Olive Mill Wastewaters Total Organic Carbon Degradation using TiO_2 Nanoparticles

Iliopoulos I.[1], Kourkouta E.[1], Bekiari V.[2], Stathatos E.[3], Panagopoulos G.[1] And Panagiotaras D.[1,*]

[1]Department of Mechanical Engineering, Technological Educational Institute (TEI) of Western Greece, 263 34 Patras, Greece.

[2]Department of Fisheries & Aquaculture Technology, Technological Educational Institute (TEI) of Western Greece, Messolonghi, Nea Ktiria, 302 00 Messolonghi, Greece.

[3]Department of Electrical Engineering, Technological Educational Institute (TEI) of Western Greece, 263 34 Patras, Greece.

*corresponding author:

e-mail: sakpanag@teiwest.gr

Abstract

Olive mill wastewaters (OMW) constitute an important pollution factor for the olive oil-producing regions but also a significant problem to be solved for the agricultural industry. The main reason is the large wastes amounts produced in relatively small time interval, which should be processed with safety for the environment. Because of the high organic content, it is imperative to use Advanced Oxidation Technologies in order to reduce the organic load of these wastewaters. We used TiO_2 nanopowder (Degussa P-25) as a low cost, low toxicity and effective photocatalyst for the degradation of the organic load of the wastewaters in an olive oil production facility at the prefecture of Ileia Western Greece. The treatment of OMW showed that the Total Organic Carbon (TOC) can be reduced over 44% after 300 minutes under UV irradiation. In addition we studied the effect of the TiO_2 mass in respect to the total volume ratio of OMW as a critical factor for the effective degradation of the TOC. The sample with a mass/volume = 15 mg/ml shows the highest photocatalytic decomposition efficiency (44%) in comparison to the mass/volume = 0.5 mg/ml which shows a 30% efficiency after 300 minutes of UV exposure.

This easy-going treatment technology, aim to transform resistant organic molecules into others which could be further biodegraded in the natural environment.

Keywords: Olive Mills Wastewater, Photocatalysis, TiO_2 nanopowder.

1. Introduction

Olive mill wastewaters (OMW) are of the major environmental problems in Mediterranean countries where large quantities of olive oil are produced (1-5). The acidic pH values, the high organic load and the large quantities are the major characteristics that constitute olive mills wastewaters, hazardous wastes (6).

The OMW produced during the treatment of the olives, in different stages, in traditional, and/or two-three phase centrifugal systems (7-8). An estimation of the OMW produced under these facilities in the Mediterranean is about 30 million m^3 (9). However, the composition of the OMW exhibits variations in regard to the methodology of the oil extraction, the age of the trees, the soil characteristics and other environmental factors (10).

In general, for each 100 kilos of olive-crop, 100-120 kilos of humid wastes are produced.

The substantial high organic load constitutes by substances like sugars, organic acids, amino-acids, proteins, fats and polyphenols. Wastes contain high concentration of polyphenols, which may cause the appearance of bio-toxic phenomena in the natural environment.

A typical composition of the OMW is organic matter of about 4-16 %wt, minerals 1-2 %wt and water 83-92 %wt (11-13). Total phenols are between 10.6-17.2 g/l, BOD_5 45.5-68.7 g/l and COD 85.7-158 g/l (11-12).

The illegal discharge of the OMW without pretreatment is of a major concern in oils produced countries in the Mediterranean region and causes a lot of environmental problems such as eutrophication, toxic phenomena to the aquatic fauna, phytotoxicity, aesthetic degradation, as well as socioeconomic impacts in a regional scale (13-15). During the past, much research has been conducted in order to achieve an efficient degradation method of the high organic load of the OMW.

These methodologies used various techniques such as the aerobic-anaerobic treatment (16-18), enzymatic catalysis (19), composting (20), membrane ultra-filtration (UF) combined with centrifugation (21) or UV/H_2O_2 oxidation (22), advance oxidation using O_3/UV (23), photocatalysis (24), Fenton and electrochemical oxidation (25, 26).

However, a major disadvantage of the above mention techniques is the up-scaling application, and their use in real conditions olive oil production units.

Table 1. Mass to volume ratio of the samples analyzed

Sample Number	Sample ID	Mass TiO_2 (mg)	Volume Wastewater (ml)	Mass/Volume (mg/ml)
1	OMW1	100	200	0.5
2	OMW2	500	200	2.5
3	OMW3	1500	200	7.5
4	OMW4	3000	200	15

Taking into consideration the limitations of the use of advance oxidation technologies for OMW in large scale applications, we propose a simple methodology based on the photocatalytic degradation of the total organic load using TiO_2 as the photocatalyst for OMW effective treatment.

2. Methodology, Results and Discussion

2.1. Materials and Methodology

Samples were collected from a two phase centrifugal system, oil production facility, located in Pyrgos municipality, Ileia prefecture Western Greece. After collection, the samples were deep frozen until their treatment to the laboratory. The raw sample was processed to a 9 mesh, 2 mm pore size strainer (Fig. 1). The wastewater was then centrifuged two times (10 minutes each) using a speed of 3000 r/min. Aliquots of the sample were used for the photocatalysis.

Figure 1. Photographs showing the treatment of the samples analyzed.

In Table 1 we present the samples identification and the mass of TiO_2 nanopowder and volume of sample used. Commercially available TiO_2 -Degussa P-25 was used as the photocatalyst. The Degussa P-25 characteristics are anatase to rutile ratio 80:20, particle size 20 nm and particle specific area 50 m^2/g.

A cylindrical reactor was used in all experiments (Fig. 2). Four black light fluorescent tubes of 4 W each nominal power, were placed around the reactor. The whole construction was covered with a cylindrical aluminum reflector. Cooling was achieved

by air flow from below the reactor using a ventilator. Continuously stirring of the samples in the reactor was achieved with a magnetic stirrer.

Figure 2. Photographs showing the photocatalytic system used.

The intensity of radiation was measured with a Solar Light PMA-2100 UV-Photometer and found equal with 0.9 mW/cm^2. The reactor was filled with 200 ml of the sample and the irradiation applied for a total of 300 minutes. TOC analysis was performed using the Combustion-Infrared method, Standard Method (SM) 5310B (Standard Methods for the Examination of Water and Waste Water, American Water Works Association) (27, 28). All analyses were carried out using a Shimadzu TOC analyzer (TOC-VCSH).

2.2. Results and Discussion

The use of TiO_2 powder as the photocatalyst was decided because titanium dioxide is a well-known low cost nontoxic photocatalyst for a variety of pollutants. Also it can be used with success in many photocatalytic cycles and can be easily handled by an unskilled worker in an oil production unit. The high efficiency of TiO_2 to produce hydroxyl radicals in solution under UV light illumination, the high stability in water and the nontoxic response are major characteristics. In addition TiO_2 is a cost efficient and very effective photocatalyst for the decomposition of organic substances in water and air (Fig. 3; 29, 30).

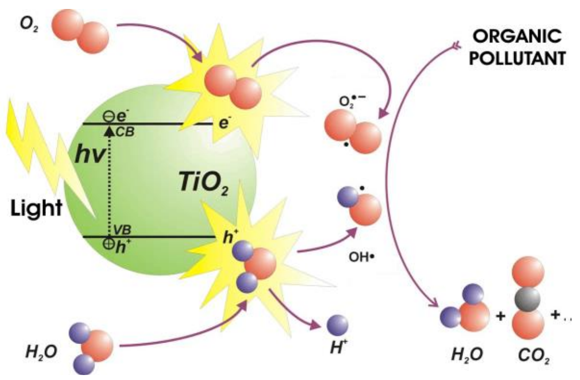

Figure 3. Schematic presentation of ●OH generation through TiO_2 photoexcitation and organic pollutants degradation (adopted from 30).

Hydroxyl radicals (●OH) can be generated from water using TiO_2 as a photocatalyst. The ●OH compounds are very reactive chemicals with a redox potential of +2.8 V (vs. Nernst Hydrogen Electrode) and they can react with the organic pollutants with a 10^7-10^{10} M^{-1} s^{-1} constant reaction rate. The end product of the reaction of the ●OH radicals with the organic compounds are CO_2, H_2O and inorganic salts (29, 30). Because of hydroxyl radicals' high redox potential (+2.8 V), they are more effective for the decomposition of organic pollutants than other oxidants like O_3 (+2.07 V), HOCl (+1.49 V) and H_2O_2 (+1.78 V) used for water purification and disinfection (29, 30).

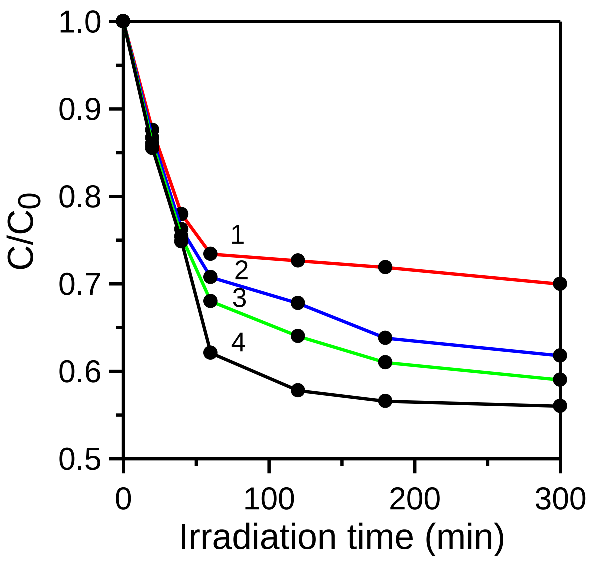

Figure 4. Decomposition rate of TOC in relation to the irradiation time.

The effectiveness of semiconductors for photoactivation is a function of the energy required for the excitation of their crystals. For TiO_2 in the anatase form this energy must be higher than the E_g=3.2 eV and for the rutile higher than E_g=3.0 eV. As a conclusion TiO_2 nanocrystals excitation requires energy in the near UV region (radiation with $\lambda \leq 380$ nm for anatase and $\lambda \leq 400$ nm for rutile). This limitation is a major disadvantage of the use of TiO_2 as a photocatalyst because only 5% of the solar light radiation is in the UV region (31).

In order to estimate the photo-degradation rate (R) of the TOC we employ the following equation:

$$R = (C_o - C)/C_o$$

Where C_o is the initial concentration of the pollutant measured in solution and C is the final concentration after irradiation with UV light. Then we can calculate the degradation efficiency (E%) as:

$$E\% = [(C_o - C)/C_o] \times 100\%$$

Our experiments reviled that the photocatalytic efficiency of the TiO_2 used for the degradation of the TOC in the samples analyzed is related to the time of irradiation and the mass of the material used. In particular after more than 150 minutes of illumination all the samples showed no difference in the photo-degradation rate of TOC (Fig. 4).

The mass of the catalyst to the total volume of the sample, indicates that the higher mass/volume ratio causes the most efficient degradation of the TOC among all measured samples (Fig. 5).

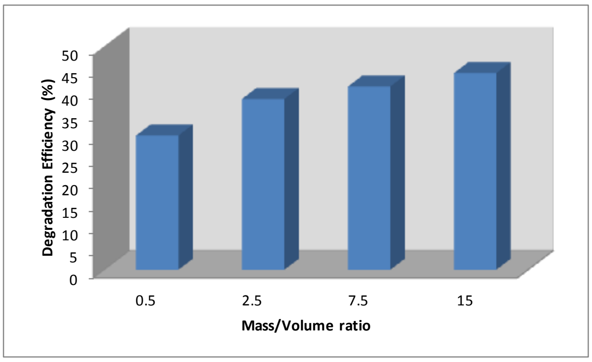

Figure 5. Degradation efficiency of the catalyst after 300 min of irradiation with respect to the mass/volume ratio.

High TOC decomposition efficiency 44% is apparent when we use the higher mass/volume ratio while the lowest mass/volume ratio shows a degradation efficiency of 30% after 300 min of illumination (Fig. 5). Higher mass/volume ratio could be used and repetition measurements could be helpful

3. Conclusions

The data presented here show that TiO_2 can be efficiently used for the photocatalytic treatment of Olive Mills Wastewaters. The degradation efficiency of the photocatalyst used for the decomposition of the Total Organic Carbon of the samples is accelerated when high mass TiO_2/volume sample ratios have been used. After 150 minutes of UV irradiation there is no change of the decomposition rate of TOC.

Degussa P-25 can be used as a low cost, efficient and environmental friendly material for the treatment of the olive mills wastewaters generated in an olive oil production facility. The procedure we propose for an easy going process is illustrated in figure 6. To this perspective, the OMW treatment includes physical sedimentation in the first concrete tank in order for the heavy solid particles to precipitate and a second step with stirring, oxygenation and photocatalytic treatment with Degussa P-25 under UV illumination for 150 minutes.

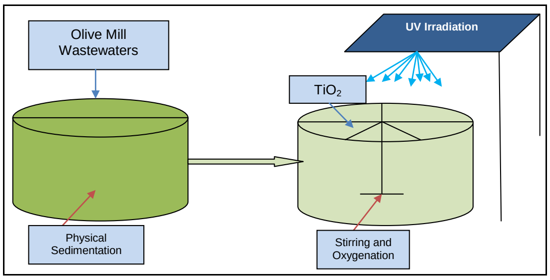

Figure 6. Shematic illustration of a cost effective, efficient and easy going procedure for OMW treatment.

Oxygenation can further facilitate the TOC photocatalytic degradation because of the major reactive oxygen species (ROS) produced (32).

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