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Characterization and treatment of effluents loaded with sulphides from two tanneries: Modern and Artisanal

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Abstract

The objective of this work is to characterize and treat wastewater loaded with sulphide ions from two types of modern and artisanal tanneries. A preliminary diagnosis was made of both types of artisanal and modern tanneries and showed that modern tanneries consume more water and chemicals than traditional tanneries. The most sulphide-laden steps are those of unhairing-liming and lime baths for modern and artisanal tanneries respectively. The physicochemical characterization of the wastewater from the different operating units of the two types of tanneries shows that the unhairing-liming and lime baths steps are the most loaded with sulphides, in addition to their high load of non-biodegradable organic material. Wwe note that wastewater from artisan tanneries is less polluting than that from modern tanneries. The treatment of sulphide ions was first carried out on a synthetic solution at different concentrations by precipitating sulphides with ferric chloride at pH adjusted according to the Pourbaix diagram. The results of the treatment of the synthetic solution of concentration 1500 $mg.L^{-1}$ allowed the reduction of 91% of sulphide to pH = 8.5.The analysis by the X-ray diffraction records the presence of gypsum. The treatment of wastewater from the unhairing-liming units of modern and artisanal tanneries by ferric chloride 1.2 and 0.8 mol.L-1 respectively under the optimum conditions raised leads to a reduction of the non-biodegradable organic load of almost 96% and those of sulphide ions of about 90% for both types of tanneries.

Keywords: *Tannery wastewater; Sulphide removal; Chemical treatment; Ferric chloride.*

1. Introduction

The leather tanning industry is the most important industry in the Mediterranean countries [1–3]. Although the leather tanning is one of the most important industries to the Moroccan economy, particularly in Fez city where it contributes to 24% of industrial production and 53% of the city employment [4]. This plant has a capacity of 50000 kg/day of sheep and bovine skin, and produces 6000 m^3/day of effluent [5]. However, in the leather industry workers must stand in toxic and prolonged sulphide exposure which causes serious health and environmental problems due to the their untreated effluents [6–8]. Consequently, a treatment method for these effluents is necessary. The characteristics of leather tanning waste water depend on the nature of the tanning process [8]. There are two methods of tanning ; the modern technique which uses chromium in the finishing process and the traditional method using plant extracts in the finishing product to stabilize leather [4,9,10]. In these methods a large number of organic and inorganic compounds are employed, such as natural or synthetic tannins, organic acid, as well as chloride, chromium III and sulphide salts [11,12]. Several studies have been devoted to analyse the characterization and treatment of this type of waste by the biological application or physicochemical processes [13–17]. All these processes require a good knowledge of the treated water pollution load for the sake of choosing and applying a suitable and effective method for processing. Chromium and sulphide are removed by 98% and 90% respectively by the use of the precipitation method under the already determined pH and coagulant charge conditions [4,18]. Then, our aim is to minimize the sulphide concentration in the waste water from unhairing liming and lime units in the respectively modern and artisanal tanneries by using ferric chloride, which has proved its effectiveness on several types of effluents [19–21]. In this respect, we proceed by first analysing the different processes of modern and artisanal tanneries effluents in Fez after having conducted a diagnostic at the level of the two types of tanneries to detect the chemical or natural products and water consumption during the tanning process. The second step consists of varying the parameters, such as pH, precipitation period, concentration of Fe^{3+} and speed, to determine the optimum conditions to remove the sulphide of synthetic tannery waste water by using jar test methodology. The present work scope also includes the study of sulphide and DCO removal from the units unhairing liming and lime bath waste water under the optimum conditions found in the differents concentration treatment of sulphide in synthetic waste water.

2. Materials and methods

2.1. State of the art

The findings from the diagnosis reveal that modern tanneries exist at the industrial district Dokkarat, Sidi Brahim, Ain Chkef, Ain Nokbi while the artisanal are located in the Medina-Fez. Modern tanneries use approximately 680 kg of chemical products and consume about 29 m^3 of water per tonne of skins. The products implemented in modern tanneries are sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), the dichromate potassium ($K2Cr_2O_7$), the lime ($Ca(OH)_2$), sulfuric acid (H_2SO_4) ,formic acid (HCOOH), sodium sulphide (Na2S) and ammonium salts. While craft tanneries exploit extracts of natural plant products [1] such as takeout, flour, bran, virgin oil, mimosa bark, grenadine bark, cork oak bark, pigeon droppings and the only chemical used is sodium sulphide (Na2S). In addition, we note that modern tanneries are known by excessive consumption of water and chemicals compared to traditional tanneries. Wastewater is dropped from these industries into streams without prior treatment, which is the main cause of water pollution at both the surface and underground. In this study, we have selected two types of tanneries, a modern one located at the Dokkarat Industrial District and the Chouara tannery located in the Old Medina. These tanneries have a very high daily production of 2.5 tons per day, which requires large quantities of chemical or natural products as well as a high consumption of water.

2.2. Sampling

This study was carried out by the prepared synthetic solution and two waste water tanneries which are taken from tannery leather works located in the industrial area of Dokkarat: Fez, and the traditional Chouara tanneries located in the medina of Fez Morocco which were selected following the diagnosis made.A Synthetic wastewater was prepared by diluting $Na_2S.9H_2O$ stock solution and lime to obtain different sulphide concentration of 500, 1000, 1500 and 2000 $mg.L^{-1}$. The wastewater tannery samples were taken from the end of the operations unhairing-liming (R1M), rinsing (R2M), deliming-bating (R3M), and chrome tanning (R4M) in modern tannery according to the ISO 5667-10 standard [22]. Other four effluent samples were obtained from the Lime Baths or unhairing-liming (R1A), Pigeon Faecal Unit (R2A): (PFU: Pigeon Faecal Unit means where tannery works keep the pigeon faecal for use in the treating bovine skin), the bran (R3A) and Tanning (R4A) steps were taken from artisanal tannery according to the ISO 5667-10 standard [21]. While the effluent from the total rejection (RTM = R1M + R2M + R3M + R4M and RTA = R1A + R2A + R3A + R4A) were taken by the composite method [23]. All samples were transported in polyethylene containers and immediately stored in a refrigerator at a temperature of 4°C according to AFNOR standards set by Rodier [23] and are warmed to ambient temperature before use.

2.3. Physicochemical analyses

The wastewater samples from the different sampling points of the two types of tanneries(modern and artisanal) were analyzed by pH, EC (Electric Conductivity), suspended solids (SS), chemical and biological oxygen demand COD-DBO_5, sulphate ions SO_4^{2-} , nitrite NO_2^-, nitrate NO_3^-, ammonium NH_4^+, orthophosphate PO_4^{3-} and sulphide ions S^{2-} according to the methods of AFNOR issued by Rodier [23].

2.4. Synthetic and tannery wastewater precipitation treatment and the solid phase analysis

Effluent treatment consists of sulphide compounds elimination. The protocol generally comprises introducing into each beaker 200 mL of synthetic waste water having fixed sulphide concentrations and were tested by the following procedures:

- The first procedures consisted of the treatment method optimization which involves varying the synthetic waste water (1500 $mg.L^{-1}$ in sulphide) pH in order to have an optimum pH by addition of HCL (0.1 M) or the base NaOH (0.1 M) and we added a concentration of Fe^{3+} ions until precipitation to get a good removing of sulphide [18].
- For the second one, we optimized the Speed and time of treatment. Finally, we treated each sulphide concentration of synthetic wastewater by using different concentrations of Fe^{3+} (ranging from 0.1 to 1.2 $mol.L^{-1}$).

Whenever, a parameter is optimized we take it into consideration for the next procedures.

These two treatments were made in Jar-test; which is cheap and easy method, producing two phases which were separated mechanically. Sulphide ions were measured only in the liquid phase by the indirect method according to standard NFT 60-203 [23] and the solid phase was determined by XRD (PANalytical XPERT-PRO) which can be used to identify chemicals from the sludge. Finally, we took wastewater from artisanal lime bath and modern unhairing liming effluent and we applied the optimal results found in the treatment of synthetic wastewater.

3. Results and Discussions

3.1. Physical-chemical characterization of tanneries waste waters

The wastewater of the units unhairing liming (R1M) and lime baths (R1A) from respectively modern and artisanal waste tanneries were characterized by high alkalinity but those of other modern tanneries units were slightly alkaline.

The effluent of R2A, R3A and R4A were characterized by a very acidic pH (Figure 1) revealing that they go far beyond the prescribed Morocco's standards 2013 (which are between 5.5 and 8.5 [24]). Effluents with similar pH characteristics were found in previous works [2,25,26]. As for the conductivity, it ranges between 4 and 39 ms/cm and the conductivity highest value was found in R1M and R1A with respectively 39 and 22 ms/cm values (Figure 2). These high conductivity values were showed a significant use of salt for preserving animal skins during the tanning process and it was removed during the rinsing [2,3,16,27]. The wastewater contains also suspended solids (SS), which were confirmed by the different values obtained with the modern and artisanal tanneries wastewater (Figure 3).

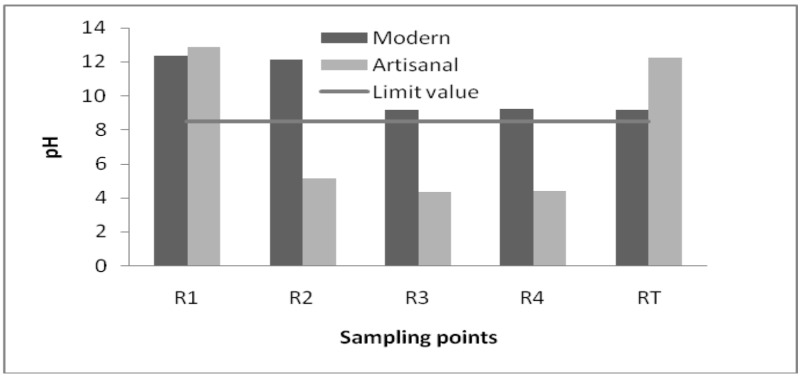


Figure 1: pH of the wastewater studied in modern and artisanal tanneries.

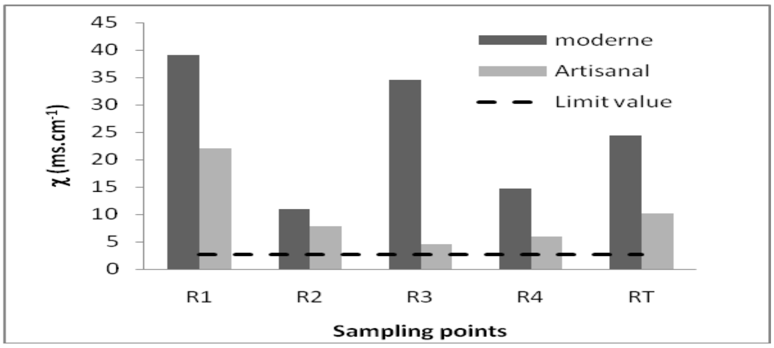


Figure 2: Conductivity of the wastewater studied in modern and artisanal tanneries.

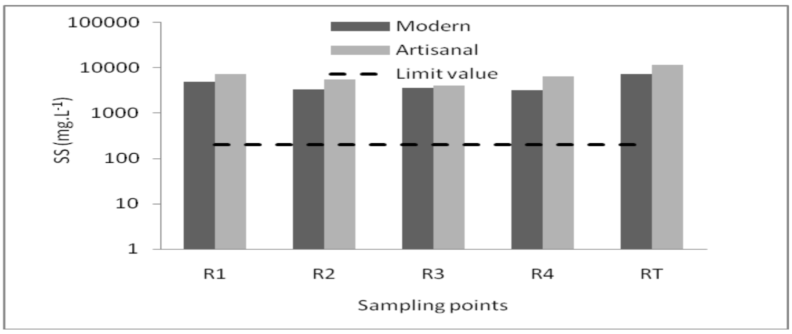


Figure 3: Suspended solids of the wastewater studied in modern and artisanal tanneries.

For all the sampling points, the COD values of the modern and artisanal units were found to be between 400 and 18000 mg O_2/L (Figure 4). This is very high compared to Moroccan standards of discharges into receiving environment [24].

The results were similar to BOD_5. They showed that the higher values were obtained in sample points R1M and R4M (Figure 4).

The significant value of BOD_5 in the Pigeon Faecal Unit (R2A) compared to the other samples points were due to the presence of pigeon faecal matter rich in biodegradable organic matter. Indeed, All units of modern and artisanal tanneries were characterized by a low BOD_5 and a high COD ; the same results were reported by [8,17,28–30].

Additionally, the relationship between COD and BOD_5 were 11.81 $mg.L^{-1}$ for R1M, 7 $mg.L^{-1}$ For R4M and 7.64 $mg.L^{-1}$ for R2A (Figure 5), and were higher than the normalized value (≈ 2.5), that showed the effluent biodegradation.

The examination of the nitrogenous load showed that the concentration of NO_3^- was about 23 $mg.L^{-1}$ in the final effluent of artisanal tannery (RT) and the lowest values were observed in all sampling points and the same for the results of nitrite and ammonium ions (Figure 6). The nitrogenous load was very low compared to Moroccan standards of wastewater discharges into surface waters [24]. The results obtained in terms of nitrate, nitrite and ammonium ions were consistent with those of some authors [12,15].

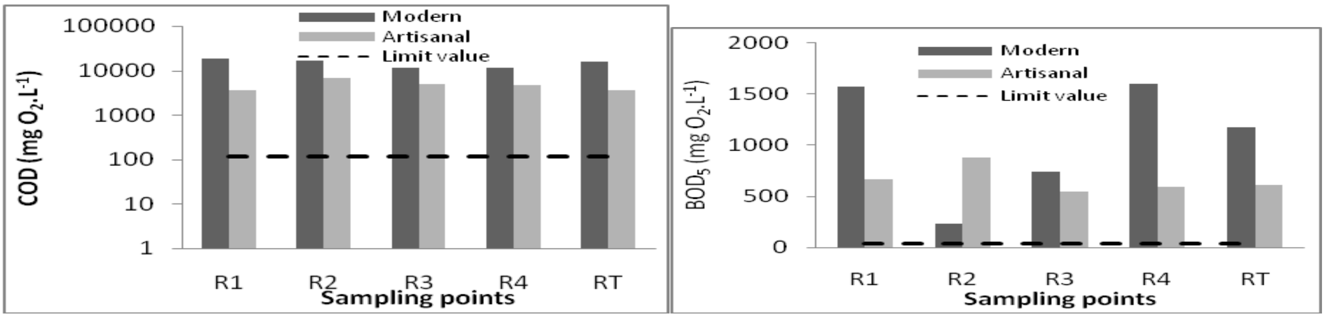


Figure 4: Physical and chemical water quality values in the two tanneries modern and artisanal. COD ($mgO_2.L^{-1}$); BOD_5 ($mgO_2.L^{-1}$).

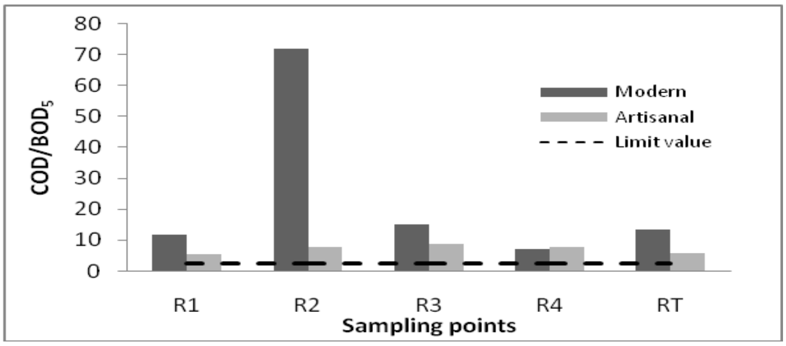
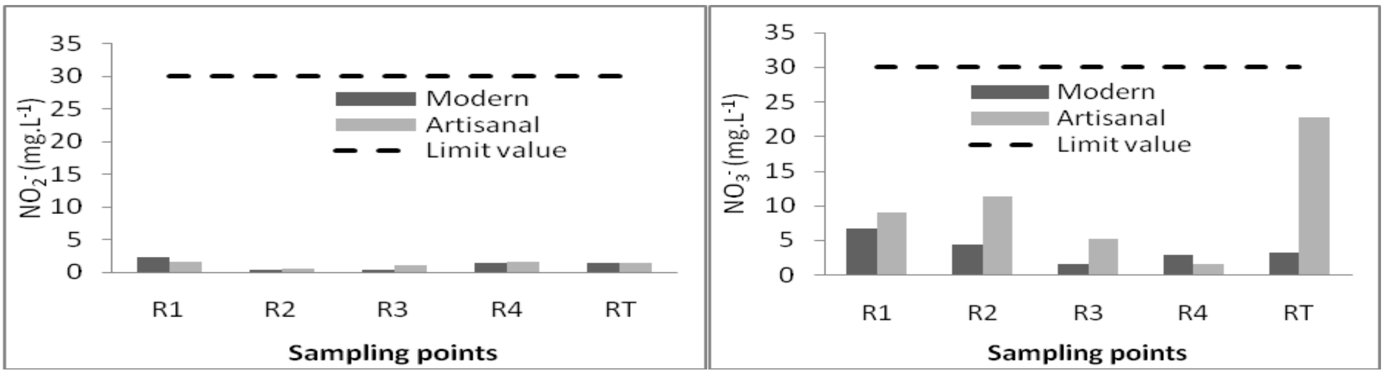


Figure 5: Ratio COD/BOD_5 of the effluent studied in modern and artisanal tanneries.



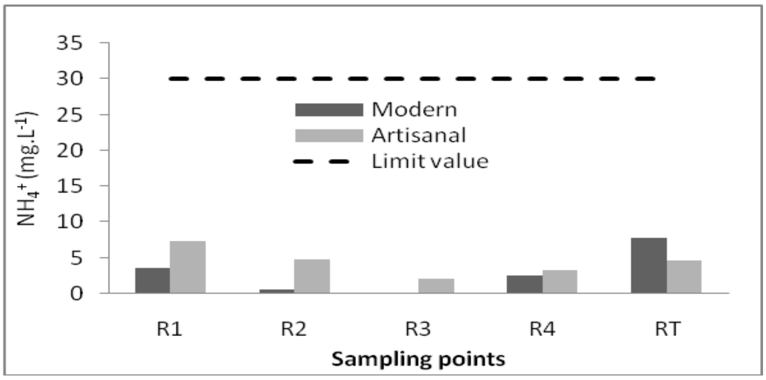


Figure 6: Chemical water quality values in the two tanneries Modern and Artisanal. NO_3^- ($mg.L^{-1}$) ; NO_2^- ($mg.L^{-1}$); NH_4^+ ($mg.L^{-1}$).

In the same way the effluent from all units, modern and artisanal, were characterized by low phosphate concentration (Figure 7). They were lower than the Moroccan standards [24].

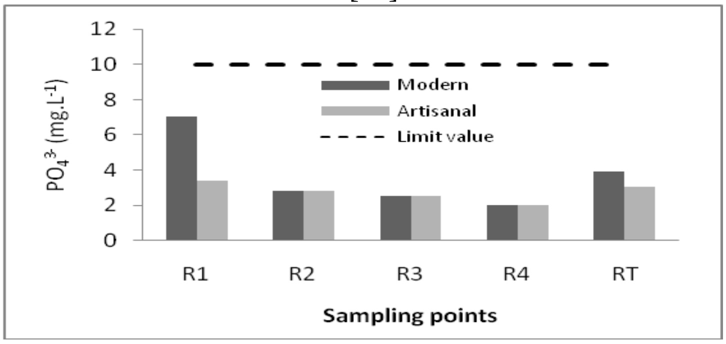


Figure 7: Chemical water quality values in modern and artisanal tanneries: PO_4^{3-}.

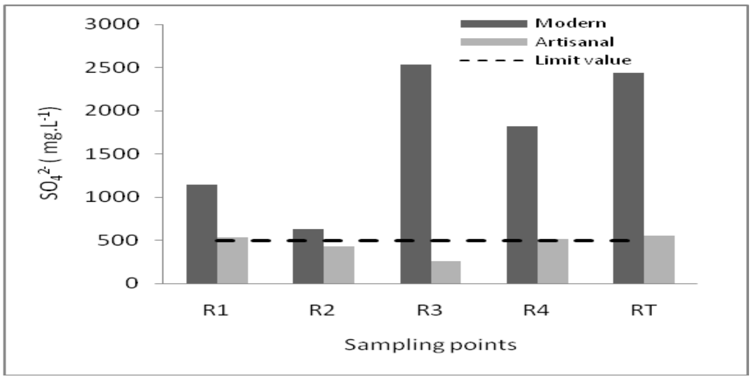


Figure 8: Concentration of Sulphate in Waste Solution derived from different sampling points in Modern and Artisanal tanneries.

The highest sulphate concentration was observed in all release of operating units investigated of the R2 for the modern tanneries because in these units the skin is treated by the use of deliming agents and chromium sulphate, and lowest value was found in all units for artisanal tannery (Figure 8) The same results were found by several researches [15,31–33]. The effluents of modern and artisanal tanneries were all characterized by high concentrations of sulphide. The highest values were 1500 and 800 $mg.L^{-1}$ in respectively the unhairing-liming (R1M) and batch lime effluents (R1A) (Figure 9). Concentrations found in sulphide in different units of modern tanneries were comparable to the results obtained in previous works [18]. The effluents from the R2, R3 and RT units of the modern tannery have almost half

the load of that of unit R1 because sodium sulphide is used only during the unhairing liming and batch lime steps of the modern and artisan tannery respectively. R4's load sounds lower than other units, but it remains significant. The exposure to hydrogen sulphide causes watery eyes shallow breathing, and pulmonary disease. Thus, Hydrogen sulphide is considered as a poisonous substance, and it may generate knowledge loss or death after some breathing movements, which may have an impact on the fauna and flora. Consequently, this swage contaminates other water streams, so rational management of water resources and the preliminary treatment of sulphide will decrease environmental risks associated with the upload of wastewaters in the raw state of water sanitation. As to the R3 and R4 units of the artisanal tannery, there is an absence of sulphide ions because sodium sulphide is used at a lower degree.

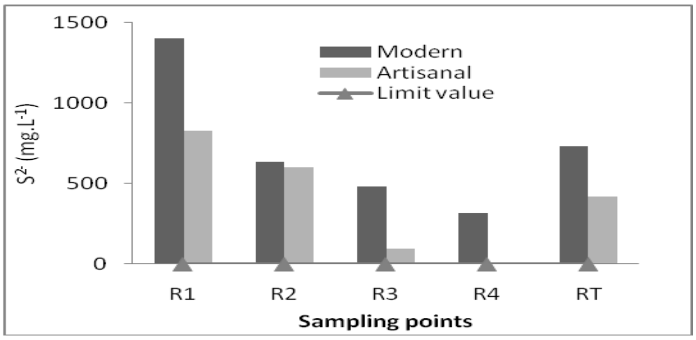


Figure 9: Concentration of Sulphide in Waste Solution Derived from different sampling points in Modern and Artisanal tanneries.

3.2. Optimum sulphide removal's conditions of synthetic and real wastewater by precipitation

Experiments with synthetic wastewater were conducted to determine the optimal pH for sulphide removal. The pH medium adjustment was controlled by addition of HCl or NaOH (0.1M) to attain pH values from 4.5 to 12.5. Optimization of pH was studied for fixed sulphide ions concentration (1500 mg.L^{-1}) in synthetic wastewater and ferric ions concentration of 1.2 mol.L^{-1}. Analysis of the results listed in Figure 10 allowed us to conclude that the higher removal obtained was about 90% for an optimum pH of 8.5. In acidic medium, the sulphate was formed and observed during the adjustment of pH with a white colour in the beaker.

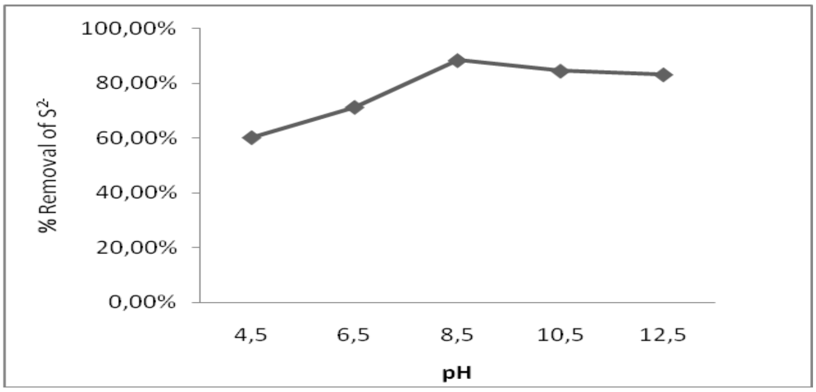


Figure 10: Effect of pH on % of sulphide removal of synthetic solution.
Operating Conditions: [Fe^{3+}] = 1.2 mol.L^{-1}, T = 24 ° C, t= 10 min, V= 150 rpm, [S^{2-}]$_{Synthétique}$ = 1500 mg.L^{-1}.

Figure 11 below illustrates the effect of time and speed and its dosages on sulphide removal. We can observe that in optimum pH and dosage of ions Fe^{3+}, the time and the speed have almost no influence on the quality of treatment [34].

10 min of rapid stirring (150 rpm) is enough for destabilization of colloidal particles and suffice to growth of floc pollutants in studied wastewater to reduce the abatement rate of the sulphide.

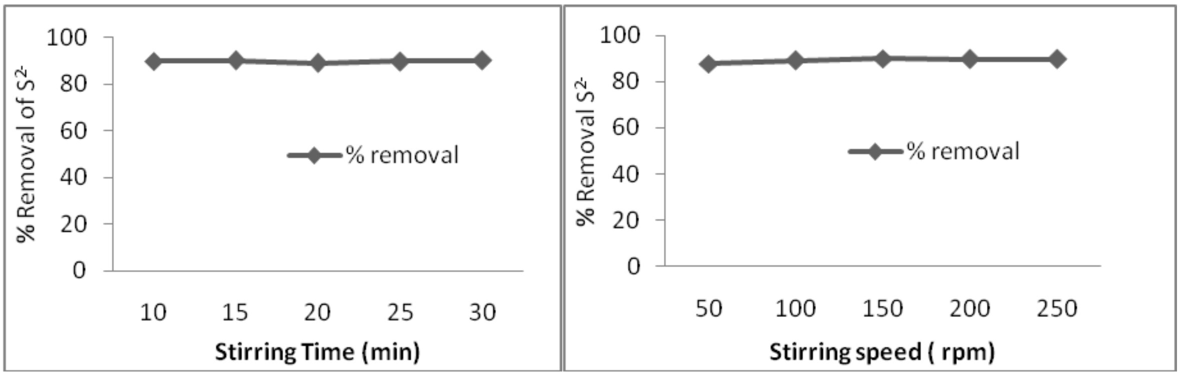


Figure 11: Effect of the time and speed on Sulphide removal of synthetic solution.Operating Conditions: $[Fe^{3+}]$ = 1.2 $mol.L^{-1}$, pH= 8.5, T = 24 ° C, $[S^{2-}]$ Synthétique = 1500 $mg.L^{-1}$.

Figure 12, the effect of the ions ferric dose and its dosage on the sulphides removal for each initial sulphide concentration in synthetic wasterwater (from 500 to 2000 $mg.L^{-1}$). As it is seen in Figure 12, the removal efficiency of sulphide increased proportionally by increasing the dosage of ions ferric (Fe^{3+}) concentrations until stabilisation for the same concentration of the sulphide ion solution. For the focus on sulphide ions is weak ; they are respectively of 0,6 ; 0,8 ; 1,2 et 1,4 $mol.L^{-1}$ of Fe^{3+} for charged solutions in 500, 1000, 1500, 2000 $mg.L^{-1}$ of sulphide ions respectively. The treatment is followed by decrease of the pH at values lower than 4. Last, time and stirring speed are reported not to have a huge influence on the sulphide precipitation. Reduction or even suppression of these effluents required removal of HS^- ions by precipitation, although the reason for this high removal is not clear. The same phenomenon was also reported by [20,21].

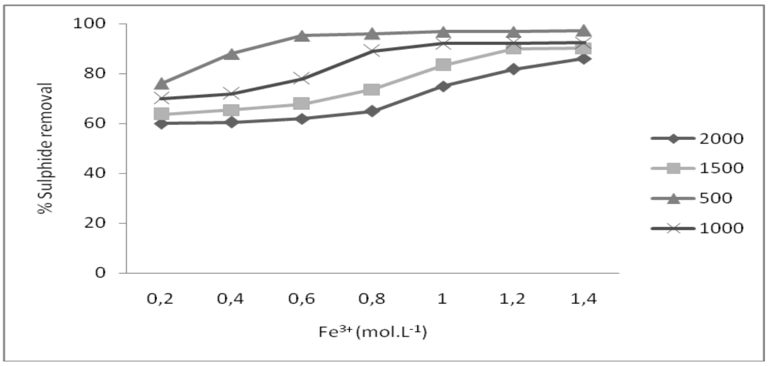


Figure 12: Effect of the dose of Fe^{3+}on sulphide removal of differentssulphide concentration of synthetic solution. Operating Conditions: pH= 8.5, t = 10 min, V= 150 rpm, T = 24 ° C, $[S^{2-}]_{Synthétique}$ = 500 ; 1000 ; 1500 ; 2000 $mg.L^{-1}$).

The pH in this type of treatment is very important since we seek to make ferric ion (Fe^{3+}) react with sulphide (HS^-) in this slightly basic medium (8.5) as it can be seen in the reactions 1 to 3 [19–21,35–37].

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

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

$$FeS + S^0 \rightarrow FeS_2 \quad (3)$$

According to reaction 1, ferric ion was first reduced to ferrous ions and oxidized sulphide into elemental sulfur. Then the product ferrous ions reacted with the hydrogenosulfure (HS^-) to produce FeS precipitate (Reaction 2), next the FeS

was converted to pyrite FeS_2 (Reaction 3). However, the reaction between ferric and sulphide was believed to be the dominant mechanism for sulphide removal. This was also supported by the change of the color of wastwater to black and after few second it changed into brown which was a typical color of respectively FeS and FeS_2, excess turbidity and a solid-liquid separation were observed with naked eyes. Even if very low O_2 in solution allowed dissolution of pyrite and a highly acidic solution form, in which H^+, SO_4^{2-}, Fe^{2+} were the major ions (Reaction 4). These results were generally consistent with experimental studies [38,39].

$$FeS_2 + 3{,}5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4)$$

Fe^{2+} formed in reaction 4 was oxidised to Fe^{3+} by O_2 (Reaction 5) and SO_4^{2-} produced in reaction 4 reacted with Ca^{2+} from the solution to form gypsum (Reaction 6).

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (5)$$

$$SO_4^{2-} + Ca^{2+} + 2H_2O \rightarrow CaSO_4{,}2H_2O \quad (6)$$

3.3. Caractérisation of precipitate by X-ray diffraction

Typical diffractogram for the solid reaction products is presented in Figure 13 and showed that gypsum was produced. This result was confirmed by the reaction 6.

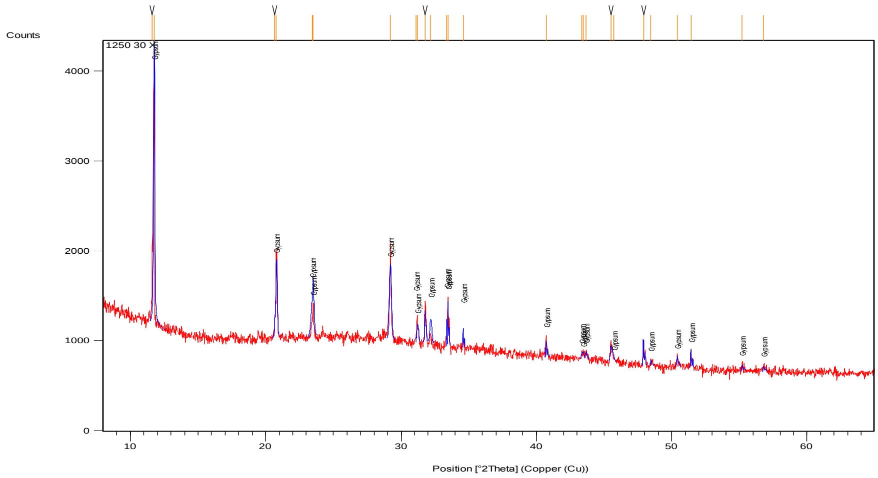


Figure 13: XRD spectra of the precipitate after treatment.

3.4. Treatment of the modern (R1M) and artisanal (R1A) tanneries's wastewater by precipitation

The results of the physicochemical characterization of the effluents of the different operating units of modern and artisanal tanneries reveal that the most polluted and sulphide-loaded effluents emanated from unhairing R1M and batching R1A units. The treatment of such effluents with ferric chloride under the optimal conditions obtained after the treatment of synthetic solutions (Figure 14) records that sulphide and COD abatement rate in the wastewater from the unhairing units of the modern and artisanal tanneries at optimum parameters that are found in the synthetic effluent. The sulphide removal reached about 90 and 92% at the optimum dose of 1.2 and 0.8 $mol.L^{-1}$ of Fe^{3+} for respectively modern and artisanal tanneries. Therefore, a maximum COD removal (92% for R1M and 96% for R1A) was achieved by optimal conditions followed by synthetic effluent.

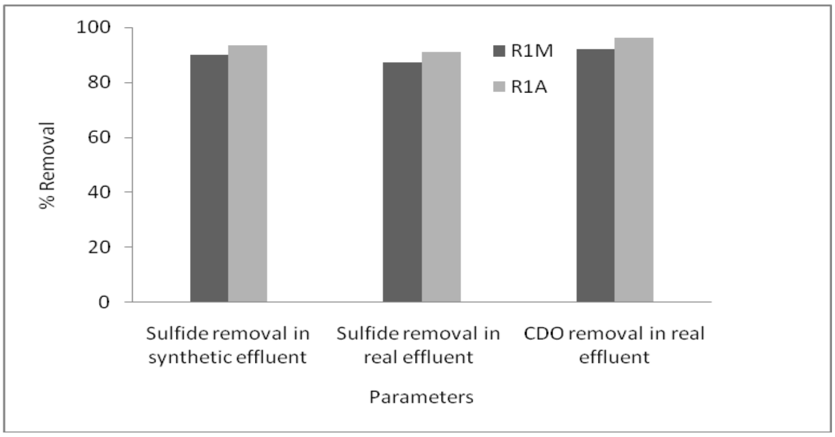


Figure 14: S^{2-} and COD abatement rate in the wastewater from the unhairing-liming units of the modern and artisanal tanneries. Operating Conditions: $[Fe^{3+}]_{Modern}$ = 1.2 mol.L^{-1}, $[Fe^{3+}]_{Artisanal}$ = 0.8 mol.L^{-1}, T = 24 ° C, $[S^{2-}]_{0(Synthetic\ Modern)}$ = 1500 mg.L^{-1}, $[S^{2-}]_{0(Synthetic\ Artisanal)}$ = 500 mg.L^{-1}, $[S^{2-}]_{0(Modern)}$ = 1500 mg.L^{-1}, $[S^{2-}]_{0(Artisanal)}$ = 820 mg.L^{-1}.

4. Conclusion

Bearing in mind that the leather industry has complex processes and use considerable chemical and water quantities, the physicochemical characterization of the effluents of the various skin treatment operating units shows that the wastewater of the different operating units is characterized by a variable load and different from one unit to another. This heavily depends on the treatment process and the chemicals used in each operating unit. In fact, they are generally basic and carry an organic, non-nitrogen and mineral load exceeding the standards for the discharge of wastewater into surface water. However, we note that wastewater from artisan tanneries is less polluting than that from modern tanneries and is slightly acidic. We also note that the wastewater from the unhairing of modern tannery and lime bath of the artisanal tannery units are heavily loaded with sulphide in addition to their high load of non-biodegradable organic matter.

For the removal of sulphide and COD from the effluent of these units by precipitation, we come across the following conclusions:

- Experiments with synthetic effluent showed that sulphide removal was almost complete and depended on the dose of Fe^{3+} and the concentration of sulphide in the initial effluent. Indeed, the reaction of sulphide ions with Fe^{3+} had the advantage of a distinct colour change due to the formation of FeS_2 which was oxidised to Sulphate to form Gypsum. The efficiency of the sulphide removal of effluent was highly dependent on the control of pH and Fe^{3+} doses.
- In optimum pH (8.5), time and speed (10 min, 150 rpm), the treatment of each sulphide concentration using the following sequences 500, 1000, 1500, 2000 mg.L^{-1} contained in the synthetic effluent with the respective dosage of 0.6, 1, 1.2, 1.4 mol.L^{-1} of Fe^{3+}. This demonstrated a sulphide removal of about 90%.
- The use of optimum results of synthetic effluents provide the following results:
- The concentration of sulphide and COD in real effluent of R1M was reduced with respectively corresponding removal of 87% and 92%.
- The concentration of sulphide and COD in real effluent of R2A was greatly reduced with respectively corresponding removal of 91% and 96%.
- The quantity of ferric ions depends on the charge of sulphide compounds, so that where the sulphide concentration increased, the demand for ions ferric grew.

We conclude by stating that treatment of the precipitation with the use of Fe^{3+} allows the simultaneous removal of sulphide and COD in the unhairing-liming and lime bath effluent in respectively modern and artisanal tannery. Thus, this can be an alternative solution for the treatment of sulphide in waste water from tannery processes.

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