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Evolution of Phenol and Surfactant Along the Different Wastewater Treatment Process STEPS

H. Oubrayme * [1,2]
[1] Laboratory of Materials Membranes and Environment, Department of Chemistry, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca ,28806, Mohammedia, Morocco.
[2] Laboratory of Water and Environment Engineering, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca, 28806, Mohammedia, Morocco

S. Souabi
[2] Laboratory of Water and Environment Engineering, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca, 28806, Mohammedia, Morocco

M. Bouhria
[1]Laboratory of Materials Membranes and Environment, Department of Chemistry, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca ,28806, Mohammedia, Morocco

A. Jada
[4] Institut de Sciences Des Matériaux De Mulhouse (IS2M-UMR 7361 CNRS - UHA) 15, rue Jean Starcky, BP 2488 68057 MULHOUSE Cedex France

M. Tahiri
[3] Industry Refining SAMIR, 20800, Mohammedia, Morocco

S. Alami Younssi
[1] Laboratory of Materials Membranes and Environment, Department of Chemistry, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca ,28806, Mohammedia, Morocco

A. Albizane
[1] Laboratory of Materials Membranes and Environment, Department of Chemistry, Faculty of Science and Technology of Mohammedia, Hassan II University of Casablanca ,28806, Mohammedia, Morocco

***Abstract*—Aromatic compounds, including phenol and surfactant, are among the most common organic pollutants in effluents, mainly from oil industries and also plastic, paper, dyes, resin and wood industries. Wastewater is generally a mixture of pollutants originating from these industries. These pollutants are used for domestic or industrial needs, may be either dispersed or dissolved in water. The objective of the present work, carried out in the refining company SAMIR aims to make a diagnostic assessment of the phenol and surfactant elimination during the various processing steps within the wastewater treatment plant. The crude that was used at that period was too loaded with organic matter. The removal of phenols by STEP showed removal exceeding 97 % , as well as the removal of surfactant STEP showed removal exceeding 88 % , which shows that justifies the optimization of the coagulation /flocculation and therefore biological aeration tanks may be useful to ensure good biodegradability phenol and surfactant.**

Keywords—Wastewater; Refinery; Phenol; Surfactant; Coagulation/flocculation

I. INTRODUCTION

The rejections of water which were not treated can produce certain problems on the human being, these problems caused by discharges contaminated, industrial and agricultural discharges. Industries produces about 300-400 millions of waste polluted in the seas and the oceans as each year approximately 80% of sewages in the developing countries is unloaded directly without being treated [1]. Wastewater is generally a mixture of pollutants with these categories, dispersed or dissolved in the water used for domestic or industrial needs. So in the wastewater terminology, one group of waters of very diverse origins has lost their purity; that is to say, their natural properties by the effect of pollutants after being used in human activities (domestic, industrial or agricultural). Phenols are important industrial chemicals of environmental concern since they are involved in many industries such as coke, refineries, manufacturers of resin, pharmaceuticals, pesticides, dyes, plastics, explosives and herbicides, and can also occur in their wastewaters. Phenols are produced in very large quantities for use as solvents, and starting materials for chemical synthesis [2]. Aromatic compounds, including phenol, are among the most common organic pollutants in effluents from industries of paper, plastic, oil, dyes, resin and wood [3, 4, 5]. Phenol is considered a toxic compound, requiring the development of an effective technology to eliminate from waste waters [6, 7]. Phenolic compounds are some of the major hazardous compounds in industrial wastewater due to their poor biodegradability, high toxicity and ecological aspects. Petroleum refineries are the main sources of phenolic wastewaters. For instance phenols are released into water from industrial effluent discharges such as petroleum refinery wastewater Phenol is classified by the European Union as a mutagen category 3. Because of its high toxicity in water, it is necessary to treat aqueous solutions of phenol, before being discharged into the natural environment. [8]. The presence of phenols in the effluent, even at trace poses great problems since these compounds, particularly chloro- and nitrophenols are toxic to living organisms including humans. The toxicity of phenols increases their acidity, so nitrophenols and polychlorophenols are the most toxic. However, nitrophenols

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are more readily biodegraded in the environment by reduction of their corresponding amines, but, chlorophenols are highly persistent and may pollute the environment [9, 10]. For this, various methods have been developed such as solvent extraction, the microbial degradation, activated carbon adsorption and chemical oxidation [11, 12, 13].

There are different methods for the separation of phenols in wastewater, physical, chemical and biological [14], Separation by extraction [15], by adsorption [16], by membrane [17], electro-coagulation [18]. Surfactants are in widespread use throughout the world. The use of surfactant is gradually increased day by day; the world surfactant production was 1.7, 1.8 and 9.3 million tons in the years 1984, 1987 and 1995, respectively. Surfactant discharge of wastewater may cause serious environmental problems because surfactant product and ingredients may be relatively toxic to aquatic life [19]. Anionic and nonionic surfactants are principal components of synthetic detergents. In order to protect water environment, a cure process should be applied. Owing to its intricacy, surfactant wastewater is very difficult to deal with it [20]. Surfactant removal operations involve processes such as chemical and electrochemical oxidation [21, 22], membrane technology [23, 24, 25], chemical precipitation [26, 27]. Many problems associated with the above mentioned methods have been reported in the literature such as high cost, low efficiency and generation of toxicity products [28]. The objective of this work, carried out in the SAMIR refinery aims to make a diagnostic assessment of the removal of phenol and surfactant during the various processing steps within the station.

II. EXPERIMENTAL PART

A. *Description of SAMIR WWTP*

SAMIR refinery is located on the western edge of the city of Mohammedia, bordering the Atlantic Ocean. Its refining capacity is 200,000 bbl / day with a storage capacity of 2 million cubic meters. It supplies 80 to 85% of the Moroccan market needs in petroleum products. The diagram of the wastewater treatment plant of the SAMIR Company is illustrated in Fig 1 [29]. The floating oil and grease is collected with the half-pipes and pumped into the recovery tanks.

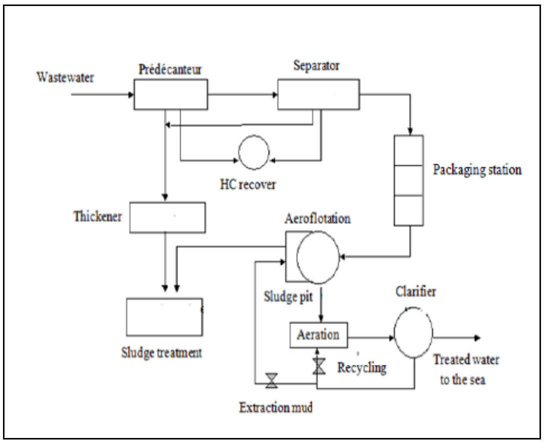

Figure 1. Schematic of wastewater treatment SAMIR plant

B. *Nature of effluents*

Effluent from the Mohammedia refinery is treated according to the origin of each effluent. Table 1, illustrates the nature and origin of the waste, the types of the most representative pollutants and types of treatment adopted.

TABLE I . TYPES OF POLLUTANT AND TREATMENT PROCESSES ADOPTED DEPENDING ON THE ORIGIN AND QUALITY OF THE EFFLUENT

Type of effluent	Origin	Type of pollutant	Treatment
Clean Water	Cooling water	nothingness	Basin Inspection
Oily Water	Purges bins Washing units loading station Rainwater	Hydrocarbons, sulphides, H_2S solvents	Oiling ((pre-treatment) • Settling-Separation Physicochemical (primary): •Coagulation •Flocculation • Air flotation Biological (secondary) •Ventilation • Clarification
Process water	steam condensate stripping Water desalting	Hydrocarbons, sulphides, H_2S, $NH^{4+,}$ phenols, salts	
Acid water	Regeneration of water channels demineralization	Acid H_2SO_4	Neutralization in basins with sodium hydroxide

C. *Sample Points and Methods of analysis*

To perform this study, eight samples were collected from five points along the processing of the STEP:

-Water station entrance (raw water) (A)
-Water inlet coagulation /flocculation (B)
} Points before treatment ((A & B)) I

-Water output coagulation/flocculation (C)
-Water output biological basin (D)
-water clarifier output (E)
} Points after treatment ((C, D & E)) II

D. *Physical parameters*

-Temperature was measured with an ASTM 5C thermometer
-Conductivity was measured by Hach type conductivity (Hach Sension 7).
-MES were determined by filtering 100 ml of water to be analyzed through a 47µm porosity filter, the filter was dried at 105 ° C for 2 hours. The amount of solids was obtained by the weight difference of the filter before and after drying (NF T 90-202), [29].

E. *Chemical parameters*

-Turbidity was determined by a turbidity meter (Model 2100N HACH)
-PH measurement was performed using a pH meter type Oakton-Metrohm with a glass electrode.
-COD was based on the oxidation of organic material by an excess of potassium dichromate ($K_2Cr_2O_7$), in acid and boiling medium in the presence of silver sulfate and mercury sulfate according to the standard (NF T90-101) . COD was measured by a spectrophotometer DR 2800. [29]

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-BOD_5 was measured using a thermo Aqualytic (BOD) Trak Hach. The measurement of BOD5 was obtained after 5 days of incubation at 20 ° C in the dark (NF EN 1899-2) [29].

-Hydrocarbons were analyzed by infra-red after extraction with tetracloro-ethylene. The monitoring of these physico-chemical parameters was performed over several months. (Norme AFNOR 1999) [29].

-Total Phenols

The experimental conditions proposed for the determination of total phenols: 1 ml of sample (blank) was added to at least 9 ml of distilled water. The process involved the following: add 0.5 ml of FC reagent and mix. After 5 minutes, 0.5 ml of sodium carbonate at 20%. The absorbance of the solution was mixed loft and leave standing for an hour. The absorbance measurement was thus carried out in the following terms: (725 nm; tank with a diameter of 2.5 cm). [30]

-Surfactants

Analysis of Surfactants was conducted by crystal violet (Method 8028) [31].

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

The elimination of wastewater pollutants (Ammonia, phenol, sulphur and oil and grease…) at the outlet of the treatment plant is necessary for the proper functioning of the treatment steps. The wastewater parameters that will be treated by the plant must be limited before discharge into the marine environment according to the World Bank of refineries. The processing of crude oil; petroleum refining is among the ones that consume the highest amount of water per barrel of crude oil. The results of physico-chemical parameter of the refining effluent at the entrance of the stations during the period of February 2014 to June 2015 are shown in Table 2. Fluctuation range of the measured values for COD, BOD, surfactants, phenol….etc, is given in Table 1. The wastewater is characterized by substantial organic matter and high surfactants, phenol and hydrocarbons.

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 [32].

SAMIR wastewater is characterized by an average concentration of 635 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). [33]. COD was 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.

The COD values range from 4890 to 600 mg /L. These values were greater than 2745 mg/L, (which is the limit for direct discharge), but well below 1000 mg/l (which is the limit for indirect discharge) [33]. BOD5 values vary between 250 to 690 mg/l with an average of 470 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) [33]. The hydrocarbon content varied between 52 and 96 mg /L with an average of 74 mg/l. The concentrations of phenols were between 25.98 and 73.2 mg /l.

SAMIR wastewater is characterized by surfactant contents between 4.8 and 53.56 mg / L with an average of 29.18 mg / L.

Should every time to do maintenance repairs in the factory , the spectrum to improve quality and remove contaminants with sampling to be analyzed to fully understand exactly what is going on at each stage of treatment.

In the refining process of crude oil, the oil is converted into more than 2,500 products by using several chemical processes such as distillation, cracking, alkylation, polymerization, coking, and hydro treating, among others [1].

Wastewater is generated in several of these different processes done daily in the refinery and, based on where this polluted water is generated. It can be classified into two types: process and non-process wastewater.

Table 2: Physico-chemical parameter of the refining effluent at the entrance of the stations during the period of February 2014 to June 2015.

	Azote amonical (mg/L)		Total Phosphore (mg/L)		Nitrate (mg/L)	HC (mg/L)	TSS (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Turbidity (mg/L)	pH	Phenols (mg/L)	Surfactant (mg/L)
	680 nm	415 nm	880 nm	700 nm									
Max	3.89	42,6	2,99	3.51	3,985	96	850	4890	690	780	8,3	73.2	53.56
Average	3.835	41.4	2.91	3.365	3.059	74	635	2745	470	491	7.4	49.59	29.18
Min	3.73	40.2	2.83	3.22	2.134	52	420	600	250	101	6,5	25,98	4.8

These results show that the pH ranges from 6.5 to 8.3 with an average value of 7.4. 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 101 to 780 NTU. This is related to the instability in the quality of the effluent over time.

Process wastewater is the one that is generated during the refining process itself and that Drainage operations are always connected with the hydrocarbons while they usually come from the cooling towers, and the flow of surface water, cleaning equipment, containers clean equipment and offices [34]. Normally, these streams are separated in order to

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accomplish the best treatment possible and to avoid the contamination of a higher volume of water with harsh pollutants.

The pollutants found in the wastewater will depend on the type of oil being refined, the plant configuration and the processes found in the installation [35].

For instance, when water vapour is used for distillation and/or cracking units, the vapour is condensed in an environment where hydrocarbons that contain hydrogen sulphide and ammonia are present, thus the produced wastewater has a high concentration of them. The presence of oil in the treated water discharged into water bodies is detrimental for the aquatic life as a layer of oil is formed in the water surface that decreases the penetration of light and consequently reduces photosynthetic activity and oxygen production.

In general, the contaminants that are found in oily wastewater coming from refineries and that are of concern are: suspended solids, phenols, benzene, ethylbenzene, xylenes, sulphides, ammonia, polyaromatic hydrocarbons (PAH) and chemical oxygen demand [36].

Removal efficiency of the parameters (Phenol and Surfactant) was obtained using the following equation:

$$\mathrm{Re}\,moval(\%) = \left[\frac{(Ci - Cf)}{Ci}\right] * 100 \qquad \text{Eq . (1)}$$

Where C_i and C_f are the initial and final concentrations of the five processing steps [Water station entrance (raw water), Water inlet coagulation /flocculation, Water output coagulation/flocculation, Water output biological basin, and water clarifier output], respectively.

III. VARIATION OF THE FLOW RATE OVER TIME IN THE SAMIR WASTEWATER TREATMENT PLANT

Fig 2 shows the variation of flow received by the station. These results show that the flow rate varies between 200 and 400 m^3/h.

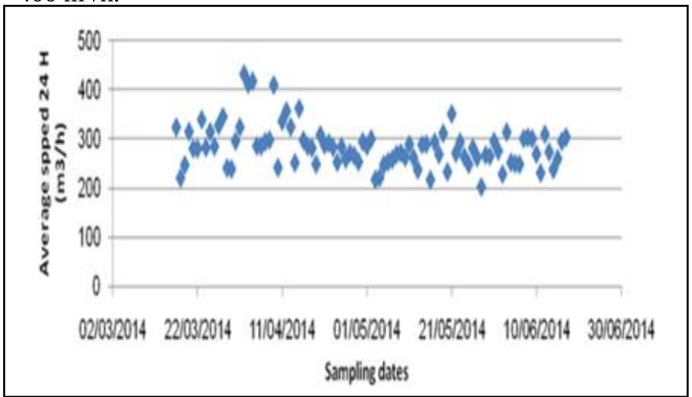

Figure 2. Variation of flow received by the station

is a function of the flow and the pollutant content. The establishment of a neutralization and homogenization basin would ensure a good coagulation-flocculation and subsequently protect the biological basin of attacks due to the hydrocarbons. [29]

SAMIR Company operates 24H / 24H. The treatment plant must be optimized to significantly reduce pollution of the marine environment since the treated water is discharged after treatment in the marine environment.

Water contamination not only affects negatively the natural ecosystems by decreasing its biodiversity but it also affects human health as the amount of people dying or getting sick by its consumption increases with it.

Industrial waste toxins can be broadly grouped into toxic chemicals and toxic metals. In refinery wastewater, the toxic chemicals are phenol, surfactant, compounds such as organochlorine compounds, organophosphates and complex inorganic compounds, while Pb, Cd, Hg, As, Se, Cr, Bi, Pt, Ni and many other metallic elements are the toxic metals prevalent in industrial waste. [37]

The persistence and bioaccumulative tendency of these substances, their metabolite and residues in the environment (air, land and water) endangers the environmental ecosystem and human health. [38]

Wastewater is generated by different processes done daily in the refinery and, based on where this polluted water is generated; it can be classified into two types: process and non-process wastewater. Process wastewater is the one that is generated during the refining process itself and that has been in direct contact with hydrocarbons of equipment flushing, containers cleanse and office facilities [34].

IV. VARIATION THE COD, BOD5, TURBIDITY, HC, PHENOL AND SURFACTANT OF THE RAW EFFLUENT IN OVER TIME IN THE WASTEWATER TREATMENT SAMIR PLANT

Water scarcity is a problem that is currently lived in several countries of the world. The Lack of water is one of the most important problems facing many countries. Saluting the level of water scarcity varies depending on the region where it is located. On the other hand, the amount and type of pollutants those are significantly dependent on various industrial activities in the region.

Fig 3 shows the variation of COD, BOD5, Turbidity and Hydrocarbons of the raw effluent in over time in the wastewater treatment SAMIR plant.

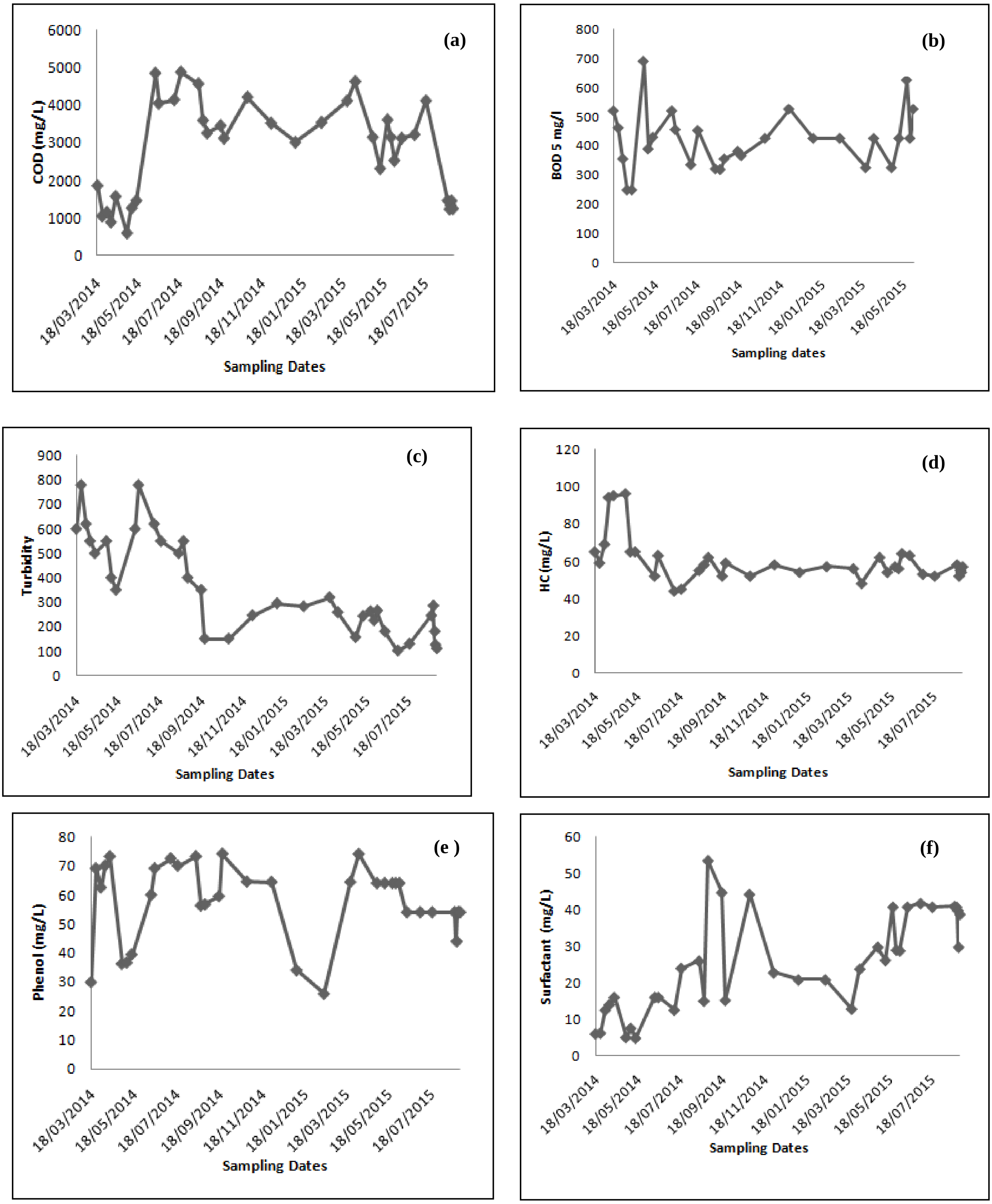

Figure 3. Variation the COD (a), BOD_5 (b), Turbidity (c) ,HC (d), Phenol (e) and Surfactant (f) of the raw effluent over time in the SAMIR wastewater treatment plant.

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Often estimated in a treatment plant, pollution of water directly through the measurement of global parameters COD and BOD_5 which offer a more or less complete representation of oxidized and biodegradable material present in a sample. [38] It was necessary to measure the COD samples of the raw effluent over time in the SAMIR wastewater treatment plant to indicate the purpose the degree of pollution.

Fig 3 shows the variation of the COD obtained during this study period. It shows that the value range between 600 to 4890 mg /L, while the values of BOD_5 obtained show enough considerable changes. The values are between 250 to 690 mg. The Moroccan regulations oblige industry to measure the COD parameter because it will make it possible to evaluate the quality of organic pollution. [39].

COD is an important factor in the petroleum industry because it can be found in high concentrations of refinery effluents [40]. This parameter would be useful to evaluate the BOD / COD ratio needed for an efficient biological treatment [41].

On the other hand the turbidity of water is mainly caused by colloidal particles. These particles, which can stay suspended in the water for very long periods of time and can even cross a very fine filter. [29]. Fig 3, shows the considerable turbidity. The values are between 101 to 780 NTU.

Otherwise, the hydrocarbons constitute a screen to the water surface that inhibits the exchange with the air, which can cause problems in the aeration tank. Fig 3 shows the Hydrocarbons concentration in refinery wastewater varies from 52 and 96 mg /L .

In addition, Phenol is a major pollutant in the wastewater because of its presence in the effluent of major processing and refining plants [42]. The considerable Phenol concentration shows the values are between 25.98 and 73.2 mg /l (Fig 3).

In addition, surfactants are among the most widely disseminated xenobiotics that contribute significantly to the pollution profile of sewage and wastewaters of all kinds. [43]. As shows in Fig 3, the surfactant concentration, shows that the values range between 4.8 and 53.56 mg / L.

In this study the changes in parameter (COD, BOD_5, Turbidity and Hydrocarbons, Phenol and Surfactant) measurement at the raw effluent over time depends on the quality of crude that was used at the Company SAMIR.

V. EVOLUTION OF PHENOL AND SURFACTANT ALONG THE DIFFERENT STAGE OF STEP

Phenols are compounds that can be highly toxic for humans even when consumed at small concentrations. Chronic toxicity of phenol can cause sour mouth, diarrhea, impaired vision and dark urine in humans and it is also highly toxic for aquatic fauna [44]. These compounds are very soluble in water and can serve as precursors for the formation of other toxic compounds [40].

In general, the contaminants that are found in oily wastewater coming from refineries and that are of concern are: suspended solids, phenols, benzene, ethylbenzene, xylenes, sulphides, ammonia, polyaromatic hydrocarbons (PAH) and chemical oxygen demand [45, 46].

If all these compounds are discharged continuously over time in a water body, they can affect quite drastically the health of the ecosystem [47]

The evolution of Phenol and surfactant along the different stages of the STEP illustrated in Fig 4. Phenol is classified by the European Union as a mutagen category 3.

Due to its high toxicity in the water, it is necessary to treat aqueous solutions of phenol, before being discharged. The presence of phenols in the effluent, even at trace levels pose big problems for these compounds, particularly chloro- and nitrophenols which, are toxic to living organisms, including humans.

Fig.4 illustrates the evolution of phenol concentration before treatment (A, B) and after treatment (C, D and E) throughout the process step.

The values before treatment (A, B) showed that the phenol concentration of the entry recorded in the Step was between 30 and 73.2 mg / L with an average of 51.6 mg / L , as well as after treatment (C, D & E) value decreases, at the outlet of the clarifier. In there is flocculation over time which requires optimization at the level of flocculation coagulation to eliminate a large amount of phenol.

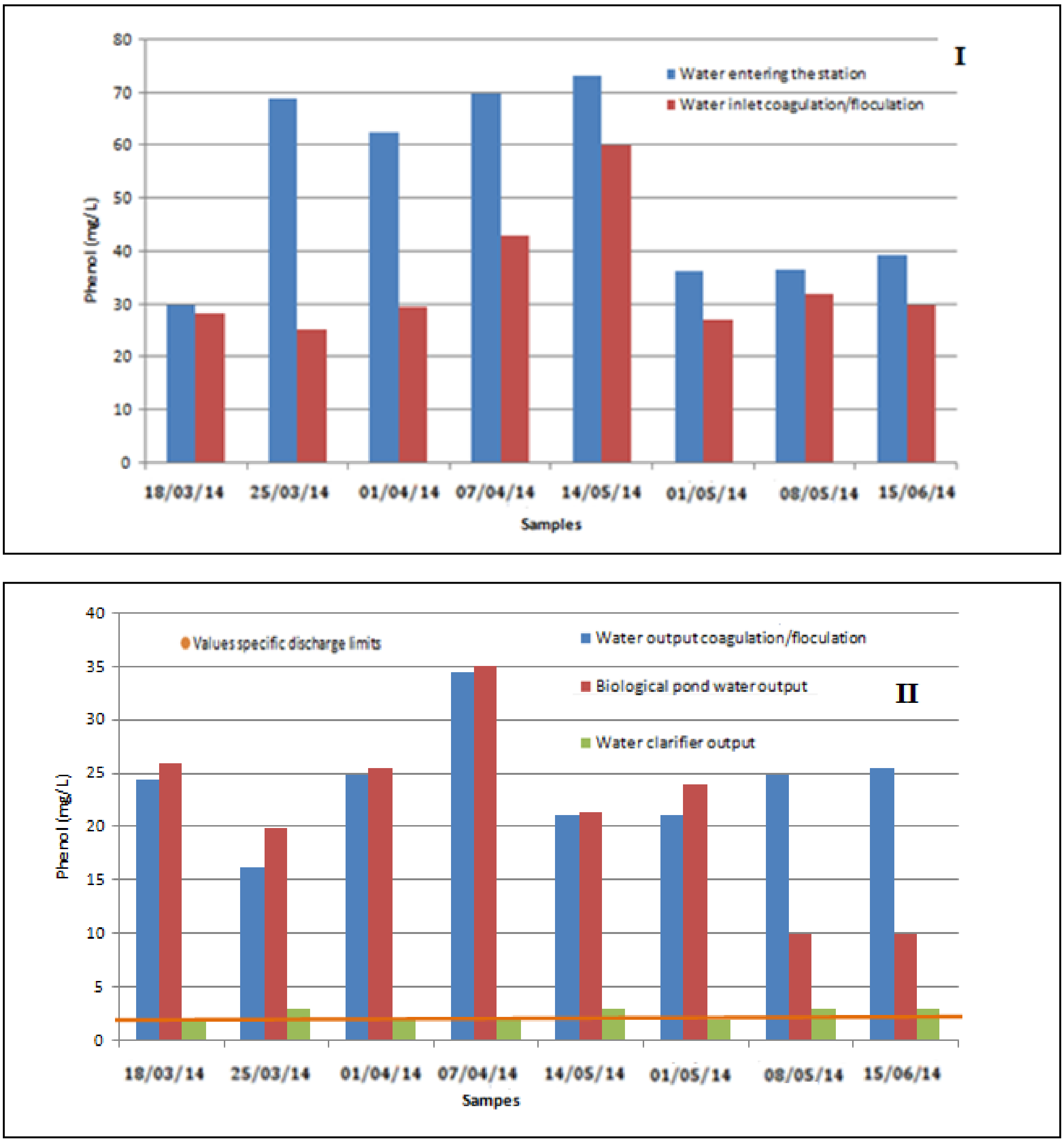
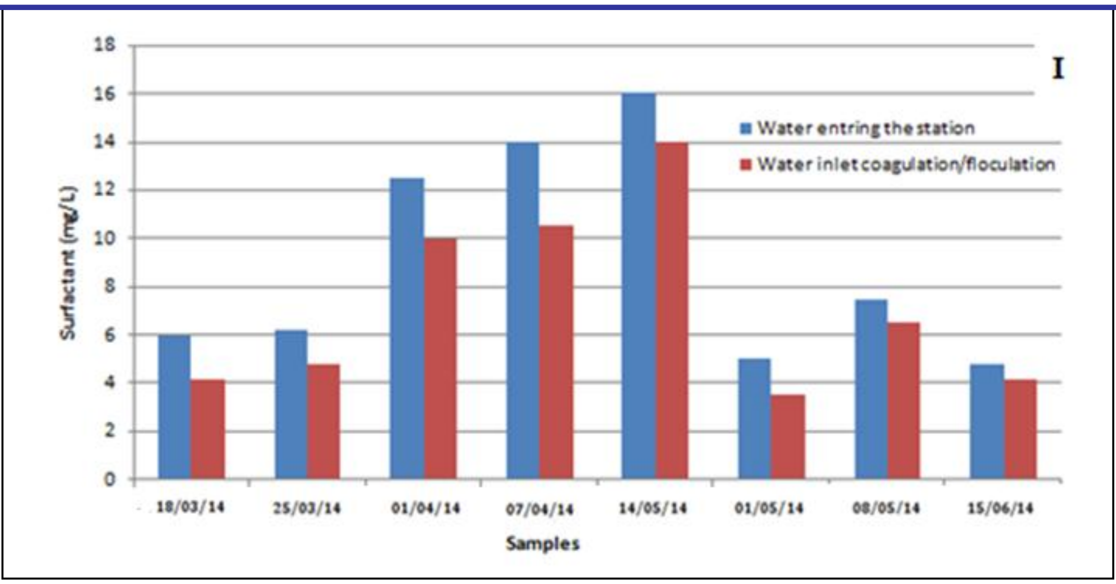


Figure 4. Evolution of phenol concentration before treatment I ((A, B)) and after treatment II ((C, D & E)) along the process STEP

The results of the work carried out by Kulkari and Kaware (2013) on the treatment of rich refiners show that in the lagoon system the reduction in phenol concentration reaches 74% [44]. This reduction is due to the aerobic biodegradation of the compound in the stabilization ponds due to the photo-degradation of organic compounds [48]. Different studies have shown that up to 70% of phenol can be removed in wastewater due to stabilization ponds [49]. The following table lists the standard deviation, maximum and minimum values for phenol between March to May 2014. It is observed frome this table that the range of values found for the effluent from the stabilization basin and from the discharge into the water body is very high especially of the stripped water. As well as each parameter to data very close to the limit. The crude that was processed at that time was too loaded with organic material and two days were required to fine timing of the station processing in order to WWT optimize the treatment. The evolution of surfactant is illustrated in Fig 5



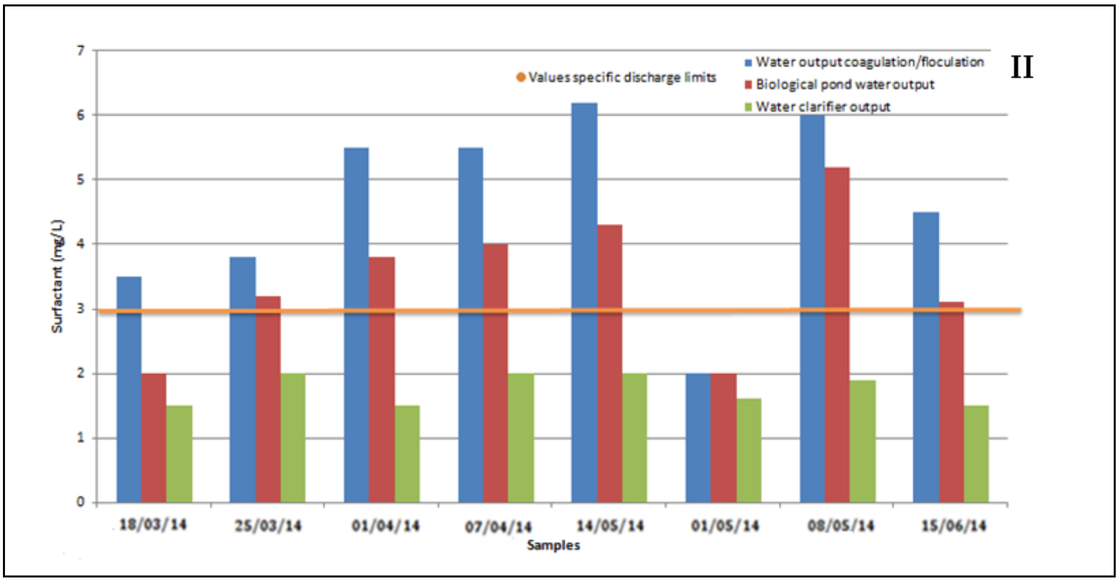


Figure 5. Evolution of surfactant before treatment I ((A, B)) and after treatment II ((C, D & E)) along the process STEP

Surfactants are components that come from both industrial and domestic activities. Their active voltage property attributes their large flotation capacity, and poses a risk to the operations of decanting and aeration of wastewater treatment plants (for foam protection). [51].

Their reluctance to biodegradation makes compounds that will eliminate the early stages of treatment. Currently, European and American regulations encourage the use of biodegradable detergents. [52].

Fig.5 illustrates the evolution of surfactant before treatment (A, B) and after treatment (C, D and E) throughout the process step, for after this figure is observed the values before treatment (A, B) note that the raw water at the entrance of the station has a content of surfactant which varies between 4.8 and 16 mg / L.

These values were greater than 3 mg / L values required by Moroccan standards but it is normal since the effluents that have not yet processed at the two points (A and B), but after treatment (C, D and E) the values decrease and reach 1.5 mg /L The physico-chemical treatment followed by biological treatment can reduce this excess surfactant. The registered values the output of a clarifier is less. Surfactants are components that come from both industrial and domestic activities.

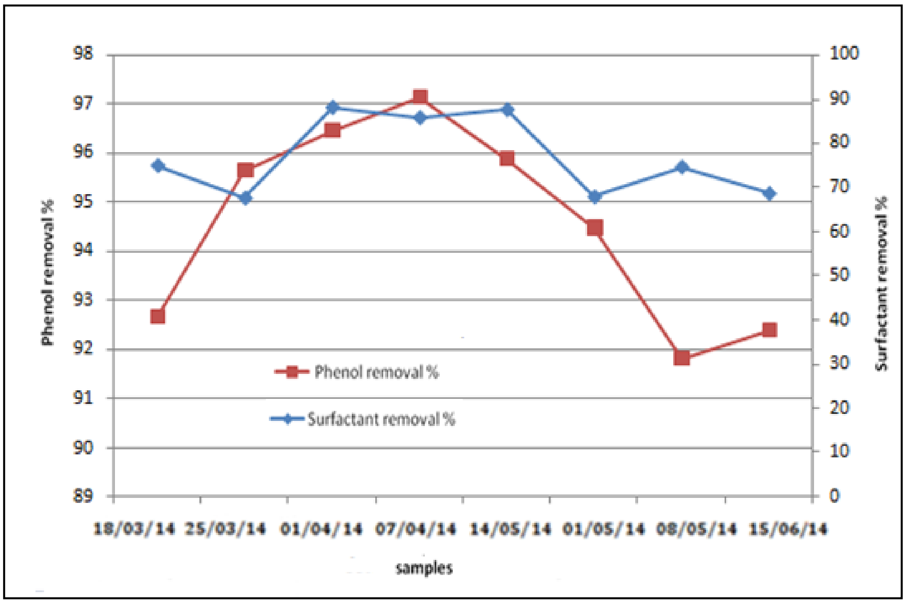


Figure 6. Removal of the phenol and surfactant along the process STEP

Fig 6, illustrates the removal of the phenol and surfactant along the STEP process. Results the removal of Phenol by STEP exceeded 97% which justifies the optimization of the coagulation /flocculation and therefore biological aeration tanks may be useful to ensure good biodegradability phenol. In addition to monitoring the removal of surfactant by STEP showed removal exceeding 88 % (Fig.6) which justifies the optimization of the coagulation /flocculation and therefore biological aeration tanks may be useful to ensure good biodegradability surfactant. [52].

VI. CONCLUSIONS

This study was conducted in the SAMIR refining company aiming to make a diagnostic assessment for phenol and surfactant removal from wastewater during the various treatment plant steps.

It is then concluded that the physico-chemical treatment followed by biological treatment can reduce the surfactant amount present in the wastewater, so that the registered values of the clarifier output is less than the standard value.

Moreover, SAMIR treatment plant showed that the removal of phenols is exceeding 97 % of its initial amount. This treatment showed also that the removal of surfactant is exceeding 88 % of its initial value. Finally the wastewater treatment presented in this work justifies the optimization of the coagulation /flocculation processes and therefore the biological aeration is required to ensure good biodegradability of phenol and surfactant compounds.

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