Journal of Materials and Environmental Sciences
ISSN : 2028-2508

Copyright © 2017,
University of Mohammed 1er
Oujda Morocco

JMES, 2017 Volume 8, Issue 4, Page 1434-1447

http://www.jmaterenvironsci.com /

Analytical and statistical study of the impact of artisan activities in the period of Eid all Adha on Fez city effluents

N. El Allaoui*[1], Z. Rais[1], M. El haji[4], A. Omor[1], M. Nawdali[3], H. Bouka[2], M. Taleb[1]
1Laboratory of Electrochemistry, Engineering, Modeling and Environment (LIEME), Faculty of Sciences Dhar El Mahraz - Fez. Dhar El Mahraz, Fez, Morocco
2Laboratory natural Resources and Environment, Faculty Disciplinary Poly Taza . , Taza, Morroco
3Laboratory of Chemistry of Condensed Matter (LMCC), Faculty of Science and Techniques Fez, Morocco
4Laboratory of Industrial Management, Energy and Technology of Plastics and Composites materials, National School of Electricity and Mechanics (ENSEM) - Hassan II University, Casablanca, Morocco

Received 23 Sep 2016,
Revised 15 Nov 2016,
Accepted 17 Nov 2016

Keywords
- ✓ Effluent,
- ✓ Monitoring space-time,
- ✓ Pre-treatment,
- ✓ Environment.

nouhaelallaoui@gmail.com
Phone: +212 675244539

Abstract

The sewerage of Fez City receives different industrial effluents (tannery, brassware, dyeing, pottery...). The district of Ain Nokbi includes most of the craft activities, which discharge untreated into public networks or directly to Oued Sebou. The space-time monitoring of physical-chemical parameters, compared to Moroccan standard of rejection, reveals that the wastewaters from this district and surroundings, containing huge quantities of SS, cyanide, mineral and organic matter with variable biodegradability, and a very high metal load in chromium presented as chromium III which can reach as average values (4009 ; 927mg.L-1) in SS , (3329 ; 1342 mgO2.L-1) in COD, (251.1 ; 171.7 mg.L-1) TKN, (307 ; 101 mg.L-1) in CN- and (97 ; 12 mg.L-1) Cr III respectively for P1 and P2. While statistical analysis revealed a strong positive correlation between the chemical parameters. They are opposed to the physical parameters of the (F1 * F2) CPA plan. Disposing of this wastewater, either in networks or consolidations in nature can have adverse effects on the biological treatment station of Fez city, also on the health of the population and the aquatic life of Oued Sebou. In this sense a physic-chemical pre-treatment of these effluents is a must to ensure a healthy environment in this town.

1. Introduction

In Morocco the natural water resources are among the lowest in the world. Indeed, the potential of natural water resources are estimated at 22 billion m^3 per year, the equivalent of 750 m^3 / Inhabitant / year [1]. This water resource restriction is compounded by the degradation of the water quality due to the increase of the degradation of pollution. The annual volumes of wastewater discharges in recent decades have substantially expanded, they went from 48 to 506.2 million m^3/ Year between 1960 and 2012 [2]. A large part (61%) of these volumes is discharged directly into the ocean; the rest (39%) is released into the water system or directly in the ground [2]. Similarly, the established forecasts indicate that such discharges will continue to grow rapidly to 741 million m^3 / year in 2030 [3].

According to the autonomous inter-communal water and electricity distribution of Fez region, the total volume of the pollution generated by the city of Fez is about 37 million m^{3}coming from the domestic pollution and wastewater discharge from different industries. Nowadays, these effluents are collected and transported to the treatment plant of the city. This plant treats about 100 000 m^3 per day and the rest estimated at nearly 70 000 m^3 per day is evacuated directly in the Sebou river without any treatment [4].

These effluents are generally loaded with non-biodegradable pollutants and heavy metals. In fact, the metallic pollution of Fez city is estimated at 400 kg per day of which the chromium represents 350 kg.d^{-1} of the total pollution [4]. Thus contributes to 40% of the pollution generated in the Sebou basin. The medium part of this river presents a poor water quality which affects the different water uses downstream the river [4; 5].

The standards of these releases are becoming stricter and reducing environmental footprints, carbon and water, has become a priority. Several studies are interested in the characterization and treatment of this type of waste by biological processes [6; 7] or physicochemical [8; 9]. All these processes require a good knowledge of the pollution load of treated water to choose and apply a non-expensive, effective and suitable method for processing.

This study seeks to evaluate the degree, nature and behavior of different physical-chemical parameters of effluents of the most polluted sites in the city of Fez. To achieve this, we opted for a space-time monitoring that allowed us to have a thorough data base for statistical tests , which have proven effective in several studies [10 ;11 ;12], to determine the correlation between the parameters and also to know the significant effect of explanatory variables (time and site samples) on the dependent variables (pollution parameters : COD, BOD 5 , NTK …) . In our case we used two statistical tests which are the Principal Component Analysis (PCA) and analysis of variance (ANOVA), by exploiting the SPSS software (SPSS Statistics 20).

2. Materials and methods

2.1. *Study area*

The wastewater was collected from Ain Nokbi district (Morocco, Fez) and surroundings collector, this area is estimated as the most polluted area of Fez city (Morocco) which groups domestic and industrial wastewater from tanneries, brassware and pottery. The sampling points are illustrated in Figure 1; these effluents require a pretreatment before connecting them to the biological treatment plant for the city of Fez.
In this regard two sites were selected:

- P1: effluent from discharges tanneries of Ain Nokbi district, discharged directly into Oued Sebou, (Distance from the STEP 2.28 Km).
- P2: effluent from 1200 collector .coming from the entire Ain Nokbi neighborhood and its surroundings. Most of it passes through Oued Sebou, (Distance from the STEP 130.59 m).

The sampling campaign began 15 days after Eid al Adha. This period is chosen in order to make a follow-up of the 4 months which the city of Fes receives the highest level of pollution coming from artisan activities and especially of dyeing and tanning. The monitoring was extended over duration of 14 weeks from October 12th, 2015 until January 21th, 2016.

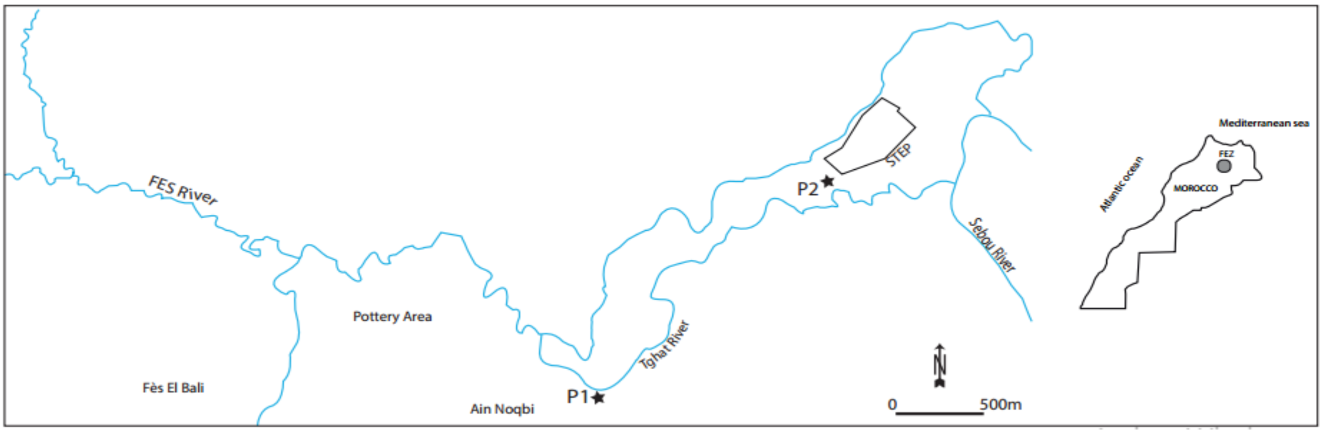


Figure 1: Overview of the study area. Sampling locations are indicated with (★).

2.2 *Sampling*

The sample was carried out by the composite method because of the variability of activities and the composition of effluents. The samples were taken by an automatic sampler of 24 vials (ISCO 3700).
All controlled parameters were analyzed in the laboratory. Transportation and packaging of samples were made according to the AFNOR standards set by Rodier [13].

2.3 *Physicochemical analyses Water*

Seventeen parameters were measured including four were performed on site: temperature, conductivity, pH measured using a multi-parameter analysis Type CONSORT model C535, and flow measured by an air-speed Doppler flow-meter (ISCO 4250).
BOD_5 was determined by the method Oxitop, COD was performed according to the standard NF T90-101. The suspended material (SS) was determined gravimetrically after filtration on a 0.45µm membrane. Sulfate, nitrate, nitrate, and orthophosphate were determined by molecular absorption spectrophotometer. Nitrogen kjeldhal was measured according to NF EN 25663 (Rodier, 2009). Cu^{II} was determined by colorimetric method using sodium thiosulfate. Cyanide was measured by potentiometer (selective electrode readily liberated cyanide). Nickel was determined according to standard EN ISO 15587-2 / EN ISO 11885. The Cr^{VI} was measured according to

standard NF T 90-043. . And Cr^{III} was determined by subtracting the total Cr of Cr^{VI}: EN ISO 15587-2 / EN ISO 11885.

3. **Results and discussion**

3.1. *Spatio- Temporal Monitoring*

All the analysis results are listed in the graphs below which represent the value of each parameter characterizing the effluents from the sites P1 and P2 for all sampling.

3.1.1 Flow

On the figure 2(a) we can observe that the pollution load of the two effluents has the same tendency of evolution because of the discharge of wastewater craft enterprises (consisting of tannery effluents, pottery, copperware, textile dyeing ...) into the sewerage system. The counting of the results shows that the flow of the point P2 is almost 8 times larger than the P1 point because it collects industrial and domestic effluents from all areas of Ain Nokbi and could reach up to 3560 m^3 / day depending on the daily craft activities .

3.1.2 Temperature

The temperature of the wastewater at the site P1 is between and 16.87°C and 26.6° C as minimum and maximum extremes and 22.9°C as average value (Figure 2 (b)). For the site P2 the minimum and maximum values are respectively 17.85 and 27°C with an average of 23.29° C. These temperature variations follow those of the climate of the region. Generally temperatures recorded at both sites are below 30°C which is the direct discharge limit value according to Moroccan standards [14].

3.1.3 pH

The average pH values found in two locations P1 and P2 are respectively 9.5 and 7.9; they can reach 12.17 for P1 because of the disposing of tanneries (Figure 2(c)). They go far beyond the prescribed Morocco‘s standard in 2013 bulletin which is between 5.5 and 8.5. The two effluents are of medium to strong basicity because sulfide, cyanide and lime used in some operating units of tanneries, copperware, stains ... found in the area of Ain Nokbi and discharge their effluents without any treatment. That influences most of chemical reactions and controls the heavy metal toxicity in aquatic environment [15].

3.1.4 Electrical conductivity

Figure 2(d) shows that the mineral filler of effluents from the point P2 is close to the norm in most of the time, while that of P1 exceeds 2 to 5 times the load of P2 and fluctuates between 10 $mS.cm^{-1}$ and 27 $mS.cm^{-1}$ exceeding largely the Moroccan standard of rejection (2.7 $mS.cm^{-1}$) [14], thus indicating an excessive mineralization attributed to the salts used in the tanning process.

3.1.5 Suspended Solids (SS)

The result shown in Figure 2(e) reveals a very high concentration of SS in both sites their average is around 4009 and 927 $mg.L^{-1}$ respectively, for P1 and P2, while the standard of Moroccan discharges is 30$mg.L^{-1}$. The presence of these SS in the releases may affect significantly the functioning of the sewage system causing sludge deposits and clogging of aquatic receptors funds [16].

3.1.6 Chemical and Biological oxygen demand

Figure 3 (a) depicts that the high values of COD is at the beginning of the campaign in October (the beginning of the crafts after the feast of Eid Adha which reaches more than 5200 $mgO_2.L^{-1}$ in P1 and 1472 $mgO_2.L^{-1}$ in P2, these values decrease in November and re-increase in December and mid-January. This variation depends practically on craft activities (tanneries, brassware, pottery, paintings ...) of the area. Overall, these values are very high compared with discharge limits which are 120$mgO_2.L^{-1}$[14]. The values obtained for the COD explain the presence of non-biodegradable and oxidizable material. The temporal evolution of biological oxygen demand BOD_5 (Figure3(b)) is characterized by significant fluctuations in particular for the P1 site with 356$mgO_2.L^{-1}$ as a minimum and 3000 $mgO_2.L^{-1}$ a maximum value, while the values of P2 Site oscillate between 150 and 1550 $mgO_2.L^{-1}$. These values obtained are much higher than the discharge standard which is 40$mgO_2.L^1$. In general we see that the values found at the Site P1 are higher than P2 Site with the exception of a few days in October, November and December. This is probably due to a lack of tanning activity, or that most tanneries do not proceed to depilation and planning step of skin, which prevents the greater amount of the organic filler.

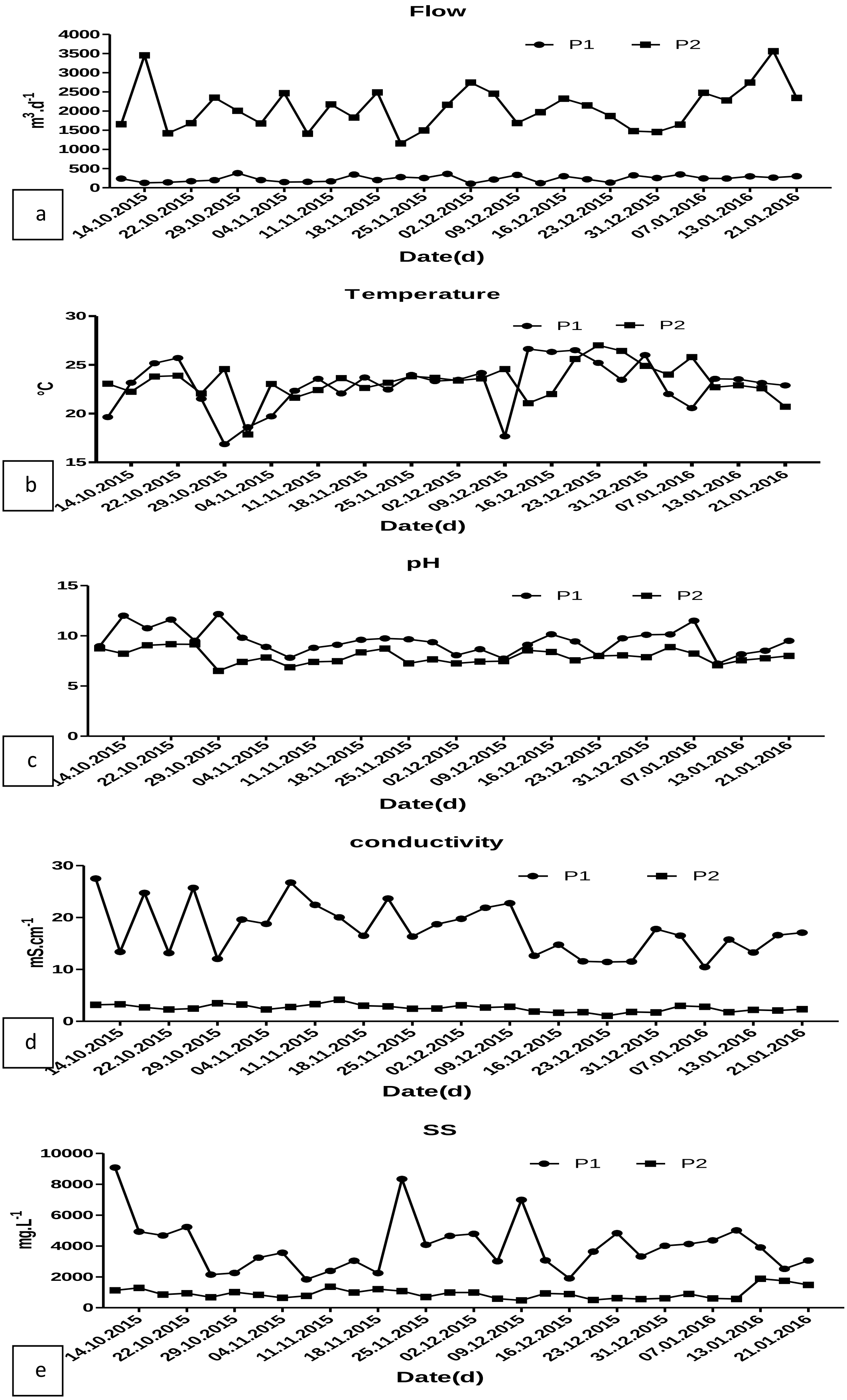


Figure 2: physical and chemical water quality values in the two sites P1 and P2 from October 2015 to January 2016. (a) Debit (m^3.d^{-1}); (b) Temperature (°C); (c) pH; (d) Electrical conductivity (mS.m^{-1}); (e) Suspended Solids (mg.L^{-1}).

The ratio (COD/BOD$_5$) as shown in Figure3(c) notoriously evolves with time; it goes from 1.2 to more than 6 on P1 and from 0.3 to 5 on P2. The biodegradability ratio peaks at the beginning of the season and at the beginning and the end of December, which implies the depletion of effluents from biodegradable organic materials. The average value of the both sites is 2.56 and 1.16 on P1 and P2 respectively. This variation influences the nature of organic matter biodegradation of wastewater. The latter pass from a biodegradable to a non-biodegradable effluent from one day to another, the variation of this parameter is very significant over time and with the sampling sites.

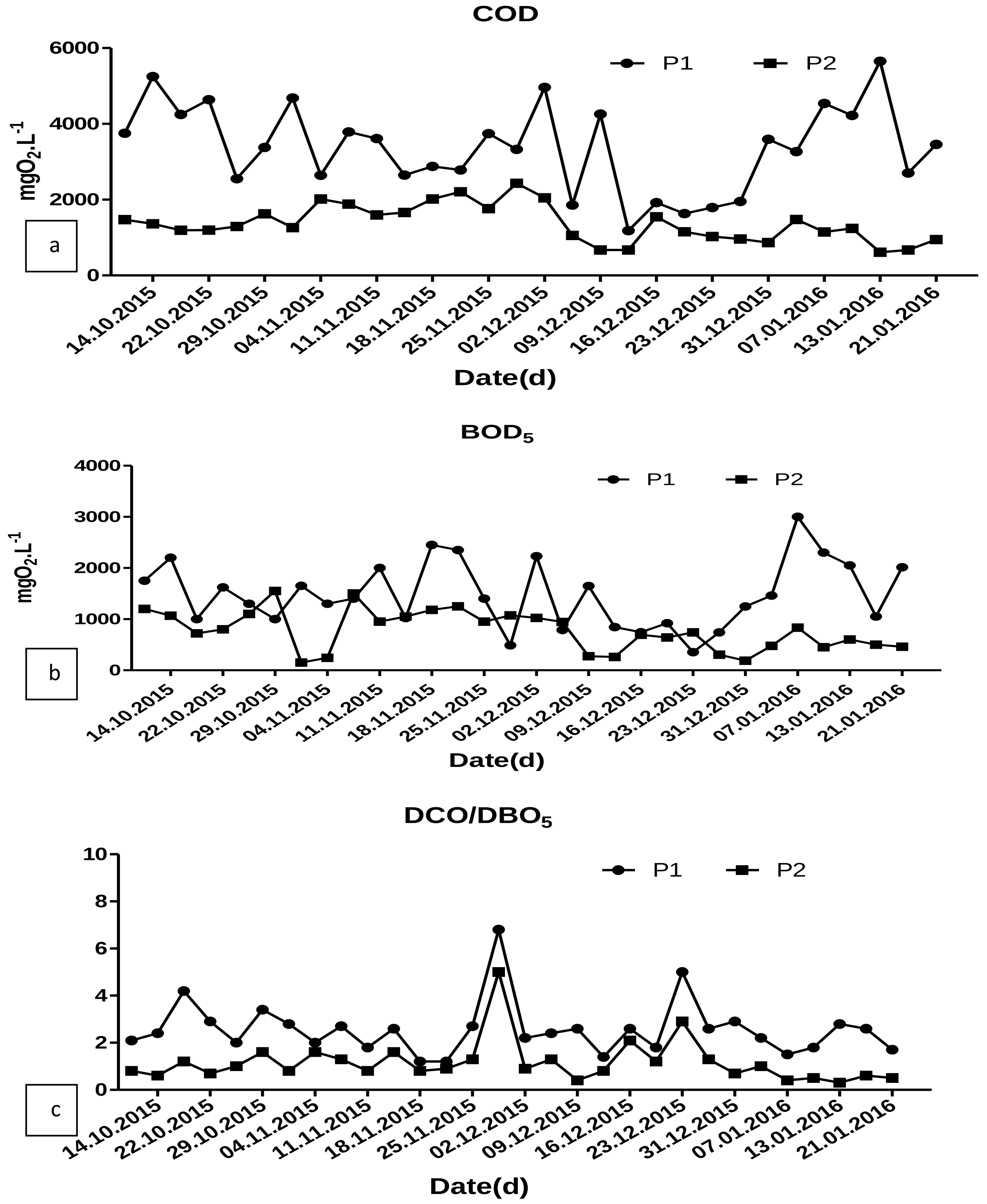


Figure 3: physical and chemical water quality values in the two sites P1 and P2 from October 2015 to January 2016. (a) COD (mgO$_2$.l^{-1}); (b) BOD$_5$ (mgO$_2$.l^{-1}) ; (c) DCO/DBO$_5$.

3.1.7 Nitrogen and Phosphorus elements

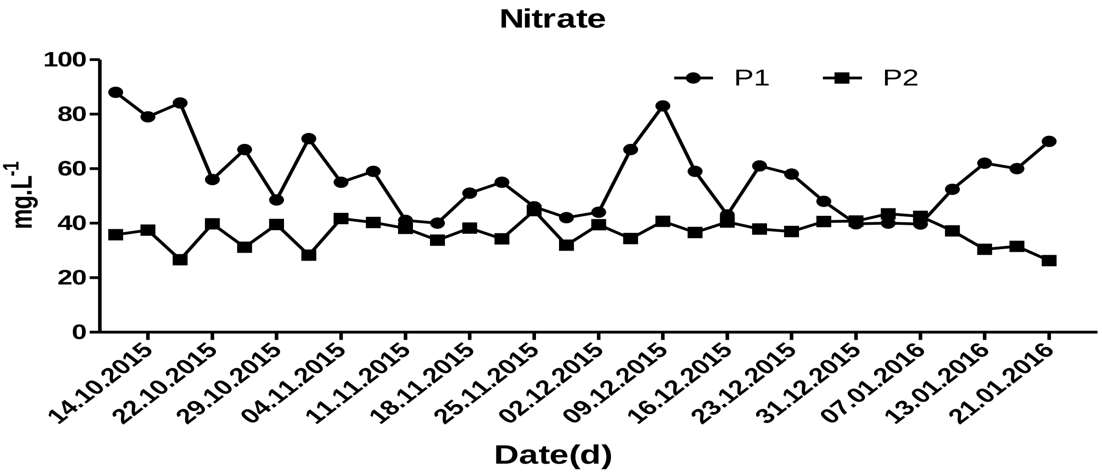
Nitrogen pollution effluent evaluated on nitrites, nitrates and nitrogen kjeldahl (TKN) has the same tendency of evolution for the three elements. The concentrations of nitrogen elements is very high in the period after Eid Adha (Figure 4(a),(b) and (c)), it is around 88 mg L^{-1} on nitrate 2.52 mg L^{-1} on nitrite and 362.67 mg.L^{-1}on TKN for the site P1. In P2 the maximal values are on the order of 44.61 mg L^{-1} on nitrate 1.31 mg L^{-1}on nitrite and 248.33 mg L^{-1}on TKN. The average values of the three nitrogen elements on P1 and P2 are, respectively (56.98; 36.07 mg L^{-1}) of nitrate (1.2; 1.1 mg.L^{-1}) of nitrite (251.1; 171.7 mg.L^{-1}) of TKN. Overall the concentrations nitrate and nitrite are close to the discharge limits on P1 and P2 with the exception of some fluctuations.

The low concentrations of nitrite encountered in wastewater studied could be explained by the fact that the nitrite ion (NO_2^-) is an intermediate composed, unstable in the presence of oxygen, whose concentration is generally much lower than other forms related to it [17].

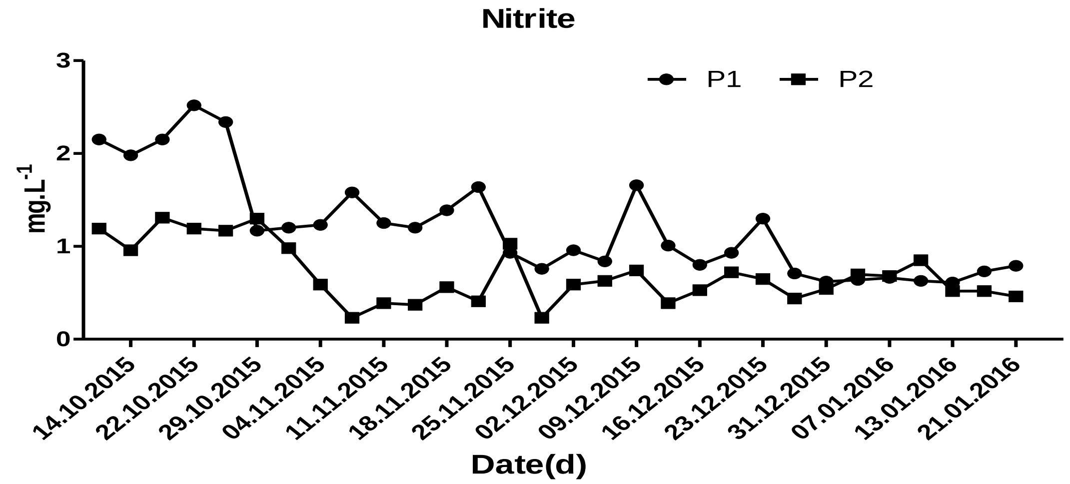
However, the concentration of nitrogen kjeldahl is 4 times higher than the limit value of discharge (40mg.L^{-1}) [14] on P2 and 9 times on P1. This could be resulting from the proteins, polypeptides, amino acids coming from the skin of cattle, droppings pigeons used during the traditional tanning, or from urea coming from domestic wastewater. The reduction of nitrites to nitrogen produce the formation of methemoglobin that can contribute to the endogenous synthesis of N-nitroso compounds [18].

The orthophosphate remain more or less stable during the sampling campaign (Figure 4 (d)), for both sites P1 and P2. The minimum and maximum values are respectively (1.52; 19.19 mg.L^{-1}) for P1 (4.17; 9.66 mg.L^{-1}) for P2.The average values are on the order of 15.09 mg.L^{-1} (P1) and 7.34 mg.L^{-1} (P2). These values revolve around the discharge standard which is 10mg.L^{-1}. The large part of the phosphorus pollution comes from industrial or domestic detergents, waste of protein metabolism and disposal in the form of phosphates in the human's urine [19].

The high amounts of nitrogen and phosphorus elements can lead to eutrophication of Oued Sebou River which could lead to production of excessive and imbalanced algal biomass and a severe hypoxia resulting of the degradation of this excess of organic matter [20].



a



b

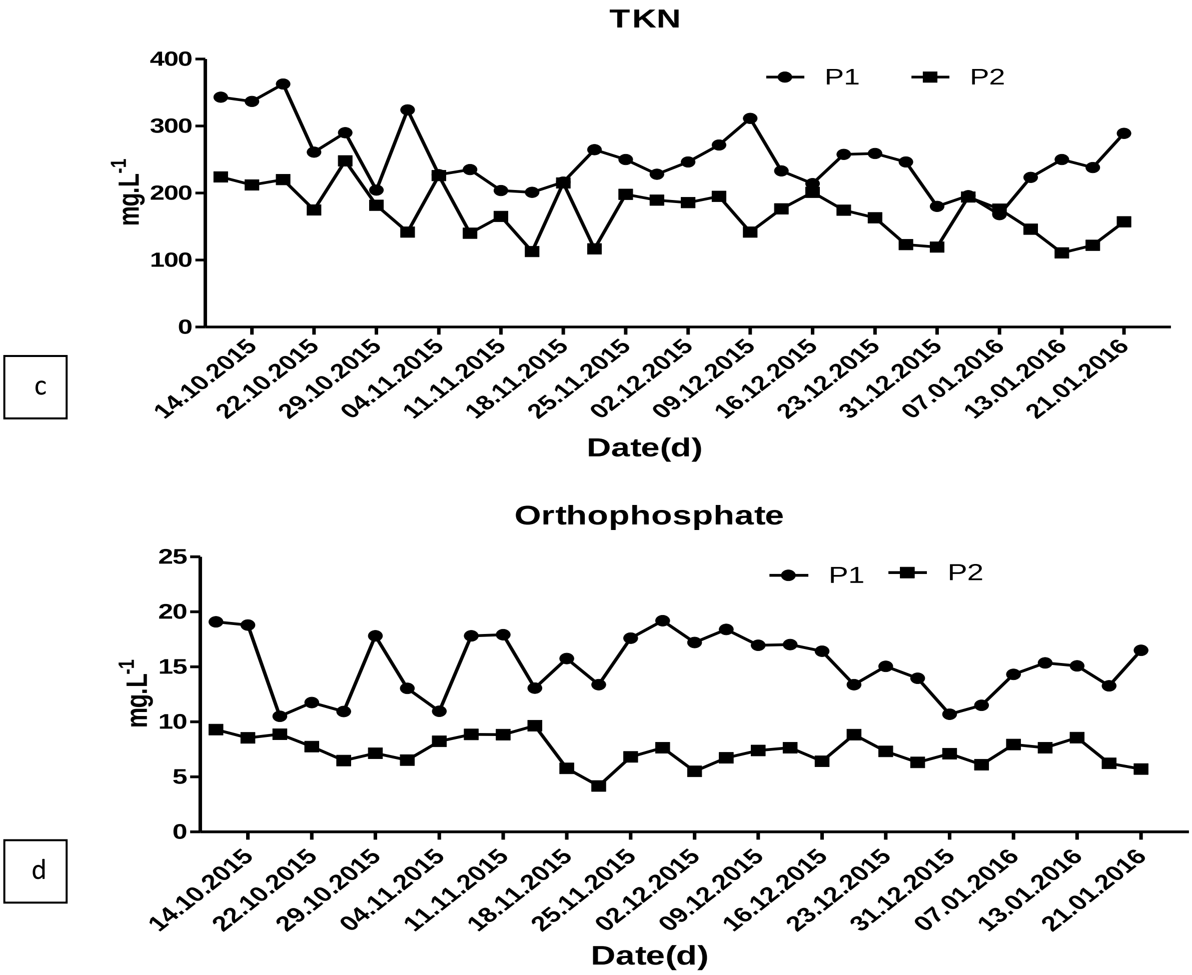


Figure 4: physical and chemical water quality values in the two sites P1 and P2 from October 2015 to January 2016. (a) NO_3^- (mg.L^{-1}) ; (b) NO_2^- (mg.L^{-1}); (c) TKN (mg.L^{-1}); (d) PO_4^{2-}(mg.L^{-1}).

3.1.8 Sulphate

Figure 5 (a) indicates that the average concentrations of sulphate (SO_4^{2-}) found in both sites P1 and P2 are 638 and 228 mg.L^{-1}respectively. The highest values were recorded at the beginning of the campaign, 1310 mg.L^{-1}on P1, and 390.67mg.L^{-1} on P2. In general the sulphate concentration exceeds the recommended standard which is500 mg.L^{-1} [14] on the P1site (tanneries wastewater). These concentrations are related to the use of mineral salts in the different steps of leather processing.

They come mainly from pickling step they used for maintaining the skin by preventing the development of putrefaction bacteria. Chromium sulfate is used as a tanning agent when the aluminum sulphate is used in deliming step [21].

3.1.9 Cyanide

Concerning cyanide, presented in Figure 5 (b) they are excessively high in both sites P1 and P2 in comparison with the discharge standard of wastewater (0.1mg.L^{-1}), and reach as average values 307mg.L^{-1} and 101mg.L^{-1}, respectively for P1 and P2.

This could be from pools of cyanide used in brassware or as stains and cyanide-based varnishes used in tanneries and textile industries.

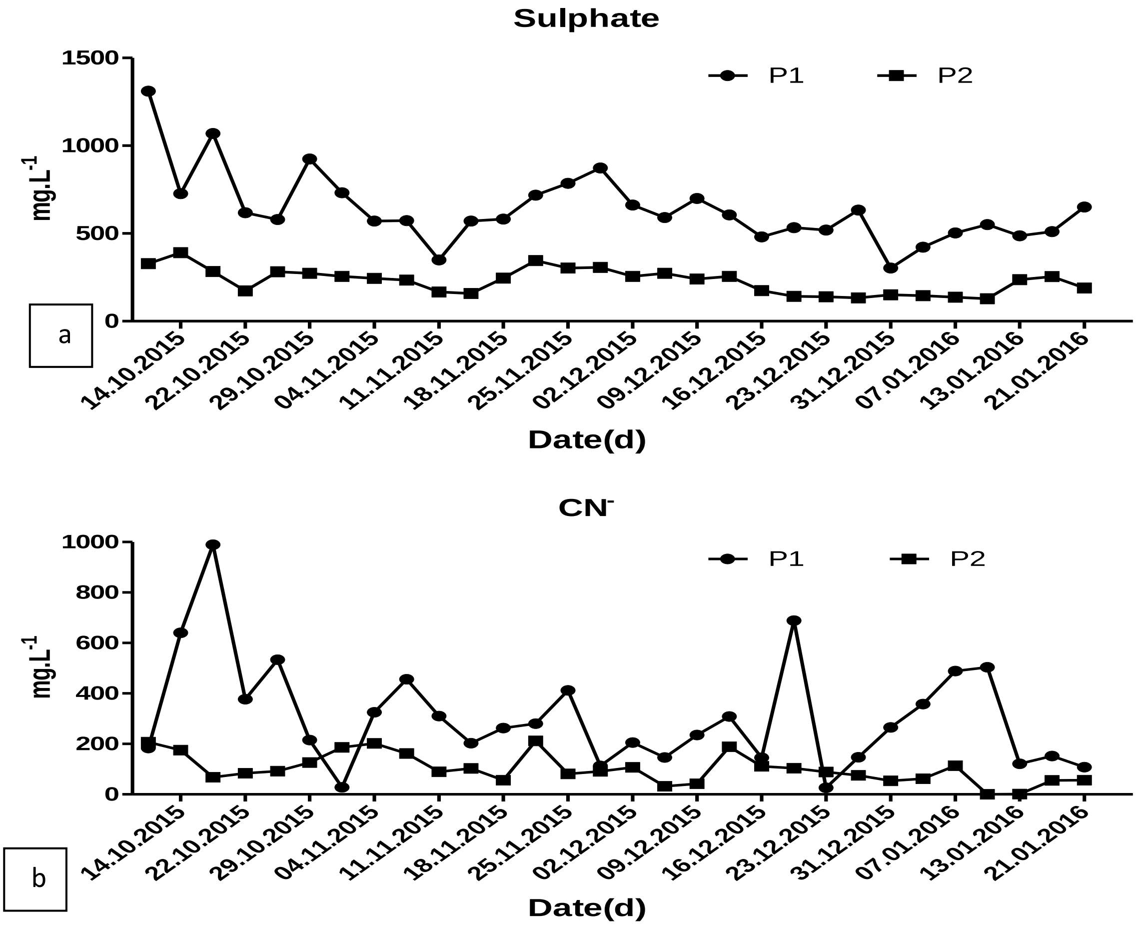


Figure 5: physical and chemical water quality values in the two sites P1 and P2 from October 2015 to January 2016. (a) SO_4^{2-} (mg.L^{-1}); (b) CN^- (mg.L^{-1})

3.1.10 Metal elements

The metal elements followed in this campaign are the cupric ion, nickel, hexavalent and trivalent chromium:

Concentrations of copper ion and nickel in both sampling sites (Figure 6 (a);(b)), show very large variations in the level of cupric ion in function of time, ranging between 0.72 and 3.15 mg.L^{-1} (P1) and 0.2 and 2.23 mg.L^{-1} (P2). The nickel values remain more or less negligible during this campaign except some fluctuation that does not exceed 0.19 mg.L^{-1} in the P1 site. The concentrations of nickel remain much lower than Moroccan discharge standard which is 5 mg L^{-1}[14].

Figure 6 (c) and (b) illustrate the effect of time on Cr^{III} and Cr^{VI} on the two sites P1 and P2. Hexavalent chromium Cr^{VI} ranges between 0.78 - 2.54 mg.L^{-1} in P1 and 0.23 - 1.85 mg.L^{-1} in P2. These levels are higher than the discharge standard (0.1mg.L^{-1}). Trivalent chromium Cr^{III} is between 4.1 - 482 mg.L^{-1} with an average of 115mg.L^{-1} P1. And between 0.05 - 38.4mg.L^{-1} with an average of 13.51 mg.L^{-1} in P2. From the graphs we can see very significant changes in function with time probably due to the nature and frequency of daily craft activities in the area.

The very high concentrations of chromium especially in P1 (discharge from tanneries) endorse the results found by Hayzoun [21] which show that most concentrated chrome rejection is that of tannery industry because of the different products used in the tanning, such as chromium sulphate.

Hexavalent chromium has no tanning action and is not used in tanning. Alone the trivalent chromium in the form of chromium III sulphate has a tanning action and allows the transformation of the raw skin into leather. The speciation of chromium (VI) and (III) depends on several parameters, such as pH, concentration and availability of ligand. In environments, in pH between 8 and 10, hexavalent chromium is mainly in the form of CrO_4^{2-}. Reduction of hexavalent chromium is possible in the environment under the reducing conditions encountered in many low oxygenated media [22].

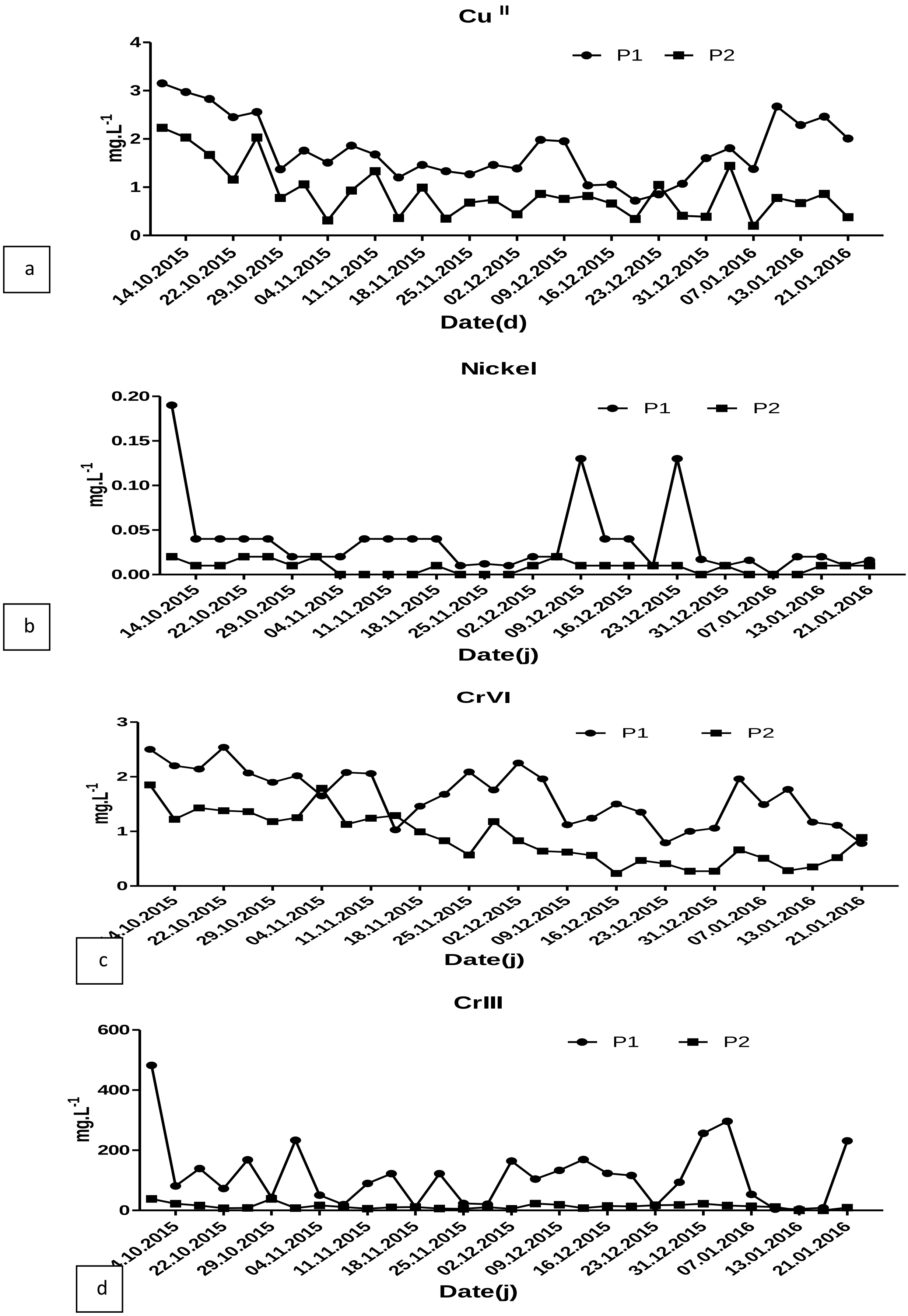


Figure 6: physical and chemical water quality values in the two sites P1 and P2 from October 2015 to January 2016. (a) Cu^{II} (mg.l^{-1}); (b) Ni (mg.l^{-1}); (c) Cr^{VI} (mg.l^{-1}); Cr^{III} (mg.l^{-1})

3.2. *The average pollution load of P1 and P2 on kg per day*

Table (1) depicts the results of the average pollution load of the both sites P1 and P2 on kg per day. The values of all the parameters are calculated using the estimated average flow from Figure 2 (Figure 2a). Again, the high BOD_5 and COD values show effluent's strong contamination with organic matter. As was aforementioned, the wastewater also presents high values of SS, TKN, CN^- and Chromium. Average values in kg per day are in the order of 2632 $Kg.d^{-1}$ on P2 and 917 $Kg.d^{-1}$ on P1 of COD, more than 1788 $Kg.d^{-1}$ of BOD_5 on P2, 503 $Kg.d^{-1}$ of cyanide on P1, 1843 $Kg.d^{-1}$ of suspended solids on P2, over 323 $Kg.d^{-1}$ of TKN on P2 and almost 23 $Kg.d^{-1}$ of trivalent chromium on the both sites. These results are very alarming and require an adequate physic-chemical treatment.

Table 1: Pollution load of P1 and P2 ($Kg.d^{-1}$)

Sampling points Parametres	P1 ($kg. d^{-1}$)	P2 ($kg. d^{-1}$)
COD	917.2 ± 277	2632 ± 210
BOD_5	1185 ± 145	1788.5 ± 162
CN^-	503.8 ± 32	197.8 ± 36
Sulphate	189.7 ±55	469.3 ± 30
Orthophosphate	4.5 ±1	14.6 ± 3
TKN	73.2 ± 21	323.8 ± 17
Nitrate	15.9 ± 5	70.8 ± 2
Nitrite	0.4 ± 0,1	1.2 ± 0.16
Cu II	0.5± 0,15	1.8 ± 0.21
Cr VI	0.5 ± 0,14	1.7 ± 0.19
CrIII	22.8 ± 7	23.2 ± 6
Ni	0.014 ± 0.004	0.039 ± 0.001
SS	1185 ± 342	1843.3 ± 172

3.3. *Statistical analysis*

Multivariate statistical methods are useful for the interpretation of large and complex water and wastewater quality data sets, evaluating redundant measurements in the environment, allowing, this way, the classification and the grouping of pollutants according to their sources, achieving a small number of underlying factors without losing too much information [23].

3.3.1 Analysis of variance (ANOVA)

Correlation analysis was conducted to investigate the spatial and temporal variation of physicochemical parameters; we analyzed, initially, the evolution of each parameter in function with time. Secondly, we studied the variation of these parameters according to sites.

Table (2) shows the results of the analytical bivariate test, fixed model applied to each of the 17 measured variables during the studied period. The bivariate analysis of variance ANOVA aims to identify the existence of differences between the various sites studied and the different campaigns sampling.

Table 2 shows the results of the quadratic means applied for the study of the spatio-temporal variations of the physicochemical parameters. We observe that the mean square of all the parameters are superior to sites compared with the time factor (flow$_{(site)}$ M.S : 51420000, flow $_{(time)}$ M.S : 161500 ; DCO$_{(site)}$ M.s : 59660000, DCO$_{(time)}$ M.S : 790400 etc.)

The Fisher (F) statistic is the sum ratio of the inter and intra-group mean squares. The P value indicates the probability of finding the F value. This value is accepted when the null hypothesis is true and smaller than 0.05%.[24]

Table 2: Bivariate analysis ANOVA

Parameters	Sites				Time			
	M.S	F	P value summary	Significant	M.S	F	P value summary	Significant
Flow	51420000	290.5	P<0.0001 ***	Yes	161500	0.9123	0.5968 ns	No
Temperature	2.329	0.5638	0.4588 ns	No	5.452	1.320	0.2295 ns	No
pH	35.17	49.33	P<0.0001 ***	Yes	1.327	1.861	0.0499 *	Yes
EC	3475	312.6	P<0.0001 ***	Yes	13.85	1.246	0.2789 ns	No
COD	59660000	77.98	P<0.0001 ***	Yes	790400	1.033	0.4653 ns	No
BOD_5	7302000	19.54	0.0001 ***	Yes	369500	0.9889	0.5118 ns	No
NTK	94570	67.46	P<0.0001***	Yes	2402	1,.713	0.0766 ns	No
Nitrate	6172	42.08	P<0.0001 ***	Yes	78.51	0.5354	0.9510 ns	No
Nitrite	4.009	37.21	P<0.0001 ***	Yes	0.3009	2.793	0.0036 **	Yes
Orthophosphate	902.4	210.2	P<0.0001 ***	Yes	4.977	1.159	0.3468 ns	No
Sulphate	2516000	179.5	P<0.0001 ***	Yes	32620	2.327	0.0131 *	Yes
Cu^{II}	1164	102.9	P<0.0001 ***	Yes	0.6019	5.320	P<0.0001***	Yes
Cr^{VI}	9.228	93.77	P<0.0001 ***	Yes	0.3688	3.748	0.0003**	Yes
Cr^{III}	154300	29.33	P<0.0001 ***	Yes	6006	1.142	0.3619 ns	No
Ni	0.01236	15.88	P<0.0001 ***	Yes	0,0009883	1.271	0.2616 ns	No
Cyanide	641600	26.68	P<0.0001 ***	Yes	24630	1.024	0.4743ns	No
SS	142500000	84.34	P<0.0001 ***	Yes	1460000	0.8641	0.6517 ns	No

p> a = 0.05 (ns) no significant difference
p <0.05 a = (*) just significant difference
p <0.01 a = (**) highly significant difference
p <a = 0.001 (***) very highly significant difference
F: Fisher value
M.S: Mean Square

In our case we find that the analysis of the table results reveals a very highly significant correlation between P1 and P2 sampling sites for the parameters: Debit, pH, EC, COD, BOD_5, TKN, NO_2^-,NO_3^-,PO_4^{2-} , SO_4^{2-} , Cu^{II} , Cr^{III}, Cr^{VI} , Ni, CN^-, SS ($P <0.0001$) . However, for the temperature we can accept the null hypothesis (P value = 0.46), this parameter varies insignificantly with sampling sites.

The copper ion varies very significantly with time, chromium VI and Nitrite is highly significant, and the difference of sulphate is just significant. While, the remaining parameters Debit, pH, CE, COD, BOD_5, TKN, NO_3^-, PO_4^{2-}, Cr III and T° do not vary significantly with time their P values is higher than 0.05%.

From the previous test results, we conclude that the factor of site has more influence on each of the parameters studied than time, since the quadratic mean of all the parameters in the site is higher than the time.

Most parameters vary significantly with sampling sites but not with time because the effluents from sites do not have the same background or the same human activities. The significant differences observed are related to the nature of the activity in each site, the different types of water discharged and characteristics of each environment [25].

The temperature varies independently at site and time since the climate of the region is the most influential factor on this parameter [26].

3.3.2 Principal Component Analysis (PCA)

PCA is a statistical technique that transforms the original set of inter-correlated variables into a new set with a small number of independent uncorrelated variables or principal components (PCs) that are linear combinations of the original variables and account for most of the variance in the observed variables [27].

PCA was conducted with the samples of P1 and P2 sites. The results show in Figure 7. The first two axes were chosen for the graphical representation. Both axes represent 58.13% of the information contained in the data matrix.

The Kaiser-Meyer-Olkin (KMO) index is 0.82 (Table 3). We can then judge that the correlation between items is excellent. The result of the Bartlett's test of sphericity was significant ($p < 0.0005$). We can therefore say that the correlations are not all equal to zero. The variables depend on each other.

Table 3: KMO Index and Bartlett's test

Sampling precision measurement de Kaiser-Meyer-Olkin.		0.827
Bartlett sphericity test	Khi-deux approximé	295.020
	Ddl	120
	Significance Bartlett	0.000

Figure 7 illustrates Projection of physico-chemical factors of effluents on the first two axes of Principal Components Analysis (PCA) plan. The review of digital results PCA showed that parameters BOD_5, pH, Cr^{III} ,Cr^{VI}, Cu^{II}, TKN, NO_3^-,DOC, SO_4^{3-}, PO_4^{2-},CE are increasing in a positive correlation from 0.5 to 0.89 on the axis F1 which represents 42.95% of the inertia. The latter oppose on the same axis the temperature (-0.36) and flow (-0.83) negatively related to the first component. While Cyanide (0.8) is positively related to the second component, which represents 15.17% of the overall inertia.

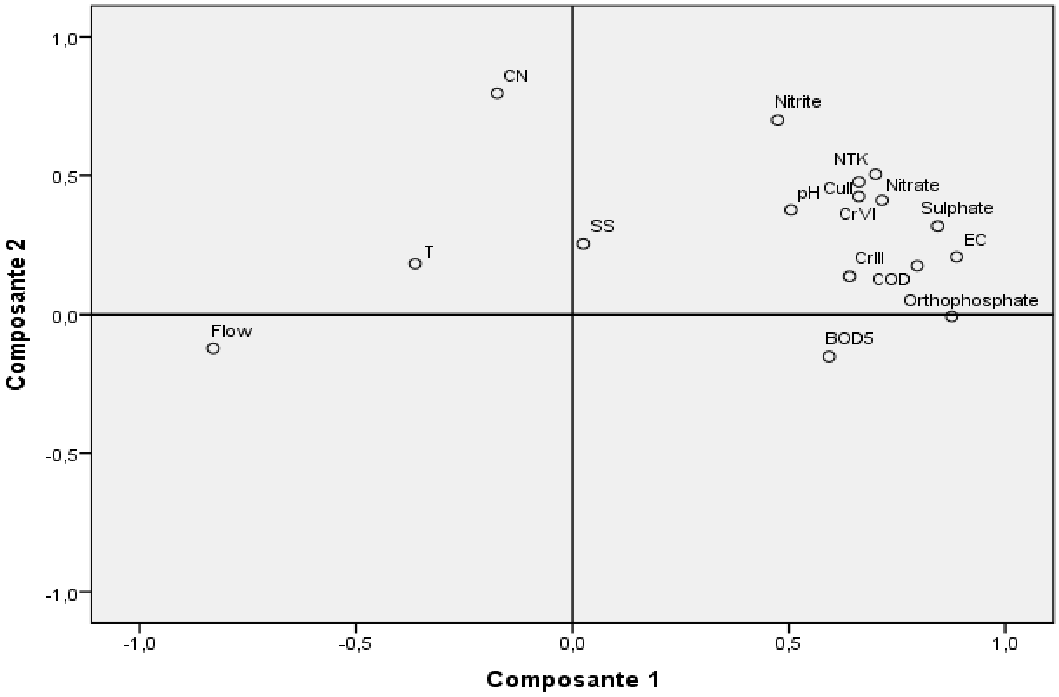


Figure 7: Projection of physic-chemical factors of effluents on the first two axes of Principal Components Analysis (PCA) plan.

The grouping and positioning of variables in the correlation circle allow us to distinguish three groups of variables: the first which is positively related to component 1 may be termed chemical parameters and encompasses most chemical parameters indicating the quality of the water. While the second group can be termed physical parameters is opposed to the chemical parameters on the same component. The third group is the cyanide-variable related to axis F2 and varies independently of the other parameters.

On the first 2 factorial axes of the PCA in a matrix (site / physicochemical characteristics) it's clear (Figure 7) that the two descriptors SS and NO_2^- show a very little variation from one station to another and cannot significantly discriminate these stations. Contrary to all other chemical descriptors they all have positive coordinates and present important variations in the site P1. While most imperative changes in P2 site are those of Group 2 physical parameters.

In fact, effluent discards of tanneries on P1 (Figure8) generally exhibit significant variations which depend on the steps of tanning. The tanneries in the area Ain Nokbi are not working in a synchronized manner, so the release of the collector collects the discharge of all the tanning steps. This enables most of the chemical parameters assemble and relay on each other. The Cyanide depends essentially of releases of dyeing and brassware basins. So the existence of this parameter is occasional and its variation is independent of other parameters.

P2 site, collector of industrial and domestic wastewater in the area, includes releases of a very large area which has an uncontrollable flow rate. It hinges primarily on the daily human activities. This affects in a very meaningful way the flow variation (Figure8).

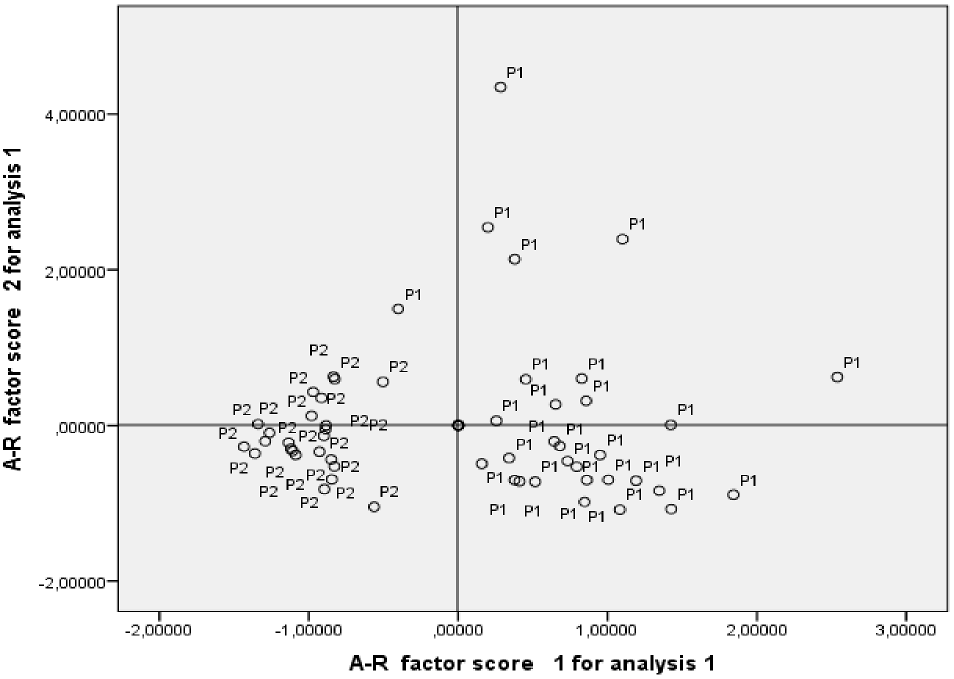


Figure 8: Projection of P1 and P2 on the first two factorial axes of PCA plane of the matrix Sites / Physic-chemical characteristics.

Conclusion

The present study shows that effluents of the two sites P1 and P2: rejection tanneries Ain Nokbi and Fez City collectors were characterized in terms of physicochemical parameters. The spatiotemporal evaluation shows that the load on both effluents has the same tendency of evolution proving that parts of releases craft activities; especially tanneries are discharged into the collector 1200 upstream of STEP.

Wastewaters of the two sites are basic, they have a very high load of suspended solids, cyanide, mineral and organic matter, and high metal loaded with chromium presented as Chromium III and lesser as chromium VI. The different sources and types of pollutants (organic, chemical, toxic, etc.) cause a negative impact that affects several sectors such as water resources management, drinking water production, agriculture, human health and Ecological balance of the environment.

The results of statistical tests reveal that most of the parameters vary significantly with the site factor that has more influence on the variability of pollution that the time factor. The ACP shows a strong positive correlation between the chemical parameters at P1 opposed to the physical parameters which have more influence on the P2 site.

Despite the fact that effluent from point P1 are more loaded than the point P2. The impact of the point P2 is more intense because the effluent is 8 times higher than the P1 site.

Arguably the pollution in the effluents from the city of Fez is of the chronic type. Generally it’s caused by industrial and especially artisanal releases of the city which reject their effluents without any treatment; this discharge has great adverse effects on the aquatic environment and on the biological treatment with activated sludge of sewage. It is imperative to provide a physic-chemical pre-treatment to reduce the load of this pollution and be able to be discharged into water courses or be treated by treatment plant of the city.

References

1. Salama Y., Chennaoui M., Sylla A., Mountadar M., Rihani M., Assobhei O., *J. Environ.and Poll. Res.* 2 (2014) 9-25.
2. DRPE. Etude stratégique de réutilisation des eaux usées déversées en mer. Mission I (2012).
3. Ministère délégué auprès du Ministère de l'Energie, des Mines, de l'Eau et de l'Environnement., (2014).
4. Sebou basin Agency and Autonomous electricity and water distribution company,. 6 (2015).
5. RADEEF., *Assistance à la RADEEF pour l'exploitation de la station d'épuration des eaux usées de la ville de Fès.* (2014) 2-4.
6. El Kadiri Boutchich G., Tahiri S., Mahi M., Gallart-Mateu D., de la Guardia M., Aarfane A., Lhadi EK., El Krati M., *J. Mater. Environ. Sci.* 6 (8) (2015) 2206-2220.
7. Zupanc M., Kosjek T., Petkovšek M., Dular M., Kompare B., Širok B., Blažeka Ž., and Heath E., *Ultrason. Sonochem.* 4 (2013) 1104–1112.
8. Nassar A.M., Smith M., Afifi S., *J. Water Environ.* 23 (1) (2009) 75–82.
9. Aoudj S., Khelifa A., Drouiche N., and Hecini M., *J. Desalin. Water Treat.* 6 (2015) 1422–1432.
10. El Adnani M., Boughrous A., Khebiza M. Y., El Gharmali A., Sbai M. L., Errouane S., Idrissi L. L., and Nejmeddine A., *J. Environ. Technol.* 28 (2007) 71–82.
11. Morhit M. E. L., Fekhaoui M., Serghini A., Blidi S. E. L., Abidi A. E. L., Yahyaoui A., Hachimi M., V-agdal U. M., Scientifique I., Zoologie L., Pollution U., and Agdal B. P., *Bulletin de l'Institut Scientifique.* 34 (2012) 151–162.
12. Nuto Y., And Guenda W., *J. Europ. Sci*. 11 (2015) 204–225.
13. Rodier.J, "*L'analyse de l'eau – eauxnaturelles, eauxrésiduaires, eau de mer,*" 9ème édition, Paris, Dunod, (2009) 1475.
14. Official Bulletin of the Minister of the Interior, the Minister of Energy, Mines, Water and Environment., the Minister of Industry. (2013) N° 2942-13.
15. Lokhande R. S., Singare P. U., and Pimple D. S., *J. Ecosyst.* 9 (2012).
16. Bordjiba. O., Bekhouche. F., Hassaine. A., Djenidi. R., *J. Europ. Sci. Res.*. 26 (2009) 87-97.
17. Belghyti D., Guamri Y. E. L., Ztit G., Lahcen M., Maroc K., *Sci.* (80).5 (2009) 199 – 216.
18. Tahiri A.A., Laziri F., Yachaoui Y., El Jaafari S., Tahiri A.H., *J. Europ. Sci. Res.* 35 (2014) 1857 – 7881.
19. Lemercie R., Legube G., Caron C., louwagie M.E., garin J., trouche D., khochbin S., *J. Biol. Chem.* 278, 7 (2003) 4713- 4718.
20. Ménesguen.A , *Direction de l'Environnement et de l'Aménagement Littoral DEL/EC,* Rapport IFREMER DEL/EC/01.02 (2001).
21. Hayzoun H., Ouammou A., Saidi O., Khalil F., Bouayyadi L., J. *Mater. Environ. Sci.* 5 (S2*)* (2014) 2438-2443.
22. Samake D., Traitement des eaux usées de tanneries à l'aide de matériaux à base d'argile. Sciences de la Terre. (2008) Université Joseph-Fourier - Grenoble I.
23. Singh K.P., Malik A., Sinha S., *Anal. Chim.* 7 (2005) 355-374.
24. Feng X., Thomas R. H., Matt F. S., John S., *J. water res.* 46 (2012) 3101-3109.
25. Bliefert C., and Perraud R., *J. Chim. de l'environ.* 477 (2001) 256-259.
26. Rim M. B. A., *Mémoire de fin d'étude en Ecologie et Environnement.* Université Constantine 1 (2014).

22. Cristovao R.O., Pinto V.M.S., Gonc alves A., Martins R.J.E., Loureiro J.M., Boaventura R.A.R., *Proc. Saf. and Environ. Protection* (2016) http://dx.doi.org/10.1016/j.psep.2016.03.016/ .

(2017) ; http://www.jmaterenvironsci.com