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Study of refining wastewater pollution: case of vegetable oil refining industry Morocco

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Abstract
Rapid industrial development and growth of cities throughout the world especially in developing nations have led to the recognition and an increase in understanding of the relationship between pollution, public health and the environment at large. Generally, industries produce more pollutants than any other sector in society. Previously, effluents from the vegetable oil industry were directly discharged into the soil or ground water. However, due to their important environmental impact, national legislations have become stricter and imposed stringent norms. The oleaginous industry produces large volumes of aqueous wastes that must be first characterized as a step to their management. This study is focused on the sources, characteristics, and composition of vegetable oil refinery wastewaters. The obtained results were very much useful in identification and rectification of operational and maintenance problems as well as the future expansion to be carried out in the plant to meet the increased hydraulic and organic loadings. Types of wastewaters evaluated are refinery, soap, acidic and process wastewater. Samples were collected and analysed for the following water quality parameters: biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and oil & grease phenol and surfactant. Results present data for 13 week sampling period. In our characterization studies, the maximum values COD were 205800 mgL^{-1} and 240500 mgL^{-1} for acidic and soap wastewater respectively. These results confirm that the vegetable oil refinery wastewater has a high organic pollution load. Knowledge of the effluent quality parameters and subsequently the treatability of wastewater would help for the development of sustainable treatment strategies.

Key words: vegetable oil refinery, wastewater, biological oxygen demand, chemical oxygen demand.

1. Introduction

Pollution generally may be defined as the total disturbance of the natural environment. Water pollution may be defined as the presence of Chemical, Physical and/or Biological elements that exceeds the allowable standard limits. The presence in significant quantity of any extraneous material (solid, liquid, gas) in any particular location may therefore constitute pollution. One of the important sources of pollutants is the oil refinery industry, being a significant water consumer and consequently a large wastewater producer.

The treatment of vegetable oil refinery effluent has been a major issue of environmental concern in developing countries for the last three decades. The waste streams which come out of vegetable oil refinery without any treatment create environmental problem such as threat to aquatic life due to their high organic content. Refining of crude vegetable oils generates large amounts of wastewater [1]. In oil industry, wastewaters mainly come from the degumming, deacidification, deodorization and neutralization steps. In the neutralization step, sodium salts of free fatty acid (soap stocks) are produced and generate highly acidic and oily wastewaters [2]. Its characteristics depend largely on the type of oil processed and on the process implemented that are high in COD, oil and grease, sulphate and phosphate content, resulting in both high inorganic as well as organic wastewater. Many methods are available to treat the organic content and a great deal of literature is available on this aspect [3-7]. The selection of proper treatment method is crucial in effluent treatment. However, there is still a waste generated that poses a major challenge in the vegetable oil processing industry [8].

As a result, studies on the treatment of oily wastewaters have gained increasing importance. Oil effluents can be treated either separately or in conjunction by chemical or biological means. The problems with chemical treatment are the increased handling costs and the production of chemical sludge that is difficult to treat [9]. Biological treatment methods offer an easy and cost effective alternative to chemical methods of treatment. Biological treatment of oil wastewater could be done by Conventional Activated Sludge Process and Sequencing Batch Reactor [10]. Mkhize et al. [11] observed that 75% influent COD reduction and more than 90% removal of oils and suspended solids have been achieved for edible oil effluent by using an anaerobic/aerobic sequencing batch reactor. Characterization of wastewaters is important for control and development of treatment processes [12]. Total suspended solids (TSS), biological oxygen demand and chemical oxygen demand are the most common parameters used for measurements of organic materials in characterization studies. In this study, biological treatability of wastewaters coming from vegetable oil refinery was investigated by determining COD fractions. Characterization studies were also done in order to define the properties of the wastewater.

2. Materials and methods

2.1. Industrial unity presentation.

The refinery (mentioned herein as the company) is one of the leading agro industrial companies in the continent of Africa. The company has two processing units in Morocco, located in the region of Casablanca. The company manufactures and markets oils and soaps in Morocco. The company operates in: Oilseed Milling, Oil Refining Process, and Soap Making Process. It produces olive oils and other edible oils, as well as various soaps.

The refinery uses chemical and physical methods for the refining of oils (rapeseed, sunflower, soybean, palm, and hydrogenated). On average, the refinery generates 1200 m^3 of wastewater daily, which includes acid wastewater (80 - 270 $m^3 \cdot d^{-1}$) and process wastewater (570 - 1000 $m^3 \cdot d^{-1}$). The acid wastewater is that stream coming from the soapstock splitting process, whereas the process wastewater is that stream originating from all the factory's process installations and equipment (Fig.1).

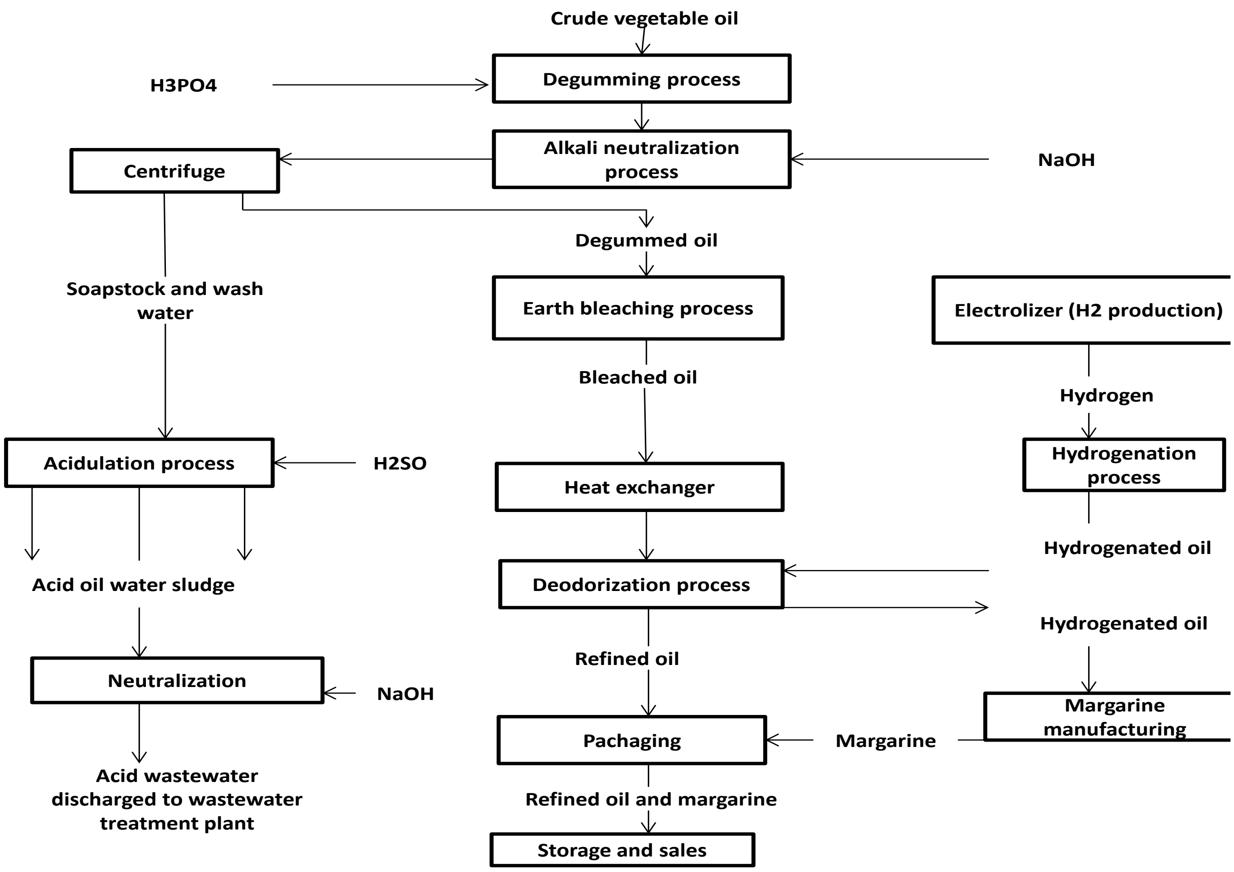


Figure 1: Simplified schematic diagram of vegetable oil refining processes: source of vegetable oil refinery wastewater (Acid and process wastewater). [13]

The investigations were carried out on freshly collected untreated wastewater samples coming from the company. Sampling locations are shown in Fig. 2 as A, B, C and D for refinery, soap, acidic and process wastewater respectively. The process wastewater is a mixture of refinery; soap and glycerin wastewater. Acidic and process wastewaters are the influents which enter into the wastewater treatment plant.

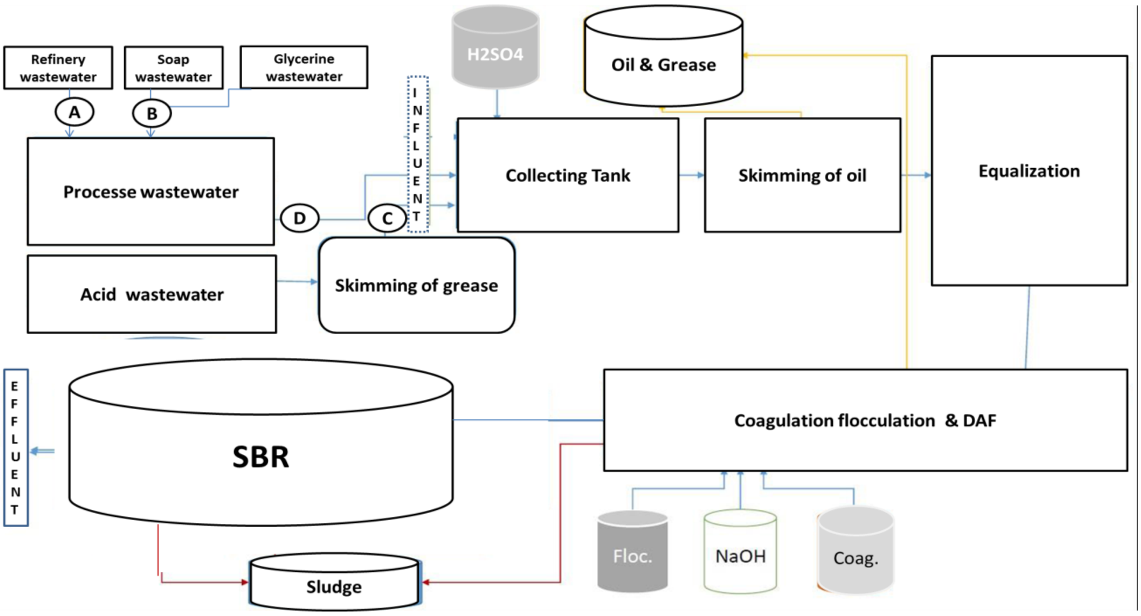


Figure 2: Treatment system for the vegetable oil refinery wastewater showing sampling station: A, refinery wastewater; B, soap wastewater; C, acid wastewater; D, process wastewater.

2.2. Sampling strategy and analytical methods.

Weekly sampling began in April 2013 and continued until June 2013. A total of 52 samples were taken simultaneously from refinery wastewater outflow (sampling station A), soap wastewater outflow (sampling station B), acidic wastewater outflow (sapling station C), and process wastewater outflow (sapling station D) (Fig. 2.). Samples were taken before treatment in order to obtain a clear picture of the quality of each influent alone. All samples were analyzed for physico-chemical variables in accordance with the procedure laid down in Standard Methods for the Examination of Water and Wastewater [14]. The pH and Temperature of all samples were measured in situ.

Temperature was measured with an ASTM 5C thermometer. The pH was measured according to the NF T 90-008 February 2001 (T 90-008). DO was measured with a dissolved oxygen probe HI 9143. The Chemical Oxygen Demand (COD) was performed according to standard AFNOR in force (NF T90-101 February 2001 (T90-101)). Measuring the biological oxygen demand after 5 days (BOD5) was facilitated by the use of the method manometric ((NF EN 1899 May 1998) (T90-103)). The turbidity was measured according to standard NF EN ISO 7027 March 2000 (T 90-033). The determination of suspended matter was conducted by the centrifugation method according to standard (NF T 90-105 January 1997 (T 90-105)).The oil and grease were measured according to standard method 1164, EPA. The surfactant concentration was analysed by using solvent extraction and spectrophotometric quantitative determination with ethyl violet method [15]. Phenolic compounds were determined by the colorimetric method using the Folin-Ciocalteu [16].

3. Results and discussion

3.1. Characteristics of Lesieur-Cristal wastewater

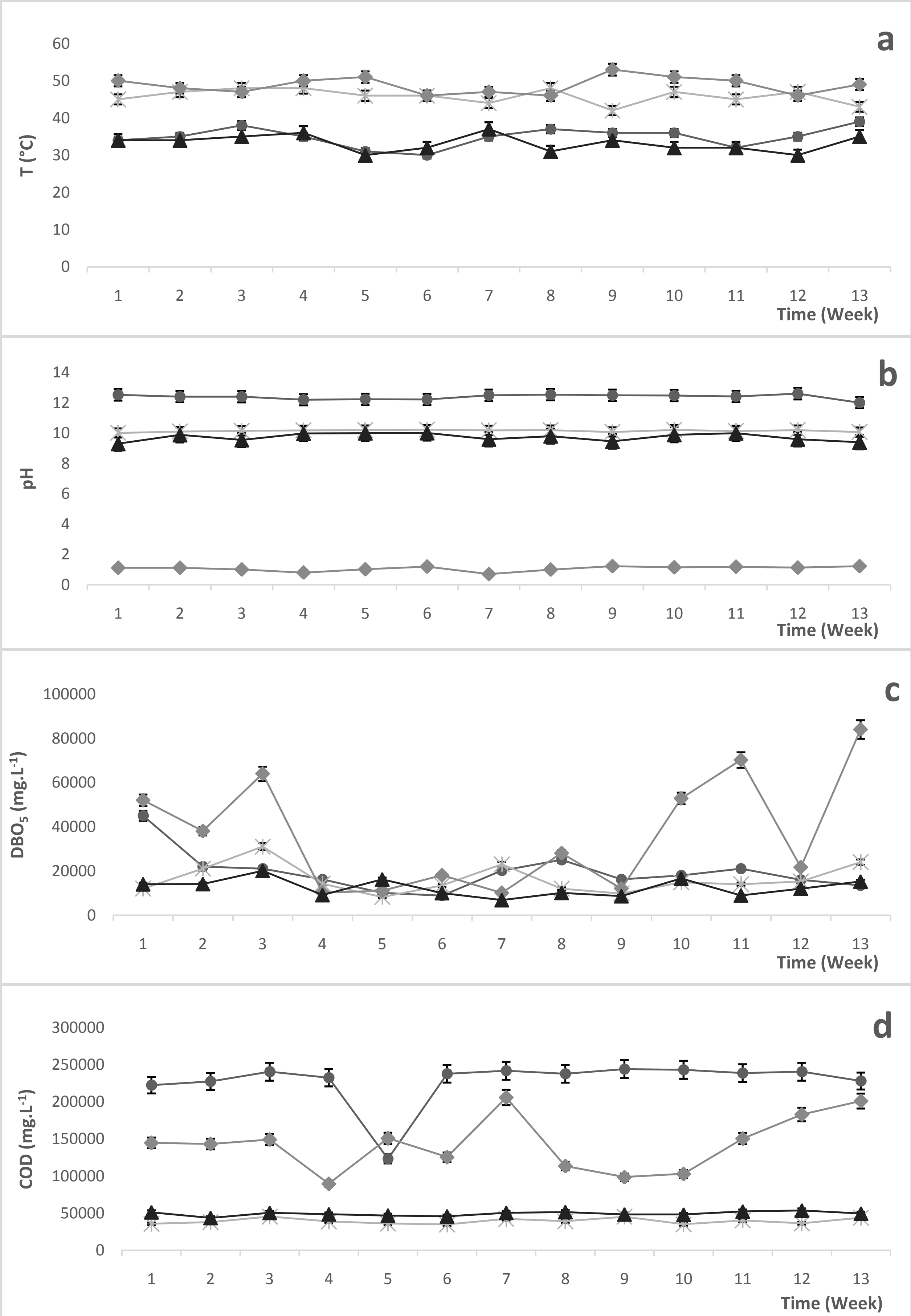
The refinery wastewater is a complex mixture of organic and inorganic matter. The removal of the pollution load by physicochemical and biological treatment (SBR) is affected by many factors such as the characteristics of the organic matter, the nature and concentration of other components, and the design and operation of the treatment facility. As a result, the performance of the process may widely vary. The characteristics of wastewater samples are summarized in Table 1. Results presented are for samples taken over a 13 week period. Mean values of BOD5 and COD confirm that the refinery wastewater has a high organic pollution load. With respect to COD values given in Table 1, it can be stated that wastewaters of this sector have high organic loads.

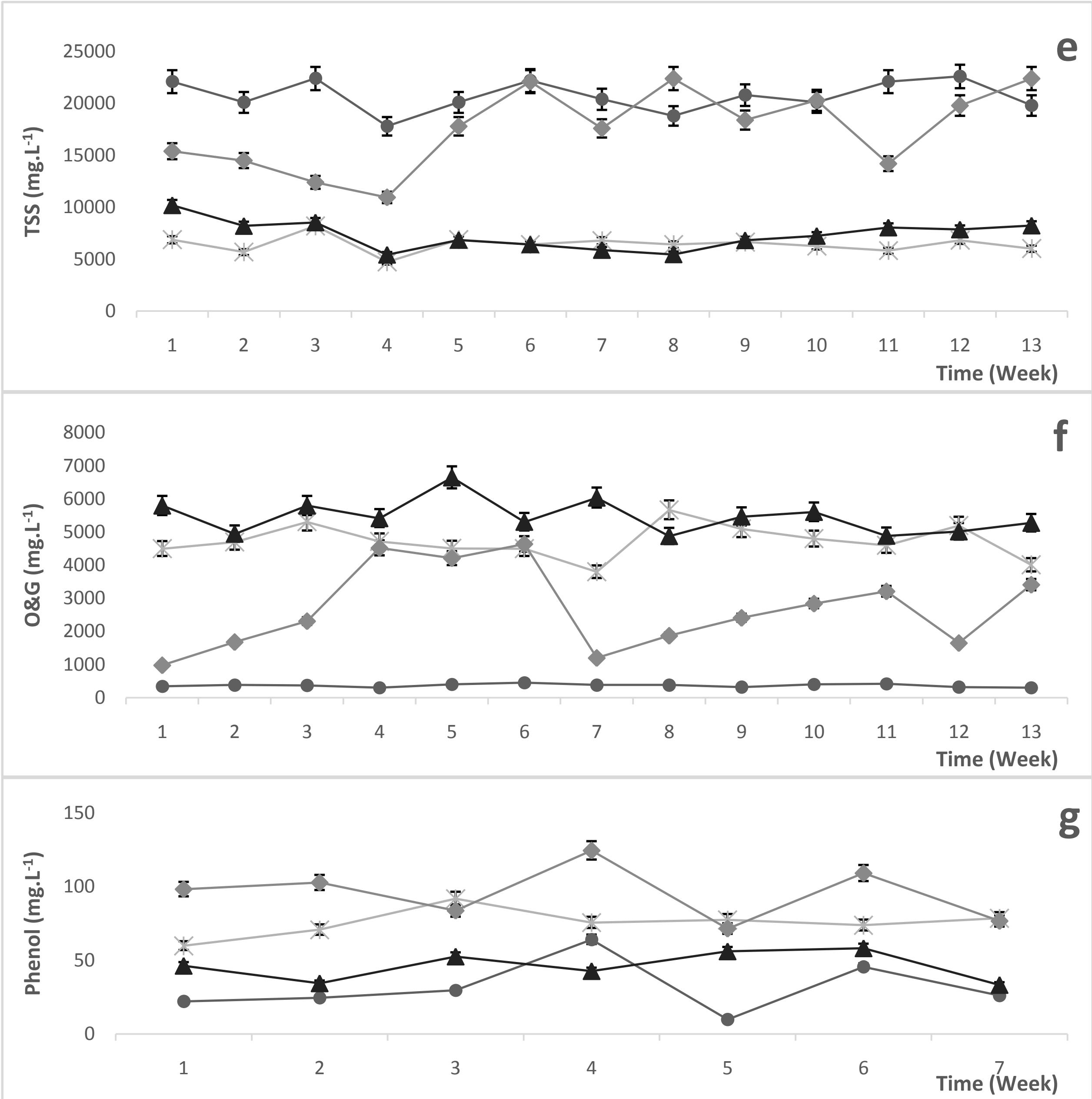
Table 1: wastewater parameters at different sampling stations

Parameters	Soap wastewater				Refinery wastewater				Acidic wastewater				Process wastewater			
	Mean	**Min.**	**Max.**	**S.D**	**Mean**	**Min.**	**Max.**	**S.D**	**Mean**	**Min.**	**Max.**	**S.D**	**Mean**	**Min.**	**Max.**	**S.D**
pH	12.39	12.01	12.06	0.171	10.15	10.01	10.23	0.066	1.07	0.7	1.23	0.162	9.73	9.4	10.01	0.253
Temperature (°C)	35	31	39	2.609	46	42	48	1.95	49	46	53	2.278	33	24	37	2.241
TSS (mgL^{-1})	20715	17800	22600	1491	6419	4720	8200	812	17558	10950	22400	3834	7322	5460	10200	1374
COD (mgL^{-1})	227508	123100	240500	32076	39138	34600	45400	3890	142858	89450	205800	37320	49192	43500	53600	2794
BOD_5 (mgL^{-1})	19454	8800	25000	8981	16363	8200	31000	6509	36302	10060	84000	25709	12446	6800	20100	3930
Oil & grease (mgL^{-1})	366	300	450	47	4725	4010	5670	511	2687	1200	4640	1238	5471	488	6650	514
Phenol (mgL^{-1})	31.8	9.9	64.2	17.79	75.5	59.9	91.9	9.58	95.3	71.5	124.6	18.98	46.3	33.4	58.3	10
Surfactant (mgL^{-1})	67	31	94	22.61	7.6	3.9	13.7	3.84	11.2	6.5	16.5	3.37	11.8	6.6	17.6	3.81
DO (mgO_2L^{-1})	1.16	0.56	1.87	0.54	0.88	0.22	1.70	0.43	0.51	0.20	0.86	0.29	1.28	0.11	2.20	0.74
Turbidity (NTU)	> 1000	-	-	-	> 1000	-	-	-	> 1000	-	-	-	> 1000	-	-	-

Weekly variations of physical and chemical parameters at different sampling station are given in Fig. 3. At the refinery wastewater outflow , the concentrations of TSS, BOD5 , COD, phenol, surfactant and oil & grease were 4720-8200 mgL^{-1}, 8200-31000 mgL^{-1}, 34600-45200 mgL^{-1}, 59.9-91.9 mgL^{-1}, 3.9-13.7 mgL^{-1}, and 3800-5670 mgL^{-1}, respectively. The mean temperature was 46 °C (fig. 3.) and the pH varied from 10.01 to 10.23. At the soap wastewater outflow, the concentrations of TSS BOD5, COD, phenol, surfactant and oil & grease values ranged between 17800-22600 mgL^{-1}, 8800-45000 mgL^{-1}, 34600-45400 mgL^{-1}, 9.9-64.2 mgL^{-1}, 31-94 mgL^{-1}, and 300-450 mgL^{-1} respectively. The mean temperature was 35 °C, while the pH varied from 12.6 to 12.0. Industrial production of soap is done through four basic steps. These are saponification, glycerine removal, soap purification and finishing [17]. In the saponification phase, a mixture of oils and tallow are mixed with sodium hydroxide and heated [18]. The soap which is formed is the salt of a long chain carboxylic acid. Salt is added to wet soap causing it to separate into soap and glycerine in salt water as soap is not very soluble in salt water, whereas glycerine is soluble. The remaining sodium hydroxide is neutralized with a weak acid such as citric acid and two thirds of the remaining water is removed. In the final phase, additives such as preservatives, color and perfume are added and mixed with the soap and it is shaped into bars for sale.

Two types of wastewater are generated from vegetable oil refinery, namely, acid and process wastewater. The acid wastewater is generated from the soap-stock splitting process, where as the process wastewater is generated from all the factory's process installations and equipment. That wastewater has a varying high pollution load (organic materials, sulphates, phosphates, and chloride). The highest values of total suspended solids (17558 mgL^{-1}), BOD5 (36302 mgL^{-1}), COD (142858 mgL^{-1}), phenol (95.3 mgL^{-1}), surfactant (11.2 mgL^{-1}) and oil & grease (2687 mgL^{-1}), noticed in Acidic wastewater outflow can be attributed to heavy organic and inorganic loading. The average Temperature was 49 °C, while the pH varied from 0.7 to 1.23. In this study, it is clear that BOD5 concentrations are low despite high COD values. In literature, Sulfate contents of wastewaters are also high due to usage of sulfuric acid during degradation of soap stock in the neutralization process [19, 20]. In this step, extraction effluent consisting of fatty acid (RCOOH) and NaSO4 forms during degradation of soap stock in the form of RCOONa. This process generates acidic wastewaters. Lower pH value of acidic wastewaters is related to a higher concentration of fatty acid. The formation of more soap stock increases the amount of acid used for oil production. Raw vegetable oils contain phospholipids. Furthermore, in the degumming step, phosphoric acid is widely used for removal of phospholipids and lipoproteins. These induce high phosphor concentration in wastewaters. Also, high values were found for TSS (7322 mgL^{-1}), BOD5 (12446 mgL^{-1}), COD (49192 mgL^{-1}), phenol (4.63 mgL^{-1}), surfactant (1.18 mgL^{-1}) and oil & grease (5471 mgL^{-1}) in the Process wastewater, which is also due to heavy organic and inorganic loading. The average Temperature was 33 °C, while the pH varied from 9.3 to 10.01. Generally, it can be seen that the wastewaters varies both in quantity and characteristics from acidic and process wastewater. The composition of wastewater from the same effluent also varies widely from day to day. These fluctuations may also be attributed to different types of oils processed and to operating conditions and processes [21]. Wastewater characteristics are not only influenced by raw materials and products processed, but also by water used in washing procedures during and after the production [22]. These factors apparently influenced the observed variation in the COD and BOD5 values of each wastewater sample.


a
T (°C)
Time (Week)
b
pH
Time (Week)
c
DBO5 (mg.L-1)
Time (Week)
d
COD (mg.L-1)
Time (Week)


e
TSS (mg.L-1)
25000
20000
15000
10000
5000
0
1 2 3 4 5 6 7 8 9 10 11 12 13
Time (Week)
f
O&G (mg.L-1)
8000
7000
6000
5000
4000
3000
2000
1000
0
1 2 3 4 5 6 7 8 9 10 11 12 13
Time (Week)
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150
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Time (Week)

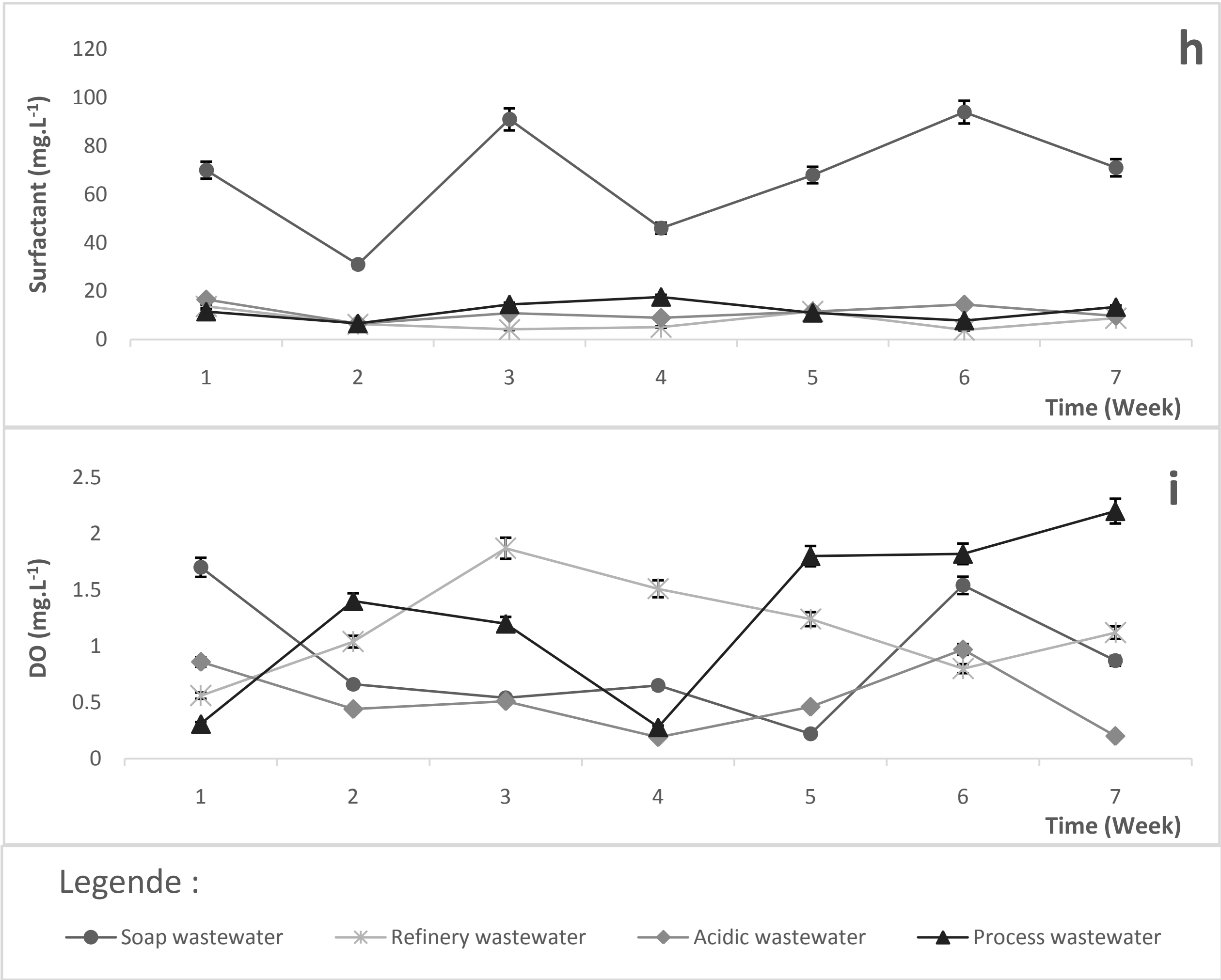

Figure 3: Weekly evolution of temperature (a) pH (b), BOD5 (c), COD (d), TSS (e), O&G (f), phenol (g), surfactant (h), and DO (i) at Refinery wastewater (A), Soap wastewater (B), Acidic wastewater (C), and Process wastewater (D).

3.2. Relative biodegradability

A biodegradability index helps in predicting the measure of chemical stability/resistance to biological degradation of organic pollutant in the environment, which can be evaluated by the biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The strength of wastewater is judged by its BOD. This is defined as oxygen required by bacteria while stabilising the organic matter in the waste water under aerobic conditions at a particular time and temperature. The ratio of COD to BOD of wastewater and its indication for biodegradability is shown in Table 2.

Table 2: Ratios of wastewater COD to BOD and their indication. Source: [23]

BOD/COD ratio	**Indication**
More than 0.3	Effluent readily biodegradable
Between 0.2- 0.33	Effluent medium biodegradable
Less than 0.2	effluent non-biodegradable

In this respect, COD/BOD5 ratios of the untreated wastewater were calculated in order to evaluate the potential biodegradability of the organic compounds in the wastewater. Results illustrated in fig. 4 show that the value of

COD/BOD5 was greater than 2. However, the relative biodegradability of the wastewater samples fluctuated weekly.

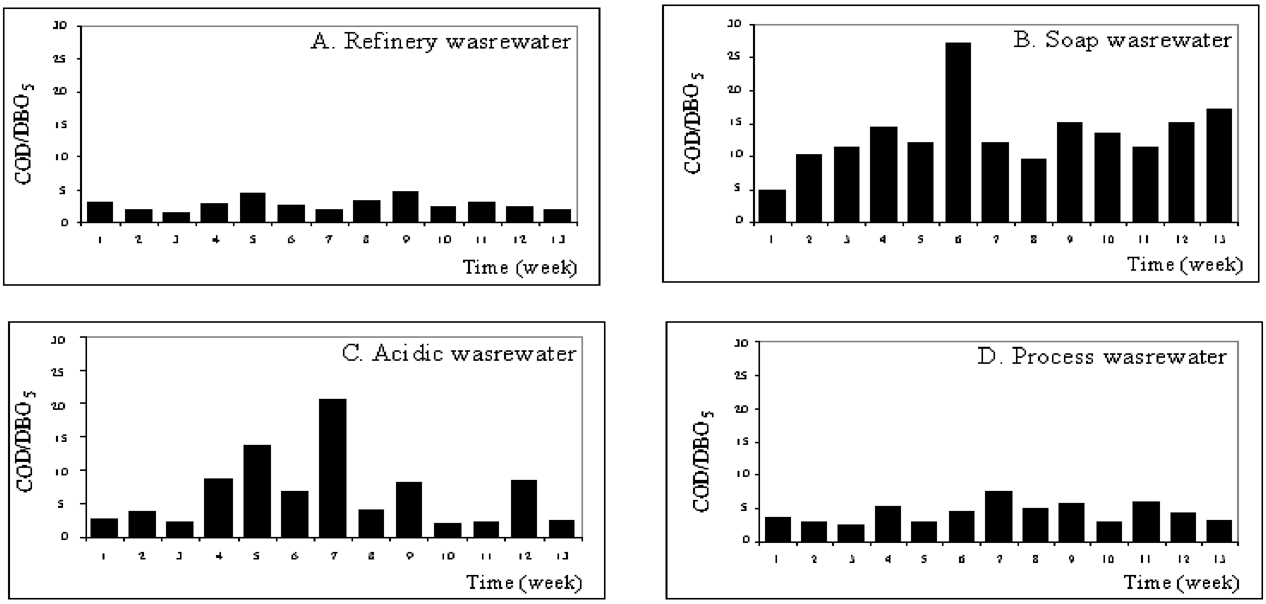

Figure 4: Relative biodegradability of wastewater at sampling station A, B, C and D

COD/BOD5 ratios calculated with mean concentrations are 13.37, 6.61, 4.35 and 2.69 for soap, acidic, refinery and process wastewater, respectively (Fig. 5). COD to BOD ratio reveals the treatability. The wastewater is deemed to undergo a chemical treatment before the routine biological treatment.

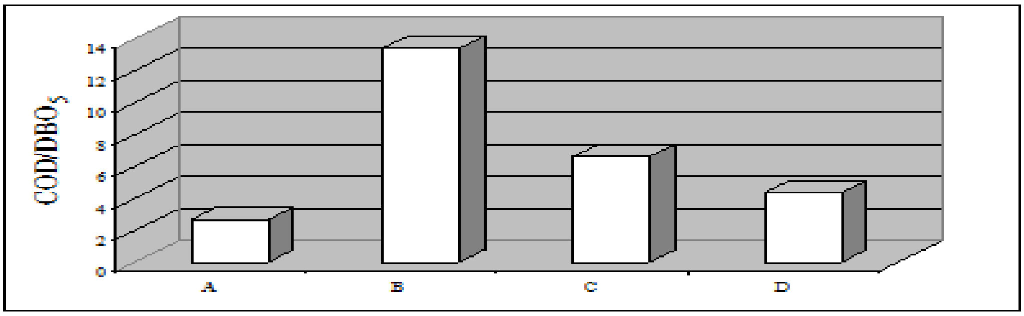

Figure 5: Average COD/BOD5 values at different sampling station (A, B, C, and D)

Other researchers attribute fluctuation in vegetable oil wastewater characteristics to differences in the refined oils and to the operating conditions and processes [24]. Wastewater characteristics are not only influenced by raw materials and products processed, but also by water used in washing procedures during and after the production [25]. These factors apparently influenced the observed variation in the COD/BOD5 values of each wastewater sample. In Fig 4, the COD/BOD5 values for wastewater were high. Therefore, acid wastewater, which is characterized by a high rate of oxidizable substances, fats, fatty acids, sulfates and phosphates as well as low pH values, would be less biodegradable. Wastewater had the highest COD/BOD5 values in soap wastewater, but at refinery wastewater the values were significantly low. The mixture of Acidic and process wastewaters (B+D) constitutes the influent into the wastewater treatment plant. COD/BOD5 of the influent was found to be 12.5, which indicates that most of the organic compounds in the wastewater from vegetable oil refinery industry are not easily biodegradable. The combined wastewaters from these sections of refined vegetable oil are acidic and contaminated with colloidal particles. For the treatment of an effluent by conventional methods such as aerobic or anaerobic digestion the ratio of BOD to COD should be >0.6.

However, an effluent from the vegetable oil industry usually has its BOD/COD ratio around 0.2 which could cause destruction of micro-organisms useful for the biodegradation [26]. Physical and chemical pretreatment are the most commonly used methods for this wastewater [27]. But generally, the most common treatments of the raw VORW are based on physicochemical processes or biological degradation with previous screening and pH-adjusting steps. Physicochemical treatment methods allow reducing dissolved, suspended, and colloidal materials from water through chemical coagulation flocculation followed by gravity settling. These processes can completely eliminate the color, but have the major drawbacks of difficult sludge management and high chemical costs [28, 29]. On the other side, the biological treatment remains the most practical and cheaper process to treat this kind of wastewater. However, biodegradation by conventional activated sludge systems is usually a slow process due to the inhibitory effect of phenols on the microbial metabolism [30]. Other separation and destruction processes such as advanced oxidation process [31-33] and electrochemical treatment [34-36] were proposed as alternative for better treatment of oil wastewater.

Conclusion

Vegetable oil refinery wastewaters are a complex mixture of widely-distributed particle sizes influencing each unit operation of the treatment process. The wastewater varies both in quantity (800 to 1700 $m^3 day^{-1}$) and characteristics from one unit to another. The composition of wastewater from the same unit also varies widely from day to day. These fluctuations may be attributed to different types of oils processed. The elimination of the pollution load is affected by many factors such as the characteristics of the organic matter, the nature and concentration of other components, and the design and operation of the treatment facility. Considerations to be made for the treatment of oily wastes have been outlined. A physico-chemical treatment followed by a biological process should be used to treat the wastewater of oil refinery industry.

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