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Valorization of two biological materials in the treatment of tannery effluents by filtration Treatment of tannery effluents by filtration

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Abstract

The present study aims at the valorization of two natural materials such as marine sand and wood sawdust in the treatment of tannery effluents taken directly from an industrial unit located in the Dokkarat, district of Fez. The technique used is that of column filtration. Physicochemical characterization such as COD, BOD_5, NH_4^+, Cr, etc. as well as microbiological analysis such as total germs (TG), Total Coliforms (TC), Faecal Coliforms (FC), etc. of the effluent, before and after filtration by the two supports used, were performed. The two filtering materials were previously characterized by DRX, IR-FTIR and SEM-EDX. The results obtained show that the latter two are effective in the treatment of the effluent, especially with the wood sawdust filter. Indeed, the removal rate (RR) of COD, BOD_5, SS, EC, SO_4^{2-} and Cr is in the order of 90.79%, 86.04%, 83.3%, 80%, 96.7% and 84.07% for the sawdust filter, while for the marine sand filter these values are of 81.5%, 79.9%, 79.2%, 66.6%, 94.4% and 56.15%, respectively.

Keywords: Tannery effluents, column filtration, characterization, marine sand, wood sawdust.

1.Introduction

Water was always inseparable from human activity; it is the essential element in all socio-economic processes, whatever the degree of development of society. Water requirement maintains its growth simultaneously to economic growth, which is creates an increasing pressure on the world's freshwater reserves [1]. Unfortunately, most industries discharge their effluents without any prior treatment [2]. Therefore to search for an effective alternative means to reduce negative effects has become a major global concern [3], forcing manufacturer to adopt water conservation and control technologies against pollution [1]. In Morocco, the tanning industry is one of the most active sectors; Its role in the economy of a country is far from negligible [4]. The Sebou basin is one of the most important water resources in Morocco [5]. It is considered to be a home to many industrial units concentrated especially in the districts and wilayas of Fez, Meknes, Kenitra and Sidi Kacem [4]. Fez is among the cities that pose a major pollution problem, whose discharges account for 40% of the total impact in the Sebou basin [6]. The aim of this work is to treat an effluent from a tannery in Fez city using the column filtration process with two different supports namely: wood sawdust (WS) and marine sand (MS). In order to obtain a very significant reduction in the organic, mineral and microbiological load of the effluent which is perfectly adapted to the socio-economic context of Morocco and which meets the general discharge standards given in the official bulletin 2013 [7]. The study consists of a characterization of the two supports by: X-ray Powder Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) Spectroscopy. The physico-chemical parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD_5), suspended solids (SS), ammonium ions (NH_4^+), nitrate(NO_3^-), nitrite (NO_2^-), sulfates (SO_4^{2-}), chromium (Cr), etc. and microbiological parameters such as TG, TC, FC, FS, SRC, E-coli were measured on the effluent sampled and the treated effluent. The RR relative to each parameter, making it possible to follow the efficiency of the latter two, is calculated from values found.

2. Material and methods

2.1. Material

2.1.1. Effluent used

We used synthetic waste obtained by mixing an equal volume of four effluents from different stages of tanning activity (Fig.1). These were previously taken from an industrial unit located in the Dokkarat district of Fez, in polyethylene bottles, transported to the laboratory in a cooler and stored at a temperature of 4 °C until use [8].

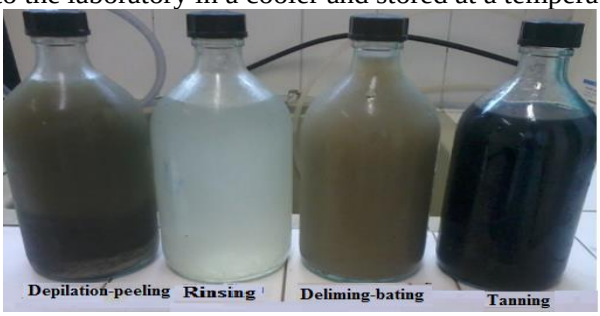

Figure 1: Effluent collected from four stages of the activity of the tannery

2.1.2. Filters used

The filter materials used are (MS) from Rabat city and (WS). These materials were crushed, sieved to obtain a fraction of diameter in the order of 63µm and then washed with MLLIPORE ultrapure water and dried in a MEMMERT oven overnight at 80 ° C [9].

2.2. Methods

2.2.1. Filtering materials characterization Techniques

The analytical techniques used for the characterization of filtering materials are:

- Structural Analysis by Infrared Transformed Spectroscopy of Fourier FTIR Bruker (Vertex70), coupled to a digital computer for plotting spectra between 400 and 4000 cm^{-1}.
- Morphological analysis by Quanta 200 FEI Scanning Electron Microscope, equipped with EDAX probe for surface microanalysis. Quantitative analysis of the elemental composition were studied using an energy dispersive X-ray system (EDX).
- Mineralogical analysis of sand by X-ray powder diffraction (X'Pert PRO diffractometer), operating with Cu radiations, functioning to 40 kV and 30 mA, in the range of 2θ between 4° and 79° with a pitch of 0.0170 .

2.2.2. Effluent Characterization Techniques

The pH of the effluent was measured using a pH meter XS instrument. The EC was measured using conductivity meter WTW LF 197.*3*, TetraCon 325 based type and the results were obtained at 25°C in mS/cm. SS, nitrogen ions such as NO_2^-, NO_3^-, NH_4^+, in addition to SO_4^{2-} and ortho-phosphate PO_4^{3-} were determined according to AFNOR standard techniques [10]. The determination of COD was performed by the potassium dichromate method with a COD meter of the HACH type and BOD_5 was measured by an OxitopR IS6 type BOD meter (ET 618-4 / 619-4). The analysis of some elements such as Arsenic (As); Beryllium (Be); Calcium (Ca); Cadmium (Cd); Cobalt (Co); chromium (Cr); Copper (Cu) and Iron (Fe) were realized by Atomic Emission Spectrometry with induced Plasma from the Innovation Center. Microbiological analyzes consist of counting total germs (TG), Total Coliforms (TC), Faecal Coliforms (FC), Faecal Streptococci (FS), staphylococcus, sulfito-reducing clostridia (SRC) and E-coli.

3. Results and discussions

3.1. Results

3.1.1. Characterization of filtering materials

3.1.1.1. Analysis by X-ray powder diffraction

Mineralogical analysis of the (MS) by X-ray powder diffraction is shown in Fig.2. The X-ray diffractogram shows the presence of several characteristic peaks of quartz and calcite. The peaks located at position 2θ such that: 20.92; 26.67; 27.27; 42.47; 50.18; 54.89; 59.97; 67.79 and 68.33 relate to Quartz. On the other hand, the peaks corresponding to position 2θ such that 23.11; 29.47; 33.14; 36.04; 39.50; 45.86; 47.56;48.46; 48.58; 56.73 and 77.33 are attributed to Calcite. These results are consistent with data from the literature [11]. The X-ray diffraction is a technique used to identify both the crystalline phases and the mineralogy of products [12]; the fibrous composition of (WS) is not appropriate for this type of analysis.

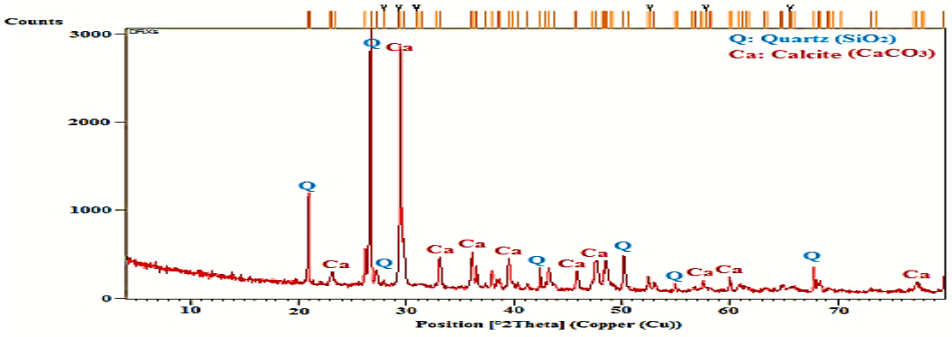

Fig 2: Diffractometric analysis of marine sand.

3.1.1.2. Analysis by Infrared Spectroscopy

- ***Marine Sand***

Examination of the MS spectrum illustrated in Fig.3 and obtained by FTIR exhibits a peak at 1791.92 cm^{-1} characteristic of OH stretch group, peaks located at 1411.49 and 866.61 cm^{-1} relating to CO_3 elongations vibration specific to calcite. In addition to this, the presence of the Si-O bond vibrations is confirmed by the peak at 787.13 cm^{-1} [13]–[15]. All of the groupings found are characteristics of Calcite and Quartz previously revealed by diffractometric analyzes.

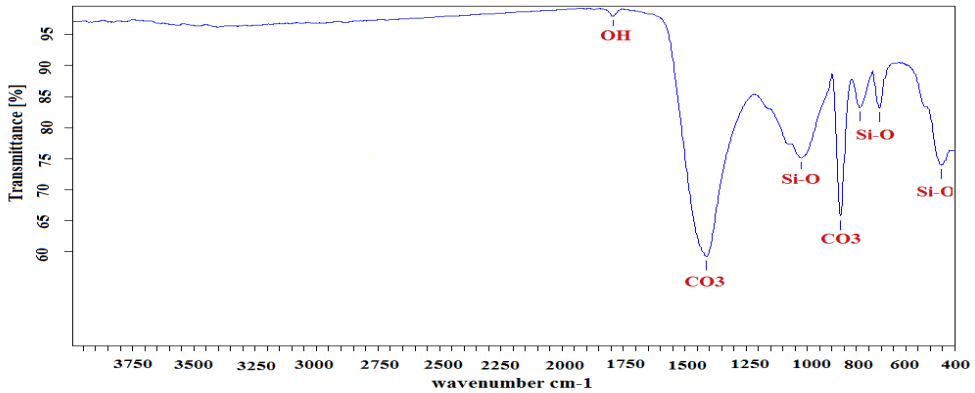

Fig 3: Infrared Spectroscopy Analysis of marine sand.

- ***Wood sawdust***

The transmission infrared spectrum; obtained for the (WS) is exhibited in Fig.4. The band at 3333.05 cm^{-1} corresponds to the OH stretch group of the aromatic and aliphatic structures of phenol is a group of lignin and cellulose. The absorption band which appears at 2894.72 cm^{-1} is assigned to the C-H asymmetric stretching vibration of the cellulose and the vibration located at 1506,552 cm^{-1} is attributed to the C=C deformation indicating the presence of an aromatic ring of lignin. The peak at 1021.68 cm^{-1} related to C-O and C-O-C stretching vibrations of cellulose. The peak at 893.28 cm^{-1} and the bands that appear in the frequency between 720-400 cm^{-1} are characteristics of C-H group in the cellulose. These results are in agreement with the data of the literature [16]–[21] . All the bands observed characterize the fibrous structure rich in cellulose, lignin and hemicellulose.

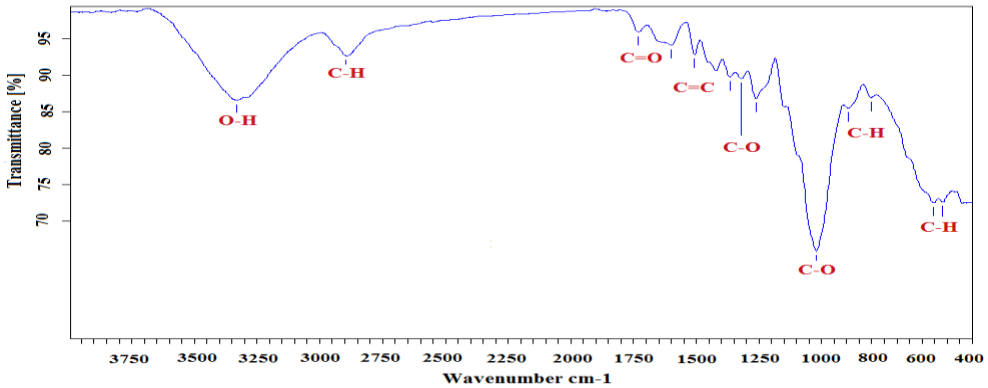

Fig.4. Infrared spectrum of wood sawdust.

3.1.1.3. Scanning electron microscopy coupled to EDX

- ***Marine Sand***

The elemental composition and morphology examination of the natural (MS), represented in Fig.5, displays that the surface microstructure has a porous and luminous appearance indicating the presence of crystals.

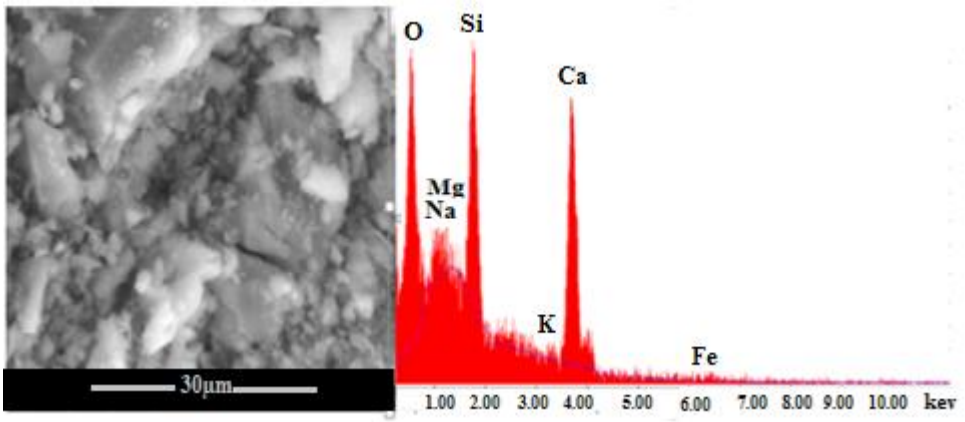

Fig 5: Morphological examination of sand by SEM-EDX.

The chemical composition of the sand as well as the percentage of the elements found by EDX shown in Table 1 prove the validity of the spectral analysis.

Table 1: Percentage of the elements found by EDX in marine sand.

Elements	Weight %	Atomic %
C	27.44	38.30
O	45.38	47.54
Na	3.55	2.59
Mg	0.96	0.66
Si	8.72	5.21
K	0.51	0.22
Ca	12.33	5.16
Fe	1.11	0.33
Total	100	100

- ***Wood sawdust***

The image of the WS obtained by SEM and the chemical composition found by EDX are illustrated in Fig.6 and Table 2. It has been infered that the latter appears to have both a fibrous and a branched appearance with the presence of certain intercalary spaces, which appear as luminous spots.

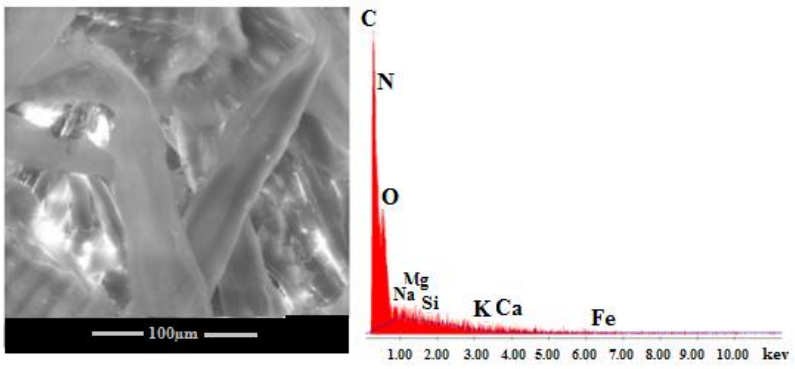

Fig 6: Morphological examination of wood sawdust by SEM-EDX.

Table 2: Percentage of the elements found in sawdust sand by EDX.

Elements	Weight %	Atomic %
C	33.66	38.70
O	37.79	37.27
Na	26.92	23.24
Mg	0.61	0.36
Si	0.30	0.17
K	0.15	0.07
Ca	0.19	0.07
Fe	0.27	0.09
Total	0.11	0.03

3.1.2. Characterization of the tannery effluent and removal rate

3.1.2.1. Raw effluent physico-chemical characterization

Table 3 displays the physicochemical characterization results of raw tannery wastewater. Moroccans discharge norms mentioned in the right most column are stipulated by the official bulletin 2013 [7]. In this respect, some values found are high and exceed the standards set by the official bulletin 2013 [7]. Therefore, the average value of the EC, which expresses the ionic concentration, achieved 15 µS/cm indicating that the effluent is rich in minerals [11]. Consequently, this important value is due to the use of significant quantities of salts during the leather manufacturing process. The average concentration of the SS exhibits a higher value in the order of 1500 mg/l, which explains the unclear appearance of the effluent [22]. The values of the average concentration in terms of BOD and COD_5 are 1025 mg O_2/l and 11439 mg O_2/l respectively with a BOD_5/COD ratio in the order of 0.09 mg O_2/l. In this case a low value of the latter can be explained by the excessive use of chemicals during the different tanning process [23]. As a result, the effluent cannot undergo biological treatment [24]. The SO_4^{2-} content reached 4200 mg/l ,this value is due in particular to the use of chromium sulfate as the tanning agent and aluminum sulfate during the deliming step [24].

Table 3*:* Physico-chemical characterization of the raw effluent from tanneries.

Parameters	Min values	Max Values	Average values	Moroccans discharge norms
pH	8.17	8.25	8.21	5.5-8.5
EC (mS/cm)	12	20	15	2.7
SS (mg/l)	1000	2000	1500	30
BOD_5(mg O_2/l)	850	1200	1025	40
COD (mg O_2/l)	9000	13878	11439	120
NO_2^- (mg/l)	0.9	1.26	1.08	-
NO_3^- (mg/l)	2.7	3.5	3.1	-
NH_4^+ (mg/l)	29.6	32	30.8	-
SO_4^{2-} (mg/l)	3900	4500	4200	500
PO_4^{3-} (mg/l)	2.3	4.2	3.25	-

Heavy metals concentrations detected in the raw effluent are shown in Table 4. The analysis of the values presented in the Table 4 show that Cr has a value outside the norms that is of the order of 4.42 mg/l. This result is expected because Cr is the essential element during the tanning step [24]. Other elements such as Ca, Cu, Fe, As, Be, Cd and Co are also presented but in reasonable quantities and comply with Moroccan discharge standards. However, the physicochemical characteristics do not meet the general discharge standards and are difficult to biodegrade showing a complex nature of the rejection which is very rich in chromium. Therefore, the latter necessarily requires a set of treatments able of rendering permissible the general discharge standards. Thus, the choice of filtration, using natural materials, would seem to be a primary and efficient treatment process that will allow us to follow the RR of the parameters which present unusual values.

Table 4: Heavy metals concentrations detected in the raw effluent.

Heavy metals	Concentration mg/l	Moroccan Releases Standards
As	<0.01	0.05
Be	<0.01	-
Ca	1447.24	-
Cd	<0.01	0.2
Co	<0.01	0.1
Cr	4.42	0.5
Cu	2.01	3
Fe	3.97	5

3.1.2.2. Removal rate after treatment

- ***Removal rate of SS and EC***

The outcomes of the abatement of the SS and the EC after treatment are shown in Fig.7. As shown in the histograms in the Fig.7 both filter substrates contribute to maximum reduction of (SS) and (EC) with respective RR of 79% and 67% for (MS) and 83% and 80% for (WS). According to these consequences, it is deduced that the SS is better trapped in the granular mass of the WS filter and hence the chemical exchanges between the effluent and this filtering material allow a maximum reduction of the EC [25]. The achieved concentrations exhibit values very close to the standards that are 250 mg/l and 3000 mg/l, respectively.

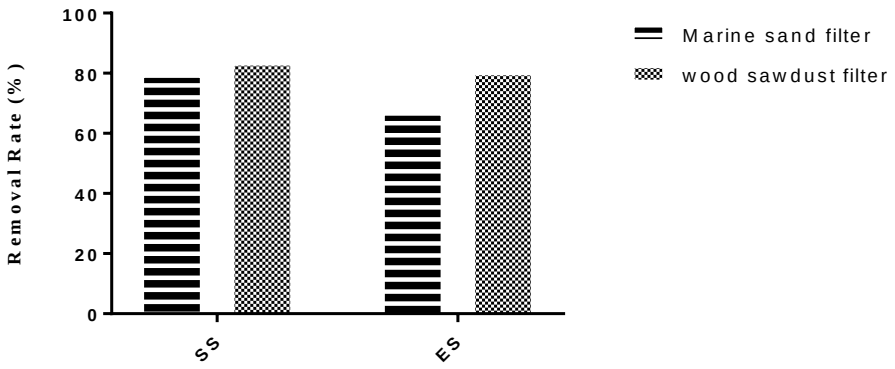

Fig 7: Removal rate of the SS and the EC.

- ***Removal rate of Sulfate***

The RR of SO_4^{2-} is given in Fig.8. According to the data, (MS) and (WS) contribute to a very satisfactory decrease of the SO_4^{2-} and the characterization values give a RR of 94.4% and 96.7% with grades below the standard, which are 233.125 mg/l and 136.87 mg/l, respectively.

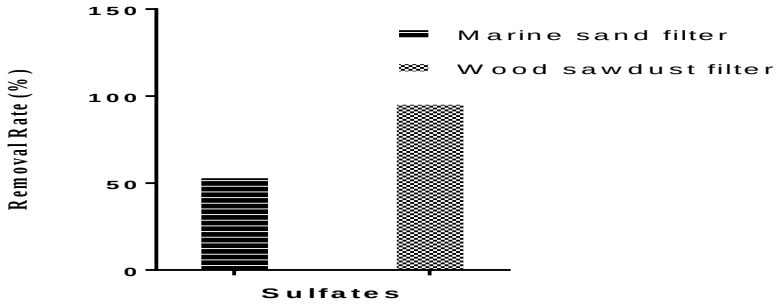

Fig 8: Removal rate of Sulfates.

The histograms obtained for the relief of Cr with (MS) and (WS) are displayed in Fig.9. Hence, the results show that the RR of Cr is about 56% for (MS) and 84% for (WS), with final concentrations closer to the discharge standards. Therefore, the best value found is the one that acquired by the WS filtrate, which is of the order of 0.704 mg/l.

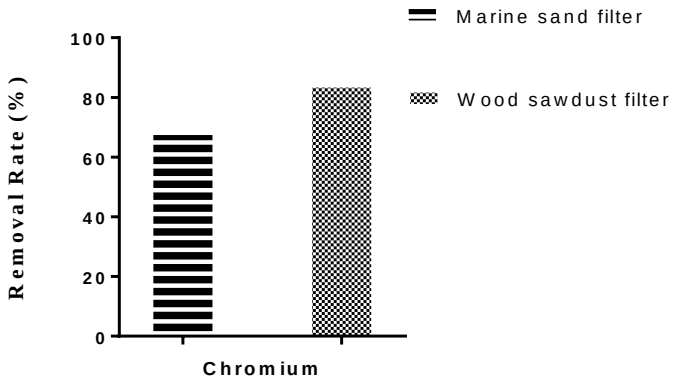

Fig 9: Removal rate of chromium.

- ***Removal rate of BOD_5 and COD***

The results of the reduction of BOD_5 and COD accomplished after treatment of the mixture of the four discharges are shown in Fig.10. In this respect, the analysis of the histograms shows that the effluent filtered by the marine sand bed yields RR of 80 % for BOD_5 and 81% for COD, while the WS filter bed gives best RR, which is 91% and 86% for BOD_5 and COD respectively. So the comparison between the two filter signifies a lessening of organic pollution in terms of BOD_5 and COD; whereas the WS filter represents the maximum RR. In this case, the concentrations of these two parameters have been reduced to 301 mg/l and 2115 mg/l respectively for the MS bed, and they are even highly reduced and reached 143 mg/l and 1057.5 mg/l respectively, for the WS bed. However, it has always been remained above standards.

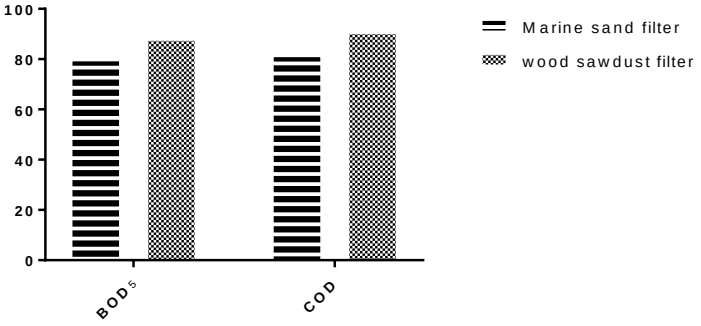

Fig 10: BOD_5 and COD abatement.

3.1.2.2. Raw effluent microbiological characterization

The microbiological characterization of the raw effluent shows a total absence of fecal germs such as TC, FC including E-coli and FS. Besides, there is also a lack of staphylococci. Therefore, this absence is probably due to both the high concentration of heavy metals and the high load of the raw effluent, which act on these microorganisms and disadvantages of their growth. In addition, SRC are present; their concentration is in the order of $0.6.10^4$ CFU/20 ml. In this respect, these germs are well known for their ability to sporulate and persist long in the water. They are, therefore, witnesses of an old pollution. The value of TG counted reach $0.18.10^4$ CFU/100ml. Moreover, the RR of the different germs detected in the raw effluent after filtration by (MS) and (WS) are shown in Fig.11. The histograms display that the number of SRC undergoes a significant reduction in the treated effluent. Indeed, the RR is more important for the WS filter than that of the MS filter with values of 96% and 85% respectively. The RR corresponding to the TG is maximum; these germs disappear definitively as soon as the effluent is treated.

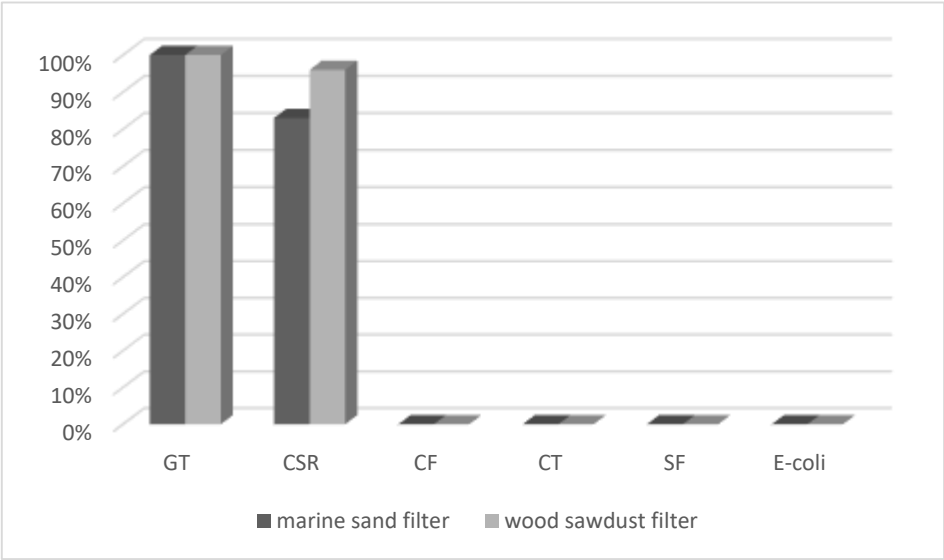

Figure 11: Germs abatement.

4. Discussion

The results obtained after filtration of the tannery effluents exhibit the ability of (WS) to improve both the physicochemical and microbiological quality of the treated effluent; this material generally has higher values compared to (MS). This can be explained by the chemical composition of WS, which is rich in cellulose, hemicellulose and lignin [9]. For this reason, this fibrous composition gives the material a large specific surface area,

which permits maximum retention of the elements of the solute. while the sand shows a remarkable filtering power, the porous micromorphology of this material has a very small specific surface area and does not authorize maximum retention. Therefore, the saturation of the filter bed is fast. The RR are very satisfactory in terms of all physicochemical parameters, they are suitable for (WS) as for sands according to the results found by [11]. In this study, they proceeded to filtration of the leachates by beach sand and wood sawdust of the *Cidrus.atlantica* species. Whereas the RR of SS, EC, BOD_5 and COD were 87%, 31%, 48% and 28% respectively for the sand filtrate, it were 88%, 39%, 74% and 54% for wood sawdust respectively. Another study by [6] showed a very significant decrease in the values of physicochemical parameters of a tannery effluent containing 500 mg/l of total chromium (Cr_T) and treated by sequencing batch reactor (SBR). Therefore, the recovered RR is 100% for SS, Cr_T and soluble DCOs and it is of the order of 95% for the PO_4^{3-}. In our study, the maximum RR of the PO_4^{3-} recorded a value of 65% for the sawdust filtrate. The microbiological characterization of the two filtrates displayed an elimination of TG and the RR was 100%. Besides this, a similar value was found by [26], which treated the effluents of carbonated drinks by SBR. Hence, the recovered RR is Close to 100% with a value of around 98.7%.

5. Conclusion

At the end of this work, we have shown the possibility of filtering an effluent taken from a modern tannery located in the Dokkarat district by two types of natural materials, (MS) and (WS). At a first place, the different results of the characterization of the adsorbent materials before saturation allowed us to distinguish between the composition of each. In addition, they also made it possible to say that the MS is depicted by its both porous and crystalline forms, which are rich in quartz and calcite on the other hand, the WS is portrayed by its fibrous structure that is rich in cellulose, lignin and hemicellulose. Further, after the characterization of the two filtrate obtained, it was found that the two natural filtering agents show a reduction in the organic, mineral and microbiological pollution. Thus, the treatment of the effluent with a MS filter did not result in maximum RR of COD, BOD_5, SS, EC, Sulfates and Cr, average RR for these parameters are 81.5%, 79.9%, 79.2%, 66.6%, 94.4% and 56.15%, respectively. However, the RR recorded an increase for filtrate treated on a WS bed and their values were 90.79%, 86.04%, 83.3%, 80%, 96.7% and 84.07% for COD, BOD_5, SS, EC, SO_4^{2-} and Cr, respectively. Furthermore, the microbiological outcomes also exhibit a decrease in SRC in both filtrate and a total elimination of the TG; However, it is noticeable that the filtrate, which underwent a treatment on (WS), presents only $0.02.10^4$ CFU/20ml against $0.1.10^4$ CFU/20ml for (MS) filtrate. Hence, the microbiological characterization shows a total absence of fecal germs in the crude effluent and the two filtrates. The characterization of the physicochemical parameters display that the tannery effluent is a highly charged reject of organic and mineral matter, especially chromium. From these results, we can come to the conclusion that column filtration shows a very important organic and mineral depollution for the two natural filters. Additionally, the values found are approximate to the general discharge standards. Moreover, the highest RR were recorded by sawdust filtrate.

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