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Combination of chemical and biological processes for the treatment of tannery effluent of Fez city in Morocco

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ABSTRACT

Several tannery effluent treatments were studied, but there was no process that could remove the total pollution of these effluents. Besides, most of those processes are expensive. In this study, a promising coupled treatment of tannery effluents was performed to eliminate the entire pollution load of these toxic effluents. The treatment of these effluents was by precipitation using ferric chloride coupling with the sequencing batch reactor (SBR) process. For the SBR system, a daily cycle treatment and a high organic load of 1.5 kg of COD d^{-1} m^{-3} were used. Concerning the results, this combined system provided very satisfactory outcomes, wherein removals were 99.89%, 99.98%, and 99.99%, respectively, for the chemical oxygen demand (COD), the sulfide ions, and the total chromium. Thus, the treated effluent is strongly conformed to the Moroccan standard of discharge. This result was not reached when these two systems were applied separately in previous studies. Therefore, this combined treatment can be an attractive and economic treatment for tannery effluent treatment.

Keywords: Tannery effluents; Toxicity; Coupled treatment; Precipitation; Ferric chloride; Sequencing batch reactor

1. Introduction

Chromium and sulfide are the major problems of tannery effluents [1]. In fact, chromium was known for its toxicity, especially its form VI. The hexavalent chromium is very carcinogenic and had harmful effects on human health [2]. Likewise, the oxidation of sulfides produces hydrogen sulfide (H_2S) gas, which is toxic and belonging to the greenhouse gases. This gas causes several serious human diseases such as the irritation of the skin and eyes, lung diseases, or respiratory paralysis [3]. For that reason, the remediation of these effluents before their discharge into the environment has been mandatory.

On the other hand, several chemical and biological treatments have been recently studied, namely, the precipitation using ferric chloride [4], the electrocoagulation [5], the coagulation [6], the activated sludge [7], and the sequencing batch reactor (SBR) using a high organic load [8] and a low organic load [9]. However, these processes have some operation limits. For example, although the treatment of tannery effluents by the SBR process gave the best removals using a low organic load, the treated effluent could not

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satisfy the Moroccan discharge standard in terms of sulfides and suspended matters [9]. Therefore, a combination of different techniques is recommended. In fact, there are also some combined treatments for the tannery effluents, such as the combination of two stages up-flow anaerobic sludge blanket (UASB)-ozonation-a biological aerated filter (BAF) systems [10], the coupling of coagulation and activated carbon adsorption [11], etc.

In Morocco, and Fez city, in particular, the tanneries cause many pollution problems. Consequently, many projects had been suggested for the treatment of tannery effluents. Among these projects, the combination of the precipitation with ferric chloride and the SBR was selected for the treatment of these tannery effluents of this city. In fact, these two treatments are inexpensive than other systems. Furthermore, this project will be performed at a high scale to reduce tannery pollution in this city.

Accordingly, the main objective of this study is the treatment of tannery effluents by coupling chemical and biological systems. It is worth mentioning that the chemical process was by precipitation using ferric chloride, whereas the biological process was through the SBR process using a high organic load and a daily cycle treatment.

2. Materials and methods

2.1. Sampling

Tannery effluents were collected from a tanning industry located in the industrial area "DOUKKARAT" in Fez city. Moreover, the sampling was a composite of four rejects and it was performed using the method described by Rodier [12]. As mentioned below, Table 1 demonstrates the physicochemical characterization results of these effluents.

2.2. Coupling of chemical and biological processes for the treatment of tannery effluents

2.2.1. Chemical system

In a beaker of 1 L (Fig. 1a), a volume of 400 mL of tannery effluent (pH = 9 ± 0.2) was added to a volume of 25 mL of ferric chloride solution (1.4 mol L^{-1}); under magnetic stirring at 150 rpm. The pH of this effluent was adjusted with a sulfuric acid solution (2 M) to achieve the optimum pH 8. After 15 min of agitation, the flocs or agglomerated substances were formed, and then, these flocs were precipitated pending

Table 1
Results of the physicochemical parameters of composite tannery effluents of Fez city in Morocco [8]

Parameters	Average values	Moroccan standard [13]
SS (mg L^{-1})	4,000 ± 100	30
COD (mg O_2 L^{-1})	14,500 ± 250	120
BOD_5 (mg O_2 L^{-1})	1,460 ± 90	40
PO_4^{3-} (mg L^{-1})	12.8 ± 1	2
S^{2-} (mg L^{-1})	410.6 ± 12.4	0.5
TKN (mg L^{-1})	698.48 ± 1.63	2
Total Cr (mg L^{-1})	920 ± 20.04	0.5

Fig. 1. Combination of precipitation and SBR systems for treatment of tannery effluent in the laboratory. Beaker for (a) chemical process, (b) pH neutralization, and (c) SBR process.

1 h. Otherwise, the effluent pH, the volume of ferric chloride solution including its concentration, and the stirring speed and time were optimized in a previous study [4].

After the decantation of those flocs (Fig. 1b), the supernatant was transferred to another beaker to adjust its pH because the supernatant was highly acidic. Therefore, the pH was adjusted to tolerated pH by microorganisms (pH = 7) using a sodium hydroxide solution (2 M). Finally, the effluent was passed to the SBR to eliminate the remaining pollution load.

2.2.2. Biological system

The SBR (Fig. 1c) is of pyrex and it has a capacity of 4 L. This reactor was attached to the peristaltic pumps (7554-95 Master flex L/S) to supply and withdraw the effluent. The aeration was maintained by a compressor (Snorkels TÜBAS FH 255-2050C), whereas the stirring is performed by a magnetic stirrer [9]. The treatment through this biological process involves four phases, which are: supply of the raw effluent, treatment, or aeration phase, decanting phase, and withdrawal of the treated effluent. These four phases compose a treatment cycle. Indeed, the treatment was performed according to the characteristics mentioned in Table 2. Meanwhile, it should be noted that the duration of each phase was maintained by timers.

This biological process is based on treatment with activated sludge in aerobic. The activated sludge was collected from the wastewater plant. Moreover, it should be highlighted that the station aims to treat the city's wastewaters before their discharge into the Sebou River.

2.3. Analysis method

The physicochemical parameters were analyzed, before and after this integrated treatment, to determine the abatement rates for each parameter and to show the effectiveness of this combined system. The chemical oxygen demand (COD), the biological oxygen demand (BOD_5), the total Kjeldahl nitrogen (TKN), the suspended solids (SS), the color, and the sulfide ions, were performed according to standard methods [12]. The pH was measured by pH-meter (Adwa pH-meter, model AD1000, Romania). Dissolved oxygen was determined by an oxygen-meter (AD630, Hungary). Mohlman index was determined according to the standard method. Meanwhile, the total chromium was analyzed by atomic absorption spectroscopy (ICP) (type Jobin Yvon Horiba) in the laboratory of innovation of Fez city.

Table 2
Characteristics of the SBR process

Volumetric organic load	1.5 kg of COD d^{-1} m^{-3}
Supply volume	200 mL
Activated sludge volume	600 mL
Working volume	3 L
Supply and withdraw time	5 min for each phase
Aeration phase	22 h 20 min
Decanting phase	1 h 30 min

2.4. Statistical analysis

ANOVA one way test was performed to compare this combined process and these processes applied separately (alpha value is 0.05). Moreover, *t*-test was also carried out to check which process was different. These tests were carried out in Microsoft Excel 2007.

3. Results and discussion

The results of the coupled treatment for tannery effluent are shown in Fig. 2. As demonstrated in Fig. 2a, the COD concentration was decreased during this combined system and it reached 12.12 mg O_2 L^{-1} after 1 week of treatment. Moreover, the average abatement rate was 99.89%. Indeed, this removal is higher than that found by the chemical process alone [4] even that of the biological process using the same conditions (high organic load and a daily treatment cycle) [8].

Concerning BOD_5, its concentration was also decreased during this integrated treatment. After that, the concentration was stabilized at 19 mg O_2 L^{-1} (Fig. 2b). In addition, the removal reached an average value of 98.84%. Likewise, this decrease rate is higher than that obtained by the SBR alone using the same processing conditions [8].

These abatements of COD and BOD_5 could be explained by the precipitation of organic or/and inorganic substances as flocs, which were formed by the addition of the ferric chloride solution within the effluent. Then, the remaining pollution was probably biodegraded within the SBR by microorganisms of the sludge, and/or these particles could be decanted as bioflocs during the settling phase which could be grouped through the sludge's microorganisms.

As well, the concentration of sulfide ions decreased from 410.6 to 0.08 mg L^{-1} (Fig. 2c), with an average removal of 99.98%. This removal was higher compared to that found using the same processes, wherein the abetment rates were 90% and 98.8%, respectively, for the precipitation and the SBR [4,8]. However, the major sulfide ions (S^{2-}) amount was removed during the chemical system. This could be explained by the reaction between the ferric chloride and sulfide ions (S^{2-}). This reaction produced the ferrous sulfur (FeS) and elemental sulfur (S°), and then, these elements were precipitated as flocs. These results are consistent with other studies [14–16], in which the reaction was strongly dependent on the ferric ions concentration and the pH as well [17,18]. After this chemical system, the treated effluent did not conform to the Moroccan standard [13], although the removal was more than 90%. So, the remaining amount of these sulfide ions was removed within the SBR, consequently, the treated effluent was strongly consistent with this release standard. Within the SBR process, the decline of sulfide ions could be related to the oxidation of these ions through the chemotrophic bacteria existing in the activated sludge [19].

As for pH (Fig. 2d), there was a high decrease within the effluent pH after the chemical precipitation. Thus, this decrease could be explained by the use of two acids, namely, sulfuric acid (used during the adjustment of optimum pH) and ferric chloride (used as a precipitating agent). After this chemical treatment, the effluent was severely acidic (pH = 3), and then it was adjusted to 6.5–8 for optimal bacterial

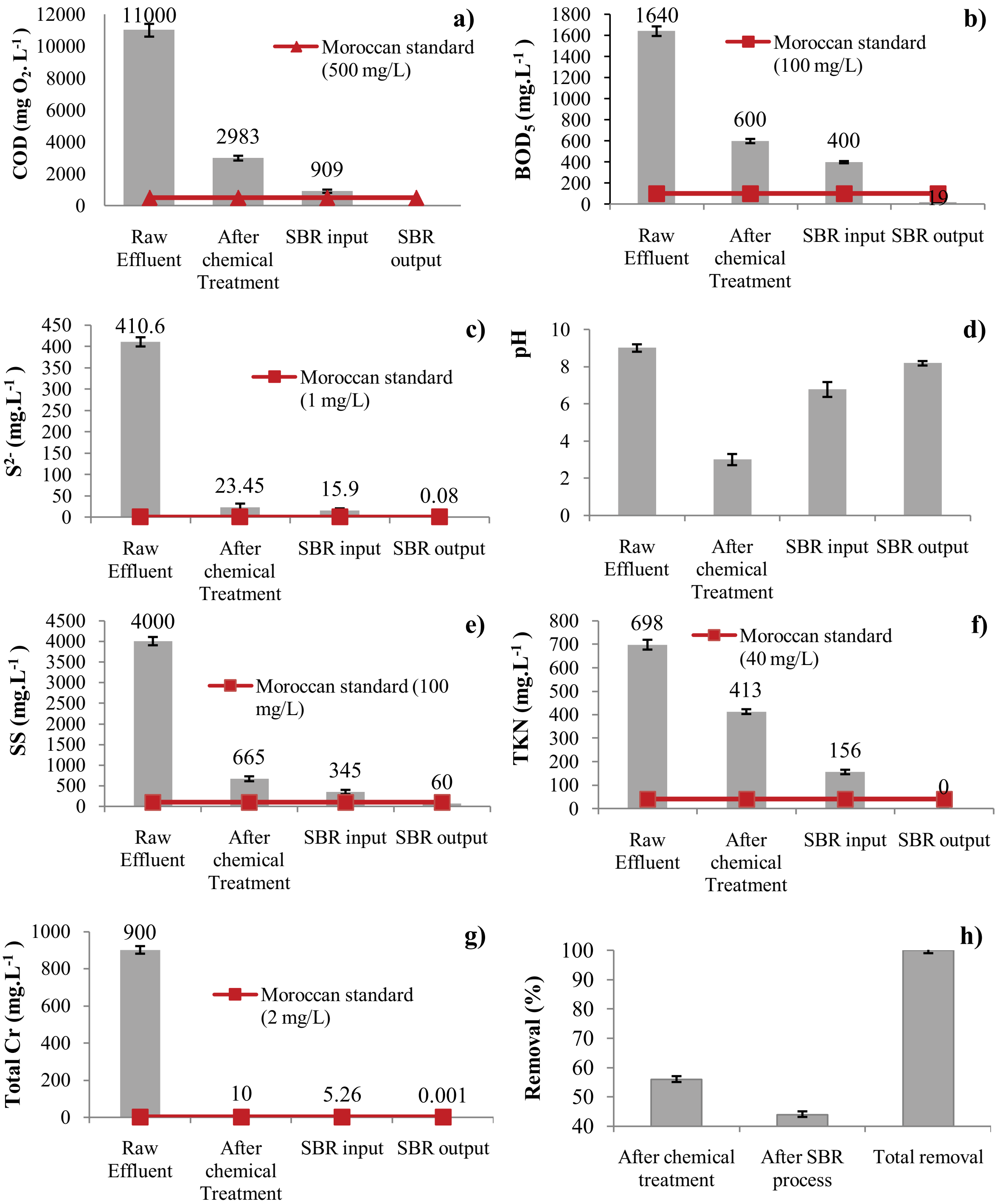

Fig. 2. Evolution of COD (a), S^{2-} (b), BOD_5 (c), pH (d), SS (e), TKN (f), total Cr (g), and color (h) during the coupled systems for tannery effluent treatment. *Hydraulic retention time (HRT) was 2 h for precipitation and 24 h for the SBR process. *Physicochemical analysis was daily performed before and after each treatment process. *These average values were results of 1 month of treatment. *SBR input values are the parameter values at the beginning of the treatment cycle (the decreased values are due to the effluent dilution within the reactor).

growth [20]. However, an increase in pH was observed in the treated effluent after the SBR. This was consistent with previous studies, wherein they explained this increase by the release of OH^- groups pending aerobic denitrification [8].

The concentration of suspended solids was also lowered (Fig. 2e), which reached 60 mg L^{-1} with an average abatement rate of 98.5%. Indeed, the chemical precipitation process removed an important part of the suspended solids. This could be explained by their precipitation as agglomerated substances after adding ferric chloride. Furthermore, this combined treatment increased the removal of suspended solids while comparing it to these two systems applied separately [4,8].

The TKN was completely removed within this integrated treatment (Fig. 2f). Otherwise, the TKN removal did not exceed 44% after the chemical precipitation, whereas the remaining amount was removed during the SBR treatment. This abatement could be due to the precipitation of nitrogen compounds through the agglomerated substances within both processes. Moreover, the TKN could be removed by the activated sludge's microorganisms, which could have a high ability to convert the organic and ammoniacal nitrogen to nitrogen gas through the nitrification and denitrification reactions. A recent study shows that simultaneous nitrification and sulfide oxidation processes could occur in an SBR process [21]. This could explain our high removals of nitrogen compounds and sulfide as well.

Fig. 2g shows the evolution of the total chromium concentration through this combined process. In fact, its amount was lowered from 900 to 10 mg L^{-1} after chemical precipitation and it reached 0.001 mg L^{-1} after the SBR system. Therefore, the chromium removal reached 99.99% after this coupled treatment, and then the treated effluent has been conformed to the Moroccan standard [13]. However, the SBR alone gave a lower abatement rate than that found in this study. As well as, the treated effluent could not satisfy the Moroccan discharge standard [8]. This abatement rate of chromium could be justified by the decantation of this metal pending the chemical process and the settling phase within the SBR treatment. In addition, other studies showed that the chromium can be precipitated within the solution having a pH between 6 and 10 [22]. Therefore, this metal removal could be also explained by the bioaccumulation and/or biosorption by the activated sludge bacteria in the SBR [23]. As a mass balance of chromium, 98.89% were removed through the precipitation process and 1.1% were removed within the SBR process, in which 99.9% were biosorbed by microorganisms. This result was confirmed by the isolation of three strains from tannery effluents, which have shown a high capacity of total and hexavalent chromium removal [24]. These strains were identified as *Bacillus* sp., *Enterobactera erogenes*, and *Bacillus pumilus.*

Figs. 2h and 3 present the color removal of the tannery effluent over this study, where the treated effluent looks as freshwater. As shown, the combination of the precipitation and the SBR processes gave a high color removal, which was 99.98%. In fact, the chemical process removed only 56% of color, then, the remained color was eliminated by the biological process. Additionally, the discoloration rate of our coupled treatment is higher than that obtained by the biological treatment alone [8].

Fig. 4 reveals the evolution of dissolved oxygen, suspended solids, Mohlman index, and pH within the mixed liquor. As shown, the dissolved oxygen values were higher than 6 mg L^{-1} over the treatment period; consequently, these values indicate good aeration in our reactor. The pH values were around 7.4 ± 0.4 which is an optimum pH for bacterial growth. Concerning suspended solids, their amount increased from 4 to 7 g L^{-1}, and hence this increase reflects the bacterial growth of sludge's microorganisms within mixed liquor. As for Mohlman index, their values were between 110 and 124 mL g^{-1}. These values show a good decantation phase in the SBR process, the presence of filamentous bacteria (responsible for the formation of bioflocs) with a sufficient amount, and the absence of bulking phenomenon. These parameters were optimum for greater treatment of our composite tannery effluent. Also, they could explain and confirm our treatment results.

Otherwise, ANOVA one way test confirmed that the combination between the precipitation and the SBR systems affected significantly on the removal of all physicochemical parameters ($P = 0.001 < \alpha = 0.05$).

Otherwise, a combination of a two-stage UASB reactor, an ozonation reactor, and a BAF in series, gave high abatement rates which were 97.5%, 95.6%, 94.6%, 93.5%, and 97.4% for COD, total Cr, TSS, total nitrogen, and color, respectively [10]. Moreover, a coupling of coagulation and adsorption systems showed also huge removals, which were 97%, 99%,

Fig. 3. Color removal of the composite tannery effluent during the combined treatment.

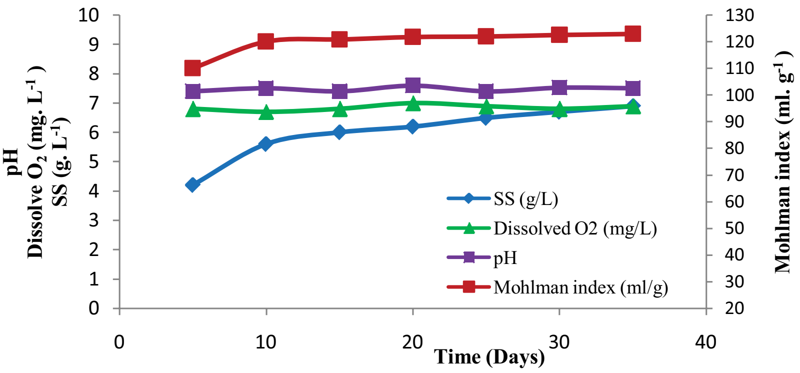

Fig. 4. Evolution of dissolved oxygen, suspended solids, Mohlman index, and pH within the mixed liquor over the treatment of tannery effluent by SBR.

and 99.7% for TSS, color, and total chromium, respectively [11]. The combination of sequential electrocoagulation and UV photolysis processes afforded 94.1% of COD reduction [25]. Pire-Sierra et al. [26] also coupled the coagulation with ferric chloride and the SBR process, but they performed firstly the biological process following by the chemical treatment [26]. This combined treatment gave 80%, 82%, and 99.6% for COD, TN, and N–NH^{4+}, respectively.

As shown, although two inexpensive processes were used, the coupled treatment demonstrated great removals than these all combined processes above-mentioned. Thus, this combined treatment will be a promising treatment for tannery effluents and could be performed at a large scale.

4. Conclusion

The coupling of chemical and biological systems for the tannery effluent treatment gave excellent results. The chemical treatment was with precipitation using ferric chloride, whereas the biological treatment was with the SBR using a high volumetric organic load and one daily cycle. This combined process had a significant effect on all removals of physicochemical parameters. Moreover, the abatement rates were 99.89%, 99.98%, 98.84%, 98.5%, 100%, and 99.99%, respectively, for COD, sulfide ions, BOD_5, suspended solids, NTK, and total chromium. Besides, the treated effluent could strongly satisfy the Moroccan standard of discharge. In conclusion, this combined treatment could be a promising and new approach for the treatment of tannery effluents of Fez city in Morocco.

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