Chapter

Treatment of Tannery Effluent of Unit Bovine Hides' Unhairing Liming by the Precipitation

Anass Omor, Karima Elkarrach, Redouane Ouafi, Zakia Rais, Fatima-Zahra ElMadani and Mustafa Taleb

Abstract

The tannery effluents are characterized by high toxic pollutants such as sulfides; used in the tanning of animal's skin. The mean objective of this work is the evaluation of the pollution degree of various operating units, and the treatment of tannery effluent generated from unhairing-liming unit. According to physicochemical characterization, this effluent was largely basic and very loaded in sulfides, which have harmful effects on human health and the environment as well. Otherwise, the microbiological characterization showed an absence of pathogenic bacteria and a low concentration of mesophilic aerobic flora, because of this effluent toxicity. Thus, the treatment of this effluent is indispensable before its reject into the environment. In fact, chemical precipitation is a promising approach for the treatment of this effluent. In this regard, ferric chloride was used as chemical agent to reduce and removal sulphide ions from this effluent. As result, this treatment gave an excellent abatement rate of sulphide, which reached more than 90% using a pH of 8.5 and a ferric chloride concentration of 1.4 mol/L.

Keywords: Tannery, sulfides, characterization, chemical precipitation, ferric chloride

1. Introduction

The leather industry plays an important role in the global economy, particularly in African countries [1, 2], particularly in Morocco [3]. Besides, the tanning industry is an important activity, which involves the processing of leather animal skin by removing fat and hair through different operations namely unhairing-liming, rinsing, deliming-bating and tanning … etc. This tanning process led skins unalterable and rigid [4]. Two methods of tanning are used, chrome tanning and vegetable tanning. At a global level, between 70% and 80% of leather is produced by chrome tanning [5, 6]. Tannery industries use a lot of chemicals and produce huge volumes of wastewater and solid waste [7]. Consequently, tanning industries have been known as a pollution source in the whole world, including Morocco. In fact, they always reject into the environment a large amount of wastewaters, which is loaded with toxic pollutants such as sulfides.

Sulfides can be reduced to hydrogen sulfide (H2S). This toxic gas can poison all living beings, especially humans. Indeed, prolonged sulfide inhalation may cause degeneration of the olfactory nerve and cause death just after few breaths. Plus, the inhalation of this gas even in small amounts can lead to a loss of consciousness [8–13].

Thus, the discharge of these tannery effluents, without prior treatment, harms human health and the environment too. For that, the treatment of these effluents has been very necessary.

Several previous research works have proven some treatment processes for these effluents such as activated carbon adsorption [14], ions exchange [15–18], chemical precipitation using ferric chloride [19, 20], coagulation [21], electrocoagulation [7, 22], sequencing batch reactor [23], bio-augmentation [24] ... etc. However, all these studies are only focused on chromium removal from these effluents, and they ignored the elimination of sulfides even they also very toxic.

In this regard, the objective of this chapter was the evaluation of the quality of tannery effluents rejected from different tanning operations. Then, the treatment of wastewater loaded in sulfide and generated from unhairing-liming operation.

2. Chemical consumption and generated pollution of modern tanning industry

Leather is obtained by treating the skin to keep it in good condition. The tanning process consumes a large quantity of chemical products and water according to tanning

Operation	Products used	Quantity (Kg)	Quantity of water consumed (m^3)	Quantity of water discharged (m^3)
Preparation	Savon	3	2,5	2
Unhairing-liming and rinsing	Sodium sulfide	42,5	20	19,5
	Sodium carbonate	6		
	Lime	20		
Deliming-bating	Sulfate of ammonia	5		
	Sodium metabisulphite	50		
	Sulfuric acid	56		
	Salt	140		
Chrome tanning	Chromium	100	2	1,5
	Sodium bicarbonate	12,5		
	Tanning oil	6		
Retanning and finishing	Soap	0,5	4,5	4
	Formic acid	0,5		
	Sodium bicarbonate	34		
	Tannins	64		
	Oil	73		
	dyes	8		
	Pigments, Resins, Waxes	17	0,02	0,01
	Matting agents, Touching agents	11		
	Lacquers	26		
Total	**680 Kg Chemical products**		29	27

Table 1.
Quantity of chemicals and water consumed during the treatment of 1000 kilograms bovine hides in tannery.

type (Traditional or modern). For a modern tannery, the treatment of 1000 kg of bovine hides consumes around 680 kg of chemicals (**Table 1**) and 29 m^3 of water. These amounts were used during several operations such as unhairing-liming, rinsing, deliming-bating and chrome tanning; in which 46% of these amounts of chemicals and water were used during correspond unhairing-liming unit (**Table 1**). Otherwise, this tannery rejects around 27 m^3 of wastewaters, which is a huge amount. These wastewaters are loaded with excess chemical products, which are not absorbed by skins, and organic matter eliminated from skins during unhairing-liming operation.

3. Wastewaters of modern tannery

A modern tannery was selected to study the quality of tannery wastewater. This industries located in industrial area of Doukkarat in Fez city, Morocco. This latter trait bovine hides only. As mentioned above, the tanning process involves several operations namely unhairing-liming (R1), rinsing (R2), deliming-bating (R3) and chrome tanning (R4) (**Figure 1**). So, the samples of wastewater were collected from the fuller of these units. The samples were monthly collected starting from February 2015. The sampling and conservation conditions were performed according to the ISO 5667-2 standard [25]. The physical parameters: temperature, pH and conductivity were directly measured after sampling. All samples were stored in a refrigerator at a temperature of 4°C according to AFNOR standards set by Rodier [25].

4. Characterization of industrial tannery wastewaters

Tannery wastewater contains significant content of chemical substances, including toxic compounds. Thus, several parameters were carried out to characterize these tannery wastewaters. Among these parameters, there are physicochemical analyses such as pH, temperature, electrical conductivity, turbidity, suspended solids (SS), chemical oxygen demand (COD), sulphate ions (SO_4^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}) and sulfide ions (S^{2-}).

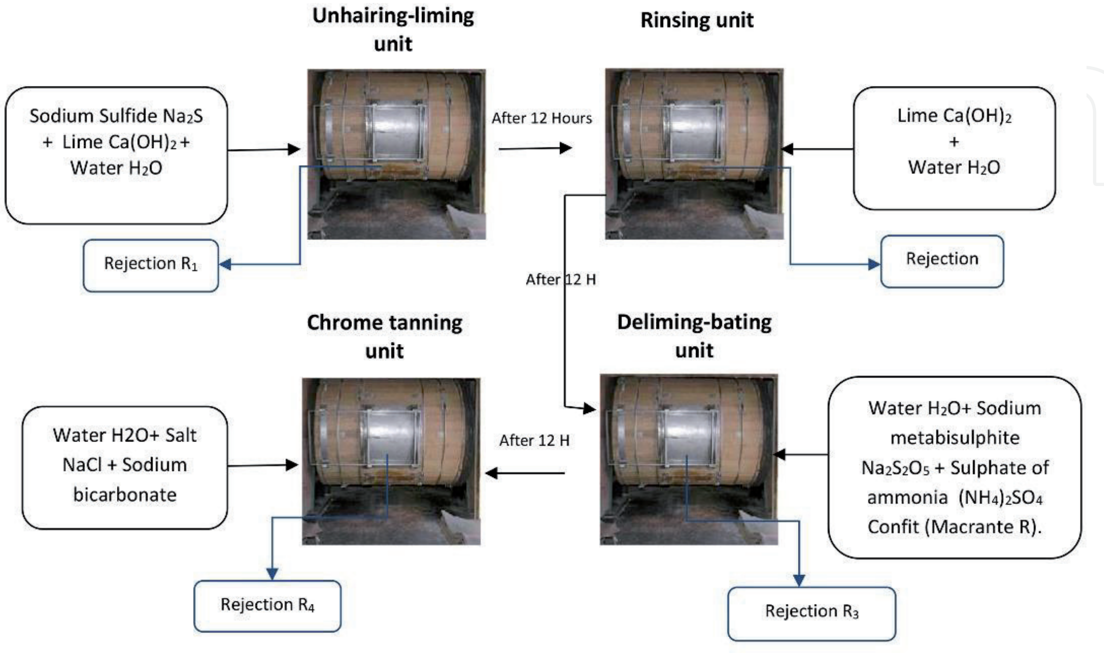

Figure 1.
Tanning process and sampling method of wastewater rejected by a modern tannery.

The pH was measured using a pH meter HANNA with a type electrode Senti X 22 according to NF T90.008 [25]. Conductivity and turbidity were measured by ORION type conductivity. Suspended solids (SS) were determined by centrifuging a wastewater volume according to standard NF T90.105 [25]. Sulfide ions were measured by the indirect method according to standard NF T 60–203 [25]. Ammonium, orthophosphate, nitrate, nitrite, sulfate, BOD_5 and COD were carried out by the spectrophotometric method using a DR/2005HACH at a fixed wavelength and according to AFNOR standards issued by Rodier J. et al. [25]. The bacteriological parameters were also evaluated, especially total coliform (TC), fecal coliform (FC), fecal sterptocoques (SF), total aerobic mesophilic (FMAT) and staphylococci. The enumeration of these bacteria was performed using desoxycolate lactose, slanetz, lauriabertani and Chapman respectively [25].

In general, the average temperature of R1, R2, R3 and R4 was between 24 and 27°C. In fact, these effluents take usually the environmental temperature, because of the absence of heating or cooling operations. The **Figure 2** shows the results of pH, conductivity and suspended solids for the fourth rejects (R1, R2, R3 and R4). So, R1 was largely basic, R2 had also a basic pH, R3 was slightly basic, whereas R4 was acidic (**Figure 2a**). The use of sodium carbonate and bicarbonate, during the first operations, could explain this basic pH of R1, R2 and R3. Concerning R4, the use of acids, for the solubilization ofchromium salt, could explain its acidic pH. The values obtained are comparable to those found in previous work on wastewater from tanneries that have a weakly basic pH [4, 26–28].

As for the conductivity, its average value was around 10 and 30 ms/cm, and then it was largely exceeding the Moroccan standards [29]. The largest values are recorded for unhairing-liming reject (R1), deliming-bating reject (R3), and

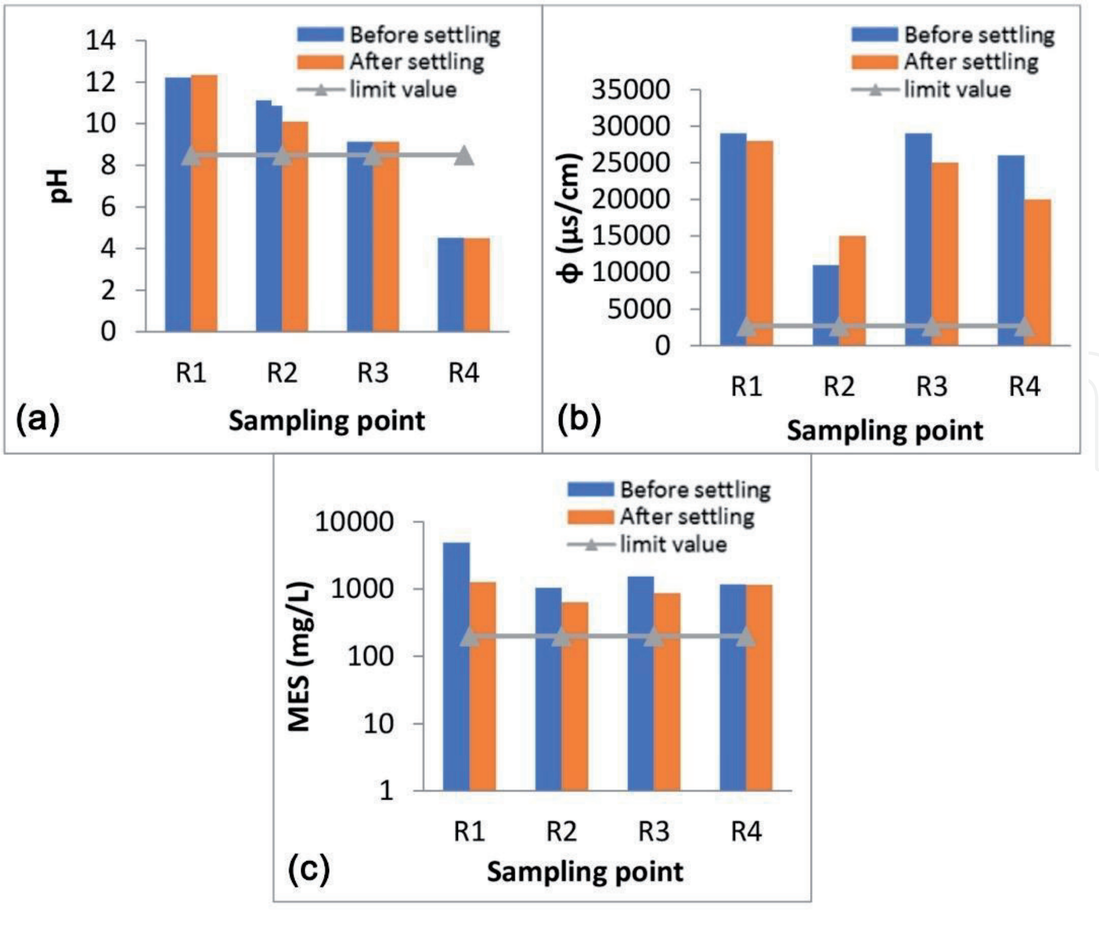

Figure 2.
Results of physical parameters within the fourth rejects of a modern tannery before and after settling: (a) pH; (b) conductivity; (c) suspending matter.

chromium tanning reject (R4) (**Figure 2b**). These high values of conductivity show significant use of salt during these tanning operations (**Table 1**). For suspended solids (SS), they had a high amount, which achieved more than 5000 mg/L for all effluents (R1, R2, R3 and R4) (**Figure 2c**). However, R1 had the highest amount of SS; this could be justified by the huge organic matter (Proteins, hair, fat ….) eliminated from animal skin during this step.

Concerning nitrogen compounds, ammonium, nitrate and nitrite have been followed and their average concentration has shown in **Figure 3**. R1 had again a high concentration of nitrate, nitrite and ammonium compared to R2, R3 and R4 (**Figure 3a–c**). This could be explained by the use of ammonium during unhairing-liming unit (**Table 1**). Indeed, nitrate amount was higher than nitrite and ammonium amount, this could be explained by the reduction of ammonium to nitrate passing by nitrite. This reduction could be through chemical reactions or bacteria such as *Nitrobacter, Nitrosomonas* … etc. [29]. On the other hand, these fourth rejects were conformed to Moroccan standards of discharge in term of nitrogen compounds [29]. These results of nitrate, nitrite and ammonium ions are consistent with those of some authors [30, 31].

Figure 4 presents the result of phosphate ions. As shown, their amount was largely lower than the Moroccan standards reject for all tannery effluents (R1, R2, R3 and R4). Furthermore, R1 had the highest phosphate amount due to the use of some phosphate chemicals in this unit.

Concerning sulfate ions, **Figure 5a** shows that R3 and R4 were very loaded in sulfate than R1 and R2. This could be due to the use of sulfate chemicals in these units. Nevertheless, the tannery effluents were exceeded the Moroccan standards except for the reject R2 (**Figure 5a**). These high loads were due to the use of many

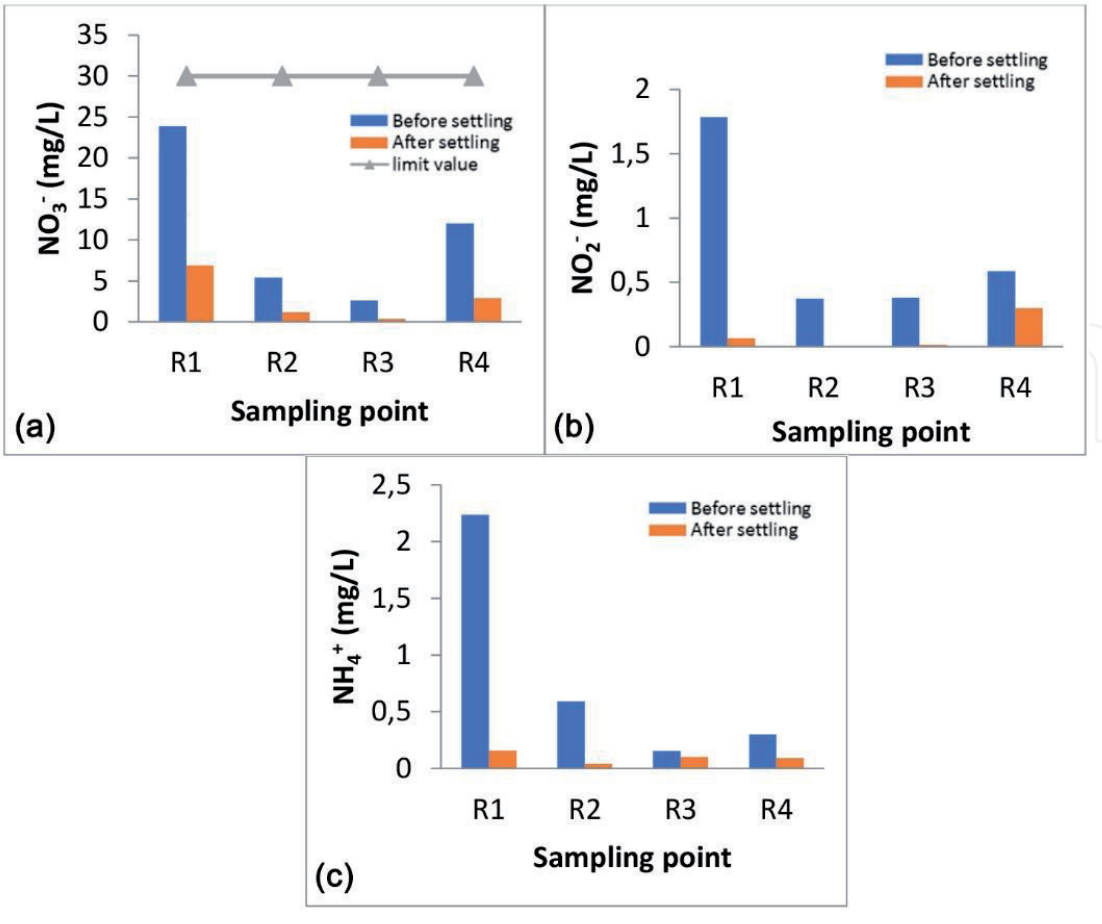

Figure 3.
Nitrogen compounds of tannery effluents before and after settling: (a) nitrate; (b) nitrite; (c) ammonium.

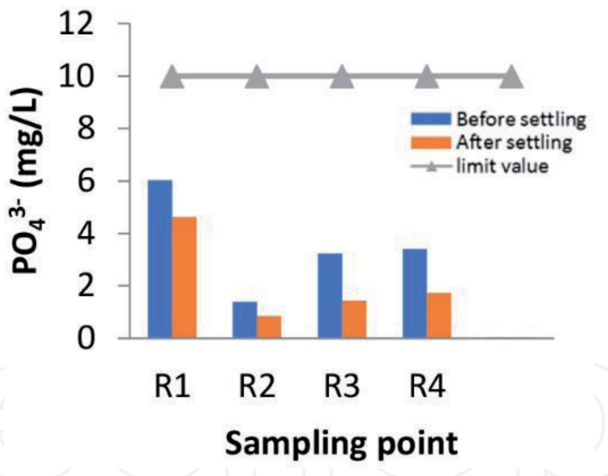

Figure 4.
Composition of the effluent studied before and after settling: Orthophosphate ions.

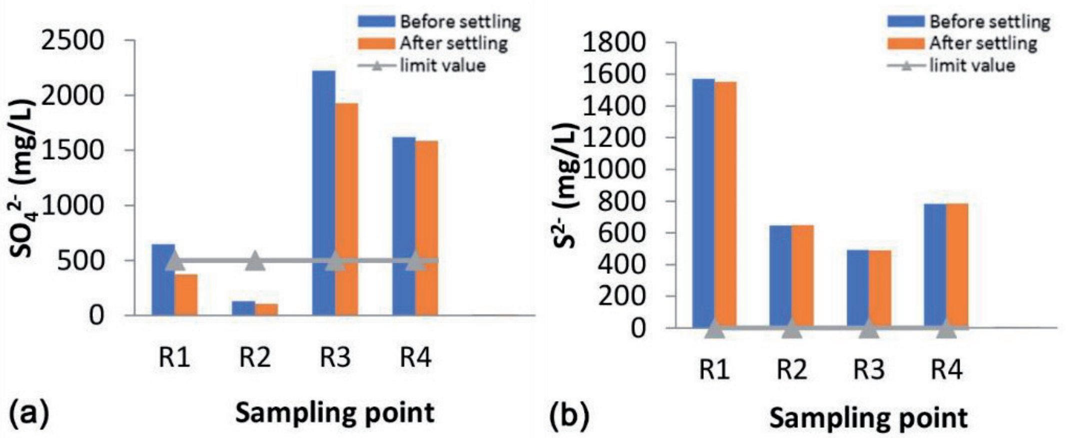

Figure 5.
Composition of the effluent studied before and after settling: (a) Sulfate ions; (b) Sulfide ions.

sulfate products during deliming and tanning units as chromium sulfate [32]. Concerning sulfide, the R1 had the highest load which approximates 1600 mg/L (**Figure 5b**). This huge amount could be justified by the use of the sulfide and sulfuric acid during the unhairing-liming step to eliminate hair of the animal skin. Indeed, the effluent of R1 is largely alkaline; which proves the presence of hydrosulfide HS- ions according to the Pourbaix diagram [33]. The results obtained are consistent with those found by [30] for the final rejection and those found by [34].

On the other hand, the organic load of the effluent is evaluated by measuring the chemical oxygen demand (COD) (**Figure 6a**) and biological oxygen demand BOD5 (**Figure 6b**). The **Figure 5** shows that R1 is very loaded in COD and BOD_5 than others (R2, R3 and R4) exceeding Moroccan standards reject [29]; this could be justified by the high amount of chemicals used in this first unit and the organic matter eliminated as well. The same figure reveals that all effluents are non-biodegradable because of the report COD/BOD_5, which was higher than 4 (**Figure 6c**). The concentrations found in COD are comparable to results obtained by several authors [30, 31].

Even if the characterization of these four rejects after settling shows a slight reduction of all physicochemical parameters, their amount did not meet Moroccan standards.

The microbiological analyses showed a low concentration of the total aerobic mesophilic flora (FMAT), which the average value was 300, 400 and 700 CFU/mL

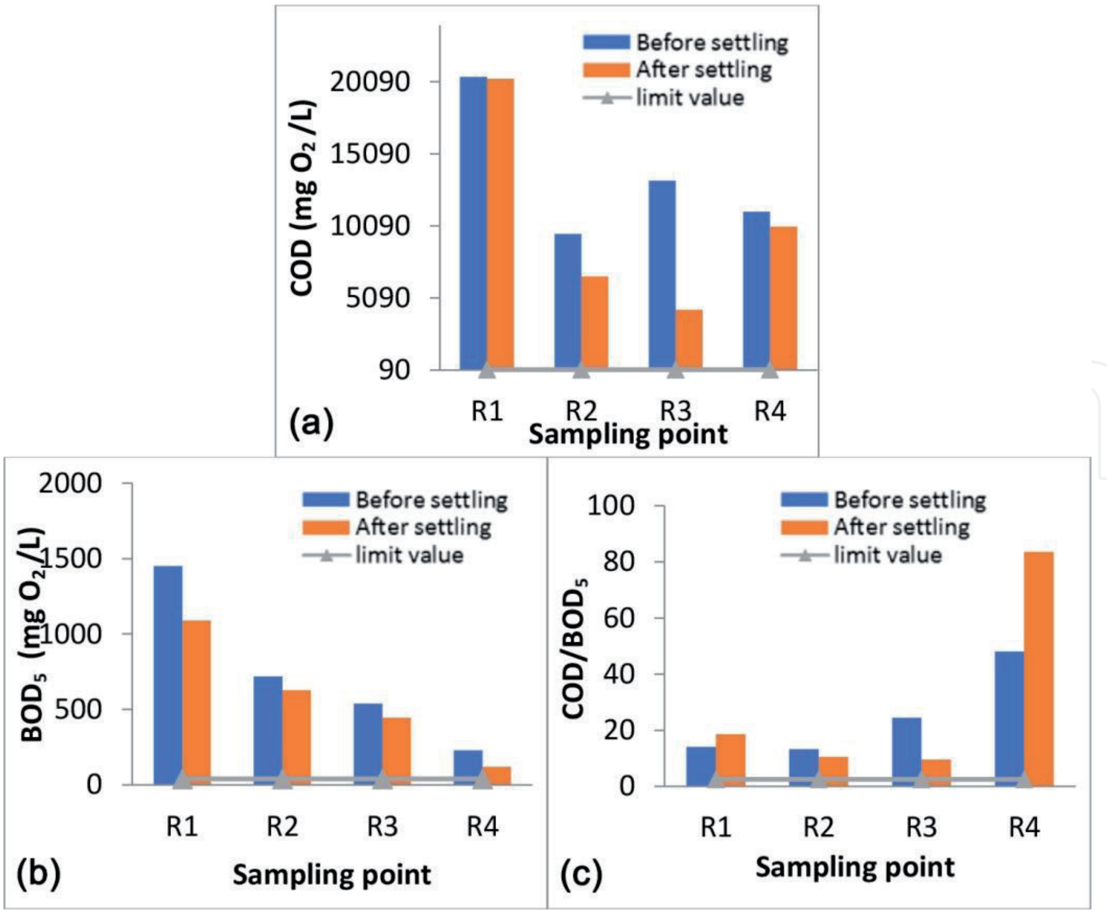

Figure 6.
Composition of the effluent studied before and after settling: (a) chemical oxygen demand; (b) biological oxygen demand; (c) ratio COD/BOD$_5$.

respectively for R1,R2 and R4 (**Table 2**). For pathogenic and fecal germs (Staphylococci, fecal streptococci, and the fecal coliform), **Table 2** reveals an absence of all of them. This could be explained by the high concentration of salts that may inhibit bacterial growth [35], and also by the toxicity of chromium which is present with a very high concentration [36]. However, we can conclude that the obtained germs (MTAF) may be halophilic and chromium bacteria.

In conclusion, tannery effluents are very complex, toxic and loaded in organic and inorganic matter, especially the first reject R1 of the unhairing-liming unit. Furthermore, R1 had a huge amount of sulfide, which could easily reduce to hydrogen sulfide under anaerobic conditions. As mentioned above, this toxic gas harms all living organisms, including human health. Therefore, the treatment of R1 has been very essential to remove sulfide ions.

Effluents	FC	TC	SF	FMAT	Staphylococci
R_1 (CFU/mL)	0	0	0	300	0
R_2 (CFU/mL)	0	0	0	400	0
R_3 (CFU/mL)	0	0	0	700	0
R_4 (CFU/mL)	0	0	0	0	0

CFU, colony forming units; FC, fecal coliform; TC, Total coliform; SF, Fecal sterptocoques; FMAT, total aerobic mesophilic.

Table 2.
Microbiological characterization of the wastewater of different operating tanning units.

5. Treatment of the unhairing-liming unit wastewater by precipitation

Several processes have been studied for the treatment of tannery wastewater, using simple and advanced methods. These processes include physicochemical treatments such as electrochemical methods [37, 38], filtration [28, 39], ion exchange [40], membrane filtration [41, 42], precipitation [43, 44], coagulation [5, 45], solvent extraction [46, 47], reverse osmosis [48, 49], adsorption [45, 50] and aerobic or anaerobic biological systems [51–53].

However, the high operating costs, the large amount of used chemicals, and the production of sludge are the main disadvantages of traditional chemical processing [2, 54]. On the other hand, advanced treatment techniques, such as reverse osmosis, ion exchange and membrane filtration are very expensive and generate another waste [54–56].

In fact, a dechromatization station was performed to remove the chromium from R4 of tannery industries in Doukkarat area in Fez city, Morocco. Nevertheless, there is not any plant to reduce sulfide toxicity in this Moroccan city. Thus, the elimination of sulfide ions is mandatory, but the removing process should be non-expensive and efficient. As mentioned above, R1 is non-biodegradable, and then, the physicochemical treatment is the best adequate treatment.

The chemical precipitation process is relatively simple and inexpensive. There are many precipitant agents such as ferric chloride, aluminum sulfate … etc. [21]. The principle of this treatment is based on the production of the insoluble complex from pollutants and chemical agent. Furthermore, the conventional chemical precipitation processes include hydroxide precipitation [57] and sulfide precipitation [58, 59]. According to the literature, ferric chlorides can react with sulfide ions to produce a complex compound. For this reason, chemical precipitation using ferric chloride may be a great process to remove sulfide ions from R1.

Khatoon et al. [60], showed that COD and chromium could be treated by coagulation with an elimination rate of 38 to 46% for the suspended matter and 30 to 37% for the Total COD. The chromium elimination rate is 74 to 99% for an initial concentration of 12 mg/L using a coagulant dose of 800 mg/L with an optimal pH of around 7.5. This study showed also that ferric chloride gave better results than aluminum sulfate.

Other studies [61, 62] consist of the elimination of sulfur compounds from unhairing-liming effluent after a preliminary settling for one hour, following by filtration in a sintered glass. This glass had a porosity of 10 microns and a diameter of 70 mm.

For the treatment of tannery effluent [61, 63], particularly unhairing-liming effluent, a volume of a $FeCl_3$ solution was gradually added to 200 ml of this effluent until the formation of an insoluble complex. Afterward, these two phases (Liquid/solid) are separated mechanically and the liquid phase was only analyzed.

This treatment is based on the reduction of sulfide ions by ferric chloride $FeCl_3$ in a slightly basic medium according to these reactions, which were established by those authors [20, 64–67].

$$2Fe^{3+} + HS^{-} \rightarrow 2Fe^{2+} + S^{0} + H^{+} \quad (1)$$

$$Fe^{2+} + HS^{-} \rightarrow FeS + H^{+} \quad (2)$$

$$2Fe^{3+} + 3HS^{-} \rightarrow 2FeS + S^{0} + 3H^{+} \quad (3)$$

$$FeS + S^{0} \rightarrow FeS_2 \quad (4)$$

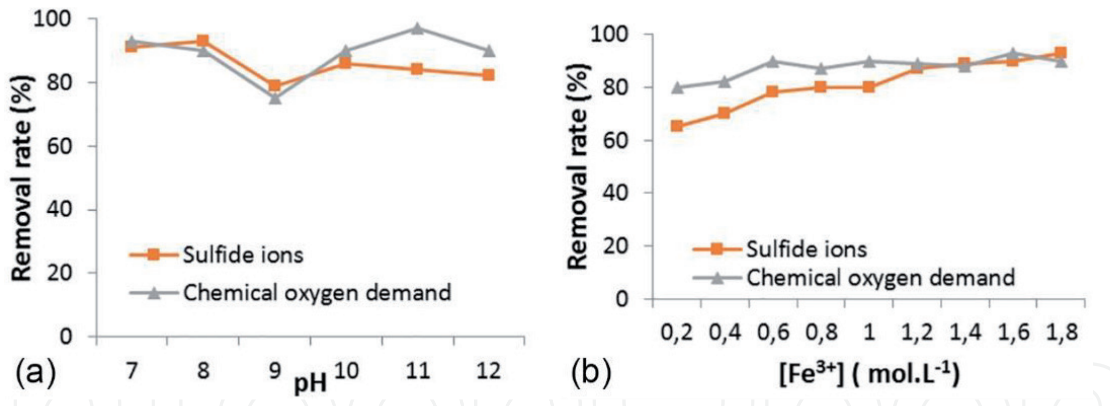

Figure 7.
(a) Effect of pH on the removal of sulfide ions and COD of effluent unhairing-liming; (b) elimination rate of sulfide ions in terms of the concentration of ferric ions at the pH of the medium (operating conditions: pH = 8.5, T = 24°C, $[S^{2-}]_0$ = 1570.94 mg/L).

According to the first Eq. (1), ferric ions react with sulfide ions to produce elemental sulfur. Afterward, the product ferrous ions will also react with sulfide ions to produce FeS precipitate. Otherwise, the reaction between ferric ions and sulfide ions may produce FeS and elemental sulfur according to the third Eq. (3). Finally, the FeS is converted to pyrite (FeS2) according to the fourth reaction (4). The precipitation depends strongly on the medium pH and the concentration of ions ferric [37–40].

Figure 7a reveals that the best removal rate of sulfide ions and the chemical oxygen demand was at the pH 8.5. Meanwhile, **Figure 7b** shows that the abatement rate of sulfide ions and COD increases when ferric ions (Fe^{3+}) concentrations increase too, and then this removal stabilizes at a value around 85% and 90% respectively for sulfide ions and COD, starting a ferric ions concentration of 1.4 mol/L. This could be explained by the high presence of hydrogen sulfide ions (HS^-)at pH of 8.5 according to the Pourbaix diagram [33].

The adjustment of pH effluent was performed by the addition of sulfuric acid (H_2SO_4) at a concentration of 1 N to obtain pH values between 7 and 12. For optimization of ferric chloride concentration, different concentrations were carried out ranging from 0.2 to 1.8 mol/L and using a pH effluent of 8.5 (**Figure 7b**).

The results show that the COD and sulfide ions had the same evolution of elimination depending on the pH and concentration of ferric ions. COD removal reached 90% at pH 7, 8 and 11 for ferric ion concentrations of 1, 1.2 and 0.8 mol/L respectively. As to sulfide ions, their removals achieved 90% and 84% at pH 7 and 8 using ferric ion concentrations of 1.6 and 1.8 mol/L respectively.

6. Conclusion

The main objective of this chapter was the characterization of different effluents of a modern tannery, giving a Moroccan modern tannery of Fez city as an example, and the treatment of unhairing-liming effluent, which was very loaded in sulfide.

The physicochemical characterization, of the fourth rejects of this modern tannery, showed a huge organic and inorganic pollution of these effluents, particularly unhairing-liming effluent that is largely alkaline and characterized by a huge organic and mineral pollution such as sulfides. However, the biological characterization revealed that these four effluents were empty from fecal and pathogenic germs due to their high inorganic toxicity. Otherwise, chemical precipitation using ferric chloride could remove a big amount of COD and sulfide ions during the treatment of unhairing-liming effluent. The abatement rate of sulfide ions reached 90% using a pH effluent of 8.5 and a ferric ions concentration of 1.4 mol/L.

In conclusion, the treatment of unhairing-liming wastewater could contribute to the protection of wildlife from the toxicity of sulfide ions through the reduction of the emission of greenhouse gases (Hydrogen Sulfide). Furthermore, chemical precipitation may be the best treatment for this type of effluent due to the high sulfide removal.

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