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Optimization of the method wastewater treatment of unit bovine hides's unhairing liming

A. Omor[1*], Z. Rais[1], K. El Rhazi[2], M. Merzouki[3], K. El Karrach[3], N. Elallaoui[1], M. Taleb[1]

1: Laboratory of Electrochemistry Engineering, Modeling and Environment. Science Faculty of Dhar El Mahraz, University Sidi Mohamed Ben Abdallah, Fez, MOROCCO
2: Laboratory of Epidemiology, Clinical Research and Community Health. Faculty of Medicine and Pharmacy, University Sidi Mohamed Ben Abdallah, Fez, MOROCCO
3: Biotechnology Laboratory. Science Faculty of Dhar El Mahraz, University Sidi Mohamed Ben Abdallah, Fez, MOROCCO

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anassomor@gmail.com;
Tel: +212 6 20 18 59 11

Abstract

The mean object of this work is to evaluate the pollution degree of the various operating units (capacity of 2.5 tons of cattle/day) of tanning hide treatment, and treat effluents of the unit unhairing-liming by precipitation. The physico-chemical and biological characterization of wastewater studied operating units and the final discharge shows that the waters of all units are slightly basic, with a low biodegradable organic load and absence of fecal bacteria, but with a low concentration of flora mesophilic aerobic total. Settling of all characterized wastewater for one hour allowed a polluting load reduction of 10 to 35% with the exception of sulfide ions and electrical conductivity of the effluent have not changed almost their concentrations. The treatment of settled effluents, characterized by high load sulfide ions, of unhairing-liming unit by ferric chloride in basic medium has contributed to the elimination of approximately 90% of these ions as a precipitate.

1. Introduction

The tanning industry is an important activity which involves the processing of leather animal skin by removing fat and hair by different processes and treatments of the skin to make it unalterable and rigid [1]. Two methods of tanning are used, chrome tanning and vegetable tanning. At a global level, between 70% and 80% of leather are produced by chrome tanning [2, 3].Tannery industries use a lot of chemicals and produce huge volumes of wastewater and solid waste [4].

Tanneries effluents are highly polluted. They contain fragments of flesh and hair, protein colloids, fats, tannins, dyes and toxic elements such as sulphide and chromium [5, 6]. These various loads have an impact on the environment and on health. Chromium is found naturally in many vegetables, fruits, meats, grains and yeasts. Chromium III is an essential nutrient for humans. An excessive absorption of chromium III can cause health problems (metabolic disruption and diabetes) [7]. Under certain conditions, the trivalent chromium the most common form in tanning can oxidize on chromium VI which is carcinogenic and harmful to humans and animals when it seeps into the water supply [8-12]. Hydrogen sulfide can poison various organs, prolonged sulfide inhalation can cause degeneration of the olfactory nerve and cause death just after few breaths. Inhalation of the gas even in small amounts can lead to a loss of consciousness [13-16].

Several previous research works have proven the effectiveness of certain chromium treatment processes such as activated carbon adsorption, ions exchange [17-19] and precipitation with ferric chloride [20,21].Currently, a dechromatation station is installed at Dokkarat industrial district of Fez with a treatment capacity of 50 m^3/day. Chromium is 98% recovered by precipitation under conditions of pH and coagulant charge, although determined. However, sulfides used during the tanning process are not treated and have critical impacts on health and the environment.

The objective of this study is, in the first part, evaluating the pollution load of different wastewater operating of a hide tannery processing units. In the second, studying aims to treatment of wastewater loaded with sulfide of unhairing-liming units.

2. Materials and Methods

2.2. Sampling

Industrial effluents used in this work come from the river of a tannery workshop located in industrial area of Dokkarat: Fes, Morocco, which deals essentially bovine hides.

The samples were collected in the month of February 2015 at the end of the operations unhairing-liming (R1), rinsing (R2),deliming-bating (R3)and chrome tanning (R4) (figure 1) according to the ISO 5667-2 standard [22]. While the effluent from the mixture M (R1 + R2 + R3) and total rejection (RT = R1 + R2 + R3 + R4) were taken by the composite method [22].

The physical parameters: temperature, pH and conductivity were measured after sampling. All samples were stored in a refrigerator at a temperature of 4°C according to AFNOR standards set by Rodier [22] and are warmed to ambient temperature before use.

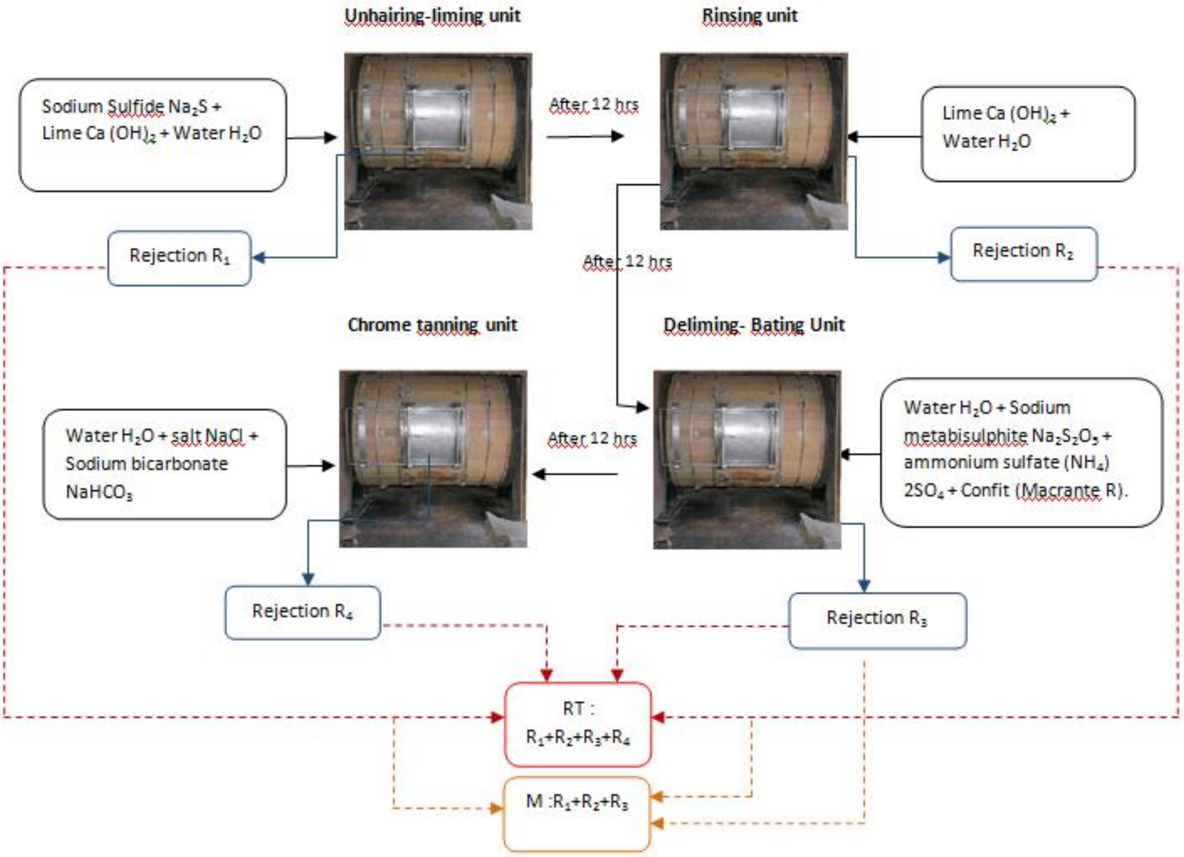

Figure 1 : Sampling Method discharges of tanning and sampling points

2.2 Methods

All samples were characterized by physicochemical and bacteriological parameters in accordance with standards [22] before and after settling of effluents for one hour and filtration except for bacteriological parameters.

2.2.1. *Physicochemical characterization*

The measured parameters are pH, temperature, 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-}.

The pH was measured using a pH meter HANNA with a type electrode Senti X 22 according to NF T90.008 [22]. 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 [22].

Sulfide ions were measured by the indirect method according to standard NF T 60-203 [22].

Ammonium, orthophosphate, nitrate, nitrite, sulfate, and the chemical demand for oxygen COD were carried out by the spectrophotometric method using a DR/2005HACH at a fixed wavelength. The concentration of a substance is proportional to its optical density according to the Beer-Lambert law and to the standards approved by AFNOR T90-101 [22].

2.2.2. *Bacteriological characterization of effluents from tanneries*

The bacteriological parameters evaluated are biological oxygen demand BOD_5, *total coliform* (TC), *faecal coliform* (FC), *fecal sterptocoques* (SF), *total aerobic mesophilic* (FMAT) and *staphylococci*.

The samples were collected in sterilized bottles of 1 L.

The biological oxygen demand in 5 days (BOD_5) was measured by the incubation method during 5 days using an OxiTop IS6 device according to standard NF EN 1899-1 [22].

The counting of FC and TC were held under the indirect method of multiple tube fermentation in lactose broth. The number was deducted following statistically most probable number method [22].

The enumeration of *staphylococci* and *fecal sterptocoques* (SF) were performed respectively on medium Chapman and Slanetz [22].

Enumeration of *total aerobic mesophilic flora* and *yeast* were made respectively on nutrient *agar* and *Peptones Yeast Glucose* (YPG) which is added *chloramphenicol* and *ampicillin* as antibiotics to inhibit bacterial growth [22].

2.2.3. *Effluent treatment of the unit unhairing-liming*

Effluent treatment of the unhairing-liming unit consists of elimination of sulfur compounds after a preliminary settling for one hour and filtration in sintered glass of porosity 10 microns and diameter of 70 mm.

In a beaker of 300 mL, a volume of 200 ml of waste water is added to V ml of a $FeCl_3$ solution until precipitation to a well studied pH as Pourbaix diagram [23]. The two phases are separated mechanically and only the liquid phase was analyzed.

3. Results and discussion

3.2. Characterization of discharges studied

The results of the physico-chemical and biological characterization of the wastewater of different operating tanning units studied before and after settling for one hour and filtering are listed in Figures 3 to 12 and in Table 1.

Table 1: Characterization of bacterial wastewater operative units studied of leather tanning.

Effluents	Faecal coliform(FC)	Total coliform (TC)	Fecal sterptocoques(SF)	FMAT	Staphylococci	Yeast
R_1 (UFC/mL)	0	0	0	300	0	0
R_2 (UFC/mL)	0	0	0	0	0	0
R_3 (UFC/mL)	0	0	0	100	0	20
RT (UFC/mL)	0	0	0	700	0	10

The analysis of the results of the various figures and table shows that wastewater from all study units are a temperature between 24 and 27 °C and don't contain a load of fecal origin, but microbial FMAT load (*Flora Mesophilic aerobic Total*) 300 CFU/mL for wastewater from the unhairing-liming unit, 100 CFU/mL for sampling points R3 corresponding wastewater from the deliming-bating unit and 700 CFU/mL for the total rejection RT (Table 1). This is explained by the concentration of dissolved salts of these discharges. These can inhibit microbial activity and cause a rise of suspended solids in the effluent [24]. Indeed, from 10 to 12 mg of chromium (VI) per liter may inhibit the development of soil bacteria. Whereas, the same concentrations of chromium (III) have no effect on this growth [25].

The rejects of the units unhairing-liming and rinsing are characterized by high alkalinity and those of others units are slightly alkaline (Figure 2). The values obtained are comparable to those found in previous work on wastewater from tanneries that have a weakly basic pH [26, 27].

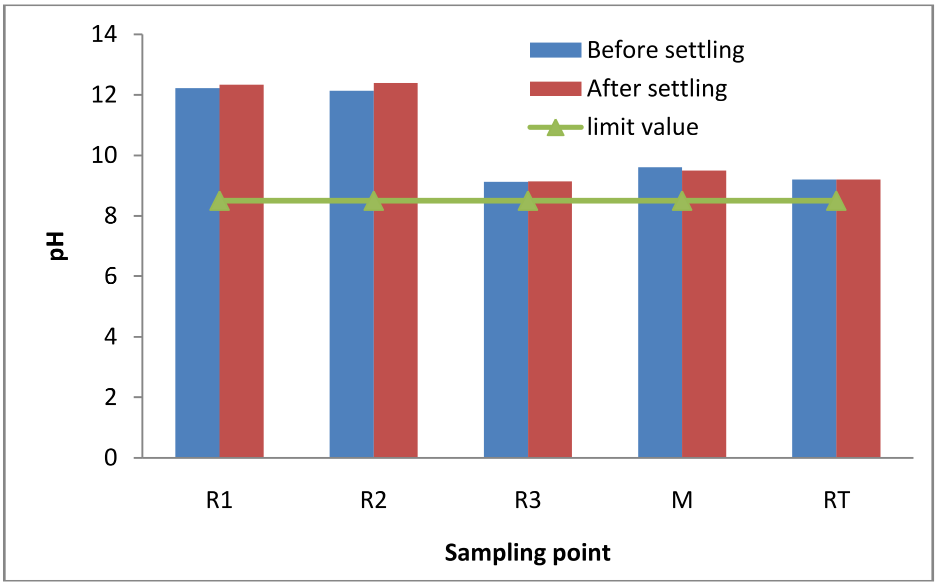

Figure 2 : pH of the wastewater studied operation units of leather tanning before and after settling.

As for the conductivity it ranges between 10 and 30 ms/cm largely exceeding the Moroccan standards [28]. The largest values are recorded for effluent from units of the unhairing-liming (R1) and deliming-bating (R3) (Figure 3). These high values of conductivity show a significant use of salt during the tanning process.

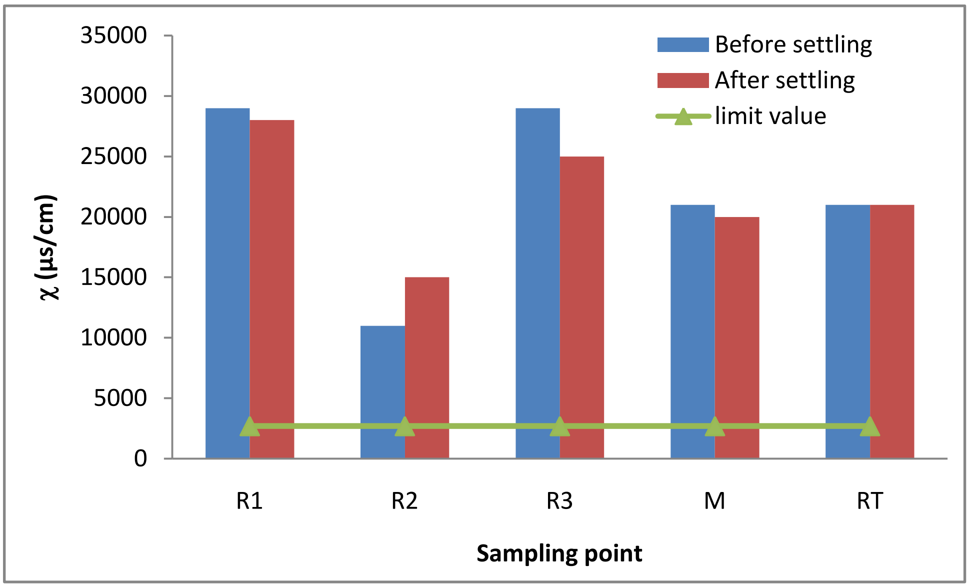

Figure 3: Wastewater conductivity of the studied operative units of leather tanning before and after settling.

For suspended solids (SS), they are around 5000 mg / L for wastewater from the all units except those of the final reject which is almost 10 times higher (Figure 4).

The examination of the nitrogenous load (Figure 5) reveals that the nitrate levels recorded at the R1 discharges is about 24 mg.L^{-1} for raw waters and are reduced by about 80% after settling.

For other sampling points, the nitrate is very low compared to Moroccan standards of wastewater discharges into surface waters [28]. Similarly to the results for nitrite and ammonium ions (Figure 5). The results thus obtained in terms of nitrate, nitrite and ammonium ions are consistent with those of some authors [29, 17, 1].

Concerning the phosphate load (Figure 6), it is lower than the Moroccan standards of discharges into the receiving environment for the effluents of all sampling points [28]. Whereas their load of sulfate ions exceeds the standards for all wastewater studied [28] except for the second sampling point R2 (Figure 7). These high loads are due to the use of weak acids-based deliming agents to neutralize the lime when the hair and flesh adhered to the skin are removed [30]. For the final discharge effluent (RT), they are very rich in chromium sulphate not absorbed by the leather (30-50%) [30]. The same results were found by [17, 19, 31, 32].

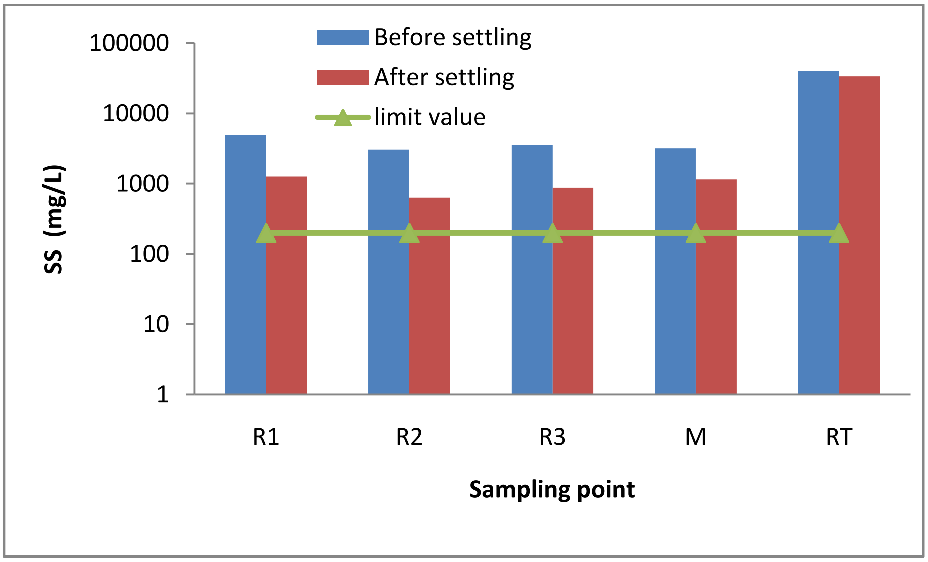

Figure 4 : suspending matter from wastewater studied operation units of leather tanning before and after settling.

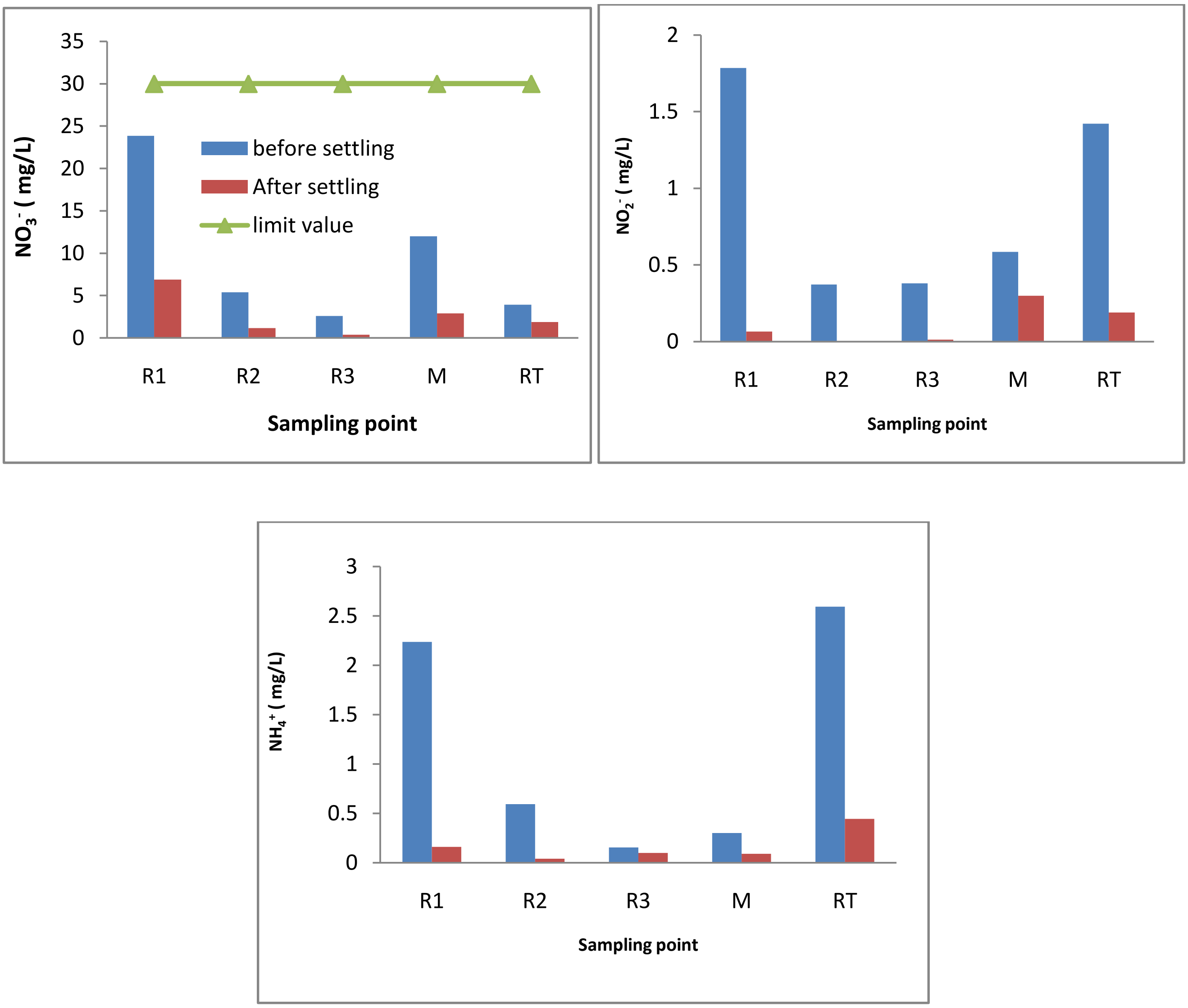

Figure 5 : Nitrogenous feed of effluents studied before and after settling.

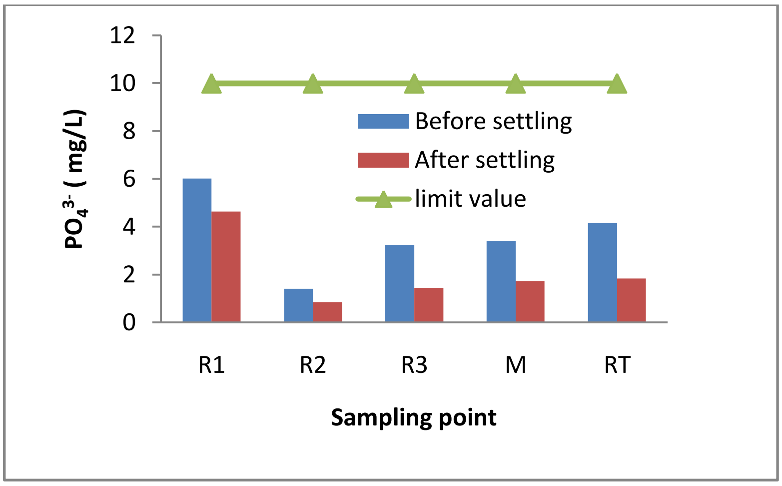

Figure 6 : Orthophosphate ions of the effluent studied before and after settling.

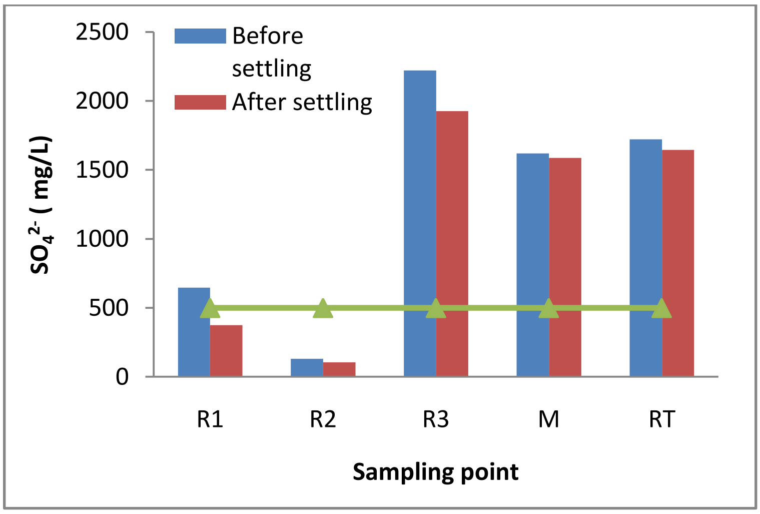

Figure 7 : Sulfate ions of the effluent studied before and after settling.

Similarly to the organic load of the effluent that is evaluated by measuring the chemical oxygen demand COD and biological oxygen demand BOD_5 (Figure 8). The Figure 8 shows that all effluents are a no biodegradable organic load considerably exceeding the standard Moroccan rejection of wastewater in the receiving environment [28] (VLRE, 2013); 100 times for COD and 50 times for BOD5. In addition to the report, 9≤ COD / BOD 5 ≤50 is much higher (Figure 9) to the normalized value (≈ 2.5) corresponding to the boundary of organic matter biodegradation. This high load is mainly due to biogenic materials skins and organic chemicals. The concentrations found in COD are comparable to results obtained by [33, 34].

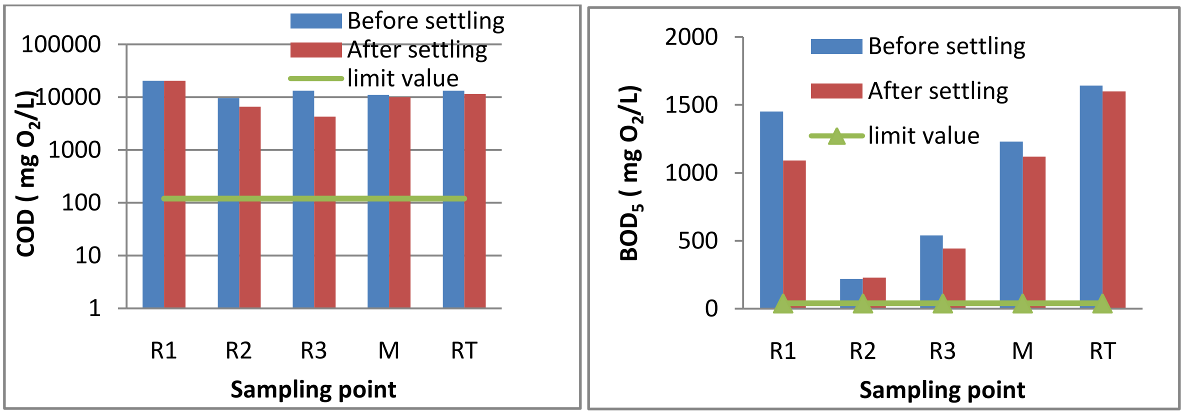

Figure 8: Chemical and biological oxygen demand (COD and BOD_5) of the effluent studied before and after settling.

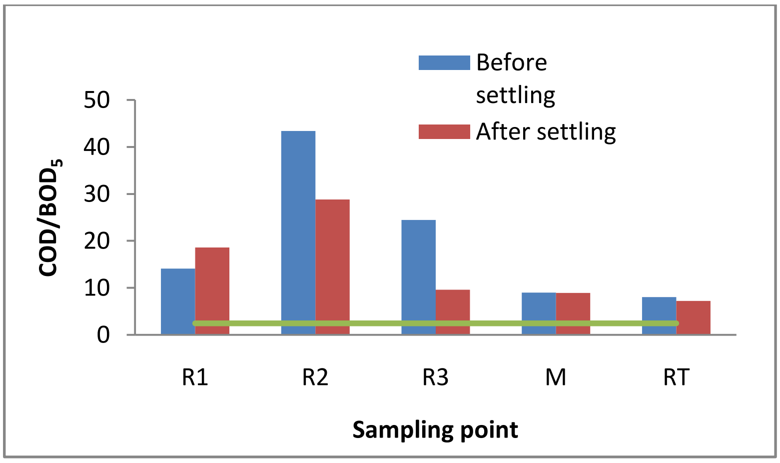

Figure 9 : Ratio COD/BOD$_5$ of the effluent studied before and after settling.

For sulfide ions load, effluents from the units unhairing liming R1 and final rejection RT have the highest load which approximates respectively 1600 and 600 mg.L^{-1} (Figure 10).

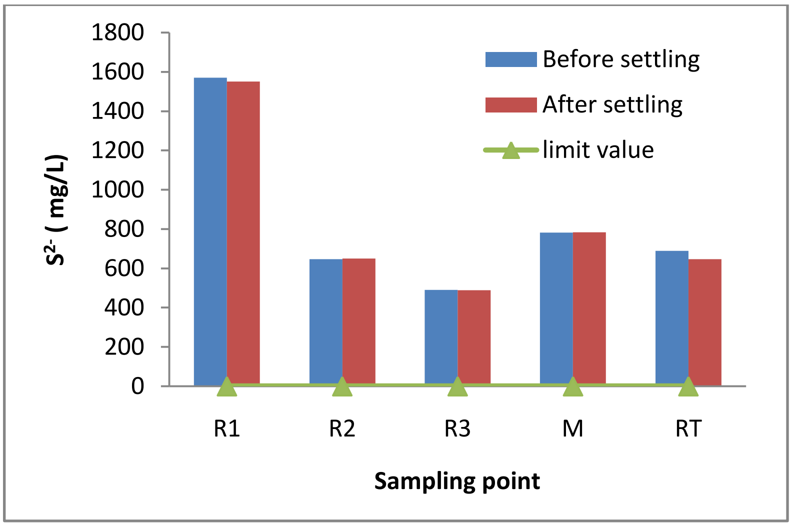

Figure 10 : Sulfide ions of the effluent studied before and after settling.

Indeed, discharges of the R1 unit are alkaline; which proves the presence of hydrosulfide HS$^-$ ions according to the Pourbaix diagram [23]. The results obtained are consistent with those found by [33] for the final rejection and those found by [29].

Furthermore, the settling of all effluents for 1 hour reduced their pollutant load from 10 to 35% except for the sulfide ions, pH and conductivity.

3.3. Treatment of settled effluents of the unhairing-liming unit

The treatment concerning wastewater of the unit unhairing-liming and consists to reduce non-biodegradable organic load and sulfide ions by ferric chloride FeCl$_3$ in slightly basic aria according to the reactions established by [35, 36, 21].

$$2Fe^{3+} + HS^- \longrightarrow 2Fe^{2+} + S^0 \downarrow + H^+ \qquad (1)$$

$$Fe^{2+} + HS^- \longrightarrow FeS \downarrow + H^+ \qquad (2)$$

$$2Fe^{3+} + 3HS^- \longrightarrow 2FeS \downarrow + S^0 + 3H^+ \qquad (3)$$

$$FeS + S^0 \longrightarrow FeS_2 \qquad (4)$$

According to equation (1), ferric ion oxide sulfide to elemental sulfur. Afterwards the product ferrous ion reacts with the sulfur to produce FeS precipitate. Therefore, the third of the sulphide is converted to elemental sulfur and the other two thirds are converted to FeS according to reaction (3). Finally the FeS is converted to pyrite (FeS$_2$) according to reaction (4). The precipitation strongly depends on the pH of the medium and the concentration of ions ferric [37, 38, 39, 40].

Analysis of the results of Figure 11 reveals that the removal rate of sulphide ions and the chemical oxygen demand at the pH of the medium increases with the concentration of ferric ions (Fe^{3+}) to stabilize at a value of about 85% and 89 % respectively for a ferric ions concentration of 1.4 mol L^{-1}. This is explained by the presence of hydrogenosulfide (HS^-) ions according to the Pourbaix diagram Figure 12 [23] and the oxidation of sulphide to elemental sulfur according to reaction (1).

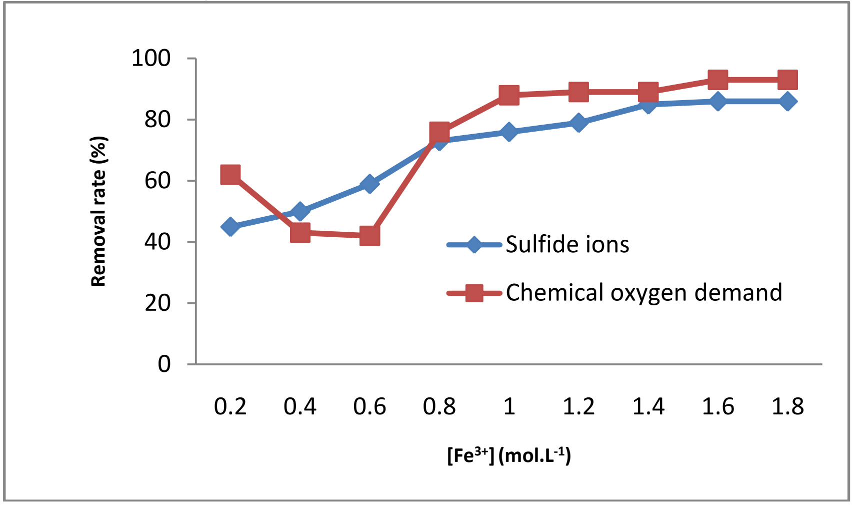

Figure 11 : Elimination rate of sulfide ions in terms of the concentration of ferric ions at the pH of the medium (Operating Conditions: pH = 12.14, T = 24 ° C, $[S^{2-}]_0$ = 1570.94 mg.L^{-1}).

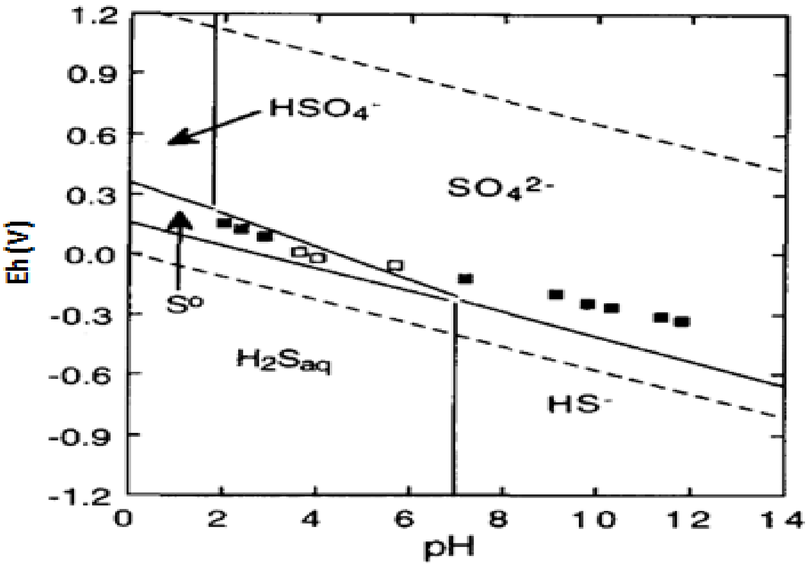

Figure 12 : Potential-pH diagram of the sulfur [23].

3.3.1. pH optimizing

The pH aria adjustment was conducted by addition of sulfuric acid (H_2SO_4) at a concentration of 2 mol.L^{-1} to attain pH values between 7 and 12.Optimization of pH was studied for different ferric ions concentrations ranging from 0.2 to 1.8 mol.L^{-1} (Figure 13).

Analysis of the results listed in Figure 13 shows that the no biodegradable organic matter evaluated by measuring the COD and sulfide ions has the same tendency of elimination depending on the pH and concentration of ferric ions. However, the rate of COD removal is greater than that of the sulfide ions to all pH with the exception of the pH = 9. It reaches 90% for pH 7, 8 and 11 at concentrations of ferric ion 1 mol.L^{-1}; 1.2 and 0.8 mol.L^{-1} respectively. As to sulfide ions, there is a reduction of 90% and 84% only at pH = 7 and 8 for ferric ions concentrations of 1.6 and 1.8 mol.L^{-1} respectively.

Figure 14 summarizes the results treatment of unhairing-liming effluent unit with a concentration of ferric chloride (1.4 mol.L^{-1}) depending on the pH of the medium, and allowed us to conclude that the optimum pH is between 7 and 8. The Pourbaix diagram confirms the result obtained [23]. Note further that the final pH values were lower than initial values. This is due to the consumption of sulfide ions by ferric ions.

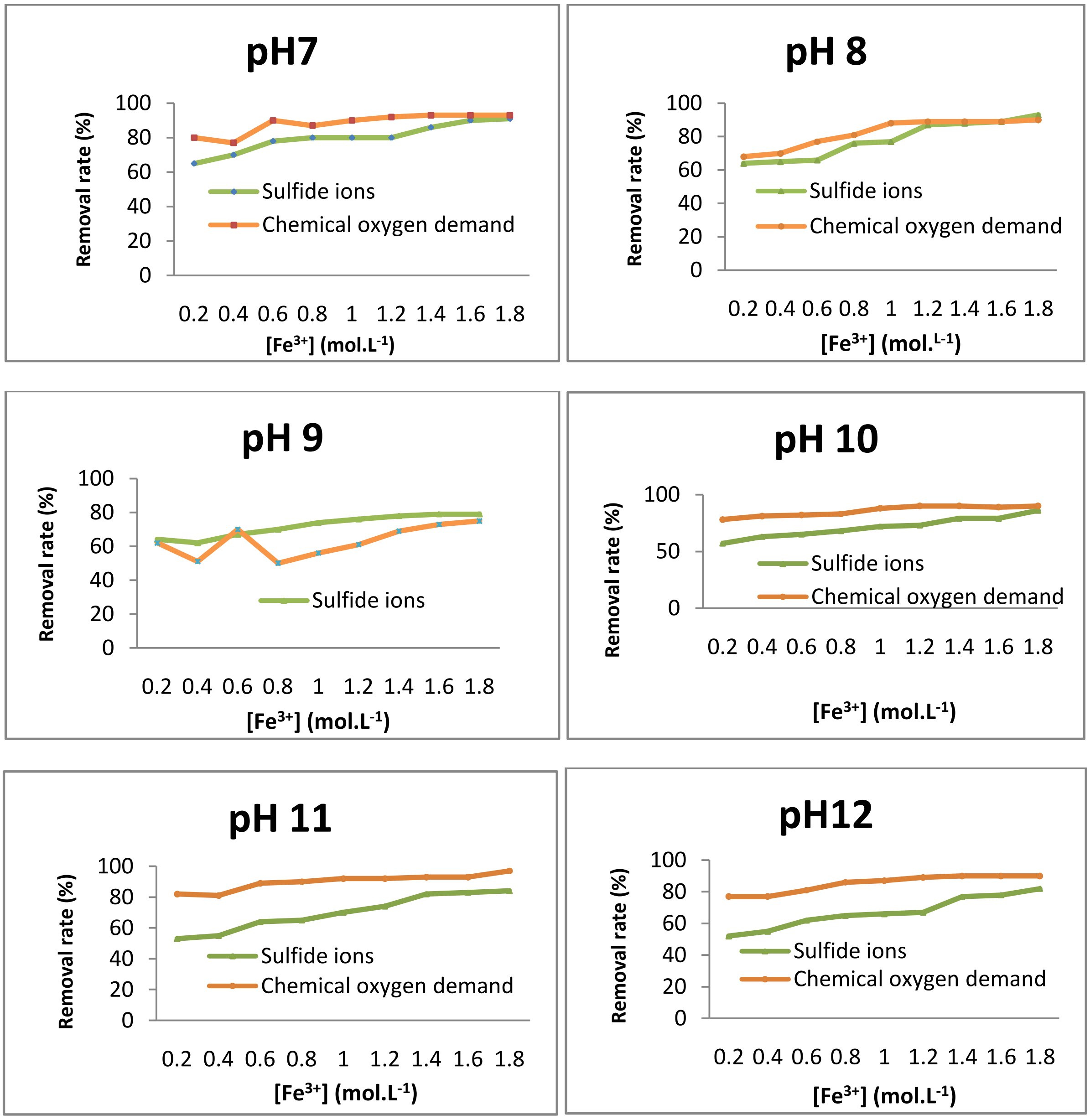

Figure 13 : COD and sulfide ions removal rate depending on the pH and the concentration of Fe^{3+} ions.

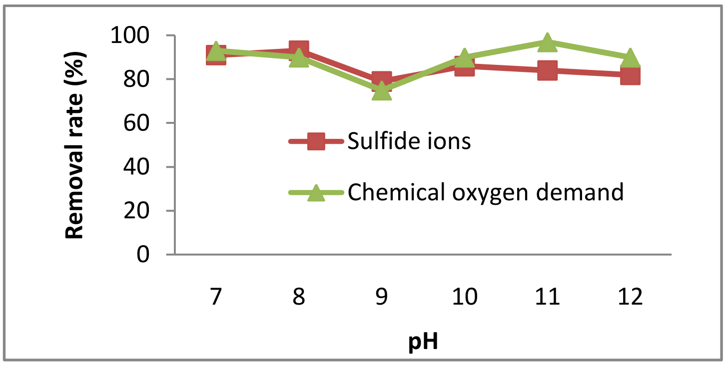

Figure 14 : Effect of pH on the removal of sulfide ions and COD of effluent unhairing-liming.

3.3.2. Concentration of ferric ions optimizing

The removal of sulfide ions and COD of the unhairing-liming effluent of the hides was evaluated at various concentrations of ferric chloride $FeCl_3$ to pH 8 and are illustrated in Figure 15.

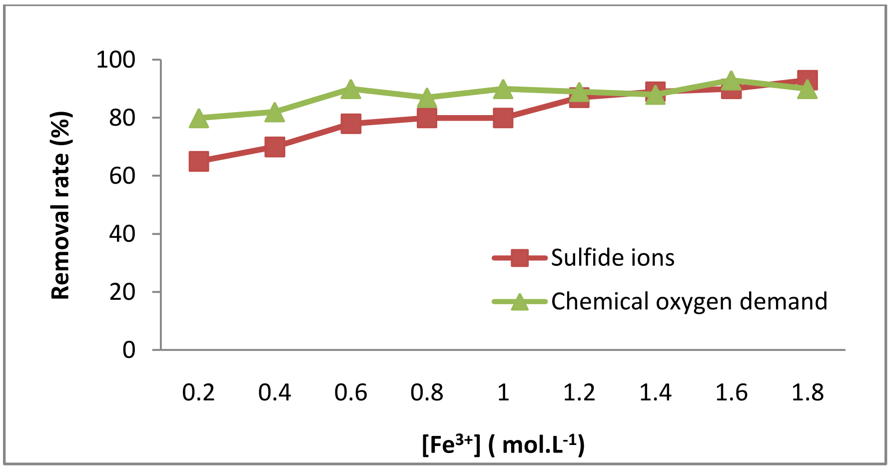

Figure 15 : Effect of the ferric ions concentration on the removal of sulfide ions and COD.

The curves of Figures 14 and 15 show that at pH 8, the two parameters are stabilizing at the same rate of reduction by about 90% with Fe^{3+} ions concentration of 1.4 mol L^{-1}.

3.3.3. Effect of time and the stirring speed

In addition to optimizing the pH and the concentration of ferric ions, we sought to improve the reduction yields of sulfide ions and the chemical oxygen demand (COD) depending of the duration and the rate of agitation. The main results are shown in the curves 16 and 17 which show that the maximum removal is obtained after 15 minutes with a stirring speed of 150 rpm.

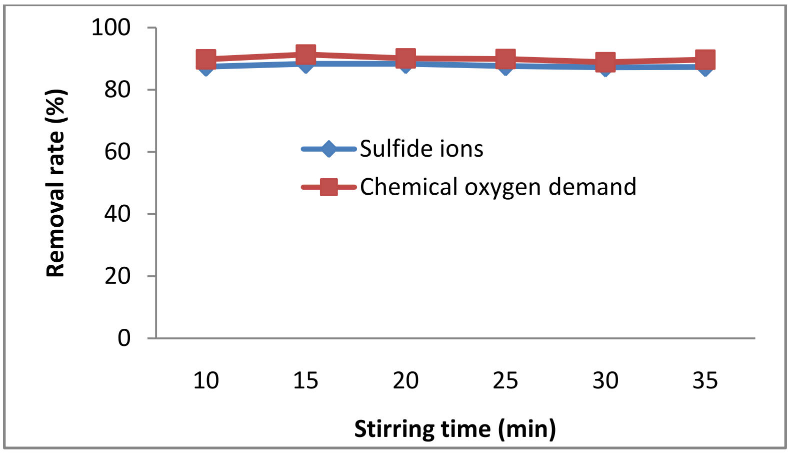

Figure 16 : Effect of the stirring time on the removal of sulfide ions and chemical oxygen demand.

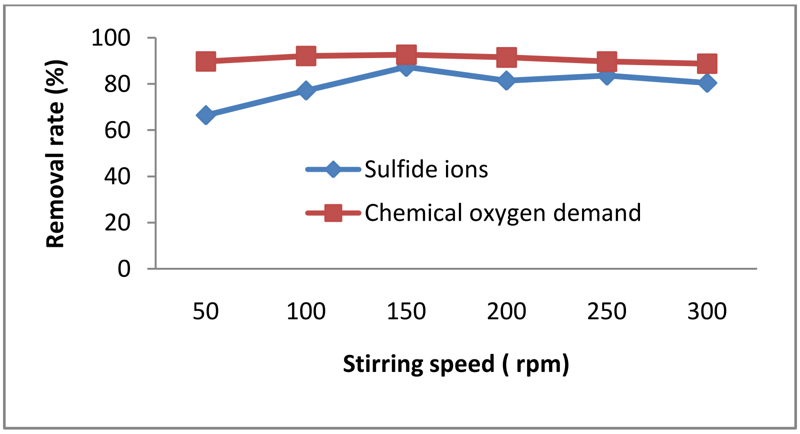

Figure 17 : Effect of the stirring speed on the removal of sulfide ions and chemical oxygen demand.

Beyond the 150 rpm, the rate of removal of the sulphide ions and chemical oxygen demand stops increasing and then stabilizes. This period of 15 minutes and a stirring speed of 150 rpm would therefore the time and speed necessary for the iron flocs adsorb a fraction of the pollution expressed in terms of the chemical Demand oxygen (COD) and ions sulfide (S^{2-}).

Conclusion

The study of tannery effluent has led to the following conclusions:

The physicochemical and bacteriological characterization carried out for the wastewater of different operating units and the final rejection before and after settling for one hour and filtration, shows that the wastewater from all units are basic, pH ranging from 8 to 12, temperature between 24 °C and 27 °C, don't contain any load of the nitrogen, phosphate and fecal. However, wastewater from all units are characterized by FMAT microbial load, heavy load of the suspended matter (SS), mineral and organic matter no biodegradable and sulphide and sulphate for especially unhairing-liming units (R1).

The treatment of settled sewage of the unit unhairing-liming by ferric chloride under optimal pH conditions (8) and ferric ions concentration (1.4 mol.L^{-1}) has reduced the load organic and a desulfurization by about 90%.

In conclusion, the wastewater from the unhairing-liming unit of the hides can be separated from those the other operating units and treated separately by the precipitation method. This solution could contribute a part in the protection of wildlife and flora of the intense pollution from sulfide ions. On the other hand, it will participate in the reduction of the emission of greenhouse gases (Hydrogen Sulfide).

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