Combining Chemical Treatment and Sand Filtration for the Olive Mill Wastewater Reclamation

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Abstract: Olive oil production is a significant agricultural activity with great economic importance. The growth of the olive oil production in Al-Jouf region in recent years has been accompanied by an increase in the volume of associated processing waste. This work aims to reduce the impact resulted from the discharge of olive mill wastewater (OMW) without treatment. Combination between chemical treatment using ferric chloride aided with lime, Fenton and photo-Fenton with sand filter was carried out. The obtained results indicated that the coagulation sedimentation (using ferric chloride aided with lime) reduced the concentration of organic load represented by COD, BOD and TSS reduced from 117900, 22174 and 15977 to 8965, 5463 and 453 mg/l, respectively. The Fenton and photo-Fenton processes showed efficient removal of organic load than the coagulation sedimentation process. The residual concentration of COD, BOD and TSS was 4563, 2683 and 378 mg/l for Fenton process and 3647, 2167 and 339 mg/l for photo-Fenton, respectively. Sand filter was used for polishing the effluent. The scheme consisting of photo-Fenton followed by sand filtration was found to be much efficient for the treatment of OMW. The residual concentration of COD, BOD and TSS was 1150, 645 and 40 mg/l. respectively. The final effluent could be discharged safely to the sewerage system.

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1. Introduction

Olive mill wastewater (OMW) is produced during the extraction of oil from the olive fruit by the traditional mill and press process. OMW has a wide range of characteristics depending on the type of the mill and the type of olive and equipment employed. Most of the mills are 3-phase extraction process. However, some of the newer ones use the 2-phase extraction process [1]. The olive itself consists of pulp (75-85% weight), nut (13-23% weight) and seed (2-3% weight). Typically, the weight composition of OMW is 80-96% water, 3.5-15% organics, and 0.5-2% mineral salts [2].

OMW is characterized by its black brownish color that is considered undesirable property. Another negative impact of this wastewater is its extremely high content of organic compounds, which is reflected by the high values of COD and TOC, most of which are refractory or toxic to micro-organisms. Mean concentration values of COD and BOD are 139,575.0 and 83,780.3 (mg/l). The COD/BOD ratio ranges from 2.1:1to 4.4:1 with an average value of 2.7:1, which indicates the presence of poor biodegradable organic compounds and/or toxic once [3-5].

Deterioration of natural water bodies due to OMW is a serious problem. It affects the soil quality, toxic to plants and soil micro flora when disposed into the soil. Therefore, direct discharge of olive mill wastewater into receiving media is not permissible and certain measures must be taken before disposal of the OMW into the environment [3.4,6].

El-Gohary *et al.,* [3] examined the use of an integrated treatment system consisting of wet hydrogen peroxide catalytic oxidation (WHPCO) followed by two-stage upflow anaerobic sludge blanket (UASB) reactor (10 l each) for the treatment of OMW. The diluted wastewater (1:1) was pre-treated using Fenton's reaction. Optimum operating conditions namely, pH, H_2O_2 dose, Fe^{+2}, COD:H_2O_2 ratio and Fe^{+2}:H_2O_2 ratio were determined. The UASB reactor was fed continuously with the pre-treated wastewater. The hydraulic retention time was kept constant at 48 hrs (24 hrs for each stage). The results indicated a good quality final effluent. Residual concentrations of individual organic compounds ranged from 0.432 mg/l for p-hydroxy-benzaldhyde to 3.273mg/l for cinnamic acid.

El-Gohary *et al.,* [4] studied the treatment of catalytically oxidized OMW with continuous anaerobic treatment using two treatment schemes.

The 1st step in both schemes was an UASB reactor (20 l). The 2nd step was either a hybrid UASB reactor or a classical one (10 l, each). The 1st stage was operated at constant hydraulic retention time (HRT) of 24 h. The organic loading rate (OLR) varied from 3.4 to 4.8 kg COD/m^3 d depending on the quality of the pretreated wastewater. The results obtained indicated that, the 1st step UASB reactor achieved a COD percentage removal value of 53.9%. Corresponding total BOD and TSS removal were 51.5% and 68.3%, respectively. It was noted that the hybrid UASB reactor as a 2nd step produced better quality effluent as compared to the classical one. This could be attributed to the presence of the packing curtain sponge with active biomass in the sedimentation part of hybrid UASB reactor which minimizes suspended solids washout, consequently enhancement of the efficiency of the reactor. The combination of two stage system consisting of a classical and a hybrid UASB reactor operated at a total HRT of 48 h and OLR of 2.0 kg COD/m^3.d provided a good quality effluent.

In an attempt to reduce the environmental impact resulted from OMW, treatment is of utmost important. Combination of chemical followed by physical treatment techniques is the main objective of this study.

2. Materials and Methods

Field trips were carried out for collecting OMW. Samples were collected to study the physico-chemical characteristics of the OMW. The efficiency of some coagulants such as ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4$), lime (CaO) as well as some methods of chemical oxidation for the treatment of OMW. Chemical oxidation will be carried out using advanced (Fenton and photo-Fenton) oxidation.

The physico-chemical analysis will cover: pH, chemical oxygen demand (COD) biological oxygen demand (BOD), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and TSS.

The analyses were carried out according to the American Public Health Association for Examination of Water and Wastewater [7]. Statistical analyses were carried out using Microsoft Excel 2003.

Treatment steps

Three treatment approaches were investigated. The 1st approach is the pre-treatment of wastewater using chemical coagulation-sedimentation, the 2nd treatment approach was direct catalytic oxidation and the 3rd treatment approach was photocatalytic oxidation. The secondary treatment step was sand filtration technique. The treatment train is described in the following schematic diagram (Figure 1).

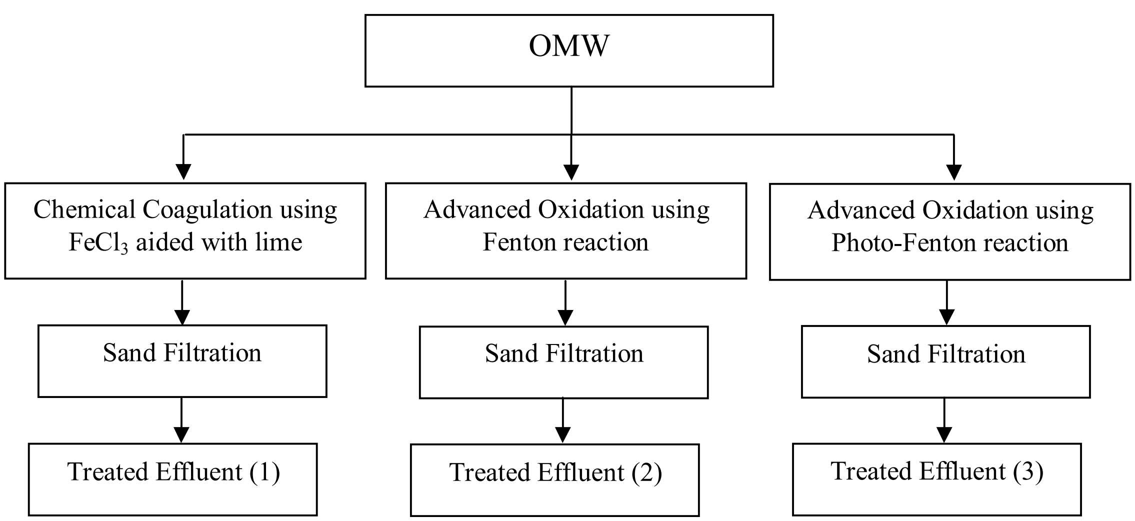

Figure 1: Schematic diagram of the two treatment approaches

Coagulation-sedimentation

Different doses of coagulant were applied for the treatment of OMW. Also, different contact time of the coagulant was studied. Bench scale chemical coagulation process was carried out using Jar test procedure. $FeCl_3$ aided with lime was chosen as an efficient coagulant for this type of wastewater. The pH was raised to 11.5 with lime followed by addition of $FeCl_3$ to pH 8.5. Flash mix (200 rpm) for 2 minutes was carried out after which slow mixing was applied (40 rpm) for 15 minutes. The resulting flocs were allowed to settle for one hour.

Catalytic oxidation

The optimum operating conditions for advanced oxidation (Fenton) processes was selected according to El-Gohary *et al.,* [4]. Fenton's reaction was carried out at room temperature by adding various doses of

$FeSO_4$ at the predetermined optimum pH value (3.0±0.2). The required amount of H_2O_2 was fed under continuous stirring for a period of 120 min. To complete the reaction, stirring was continued for another 120 min. This step was followed by the addition of lime to raise the pH to 10. Lime was added under continuous stirring for 5 min at 100 rpm, this was followed by 20 min of slow mixing (30–40 rpm) and 60 min of settling. The supernatant was withdrawn for the second step treatment.

Photo-Fenton oxidation

$FeSO_4/UV/H_2O_2$ process is used to oxidize the high organic content present in the raw wastewater as well as the pre-treated effluent using coagulation-sedimentation. The optimum operating conditions which produce the best oxidation, such as the doses of $FeSO_4$, H_2O_2 and contact time were previously investigated by El-Gohary *et al.,* [4] (as described in the previous section). The reaction vessel used was a glass vessel with a volume of 1000 ml. The samples were subjected to UV source using medium pressure mercury lamp acted as a UV source generating output between 320 – 400 nm. This lamp was located above the reaction vessel. Hydrogen peroxide was used as an oxidant aided with activated TiO_2 as a catalyst. The reaction media was stirred using magnetic stirrer to ensure good mixing of the reactants.

The optimum operating conditions (for Fenton and photo-Fenton oxidations) Table 1 summarizes the optimum operating conditions. All the experiments were carried out in a bench scale batch mode.

Table 1: Operating conditions for catalytic as well as photocatalytic oxidation

Parameter	Value
pH	3.0 (±0.1)
Fe^{2+}:H_2O_2	1:50
COD: H_2O_2	1:3.3

Sand filter

The dimensions of the sand filter unit are shown in Figure 2. The media used throughout the study was pea gravel (1-2 ml). The flow rate was 0.5 liter/min.

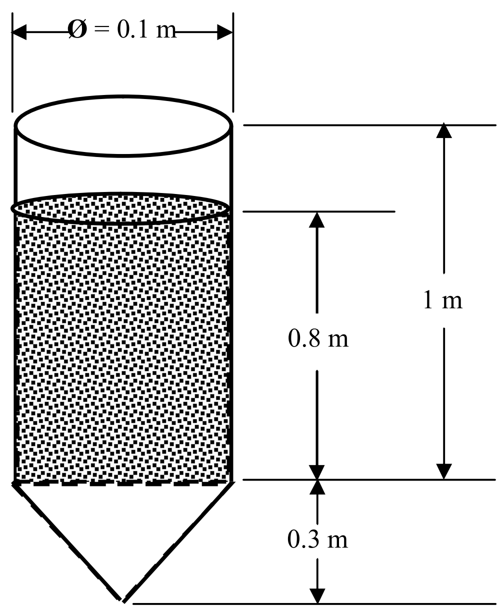

Figure 2: Dimensions of the sand filter unit

Table 2: Operating conditions for column experiment

Parameters	Unit	Coagulation-sedimentation	Catalytic oxidation	Photo-catalytic oxidation
Surface area (SA)	m^2	0.27	0.27	0.27
Volume (liter)	m^3	0.1256	0.1256	0.1256
Hydraulic surface loading rate (HSLR)	$l/m^2/h$	9.3	9.3	9.3
Organic surface loading rate (OSLR)	$gBOD/m^2/h$ $gCOD/m^2/h$	328 538	161 274	130 219
Flow rate	m^3/day	0.22	0.22	0.22

3. Results and Discussion

The obtained results indicated that OMW under investigation is characterized by its extremely high content of organic compounds, which is reflected by the high values of BOD, COD and TOC. During the study period, the COD, BOD and TOC values, ranged from 103934 to 199800 mgO_2/l, from 31098 to 65035 and from 28765 to 51987 mgO_2/l, respectively. The BOD/COD ratio ranges from 0.22 to 0.54 with an average value of 0.4, which indicates the presence of poor biodegradable organic compounds and/or toxic ones [5]. Total suspended solids concentrations ranged from 14463 to 19433 mg/l most of which are colloidal in nature making its settleability very difficult. Variation in physico-chemical characteristics of OMW is presented in Table 3.

Application of biological treatment requires dilution of OMW more than 70 times in order to keep the concentration of toxic compounds at a biologically tolerable level for anaerobic treatment [8,9]. Consequently, Chemical treatment is an essential possible solution to reduce the toxicity hence increases the biodegradability of OMW [4].

Table 3: Characteristics of OMW*

Parameter	Minimum	Maximum	Average
pH	3.6	5.66	
COD	103934	199800	117900 (±26099)
BOD	31098	65035	22174 (±9564)
TOC	28765	51987	39445 (±10716)
TKN	456	642	532 (±54)
TP	120	151	130 (±10)
TSS	14463	19433	15977 (±6451)
TR	42526	56473	48264 (±4761)
Oil and Greases	2341	3657	2860 (±1276)

*Average of 19 samples

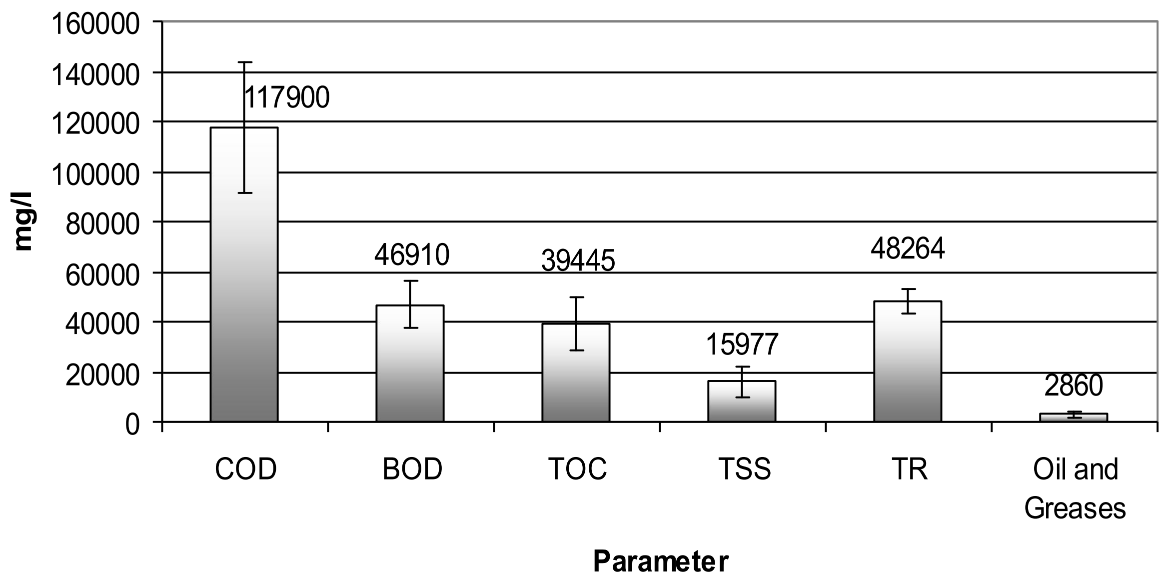

Figure 3: Characteristics of OMW

Coagulation-sedimentation:

Chemical coagulation-sedimentation process followed by sand filter for the treatment of OMW.

Table 4 shows the performance of the combined.

Table 4: Efficiency of coagulation-sedimentation process

Parameter	Unit	OMW*	Coagulation-sedimentation**	%R
pH	-	4.97	8.32	
COD	mgO_2/l	117900 (±26099)	8965 (±2345)	92.4
BOD	mgO_2/l	22174 (±9564)	5463 (±1938)	88.4
TOC	mgC/l	39445 (±10716)	2341 (±867)	94.1
TKN	mgN/l	532 (±54)	120 (±32)	77.4
TP	mgP/l	130 (±10)	8 (±3)	93.9
TSS	mg/l	15977 (±6451)	453 (±198)	97.2
TR	mg/l	48264 (±4761)	4536 (±2121)	90.6
Oil and Greases	mg/l	2860 (±1276)	34 (±18)	98.8

The level of COD, BOD and TSS was reduced from 117900 to 8965, 46910 to 5463 and 15977 to 453 mg/l, with removal efficiency of 92.4, 88.4 and 97.2%, respectively. The removal of COD was found to be higher than the removal of BOD. This may be attributed to presence of phenolic compounds which inhibit the biodegradation of organic compounds in OMW. The removal of phenolic compounds during the chemical treatment of OMW enhances the biodegradability of the chemically treated effluent [4-10]. The removal of organic materials (COD and BOD) is due to lime precipitation. Therefore, lime is a safe substance for organic stabilization because nothing is oxidized and no dangerous compounds are formed [11]. The phosphorus content was highly affected by the chemical treatment process, the removal of TP was found to be 93.4% while, the removal of TKN didn't exceed 71%. The residual level of TP and TKN was 8 and 120 mg/l, respectively. The lime treatment of OMW increased the pH from 4.97 until 12. This treatment volatilizes the nitrogen and precipitates the phosphorous along with other suspended and dissolved solids. After the lime treatment the effluent should be re-carbonated with Ferric chloride to precipitate out the excess lime and lower the pH to about 8 [12].

Fenton Oxidation:

Fenton oxidation reaction was used for the treatment of OMW. Table 3 shows the performance of Fenton oxidation reaction for the treatment of OMW. The level organic load represented by COD, BOD and TSS was reduced 96, 94 and 98% with residual concentration of 4563, 2683 and 378 mg/l, respectively. The nutrient level namely, TP and TKN was reduced from 130 and 532 mg/l to 6 and 68 mg/l with removal of 95 and 87%, respectively.

Table 5: Efficiency of Fenton oxidation process

Parameter	Unit	OMW*	Fenton Oxidation**	%R
pH	-	4.97	7.21	
COD	mgO_2/l	117900 (±26099)	4563 (±1999)	96
BOD	mgO_2/l	22174 (±9564)	2683 (±665)	94
TOC	mgC/l	39445 (±10716)	1435 (±564)	96
TKN	mgN/l	532 (±54)	68 (±24)	87
TP	mgP/l	130 (±10)	6 (±3)	95
TSS	mg/l	15977 (±6451)	378 (±119)	98
TR	mg/l	48264 (±4761)	3564 (±2100)	93
Oil and Greases	mg/l	2860 (±1276)	24 (±15)	99

*Average of 19 samples, ** average of 5 samples

Photo-Fenton Oxidation:

In an attempt to enhance the efficiency of Fenton oxidation reaction the use of UV light was done. Figure 4 shows the characteristics of the photo-Fenton oxidation process. The level of COD, BOD, TOC and TSS was reduced form 117900, 46910, 39445 and 15977 to 3647, 2167, 1243 and 339 mg/l, respectively.

Table 6: Efficiency of photo-Fenton oxidation process

Parameter	Unit	OMW*	Photo-Fenton Oxidation**	%R
pH	-	4.97	7.10	
COD	mgO_2/l	117900 (±26099)	3647 (±1675)	97
BOD	mgO_2/l	22174 (±9564)	2167 (±653)	95
TOC	mgC/l	39445 (±10716)	1243 (±521)	97
TKN	mgN/l	532 (±54)	59 (±21)	89
TP	mgP/l	130 (±10)	6 (±3)	96
TSS	mg/l	15977 (±6451)	339 (±111)	98
TR	mg/l	48264 (±4761)	3254 (±2024)	80
Oil and Greases	mg/l	2860 (±1276)	20 (±14)	100

*Average of 19 samples, ** average of 5 samples

The results presented in Tables 5, 6 show that the quality of the treated effluent is quite satisfactory. Sarria *et al.,* [13] showed that treatment of OMW with activated carbon increased the BOD/COD ratio from 0.3 to 0.53 in the effluent produced after Fenton reaction. Consequently, the BOD/COD ratio enhanced and is enhanced greatly to be comparable with the ratio of domestic wastewater, which ranges from 0.5 to 0.7 [14-16]. Hence, the Fenton reaction appears to be useful for reducing toxic compounds consequently increases the biodegradability of OMW. However, the Fenton reaction efficiency reached more than 90% (corresponding to COD) the level of organic load (COD and BOD) was found to be very high. Therefore, a post treatment step was required.

Sand filter

The effluents from coagulation-sedimentation, Fenton and photo-Fenton reaction process still contain considerable level of organic loads. Sand filter was used as a post treatment for these effluents. Table 7 and Figures 4, 5 summarize the efficiency of sand filter. Sand filter removes 76, 80 86 and 88% of COD, BOD, Toc and TSS, with residual concentration of 2134, 1089, 324 and 56 mg/l, respectively.

Table 7: Efficiency of sand filter for the treatment of coagulation-sedimentation treated effluent

Parameter	Unit	Coagulation-sedimentation*	Sand filter*	%R
pH	-	8.32	8.3	
COD	mgO_2/l	8965 (±2345)	2134 (±768)	76
BOD	mgO_2/l	5463 (±1938)	1098 (±213)	80
TOC	mgC/l	2341 (±867)	324 (±100)	86
TKN	mgN/l	120 (±32)	71 (±23)	41
TP	mgP/l	8 (±3)	4.5 (±1)	44
TSS	mg/l	453 (±198)	56 (±15)	88
TR	mg/l	4536 (±2121)	1893 (±958)	58
Oil and Greases	mg/l	34 (±18)	25 (±10)	27

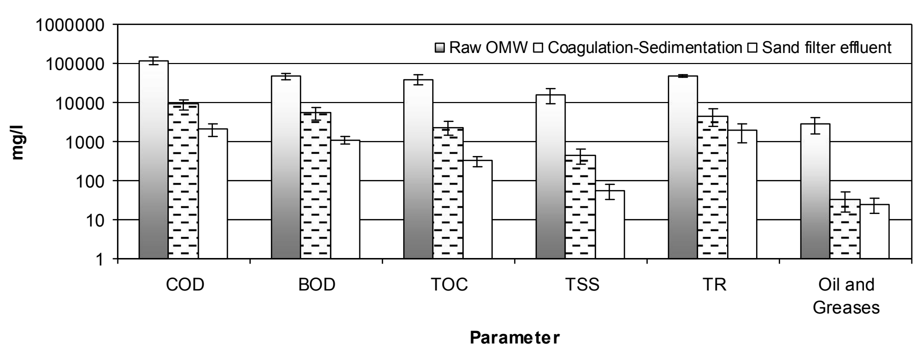

Figure 4: Efficiency of combined coagulation sedimentation and sand filter for the removal of COD, BOD, TOC, TSS, TR and oil and grease from OMW

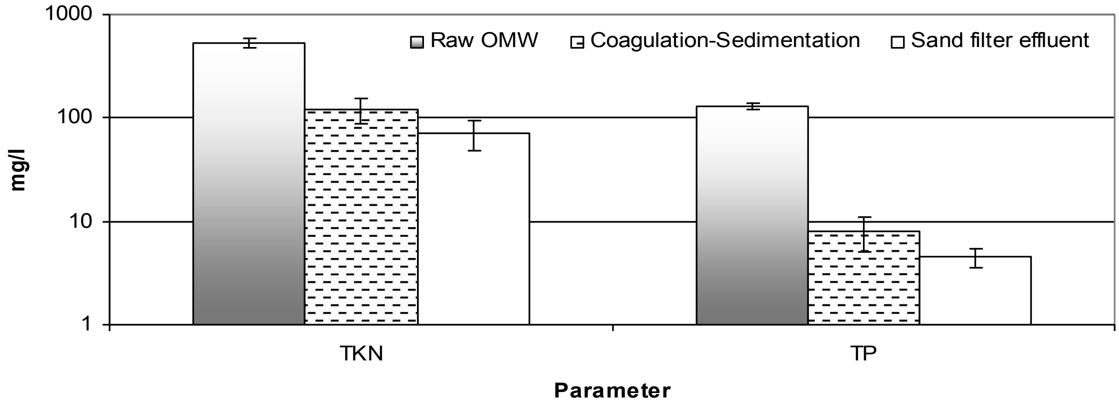

Figure 5: Efficiency of combined coagulation sedimentation and sand filter for the removal of nutrients (TP and TKN) from OMW

Table 8 and Figures 6 and 7 show the performance of the combined Fenton reaction and sand filter for the treatment of OMW. The level of COD, BOD, TOC and TSS was reduced by 69, 75, 83 and 88%, with residual concentration of 1435, 675, 243 and 44mh/l, respectively.

Table 8: Efficiency of sand filter for the treatment of Fenton oxidation treated effluent

Parameter	Unit	Fenton Oxidation*	Sand filter*	%R
pH	-	7.21	7.17	
COD	mgO_2/l	4563 (±1999)	1435 (±125)	69
BOD	mgO_2/l	2683 (±665)	675 (±98)	75
TOC	mgC/l	1435 (±564)	243 (±78)	83
TKN	mgN/l	68 (±24)	50 (±20)	26
TP	mgP/l	6 (±3)	4 (±1)	38
TSS	mg/l	378 (±119)	44 (±17)	88
TR	mg/l	3564 (±2100)	2435 (±758)	32
Oil and Greases	mg/l	24 (±15)	17 (±6)	29

*Average of 5 samples

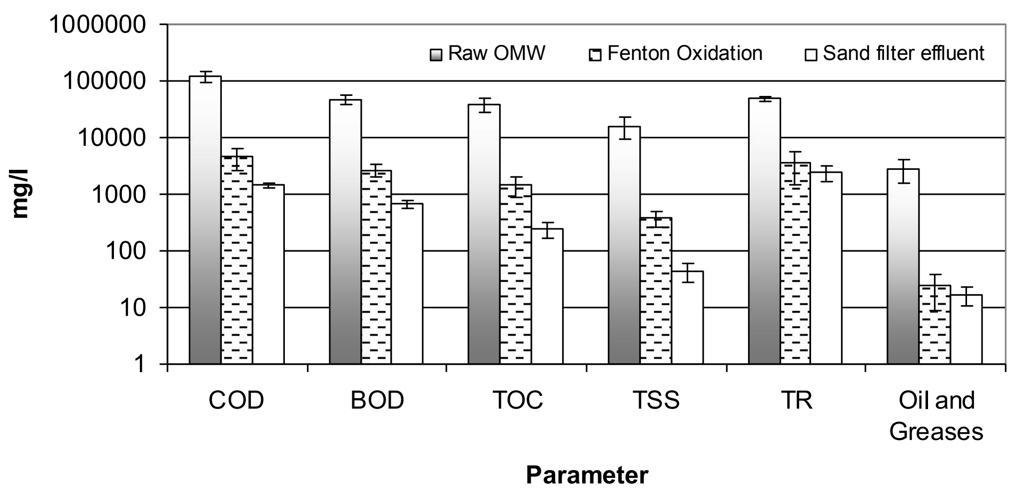

Figure 6: Efficiency of Fenton oxidation and sand filter for the treatment of OMW

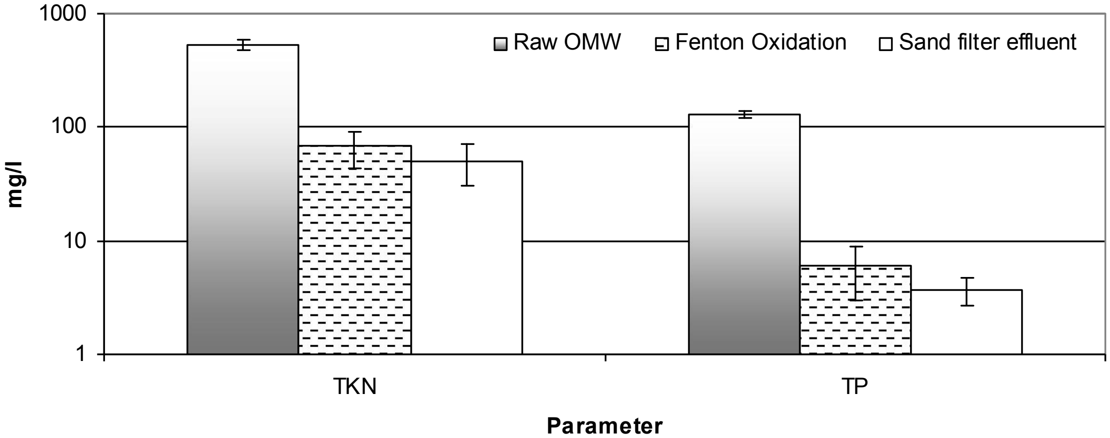

Figure 7: Efficiency of combined Fenton Oxidation and sand filter for the removal of nutrients (TP and TKN) from OMW

In an attempt to enhance the performance of Fenton reaction the use of photo energy was combined with the reaction. Table 9 and Figures 8 and 9 show the efficiency of the photo-Fenton reaction. The organic load represented by COD, BOD, TOC and TSS was reduced from 8965, 5463, 2341 and 453 to 1150, 645, 215 and 40 mg/l, respectively.

Table 9: Efficiency of sand filter for the treatment of photo-Fenton oxidation treated effluent

Parameter	Unit	Photo-Fenton Oxidation*	Sand filter*	%R
pH	-	7.10	7.04	
COD	mgO_2/l	3647 (±1675)	1150 (±122)	68
BOD	mgO_2/l	2167 (±653)	645 (±100)	70
TOC	mgC/l	1243 (±521)	215 (±71)	83
TKN	mgN/l	59 (±21)	45 (±17)	24
TP	mgP/l	6 (±3)	4 (±1)	35
TSS	mg/l	339 (±111)	40 (±15)	88
TR	mg/l	3254 (±2024)	2353 (±123)	28
Oil and Greases	mg/l	20 (±14)	15 (±6)	25

*Average of 5 samples

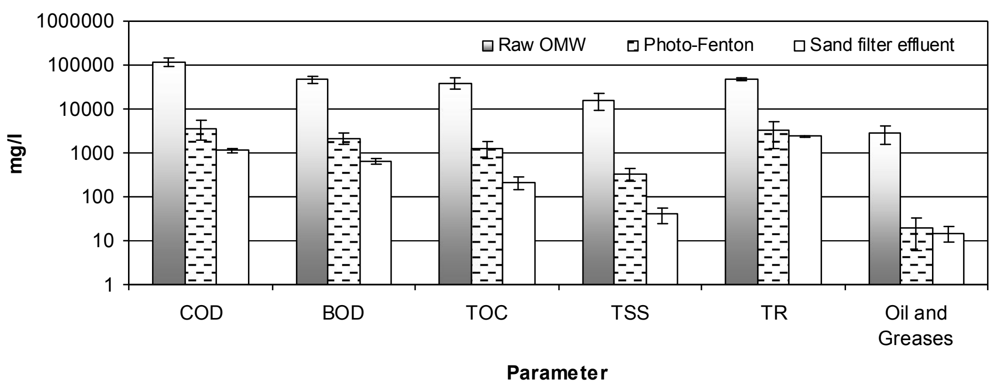

Figure 8: Efficiency of combined photo-Fenton oxidation and sand filter for the treatment of OMW

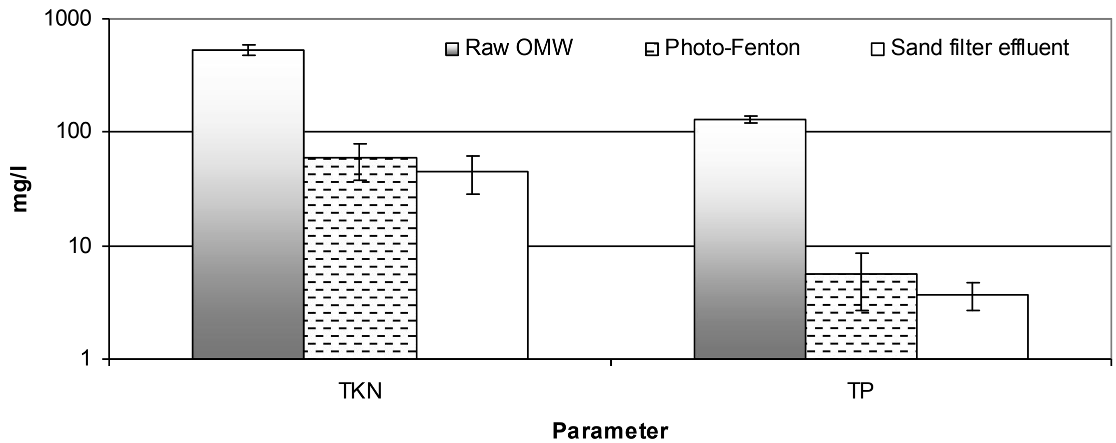

Figure 9: Efficiency of combined photo-Fenton oxidation and sand filter for the removal of nutrients (TP and TKN) from OMW

The concentration of COD and BOD was found to be similar to that concentration in high strength sewage water. Consequently, for safe discharge of the treated effluent from the above mentioned processes, it could be mixed with raw sewage and treated in wastewater treatment plant. Achak *et al.,* [15] examined the performance of a sand filter in treating OMW effluents after dilution with domestic wastewater on a one-to-one basis. The experimental pilot consisted of a column of opaque PVC, and the sand filter was filled with 50 cm of sand and 10 cm of gravel in the top and the bottom of the filter. The percolation of the diluted OMW through the sand filters caused 90% removal of total suspended solids. The sand filter treatment also led to important reductions in organic matter (90% of total COD, 83% of dissolved COD and 92% of phenolic compounds) and nutrients (91% of TKN and 99% of phosphates).

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