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Performance of Wastewater treatment in Petrochemical Refinery Plant SAMIR

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Abstract*— This study focuses on the diagnostic evaluation of the SAMIR wastewater treatment plant, and aims to identify the steps needed in order to improve performance with respects to the elimination of pollution. The results obtained showed that the variation in flow rate varies over time and reaches up to 400 m3 /h. This has consequently a variation of the organic load which is a function of the flow rate and content of the pollutant. By monitoring the sludge index in wastewater in the biological basin shows that the value varied between 20% and 40% which justifies the effectiveness of the biological treatment. In addition, the COD removal by the STEP yield varied between 50% and 94% while the BOD removal varied between 60 and 92%. On the other hand, the removal of turbidity by STEP yield varied between 92% and 96 % while eliminating of TSS varied between 92% and 95%. Additionally, the results obtained while monitoring changes at different wavelength (254 436 540, 660) showed there was an increase in light intensity during the first four steps, which indicates that water in this case is very rich in organic matter. On the other hand, it was found that the water outlet of the clarifier always takes the minimum value of the light intensity for each sample. The removal of hydrocarbons by STEP fluctuates over time which justifies optimization of coagulation/flocculation process and therefore the biological aeration basins could be useful to ensure good biodegradability of hydrocarbons.

Index Terms— **Wastewater, activated sludge, Hydrocarbon, coagulation/flocculation.**

I. INTRODUCTION

The treatment of wastewater generated by industrial activity is a major concern for plant operators and in particular those of refineries and petrochemical units. The petroleum refining industry produces a large amount of wastewater due to the amount of water used in refining the processes particularly for cooling systems [Nashwan et al , 2013] ;[Al-Malack, et al , 2013]

Untreated wastewater discharged by refining causes the large environmental problems with the decrease in oil yield [Jing et al, 2003]. The extraction of sediments and marine various transportation process are among the causes that lead to contamination of oil components [A. L. N. et al, 2008]. On the other hand, untreated wastewater from petroleum refining generated some contaminants for example Phenol, dissolved minerals and hydrocarbons; the latter cause’s grave affects because of their toxicity. [Ishak et al , 2012]

Generally, petroleum refineries generate polluted wastewater containing approximately 150-250 mg/L of biochemical oxygen demand (BOD) and 150-250 mg/L of chemical oxygen demand (COD), phenol and oil levels of 20-200 mg/L and 100-300 mg/l, by against desalted water in tank’s bottoms and up to 5,000 mg/ L [Al-Malack et al , 2013]. Moreover, Approach should be developed in order to effectively remove organic and inorganic pollutants to improve the general quality of discharged wastewater [Won, 2013]

For this reason, most countries have made efforts to solve this problem mostly rarities and alteration in water quality due to the diversity of sources of water pollution. The difficulty of managing this pollution in developing countries is that it requires projects with large budgets. Most of these countries have installed sewage treatment stations but they are managed differently depending on the type of activities in each country.

There are several technologies and processes used in the treatment of refinery wastewater, such as, chemical coagulation/flocculation, treatment membranaire, adsorption and photo catalytic oxidation [Muftah, 2014].

Morocco has realized that its socio -economic development is conditioned by the integrated management and conservation of its water resources. According Reffouh. A. (2007), the volume of wastewater was estimated at 600 million m3/year in 2005 and will increase to 900 million m3/year in 2020 [Reffouh, 2007]. .

A national program of sewerage and wastewater treatment with a budget of 43 billion dirhams for 260 cities and centers was established in 2009. It aims for 80% urban sanitation, 60% reduction of pollution from reused agriculture wastewater and 40% treatment of wastewater by 2020 [National Council of The Environment , 2007]. It is therefore clear that the development of purification techniques adapted to the national context , taking into account both the technical and financial capacities of the Moroccan towns and other targets, purified effluent reuse in agriculture remains a valid option and will be implemented in the national strategy for the preservation of water resources of the country.

SAMIR Refining, in Morocco transforms crude oil into various end products (gas, gasoline, naphtha, kerosene, diesel, fuel oil…), this process contributes to water contamination resulting from usage in different treatment of petroleum.

To meet environmental requirements, SAMIR devotes all means and human resources to the treatment of wastewater produced by the refinery. It is for this purpose that the effluent treatment station was designed. This treatment plant is managed to ensure the daily monitoring of the treatment of wastewater from septic pumping.

The objective of this work, carried out in the SAMIR Refining company , aims to make a the diagnostic evaluation of the treatment plant in order to identify the steps on which we can act upon to generally improve the eliminating of pollution within the station .

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II. MATERIALS AND METHODS

A. Description of SAMIR WWTP

The design layout of the wastewater plant consists of a minimum of 20 m3 / h and a maximum of 550 m3 / h, with an average reach daily rate of 230 m3 / h. Water flows from production facilities, first passing through the nasal lift before being evacuated and transported to pre-settlers. The diagram of the wastewater treatment plant of the company SAMIR is illustrated in Figure 1

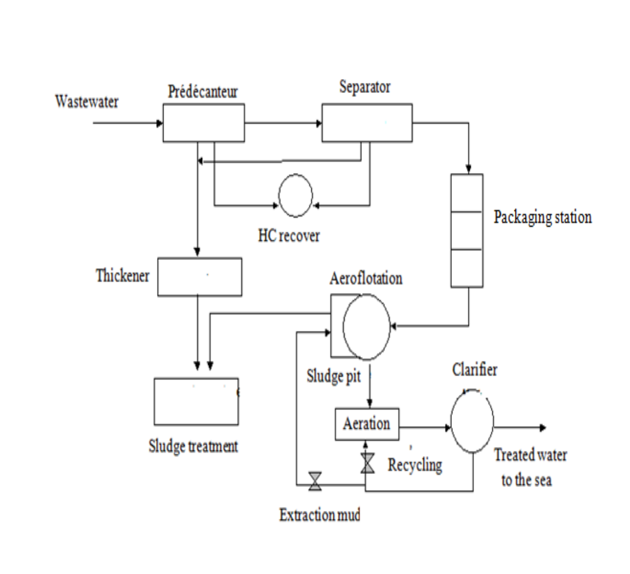

Fig.(1) : Schematic of wastewater treatment plant SAMIR

B. Sampling points and Analytical methods

To perform this study, eight samples were collected from five processing steps [Water station entrance (raw water), Water inlet coagulation /flocculation, Water output coagulation/flocculation, Water output biological basin, and water clarifier output]

These samples were then analyzed for water analysis at the laboratory of the Faculty Science and Technology of Mohammedia. The following parameters are determined: turbidity, COD, BOD, T°C, pH, Temperature, Total suspended solid (TSS), and hydrocarbon.

- Turbidity: The turbidity measurement is performed using a turbidimeter Hanna kind. The measured value of the turbidity in NTU

-COD, BOD, T°C, pH, Conductivity and Total suspended solid (TSS) are determined according to standard method AFNOR [AFNOR technical quality of the water, 1999]

-Color is determined using a UV/Visible (Model 7800 UV/VIS spectrophotometer) by gauging the absorbance at four wavelengths (254,436,540, 660) [P.Aysegül and T.Enis, 2002]

- Hydrocarbons were analyzed by IR after extraction with tetrachlorethylene. This parameter was analyzed using the method AFNOUR [AFNOR, 1973]

These parameters were chosen in order to analyze the operating conditions at the station.

III. RESULTS AND DISCUSSION

A. Physicochemical Characteristics of the wastewater received by the treatment plant

The results of physico-chemical analyzes of raw sewage produced by the STEP Company SAMIR, taken from weekly samples between March to May 2014 are shown in Table 1.

Table 1: Physico-chemical parameters analyzed in the raw wastewater received by the STEP Company SAMIR

		Moy	Min	Max
HC	mg/l	8500	4475	2000
TSS	mg/l	850	634	420
COD	mg O_2/l	1860	1200	600
BOD_5	mg /l	690	418	250
COD/ BOD_5	--	2,69	2 ,87	2,4
pH	--	8,3	7,44	6,5
Turbidity	NTU	780	543	350
Phenols	mg/l	74,51	52,53	29,58
Detergents	mg/l	16,05	9,04	4,67

These results show that the pH range from 6.5 to 8.3 with an average value 7.44. The pH is an important element for the interpretation of the corrosion in the piping facilities. The monitoring of the variation of turbidity over months showed a significant variation between 350 to 780 NTU. This is related to the instability in the quality of the effluent over time. Suspended solids are all inorganic and organic particles in the wastewater. Because of their effects on the physicochemical characteristics they hinder the penetration of light, thus hampering photosynthesis [EL GOUAMRI et al , 2006]. SAMIR wastewater are characterized by an average concentration 634 mg / L of TSS with a maximum concentration of 850 mg / l and a minimum concentration of 420 mg / l. Levels recorded in suspended solids are above the limit of direct discharge concentration (50 mg / l) and concentration for indirect discharge (600 mg / l). [Ministry of environment of Morocco, 2002] . COD used to assess the concentration of dissolved inorganic or organic materials, or in suspension in water, through the amount of oxygen required for the total chemical oxidation. [Rodier et al , 1996] COD values range from 1860 mg /l to 600 mg /l .

These values were greater than 200 mg / L, (which is the limit for direct discharge), but well below 1000 mg / l (which is the limit for indirect discharge) [Ministry of environment of morocco, 2002]. BOD5 values vary between 250 mg / l to 690 mg / l with a mean of 418 mg / l . These values were greater than 100 mg /l (which is the limit for direct discharge) but less than 500 mg /l (which is the limit for indirect discharge) [Ministry of environment of morocco, 2002]. COD/BOD5 the report shows that the effluent received by STEP is biodegradable with selected strains.

The hydrocarbon content varied between 2000 and 8500 mg /l with an average of 4475 mg / l. The concentrations of phenols was between 29.28 and 74.51 mg /l. SAMIR wastewater is characterized by detergents contents between 4.67 and 16.05 mg / L with a mean of 9.04 mg / l .

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C. Variation of the flow rate over time in the wastewater treatment plant SAMIR

Monitoring the elimination of pollution by sewage treatment plant of the company SAMIR was performed by measuring the physico-chemical parameters such as COD, PH, T°C… The variation of the flow received by the station of various is given in Figure 2.

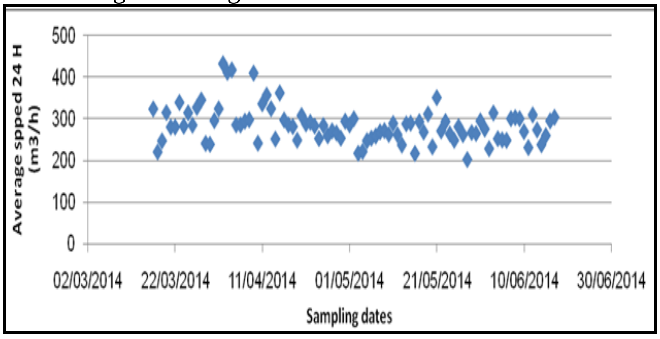

Fig. (2): Variation of flow rate over time

The variation of the flow illustrated in Figure 3 shows that it changes over time and up to 400 m3 / h. This is consequently a variation of the organic load which is a function of the flow rate and content of the pollutant matter. Reparation of the buffer tank is needed in order to ensure a good coagulation/flocculation and subsequently a good biodegradability of hydrocarbons within the biological basin.

D. Variation of the PH and Temperature along the different stages of the STEP

The variation of the pH and temperature of the raw wastewater received by the processing station are illustrated in Figures 3 and 4.

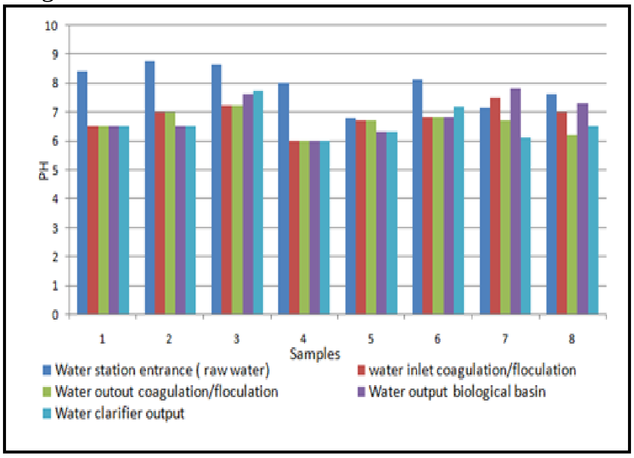

Fig. (3): PH in relation to Samples

PH is defined as the negative log of hydrogen ion concentration. It indicated the acidity and alkalinity of water samples [Kolhe et al , 2011] ;[Sharma, et al , 2014]. The results obtained concerning the change in pH at the entrance to the purification plant shows that it varies from 6,5 to 8,3 (Figure 3). This pH change can greatly disrupt the biological treatment as was shown [Khallaki , 2000] . It is also worth noting that the pH during the various sampling sectors were between 6.2 and 7.

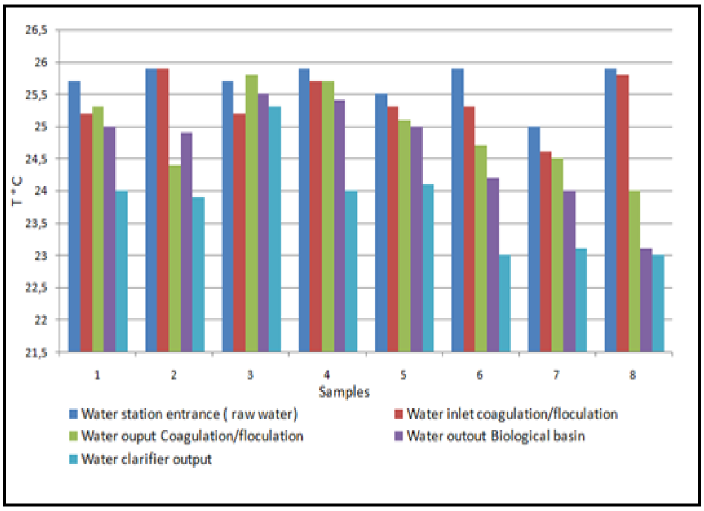

Fig.(4): Temperature in relation to Samples

Temperature is also an important factor; it has an effect on certain chemical and biological reactions which takes place in water and in organisms inhabiting an aquatic media. It depends upon the seasons and time of sampling [Sharma, et al, 2014]. In this study the temperature along different steps of treatments varied between 23 ° C and 25.8 ° C (Figure 4).

E. Evolution of Turbidity

The evolution of turbidity and performance along the processing steps is given in Figure 5

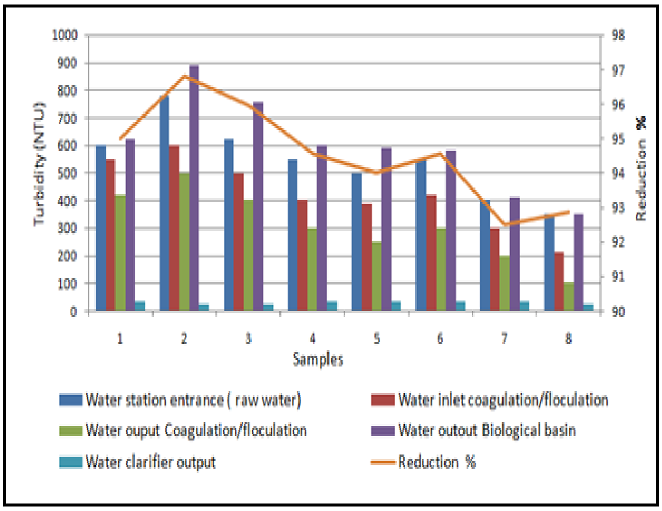

Fig.(5): Evolution of turbidity and performance along the processing steps

Turbidity of water is mainly caused by very small particles, such as colloidal particles. These particles can remain suspended in the water for very long periods of time, can even penetrate a very fine filter [CHAOUKI.I et al, 2013]. From the diagram above it is observed that the turbidity values at the entrance of the station are between 350 and 780 NTU, while values at For against the output of the biological basin

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were between 388 and 890 NTU . This indicates that there is a problem with the biological basin. At the outlet of the STEP the recorded values were between 25 and 30 NTU. The removal of turbidity by STEP yield varies between 92% and 96% (Figure 5).

F. Evolution of TSS

The evolution of the TSS and performance along the processing steps over time is illustrated in Figure 6

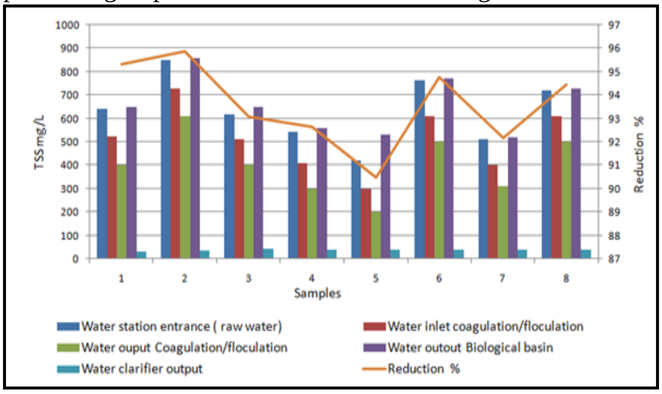

Fig.(6): Evolution of TSS and performance along the processing steps

Total suspended solids consist of silt, clay and fine particles of organic and inorganic matter [Ogunlaja et al, 2009] .In this study the TSS content at the entry of the station varied between a maximum value of 850 mg / l and a minimum value of 420 mg /l , averaging 634 mg / l .

These values far exceed the general disposal limits of treated wastewater which is 50 mg / l. This content has been declining at the die exit and passes to 40 mg / L meet discharge standards Moroccan. The abatement rate of TSS by STEP varied between 92% and 95%, which remains above the minimum treatment efficiency for effective treatment which is 90% [Rejsek , 2002]. This implies that the solids contained in the effluent are readily settle able solids.

G. Evolution of the COD and BOD5 along the different stages of the STEP

The evolution of the chemical oxygen demand (COD) and biological oxygen demand (BOD5) along the different stages of the STEP respectively are given in Figures 7 and 8

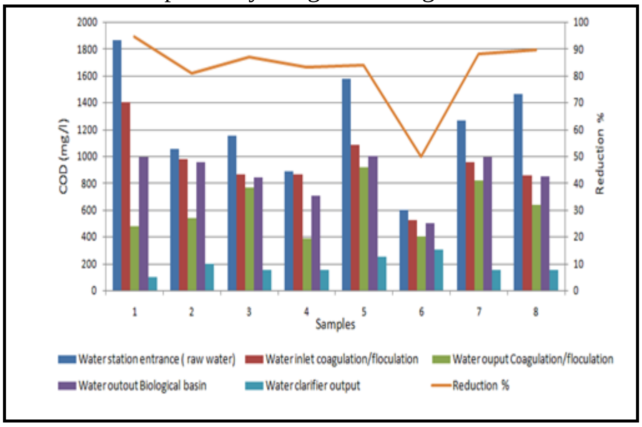

Fig.(7): Evolution of DCO and performance along the processing steps

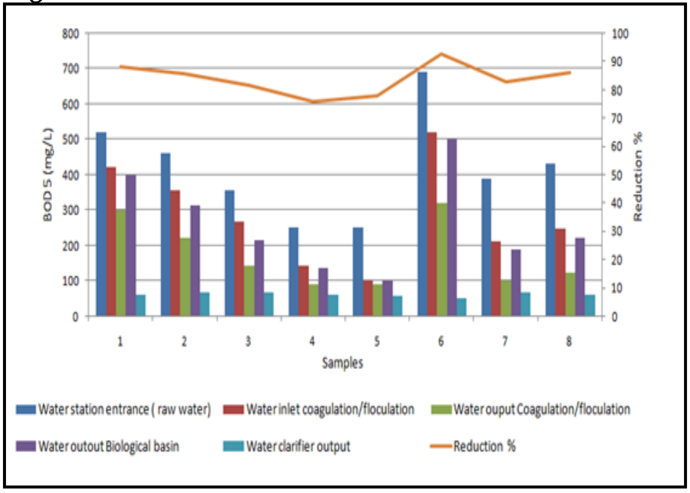

Fig.(8): Evolution of BOD5 and performance along the processing steps

Chemical oxygen demand (COD) is the main parameter which is widely used to estimate the organic content of wastewater [Vyrides, , 2009].

I.CHAOUKI et al , (2013) studied the performance of the WWTP filling station in society Salam Gaz-Skhirat.Morocco and reported COD content at the entry of the Step is between 432 and 860 mg / L with a mean of 698.09 mg / L. Figure 7 shows that the COD content at the entry of the STEP was between 600 and 1860 mg /l with a mean of 1200 mg /l , the content was significantly reduced during the processing steps. Furthermore the COD value of water at the output of the biological basin varies significantly after coagulation /flocculation. Biochemical oxygen demand (BOD) is one of major physico-chemical parameter used to determine the quality of effluent. [Akilandeswari1 et al , 2013];[DJERMAKOYE ,2005] .

Rafa H .Al-Suhaili and Muwafaq A. Abed , (2008) studied of the performance of the dora refinery wastewater treatment plant , and reported that the effluent (BOD5) values from the aeration tank were high in all tested samples . This is normally as result of related to the suspended organic load from of the biological floc which recirculates from the final settling tank back to the aeration tank . However , these high suspended (BOD5) values were reduced again in the final settling tank , which were less than the design limit of 20 mg/l . Figure 9 represents the variation of BOD5 during processing. Note that the raw water entering the station has a BOD5 varying between 250 to 690 mg / l (Figure 8). Additionally , the BOD5 at the clarifier outlet does not vary much over time. It meets the standards of treated wastewater discharges proposed by the World Health Organization. Also, COD removal by the STEP reduction varies between 50 and 94% (Figure 7) while the BOD5 removal varies between 60 and 92% (Figure 8). This fluctuation may be due to the change in raw water quality (pH, flow, COD, TSS ...). Therefore the physicochemical properties must be treated in order to optimize the effluent.

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H. Evolution of the index of sludge over a period of three months

To assess the quantity of settled sludge, Mohalman Index (sludge) was carried out during a period of 3 months (March to May 2014). The results over different sampling dates are shown in Figure 9.

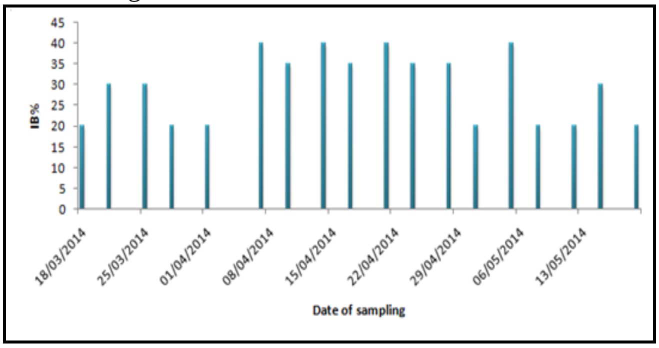


Fig.(9): Evolution of the index of sludge (IB)

IB, is are of the most practiced way of determining settling and compaction of activated sludge.

Sludge Volume Index (SVI) of 100ml/g or less is considered satisfactory while SVI of more than 150ml/g is an indication of bulking sludge [FARID AHMED, 2007] . The sludge volume index was determined according to the volume in milliliters occupied by 1 g of a biomass suspension after 30 min settling [Amaral et al , 2005] .

Many authors recognize Sludge Volume Index (SVI) as the best parameter for characterizing sludge settling properties. Sludge Volume Index (SVI) is also a good indicator of sludge bulking. [W. Janczukowicz, et al , 2001] . The results from (Figure 9), concerning the evolution of the index of sludge to the station over time shows that it varies from 20 to 30% during the months of March and May while the maximum value of 40% was obtained in April. This increase could improve the physico-chemical characteristics of the water discharged in terms of removal of organic pollution, but in general this value shows a good sludge settling in the clarifier.

I. Evolution of the hydrocarbon

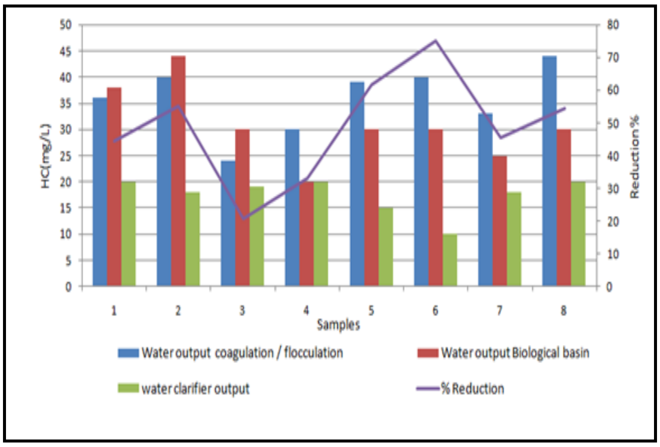


Fig.(10): Evolution of hydrocarbon (HC)

Hydrocarbons are destroyed during biodegradation, but sulphur-, oxygen- and nitrogen-containing compounds can also be degraded [Ian et al, 2003]. Pauline et al , (2010) reported that the emission of hydrocarbons in the environnement causes pollution of the air , soil, the underground nape and contaminants the food chain in living organisms . From Figure 10 we observe that the evolution of hydrocarbons along the treatment steps varies over time also the abatement rate of HC by STEP varies between 20 and 75%. This justifies optimization by coagulation/flocculation and biological aeration basins could be useful to ensure good biodegradability of hydrocarbons.

J. Removal efficiency of the COD by the biological stage in accordance with the dissolved oxygen

The variation of COD content and its correlation with the oxygen dissolved in the biological basin is given in Figure 11.

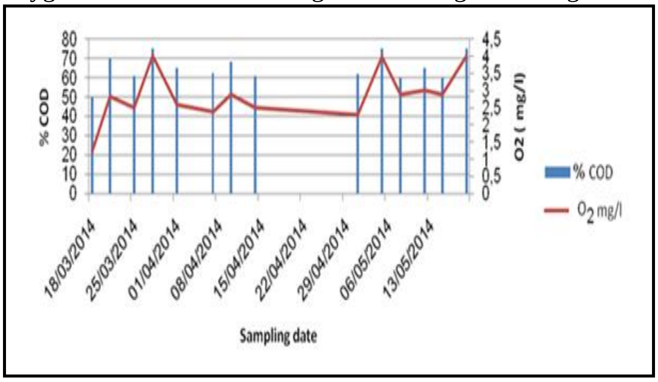
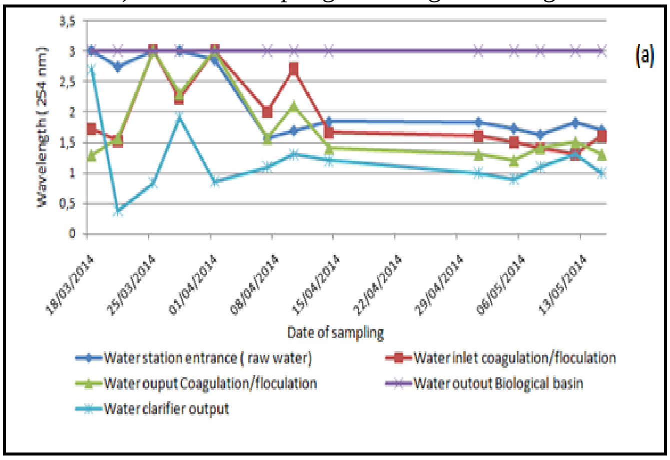


Fig.(11): Variation of the COD content and its correlation with the oxygen dissolved in the biological

The removal efficiency of the organic pollution (COD) in the biological treatment tank by the biomass is attached to the oxygen concentration as shown in Figure 11. Reduction increases with the increase of the oxygen concentration decreases and with it above. This is related to the development of microorganisms in the aeration tank. Sewwandi, et al, 2010, reported that dissolved oxygen in water is essential for the biochemical processes which determine the fate of nitrogen and organic pollutants of wastewater.

K. Variation of color and absorbance

The evolution of differences wavelength (254, 436, 540 and 660nm) based on sampling dates is given in Figure 12.



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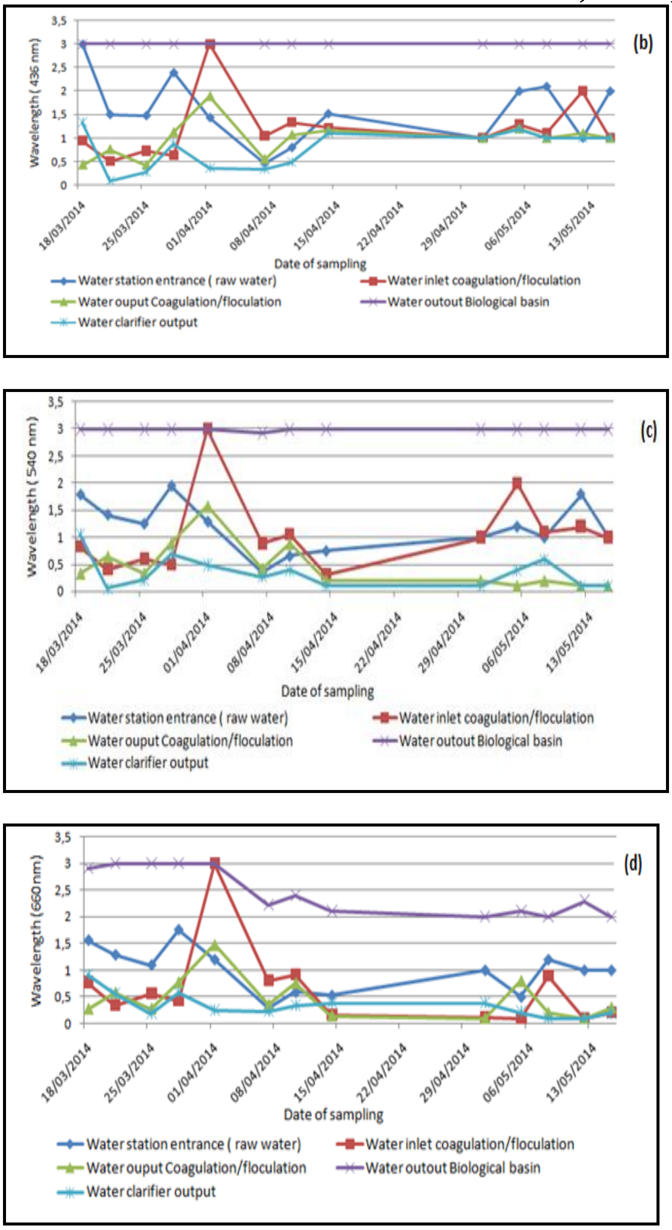

Fig.(12): [(a),(b),(c),(d)]: Evolution of differences wavelength (254, 436, 540 and 660nm) based on sampling dates

When radiation of a given wavelength length passes through a medium, its intensity decreases as a function of the density of the absorbing components and thickness of the medium. This property is used to determine the concentration of the chemical components absorbing a predetermined wavelength [Rodier, 2009]. Chaparro et al , 2011 reported that radiation absorption has been widely used to study the chemical components and its derivatives . Currently this technique enables identifying organic compounds by comparison with the spectra of known compounds. UV absorbance at 254 nm is an excellent indicator, or proxy, of the natural organic matter content in natural waters. Moreover, the aromatic structures, which are practically omnipresent in humic substances, reduce at lower wavelength; though below 254 nm there is an interference with absorption by nitrate [Pauline Junquet, 2012]. The results from Figure 12 shows that there's an increase in the light intensity for the first four stages (water station entrance, entrance water coagulation / flocculation, water output coagulation / flocculation, water clarifier output) this indicates that the water in this case is very rich in organic matter. On the other hand we find that the clarifier water outlet always takes the minimum value of intensity light for each sample.

IV. CONCLUSION

This study allowed us to diagnose the state of SAMIR treatment plant, activated in the fight against pollution caused by oil sludge types. The results showed that the fluctuation of flow and organic load are the most feared for the operation of the station enemy, this requires repairing the buffer pool in the shortest time thereby allowing the bacterial population to stabilize and chemical injections (coagulant and flocculent) to give good yields.

In fact the removal of turbidity by STEP yield varies between 92% and 96%% while eliminating of TSS varies between 92% and 95% . These results explained that the solids contained in the effluent are readily settle able solids.

In addition, the COD removal by the STEP yield varies between 50% and 94% while the BOD removal varies between 60 and 92%. This fluctuation may be due to the change in raw water quality (pH, flow, COD, TSS ...) to the back of the die and physicochemical treatment by coagulation flocculation requires optimization. The results of the sludge index in the time of wastewater in the biological basin shows that the value thereof varies between 20% and 40% which justifies the effectiveness of the biological treatment.

Furthermore, the removal of hydrocarbons by STEP fluctuates over time which justifies optimization of coagulation-flocculation and biological aeration basins could be useful to ensure good biodegradability of hydrocarbons Monitoring , of the evolution of different wavelength (254 ,436, 540 and 660 nm) to show that there's an increase in the light intensity for the first four steps (input water station, water entry coagulation / flocculation, water output coagulation / flocculation, water clarifier output) this indicates that the water in this case is very rich in organic matter.

Another side we find that the water outlet of the clarifier always takes the minimum value of the light intensity for each sample.

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