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Characterization of heavy metals and toxic elements in raw sewage and their impact on the secondary treatment of the Marrakech wastewater treatment plant

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Abstract

The purpose of this study is to follow the evolution of the concentration of heavy metals (Cr^{+6}, Cu and Ni) and toxic elements (Sulfides and Phenols) in raw water at the inlet of the wastewater treatment plant of Marrakech (Morocco) and to evaluate their impact on the performance of secondary treatment with activated sludge. For this purpose, analyzes of heavy metals and toxic elements as well as other physicochemical parameters were carried out at the entry of the WWTP in 2013.The toxic elements were an annual average of 0.19 mg /L for Cr^{+6}, 3.21 mg /L for Cu, 1.98 mg /L for Ni, 3.58 mg/L For Phenol and 2.24mg /L for sulfides. The raw effluent pollution parameters are, pH 7.9, conductivity of 2711.99µS /cm, temperature 25.28 ° C, COD of 1051.67 mg O_2 / L, BOD_5 of 516.58 mg O_2 /L, an SS of 416.53 mg /L, Global Nitrogen (NGL) of 90.55 mg / L, and 11.20 mg /L for total phosphorus (Pt).The results of analyses at the exit of secondary treatment provided good elimination efficiency throughout the year for all biological treatment parameters : 90% for chemical oxygen demand (COD), 97% for 84% for suspended solids (SS), 87% for global nitrogen (NGL), and 55% for total phosphorus (Pt). However, during the month of April, the purification performance of the biological treatment was affected by the abundant presence of toxic elements that far exceeded the standards recommended by the Moroccan authorities. The purification yields were affected and reached minimum levels of 74%, 94% 75%, 49% and 40% respectively of COD, BOD_5, SS, NGL and (Pt).

1. Introduction

Currently, wastewater treatment has become necessary to address the scarcity of water resources and reduce their negative impact on the environment for a healthier lifestyle [1]. To this end, the legislator has not ceased to impose laws and new standards on treated water at sewage treatment plants before being discharged into the natural environment. But many problems can affect the process and the performance of the processing plant. Among them, for example, the capacity of Beijing's treatment facilities in 2013 was quickly overwhelmed and more than 17% of the wastewater generated by the Chinese capital was discharged without any prior treatment [2].Another example and following a shutdown of the pumping device due to a flight of copper, the processing station of Creil Montataire, in the north of France overflowed during the night of 19 to 20 May 2014, which caused the spill of a net of organic matter in the neighboring arm of the Oise [3]. Besides, there are other concerns particularly restricting the reliability of biological treatment, because at the sewage treatment plants, the control of the biological parameters is delicate [4] as in the case of electromechanical problems (cuts in electricity accidental shutdown of machines, etc.) but also the entry of the toxic elements constituting the trace metallic elements (ETM) which have an adverse effect and which results in the modification, denaturation or inactivation of enzymes, Alteration of cell membranes, as well as other hazardous substances such as hydrocarbons even at low concentrations. Generally, they are mineral or organic micro pollutants which can damage and destroy scrubbing microorganisms and which are the causes of WWTP malfunctions [5, 6, 7].

This is the case of the Fontaine station in Cros de Rotier (Hautes Alpes). On May 22, 2012, the pollution was then found in the natural environment, due to the destruction of the bacteria fixed on the pozzolana by the discharge of about fifty liters of hydrocarbons towards the station [8]. Note also the case of malfunctioning of the Sotuba treatment plant which was affected by the poorly treated effluent from the four tanneries of the city of Bamako in Mali, which did not respect the norms of indirect rejection [9].

In Morocco, as in many countries, the type of networks, mostly unitary, which receives industrial discharges without any prior preliminary treatment, in addition to domestic waste, is further reinforced by the lack of vision and global strategy on the subject as well as in an accentuation of irresponsible practices [10].

Across the Kingdom, the presence of toxic elements in the raw effluents affects negatively the performance of biological treatment of wastewater. 313 Mm^3 of urban wastewater was treated in 2015 in Morocco, representing 41.8% of the total volume generated. Until 2010, the number of WWTP s in the country was 98, including 39 with tertiary treatment. In general, the natural lagoon predominates the type of treatment processes used (82%) with 56% of the volume of water treated in 2012. On the other hand, the aerated lagoon, bacterial beds and the algal channel account for 2% each, the activated sludge represents 12% [11], including the one of the city of Marrakech. This low-load WWTP is located 2 km from the El Azzouzia collection point and just upstream from the Tensift river. The WWTP receives almost all wastewater from the city of Marrakech, about 33 million m^3 annually, which passes through the treatment process, and a good part of which is reused for the irrigation of golf courses after tertiary treatment. The station is also designed to produce biogas from the treated sludge [12].

In the presence of oxygen (artificial aeration) in the activated sludge, the biological purification of the latter is generally based on the contact of the scrubbing microorganisms with the water to be treated, which results in the elimination of the existing dissolved pollution in the latter [13]. The Marrakech WWTP presents a risk of dysfunction since the industrial discharges of the city are evacuated to the station in the initial state [14]. The objective of this work is the characterization and evaluation of the toxic elements at the level of the raw effluent entering the Marrakech WWTP and their effects on the performance of the biological treatment (secondary treatment) of the waste water during the year 2013.

2. Experimental

2.1. Site Study

The city of Marrakech is in the center of the country; it is a metropolis with dry climate and counts a population of 1330468 inhabitants [15]. It has an average annual sunshine of more than 8 hours per day and an average annual temperature that exceeds 17 °C. The regional economy is based on tourism, crafts, industry, agrifood, agriculture, Breeding and mining [14].

Marrakech has a WWTP with a capacity of 1.3 million population equivalents. This station (Figure 1) is located at the north of the city; it covers an overall area of 17 ha on the left bank of the Tensift river which runs along the NR7 to Safi [12]. Marrakech has a collective sanitation network (2284 km) with a unitary majority, a small part of this network is pseudo-separative and it is located in the Sidi Ghanem industrial zone, the M'hamid zone and newly formed areas.

Figure1: Location of the Marrakech WWTP

(www.google.com/maps/place/STEP)

2.2Description of the WWTP

Wastewater treatment plant

A conventional pretreatment consisting of a succession of screening, sandblasting and de-oiling operations.A primary treatment (TP) consisting of three conventional decanters (Figure 2).
A secondary biological treatment (TS) composed of four aeration basins and four clarification basins. The biological treatment is a low activated sludge type.Tertiary final treatment consisting of a succession of coagulation operations, flocculation, sand filtration and UV disinfection and chlorine.
Sludge: All the sludge produced in the water system is recovered and thickened by gravitation for the primary sludge and by flotation for the secondary sludge.
Biogas: The thickened sludge is returned to four digesters for the production of biogas by biomethanisation.

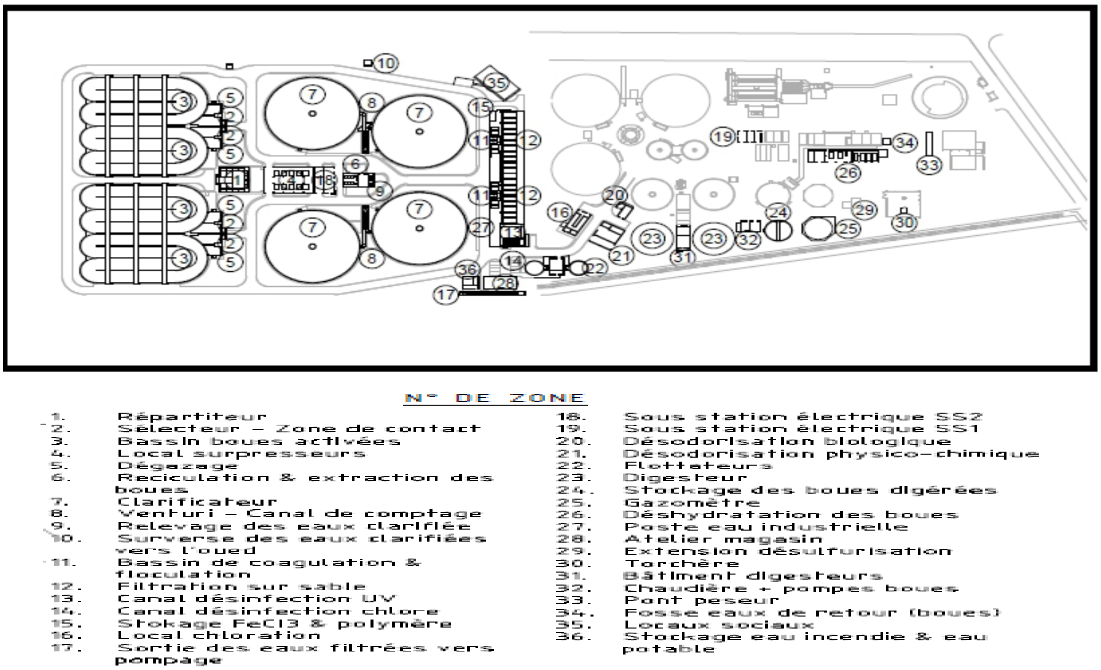

Figure. 2: General outline of the Marrakech WWTP

2.3Physico-chemical analysis

Analyses are performed daily on 24 hour composite samples taken automatically every hour. The samples are taken from two points: at the entry of the WWTP (EP) and at the exit of the secondary treatment for the analysis of the performance indicators which are: BOD_5, COD, SS, NTK and Pt. They are analyzed according to international standard methods.
In addition, the search for toxic elements including some heavy metals (MTE) was carried out only at the level of the raw effluent (EP); mainly because the MTEs precipitate and accumulate in the solid phase (sludge) via primary settlement [16] and is poorly encountered at the secondary tributary. The detected elements are: Copper (Cu), Chromium VI, Nickel (Ni), Phenols and sulfide (S °), they are analyzed according to the standardized rapid methods (the tanks) (Table 1).

Tableau.1 Toxic elements and associated analytical methods

The toxic element	**standards**	**Name of the method**	**Platform**	**Measuring range**
Chrome VI	ISO 8466-1	Diphénylcarbazide EN ISO 11083, DIN 38405-D24	Test en cuve: LCK 313	[0,03-1,0 mg/l]
Copper Cu)	ISO 8466-1	Acide bathocuproïnedisulfonique	Test en cuve : LCK529	[0,01-1,0 mg/l]
Nickel (Ni)	ISO 8466-1	Diméthylglyoxime DIN 38406-E11	Test en cuve: LCK 337	[1-60 mg/l]
Sulfide (S°)	ISO 8466-1	Diméthyl-p-phénylène-diamine ISO 10530-1991, DIN 38405-D26	Test en cuve: LCK 653	[0,1-2,0 mg/l]
Phenols	ISO 8466-1	4-nitroaniline	Test en cuve : LCK345	[0,05-5 mg/l]

3. Results and discussion

This study examines the performance of WWTP during 2013. With the monthly averages of the toxic elements which do not represent all the days of the month but depends on the number of days of the appearance of these elements in the raw water of each month.

3.1.Characterization of raw sewage at the entrance of the WWTP

3.1.1. Trace elements: Chromium VI, Nickel and Copper

Figure 3 shows the evolution of the monthly averages of the metallic trace elements: Chromium VI ($Cr+^6$), Copper (Cu) and Nickel (Ni) evaluated at the raw effluent entering the Marrakech's WWTP Other physicochemical parameters such as COD, BOD_5, SS, NGL, pT, T °C, pH and conductivity during the year of study.

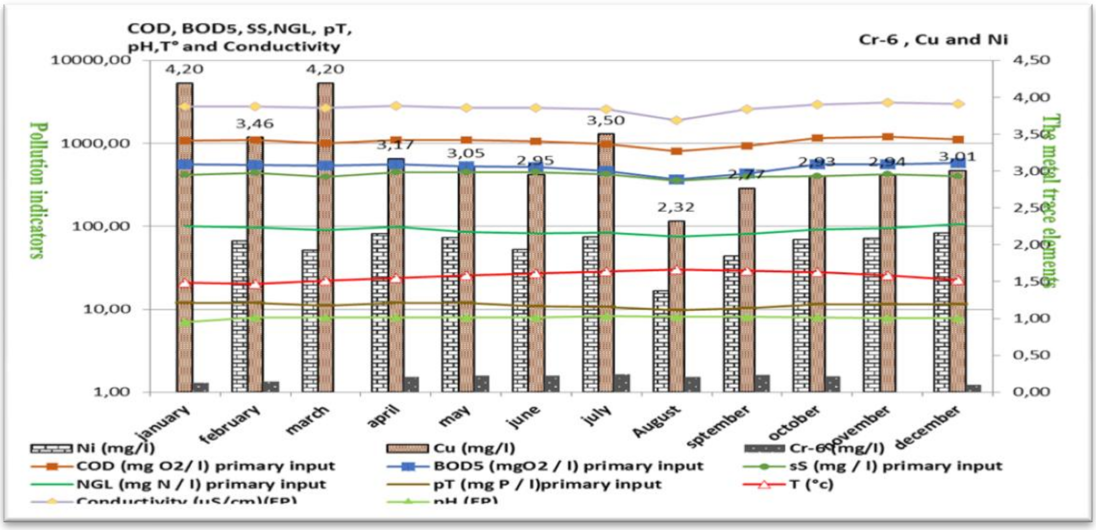

Figure 3: Evolution of monthly averages of trace metallic elements: Chromium VI ($Cr+^6$), Copper (Cu) and Nickel (Ni) as a function of physicochemical parameters in the raw effluent

Generally, the determination of chromium at the level of the sewage denounces the presence of a tannery [16]. This is the case of the city of Marrakech [17]. Chromium VI is a potent oxidant, its solubility and its mobility in the aquatic environment make it highly toxic compared to other types of chromium [18,19]. This explains its high value (among total chromium) in the aeration tanks while chromium III, which can precipitate in a pH range between 6 and 10 [20].

The months of March and November are marked by the significant absence of $Cr^{+\,6}$. This absence could be due to the stoppage of tannery activity during the holidays of the Sacrifice Feast celebrated at the end of October of this year (the handicraft workers take their annual leave during this feast). And for the month of March, this absence is probably related to the activity of the tanneries (no chromium rejection), 0.19 mg /L was the annual average of $Cr^{+\,6}$, on the other hand its minimum average value was recorded in December and is in the order of 0.10 mg /L. It coincides with the maximum monthly mean values of BOD_5, NGL and conductivity, which are in the order of 57.58 mg O_2/L, 106.03 mg N/L and 2995.22 µS /cm, respectively. Not only was the maximum concentration of $Cr^{+\,6}$ obtained in July with about 0.24 mg /L, but also from April to October the calculated monthly mean $Cr^{+\,6}$ values exceeded the limit of 0.2 mg /L authorized by Moroccan law 10-97 for indirect rejection (Decree No. 2-97-787 of 04 February 1998 concerning water quality standards and the inventory of the degree of pollution of waters [21] and 0.1 Mg /L for discharge into surface or underground waters (Order of 7 November 2013) [22].On the other hand, the presence of Nickel and Copper at the raw effluent level indicates discards from metal surface treatment industries [16].

In regards to Le Ni, except for the month of January, its monthly concentrations were observed throughout the year of study. Its annual average was of the order of 1.98 mg /L and its minimum value was observed with that of Cu during the month of August with 1.38 mg /L and 2.32 mg / l respectively. These values coincide with the lowest conductivity in the same month, 1905.74 µS /cm. This shows that these two elements are also dominant drivers. However, the maximum level of Ni 2.25 mg /L was increased in April. On the other hand, the maximum value of Cu 4.20 mg /L was recorded in March with an annual average of 3.01 mg /L.

The mean values of Ni exceed the threshold of 0.5 mg /L for indirect discharge and do not exceed the limit value (5 mg /L) of discharge and sent out into surface and ground waters recommended by the Moroccan authority. The limit of indirect discharge of Cu is around 1 mg / L according to the decree of application of Law 10-95 of 4 February A1 (Nos. 2-97-787) [21] and 3 mg / L for the recommended value for discharge and sent out into surface and underground waters according to Order No. 2942-13 of 7 November 2013 [22], it should be noted that these standards are exceeded at the level of the incoming effluent At the Marrakech WWTP.

For pollution indicators such as BOD_5 and NGL, they reached their maximum, with respectively 578.58 mg O_2 and 106.03 mg N/L during the month of December. Regarding COD, the maximum value was 1206.53 mg O_2 /L and was obtained in November. The maximum mean SS was 451mg /L, recorded in May, and pT was 12mg /L during the month of May as well. These maximum values sometimes exceed the indirect discharge standards [23]. In addition, the minimum values for these parameters were recorded in August.

3.1.2. Sulfides and phenols

Figure 4 shows the variation in monthly averages of sulfide and phenol contents with other pollution indicators during 2013. The presence of dissolved sulfides in the samples analyzed is due to the anaerobic decomposition of organic matter containing sulfur and reducing inorganic sulfates. They occur at the level of the network and the sanitation works as well as at the level of the primary settlers of the treatment plant [4, 24].

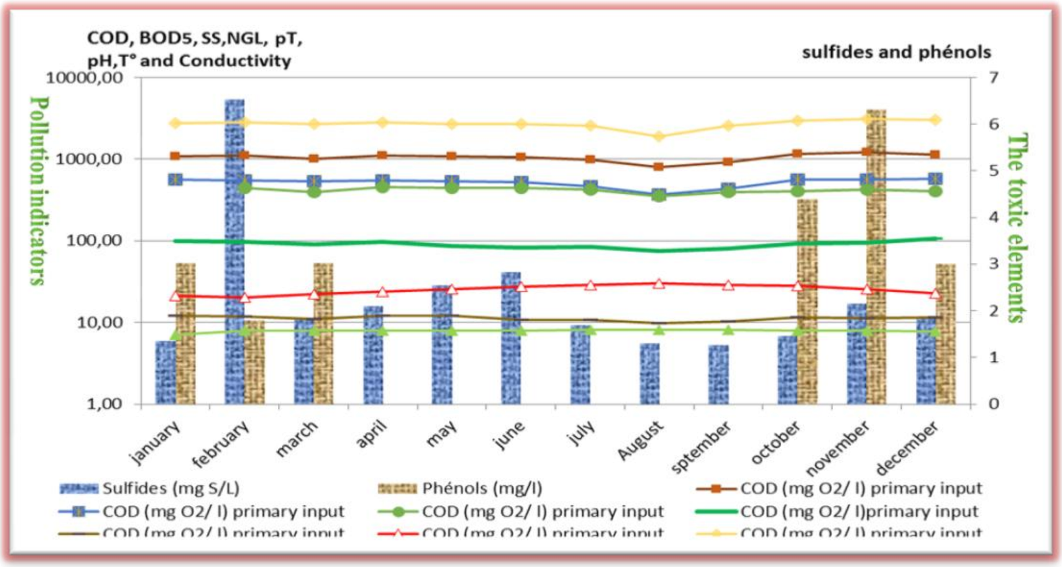

Figure.4: Evolution of the monthly averages of the toxic elements: phenol and sulfides as a function of other physicochemical parameters in the raw water entering the Marrakech WWTP.

Sulfides are found during the year in wastewater. It is in February that their value reaches its maximum with content of 6, 51 mg/L and its minimum value, which is 1.27 mg /L is increased in September. The annual average is of the order of 2.24 mg/L. This shows that the mean concentrations of free sulfides (S^{2-}) exceed the fixed direct release limit value E to 0.5 mg/L [21]. Moreover, they also exceed the threshold value 1mg/L, which is the norm for indirect rejection [22].Given the agricultural vocation of the region and particularly its olive-growing specificity, the town has several oil mills rejecting olive mill wastewater [14, 25], hence the existence of polyphenols in crude effluents [26]. Their high content is always linked to the olive period.

Phenols were observed from January to March and from October to December 2013 with an annual average of more than 3.5 mg/L. Their minimum mean concentration, 1.80 mg/L, was obtained in February. In the first place, the maximum average, which is of the order of 6, 31mg /L, exceeds the limit of indirect rejection for the index of phenol which is 5mg/L during the month of November [21]. Secondly, the phenol content is well above the standard of 0.5 mg /L of the permitted phenol content among the limit values for wastewater discharges which do not have specific discharge limits [22, 27].

3. I.1.3 Toxic elements at the entry of the WWTP and performance of the secondary treatment

Figure 5 presents a comparison of the monthly averages of the toxic elements phenols, Cu, Ni and Chromium VI that are detected at the effluent entering the treatment plant and the removal efficiencies of pollution indicators such as COD, BOD_5, SS, NGL and Pt at the secondary treatment level. The minimum removal efficiencies of COD, BOD_5, SS, NGL and pT pollution indicators were increased during the month of April, with yields of 74%, 94%, 49%, 75% and 40%, respectively.

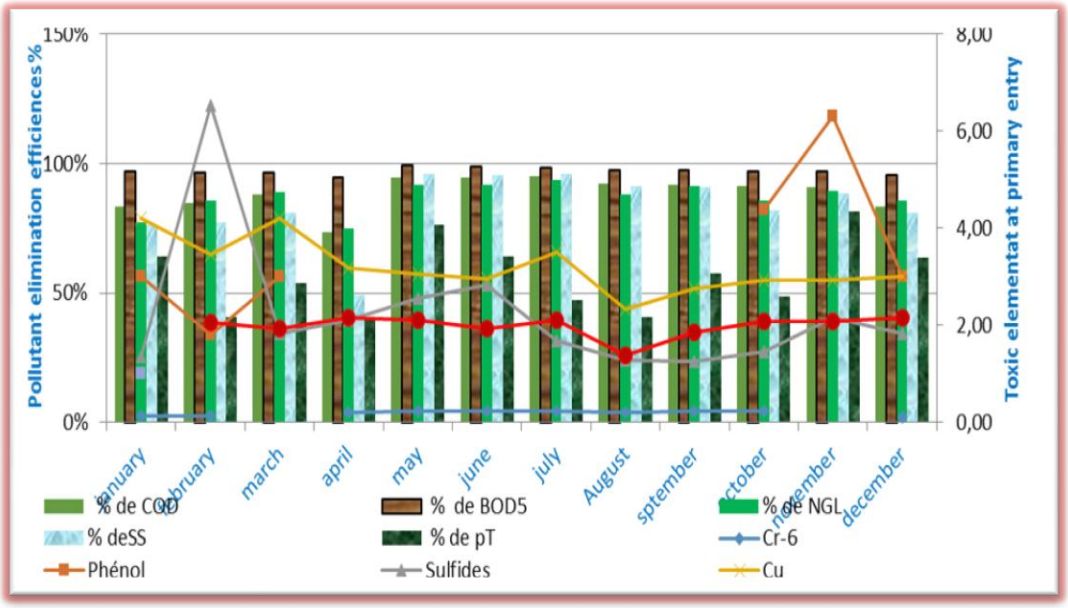

Figure 5: Evolution of the monthly averages of the toxic elements in the raw waters at the entrance of the WWTP: sulfides, phenols, Cu, Ni and Chromium VI and pollutant elimination efficiencies: COD, BOD_5, SS, NGL and Pt Secondary treatment

During this month, the raw effluent is characterized by the strong reappearance of Chromium VI with the presence of Ni, Cu and sulfides unlike phenols that disappear with the end of the olive season. The other values are represented as follows :

For COD, the maximum average of the disposal efficiency, 95%, was observed in June and July, while the annual yield was 90%. The low yields ranged between 83% and 91% and were obtained during the olive period, where the presence of phenol is important as well as that of Chromium VI. Generally, the yields obtained, with the exception of the minimum value (74%), are well above 75%, which is the minimum performance standard for the COD recommended by French legislation and laid down by the decree of 22 June 2007 [28,29].

For BOD_5, the maximum yield exceeds 99% and was obtained during the months of May and June with an annual yield of 97%. The yield obtained corresponds to the minimum limit required by the French authority and fixed at 80% [28, 29].

For SS, the maximum value reaches its maximum efficiency of 96% during the months of April and June. From January to April and from October to December, raw sewage is characterized by the presence of phenols, sulfides, Chromium VI, Ni and Cu with a total absence of Ni during the month of January and also that of Chrome VI from March to October. The efficiency elimination of the TSS varies between 49% and 82%, below the standards required by French and Moroccan legislation, respectively, by 90% [28,29] and 95% considered as a value indicating the good Operation of the purifying device [22]. However, from May to July and during September the yields are good and exceed 90%.

For the NGL, the maximum removal efficiency that was recorded was 94% during the month of July, while the annual average yield was 87%. As in the case of the SS, the lowest yields were obtained from January to April and from October to December, they ranged between 75 and 86%. However, these figures remain in line with and exceed the minimum French standard set at 70% [28, 29]

For pT, except for the maximum yield that was recorded in November and 82% (marked by the absence of Chromium VI), pT yields were above the desired standard, given that the European Directive Limited the minimum value of pT to 80% [28,29].

3.2 Discussion

3.2.1 Chrome VI

First, several research reports claim that hexavalent chromium affects the active growth of activated sludge and then the effectiveness of the treatment which is closely related to the performance of biological processes. Its inhibitory effect on respiration and microbial growth is due to the competition between oxygen and chromium VI as electron acceptors via a bond with organic substrate (such as an electron donor) Instead of the O2 molecule. This is why growth is also affected because microorganisms do not have access to the essential substrate [30, 20]. Indeed, researchers have demonstrated that hexavalent chromium has several effects on activated sludge but at different concentrations depending on the mode of analysis adopted; either by measuring the microbial respiratory rate or by other reliable and available techniques. Generally, autotrophic microorganisms in activated sludge are more vulnerable to chromium VI than heterotrophs [20, 31], especially since the growth of nitrifying bacteria undergoes a reduction in concentration from 0.2 to 0.6 mg / L of chromium VI [32]. Similarly, at a concentration of 0.5 mg / L chromium VI, the ammonia Absorption rate is also reduced [33]. On the other hand, 2 mg /L of Chromium VI resulted in a reduction in the biological oxidation of organic matter [34]. In the case of the WWTP of Marrakech, during the month of April the elimination yields of all the pollution parameters show their minimum values despite the absence of the phenol. The abrupt reappearance of chromium VI with the non-negligible presence of other toxic elements makes it the main cause of the decline in pollution abatement performance in terms of COD, BOD_5, SS, NGL and Pt. The simultaneous presence of other heavy metals with chromium 6 affects the toxicity of the latter because of the antagonistic synergy [20]. Researchers Chen and Gu recommended avoiding the sudden increase in chromium VI in raw effluent entering the treatment plant [35].

3.2.2 Copper

Copper is a well-known as an antibacterial and is used [36, 37], it is able to bind with certain proteins which can lead to their denaturation. The peroxidation of membrane lipids via the formation of highly reactive molecular species is based on the ability of copper to catalyze oxidation-reduction reactions [38]. Not to mention that at very low concentrations, copper is an element stimulating the growth of nitrifying bacteria but it is toxic on nitrosomonas at 0.3 mg / L [39]. Moreover, the results show that the addition of 20 mg of copper sulfate ($CuSO_4$) to sludge collected at the Basse-Wavre wastewater treatment plant (Intercommunale of Brabant Wallon) affects the rate of respiration; it undergoes a reduction of almost 40%, which shows the toxic effect of copper. The rate of respiration and the growth of bacteria decrease with the increase in the amount of copper added which can go as far as the complete inhibition of biological purification [40]. These results were confirmed by an experimental study of activated sludge microbial communities including the dominant bacterial taxa Proteobacteria, Bacteroidetes, Acidobacteria, Chlorobi and nitrospirae, which were continuously treated with 10, 20 and 40 mg / L of copper respectively, Causing a reduction in the elimination of the chemical oxygen demand (COD) and even affecting the elimination efficiency of ammoniacal nitrogen (NH_4^+). In general, most dominant bacterial groups are easily susceptible to copper toxicity and variously altered. Not to mention also that copper also promotes the abundance of various bacteria [41]. An earlier study showed that the simultaneous presence of chromium VI with Cu reduces the absorption capacity of BOD_5 by about 80% [20, 42]. This is also the case for the WWTP in Marrakech from January to April and during the month of December when yields of COD, BOD_5 and NGL were low.

This is explained by the antagonistic synergy between Cu and chromium VI observed in January, February and December during which COD yields were 83%, 85% and 83%, respectively. In contrast to March, characterized by significant coexistence of phenol (3.02 mg /L), copper (4.20 mg /L), sulfides (1.84 mg/L) and Ni (1.93 mg /L), the COD increased to 89% due to the absence of chromium VI. The same situation was observed for the month of November when the COD yield reached 91%. This shows the antagonistic synergy of chromium VI with other metals [20].

3.2.3 Nickel

At low concentrations, nickel could be the source of nitrite accumulation due to their Nitration [43]. Moreover, in 2004 a study confirmed that the addition of 5mg /L of Ni^{2+} caused a slight reduction in the elimination efficiency of total organic carbon in the SBR (discontinuous sequential reactor) with a reduction in the rate of specific oxygen uptake by activated sludge microorganisms. Whereas, the addition of 10mg / l of Ni^{2+} significantly affects the performance of SBR, which is reflected by the sharp drop in the elimination of suspended solids from total organic carbon [44]. Moreover, the specific absorption rate of ammonia of the bacterial species of the activated sludge thus affected by the inhibitory effect of Ni^{2+} [45].

In addition, the presence of Ni^{2+} at the same time with other toxic elements such as Cd^{2+} at total analytical concentrations of about 1.0 mM, inhibits ammonium oxidation, but does not oxidize nitrite [46]. This is not the case of our study given the absence of cadmium in the raw effluent of Marrakech. On the other hand, L. Kamikaa revealed that the toxicity of Ni^{2+} negatively affects the growth rate of isolated and studied protozoa such as *Aspidisca sp*, *Peranema sp*, *Paramécie sp* and *Trachelophyllum sp* which are characterized by their eliminatory action of nitrate and phosphate in Wastewater, although a gradual increase in the concentration of Ni^{2+} leads to a decrease in the rate of absorption and removal of nitrate and phosphorus by these protozoa. With the exception of the *Peranema sp* strain, the 10 mg /L concentration of Ni^{2+} improved its nitrate absorption capacity compared with other types of protozoa [47], however, according to the SBR study; The termination of the addition of Ni^{2+} led to the recovery of the specific microorganisms in the biodiversity [44]. On the one hand, the comparison with the results obtained in January was marked by the presence of 4 toxic elements such as Chromium VI, Cu, phenols and sulphides but nickel is completely absent, which is why the yield of pT was high, of the order of 67%.

On the other hand, the appearance of Ni^{2+} in the following month with the significant reduction in the pT removal efficiency at a value of 41% indirectly asserts the e Ni^{2+} inhibitory effect on the phosphate elimination efficiency. Then, during the months marked by the non-existence of chromium VI, the elimination efficiency of pT increased to 54% in March and 86% in November, while in its presence the yield of pT varies between 40% and 74%. This shows the antagonistic synergy of chromium VI this time with Ni^{2+}. This result is in agreement with a research carried out and which showed that the coexistence of 20 mg of chromium VI with 1 mg / L of Ni strongly inhibits the growth of cyanobacteria especially at the level of absorption of the nitrate with initial inhibition of d'Ammoniac [48].

3.2.4 Sulfides

Since sulfides create severe odor and corrosion problems in the sewer system and the works of the treatment plant whose copper-based electrical equipment through the H_2S produces. The performance of the activated sludge system is significantly affected in the excessive presence of sulfides in terms of the rate of removal of the suspended matter [49]. On the one hand, sulfides can reduce Fe^{3+} to Fe^{2+} by Fe (III) bacterium Shewanella, which has the result of weakening the floc structure responsible for decantation and the solid-liquid separation in the activated sludge system [24, 50]. On the other hand, sulfide concentrations should not exceed 1 to 2 mg /L at the entry effluent. Beyond this range, the dissolved sulfide promotes the proliferation of filamentous bacteria (Beggiata Thiotrix) which Use sulfur as a source of energy for their metabolism and are responsible for the degradation of sludge settling (sludge discharge) [4, 50]. The Sulfides at the WWTP of the Marrakech exceed the authorized limit throughout the year of study. Their negative impact affects the decantation of secondary sludge (the elimination of SS). Its maximum value (6.52mg /L) was recorded in February marked by a low SS removal efficiency (77%).

With copper, chromium, nickel and other metallic trace elements, sulfides form insoluble precipitates [51]. SS yields of 81% to 96% are obtained in months when sulfide concentrations are more or less low. Indeed, the minimum elimination value of SS was observed in April (49%) due to the coexistence of sulfides with other toxic elements, especially chromium VI, which could be the cause of this decrease with the presence of sulfides.

3.2.5 Phenols

Knowing that phenol, considered as a single carbon and energy source of many aerobic and anaerobic microorganisms [52], it makes their treatment and biological recovery an adequate solution [53,54]. However, microbial growth is affected by higher concentrations of phenol, as the latter and its derivatives are inhibitory and toxic elements that can denature the cellular proteins of bacteria by altering the membranes. They also inhibit the activity of symbiotic nitrogen-fixing bacteria by inhibiting the activity of digestive enzymes and / or by precipitating nutritional proteins, which explains the antimicrobial power of oil mill effluents [55]. At relatively low concentrations (100 mg/L), phenol is recognized as an inhibitory substrate [56]. At the level of biological treatment, a study revealed that 5mg/L (phenol, the inhibition of nitrification, occurs indirectly through the depletion of oxygen through the biodegradation of phenol [57] with concentrations (<5 mg / L) phenol gives a typical odor on chlorination [58]. Nevertheless, research was carried out on a wastewater effluent from a chemical laboratory treated with activated sludge in northern Tehran and concluded that with increasing concentrations of phenol ranging from 0 to 100 ppm, COD removal oscillates from 49.5% to 61.5%, but as the phenol concentration rises to 200 ppm, a 14% reduction in COD has been observed, Toxic effect of phenol.

The same results were obtained for total organic carbon (TOC). On the other hand, for suspended solids and volatile solids (VSS), they decreased significantly with increasing phenol concentration up to 200 ppm [59]. In our study, during the first olive-growing season, from January to February, NGL elimination yields varied between 77% and 89%, COD yields ranged between 83% and 88%, and SS yields fluctuated Between 76% and 81%, values that are more or less lower than annual returns; This decrease coincides with the presence of more or less low concentrations of phenols varying between 1.80 and 3.02 mg / l. This shows the toxic effect of phenols on the rate of pollution elimination. Unlike October to December, phenol concentrations ranged from 3.01 to 4.38 mg / l. Despite the strong presence of this element with the presence of other toxic elements, the yields are better than those of the first period. NGL yields fluctuate from 86% to 89%, COD yields range from 83% to 91%, and TSS yields range from 82% to 89%. These results are explained by the coexistence of phenols with Cu which induces an irreversible effect. Indeed, the rate of inhibition on nitrification has been greatly reduced in the complex mixtures that copper forms with phenol, which would also be the case in industrial wastewater treatment plants [57]. Without omitting, the presence of chromium VI with phenols and other toxic elements affects much more the purifying yields which is more apparent the case in April.

On the other hand, from May to September, not counting the phenols, all the other toxic elements are present at non-negligible concentrations, the yields are good thanks to the phenomenon of acclimatization of the activated sludge, Adapt to the presence of heavy metals [20,60,61]. However, the reappearance of phenols in October induces a more or less significant reduction in the purification yields.

4. Conclusions

During the year of this study, the WWTP of Marrakech received significant organic and inorganic pollution. While the pH, temperature and conductivity values remain within the indirect discharge ranges and do not interfere with biological treatment, the presence of chromium VI, nickel, copper, sulfides and phenols is The origin of the biological dysfunction of the station.

Analysis and follow-up of the toxic elements at the entrance of the WWTP and after secondary treatment concluded that:

During the first olive-growing period from January to March, the decline in COD, SS and NGL removal yields was due to the presence of phenols, sulfides and high copper or less of nickel and chromium VI.

In February, the appearance of Ni led to a marked reduction in the pT removal efficiency, which was 41%. This result shows the inhibitory effect of nickel on the removal of phosphates. It is concomitant with a minimum efficiency of the removal of the SS (77%) due to the presence of sulfides with a maximum content (6.52 mg / L) responsible for the deterioration of the settling of the sludge;

In March, the absence of chromium VI, despite the presence of nickel, copper, phenols and sulfides, resulted in increased COD (88%), BOD_5 (96%) NGL (89%), SS (81%) and TP (54%). These results show the potent toxicity of chromium VI and its inhibitory effect on purifying yields;

On the other hand, in April, the purification yields of COD, BOD_5, SS, NGL and pT are low and at their minimum value while the phenols are absent. This behavior could be explained by the reappearance of chromium VI and its effect of antagonistic synergy with the other toxic elements ;

From May to September, during which the phenols are still absent while the other toxic elements are present, the purification yields are good and exceed the averages, thanks to the phenomenon of acclimatization of the activated sludge ;

During the second olive period from October to December, the purification yields of NGL, COD and SS fluctuate, but remain slightly higher than those obtained during the first olive-growing period. These results are explained by the simultaneous presence of phenols with copper which induces an irreversible effect (the rate of inhibition of the elimination of pollution is relatively decreased). In addition, despite the presence of nickel, the maximum elimination efficiency of pT (82%) which was obtained in November is due to the total absence of chromium VI;

With the exception of April, the COD, BOD_5 and NGL elimination efficiencies are good to excellent. Furthermore, the elimination efficiency of the SS is average and that of the TP is low.

It should be noted, however, that there are other toxic pollutants that can be found in raw sewage, such as hydrocarbons, pharmaceuticals, tars, etc. These elements can interfere with the effectiveness of the treatment.

To minimize the biological dysfunction of the WWTP and to ensure a good performance, it is necessary to respect the standards of discharges of toxic elements at the source by a suitable and adequate pretreatment, especially when several toxic elements are simultaneously present.

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