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Sequencing batch reactor: inexpensive and efficient treatment for tannery effluents of Fez city in Morocco

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ABSTRACT

The toxicity of tannery effluents and the sludge (output of a wastewater treatment plant) requires mandatory treatment. In this study, the main objective was the treatment of tannery wastewater by the sequencing batch reactor (SBR) instead of the non-biodegradability of these effluents. This system was based on aerobic treatment through the activated sludge, and it was inexpensive in particular. As a result, the treatment provided excellent results by using an organic load of 0.3 kg of COD D^{-1} m^{-3} (COD – chemical oxygen demand) and a treatment cycle of 12 h. Additionally, the abatement rates were respectively 98.17%, 97.5%, 97.35%, 95.45%, 98.6%, 99.57%, and 96.1% for the COD, the biochemical oxygen demand (BOD_5), the suspended solids, the total Kjeldahl nitrogen, the orthophosphate, the sulfide ions, and the total chromium. Moreover, the treated effluents conformed to the Moroccan standards of discharge. Meanwhile, the by-product of wastewater plant showed the possibility of using this sludge as inoculums in other wastewater treatment plants.

Keywords: Toxicity; Treatment; Tannery effluent; Sequencing batch reactor; Organic load; Activated sludge

1. Introduction

Water has been a global concern in recent years. This indispensable and irreplaceable resource is particularly poorly distributed [1]. In fact, 4.3% of the world population has only 0.67% of renewable freshwater resources [1]. In addition, the necessity for water resources increases strongly. This is mainly because of human activities and industrialization in particular.

In Morocco, Fez city is considered as the city of crafts, which includes several and various traditional and modern artisanal units, namely the tanneries. These tannery industries are known as a source of pollution in the world [2] in view of the chromium and the sulfide present in their effluents. These toxic effluents have harmful impacts on human health and the environment, particularly water [3]. Therefore, the treatment of these effluents before their rejection in the natural environment is absolutely essential.

According to the literature, several treatment systems of tannery effluents were studied in Morocco, but they often were the physicochemical treatments such as microfiltration [4,5], precipitation with ferric chloride [6] and

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electrocoagulation, etc [7]. Indeed, most of those treatment systems are expensive or inefficient.

On the other hand, a previous study showed that the ratio biochemical oxygen demand (BOD_5)/COD (COD – chemical oxygen demand) is lower than 0.2 for tannery wastewater of Fez city. For that, the biological treatments were not effective for these effluents [8]. Despite that, there are few studies on tannery effluent treatments by biological systems such as the sequencing batch reactor (SBR) system. The SBR system shows various advantages especially the ease of installation, flexibility, easy control of the studied parameters, and the possibility to study the kinetics of different parameters [9]. Furthermore, the SBR was also known by its higher abatement rates for the COD, the BOD_5, the nitrogen, the phosphorus, and the suspended solids (SS) [10]. Besides, the SBR system is an inexpensive process due to the use of a single reactor for all treatment steps (aerobic treatment, nitrification/denitrification, and phosphorus elimination), and without using any chemical agent.

Otherwise, solid waste or the residue of the wastewater treatment plants is also a problem for the environment, because it includes a lot of microorganisms. Hence, we aimed to valorize this solid waste as activated sludge within the SBR system.

The objective of the present work was the treatment of inorganic effluents 'tannery wastewater' with the biologic process which is the SBR system. As well, a low organic load and two treatment cycles per day were used through this treatment to show their effect. Simultaneously, the by-product of the wastewater treatment plant of Fez city will be used as an activated sludge in our reactor.

2. Material and methods

2.1. Activated sludge

The activated sludge is either solid waste or by-products of the sludge's sector of the wastewater treatment plant in Fez city in Morocco. This plant aims to treat the city's wastewater before being released into the Sebou River.

2.2. SBR system

The reactor is of Pyrex (France) and it has a capacity of 4 L. This reactor was attached to peristaltic pumps (7554-95 Master flex L/S) for the control of the supply and withdrawal of the effluent. The air was injected by a compressor type of snorkels TÜBAS FH 255-2050C, while the agitation was performed by a magnetic agitator (Fig. 1) [8]. In addition, the treatment was carried out by using 3 L as total volume, two daily treatment cycles, and a low organic load in the order of 0.3 kg of COD D^{-1} m^{-3}. As well as, each treatment cycle was 12 h with an aeration phase of 10 h 20 min and a decantation phase of 1 h 30 min. It is worth mentioning that the duration of each phase was maintained by timers.

2.3. Tannery effluent

The tannery effluents were collected from a modern tannery located in an industrial area "DOUKKARAT" in Fez city in Morocco, which treats only the bovine hides. The sample was a composite type (Fig. 2) [8]; whose sampling and conservation were according to the method described by Rodier [11]. The composition of the tannery effluent is shown in Table 1, while the analyses of physicochemical parameters are described in the method of analysis.

2.4. Method of analysis

The performance of the SBR process was studied by physicochemical analyses. These were carried out before and after the treatment.

The analyzed parameters were pH, COD, BOD_5, SS, total Kjeldahl nitrogen (TKN), ammonium ions (NH_4^+), nitrate ions (NO_3^-), orthophosphates ions (PO_4^{3-}) and sulfide ions (S^{2-}). These parameters were analyzed using the

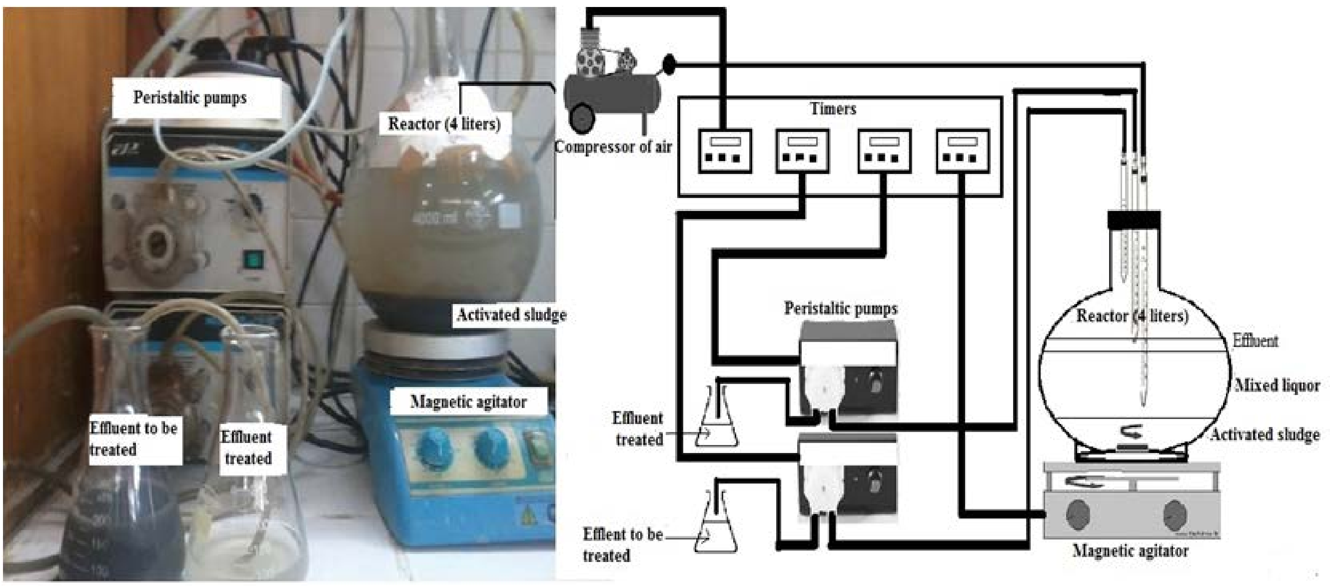

Fig. 1. Sequential batch reactor system [8].

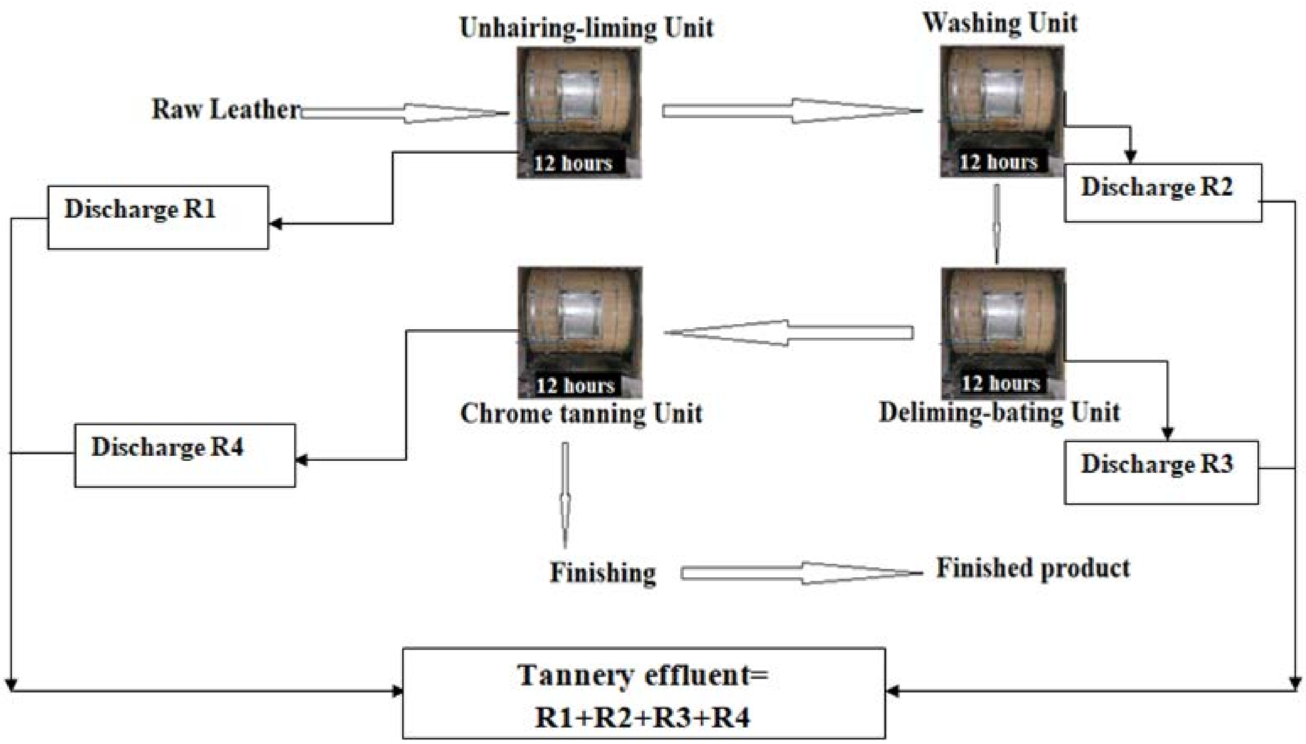

Fig. 2. The tanning process of a modern tannery industry in Fez city.

Table 1
Physicochemical characterization of composite tannery effluent [8]

Physicochemical parameters	Average values	Moroccan standard [12]	Heavy metals	Average values	Moroccan standard [12]
pH	9 ± 0.2	5.5–8.5	Cr (mg L^{-1})	920 ± 20.04	0.5
SS (mg L^{-1})	4,000 ± 100	30	Al (mg L^{-1})	5.44 ± 0.6	10
COD (mg of O_2 L^{-1})	14,500 ± 250	120	Fe (mg L^{-1})	3.9 ± 0.4	5
BOD_5 (mg of O_2 L^{-1})	1,460 ± 90	40	Ni (mg L^{-1})	0.44 ± 0.06	5
NH_4^+ (mg L^{-1})	60.6 ± 2.5	40	Cd (mg L^{-1})	0.2 ± 0.07	0.2
NO_3^- (mg L^{-1})	15.3 ± 1.5	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	20			

methods described in Table 2. On the other hand, the heavy metals were analyzed by atomic absorption spectroscopy or inductively coupled plasma - spectroscopy type Jobin Yvon Horriba (France) at the City's Innovation Laboratory (Fez, Morocco).

3. Results and discussion

3.1. Performance of the SBR process

The results of the tannery effluent treatment by the SBR system are presented in Table 3. Instead of a slight increase of pH, the treated effluent conforms to the Moroccan standard of rejection. As for the other parameters, a decrease in their amount was observed with higher abatement rates (Table 3). Thus, the treatment of these effluents through the SBR using a low load (0.3 kg of COD D^{-1} m^{-3}) gave the best removals than high and medium organic load (a high load (1.5 kg of COD D^{-1} m^{-3}) and a medium load (0.7 kg of COD D^{-1} m^{-3})), which were studied in a previous study [8]. As result, the microorganisms of activated sludge could be strongly adapted with the low organic load of this wastewater, and then, the biodegradation of our effluents. Otherwise, the polluting substances could be decanted as bioflocs during the settling phase.

3.1.1. Evolution of the COD, the BOD_5, and the SS

According to Fig. 3, the COD was decreased from 4,800 to 280 mg of O_2 L^{-1} after 5 d of treatment, while the treated

Table 2
The analysis method of physicochemical parameters

	Method and equipments	Standard
pH	Was measured by pH-meter (Adwa pH-meter, Model AD1000, Romania)	
COD	Was measured by colorimetric dosage by spectrophotometric (SELECTA LIB-030M, Spain) preceded by mineralization in COD meter (BINDER COD-meter, Model ED 53 # 02-393770, Germany)	AFNOR T90-101 [11]
SS	Were determined by centrifugation of a wastewater volume	Standard NF T90.105 [11]
S^{2-}	Were measured by titration	Standard NF T 60-203 [11]
NO_3^-, NH_4^+, PO_4^{3+}	Were determined by colorimetric dosage by spectrophotometric (SELECTA, Model LIB-030M, Spain)	AFNOR T90-012, T90-015 [11]
BOD_5	Was measured by the incubation method during 5 d using an OxiTop (Lovibond Thermostat Cabinet, Germany)	Standard NF EN 1899-1 [11]
TKN	Was measured by mineralization following by distillation (SELECTA, Spain)	AFNOR T90-110 [11]

Table 3
Results of physicochemical parameters before and after treatment of tannery effluents from Fez city by the biological system 'SBR'

Physicochemical parameters	Average values of tannery effluent	SBR input (beginning cycle)	SBR output (end of cycle)	Removal (%)	Moroccan standard [12]
pH	9 ± 0.2	7.4 ± 0.3	7.59 ± 0.2		5.5–8.5
COD (mg of O_2 L^{-1})	14,500 ± 250	4,933.4 ± 100	90.1 ± 0.1	98.17	120
BOD_5 (mg of O_2 L^{-1})	1,460 ± 90	1,200 ± 40	30 ± 2	97.5	40
SS (mg L^{-1})	4,000 ± 100	3,021.3 ± 60	80 ± 3	97.35	30
TKN (mg L^{-1})	698.48 ± 1.63	286 ± 1.4	13 ± 0.5	95.45	20
NO_3^- (mg L^{-1})	15.3 ± 1.5	12.85 ± 0.24	0.7 ± 0.04		40
NH_4^+ (mg L^{-1})	60.6 ± 2.5	50.4 ± 0.2	1.35 ± 0.04		40
PO_4^{3-} (mg L^{-1})	12.8 ± 1	4.3 ± 0.3	0.06 ± 0.005	98.6	2
S^{2-} (mg L^{-1})	410.6 ± 12.4	140 ± 3	0.6 ± 0.05	99.57	0.5
Cr (mg L^{-1})	920 ± 20.04	12.4 ± 0.1	0.484 ± 0.05	96.1	0.5

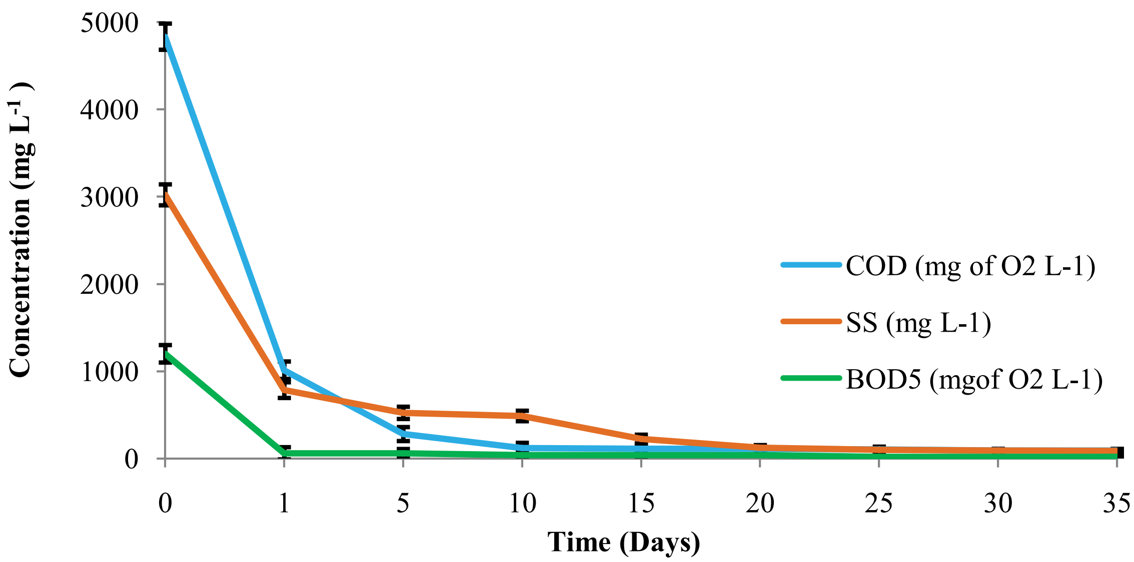

Fig. 3. Evolution of the COD, the BOD_5, and the SS during the treatment of tannery effluents by the SBR.

effluent is still out of the Moroccan standard of rejection (120 mg of O_2 L^{-1}). The abatement was progressively increased until the stabilization of COD concentration. Consequently, its amount achieved 90 mg L^{-1} with 98% of removal. This decease rate is higher than that found by other researchers [13]. This difference could be because of the use of a high organic load (1.9–2.1 kg of COD D^{-1} m^{-3}).

As for the BOD_5 (Fig. 3), its concentration was also decreased from 1,200 to 60 mg of O_2 L^{-1} after 5 d of treatment. However, the treated effluent did not conform to the Moroccan standards (40 mg of O_2 L^{-1}). After 25 d, the BOD_5 concentration reached 20 mg of O_2 L^{-1} with a removal of 97.5%.

Concerning the SS (Fig. 3), their amount was diminished from 3 g L^{-1} to 200 mg L^{-1} after 15 d of treatment, and then it was fixed at 80 mg L^{-1} after 30 d of treatment. Besides, the abatement rate achieved 97.35%.

Fig. 3 shows that the decrease of the COD, the BOD_5, and the SS is simultaneous. This could be the result of the performance of the used sludge. Moreover, this performance is probably due to the adaptation of this sludge with our tannery effluent (as mentioned previously), which was proved by the increase of the sludge amount. In fact, this increase was reflected by the increase of the SS amount from 3 to 7 g L^{-1} (Fig. 4) in the mixed liquor over the treatment. As well as, the tannery effluent has been rich in organic and inorganic pollutants [8]. Additionally, the pH of the mixed liquor was between 7.2 and 7.6 which is an optimum pH for microbial growth (Fig. 4). Furthermore, the high concentration of dissolved oxygen has shown good aeration which was in the order of 5.8–7 mg L^{-1} (Fig. 4). Consequently, these conditions were considered as the optimum conditions for the growth of the biomass and subsequently good biodegradation of our tannery effluents.

As well, the absence of the bulking phenomenon; during the treatment period; showed the presence of the filamentous bacteria with sufficient quantity in the reactor. This was proved by the sludge index which was between 50 and 150 g mL^{-1}. These bacteria are responsible for the formation of bioflocs which can be composed of microbes, inert particles, extracellular polymers, etc. Then, these bioflocs will contribute to the good separation (solid/liquid) pending the settling phase [8]. They can also adsorb organic and inorganic substances from our effluent. Certainly, this could justify the high removals presented in Table 3.

3.1.2. Evolution of the TKN, the sulfide, and the orthophosphate ions

The nitrogen compounds are represented by the TKN in Fig. 5. After 5 d of treatment, TKN concentration was reduced from 280 to 20 mg L^{-1}, with an abatement rate of 92.8%. After that, the removal of TKN was increased to 95.45% and the TKN amount was attained 13 mg L^{-1}. In fact, the decrease of TKN was accompanied by a decrease of ammonium (NH_4^+) and nitrate ions (NO_3^-). NH_4^+ concentration was reduced from 50.4 to 1.35 mg L^{-1} with the removal of 97.32%, whereas the abatement rate of NO_3^- was 94.16% with a decrease of its concentration from 12.85 to 0.7 mg L^{-1}.

The decrease of NH_4^+ could be related to nitrification reaction, wherein NH_4^+ will be oxidized to the NO_3^-. This oxidation could be carried out by nitrifying microorganisms present in the activated sludge; such as *Nitrobacter*, *Nitrosomonas*, etc. In fact, the nitrification is influenced by the pH and the temperature. The pH in the reactor was in the order of 7.2–7.6, while the temperature was around 25°C–30°C. Concurrently, these parameters showed that the conditions are optimum for the nitrification according to various studies [14].

The denitrification could explain the decrease of NO_3^-, which will be reduced to nitrogen gas by denitrifying bacteria, in particular *Pseudomonas*. The denitrification could also explain the increase of the pH within the treated effluent (Table 3) as a result of the liberation of OH^- groups during this reaction. Moreover, aerobic denitrification can be beneficial and advantageous for decreasing the costs of wastewater treatment plants in view of the elimination of tertiary treatment.

Fig. 5 shows the decrease of PO_4^{3-} during the treatment days, whose PO_4^{3-} the amount was lowered from 4 to 0.05 mg L^{-1} and the removal reached 98.6% after 30 d. This is probably due to the assimilation of these ions through the bacteria of the activated sludge [15]. According to other studies, a good phosphate removal requires the prolongation of

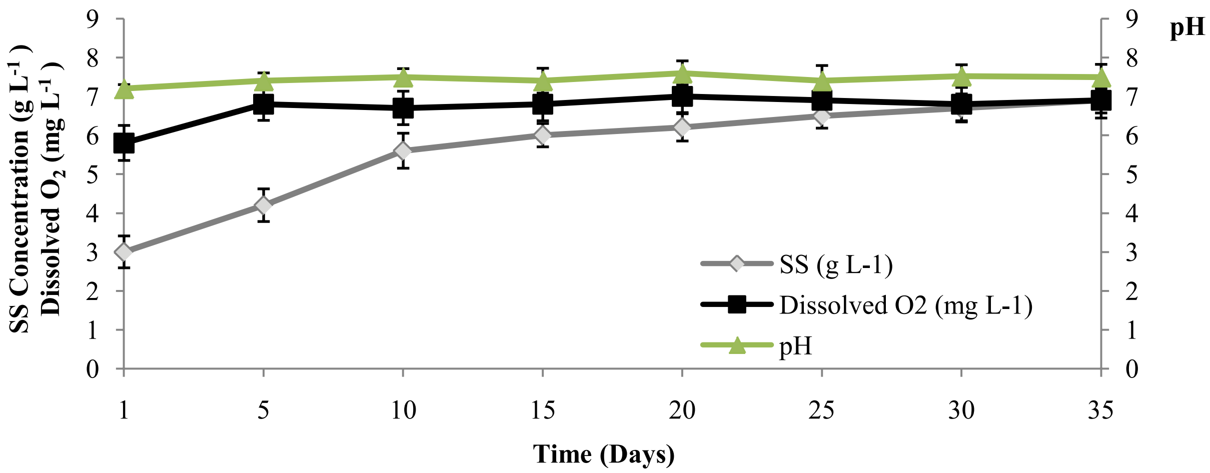

Fig.4. Evolution of the pH, the suspended solids, and the dissolved oxygen in the mixed liquor over the treatment by the SBR.

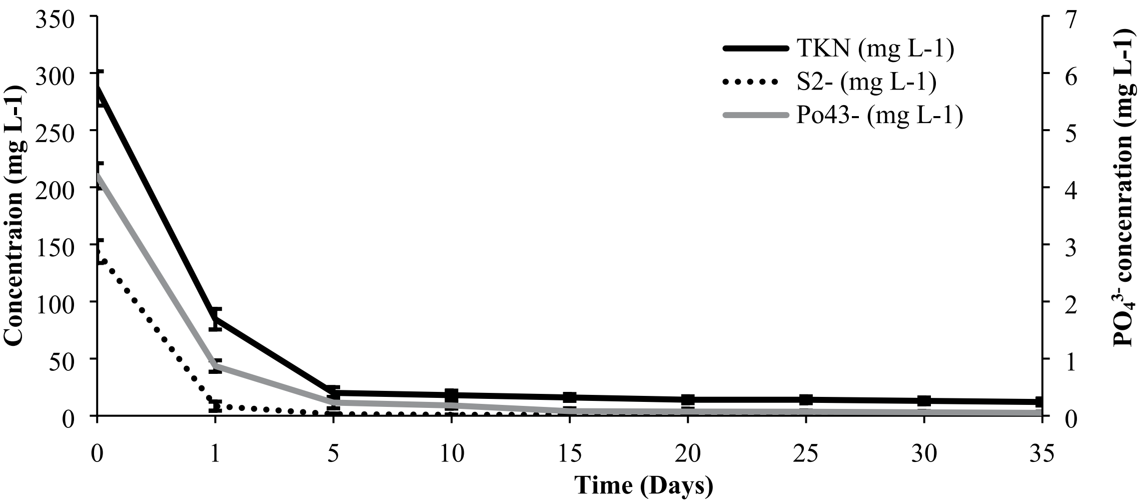

Fig. 5. Evolution of the TKN, the S^{2-} and PO_4^{3-} ions in the treatment of tannery effluents by the SBR process.

the decanting phase (anaerobic) with the extension of the aeration phase [16].

The sulfide ions have also been reduced (Fig. 5) during the treatment by SBR, in which S^{2-} concentration was decreased from 1.4 to 143.7 mg L^{-1} after 5 d. However, the treated effluent is still out of the Moroccan standard of discharge (0.5 mg L^{-1}). After 35 d, S^{2-} the amount of reached 0.5 mg L^{-1} with an abatement of 99.65%. Therefore, the treated effluent could satisfy the release standard. This removal could be related to the oxidation of these ions through the physicochemical reaction, and/or by aerobic or facultative anaerobic microorganisms present in the sludge such as *Thiobacillus* and *Pseudomonas* [17].

3.1.3. Heavy metals abatement

The results of the heavy metals are presented in Fig. 6. The total chromium concentration was reduced from 12.4 ± 0.1 to 0.484 ± 0.008 mg L^{-1} with a reduced rate of 96.1% after 30 d of treatment. Consequently, the treated effluent conformed to the Moroccan standard of rejection (0.5 mg L^{-1}). In this study, this abatement rate is higher than that found in a previous study [8].

The removal of the total chromium could be related to bioaccumulation or biosorption of this metal by the present bacteria in the activated sludge. Furthermore, the accumulation could be by adsorption, complexation, ion exchange or chelation [18]. On the other hand, studies showed that the chromium may be precipitated within the solutions, wherein the pH is between 6 and 10 [19]. Hence, this abatement could be also related to precipitation of this metal pending the decanting phase because of pH, which was between 7.2 and 7.6 in the mixed liquor.

4. Conclusion

The tannery effluent was characterized by heavy pollution load because of the massive amount of COD, BOD_5, SS,

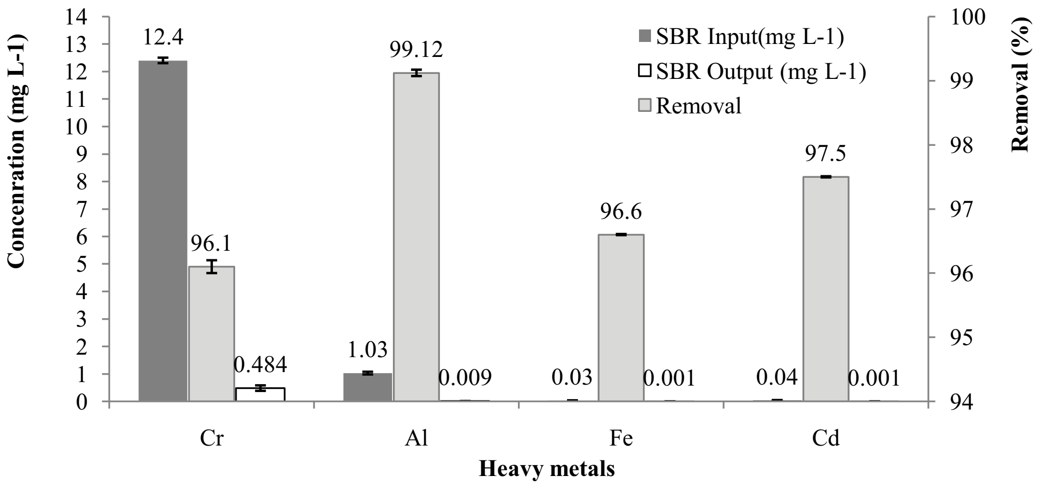

Fig. 6. Heavy metals amount before and after treatment by the SBR with their removal.

TKN, sulfide ions, and total chromium. Indeed, the treatment of effluent by SBR system gave satisfactory results after 30 d of treatment, and the abatement rates were respectively 98.17%, 97.5%, 97.35%, 95.45%, 98.6%, 99.57% and 96.1% for COD, BOD_5, SS, TKN, orthophosphate, sulfides ions and total chromium. Therefore, the effect of low organic load and a treatment cycle of 12 h on the performance of the SBR system was shown. Moreover, the treated effluent has conformed to the Moroccan standard of rejection in terms of the most parameters. However, the SS and the sulfides ions remained slightly out to this standard. Then, we envisage increasing the duration of the treatment cycle to 24 h or adding a second treatment to obtain a treated effluent which can definitely conform to our reject standard. Finally, the highest removals could reflect the performance of the activated sludge, which shows the possibility of using this waste as inoculums in other treatment plants.

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