ENVIRONMENTAL MANAGMENT OF PHARMACEUTICAL WASTES: EXPERIENCE FROM EGYPT

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ABSTRACT

Wastewater management in two companies representing the pharmaceutical industry was investigated and implemented. The results showed that the integration of the pollution prevention approach followed by an equalization tank reduced the organic load up to 70%, while further chemical treatment using either alum or ferric chloride aided with lime produced a quality of effluent suitable for restricted irrigation or safe disposal. In the second case study, the implementation of waste minimization approach followed by the construction and implementation of an equalization tank eliminated the needs for the construction of a full-scale treatment plant. All the proposed solutions were documented with cost benefit analysis and engineering designs for implementation.

Keywords: Pharmaceutical wastewater, pollution prevention, primary treatment, chemial coagulation.

1. INTRODUCTION

Pharmaceutical industry produces hazardous, toxic, and high strength organic liquid wastewater. The most toxic contaminant is antibiotics, analgesic, and anti-inflammatory drugs. The presence of these hazardous wastes can cause serious damage to the environment especially surface water, Stackelberg et. al [1]. Recently pharmaceutically active compounds such as liquid-regulating drugs, analgesics, antibiotics, antiseptics, hormones and chemotherapy and beta blocking heart drugs were detected in wastewaters streams and groundwater resources. Pharmaceutically active compounds are mainly ubiquitous at low concentrations in water bodies that receive sewerage treatment plants effluents. Also, the lake of toxicity, information in drinking water standards give rise to concern over the potential of these compounds to occur in drinking water and thus to affect human health through chronic exposures, Sim &Lee [2]. Therefore, control and treatment of such wastes are of potential concern. Pharmaceutical wastewater can be treated using different techniques. Activated sludge was used for different therapeutic groups with diverse physico-chemical properties, Horden et. al [3]. Pilot-scale membrane bioreactor exhibited enhanced elimination of several pharmaceutical residues poorly removed by the activated sludge systems, Gros et. al [4]. Solar-Photo-Fenton was studied to be used for non-biodegradable drugs. The efficiency of the system was over 95% of which 33% corresponds to the solar photochemical process, Badawy et. al [5]. Advanced oxidation treatment using low pressure UV light coupled with hydrogen peroxide (UV/H2O2) was also evaluated. The removal efficiency varied between no observed removal and 90% depending on the kind of pharmaceutical itself, Rosario et. al [6]. High pressure driven membranes such as nano-filtration membrane and a reverse osmosis membrane are considered to be effective for control and treatment of pharmaceuticals wastewater, Kimura et. al [7].

The enantio selective degradation of pharmaceuticals was evaluated, Sirton et. al [8]. It can be similar under prevailing aerobic and anaerobic conditions. Recently, the antibiotic fermentation wastewater was treated using combined poly ferric sulfate coagulation, Pengxing and Zhisum [9]. Anaerobic treatment of a chemical synthesis based pharmaceutical wastewater in a hybrid up-flow anaerobic sludge blanket (UASB) reactor was taken place lately. The hybrid UASB reactor was found to be more effective at organic loading rate of 8 kg COD/m^3.d with a COD removal efficiency of 72%. It was concluded that this system could be a suitable treatment of chemical synthesis-based pharmaceutical wastewater, Oktem et. al [10]. However, most of the previous stated works were based on laboratory scale for end-of-pipe treatment. Recently, management and in-plant control of industrial wastes is becoming a major concern, Abou-Elela et. al [11]. Due to increasing environmental awareness associated with industrial waste, companies must now incorporate waste management and prevention strategies into industrial process. A wide range of pollution prevention opportunities could be implemented with significant financial advantages for factories, as well as reducing environmental pollution Abou –Elela et. al. [12].
Therefore, the aim of this study is the application of any possible low cost/no cost pollution prevention and/or cleaner production technologies for pharmaceutical wastes prior to simple treatment approaches. The proposed solutions were implemented and documented with engineering design and it can be replicated in similar pharmaceutical industry.

2. MATERIAL AND METHODS

2.1 Industrial Auditing

The two companies under investigation produce tablets, capsules, ointments, dry and liquid syrups and creams. The first company is located at 6th of October industrial city, while the other one located in a highly density residential area in Giza Governorate. Both companies discharge their wastewater, without any treatment, into public sewage net work. Before applying any management system ,industrial auditing of the two facilities was carried out. It was a systematic review of the different manufacturing processes and operating designs to locate the sources of pollution and identify the quality of wastewater. The audit was to monitor the environmentally damaged activities, compliance with legislation, opportunities for reductions ,utilization, waste minimization strategies, effectiveness of existing management controls, potential remediation program and pollution prevention measures with relatively short payback periods.

2.2 Sampling Locations and Waste Characterization

Collection of composite samples, from different manufacturing departments, and the end of-pipe was carried out on hourly basis as well as during the working shifts. All departmental samples as well as treated effluents were subjected to physico-chemical analysis according to APHA (2005).

2. 3 in Plant Control and Treatability Studies

2.3.1 Application of in-Plant Control Measures

The opportunity of the implementation of any possible in-plant control measures was investigated. This included good housekeeping, reduction of wasted material, minimization of organic load and reuse of wastewater. All the proposed solutions were documented by engineering design for implementation.

2.3.2 Primary Treatment

Due to the great variations in the quality and quantity of the end-of-pipe during the three working shifts, design and construction of an equalization tank was recommended as a pre-request for any further treatment.

2.3.3 Post Treatment

After applying the in-plant control measures and implementation of an equalization tank, wastewater was subjected to chemical coagulation using different coagulants namely; alum alone or ferric chloride aided with lime. The pH of the end-of-pipe was raised to 10 with lime then it was decreased to pH 8 using $FeCl_3$ .In case of alum, no pH adjustment was carried out since the initial pH of wastewater was around 6.5. Optimum pH and doses of coagulants were investigated using jar test procedure. Schematic diagrams of the proposed management trains for case studies (1) and (2) are shown in Figures (1-2)

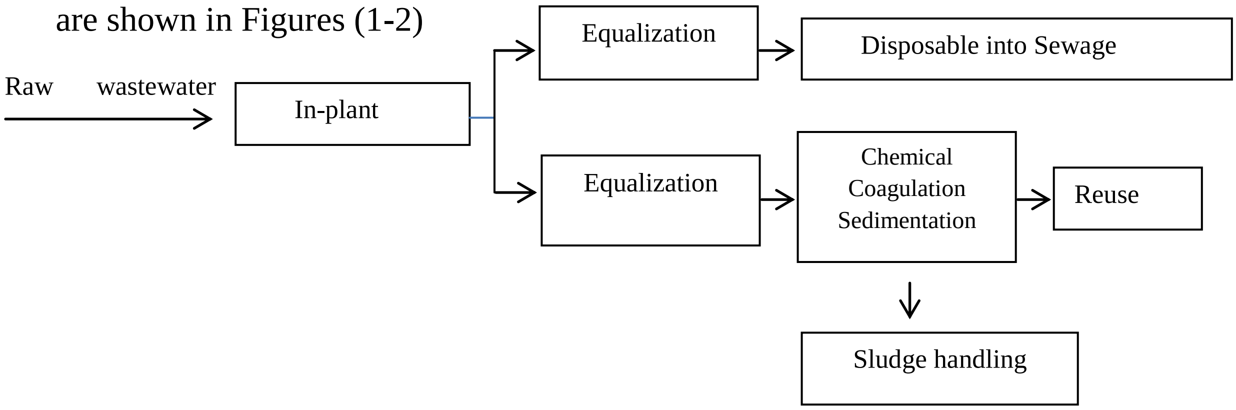

Figure (1): Treatment Train for Case Study (1)

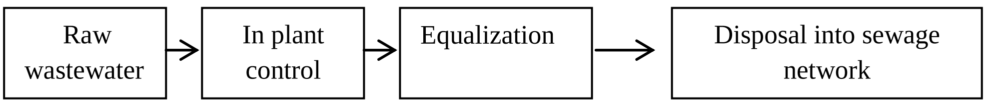

Figure (2): Treatment Train for Case Study (2)

3. RESULTS AND DISCUSSION

3.1Case Study (1)

3.1.1 Characterization of Wastewater

Industrial auditing revealed that the main source of wastewater was due to the wash and cleaning of equipments after each batch in the different manufacturing plants. The results obtained in Figure (3) indicated that the main contamination comes from ointment and syrup department due to the cleaning and washing of reaction vessels, using hot water, and prior to any new batch. Average value of chemical oxygen demand (COD) in washing water reached 35950 mg/l with a corresponding average concentration of oil and grease around 2359 mg/l. However, average results of wastewater analysis from research and development department were complying with the Ministerial Decree for wastewater discharge into public sewage network. In addition, the results showed that the end-of-pipe was violating the regulatory standards for wastewater disposal into public sewage network. The average chemical oxygen demand (COD) and biological oxygen demand (BOD) values were 2450 and 1223 mg/l, respectively.

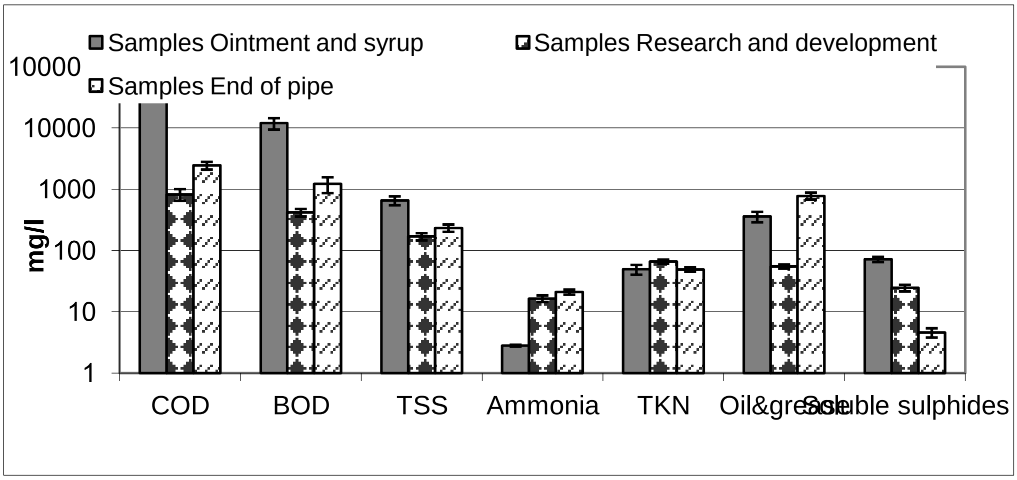

Figure (3): Characteristics of Wastewater from Different Manufacturing Plants during First Shift

3.1.2 Application of in Plant Control Measures

3.1.2.1 Oil and Fat Removal from the Ointment Manufacturing Plant

Departmental analysis showed that the main source of pollution was coming from the ointment department during the cleaning process of equipment and manufacturing tanks. The oil and fat content reached 2359 mg/l. Therefore, manual removal of residual fat in the manufacturing tanks was carried out using paper towels followed by rinsing with hot water. This approach reduced the concentration of oil and grease from 2359 mg/l to 480 mg/l. The contaminated towels were collected and sent off site for safe disposal.

The other source of pollution was the accumulation of fat on the surface of different manholes in the company. Regular cleaning for all manholes in the company was highly recommended. Application of the in plant control measure removed up to 79% of COD, 70% of BOD and 69% of oil and grease in the wastewater from ointment department as shown in Table (1) and Figure (4).

Table (1): Application of in-Plant Control Measures in Ointment Production Plant

Parameters	Units	Before in-plant control	After in-plant control	% Removal
PH		6.5	6.6	
COD	mgO_2/l	35950	7625	79
BOD	mgO_2/l	12000	3633	70
TSS	mg/l	660	488	26
Total settle able solids (10 min)	mg/l	1.6	0.85	47
Total settle able solids (10 min)	mg/l	3.5	0.87	75
Ammonia	mgN/l	2.8	5.8	
TKN	mgN/l	49.3	35	70
T.P	mgP/l	7	2	71
Oil & Grease	mg/l	2359	480	69

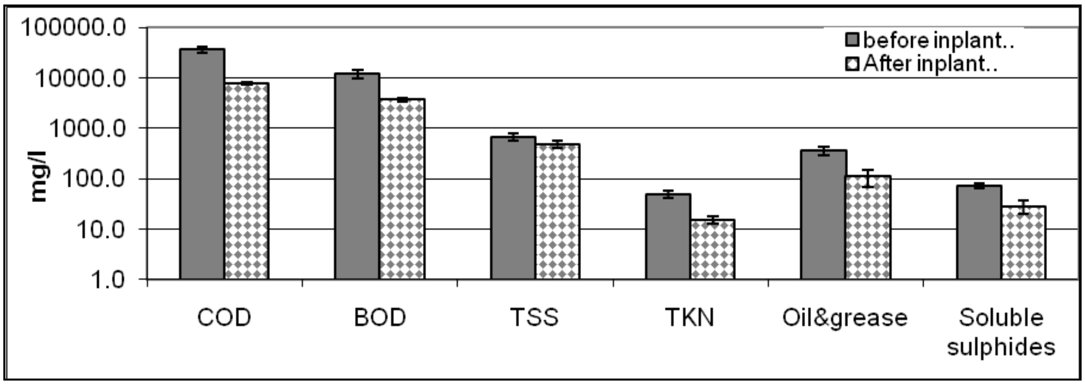

Figure (4): Application of in-Plant Control Measures in Ointment Department

3.1.2.2 Characterizations of Composite Wastewater Samples during the Whole Day

In order to get concrete performance for the quality of the end-of-pipe, composite samples were collected and analyzed during 24 hrs operation .The results obtained in Table (2) indicated that the parameters under consideration namely; COD, BOD, total suspended solids(TSS),total kjeldahl nitrogen(TKN) and total phosphorus(T.P) were complying with wastewater discharge into public sewage network. Corresponding residual average values were 574, 343, 81 and 2.2 mg/l. This indicated the need of an equalization tank.

Table (2): Characteristics of End-of-Pipe during 24 Hours Operation

Parameters	End-of-pipe (24 hours samples)			Ministerial Decree 44/2000
	Min	Max	Average	
pH	**6.3**	**7.2**		**6-9**
COD	**305**	**832**	**573.7**	**1100**
BOD	**280**	**450**	**343.3**	**600**
TSS	**46**	**103**	**81.3**	**800**
Ammonia	**6.7**	**28**	**11.2**	**25**
TKN	**16.3**	**61.5**	**23.7**	**100**
T.P	**0.2**	**4.6**	**1.2**	**25**

3.1.2.3 Equalization

The objective of equalization of flow is to minimize or control fluctuations in wastewater characteristics in order to provide optimum conditions for subsequent treatment processes, also to provide capacity for controlled discharge of wastes to municipal system in order to distribute waste loads more evenly. Therefore, design, construction, and implementation of an equalization tank were carried out. The volume of the tank was 18 $m^3$and the working hours /day was 5hrs.A schematic diagram of the proposed equalization tank is shown in Figure (5) .

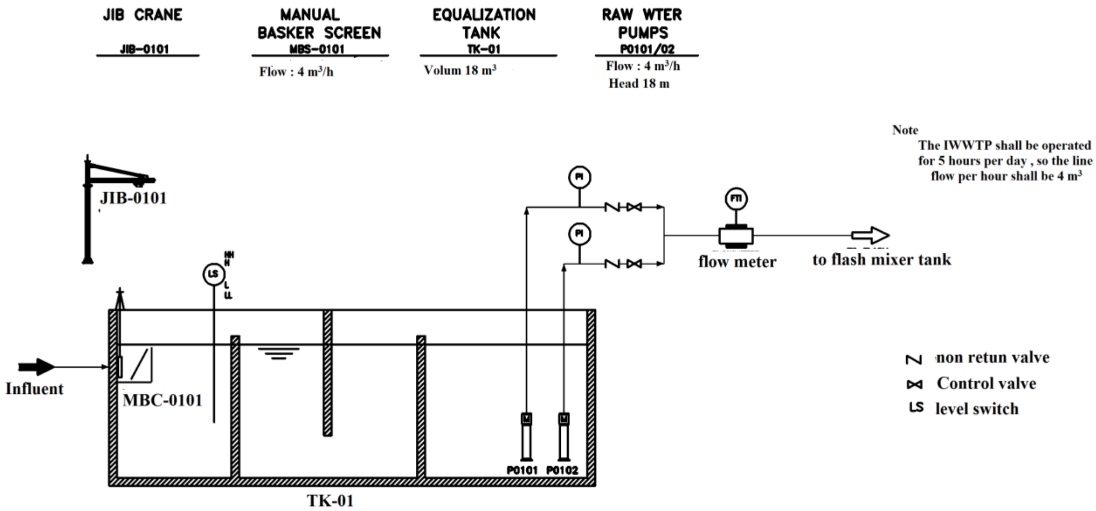

Figure (5): Schematic Diagram of Equalization Tank

3.1.3 Chemical Coagulation-Sedimentation

In order to improve the quality of the end-of-pipe for possible reuse in restricted irrigation within the facility, chemical treatment of the effluent from equalization tank was subjected to chemical treatment, using different coagulants. The coagulants used were ferric chloride aided with lime (Ferrite method), while the second coagulant was alum. The average doses of lime, ferric chloride and alum were 240, 182 and 300 mg/l, respectively. The obtained results are shown in Figure (6). The percentage removal values of COD, BOD, and TSS were 75.4, 74.3, and 96.5, respectively when ferrite method was used. Better removal values were achieved when alum was used. Removal rates of COD, BOD and TSS were 84,94,and 96 %. However, ferric chloride aided with lime was recommended due to the quality of the sludge produced, which was more stable and settled easily compared with the sludge produced from alum. A schematic diagram of the proposed chemical treatment unit is shown in Figure (7)

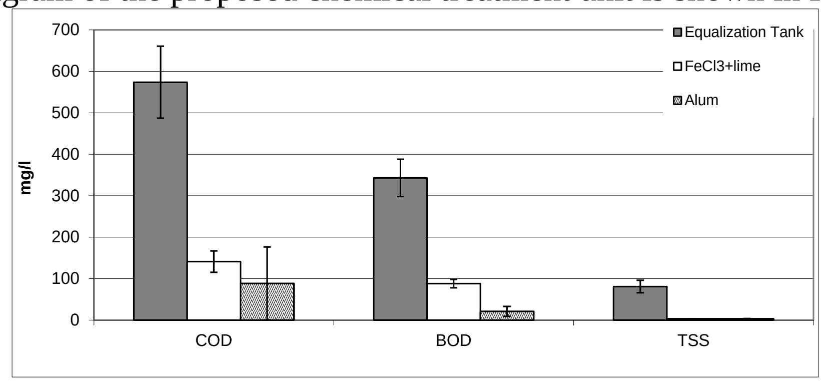

Figure (6): Residual concentration of COD, BOD, and TSS in the Chemically Treated Effluent

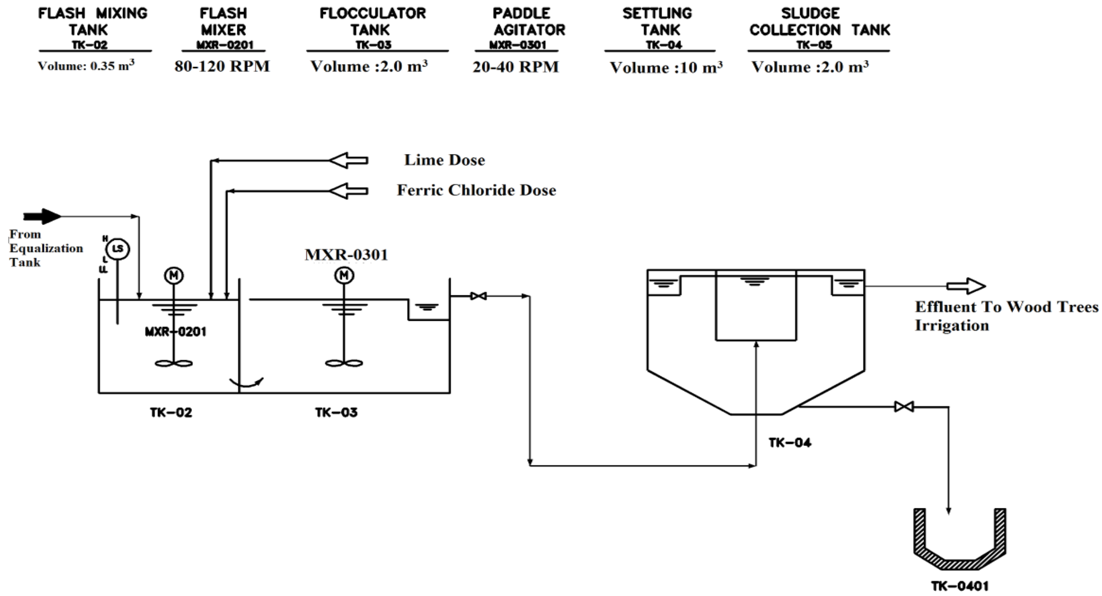

Figure (7) Schematic Diagram of the Chemical Treatment Unit

3.1.4 Overall Efficiency of the Management System for Case Study (1)

Average overall efficiency of the control and treatment of wastewater in the first company is shown in Figure (8). TSS was almost removed, while the COD and BOD percentage removals were 92.3 and 92.8 %, respectively.

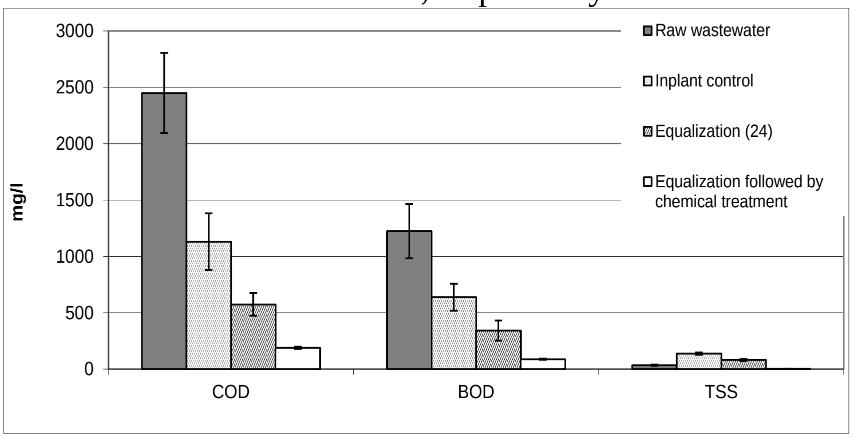

Figure (8): Efficiency of the Proposed Management System

3.2Case Study (2)

This is a very old and huge company located in a highly populated residential area. The number of employees is 3000, distributed in three shifts. Wastewater discharged from the company (500 m^3/day) was highly contaminated with organic matters as presented by COD, BOD and fats.

3.2.1 Sources of Pollution in the Company

From the plant survey, it was found that the main sources of pollution are:

- Maintenance of cars and buses, washing of cars and changing oil in garage.
- Washing of manufacturing equipments and mixing tanks after each batch.

- Floor washing and open circuit cooling water .
- Municipal wastewater.

The results showed that the cream department and the garage are the primary sources of pollution .The concentration of oil & grease and COD reached 2272 mg/l, 9612 mgO_2/l in cream department .In addition it reached 966 mg/l, 4126 mgO_2/l in the garage. Accordingly, it was found necessary to remove fats and grease prior to any further treatment.

3.2.2 Application of Pollution Prevention and in-Plant Control Measures

3.2.2.1 Oil Removal from Garage

Plant survey indicated that bad housekeeping occurred at this site. Great seepage and spill of oil on the floor took place. Moreover, changeable oil was dumped in an open channel connected to an existing on-site payara. In addition, the washing water of cars and buses were contaminated with oil, detergent and suspended solids. These oily wastes reached the final effluent and aggravated the pollution load. Therefore, two approaches for minimizing oil wastewater were carried out.

- First approach: is the elimination of the open channel and collecting the changeable oil in barrels for sale.
- Second approach: Design, construction, and implementation of oil trap chamber within the site as shown in Figure (9). Assembling of floated oil was done at the end of the shift; then the amount collected in barrels 20 liters capacity and sent to the Petroleum Company for re- use.
- Periodical oil & fat removal from the manhole of the end-of-pipe

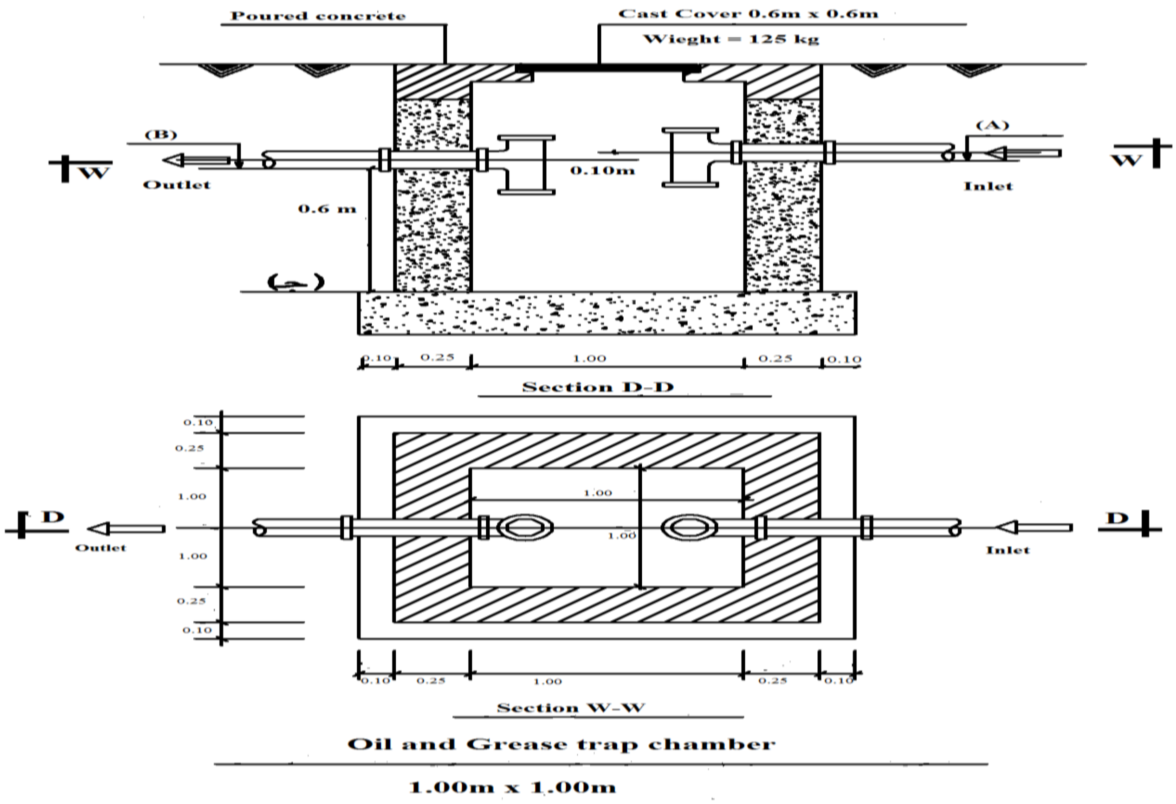

Figure (9) Oil Trap Chamber

These solutions reduced the oil & fat and COD concentrations in the garage site by 97.05%, 98.17% respectively.

3.2.2.2 Minimization of Fat Contamination in Washing Water of Equipments and Reaction vessels of Ointments & Cream

The manufacturing equipments and machines are washed with hot water after each batch. To minimize the fat concentration in washing water, cleaning of residual fat was carried out by using rolls of paper to remove residual ointments then assembled prior to safe disposal in a sanitary landfill. This was followed by hot water cleaning. By implementing this approach the organic load represented by COD and BOD were decreased from 9612, 5382 mgO_2/l to 1063, 606 mgO_2/l, while the concentration of oils and grease reduced from 2272 to 276 mg/l with a percentage removal of 87.85%.

3.2.2.3Control and Safe Disposal of Refused and Expired Medicines

The rejected medicines either liquids or solids were dumped directly to the sewage network which cause sudden chock loads to the sewage network. This problem was overcome by segregation and collection of either liquid or solids rejected medicine in separate tanks. These wastes are currently send to the Egyptian Cement Company, for safe disposal and destruction.

3.2.2.4Equalization

Composite samples collected during the working shifts on hourly basis indicated that the quality of the wastewater varied from hour to hour and even from shift to shift (Figure10).Therefore, it was found necessary to equalize the flow before final discharge. Figure (11) illustrate the engineering design of the proposed model of equalization tank.

3.2.2.5Overall Efficiency of the Management System for Case Study (2)

Application of in-plant control measures followed by equalization tank produced an effluent complying with the National Regulatory Standards and eliminated the needs for construction of a full-scale treatment plant as shown in Table (3).

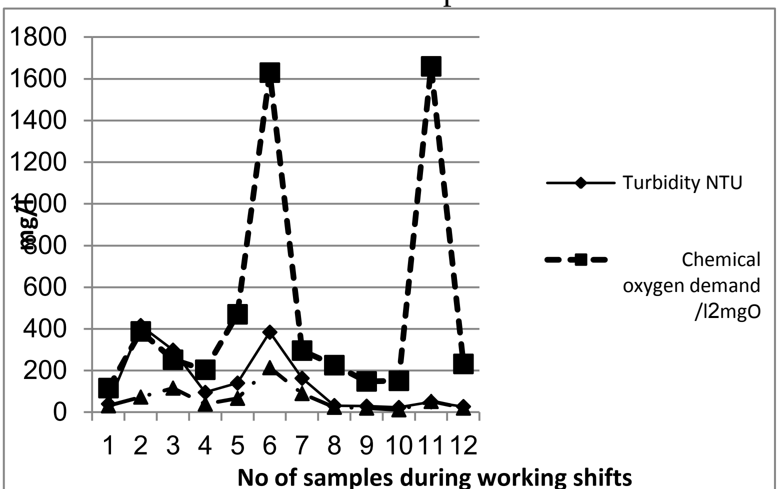

Figure ( ) Variation of COD ,TSS, Turbidity during three working shifts

Figure (10) Variation of COD, TSS, turbidity during three working

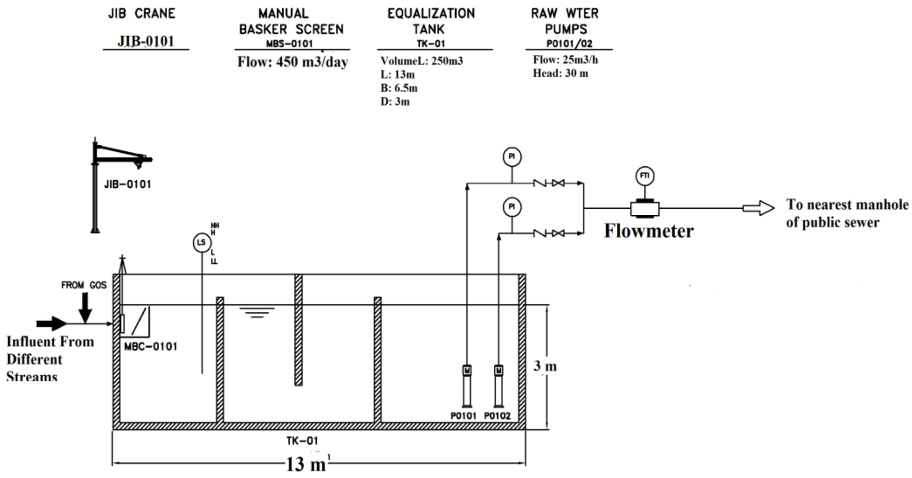

Figure (11) Schematic Diagram of Equalization Tank, Case Study (2)

Table (3) Characterization of Wastewater after Applying Management System

Parameters	Unit	Final Effluent	Ministerial Decree 44/2000
pH- value	--	6.1	6-9
Turbidity	NTU	130	---
Chemical oxygen demand	mgO_2/l	470	1100
Biological oxygen demand	mgO_2/l	205	600
Total Suspended Solids	mg/l	185	800
Oil & grease	mg/l	38	100

4. CONCLUSIONS

Application of in-plant control measures prior to treatability studies reduces the organic load as represented by COD and BOD by 78, 69.7%, respectively. By applying the in-plant control measures followed by the implementation of an equalization tank produced a quality of effluent complying with the National Regulatory Standards for wastewater discharge into public sewage network. Moreover chemical treatment using ferric chloride aided with lime after in-plant control and equalization resulted in an effluent suitable for reuse in restricted irrigation. The removal efficiencies of COD, BOD and TSS reached 98.7% , 92.3 % and 92.8%, respectively.

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