

HETEROGENEOUS AND HOMOGENEOUS PHOTOCATALYTIC TREATMENT OF WASTEWATERS FROM BLACK TABLE OLIVES PROCESSING

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ABSTRACT

The photocatalytic oxidation of an actual wastewater originating from black table olives processing was investigated. Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor. Photocatalysis was applied in the presence of TiO₂. Eight crystalline forms of TiO₂ were tested for their photocatalytic activity and a synthetic TiO₂ catalyst prepared in the laboratory was found to be more active, in terms of phenolic compounds reduction, than the other commercially available photocatalysts. The extent of photocatalytic degradation was found to increase with increasing TiO₂ concentration up to 1.5 g/L TiO₂, above which degradation remained practically constant, reaching a plateau. To assess catalyst activity on repeated use, experiments were performed where the catalyst was recovered and reused. After two successive uses, TiO₂ had sufficiently retained its photocatalytic activity. Furthermore, effluent degradation was enhanced in the presence of hydrogen peroxide at concentrations 25, 50, 100mg/L. At 100mg/L H₂O₂ the photocatalytic treatment achieved 47%, 72%, 61%, 94% reduction for COD, phenols, aromatics and color respectively. However, the use of H₂O₂ above 150mg/L suppressed degradation. Besides, the oxidative degradation of table olives wastewater was investigated by means of homogeneous photocatalysis in the presence of iron cations. Fe²⁺ and Fe³⁺ were tested in the form of FeSO₄ and FeCl₃ respectively and the latter were found more efficient for photocatalytic treatment. In general, treatment performance improved with increasing Fe³⁺ loading at values of 10, 31, 48, 104mg/L. The interference from Fe³⁺ in the estimation of phenolic compounds was pointed out. Finally, it was observed that the addition of H₂O₂ to the homogeneous photocatalytic mixture enhanced the chemical oxidation to 19%, 80%, 56%, 73% for COD, phenols, aromatics and color reduction respectively.

Keywords: photocatalytic oxidation, anatase TiO₂, photo-Fenton, edible olives

1. INTRODUCTION

The foodstuff processing industry based on olive oil extraction and table olive preparation is an economically important activity for many regions of the Mediterranean Sea area. Both processes result in large quantities of bio-recalcitrant effluents. Therefore, increasing concern has been expressed about their effective treatment and safe disposal in the environment [1].

The process through which the effluent is generated includes washing, natural fermentation in brine, air-oxidation for color improvement, sizing and packing. The washing solutions are heavily contaminated and contain a high content of sugars, organic acids and polyphenols [2]. The major polyphenolic compounds present in table olives are tyrosol, hydroxytyrosol and oleanolic acid and the concentration of these compounds depends on the degree of maturation [3]. Among the various organic compounds typically found in wastewaters originating from table olives, of particular interest is their total phenolic content, since phytotoxicity and strong antibacterial action have been attributed

to it. In particular, polyphenols eliminate abundant bacteriological populations in municipal biological wastewater treatment plants.

Due to the bio-recalcitrant nature of these wastewaters [4], research efforts have been directed towards the development of efficient treatment technologies. In recent years, advanced oxidation processes (AOPs) have been employed as alternative pretreatment methods aiming at reducing effluent organic load and bio-recalcitrance of wastewaters [5]. Various AOPs have been employed for the degradation of wastewaters from table olives processing such as chemical oxidation with Fenton's reagent, ozonation, UV radiation, combined ozonation with hydrogen peroxide or UV radiation [4; 6], electrochemical treatment in the presence of hydrogen peroxide [7], and the integration of a chemical pretreatment step followed by biological treatment [8; 9].

The aim of the present work was to study the treatment of an effluent generated from black table olives production by means of heterogeneous and homogeneous photocatalysis. Emphasis was given on the effect of key operating parameters such as crystalline form, loading and reuse of TiO_2 and addition of hydrogen peroxide. Moreover, the kind of iron cations and catalyst loading was estimated regarding homogeneous photocatalysis. The reduction of the polluting load of the effluent is expressed in terms of COD, total phenols, aromatics content and color reduction.

2. MATERIALS AND METHODS

2.1. Materials

The effluent used in the present study was kindly provided by "Charisakis S.A.", a small family-owned table olives processing company, located in Chania, Greece, and was used without any pretreatment. Regarding its physicochemical characteristics, the effluent has a dark black-brown color with maximum absorbance in the visible region at $\lambda=550$ nm, is moderately acidic with $\text{pH}=4.5$, it has a COD content of 40 g/L, a total phenol content measured as gallic acid equivalent of 1.4 g/L, a total solids content of 6.9 g/L, and contains approximately 10% w/w NaCl and 0.2% w/w CaCl_2 giving rise to a conductivity of 112 mS/cm.

For heterogeneous photocatalytic experiments, seven commercially available samples of titanium dioxide TiO_2 were used as received and screened for their relative catalytic activity. The particulars of each catalyst are shown in Table 1. In addition to the catalysts shown in Table 1, experiments were conducted with a synthetic TiO_2 catalyst prepared in the laboratory according to literature procedures [10] and its activity was compared to that of the rest. For homogeneous photocatalytic experiments, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used as catalysts and provided by Aldrich and Riedel-de Haen respectively. H_2O_2 in the form of 35% w/w solution was supplied by Merck.

Table 1. TiO_2 catalysts used in this study; nd: not determined.

Catalyst	Type	Particle size, nm	Specific area, m^2/g	Supplier
Degussa P-25	80:20 anatase:rutile	20	50	Degussa
Millenium	anatase	5-10	287	Millenium Inorganic Chemicals
Tronox AK1	anatase	20	90	Kerr McGee Chemicals
Tronox TR	rutile	300	5.5	Kerr McGee Chemicals
Aldrich	anatase	nd	nd	Aldrich
Hombikat UV100	anatase	5	>250	Sachtleben
Hombikat UV100-F	anatase	nd	nd	Sachtleben

2.2. Photocatalytic degradation experiments

Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor described in detail elsewhere [11]. In a typical heterogeneous photocatalytic run, the original effluent was diluted with distilled water and then 350 ml were loaded in the reaction vessel. The solution was slurried with the appropriate amount of catalyst and magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of organic compounds on the TiO_2 surface. After that period of time, the UV-A lamp was turned on, while air was continuously sparged in the liquid and the reaction mixture was continuously stirred. Similar procedures were followed for the homogeneous photocatalytic runs where the appropriate amount of iron salt and (if needed) hydrogen peroxide was added to the effluent while this was sparged with air. All runs were carried out at effluent's natural pH (i.e. 4.5).

UV-A irradiation was provided by a 400 W, high pressure mercury lamp (Osram, HQL, MBF-U) emitting predominantly at 366 nm. The photon flux discharged from the lamp was determined actinometrically using the potassium ferrioxalate actinometry method [12; 13] and was found $1.12 \cdot 10^{-5}$ Einstein/s.

Samples periodically drawn from the photoreactor were filtered (with $0.45\mu\text{m}$ filters) to remove solid particles and then analyzed for their residual organic concentration, color, total phenol and aromatic content.

2.3. Analytical measurements

COD was determined colorimetrically according to the standard dichromate method at 620 nm on a Hach DR/2010 spectrophotometer using standard COD digestion solutions in the range of 0-1500 mg/L. Total phenolic compounds were estimated according to the Folin-Ciocalteu protocol, using a modified micromethod [14]. The extent of decoloration that had occurred during photocatalytic treatment was assessed measuring sample absorbance at 550 nm, which is the wavelength that corresponds to the maximum absorbance in the visible region, on a UV/Vis Shimadzu UV 1240 spectrophotometer. Percent decoloration was calculated relative to the initial absorbance of the untreated effluent. The effluents' aromatic compounds were measured at $\lambda=274$ nm, which corresponds to the maximum absorbance in the ultraviolet region, on a UV/Vis Shimadzu UV 1240 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Heterogeneous photocatalytic treatment

Preliminary screening experiments were performed in order to evaluate the efficiency of various TiO_2 samples in heterogeneous photocatalysis. All runs were conducted in the presence of air sparging through the photoreactor, without any filtration of the initial effluent and at ambient pH. The effluent was diluted with distilled water to yield an initial COD value of 2g/L. As can be seen in Table 2 three catalysts, namely Synthetic TiO_2 , Degussa P25 and Hombikat UV 100 gave the best results in terms of total phenols and color removal, with Synthetic TiO_2 being superior compared to the others especially in total phenols reduction which, as it was mentioned, is of primary importance. For example, after 3 hours of photocatalytic treatment, total phenols reduction was 58% with synthetic TiO_2 , while in the case of the other two photocatalysts reduction was less than 46%. According to these findings all subsequent heterogeneous photocatalytic experiments were performed with Synthetic TiO_2 .

Table 2: % reduction of COD, color and phenolics content after 3h of treatment for various photocatalysts.

	% Reduction		
	<i>COD</i>	<i>Phenolics Content</i>	<i>Color</i>
Degussa P-25	21	33	80
Millenium	38	11	12
Tronox AK1	11	32	64
Tronox TR	3	10	33
Aldrich	12	0	26
Hombikat UV100	21	46	83
Hombikat UV100 - F	2	32	65
Synthetic TiO ₂	13	58	77

In further experiments the effect of TiO₂ loading was studied in the range of 0.25 - 3 g/L (see Figure 1). It was found that increasing catalyst loading up to 3 g/L total phenols reduction achieves an optimal increase up to 88%. However, the extent of COD, aromatic content and color degradation was found to increase with increasing TiO₂ concentration up to 1.5 g/L TiO₂, above which degradation remained practically constant, reaching a plateau. This may be due to the fact that when catalyst's concentration is above a value in the solution, the suspended solids in the effluent are so many that the radiation emitted from the lamp is prevented to go through the whole volume of the effluent. On the other hand, some polyphenolic compounds may be adsorbed on the catalyst surface resulting in an increase of polyphenols degradation.

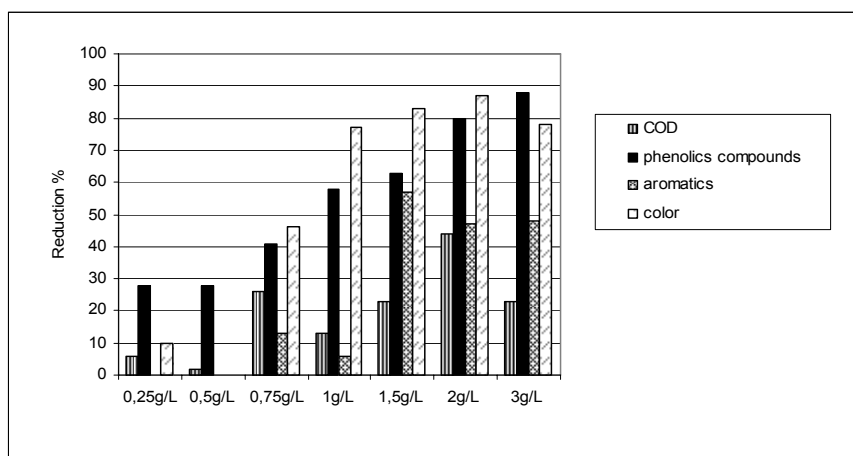


Figure 1: % reduction of COD, color, phenolic and aromatic content after 3h of photocatalytic treatment with Synthetic TiO₂ (effluent's initial COD=2g/L), for various catalyst loadings.

The possibility of catalyst recovery and reuse was also studied. A series of experiments were performed at 1.5 g/L TiO₂ loading to avoid influence of minor losses in the amount of catalyst. Experiments with recycled catalyst were performed as follows: at the end of the run with the fresh catalyst, the reaction mixture was centrifuged at 3000 rpm for 20 min and the supernatant liquid was carefully decanted. A new batch of the effluent was then added to the vessel and the used TiO₂ was slurried again under vigorous stirring. The new effluent was first filtered with an 0.45 µm filter in order to avoid the influence of wastewater's solids to the catalyst reloading. It was found that at the conditions in question, photocatalytic efficiency remained practically constant during the first recycling of the catalyst and it was marginally deteriorated after two repeated uses (see Figure 2).

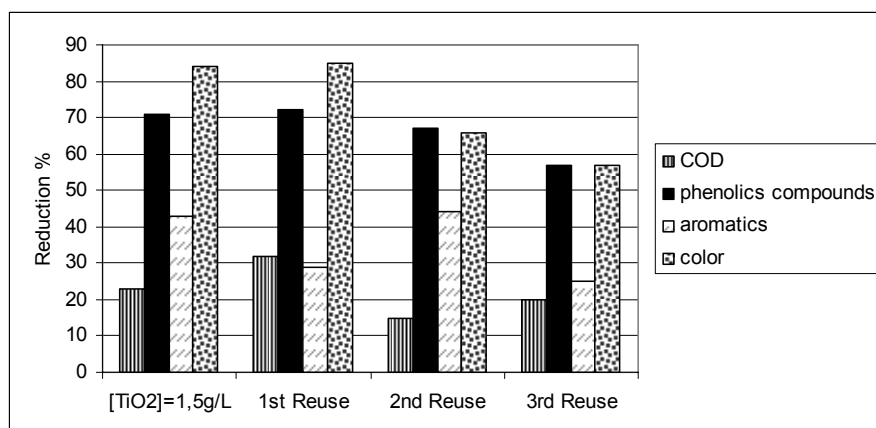


Figure 2: % reduction of COD, color, phenolic and aromatic content after 3h of photocatalytic treatment (effluent's initial COD=2g/L) for three reuses of the catalyst.

In another series of experiments, hydrogen peroxide addition to the reaction mixture was also studied. As can be seen in Figure 3 when 100mg/L H_2O_2 were added in the effluent (initial COD=1g/L), and left for 3h in the dark, phenols degradation was as low as 20%. When 100mg/L H_2O_2 are added in the effluent which is radiated by the UV-A lamp for 3h the efficiency goes up to 30% for phenols. However, when the effluent is photocatalysed in the presence of TiO_2 and hydrogen peroxide, phenols reduction increases to 72%. The same trend stands for aromatics content, COD and color.

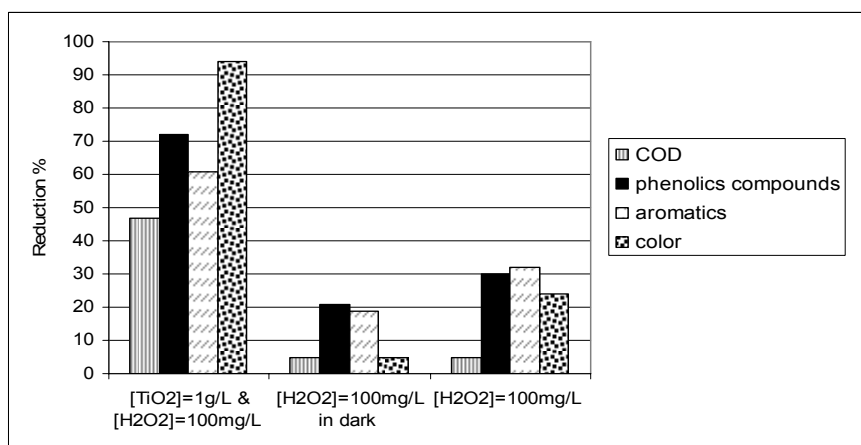


Figure 3: % reduction of COD, color, phenolic and aromatic content after 3h of photocatalytic treatment in the presence of H_2O_2 , H_2O_2 /UV, H_2O_2 /UV/ TiO_2 .

Thus, a series of experiments were conducted in order to estimate the optimum concentration of H_2O_2 needed to treat the effluent by TiO_2 photocatalysis. The experimental data, shown in Figure 4, demonstrated that H_2O_2 addition at an initial concentration from 25mg/L to 100 mg/L positively influenced photocatalytic efficiency, while further increase of H_2O_2 concentration retarded effluents' COD, total phenols and color reduction. This inhibition of mineralization is probably due to both auto-decomposition of H_2O_2 into oxygen and water and the scavenging of hydroxyl radicals by the excess of H_2O_2 according to the following reactions (eq. (1), (2)) [15, 16]. Consequently, the optimal initial concentration of H_2O_2 is 100mg/L.



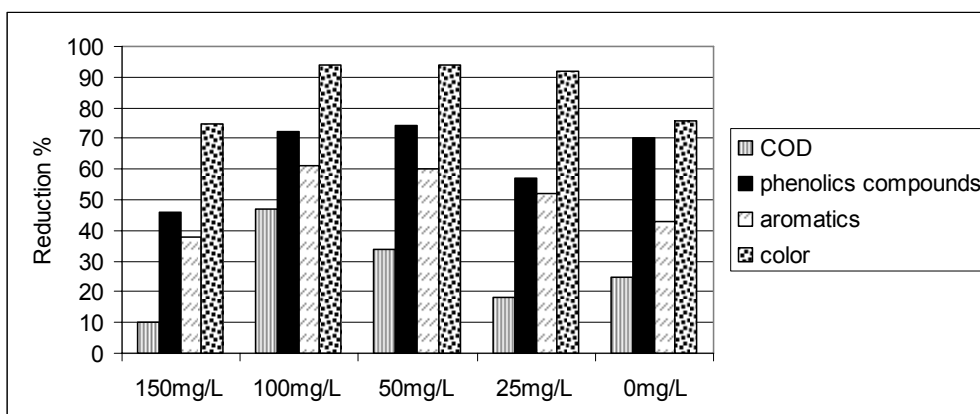


Figure 4: % reduction of COD, color, phenolic and aromatic content after 3h of photocatalytic treatment, in the presence of 1g/L Synthetic TiO_2 (effluent's initial COD=1g/L), for various hydrogen peroxide loadings.

3.2. Homogeneous photocatalytic treatment

In preliminary experiments the effluent was photocatalysed in the presence of 48mg/L Fe^{3+} or Fe^{2+} . It was found that phenols reduction after 3 h of treatment was 69% and 45% with Fe^{3+} and Fe^{2+} respectively. In terms of COD, color and aromatic compounds removal was about 30, 38 and 57% regardless the catalyst used.

A series of experiments took place to evaluate the optimum concentration of Fe^{3+} for the photocatalytic reduction of the organic pollutants, while the effluent's initial COD was 1g/L. Fe^{3+} was used as the photocatalyst, in the range of 10mg/L to 104mg/L (Figure 5). Generally, photocatalytic efficiency improved with increasing Fe^{3+} loading. However, it is worth noticing that increasing iron concentration above 31mg/L photocatalytic efficiency is negatively affected in terms of phenolic compounds. This is due to the interferences from inorganic compounds in the estimation of phenols with the Folin-Ciocalteu reagent. In particular, concentrations of iron >2mg/L as Fe^{2+} or Fe^{3+} form the insoluble iron(III) hydroxide which increases absorbance and interferes positively with the phenols measurements [17].

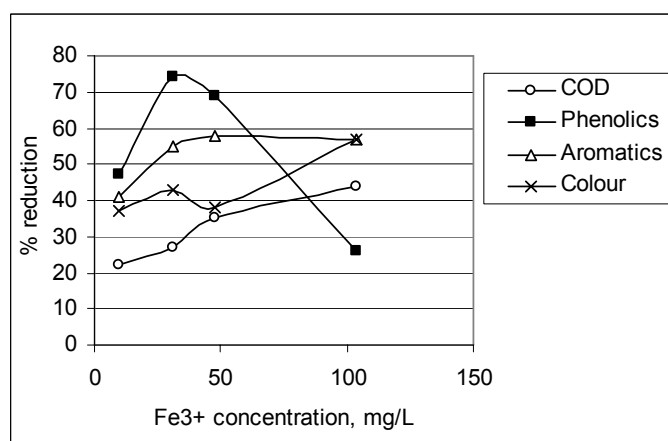


Figure 5: % reduction of COD, color, phenolics and aromatics content as a function of Fe^{3+} concentration.

Homogeneous photocatalytic treatment using Fe^{3+} as the photocatalyst can be coupled with H_2O_2 to establish the so called photo-Fenton process. Considering the fact that the optimum hydrogen peroxide loading to the heterogeneous photocatalytic treatment is

100mg/L, a final experiment was carried out in order to evaluate the effect of hydrogen peroxide addition in homogeneous photocatalysis.

Yet it was not the optimal concentration of Fe^{3+} (104mg/L) that was used for the photocatalytic treatment but the minimum (i.e. 10mg/L). The reason for this is the prospective of a resulting iron separation step required before further treatment or discharge after the photocatalytic treatment. Normally, the corresponding iron concentrations used are not much higher than the limits for direct discharge to a biological municipal wastewater treatment plant (in the range of tens mg/L, different amounts are permitted in the EU, USA, etc.) [18]. Therefore, the lower iron concentration was chosen in the way that it provided appropriate reactions rates (not the highest) for evaluating the performance of homogeneous photocatalytic mineralization under the addition of hydrogen peroxide. It was observed that when 100 mg/L of H_2O_2 was added to the effluent containing 10 mg/L Fe^{3+} , photocatalytic efficiency was significantly increased from 47% (treated with FeCl_3) to 80% (treated with $\text{FeCl}_3/\text{H}_2\text{O}_2$) for phenols, from 41% to 56% for aromatics compounds and from 37% to 73% for color. COD removal was about 20% regardless the addition of hydrogen peroxide.

4. CONCLUSIONS

In the present study the homogeneous and heterogeneous photocatalytic treatment of an effluent originating from black table olives processing was studied. It was found that, depending on the experimental conditions, both processes result in significant degree of mineralization expressed as COD removal, and a very high total phenols reduction while the effluent was almost completely decolorized after photocatalytic treatment. Consequently, it could be said that both methods are efficient provided that are used properly. This depends on the treatment that will follow after photocatalytic treatment and if an iron separation step is essential, the capacity of the wastewater produced by the process and on the economic evaluation (a prospective of catalyst reuse) of the whole treatment of the effluent. The results from the present study demonstrate that homogeneous and heterogeneous photocatalysis can be applied as alternative treatments methods for the efficient detoxification of these wastewaters thus contributing to environmental protection.

Acknowledgments

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