

Photocatalytic Degradation of Some Phenolic Compounds Present in Olive Mill Wastewater

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The olive oil industry in Palestine is an important and widely spread one and accomplished with the release of large amounts of olive-mills wastewater. This wastewater represents a significant environmental problem due to its high phenolic content. In this work, the photocatalytic degradation of the some phenolic compounds (gallic acid, oleuropein and resorcinol) present in olive-mills wastewater using the synthesized nanoparticles of mixed SnO₂-MgO catalyst and solar irradiation was performed. The nanoparticles of mixed SnO₂-MgO catalyst with different ratios were prepared by sol gel method using a modified procedure. The obtained particles were characterized by SEM and XRD. The particle size was determined as 4.32 ± 0.42 nm which is much smaller than those previously prepared by standard procedures. The degradation percentage of phenolic compounds was measured by UV spectrophotometry. The effect of time, catalyst amount and phenolic compound concentration on degradation efficiency was studied. The maximum degradation was achieved using SnO₂-MgO (4:1) catalyst, 2.5 mg catalyst per 5 mL solution, within the time of 60-120 min and ranged from 51 to 90 % for different concentrations of phenolic compounds.

Keywords: Photocatalytic degradation, Olive mill wastewater, Gallic acid, Resorcinol, Oleuropein.

INTRODUCTION

The Mediterranean region is world's leading olive growing area and olive processing has been an important and traditional industry for its countries since ancient time [1]. Countries of this region produce 98 % of the olive oil worldwide. In Palestine olive oil industry is one of the most widely spread industries. However, the problem of release of huge quantities of olive mill wastewater (OMW) is still representing a serious environmental challenge. Extremely high organic loaded aqueous waste which contains 3.5-15 % organics [2], generated from the oil extraction is directly discharged into sewerage network water or onto lands and can leakage into groundwater which used for drinking and irrigation [1,3,4].

These pollutants exhibits low biodegradability, since they include several phenolic compounds [5,6] that are highly phytotoxic and show antibacterial activity and thus resistance to biological degradation [7-9]. Therefore, treatment and managing olive-mills wastewater have been extensively investigated during the last 50 years with the aim at finding a solution,

which is technically feasible, economically viable and socially acceptable [5]. As a result, a variety of methods for olive-mills wastewater treatment were developed, namely aerobic and anaerobic treatment [10], wet oxidation [11], precipitation [12], evaporation [13], treatment by fungi [14], decolourization [3] and others. The main disadvantages of most of these methods is that they don't enable to get rid of pollutants, but they just move them from one place to another. In addition some of them are not adaptable for practical applications, or highly expensive and time consuming. So the research on finding a method that provides a suitable solution is continued.

Nowadays, one of the most intensively studied methods is the photocatalytic degradation of the phenolic compounds using metal oxides. The applicability of photocatalysis has been proven in laboratory scale for a great number of different processes [15]. A variety of catalysts was developed and found to be effective in degradation of wide spectrum of organic compounds [16-24].

Recently an intensive research is being conducted on the photocatalytic treatment of olive-mills wastewater using diffe-

rent catalysts [25-29]. However it must be ensured that in these works either the harmful UV radiation, or expensive catalysts or hazardous chemicals are used. More than 30 different phenolic compounds have been detected in olive-mills wastewater [30]. However the current work aimed at photodegradation of three representative phenolic compounds present in olive-mills wastewater that are gallic acid, oleuropein and resorcinol, using SnO_2 -MgO mixed catalyst and sunlight simulator irradiation. The method presented in this work is suggested to be a model for a simple, low-cost and applicable treatment technology for olive-mills wastewater and can contribute to the solution of one serious environmental problem related to the olive oil industry.

EXPERIMENTAL

Gallic acid, oleuropein, resorcinol, ammonium hydroxide solution, tin(IV) chloride pentahydrate, magnesium chloride hexahydrate, SnO_2 , CdS, methanol, distilled water and all solvents and other chemicals were of analytical grade and purchased from Sigma Aldrich.

Preparation of catalysts SnO_2 -MgO (4:1) and (1:1): Nanoparticles of SnO_2 -MgO (4:1) were prepared by sol-gel method using modified procedure: 3.5 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.507 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 100 mL methanol and stirred for 0.5 h. Then the mixture is added drop-wise within 1 h to solution of 8 mL ammonium hydroxide in 50 mL methanol. After the addition of 70 mL of the salt mixture solution, 2 mL ammonium hydroxide were added to keep the hydroxide excess in the solution to make sure that the hydroxides of both metals form simultaneously. Then, the obtained suspension was stirred vigorously overnight. The resultant gel was separated by the centrifuging at 6000 rpm for 10 min. The supernatant was removed and the residue was washed with methanol. Then the residue collected, dried at 80 °C for 2 h, ground using mortar and pestle and finally calcinated at 500 °C for 5 h. SnO_2 -MgO (1:1) was prepared by the same procedure using appropriate amounts of corresponding reagents.

Samples of the catalysts were characterized by scanning electron microscopy (SEM) with a Nova 200 Nano SEM (FEI) operated at 15 kV. The SEM samples were prepared by placing a thin film of the sample on a carbon tape. Crystal structure identification for the synthesized catalysts was performed by a X'Pert Pro MPD PW3040/60 X-ray diffractometer (XRD) (PANALYTICAL) with Co K_α radiation ($\lambda = 1.79278 \text{ \AA}$) in reflection geometry at a scanning rate of $0.05^\circ \text{ s}^{-1}$ in the 2θ range from 20° to 150° .

Photocatalytic degradation procedure: Photocatalytic activities of the synthesized catalysts were evaluated by the degradation of gallic acid, oleuropein and resorcinol solutions under visible light irradiation provided by sunlight simulator lamp. In each experiment, a given amount of photocatalyst was dispersed in a given volume of gallic acid, oleuropein and resorcinol solutions with certain concentrations. Before illumination, the suspension was magnetically stirred for 1 h to establish an adsorption-desorption equilibrium. At given time interval, the samples were centrifuged and the quantitative determination of gallic acid, oleuropein and resorcinol was performed by UV-visible spectrometry at wavelengths of 212, 280 and 273 nm, respectively.

RESULTS AND DISCUSSION

Preparation of catalyst: Synthesis of mixed metal oxides SnO_2 -MgO nanoparticles was previously performed by sol gel method as reported by Bayal and Jeevanandam [24] in which to a solution of salts of both metals (tin chloride and magnesium methoxide) the ammonium hydroxide is added drop-wise. The formed metal hydroxides are separated and calcinated at high temperatures. In that work, the smallest in size and the most effective nanoparticles in photodegradation of some organic dyes were those of mixed SnO_2 -MgO with the ratio of 4:1 and when the calcination was performed at 500 °C.

However, in the current work a modification on the procedure of synthesis of catalyst was made. That is the solution of metal salts (chlorides of both metals) is prepared, thoroughly stirred and added drop-wise to the solution of 2.5 M ammonium hydroxide at constant and slow rate. This enabled both ions to distribute homogenously and precipitate as hydroxides simultaneously. It is very important for the synthesis of small, with narrow size distribution and effectively mixed nanoparticles of oxides. While in the case of addition of ammonium hydroxide solution to the metal ions solution, the formation of the least soluble hydroxide [$\text{Sn}(\text{OH})_2$] will take place first resulting in bad mixing between the two oxides in the obtained particles and thus the formation of particles with larger size and less efficiency. It is explained on the basis of surface segregation of MgO on SnO_2 nanoparticles. When MgO is introduced in SnO_2 it nucleates as a second phase and migrates to the surface of SnO_2 . MgO covers SnO_2 and suppresses the crystal growth of SnO_2 leading to the reduction of the crystallite size of SnO_2 [24].

The prepared particles have been characterized by scanning electron microscope and powder X-ray diffraction. The morphology of the catalyst particles was examined by SEM (Fig. 1). Fig. 1 shows an overview image in secondary electron (SE) mode for a sample (with 1:1 ratio) after calcination for 5 h at 500 °C.

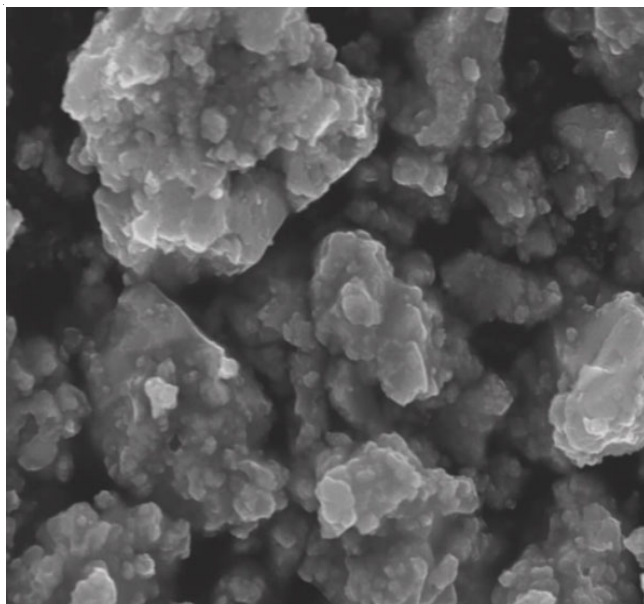


Fig. 1. SEM overview image in topography (SE) mode for the catalyst nanoparticles after calcination at 500 °C

The XRD patterns for both samples (1:1 and 4:1) were almost identical. Fig. 2 shows the diffraction pattern for the mixed SnO₂-MgO oxide particles (ratio 4:1), where the intense reflections at 2θ ~ 31° and 61° correspond to the lattice planes 110 and 211, respectively, of SnO₂ structure with space group P42/mnm (136, tetragonal, PDF No. 04-008-8133). The reflections at 2θ ~ 73° and 94° correspond to the lattice planes 110 and 002, respectively, of MgO structure with space group P3 (143, hexagonal, PDF No. 01-078-4523).

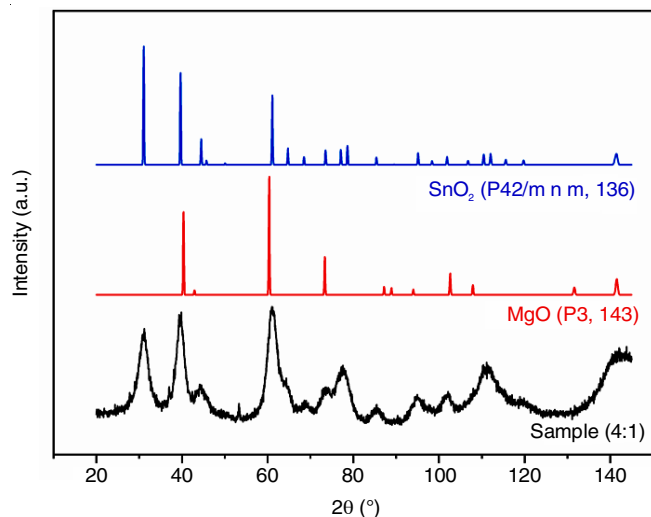


Fig. 2. XRD diffraction patterns for prepared catalysts particles (ratio 4:1) in comparison with the standards SnO₂ and MgO

Assuming the spherical shape of these nanoparticles and using Scherrer's equation [31]: $D = 0.93 \lambda / \Delta(2\theta) \cos(\theta)$, where D is the mean size of the particles, λ is the X-ray wavelength (λ is 1.7927 Å) and $\Delta(2\theta)$ is the line broadening at half the maximum intensity (FWHM) in radians, the mean particle diameter d_{XRD} of the prepared catalyst particles by the modified procedure equals to 4.32 ± 0.42 nm. Which is much smaller than the mean diameter of the particles obtained by the procedure used in work [24] that was in the range of 10-15 nm.

Photocatalytic activity of synthesized nanoparticles of SnO₂-MgO mixed catalyst: The photodegradation of gallic acid, oleuropein and resorcinol using the synthesized catalysts under the sunlight (visible) radiation was determined spectrophotometrically. The degradation percent was calculated by the equation:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t are the absorbances values measured for solutions of gallic acid, oleuropein and resorcinol before and after the degradation experiment at maximum wavelengths of 212, 280 and 273 nm, respectively.

First, in order to prove the fact that the degradation occurs due to the action of the catalyst under the sunlight (visible)

irradiation, the degradation reaction for the three compounds was carried out under the radiation but without catalyst in one case and with catalyst but without radiation in another. In both cases no significant degradation was observed which indicates that both irradiation and catalyst are necessary for the degradation process.

Furthermore, for comparative purposes, a series of catalytic reactions for gallic acid solution using nanoparticles of both synthesized SnO₂-MgO mixed catalysts, SnO₂ and CdS, for 15 min. The results presented in Table-1 show that mixed metal oxides nanoparticles exhibit better degradation efficiency compared to pure SnO₂ nanoparticles and CdS catalyst.

TABLE-1
DEGRADATION PERCENTAGES OF 4.5×10^{-5} M GALLIC ACID BY DIFFERENT CATALYSTS

Catalyst	Degradation (%)
SnO ₂ -MgO (1:1)	34.73
SnO ₂ -MgO (4:1)	40.40
CdS	8.86
SnO ₂	2.40

In addition, it can be noticed from Table-1 that the SnO₂-MgO nanoparticles prepared using $[\text{Sn}^{4+}]:[\text{Mg}^{2+}] = 4:1$ shows the better degradation than SnO₂-MgO nanoparticles with ratio of 1:1, which confirms the results reported in previous work [24]. The amount of MgO plays a prominent role in deciding the photocatalytic activity. Although when MgO is present in SnO₂-MgO, the recombination of holes and electrons decreases and hence the photocatalytic efficiency increases, but when the concentration of MgO increases beyond a certain, the excess MgO covers the surface of SnO₂ thus preventing the absorption of sunlight. This in turn reduces the photocatalytic efficiency. This explains why SnO₂-MgO prepared using $[\text{Sn}^{4+}]:[\text{Mg}^{2+}] = 4:1$ shows the better degradation than SnO₂-MgO prepared using $[\text{Sn}^{4+}]:[\text{Mg}^{2+}] = 1:1$ [24].

Therefore the subsequent photodegradation reactions were carried out using the nanoparticles of the catalyst SnO₂-MgO (4:1).

Using the optimum catalyst amount is important as it enables to minimize the excess of catalyst and to ensure maximum absorption of photons. Therefore, to evaluate the effect of the amount of catalyst used on the photocatalytic efficiency of the prepared SnO₂-MgO (4:1), the degradation % of gallic acid from its 4.5×10^{-5} M solution, with different amounts of catalyst (2.5 mg, 5.0 mg and 7.5 mg catalyst per 5 mL solution) was determined after 30 min of irradiation. The results are presented in Table-2.

The low degradation efficiency at higher concentrations of catalyst (Table-2), is related to the screening effect of excess particles and preventing light from penetration. From the results, the higher photocatalytic efficiency was demonstrated when 2.5 mg of catalyst were used. So this amount was used in subsequent reactions of this work.

TABLE-2
DEGRADATION % OF 4.5×10^{-5} M GALLIC ACID AFTER 30 min RADIATION AND USING DIFFERENT AMOUNTS OF CATALYST

Catalyst mass	Temperature (°C)			pH			Degradation (%)		
	2.5 mg	5.0 mg	7.5 mg	2.5 mg	5.0 mg	7.5 mg	2.5 mg	5.0 mg	7.5 mg
	39.4	39.1	39.9	8.12	8.37	8.79	40.4	5.8	2.9

In the next part of work, the photocatalytic degradation of the three phenolic compounds (gallic acid, oleuropein and resorcinol) using the catalyst $\text{SnO}_2\text{-MgO}$ (4:1) with the amount of 2.5 mg per 5 mL solutions was studied. In addition the influence of various parameters like radiation time, concentration of the phenolic compound on the photocatalytic activity is investigated. For this three concentrations of each compound (2.5×10^{-5} , 4.5×10^{-5} and 6.0×10^{-5}) were used in the degradation trials under the same conditions, over 2 h of exposure to the light. Also the temperature and pH of the process were monitored. The results are presented in Tables 3-5.

The degradation reaction of the three compounds was stopped after 2 h since the degradation shows only a slight increase beyond this time. Also, as can be noted from Tables 3-5, the temperature rises significantly during the reaction time (120 min) and exceeds 40°C in some cases. This takes place due to heat absorbed by the solution from the radiation source. However, the temperature remained within such a range that doesn't cause a significant effect on the degradation percentage, which was confirmed when the reaction was performed with radiation but without catalyst.

Through the degradation time, the change in pH value don't exceed one unit, which indicate that degradation not affect the pH. And this slight change in pH can be explained by the solubility of MgO in water. However, the effect of pH on the degradation efficiency could not be studied, because at high pH (> 10) the gallic acid is unstable [32] and at acidic pH the catalyst specially MgO is dissolved.

From Table-3, the final degradation percent of gallic acid after 2 h in the three concentrations was around 90 %, but it

was different during the first hour. During the first hour the concentration of the initial solution decreased, so in the second hour the reaction completes with lower concentrations.

The difference in the degradation percents during the first hour can be explained that the reaction occur on catalyst surface which has constant number of active groups and in the three trials this number is the same, so the ratio of gallic acid which absorbed on the catalyst surface to the initial gallic acid concentration present in the reaction is different in the three trials. In addition, during the first degradation hour the rate of reaction was fast, whereas the degradation during the second hour is slower. This related to that in the first hour reactants exist in higher concentrations. However, in the second hour, the concentration is lower.

Table-4 represents the degradation percent, temperature and pH data for the photocatalytic reaction of oleuropein with different concentrations, over 2 h by 2.5 mg catalyst and 5 mL of oleuropein solution. After 2 h radiation the highest degradation percent at concentration (6.0×10^{-5}) M was around 51 %, at concentration (4.5×10^{-5}) M was 16.7 % and at concentration (2.5×10^{-5}) M was 14.9 %.

Table-5 represents the degradation percentage, temperature and pH data for (6.0×10^{-5}), (4.5×10^{-5}) and (2.5×10^{-5}) M solutions of resorcinol, over 2 h by 2.5 mg catalyst and 5 mL of resorcinol solution. The maximum degradation percent was achieved during the first 30 min of reaction which was around 42 % at concentration (6.0×10^{-5}) M, 48 % at concentration (4.5×10^{-5}) M and 51.5 % at concentration (2.5×10^{-5}) M. After that period no significant change in conversion was observed. It should be noted that there is a clear difference in

TABLE-3
DEGRADATION (%) OF GALLIC ACID WITH DIFFERENT CONCENTRATIONS

Concentration $\times 10^{-5}$	Temperature ($^\circ\text{C}$)			pH			Degradation (%)		
	2.5	4.5	6.0	2.50	4.50	6.00	2.5	4.5	6.0
15 min	34.8	29.0	39.9	7.68	8.41	8.37	62.2	40.7	22.5
30 min	35.7	37.0	38.1	8.01	7.80	8.41	76.8	54.4	35.7
45 min	35.0	31.8	37.4	8.32	8.26	8.59	79.9	75.5	56.8
60 min	35.5	39.4	38.0	8.49	8.12	8.47	77.7	76.0	61.6
120 min	36.2	40.2	41.1	8.85	7.94	8.80	89.2	89.4	88.0

TABLE-4
DEGRADATION (%) OF OLEUROPEIN WITH DIFFERENT CONCENTRATIONS

Concentration $\times 10^{-5}$	Temperature ($^\circ\text{C}$)			pH			Degradation (%)		
	2.5	4.5	6.0	2.50	4.50	6.00	2.5	4.5	6.0
15 min	33.0	35.1	32.1	7.62	7.24	7.76	1.9	0.9	1.5
30 min	41.3	43.0	39.0	7.51	7.78	7.62	13.0	1.3	5.4
45 min	40.6	37.3	41.0	7.62	7.48	7.58	14.0	7.7	6.0
60 min	38.8	40.2	44.2	7.58	7.75	7.12	13.5	9.8	50.2
120 min	37.4	30.2	41.1	7.84	7.53	7.72	14.9	16.7	51.1

TABLE-5
DEGRADATION (%) OF RESORCINOL WITH DIFFERENT CONCENTRATIONS

Concentration $\times 10^{-5}$	Temperature ($^\circ\text{C}$)			pH			Degradation (%)		
	2.5	4.5	6.0	2.50	4.50	6.00	2.5	4.5	6.0
15 min	21.5	35.5	39.1	7.05	7.36	8.02	46.3	36.1	41.8
30 min	32.5	40.3	40.0	7.45	7.73	8.27	51.3	47.9	42.3
45 min	43.5	45.1	43.0	7.45	7.62	8.05	51.4	48.7	41.4
60 min	42.5	41.1	42.0	7.67	7.51	8.35	49.1	47.5	41.2
120 min	44.0	33.2	40.5	7.05	7.17	7.22	51.4	47.9	42.5

the rates of degradation reactions of the three compounds in the first and second hours of reaction time. For gallic acid and resorcinol the rate of degradation in the first 45 min was much higher than in the next period, while the oleuropein conversion occurs at a very slow rate in the 45 min. These facts can be explained basing on the exact knowledge about differences in the mechanisms of their degradation, that results from the differences in their structures, needs further specific investigation.

Conclusion

Mixed metal oxides SnO₂-MgO nanoparticles having size of 4.32 ± 0.42 nm were successfully synthesized using modified sol-gel procedure. The photoactivity of the prepared catalyst was investigated in the degradation of gallic acid, oleuropein and resorcinol as model components of phenolic compounds contained in olive-mills wastewater. Our results indicate that 50-90 % degradation occurs after 1-2 h of irradiation under visible light for different concentration of the three compounds. The optimum amount of catalyst was 2.5 mg of catalyst for each 5 mL solution. The results of current work can serve a basis for a low-cost method for olive-mills wastewater treatment.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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