Treatment of Endocrine Pollutants Upstream of the Wadis Tghat and Zhoun of the City of Fez by Coagulation-Flocculation (Morocco)

Fatima-Zahra El Madani*[1], Nisrine Idrissi[1], Nouha El Allaoui[1], Mohamed Ben Abbou[2], Zakia Rais[1], Mustapha Taleb[1],

[1]*Faculty of Sciences Dhar El Mahraz Fez, Sidi Mohamed Ben Abdellah University, 30000 Fez (Morocco).*
[2]*Faculty Poly Disciplinary Taza, Sidi Mohamed Ben Abdellah University, 35000 Taza, (Morocco)*
E-mail: fatimazahra.elmadani1@usmba.ac.ma

Abstracts: In recent years, the quality of the surface water of the city of Fez has deteriorated due to the development of various anthropic activities, ill-considered modernization, unregulated discharge of wastewater and solid waste. This is a worrying threat to human health and the environment. Previous studies on these wadis have shown that Tghat and Zhoun wadis are the most polluted **[1]**; **[2]**; **[3].** Adequate treatment of effluents upstream is therefore of crucial importance. The objective of this study is to contribute to the treatment of endocrine pollutants discharged upstream of these two wadis after their characterization and monitoring of their pollutant load for six months (El Madani et al., 2019). The most polluted wadis of the city of Fez **[2]** by coagulation-flocculation.The results showed that these effluents have a medium faecal load and are loaded by organic pollution at the limit of biodegradability rich in nitrogen and phosphorus matter and a high metallic load with endocrine disrupting effect, mainly Cr, As, Pb and Cd.The treatment of these pollutants by coagulation-flocculation with aluminum sulphate of the effluents studied under optimal conditions of pH, a dose of coagulant and flocculant and coagulation and flocculation agitation speeds, allowed the reduction of almost all the organic matter and 90 to 96% of the metal load.

Keywords: Endocrine Pollutants, Upstream Wadis Tghat And Zhoun, Coagulation-Flocculation, Treatment, Metal Charge.

1. INTRODUCTION

The effective treatment of a water requires a good knowledge of the flow, its quality (chemical composition) and the temporal variations of its composition. To this end, it is necessary to find the right treatment technology for each type of pollution. Several methods of treatment of polluted biological and/or physical-chemical water have been developed, in particular the physical-chemical treatment by coagulation-flocculation, which is considered as the most classical and most successful treatment due to its efficiency and low cost, despite the excessive generation of sludge [4]; [5]. Several studies have been carried out on coagulation aimed at selecting the coagulant, optimizing coagulation parameters or combining it with other treatment methods [6]; [7]; [8].; [1].; [9]. However, other studies propose that for water, Aluminium sulphate can considerably improve coagulation at low dosage and therefore at low cost [10].; [5].; [1].

This study shows the main test results of physical-chemical treatment by coagulation-flocculation of effluents upstream of the Tghat and Zhoun wadis, considered the most polluted, with optimization of the parameters conditioning the treatment.

2. MATERIEL AND METHODS

The treatment by coagulation-flocculation consists in reducing the pollution load of effluents upstream of the surface waters crossing the Ain Nokbi (S1) and Sidi Boujida (S2) zones, recognized by many industrial, artisanal and agricultural activities in the Fez region [3].

Water samples were taken, once a month for six months according to the AFNOR standards issued by Rodier, from the outlet pipe of each study area: upstream of the Tghat and Zhoun wadis which are downstream of the Fez wadi. They were characterized by measuring the physical-chemical parameters (Temperature, pH, Electrical conductivity, Dissolved oxygen, Chemical oxygen demand, Biological oxygen demand, Total Kjeldhal nitrogen, Total phosphorus, nitrates and trace metal elements (Arsenic, Chromium, Lead, Zinc, Cadmium, Nickel) and bacteriological (Fecal coliforms) according to the same standards. The Jar-test device type VELP SCIENTIFICA (JLT6) using Aluminium Sulphate as coagulant and Praestol as flocculant carried out their treatment.

The Jar-test is composed of 6 reactors with a capacity of one liter each in which we have:

- introduced 800 mL of decanted surface water,

- adjusted the pH of the solution by adding hydrochloric acid HCl (0.01 M) or soda NaOH (0.01 M) to the coagulation pH according to the Pourbaix diagram [7].

- added a dose of coagulant (Aluminum Sulfate (Al2 (SO_4^{3-}), 18 H_2O) under rapid agitation for a few minutes,

- added a dose of acrylamide-based flocculant (Praestol 2540 ($C_{12}H_{24}ClN_3O_2$)) under slow stirring until the flocs are visible,

- Decant the mixture for 20 minutes, then filter it and analyse the filtrate.

During the coagulation-flocculation treatment, 6 parameters were optimized at the adjusted pH: the doses of coagulant (0.10 - 0.25 g.L-1) and flocculant (0.5 - 2 mg.L-1), the coagulation (1-7 min) and flocculation (15-30 min) times, the coagulation (100-250 r.p.m.-1) and flocculation (15-30 r.p.m.-1) rates. After optimization of each parameter, we set it to its optimal value so that we can optimize the next parameter.

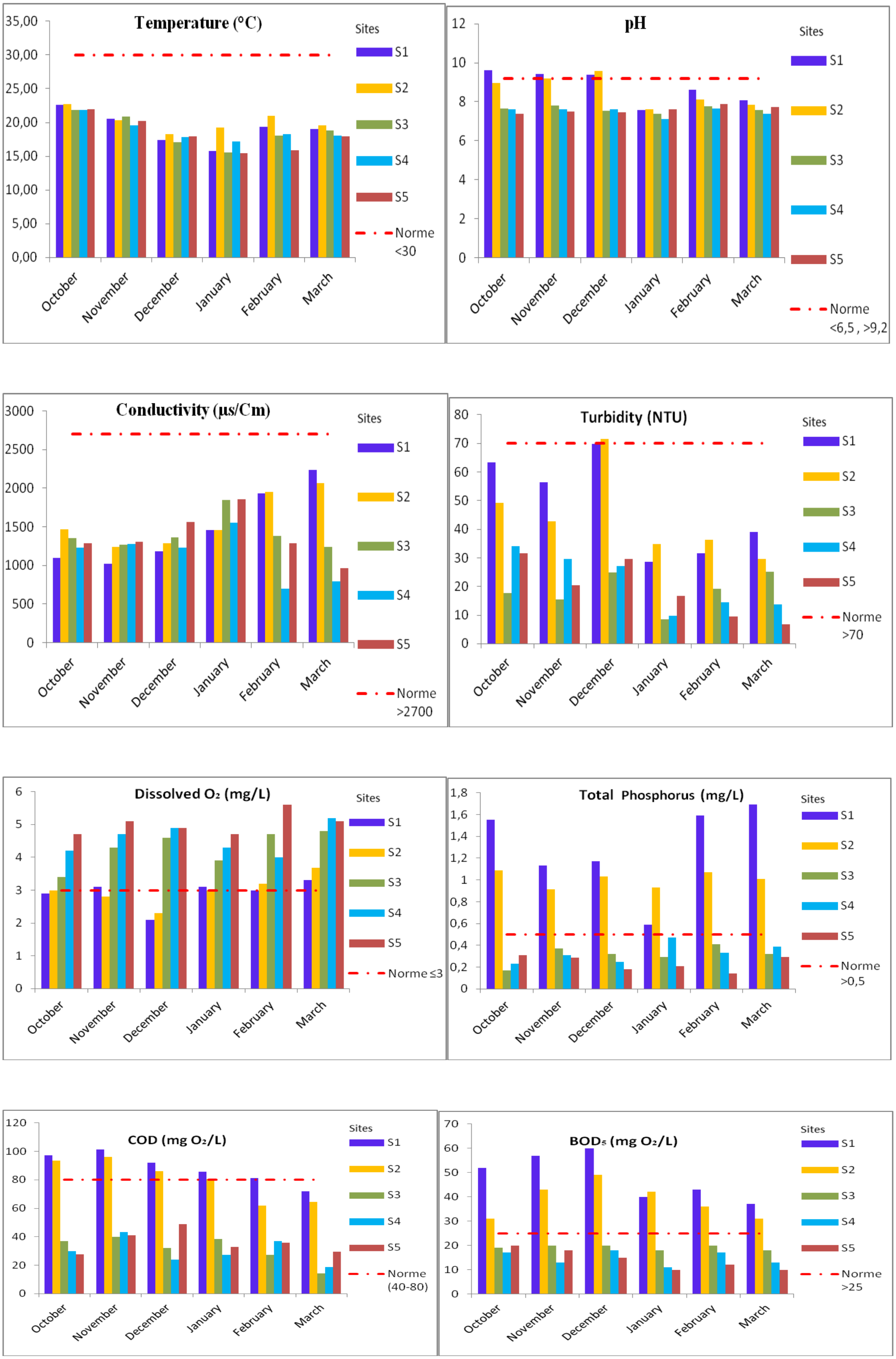
Evaluation of treatment efficiency was carried out by monitoring four metallic trace elements as a function of time: chromium, arsenic, lead and cadmium as indicators of endocrine disruptors.

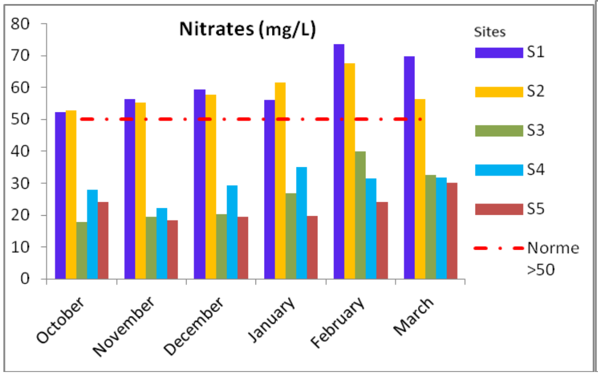
3. RESULTS AND DISCUSSIONS

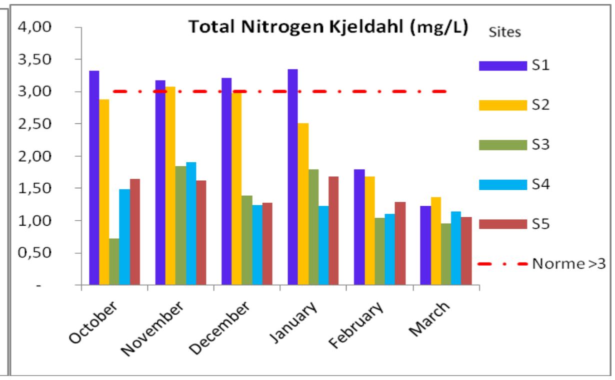
A recent study showed that the physico-chemical, bacteriological and metallic characterization of the studied effluents (S1 & S2) allowed us to identify the most polluted sites that required a spatiotemporal monitoring of their quality during the whole year of 2017 [2]; [3].

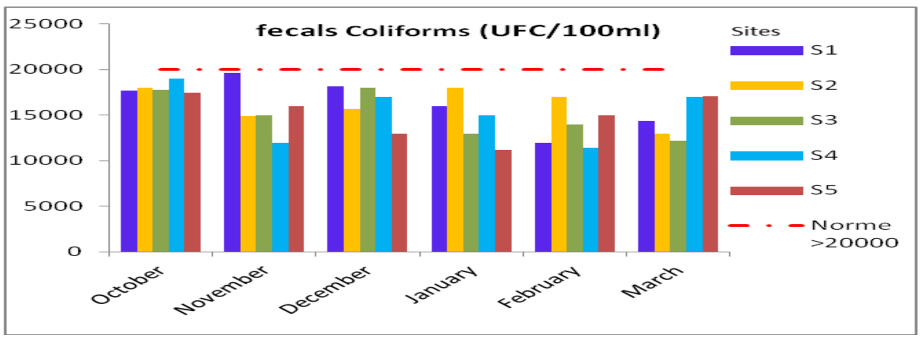
3.1. Spatiotemporal Monitoring of the Studied Effluents (S1&S2)

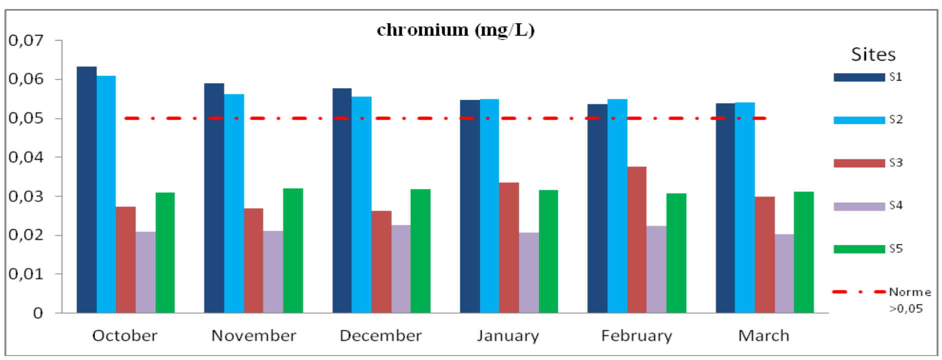
The results of the spatio-temporal monitoring of the parameters evaluating the quality of surface water at the two sites S1 and S2 are in conformity with the Moroccan standard for surface water [11]. They are represented in the figure 1.


Temperature (°C)
Sites
S1
S2
S3
S4
S5
Norme <30
pH
Norme <6,5 , >9,2
Conductivity (µs/Cm)
Norme >2700
Turbidity (NTU)
Norme >70
Dissolved O₂ (mg/L)
Norme ≤3
Total Phosphorus (mg/L)
Norme >0,5
COD (mg O₂/L)
Norme (40-80)
BOD₅ (mg O₂/L)
Norme >25
October
November
December
January
February
March


Nitrates (mg/L)
80
70
60
50
40
30
20
10
0
October
November
December
January
February
March
Sites
S1
S2
S3
S4
S5
Norme >50


Total Nitrogen Kjeldahl (mg/L)
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
-
October
November
December
January
February
March
Sites
S1
S2
S3
S4
S5
Norme >3


fecals Coliforms (UFC/100ml)
25000
20000
15000
10000
5000
0
October
November
December
January
February
March
Sites
S1
S2
S3
S4
S5
Norme >20000


chromium (mg/L)
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
October
November
December
January
February
March
Sites
S1
S2
S3
S4
S5
Norme >0,05

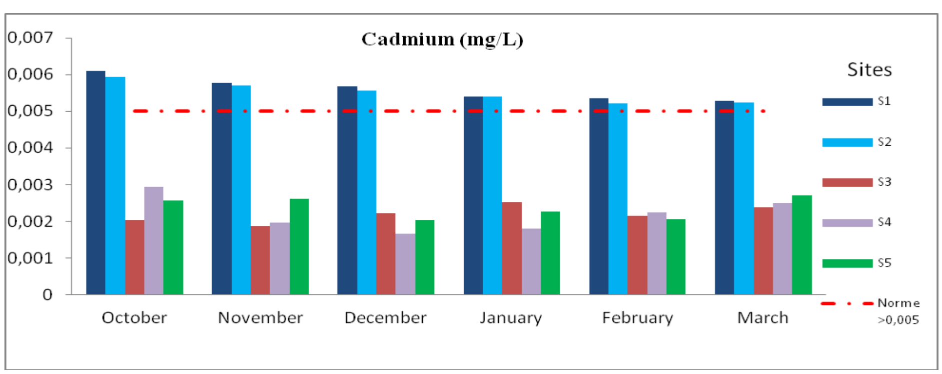

Cadmium (mg/L)
0,007
0,006
0,005
0,004
0,003
0,002
0,001
0
October
November
December
January
February
March
Sites
S1
S2
S3
S4
S5
Norme >0,005

Figure 1. Spatio-temporal monitoring of physicochemical parameters, bacteriological and metal of the monthly assessment of the water quality of river during 2017

The Analysis of the results obtained indicates that:

- Water temperatures at sites S1 and S2 are between a minimum and a maximum, with the minimum value being reached during the fall, winter and early spring seasons. The maximum value occurred at the end of the spring season and during the summer season. All values during the study period were within the surface water quality standard (<30°C).

- The pH is close to neutral during most of the period, except for the pH of the water at site 2, which is slightly basic in December.

- Dissolved oxygen has values between 1.2 mg $O_2.L^{-1}$, recorded in May, and 4.5 mg $O_2.L^{-1}$ in February. Low values were assigned during the summer season. This could probably be due to its function in the degradation of organic matter present in water by microorganisms.

- Electrical conductivity is very high during the months of June and July for sites S1 and S2. It is 2736 µs cm^{-1} and 2765 µs cm^{-1} respectively. This high mineral load could probably be due to the excessive mineralization of these waters attributed to the salts used in the majority of industrial, artisanal and agricultural activities.

- The turbidity is at the limit of the Moroccan standard during the whole study period and for the two sites S1 and S2 except for the water of site S2 that was slightly exceeded in December 2017.

- The chemical oxygen demand (COD) fluctuates between 80.5 mg $O_2.L^{-1}$ and 116 mg $O_2.L^{-1}$ exceeding the norm during the summer and autumn seasons. We note that Tghat wadi waters carry a non-biodegradable organic load to a lesser degree than that of Zhoun wadi waters. This seems to be due to discharges from the strong industrial and artisanal activities in the Ain Nokbi and Sidi Boujida areas.

- The biochemical oxygen demand (BOD_5) is well above the norm for all months of the year. It almost tripled the value characterizing good quality surface water during the months of June, July and December, and exceeded it by about 10% during the other months. However, this organic load is mostly biodegradable ($COD/BOD_5<3$) except in September and October [3].

- The high COD and BOD_5 loads could be explained by the coincidence of our study period with the period of Aid Al Adha, whose high activity of skin treatment took place during these months on the one hand, and olive crushing on the other hand.

- Ammonium indicates a maximum value in September reaching 9.23 mg $NH_4.L^{-1}$ for the waters of S1 and 7.98 mg $NH_4^+.L^{-1}$ for those of S2, showing a significant contribution of anthropic activities in the study areas. As for the Kjeldahl nitrogen results, they show fairly high concentrations throughout the study period except for the months of September and October, when they are subject to a high nitrogen load and reach values exceeding the surface water quality standard Rodier [11]; [12].

- Nitrates are at the limit of the standard for almost half of the study period outside the fall and winter seasons. This could be due to different detergents of industrial or domestic origin and to the coincidence of the Aid al Adha period between September and October [1]; [13]. In addition to the proximity of the wadis in the industrial and agricultural zones of Ain Nokbi and Sidi Boujida and the watering of animals, which is also a source of nitrate contamination of water.

- Total phosphorus is out of the norm throughout the study period for the waters of sites S1 and S2. This phosphorus pollution probably comes from detergents of industrial or domestic origin, waste from protein metabolism and its elimination in the form of phosphates in urine by humans [14].

- Contamination by faecal coliforms (FC) is unlikely because of the limit values of these parameters in the Moroccan standard for surface water in a river.

- The majority of metallic trace elements (MTEs), considered endocrine disruptors, Chromium, Arsenic, Lead and Cadmium (Figure 1), greatly exceed the Moroccan surface water quality standard for the waters of the Tghat and Zhoun wadis. As for the Zinc and Nickel load of these waters, it complies with the standards set.

- It should be pointed out that during the monitoring period we have witnessed the coincidence of the Aid Al Adha period, the olive crushing period and the discharges from tanneries and other types of industries.

- In fact, the significant variations in the monitoring are probably due to the nature and daily frequency of industrial, artisanal and craft activities in the target areas.

3.2. Coagulation-Flocculation pH Adjustment

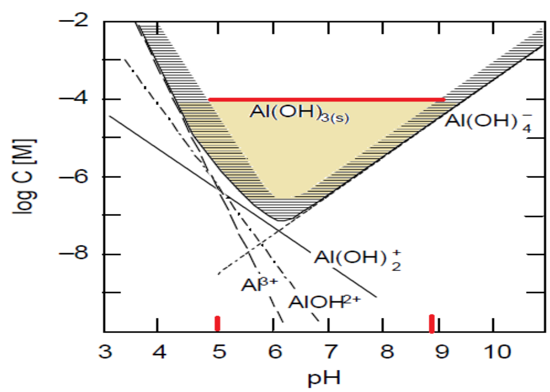


Figure 2. Aluminum Spur Diagram [7]

Has a pH between 4 and 9 :

$$Al_2(SO_4) \rightarrow 2Al^{3+} + 3SO_4{}^{2-}$$ Équation 1

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3s} + 3H^+$$ Équation 2

Has a pH between 1 and 4 :

$$Al(OH)_{3s} + 3H^+ \rightarrow Al^{3+} + 3H_2O$$ Équation 3

Has a pH between 9 and 14:

$$Al(OH)_{3s} + OH^- \rightarrow Al(OH)_4^-$$ Équation 4

For our case, we fluctuated the pH between 6 and 7.5 (Figure 3) while setting the other parameters since the transformation zone from Al3+ to Al(OH)3 at low concentrations is for pH values between 5.5 and 8.

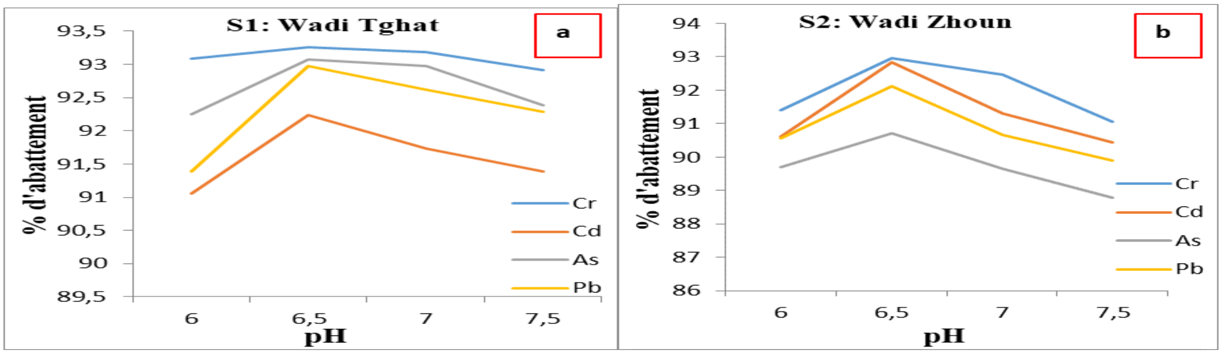


Figure 3. Adjustment of the pH of the water to be treated: (a) S1; (b) S2; Operating conditions: [Al2OH3] =0.15 g.L^{-1}, [Praestol]= 1mg.L^{-1}, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

The curves in Figure 3 show a reduction in all metallic trace elements of approximately 90-93% for effluents from the two study sites at pH 6.5.

3.3 Optimization of the Coagulant Dose

In order to optimize the coagulant dose, the pH was set at its previously identified optimal value (6.5). The results obtained for each site are presented in Figure 4 and show that increasing the coagulant dose above 0.15 g.L^{-1} diminishes the concentration of As, Cr, Pb and Cd.

The maximum removal of all metals studied took place at a concentration of 0.15g.L^{-1} of coagulant varying between 92.5% and 93.8% for Tghat wadi waters (S1) and between 90.8% and 93.5% for Zhoun wadi waters (S2).

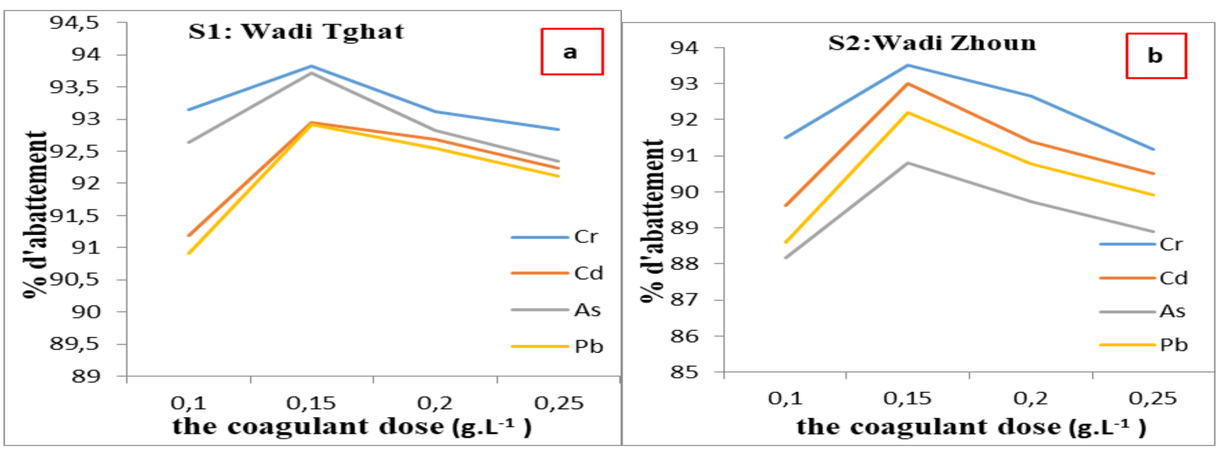


Figure 4. Effect of coagulant dose on the percentage reduction of Cr, As, Pb, and Cd: (a) S1; (b) S2; Operating conditions: pH=6.5, [Praestol] = 1 mg.L^{-1}, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

3.4 Optimization of the Flocculant Dose

In order to optimize the dose of the flocculant, we have stabilized the pH and the dose of the coagulant at their optimal values, which are 6.5 for the pH and 0.15 g.L^{-1} for the coagulant. While the dose of the flocculant was varied between 0.5 and 2 mg.L^{-1}. Figure 24 presents the results of the flocculant optimization for the effluents of the two sites S1 and S2 which record that an increase in the concentration of the flocculant (Praestol 2540 ($C_{12}H_{24}ClN_3O_2$)) from 0.5 to 1 mg.L^{-1} increases the percentage of metal removal from the effluents of S1 from 47.21% to 93.74% and those of site 2 from 58.19% to 93.69%. The treatment efficiency is slightly better, especially in Cr for Tghat wadi water. Pb was effectively eliminated by this flocculant in the incoming effluent at Wadi Zhoun. It should be noted that a concentration higher than 1mg.L^{-1} does not significantly increase the percentage of pollutant reduction. The use of

Praestol 2540 as a flocculant promotes the agglomeration of destabilized particles at low concentrations and minimizes the time of their settling.

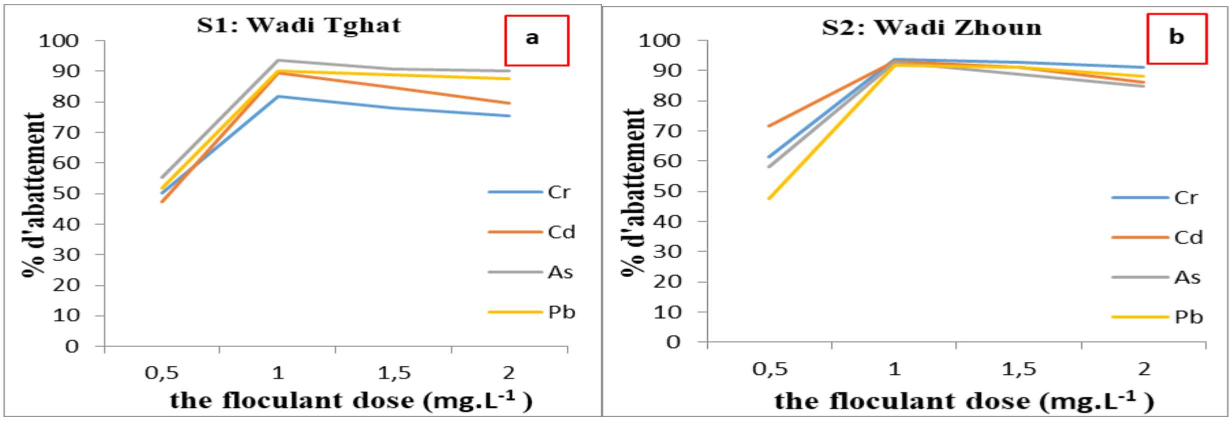


Figure 5. Effect of flocculant dose on the percentage reduction of Cr, As, Pb and Cd: (a) S1; (b) S2; Operating conditions: Al2SO4]=0.15 g.L^{-1}, pH=6.5, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

3.5 Optimization of Stirring Time for Coagulation-Flocculation

The figures 6 and 7 illustrate the effect of agitation time for coagulation and flocculation on the abatement of the pollutant load in the waters of sites S1 and S2.

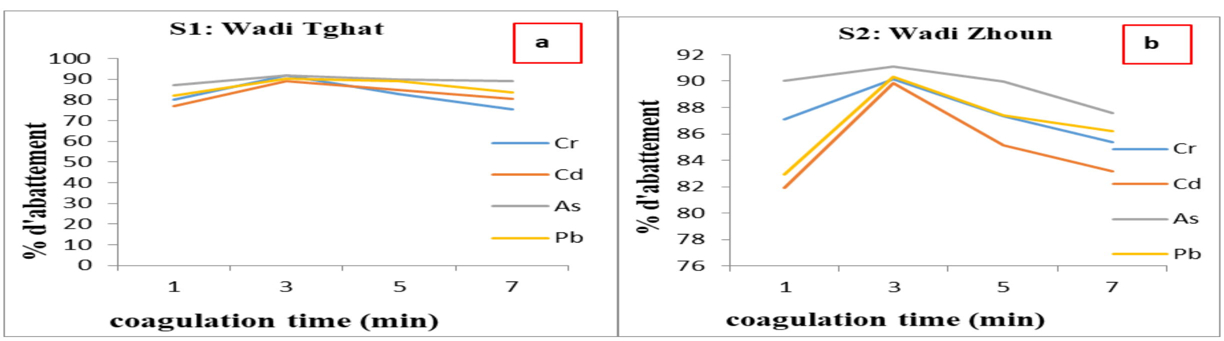


Figure 6. Effect of clotting time on the percentage reduction of Cr, As, Pb and Cd: (a) S1; (b) S2; Operating conditions: Al2SO4]=0.15 g.L-1, pH=6.5, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

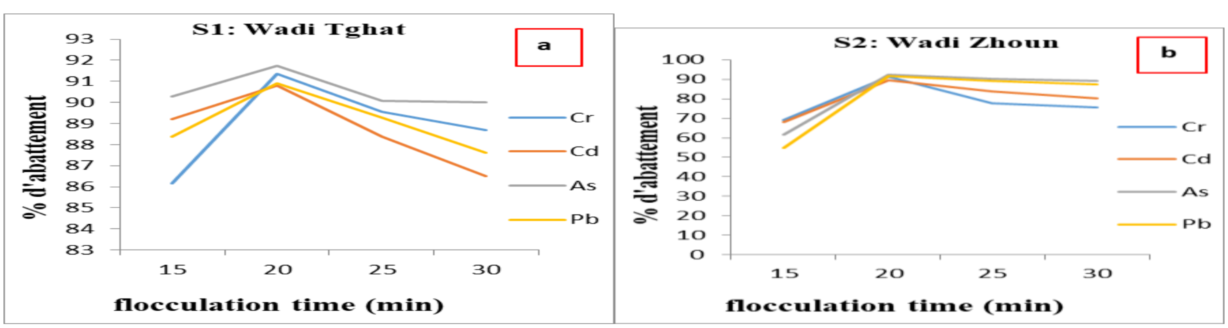


Figure 7. Effect of flocculation time on the percentage reduction of Cr, As, Pb and Cd: (a) S1; (b) S2; Operating conditions: Al2SO4]=0.15g.L^{-1}, pH=6.5, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

According to the curves in Figure 6, the maximum abatement is obtained for a coagulation time of 3 min for the waters at both sites. The removal of the various metallic trace elements is between 90% and 91%. As for the maximum flocculation time of the coagulated and floated particles, it is 20 min, corresponding respectively to a reduction of nearly 92% for almost all the metals and typical waters of the two effluents (figure 7).

In conclusion, at an optimum pH of 6.5, a time that exceeds 7 min of coagulation and 30 min of flocculation acts on the performance of coagulation-flocculation. In fact, when this optimum time is exceeded at an agitation of 150 $tr.min^{-1}$ of coagulation and 20 $tr.min^{-1}$ of flocculation, there is a dissociation of the agglomerated particles, most probably due to metal complexation; this significantly reduces the efficiency of the treatment.

The best results were recorded at a time of 3 min of rapid agitation (150 $tr.min^{-1}$) to destabilize most of the colloidal particles present in the effluents studied and a time of 20 min of slow agitation (20 $tr.min^{-1}$) is sufficient to further decant the colloidal flocs.

3.6. Optimization of the Coagulation Flocculation Rate

The figures 8 and 9 show that the removal rate of the metals studied is achieved at a maximum coagulation rate of 150 rpm.

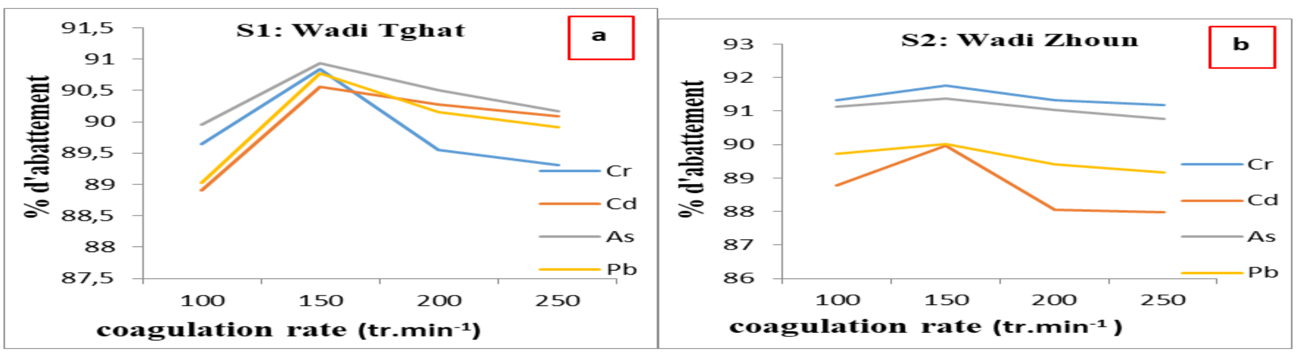


Figure 8. Effect of coagulation rate on the percentage reduction of Cr, As, Pb and Cd: (a) S1; (b) S2; Operating conditions: Al2SO4]= 0.15 $g.L^{-1}$, pH=6.5, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

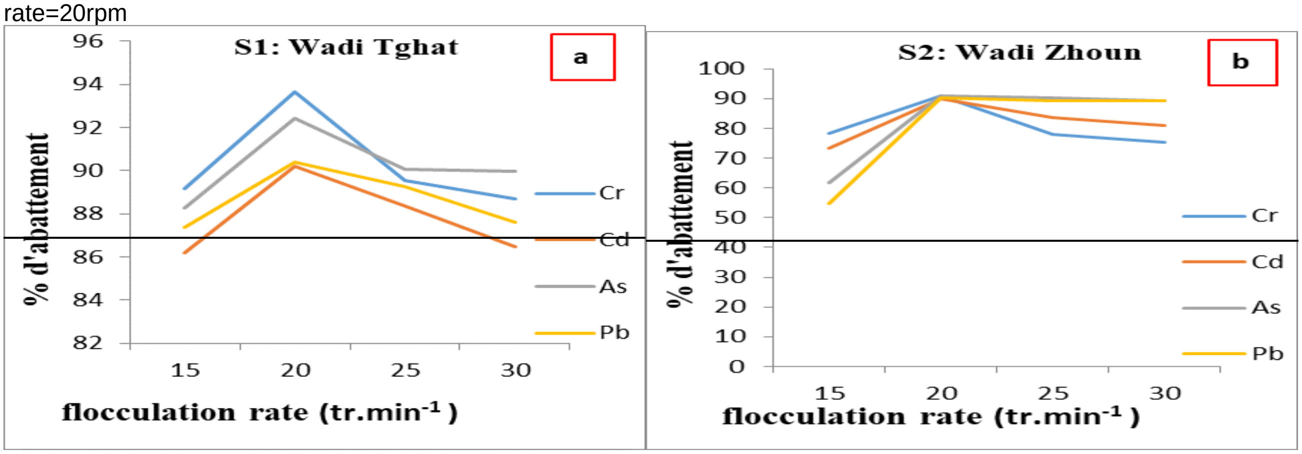


Figure 9. Effect of flocculation rate on the percentage of Cr, As, Pb and Cd abatement: (a) S1; (b) S2; Operating conditions: Al2SO4]=0.15 $g.L^{-1}$, pH=6.5, Coagulation time=3min, Flocculation time=20min, Coagulation rate=150rpm, Flocculation rate=20rpm

After having dispersed the colloidal particles present in the studied effluents and destabilized them, to gather the destabilized particles into flocs by increasing their masses to facilitate their settling and obtain the most favorable performances. According to these figures, the optimal flocculation speed was obtained at 20 rpm. Beyond this value, there was dissociation of the particles due to the complexing of the metals present in solution.

CONCLUSIONS

The waters of the Tghat and Zhoun wadis experience intense demographics and have the same sources of pollution, and almost the same anthropogenic activities (industrial, agricultural, etc.).

The spatiotemporal monitoring of the pollutant load of these effluents carry high organic, nitrogen and phosphorus loads and are rich in Chromium, Arsenic, Lead and Cadmium and to a lesser degree in bacterial load (faecal coliforms) and endocrine pollutants confirmed their permanent load in Cr, As, Cd and Pb.

The treatment tests for S1 and S2 by coagulation-flocculation, using aluminum sulfate (Al_2 ($SO_4{}^3$)$_,$ 18H2O)) as coagulant, were examined under various conditions. During the study we adjusted the pH, varied the dose of coagulant and flocculant, the coagulation and flocculation time, the coagulation and flocculation speeds. After optimizing each parameter, we subsequently set it at its optimal value to be able to move on to the next parameter.

The treatment of these pollutants by coagulation-flocculation, using Aluminium sulphate as coagulant and Praestol as flocculant, under optimal conditions of coagulation pH equal to 6.5, coagulation and flocculation concentrations of 0.15 g.L^{-1} and 1 mg.L^{-1} respectively, of coagulation stirring speeds of 3min and flocculation speeds of 20 min, and of coagulation duration of 150 tr.min^{-1} and flocculation duration of 20 tr.min^{-1}, led to an elimination of the metallic pollutant load of the effluents upstream of the two wadis studied which is in the region of 90 to 94%.

REFERENCES

[1] El Allaoui, N, *Evaluation of the pollutant load and treatment of WWTP effluents using integrated processes: optimization and modeling of results*, thesis. Sidi Mohammed Ben Abdellah University Faculty of Sciences Dhar El Mahraz Fez, 2018.

[2] EL Madani. FZ, K. Lahlou, N. Idrissi, N. El Allaoui, M. Ben Abbou, M. Merzouki, A. Chetouani, M. Taleb, Z. Rais, *Identification of the quality of surface waters in the city of Fez by the SEQ-GIS approach and ANOVA *"Mor j chem, vol 7, issue 4 2019.

[3] El Madani FZ, N. Idrissi, K. Lahlou, N. El Allaoui, M. Benabbou, M. Merzouki, M. Taleb, Z. Rais, *Spatiotemporal assessment of the quality of surface water the most polluted in the city of Fez (Morocco)*, Journal Of Biodiversity And Environmental Sciences (JBES), vol.18, N.4, P.1-10, 2021.

[4] Verma, Akshaya Kumar, Dash, R.R., & Bhunia, P, A review on chemical coagulation/flocculation technologies for removal of color from textile wastewaters, Journal of Environmental Management, 93(1), 154–168, 2012.

[5] Kulkarni, S.J. Coagulation for Wastewater Treatment: A Review on Investigations and Studies, article. International Journal of Scientific Research in Science and Technology, 3(3), 501–505, 2017.

[6] Saritha, V., Srinivas, N., & Srikanth Vuppala, N. V, *Analysis and optimization of coagulation and flocculation process*, Applied Water Science, 1–10, 2015.

[7] Boudhane Nassim & Ahmed Ammar Ikram. Optimization of biological treatment in an activated sludge treatment plant: case of the Batna WWTP, report, 2016.

[8] El Shamy, A., El Boraey, H. A., & El Awdan, H. *Chemical Treatment of Petroleum Wastewater and its Effect on the Corrosion Behavior of Steel Pipelines in Sewage Networks*, Journal of Chemical Engineering & Process Technology, 08(01), 2017.

[9] Majbar Zineb. Treatment of vegetable waters by a process combining electrocoagulation and adsorption on activated carbons of Eucalyptus sawdust and their valorization by composting of wine waste, thesis, 2019

[10] Zueva, S., Ostrokon, A., Llyina, N., De Michelis, I., & Veglio, F. *Coagulation Processes for Treatment of Waste Water from Meat Industry* International Journal of Waste Resources, 3(2), 3–6, 2013.

[11] BO. Official Bulletin, One Hundred and Fifth Year _IN° 6522, 1st Rabii 11438 (December 1, 2016), ISSN 0851 - 1217, Kingdom of Morocco. (Vol. 11438), report, 2016.

[12] Rodier, J., Legube, B., & and Merlet, N. L'Analyse d'eau,DUNOD, 9ème édition, rapport, 2009.

[13] Idrissi. N. Assessment of surface water quality and their relationships with certain water-borne diseases (case of the city of Fez): GIS-SEQ approach. Usmba-sdm, 2018.

[14] Seghairi, N. *Elimination of organic pollutants present in domestic wastewater in the commune of Sidi Okba, by a filter planted with macrophytes*, thesis, 2014

DOI: https://doi.org/10.15379/ijmst.v10i2.3342