of volatile matter. The values of TVS obtained were 6,066.67 ± 57.73, 6,300.00 ± 100, 6,833.33 ± 208.17, 5,266.67 ± 251.66 and 7,366.67 ± 115.47 mg/L for E1, E2, E3, E4 and E5, respectively. E5 presents the highest TVS value. However, E4 showed the lowest amount of TVS. E1 and E2 were statistically identical while E3, E4 and E5 were statistically different. Therefore, the effluents did not contain the same amount of volatile substances. These substances are part of the products used in chrome tanning [6]. Borba et al. [67] observed a large amount of TVS (15,810 ± 180 mg/L) in raw tannery wastewater in Paraná State (Brazil). These results illustrated the high amount of volatile matter in the total solids. The samples contained a lot of heat sensitive compounds.

3.1.9. Sedimentation speed and scour velocity

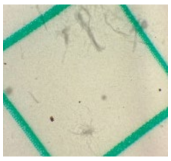
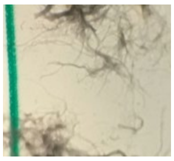
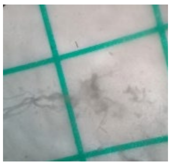
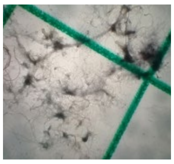
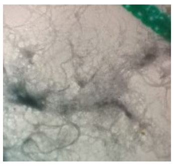
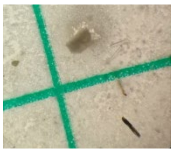
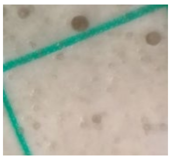
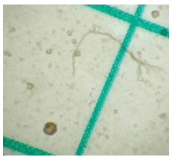
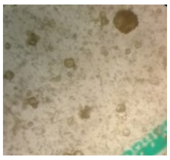
The particles of the effluent sediment after several hours to several days by vertical fall according to their shape, size, weight, and velocity. The effluent particles showed different sizes. The sizes varied from 23–90, 23–100, 23–200, 23–200 and 25–200 μm for E1, E2, E3, E4 and E5 respectively (Table 1). E3, E4 and E5 contained the largest particles, while the smallest particles were observed in E1. The particles observed would have come from animal skins or drums. Indeed, particles could have been attached to the animal hides during the stages, which preceded chrome tanning. These particles would also have come from the ingredients added during chrome tanning. Sedimentation speed of particles with a diameter of 50 μm is of 0.0019 m/s and their scour velocity is of 0.11 m/s. Particles with diameter of 200 μm have 0.020 and 0.23 m/s as sedimentation speed and scour velocity respectively. In addition, the E1 effluent contains more filaments than the other effluents. Filaments length ranged from 0.3–1.7 cm, 0.3–1.6 cm, 0.2–0.4 cm, 0.2–0.4 cm for E1, E2, E3 and E4 respectively. While filaments length of E5 effluent is of about 0.3 cm. The shape and size of filaments in each effluent would be due to the type of animal skin used or the quality of the chrome tanning process. The different of size and shape of effluent particles and filaments could contribute to adsorb the pollutants. Polycyclic aromatic hydrocarbons (PAHs) are often adsorbed by soil particles and transferred from aquatic ecosystems to sediments [68]. He and Walling [69] and Jain et al. [70] showed that particle sizes showed an effects on ammonium, phosphorus, Zn, Pb, Cd adsorption in sediments.

3.2. Chemical and trace elements

3.2.1. Cr variation in tanneries effluents

The results showed various concentrations of Cr^{6+} in tanneries wastewater (Fig. 5). The results indicated 128.02 ± 18.79, 289.48 ± 10.80, 393.37 ± 42.74, 195.65 ± 39.45 and 117.22 ± 20.19 mg/L of Cr^{6+} for E1, E2, E3, E4 and E5 respectively. The values exceed the permissible limits (0.05 mg/L) WHO [44]. E3 presented the highest Cr^{6+} concentration. This value was statistically different with E1, E2, E4 and E5. Nevertheless, E5 showed the lowest value. These differences in Cr^{6+} concentrations may be explained by the use of different amounts of Cr salts during tanning. In addition, the total Cr showed different concentrations of studied effluents (Fig. 5). Effluents E2 and E3 presented the highest concentrations of total Cr with 500 mg/L. However, total Cr of E1, E4 and E5 was of about 300, 400 and 200 mg/L respectively. A team of researchers from Fez (Morocco) showed high concentrations of Cr^{6+} with 380.86 ± 0.9 mg/L and total Cr with 597.13 ± 1.2 mg/L in a modern tannery

Table 1
Particles and filaments of various effluents from two tanneries Bab Dbagh and industrial area. Magnification 40 and Magnification 100

Magnifying glass	Magnification × 40	Magnification × 100	Effluents
			E1
			E2
			E3
			E4
			E5

[71]; these values are comparable to that of this study. In a leather manufacturing industry in the city of Mohammedia (Morocco), it was found that total Cr concentrations varied according to the leather manufacturing steps. Soaking, unhairing/scudding, deliming/Bating, pickling, tanning stages revealed different concentrations of total Cr 0.202; 0.38, 0.83, 3.20 and 4,325.75 mg/L respectively [62]. In previous studies, Yusuf et al. [72] found a total Cr in tannery effluents in Kano, Nigeria of about 42.5 ± 0.28 mg/L [72]. Vijayaraj et al. [73] reported different concentrations of total Cr in two tanneries effluents, 44.6 ± 2.3 and 50.9 ± 2.7 mg/L in Kanpur and Chennai (India) respectively. A study conducted by Yaashikaa et al. [74] revealed a low concentration of total Cr (5.46 mg/L) in the effluent of a tannery in Vaniyambadi, Vellore, India. Joyia et al. [75] collected tannery effluent in Punjab, Pakistan with 77 mg/L of total Cr. These tanneries effluents are shown to exceed the permissible limits. WHO [44] set the concentration limit for total Cr at 1 mg/L.

The presence of Cr is consistent with the leather manufacturing process involving Cr. Cr is used by tanners to obtain good quality leather. But the release of Cr into the environment can cause damage to fauna and flora.

3.2.2. Chemical elements

In all analyzed samples (Table 2), Mn, Al, Mg, Ni, Co and Pb were not detected. The concentrations of Na, K, Ca, were ranged from 2,005.46 ± 36.69 to 7,869 ± 19.41 mg/L; 3,354.74 ± 1.42 to 8,684.49 ± 15.88 mg/L; 35.59 ± 0.30 to 196.05 ± 1.66 mg/L respectively (Table 2). Several trace elements were observed in this study. These are: V: 158.94 ± 0.29 to 180.90 ± 12.87 mg/L; Fe: 156.78 ± 20.08 to 226.23 ± 2.84 mg/L; Cu: 965.92 ± 34.97 to 1,282.54 ± 26.21 mg/L; Zn: 1,422.37 ± 37.66 to 2,503.69 ± 10.72 mg/L; Cd: 2.52 ± 0.08 to 5.52 ± 0.93 mg/L (Table 2). The effluents in this study were found to have concentrations of trace elements exceed the regulatory limits set by the international organizations. Tariq et al. [76] analyzed an effluent from a tannery in Peshawar (India) and found various chemical elements. There were Na, K, Ca, Mn, Mg, Fe, Ni, Co, Zn, Cd, Pb with concentrations of 1,277 ± 103.7, 187.2 ± 248.37, 102.9 ± 71.57, 0.351 ± 0. 312, 545 ± 1,006, 14.54 ± 21.27, 0.671 ± 0.615, 0.571 ± 0.593, 0.327 ± 0.362, 0.069 ± 0.065 and 0.646 ± 0.474 mg/L respectively. Babyshakila [50] recorded a significant Mg value of 5,100 mg/L. In addition, Roy et al. [54] found chemical elements Mn, Mg, Fe, Ni, Co, Cu,

Table 2
Physico-chemical parameters of tanneries effluents and compare with standard permissible limits

Parameter	Effluent					Discharge limit values for all organizations			
	E1	E2	E3	E4	E5	USEPA [45]	WHO [44]	FAO (1985)	M.S. (2016)
Na (mg/L)	2,633.56 ± 70.12	7,869 ± 19.41	2,005.46 ± 36.69	2,192.62 ± 77.79	2,489.23 ± 21.26	–	–	–	–
K (mg/L)	8,684.49 ± 15.88	5,906.90 ± 29.52	4,365.60 ± 30.24	4,171.91 ± 20.95	3,354.74 ± 1.42	–	–	–	–
Ca (mg/L)	35.59 ± 0.30	196.05 ± 1.66	57.48 ± 5.56	67.91 ± 3.41	107.58 ± 3.42	–	–	–	–
Trace elements (mg/L)									
V	180.90 ± 12.87	166.35 ± 1.99	161.18 ± 0.87	159.99 ± 1.02	158.94 ± 0.29	–	–	–	–
Mn	0	0	0	0	0	–	–	–	1
Al	0	0	0	0	0	–	–	–	–
Mg	0	0	0	0	0	–	–	–	–
Fe	224.96 ± 20.14	169.46 ± 12.44	226.23 ± 2.84	217.30 ± 23.80	156.78 ± 20.08	5.0	–	5.0	5
Ni	0	0	0	0	0	–	–	–	5
Co	0	0	0	0	0	–	–	–	0.1
Cu	1,282.54 ± 26.21	965.92 ± 34.97	767.00 ± 32.52	1,068.76 ± 42.95	1,067.67 ± 44.50	73.3	0.2	0.2	3
Zn	2,503.69 ± 10.72	1,570.80 ± 16.92	1,507.20 ± 27.79	1,475.64 ± 31.26	1,422.37 ± 37.66	99.4	0.2	2.0	5
Cd	5.52 ± 0.93	3.91 ± 0.31	3.72 ± 0.10	3.17 ± 0.11	2.52 ± 0.08	0.2	0.01	0.01	0.2
Pb	0	0	0	0	0	0.3	0.5	–	1

Zn, Cd and Pb at 4.11, 3.87, 5.21, 11.79, 3.83, 3.12, 5.73, 2.26 and 2.98 respectively in tannery effluent collected in Ambur (India). Similarly, metals were found in wastewater from a tannery in Fez. The results showed that there were Al (920 ± 20.04 mg/L), Fe (3.9 ± 0.4 mg/L), Ni (0.44 ± 0.06 mg/L) and Cd (0.2 ± 0.07 mg/L) [5]. Yaashikaa et al. [74] mentioned different amounts of the metals, 1.66, 7.97, 6.99, 4.10, 4.54 mg/L for Pb, Ni, Cu, Zn, Cd respectively. The presence of Mn, Mg, Ni, Co and Pb could be explained by the fact that the products used in leather production vary from one stage to another. Elkarrach et al. [5] showed that the products used in the manufacture of leather varied according to the stages.

4. Conclusion

The chrome tanning industries play an important role in economic sector. Even though leather factories are important for the country's economy, their effluent is directly discharged into the nearby water body without treatment. The results of the investigations carried out in two tanneries in Marrakech, Bab Dbagh and industrial area showed that the chemical composition varied from one chrome tanning recipe to another and from one tannery to another. The analysis of 5 effluents of tanneries revealed identical temperatures (25°C), acidic pH (2.69–3.65), electrical conductivity (EC: 40.33 ± 1.21 – 90.43 ± 2.40 mS/cm), high chemical oxygen demand (COD: 939.33 ± 26.46 – 7,739.55 ± 297.68 mgO_2/L), biological oxygen demand (BOD: 24–42 mgO_2/L). The COD/BOD ration has shown that the effluent is not easily biodegradable. In addition, there were huge amounts of total suspend solids (TSS: 6,400 ± 100 – 15,700 ± 200 mg/L), total dissolved solids (TDS: 22,566.67 ± 57.74 – 50,900 ± 100 mg/L), total solids (TS: 28,966.67 ± 57.74 – 66,600 ± 264.58 mg/L), sulfate (SO_4^{2-}: 1,021.43 ± 61.86 – 2,950 ± 35.7 1 mg/L). The analyzed effluents exhibited different particles size ranged from 23 to 200 μm; and different filaments ranged in length from 0.3 to 1.7 cm. High concentrations of total Cr ranging from 200 to 500 mg/L and Cr^{6+} from 117.22 ± 20.19 to 393.37 ± 42.74 mg/L were recorded. The values of Cr^{6+} and total Cr were far above the standard permissible limits for national and international organizations. This study was necessary to assess the composition and the pollution load in the two tanneries. These finding will be helpful to set up a better environmental clean-up for tanneries wastewater in semi-arid area.

References

[1] M. Chowdhury, M.G. Mostafa, T.K. Biswas, A.K. Saha, Treatment of leather industrial effluents by filtration and coagulation processes, Water Resour. Ind., 3 (2013) 11–22.

[2] M. Umar, M.A. Ibrahim, M.B. Mustapha, I.B. Mohammed, U.T. Tashi, A. Obafemi, G.I. Ahmad, Physicochemical analysis and microbiological assessment of tannery effluent discharged from tanneries around Nigeria's Kano industrial estates, J. Adv. Microbiol., 2 (2017) 1–12.

[3] A. Balakrishnan, S.B.K. Kanchinadham, C. Kalyanaraman, Studies on the effect of pre-treatment of vegetable tanning process wastewater prior to biological treatment, J. Environ. Chem. Eng., 8 (2020) 1–10.

[4] J. Zhang, W. Chen, A rapid and cleaner chrome tanning technology based on ultrasound and microwave, J. Cleaner Prod., 247 (2020) 1–6.

[5] K. Elkarrach, M. Merzouki, O. Laidi, A. Omor, M. Benlemlih, Treatment of tannery effluents of Fez city by the sequential batch reactor, Eur. J. Sci. Res., 150 (2018) 334–348.

[6] ETSEIB, Assessment of Tannery Solid Waste Management, A Case of Sheba Leather Industry in Wukro, Ethiopia, 2018.

[7] M. Nur-E-Alam, M.A.S. Mia, F. Ahmad, M.M. Rahman, An overview of chromium removal techniques from tannery effluent, Appl. Water Sci., 10 (2020) 1–22.

[8] H. Sawalha, M. Al-Jabari, A. Elhamouz, A. Abusafa, E.R. Rene, Chapter 25 – Tannery Wastewater Treatment and Resource Recovery Options, T. Bhaskar, A. Pandey, E.R. Rene, D.C.W. Tsang, Eds., Waste Biorefinery: Integrating Biorefineries for Waste Valorisation, Elsevier, Amsterdam, 2020, pp. 679–705.

[9] G.L. Tadesse, T.K. Guya, Impacts of tannery effluent on environments and human health, J. Environ. Earth Sci., 7 (2017) 88–97.

[10] M. Gan, C. Gu, J. Ding, J. Zhu, X. Liu, G. Qiu, Hexavalent chromium remediation based on the synergistic effect between chemoautotrophic bacteria and sulfide minerals, Ecotoxicol. Environ. Saf., 173 (2019) 118–130.

[11] P. Gupta, V. Kumar, Z. Usmani, R. Rani, A. Chandra, Phosphate solubilization and chromium(VI) remediation potential of *Klebsiella* sp. strain CPSB4 isolated from the chromium contaminated agricultural soil, Chemosphere, 192 (2018) 318–327.

[12] D.K. Patra, C. Pradhan, H.K. Patra, An in situ study of growth of Lemongrass *Cymbopogon flexuosus* (*Nees ex Steud.*) W. Watson on varying concentration of chromium (Cr(+6)) on soil and its bioaccumulation: perspectives on phytoremediation potential and phytostabilisation of chromium toxicity, Chemosphere, 193 (2018) 793–799.

[13] R. Pechancová, T. Pluháček, D. Milde, Recent advances in chromium speciation in biological samples, Spectrochim. Acta, Part B, 152 (2019) 109–122.

[14] L. Ebdon, Trace Element Speciation for Environment, Food and Health, Royal Society of Chemistry, Cambridge, 2001.

[15] J. Kovacik, P. Babula, J. Hedbavny, O. Krystofova, I. Provaznik, Physiology and methodology of chromium toxicity using alga *Scenedesmus quadricauda* as model object, Chemosphere, 120 (2015) 23–30.

[16] J. Guertin, J.A. Jacobs, C.P. Avakian, Chromium(VI) Handbook, CRC Press, Boca Raton, 2004.

[17] Z. Jiang, Y. Liu, G. Zeng, W. Xu, B. Zheng, X. Tan, S. Wang, Adsorption of hexavalent chromium by polyacrylonitrile (PAN)-based activated carbon fibers from aqueous solution, RSC Adv., 5 (2015) 25389–25397.

[18] L. Anah, N. Astrini, Influence of pH on Cr(VI) ions removal from aqueous solutions using carboxymethyl cellulose-based hydrogel as adsorbent, IOP Conf. Ser.: Earth Environ. Sci., 60 (2017) 012010.

[19] R. Jobby, P. Jha, A.K. Yadav, N. Desai, Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: a comprehensive review, Chemosphere, 207 (2018) 255–266.

[20] S. Elabbas, L. Mandi, F. Berrekhis, M.N. Pons, J.P. Leclerc, N. Ouazzani, Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: eggshell and powdered marble, J. Environ. Manage., 166 (2016) 589–595.

[21] I. Chaabna, Etude de l'élimination des ions Cr(VI) par des procédés physico-chimiques application aux eaux de chromage, Université des frères mentouri-constantine, 2017.

[22] L. El Fels, M. Hafidi, J. Silvestre, J. Kallerhoff, G. Merlina, E. Pinelli, Efficiency of co-composting process to remove genotoxicity from sewage sludge contaminated with hexavalent chromium, Ecol. Eng., 82 (2015) 355–360.

[23] A. Sayari, S. Hamoudi, Y. Yang, Applications of pore-expanded mesoporous silica. 1. Removal of heavy metal cations and organic pollutants from wastewater, Chem. Mater., 17 (2005) 212–216.

[24] J.J. Coetzee, N. Bansal, E.M.N. Chirwa, Chromium in environment, its toxic effect from chromite-mining and ferrochrome industries, and its possible bioremediation, Expos. Health, 12 (2018) 51–62.

[25] K. GracePavithra, V. Jaikumar, P.S. Kumar, P.S. SundarRajan, A review on cleaner strategies for chromium industrial wastewater: present research and future perspective, J. Cleaner Prod., 228 (2019) 580–593.
[26] M. Megharaj, S. Avudainayagam, R. Naidu, Toxicity of hexavalent chromium and its reduction by bacteria isolated from soil contaminated with tannery waste, Curr. Microbiol., 47 (2003) 51–54.
[27] I. Narin, A. Kars, M. Soylak, A novel solid phase extraction procedure on Amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples, J. Hazard. Mater., 150 (2008) 453–458.
[28] S. Xia, Z. Song, P. Jeyakumar, S.M. Shaheen, J. Rinklebe, Y.S. Ok, N. Bolan, H. Wang, A critical review on bioremediation technologies for Cr(VI)-contaminated soils and wastewater, Crit. Rev. Env. Sci. Technol., 49 (2019) 1027–1078.
[29] S.S. Kahu, A. Shekhawat, D. Saravanan, R.M. Jugade, Two fold modified chitosan for enhanced adsorption of hexavalent chromium from simulated wastewater and industrial effluents, Carbohydr. Polym., 146 (2016) 264–273.
[30] P.M. Fernandez, S.C. Vinarta, A.R. Bernal, E.L. Cruz, L.I.C. Figueroa, Bioremediation strategies for chromium removal: current research, scale-up approach and future perspectives, Chemosphere, 208 (2018) 139–148.
[31] H.-W. Yen, P.-W. Chen, C.-Y. Hsu, L. Lee, The use of autotrophic *Chlorella vulgaris* in chromium(VI) reduction under different reduction conditions, J. Taiwan Inst. Chem. Eng., 74 (2017) 1–6.
[32] L. El Fels, Suivi physico-chimique, microbiologique et écotoxicologique du compostage de boues de step mélangées à des déchets de palmier: validation de nouveaux indices de maturité, Université de Toulouse, 2014.
[33] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, N. Zaim, F.Z. Bouthir, Les effluents de tannerie caractérisation et impact sur le milieu marin, Revue des sciences de l'eau, 21 (2008) 463–473.
[34] CEAEQ, Détermination de la conductivité dans les effluents; Méthode électrométrique. MA. 115 – Cond. 1.0, Ministère de l'Environnement du Québec, 2002.
[35] CEAEQ, Détermination du pH: méthode électrométrique, MA. 100 – pH 1.1, Rév. 3, Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs du Québec, 2014.
[36] I.S.A. Koralage, P. Weerasinghe, N.R.N. Silva, C.S. De Silva, The determination of available phosphorus in soil: a quick and simple method, OUSL J., 8 (2015) 1–17.
[37] CREPA, Contrôle et suivi de la qualité des eaux usées. Protocole de determination des parametres physico-chimiques et bacteriologiques, 2007.
[38] J. Rodier, B. Legube, Coll, L'analyse de l'eau Dunod, 10e édition, 2016.
[39] CEAEQ, Détermination des solides en suspension totaux et volatils: méthode gravimétrique, MA. 115 – S.S. 1.2, Rév. 3, Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec, 2015.
[40] CEAEQ, Détermination des solides totaux et des solides totaux volatils: méthode gravimétrique, MA. 100 – S.T. 1.1, Rév. 5, Ministère du développement durable, de l'environnement et de la lutte contre les changements climatiques du Québec, Centre d'expertise en analyse environnementale du Québec, 2017.
[41] I.M. Trifi, Étude de l'élimination du chrome VI par adsorption sur l'alumine activée par dialyse ionique croisée, 2013.
[42] MDDEP, Guide d'aménagement des lieux d'élimination de neige et mise en oeuvre du Règlement sur les lieux d'élimination de neige, 1997.
[43] A. Oumani, L. Mandi, F. Berrekhis, N. Ouazzani, Removal of Cr^{3+} from tanning effluents by adsorption onto phosphate mine waste: key parameters and mechanisms J. Hazard. Mater., 378 (2019) 1–9.
[44] WHO, Guidelines for Drinking-Water Quality, Health Criteria and Other Supporting Information, World Health Organization, Geneva, 1996.
[45] USEPA, Drinking Water Contaminants, National Primary Drinking Water Regulations, United States Environmental Protection Agency, Washington, DC, 2004.
[46] M.S., Norme marocaine 36–15, bulletin officiel, 2016.
[47] M. Chowdhury, M.G. Mostafa, T.K. Biswas, A. Mandal, A.K. Saha, Characterization of the effluents from leather processing industries, Environ. Process., 2 (2015) 173–187.
[48] H.R. Amanial, Physico-chemical characterization of tannery effluent and its impact on the nearby river, Open Access Lib. J., 8 (2016) 44–50.
[49] A. Aklilu, S. Mengistu, I. Fisseha, Determining the effect of tannery effluent on seeds germination of some vegetables in Ejersa Area of East Shoa, Ethiopia, Int. J. Sci. Res. Publ., 2 (2012) 1–10.
[50] P. Babyshakila, Effect of diluted effluent on soil properties and plant growth, Adv. Stud. Biol., 1 (2009) 391–398.
[51] M.M. Kabir, A.N.M. Fakhruddin, M.A.Z. Chowdhury, Z. Fardous, R. Islam, Characterization of tannery effluents of Hazaribagh area, Dhaka, Bangladesh, Pollution, 3 (2017) 395–406.
[52] R.N. Bharagava, S. Mishra, Hexavalent chromium reduction potential of *Cellulosimicrobium* sp. isolated from common effluent treatment plant of tannery industries, Ecotoxicol. Environ. Saf., 147 (2018) 102–109.
[53] Ö. Karahan, S. Dogruel, E. Dulekgurgen, D. Orhon, COD fractionation of tannery wastewaters—particle size distribution, biodegradability and modeling, Water Res., 42 (2008) 1083–1092.
[54] S. Roy, L. Nagarchi, I. Das, J.M. Achuthananthan, S. Krishnamurthy, Cytotoxicity, genotoxicity, and phytotoxicity of tannery effluent discharged into palar river basin, Tamil Nadu, India, J. Toxicol., 2015 (2015) 1–9.
[55] D. Wang, S. He, C. Shan, Y. Ye, H. Ma, X. Zhang, W. Zhang, B. Pan, Chromium speciation in tannery effluent after alkaline precipitation: isolation and characterization, J. Hazard. Mater., 316 (2016) 169–177.
[56] R. El Khalfaouy, A. Elabed, K. Khallouk, H. El Knidri, R. Belaabed, A. Addaou, A. Laajeb, A. Lahsini, Microfiltration process for tannery wastewater treatment from a leather industry in Fez-Morocco area, J. Mater. Environ. Sci., 8 (2017) 2276–2281.
[57] T. Alemu, A. Mekonnen, S. Leta, Integrated tannery wastewater treatment for effluent reuse for irrigation: encouraging water efficiency and sustainable development in developing countries, J. Water Process Eng., 30 (2019) 1–8.
[58] B. Benkaddour, Contribution à l'étude de la contamination des eaux et des sédiments de l'Oued Chéliff (Algérie), Université de Perpignan; Université Abdelhamid Ibn Badis Mostaganem (Mostaganem, Algérie), 2018.
[59] S. Banerjee, A. Misra, S. Chaudhury, B. Dam, A *Bacillus* strain TCL isolated from Jharia coalmine with remarkable stress responses, chromium reduction capability and bioremediation potential, J. Hazard. Mater., 367 (2019) 215–223.
[60] P.A. Wani, S. Wahid, M.S.A. Khan, N. Rafi, N. Wahid, Investigation of the role of chromium reductase for Cr(VI) reduction by *Pseudomonas* species isolated from Cr(VI) contaminated effluent, Biotechnol. Res. Innovation, 3 (2019) 38–46.
[61] G. Vidal, J. Nieto, H.D. Mansilla, C. Bornhardt, Combined oxidative and biological treatment of separated streams of tannery wastewater, Water Sci. Technol., 49 (2004) 287–292.
[62] I. Ilou, S. Souabi, K. Digua, Quantification of pollution discharges from tannery wastewater and pollution reduction by pre-treatment station, Int. J. Sci. Res., 3 (2014) 1706–1715.
[63] V. Sivakumar, C. Ponnusawmy, K. Sudalaimani, T. Rangasamy, C. Muralidharan, A.B. Mandal, Ammonia free deliming process in leather industry based on eco-benign products, J. Sci. Ind. Res., 74 (2015) 518–521.
[64] P. Yadav, A. Yadav, J.K. Srivastava, A. Raj, Reduction of pollution load of tannery effluent by cell immobilization approach using *Ochrobactrum intermedium*, J. Water Process Eng., 41 (2021) 1–10.
[65] A. Mekonnen, S. Leta, K.N. Njau, Anaerobic treatment of tannery wastewater using ASBR for methane recovery and greenhouse gas emission mitigation, J. Water Process Eng., 19 (2017) 231–238.
[66] A. Fouda, S. El-Din Hassan, E. Saied, M.F. Hamza, Photocatalytic degradation of real textile and tannery effluent using biosynthesized magnesium oxide nanoparticles (MgO-NPs),

heavy metal adsorption, phytotoxicity, and antimicrobial activity, J. Environ. Chem. Eng., 9 (2021) 1–15.
[67] F.H. Borba, D. Seibert, L. Pellenz, F.R. Espinoza-Quiñones, C.E. Borba, A.N. Módenes, R. Bergamasco, Desirability function applied to the optimization of the PhotoperoxiElectrocoagulation process conditions in the treatment of tannery industrial wastewater, J. Water Process Eng., 23 (2018) 207–216.
[68] R. Mu, Y. Liu, R. Li, G. Xue, S. Ognier, Remediation of pyrene-contaminated soil by active species generated from flat-plate dielectric barrier discharge, Chem. Eng. J., 296 (2016) 356–365.
[69] Q. He, D.E. Walling, Interpreting particle size effects in the adsorption of 13Cs and unsupported 210Pb by mineral soils and sediments, J. Environ. Radioact., 30 (1996) 117–137.
[70] C.K. Jain, D.C. Singhal, M.K. Sharma, Adsorption of zinc on bed sediment of River Hindon: adsorption models and kinetics, J. Hazard. Mater., 114 (2004) 231–239.
[71] K. Elkarrach, M. Merzouki, S. Biyada, M. Benlemlih, Bioaugmentation process for the treatment of tannery effluents in Fez, Morocco: an eco-friendly treatment using novel chromate bacteria, J. Water Process Eng., 38 (2020) 101589, doi: 10.1016/j.jwpe.2020.101589.
[72] R.O. Yusuf, Z.Z. Noor, M.A.A. Hassan, S.E. Agarry, B.O. Solomond, A comparison of the efficacy of two strains of *Bacillus subtilis* and *Pseudomonas fragii* in the treatment of tannery wastewater, Desal. Water Treat., 51 (2013) 3189–3195.
[73] A.S. Vijayaraj, C. Mohandass, D. Joshi, N. Rajput, Effective bioremediation and toxicity assessment of tannery wastewaters treated with indigenous bacteria, 3 Biotech, 8 (2018) 1–11.
[74] P.R. Yaashikaa, P. Senthil Kumar, A. Saravanan, Molecular characterization of chromium resistant gram-negative bacteria isolated from industrial effluent: bioremedial activity, J. Ind. Eng. Chem., 80 (2019) 640–646.
[75] F.A. Joyia, M.Y. Ashraf, F. Shafiq, S. Anwar, Zaib-un-Nisa, B. Khaliq, A. Malik, Phytotoxic effects of varying concentrations of leather tannery effluents on cotton and brinjal, Agric. Water Manage., 246 (2021) 1–7.
[76] S.R. Tariq, M.H. Shah, N. Shaheen, A. Khalique, S. Manzoor, M. Jaffar, Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water: a case study from Peshawar, Pakistan, J. Environ. Manage., 79 (2006) 20–29.