

Effect of Pretreatment on the Enhancement of Biodegradation of Olive Mill Effluent for Treatment in an Anaerobic Cross-Flow Filter Reactor

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In this study, various chemical and advanced oxidation processes were tested for enhancement of anaerobic biodegradation of olive mill effluent (OME). The experiments were carried out in a 20 L lab-scale ACF reactor packed with cross-flow filter material made of water-resistant cardboard with a specific surface area of $\sim 300 \text{ m}^2 \text{ m}^{-3}$. The ACF reactor was operated at chosen OLR conditions and fed with different pre-treated OME samples for 240 days (717 days in total). All pretreatment options used in this study improved the anaerobic biological degradation in terms of COD, phenolics and color removal efficiencies. Best effluent quality ($5700 \pm 250 \text{ mg COD per liter}$) was obtained by using the Fenton process as a pre-treatment. This effluent value is still higher than the official discharge limit for COD ($4000 \text{ mg COD per liter}$) in Turkey. Therefore, additional final treatment (e.g. membrane filtration) may be required before discharging into the sewer line.

Key words:

Olive mill effluent, up-flow anaerobic cross-flow filter, organic loading rate, chemical pre-treatment, AOPs

Introduction

In the Mediterranean countries, olive oil production is considered one of the oldest agricultural industries. It is the main olive oil production region in the world.¹ Although olive oil production is a highly significant activity for the economies of the Mediterranean countries, the process waste generates two types of pollutants, namely olive mill cake and olive mill effluent.^{2,3}

The discharging method of OME has been a very important concern for many researchers for the last few years.⁴ Physicochemical processes have been applied to OME treatment, such as flocculation,⁵ coagulation, filtration, integrated centrifugation-ultrafiltration, electrochemical oxidation,⁶ sedimentation^{7,8} and combined physicochemical process.⁹ Biological treatment combined with chemical and physical processes is an effective way of reducing OME's polluting characteristics. These processes suffer serious drawbacks such as high cost, low efficiency and sludge disposal problems. Therefore, research efforts have been directed towards the development of efficient treatment, like technologies including various advanced oxidation technologies and biological processes. Anaerobic digestion is usually the basic biological process for OME treatment since it has many advantages com-

pared to aerobic treatment. The advantages of anaerobic digestion include low levels of biological sludge, high efficiency and the production of methane, which can be used as an energy source for on site heating and electricity.¹⁰ Chemical pre-treatment methods namely Al_2SO_4 , FeCl_3 and FeSO_4 can also be used for the removal of organic matter by coagulation and flocculation techniques.^{11,12}

AOPs such as Fenton's reagent, ozone, UV, UV/ H_2O_2 , UV/Fenton and ultrasound based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to their high oxidant power. These hydroxyl radicals have a strong oxidation potential that can achieve two alternative goals: the reduction of COD content up to the desired maximum allowable concentration values through the mineralization of the recalcitrant pollutants, and the enhancement of biodegradability of treated effluents with the aim of making their subsequent biological treatments possible.¹³

Pretreatment significantly enhances the biodegradability of OME, which would be much lower if it were digested alone (without pretreatment). Over 80 % increase in biogas production was obtained when digesting OME after chemical pretreatment. The best results for enhancing the biodegradability and biogas production was taken by pre-treatment with Al_2SO_4 .^{14,15}

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Among the high-rate anaerobic processes developed in recent years, anaerobic filter reactors using various packing materials were studied for the treatment of a wide variety of wastewater including olive mill effluent.^{16,17}

Anaerobic filters are known to provide quick start-up and to be more stable during the shock organic loadings; additional advantages of fixed film over contact fermenters include the elimination of mechanical mixing and sludge settling and return. Therefore, it is of practical interest to investigate the effect of various operational parameters such as organic loading rate (OLR), hydraulic retention time (HRT) and the influent chemical oxygen demand (COD) on the performance of the cross-flow filter reactor.

In this study, in contrast to the literature reports in which were evaluated significantly diluted OME as generally employed and limited range of operational parameters, OME effluent was studied on the basis of not only COD effluent quality but other variables such as effluent volatile fatty acids, effluent suspended solids, total phenol, color, pH in details under a wide range of OLR loading conditions. The comparison of the effects of different pre-treatment methods were also studied at chosen best OLR condition.

Materials and methods

Characterization of OME

The OME studied was obtained from a local olive oil production plant located in Izmir-Turkey, which involves a three-phase olive oil extraction process with a maximum daily olive processing capacity of 60 t. The samples were taken in January and stored in a cold room at +4 °C until used. The physical-chemical and biological characteristics of the OME used in this study are given in Table 1.

Table 1 – Physical and chemical properties of OME

Parameters	Value
COD (g COD L ⁻¹)	82~110
SS (mg L ⁻¹)	1,700~2,200
Total phenols (mg L ⁻¹)	3,100~4,025
Color (Abs _{@800nm})	0.830~2.520
pH	4.9~5.4
Oil-grease (mg L ⁻¹)	400~770
Total volatile fatty acids (VFAs) (mg L ⁻¹)	1,750

Characterization of sludge

Anaerobic Cross-Flow Filter (ACF) bioreactor was initially inoculated with a granular biomass from the anaerobic digester of a local brewery plant located in Izmir, Turkey. The bioreactor volume occupied by the inoculum was 2 L, with a solid concentration of 50 g VSS L⁻¹.¹⁸

Feeding and nutrient supplementation

The COD/N/P ratio was adjusted to 500/5/1 by using NH₄Cl and (NH₄)₂HPO₄ as N and P sources. The micronutrient solution was as follows; (concentrations of the constituents are given in parentheses as mg L⁻¹): CaCl₂ (50), Fe (10) as FeCl₂, Co (1) as CoCl₂, Ni (1) as NiCl₂, yeast extract (30). Throughout the experiments, 3 g L⁻¹ of NaHCO₃ was added to the influent wastewater in order to adjust the alkalinity and pH.¹⁸

Pretreatment of OME

OME was pretreated by six different physico-chemical and advanced oxidation processes (AOP) to reduce COD and phenolic compound amounts. These were:

- 6 g L⁻¹ Al₂(SO₄)₃ was used and 40 % ±5 of the volume was sedimented,
- US (sonication) was applied for 2 hours,
- 6 g L⁻¹ FeSO₄ + 2.5 g L⁻¹ H₂O₂ was applied to OME for Fenton oxidation at pH<3,
- Combined US + H₂O₂ applied as 2.5 g L⁻¹ H₂O₂ with 2 hours US,
- During ozone experiments, 5 kg h⁻¹ O₃ was applied for 40 minutes,
- Finally, combined UV+US+O₃+H₂O₂ oxidation was applied with 2.5 g L⁻¹ H₂O₂ and 5 kg h⁻¹ O₃ for 2 hours.

All experiments, except Fenton's process, were carried out at pH 7.

Analytical methods

The samples were centrifuged at 5000 rpm for 15 min prior to analysis. COD, color and SS were measured in accordance with Standard Methods.¹⁹ The pH measurements were obtained with a pH meter (WTW pH meter and probe). Color measurements were obtained via Standard methods.¹⁹ Absorbance of OME solution was measured at their respective λ max values (800 nm) using a UV-Visible spectrophotometer.¹⁹ Total phenol concentration values as caffeic acid were measured via the Folin&Coicolteu method.²⁰ VFAs (acetate, propionate, butyrate, isobutyrate, isovalerate, valerate, isocaproate, caproate and heptanoic acid) and alcohols (ethanol, acetone and butanol) in the

mixed liquor were analyzed using a gas chromatograph (GC) (6890N Agilent) equipped with a flame ionization detector and a DB-FFAP 30 m x 0.32 mm x 0.25 μm capillary column (J&W Scientific, USA). Mixed liquor samples of 1.5 mL were first acidified with phosphoric acid and then filtered through a 0.2 μm membrane prior to analysis. The initial temperature of the column was 40 $^{\circ}\text{C}$ for 3 min followed by a ramp of 20 $^{\circ}\text{C min}^{-1}$ to 60 $^{\circ}\text{C}$ for 3 min and then increased by 30 $^{\circ}\text{C min}^{-1}$ to 120 $^{\circ}\text{C}$ for 4 min and then a final ramp of 30 $^{\circ}\text{C min}^{-1}$ to a final temperature of 240 $^{\circ}\text{C}$ for 6 min. The temperatures of the injector and detector were both 240 $^{\circ}\text{C}$. Helium was utilized as the carrier gas at a constant pressure of 103 kPa. The CH_4 content of the headspace gas was measured via the injection of a 5 mL bioreactor gas sample into the GC (6890N Agilent) equipped with a thermal conductivity detector and a Hayesep D 80/100 packed column. Injector, detector and column temperatures were maintained at 120 $^{\circ}\text{C}$, 140 $^{\circ}\text{C}$, and 35 $^{\circ}\text{C}$, respectively. Argon was utilized as the carrier gas at a flow rate of 20 mL min^{-1} .¹⁸

Configuration and operation of bioreactor

The experimental set-up (Fig. 1) consisted of a laboratory scale AFC bioreactor made of Plexiglas.¹⁸ The total volume was 20 L with 15 L working volume. The total height of the bioreactor was 102 cm with a wastewater height of 76 cm. Water-resistant cardboard, with specific surface area

$\sim 300 \text{ m}^2 \text{ m}^{-3}$, (Munster Cooling Pad, Form A.S., Turkey) used for cross-flow filter and packed in 80 % of the bioreactor. The bioreactor was fed from bottom through the Plexiglas grid by means of a peristaltic pump. Biogas was derived through a valve from the top of the bioreactor and its volume was measured via w-type gas meter (Speece Type, Nashville, TN). The bioreactor was operated in a temperature-controlled room at 35 ± 1 $^{\circ}\text{C}$.

Prior to normal operation, the reactor was operated for 3 months with a diluted OME effluent in order to acclimatize the biomass to the operating conditions. The ACF bioreactor was operated with both raw and pre-treated OME at constant hydraulic retention time (HRT) of 10 days which was determined to be the best HRT from earlier studies by varying organic loading rates (OLR) and HRTs, using raw OME as substrate. After these studies, pretreated OME was fed through the ACF reactor with 10 days HRT. pH of pretreated OME was adjusted to 7 before feeding.

Statistical analysis

All the results were statistically compared by variance analysis (ANOVA) using PAWS Statistics 18.0 software. For detailed multiple comparison of the results, the Duncan Test was used. This post hoc test (or multiple comparison test) was used to determine the significant differences between group means detected by ANOVA test at a 5 % significance level ($p = 0.05$).

Results and discussion

The main characteristics of OME are presented in Table 1. It is obvious that OME is characterized by high levels of organic and phenolic compounds, and direct discharge of OME would be highly toxic and hazardous to the receiving environment.

During the 477 days of experimental study, the samples were taken from the influent and effluent of the reactors and these measurements for COD, phenol and total volatile fatty acid levels are shown in Fig. 2. The results were obtained under two different operating conditions. In the first part of the study, OLR values corresponding to a range of 0.45 and 11 kg COD m^{-3} per day were gradually increased by increasing the influent COD at constant HRT of 10 days. During this period, COD removal efficiencies between 60–94 % were achieved (Fig. 2). It was observed that there is a significant statistical correlation between influent and effluent COD values ($R^2 = 0.88$), and increasing influent COD resulted in deterioration of effluent quality in terms of COD, which varied between 1797 and 11563 mg L^{-1} . In the second part of the study, the

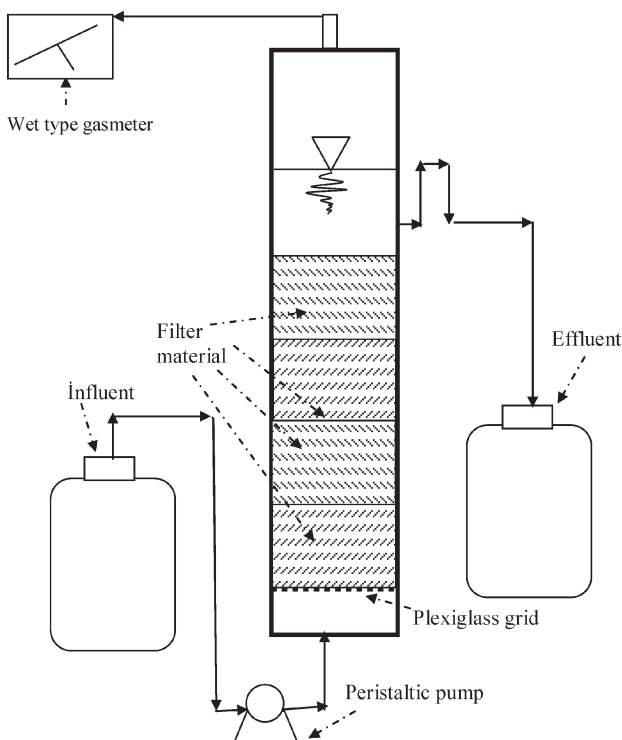


Fig. 1 – Scheme of bioreactor configuration

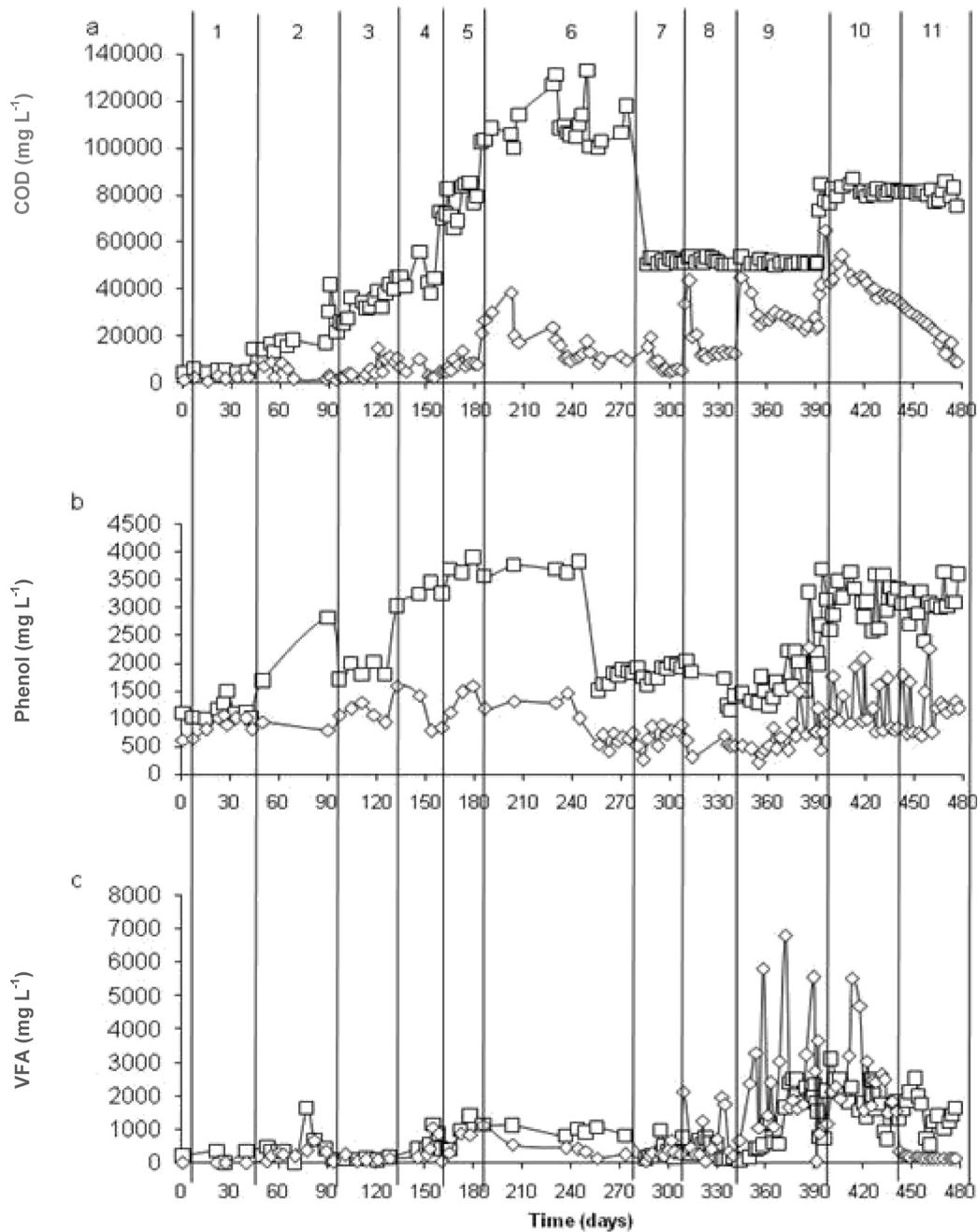


Fig. 2 – (a) COD, (b) phenolic content and (c) VFA content of influent (□) and effluent (◇) during operation

effect of higher OLR rates provided by lowering the HRT were evaluated (Fig. 2). Effluent quality significantly deteriorated when influent COD increased and HRT was lowered corresponding to OLRs between 11 – 32 kg COD m⁻³ per day (Fig. 2). HRT was found to be an important design criterion, especially for treating OME effluent with concentrated influent COD. Short HRT values resulted in poor COD removal efficiency (45 – 76 %), while HRT over 7.5 days did not alter the maximum achievable COD removal, which was around 94 % (Fig. 2). The COD removal efficiency of the reactor was reduced at OLRs over 11 kg COD m⁻³ per day,

it was observed that especially OLRs equal to or above 20 resulted in less than 50 % COD removal efficiency, possibly because of inhibition by polyphenols as suggested by Boari *et al.*,²¹ Rozzi *et al.*,¹⁷ Boari and Mancini²² (Fig. 2).

Different physicochemical and AOP procedures were also applied to raw OME. The pre-treated OME was fed to ACF reactor at an HRT of 10 h in order to monitor the effects on reactor performance parameters such as COD, phenolic compounds and color removed. Fig. 3 depicts the influent (before and after pre-treatment) and effluent values. Application of pretreatments in the form of Fenton's pro-

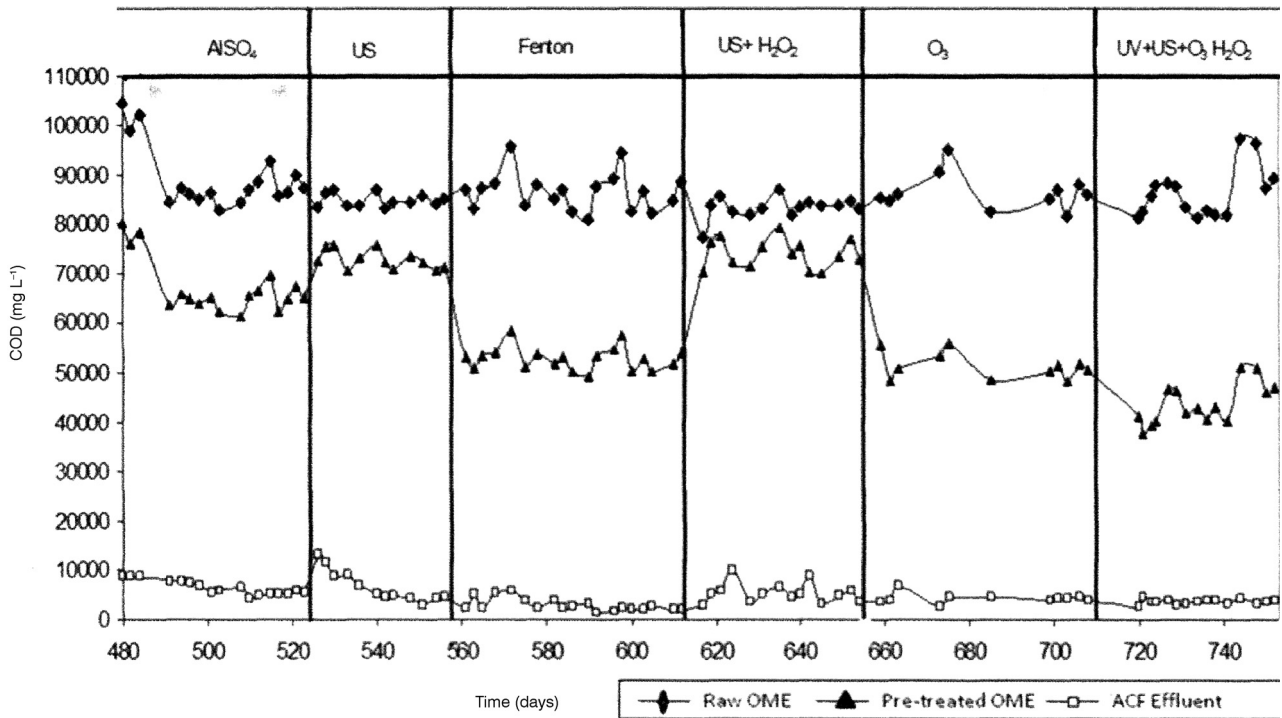


Fig. 3 – Influent and effluent of COD values of different pretreatments

cess, ozone and UV+US+O₃+H₂O₂ significantly reduced COD values from 90000±5000 mg L⁻¹ to 45000±5000 mg L⁻¹. However, COD values after pretreatment with Al₂(SO₄)₃, US, US+H₂O₂ were obtained as 65000±5000 mg L⁻¹, 70000±5000 mg L⁻¹, 80000±5000 mg L⁻¹ respectively. The best COD removal efficiency was obtained approximately 50 % and 41 % for O₃ and Fenton processes, respectively. Lucas *et al.*¹⁰ applied electro Fenton's procedure for pretreatment of OME and achieved 80 % COD and 85 % phenol removal; Rizzo *et al.*²³ reported 85 % COD removal by same procedure; Chedeville *et al.*²⁴ applied ozonation and obtained up to 80 % phenolics removed. In terms of COD removal, these results are better than our findings for the pretreatment. The effect of the pre-treatment greatly depends on the characteristics of the OME, which is a function of olive quality and the olive oil production method. A significant number of literature reports have varying results on the COD removal efficiencies depending on the conditions and materials used. Although our pretreatment results, in fact, are in parallel with most of these studies, the aim of the pretreatment in this study was to remove toxicity of the influent instead of fully destructing the influent COD, which is actually needed for a maximum biogas production. Therefore, our pretreatment values for COD destruction were kept low purposely.

According to Fig. 3, the pre-treated samples greatly enhance the COD removal efficiencies in

ACF reactor. Six different types of pre-treated samples resulted in different performances in terms of COD degradation. Using Al₂(SO₄)₃-treated OME samples as influent in ACF bioreactor resulted in the removal of COD from 65000±5000 mg L⁻¹ to 8000±500 mg L⁻¹. The effluent COD concentrations from the ACF reactor, operated by using different pre-treated (US, Fenton, US+H₂O₂, O₃, US+O₃+H₂O₂+UV) OMEs, are: 10000±2000 mg L⁻¹, 5700±230 mg L⁻¹, 7000±250 mg L⁻¹, 6850±250 mg L⁻¹, 6200±200 mg L⁻¹, respectively. According to the Turkish Water Control Regulation of the Environmental Ministry of the Turkish Republic (25687; 2004), the discharge standard for OME is 4000 mg L⁻¹ COD, and pH 6.5–9.0. The pHs of all effluents from ACF reactor comply with prescribed discharge limits. There is a great enhancement both in terms of degradation of COD and conversion into biogas, but the effluent COD concentration is still higher than the discharge limits. Best discharging condition was obtained by using Fenton pre-treated OME in ACF reactor as 5700±250 mg L⁻¹, which is higher than the limit of 4000 mg L⁻¹. Therefore, a final polishing step (such as membrane filtration etc.) may be required before discharging into sewer lines.²⁵

The results were also statistically compared by using the Duncan Test. The difference among these pretreatment processes with raw OME were found to be statistically significant ($p < 0.05$). As shown in Fig. 4, although all pretreatment processes en-

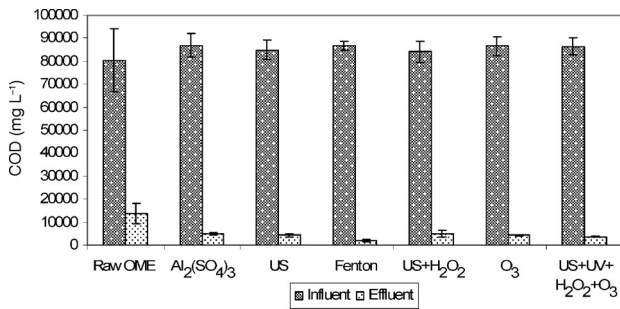


Fig. 4 – Average COD values of influent and effluent (raw OME operated at OLR = 10 kg COD m⁻³ per day).

hanced the COD removal efficiency at varying degrees, the best COD removal efficiency was obtained by Fenton process (overall COD removal efficiency 97.8 %). Khoufi *et al.*⁸ applied the electro-Fenton procedure to enhance anaerobic activity in UASB reactor and achieved 75 % COD removal efficiency at 4 days HRT. A similar study was carried out by El Gohary *et al.*²⁶ by two different pretreatments – namely, H₂O₂ and Fenton before anaerobic degradation in UASB and resulted in 77 % and 83 % COD removal, respectively. The combined system used in this study (pretreatment + anaerobic digestion) seems to work more effectively.

Fig. 5 shows the removal efficiencies for color and phenolic compounds in ACF reactor operated with raw and pretreated OME, respectively. Feeding the ACF reactor with pretreated OME significantly enhanced the phenol removal efficiency. Phenol removal efficiencies of raw OME, Al₂(SO₄)₃, Fenton, US, US+H₂O₂, O₃ and UV+US+O₃+H₂O₂ were approximately 61 %, 83 %, 73 %, 82 %, 71 %, 92 %, 87 % respectively. The best phenol removal values were achieved by ozone treatment, which were also higher than the values reported in the literature. The phenol removal potential of ozone itself was better than the other AOPs. The radicals produced during ozone treatment had a positive effect on the degradation of the long-chain phenolics. The ozone process was also found to be the most attractive option for phenol degradation in a previous study.²⁷

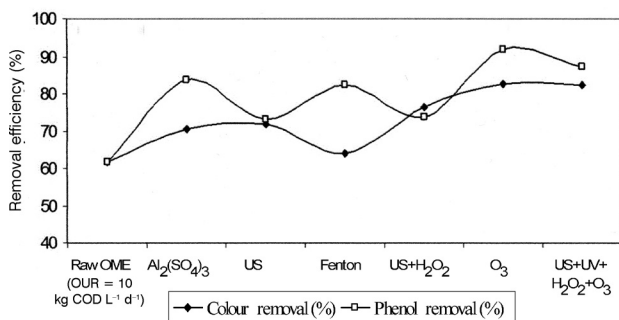


Fig. 5 – Removal efficiencies of color and phenolic compounds at effluent of ACF reactor

According to color removal efficiencies, anaerobic treatment itself (without pretreatment) was able to remove the 61 % of influent color; on the other hand, application of various pretreatments such as Al₂(SO₄)₃, Fenton, US, US+H₂O₂, O₃ and UV+US+O₃+H₂O₂, respectively, resulted in 70 %, 71 %, 64 %, 76 %, 82 %, 82 % color removal, respectively. Generally, similar trends were observed for the removal efficiencies of phenol and color. Pre-treatment greatly reduced the color of OME. AOPs and chemical pre-treatment removed the suspended solids resulting in reduced color values.

Fenton's process is one of the most common AOPs used for wastewater treatment because of its efficiency and economic advantage.^{25,28} The Fenton process also generates more compact chemical sludge than other chemical pre-treatment options, which lowers sludge disposal costs.²⁹

The evaluation of the treatment costs is today one of the most important aspects that should be taken into account. The overall cost is the sum of capital cost, operating cost, labor cost and maintenance. For a full-scale system, these costs depend on the nature and amount of wastewater. It must be emphasized that ozonation always requires significantly higher initial investments than the Fenton process.³⁰ Considering a first economic assessment of the cost of the tested treatments, it could be understood that even if it is a very effective pre-treatment operation, the Fenton treatment has a higher cost in terms of chemical reagents, which will further imply an associated higher cost of iron sludge disposal. As regards the operating costs, UV seems to be an expensive AOP due to the high nominal power of the lamp.²⁷

Conclusions

To the best of our knowledge, the cross-flow packing material made of water-resistant cardboard was used for this purpose for the first time in this study. It was demonstrated that the biodegradability of OME could be significantly enhanced by pre-treatment, therefore anaerobic biodegradation after suitable pre-treatment could be considered an efficient disposal method for OME, since a significant amount of organic destruction is achieved. Furthermore, enhanced biogas production in a novel bioreactor from OME also provides both an environmentally friendly and economically attractive solution. This is especially important considering the fact that renewable and fossil-based C-free energy alternatives are now needed more than ever before.

The ACF type reactor configuration is an efficient reactor configuration for treating OME. OLR

is a significant design parameter and should be kept at 10 kg COD m⁻³ per day or less to achieve one log treatment efficiency. HRT is another important operational parameter that should be maintained between 5 and 10 days as a function of influent organic load. All pretreatment options used in this study improved the anaerobic biological degradation in terms of COD, phenolics and color removal efficiencies. The best result for COD removal was obtained by the Fenton process. Therefore, a final polishing step (such as membrane filtration etc.) may be required before discharging OME into sewer lines.

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List of abbreviations

ACF – Anaerobic Cross-Flow Filter
 AOP – Advanced Oxidation Processes
 COD – Chemical Oxygen Demand
 HRT – Hydraulic Retention Time
 OLR – Organic Loading Rate
 OME – Olive Mill Effluent
 SS – Suspended Solids
 UV – UltraViolet
 US – UltraSound
 VSS – Volatile Suspended Solids

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