PHOTOCATALYTIC TREATMENT OF OLIVE MILL WASTEWATER BY NANO-GO/M COMPOSITE, RECOVERY AND REUSE OF NANOPARTICLES AND TREATED WASTEWATER

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Abstract- Olive mill wastewater (OMW) is an important environmental problem, particularly in the Mediterranean countries such as Turkey. In order to solve this problem, the effective performance of photocatalysis technique in the treatment of OMW has been investigated using graphene oxide magnetite (Nano-GO/M) composite. In the present work, the effects of increasing Nano-GO/M concentrations (1 g/L, 2 g/L, 3 g/L and 5 g/L), irradiation times (15, 30, 45 and 60 min) and pH (4, 7 and 10) were studied. The maximum photocatalytic pollutant removal efficiencies for COD, total phenol and TS obtained under 300 W UV light. They were 86%, 94% and 96% at the optimum Nano-GO/M concentration (2 g/L). Nano-GO/M could be reused after six sequential cycle with no significant lost. Moreover, two different polyphenol, namely gallic and p-coumaric acid, concentrations were measured. The treated wastewater can be used as irrigation purpose by measuring some additive parameters.

Index Terms— Graphene, Olive Mill Wastewater, Photocatalysis, Recovery

I. INTRODUCTION

Mediterranean countries show great potential on producing olive oil. In oil extraction processes, two type of byproducts occur, which are olive mill wastewater (OMW) and solid cake [1]. These oil extraction processes produce great amounts of OMW. OMW is a recalcitrant effluent, with a strong odor, an acidic pH, high C/N ratio and high conductivity. OMW shows phytotoxic and antimicrobial characteristics due to high concentrations of organic compounds makes OMW highly problematic wastewater [1]. OMW treatment is a very important issue for environmental protection and has been studied by several methods such as ozonation [2], physicochemical pretreatment [3], fenton [4], membrane processes [5], [6], and [7]. Alternative treatment methods such as treating OMW with nanoparticles showed a great potential. Graphene oxide (GO) is a new form of carbon materials that has unique electrical, thermal and mechanical properties [8]. As a novel two-dimensional (2D) material, graphene (G) and graphene oxide (GO) have drawn an increasing attention nowadays. GO can be obtained after oxidization of G and shares similar advantages with G. So, there are a lot of oxygen-containing surface functional groups such as epoxy (C–O–C), hydroxyl (OH) and carboxyl (COOH) on GO surfaces [9]. The existences of oxygen-containing functional groups make GO participate in various modifications, and thus lots of GO-based multifunctional materials have been prepared and used for the removal of environmental contaminants [9]. Recently, iron oxide nano particles (NPs) are being discovered for organic pollutant removals, especially for the treatment of large-volume water samples and fast separation via employing a strong external magnetic field [10]. In this work, a novel nano material, namely nano graphene oxide magnetite (Nano-GO/M), was synthesized and characterized by scanning electron micros- copy (SEM) and Fourier transform infrared (FTIR). Then, photocatalysis of OMW was studied under UV light irradiation via Nano-GO/M composite. The main objectives of our study were: (1) to obtain optimum operational conditions for the maximum treatment of OMW efficiently, (2) to recover the Nano-GO/M and (3) to investigate the polyphenol (gallic and p-coumaric acid) concentrations (4) and to determine the quality of treated effluent wastewater.

II. MATERIALS AND METHODS

A. OMW and Chemicals
OMW effluent was collected from an olive mill industry (Aydın/Turkey) and used after primary settling. Graphene (Agean Nanotech Chemical Ltd., Turkey) and Magnetite (Synergy Laboratory Products Ltd., Turkey) were bought externally. Demineralized water was used for preparation of reagents solutions. 0.1 M HCl and 0.1 M NaOH are used to adjust pH vales of OMW. Gallic acid was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). p-coumaric acid was purchased from Fluka (Buchs, Switzerland). Trifluoroacetic acid (TFA), purchased from Merck (Hohenbrunn, Germany), was of analytical grade. Methanol of HPLC grade was purchased from Fisher (Fairlawn, NJ).

B. The Synthesis of Nano-GO/M Composite
Graphene (5 g) was dispersed in 120 ml H_2SO_4 by adding 2.5 g of $NaNO_3$ in teflon coated flask on a magnetic stirrer for 30 min at 18°C. After stirring the mixture, 15 g of $KMnO_4$ was added slowly, and

continued to stir overnight, at 18°C. Then, 150 ml H_2O was added and continued to mixing a day at 98°C. Later, 50 mL 30% H_2O_2 was added to the final mixture. The mixture was washed with 5% HCl and deionized water for many times then, centrifuged and dried under vacuum for purification the GO which was obtained in a solid phase [11]. The Fe_3O_4 NPs were dispersed in 25 mL water and added to 50 mL GO aqueous solution. This mixture contained 1 mg Fe^{+3}/1mL GO and stirred at 60°C through 1 h. The nano-composite was collected by using a magnet from the outside of the glass reactor and washed with water three times [12].

C. Photocatalytic Experiments

Experiments were conducted in a system which is well-sealed and constructed with stainless steel material. Quartz glass reactors (with dimensions of 38 cm x 3.5 cm) coated with teflon and 10 UV lambs (each one has a power of 30 watt) were used at room temperature of 20-25 C. The effects of Nano-GO/M composite concentrations (1, 2, 3, and 5 g/L) irradiation times (15, 30, 45 and 60 min), pH (4, 7, 10) on the treatment of OMW were investigated. After experiments the Nano-GO/M composite separated magnetically, then supernatant was analyzed. All the experiments data were found from the duplicates analysis and the results presented as the mean values of the duplicates samples.

D. Analytical Methods

COD and TS were measured according to Standard Methods APHA 5220A and 2540B [13]. pH was measured with WTW probes. Phenols were measured using the Merck/WTW 14551 phenol reagent kits in a Photometer Nova 60/Spectroquant. Gallic and p-coumaric acid were analyzed with HPLC. Agela XBP-C18 (5 mm, 4.6 mm 150 mm, Agela, Newark, DE) was utilized for succeeding optimization. The flow rate of the mobile phase was kept at 0.5 mL/min. Mobile phase A was water containing 0.02% TFA, and phase B was methanol containing 0.02% TFA. The gradient conditions were as follows: 0-5min, 25% B; 5-10 min, 25-30% B; 10-16 min, 30-45% B; 16-18 min, 45% B; 18-25 min, 45-80% B; 25-30 min, 80% B; 30-40 min, 80-25% B. The temperature of column was controlled at 25 °C. Injection volume was 10 μL. The detection wavelengths of DAD were set at: 254 nm. Prior to each run, the HPLC-DAD system allowed to warm, and the baseline was monitored until it was stable before sample analysis.

E. Characterization of Nano-GO/M Composite

Fourier transform infrared (FT-IR): FT-IR spectra were carried out to recognize the functional groups in the synthesized composites and to confirm the chemical bonding between Fe_3O_4 and graphene. The FT- IR spectra of the Nano-GO/M before and after treatment conditions were measured with Perkin Elmer FTIR Spectrum System using BX and KBr method.

SEM: The morphological and structural observation of raw and treated Nano-GO/M composite was made on a scanning electron microscope VegaII/LMU (Tescan, Czech Republic).

F. Reusability Studies of Nano-GO/M

In order to reuse Nano-GO/M composite after first treatment step, the composite magnetically separated and then regenerated using ethanol (at pH 2.0) as eluent [14]. Nano-GO/M composite dried under vacuum then this composite reused for second treatment process to treat OMW again.

III. RESULTS AND DISCUSSIONS

G. Physicochemical Properties of Nano-GO/M

The produced nano particles (raw Nano-GO/M composite) were characterized using FTIR and SEM analysis. In the spectrum of Nano-GO/M, the peaks at 2359, 1568 cm^{-1} are the characteristics spectrum of benzene ring of Nano-GO/M while the peak at 1073 cm^{-1} is the characteristic spectrum of the C–OH rings of Nano-GO/M (Fig.1). This confirms the presence of graphene oxide peak at 600 cm^{-1} which is the characteristics of Fe_3O_4 giving an evidence of the successful preparation of the Nano-GO/M as reported by Huamin et al. [15].
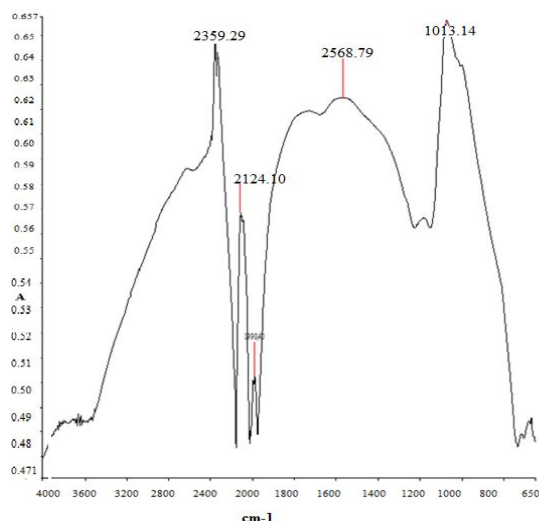

Figure 1. FTIR analysis of raw Nano-GO/M (cm^{-1}: wave number and A-%: percent transmittance)

The SEM images of synthesized GO, raw Fe_3O_4 nanoparticles, synthesized Nano-GO/M composite can be seen in Figs.2, 3 and 4. The spherical Fe_3O_4 nanoparticles are placed onto GO sheets [16]. The Fe_3O_4 particles disperse on GO and there are some interspaces among them Fe_3O_4 and GO dispersed densely and evenly on the surface of the Nano-GO/M composites and it have a core shell structure.
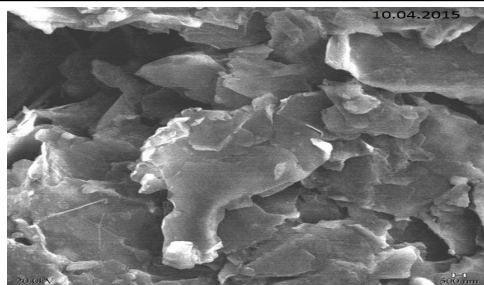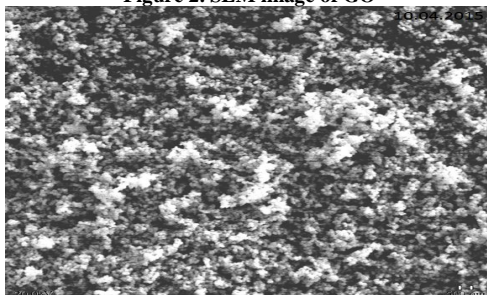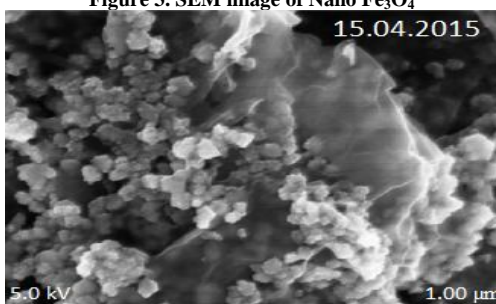
Figure 2. SEM image of GO

Figure 3. SEM image of Nano Fe₃O₄

Figure 4. SEM imagine of raw Nano-GO/M (1 μm)

H. Photocatalytic Experiment Results

The average COD, total solids (TS), phenol contents of the raw olive mill effluent were 117000 mg/L, 84250 mg/L, 660 mg/L, respectively, while its average pH value was 3.5- 4.1 (Table I). The samples were stored at room temperature.

Table I. Characterization of OMW

Parameters	Initial Value (mean ±SD)
COD	117000 mg/L± 1000 mg/L
Total Phenol	660 mg/L±100 mg/L
Total Solids	84250 mg/L±1000 mg/L
pH	3.5-4.1

After characterizing OMW, photocatalytic studies were carried out at increasing Nano-GO/M concentrations, pH
values and irradiation times.

I. The Effects of Nano-GO/M Composite Concentrations

Different catalysts dosages (1, 2, 3 and 5 g/L) were tested, and the removal of the organic pollutants in OMW was measured by following the reduction of the COD, TS and total phenol values during the photocatalytic experiments. Among the irradiation times, 45 min gave the best results. Therefore, all experiments were realized after 45 min and under 300

W UV light. The photodegradation removals of each pollutant increased rapidly and significantly with the increasing of Nano-GO/M concentration from 1 g/L to 2 g/L for all pollutant parameters (COD, TS and total phenol). The photo-removals of these pollutants increased from 60%, 68% and from 65% up to 88%, 96% and 91%, respectively. The maximum removal yields of COD, TS and total phenol were obtained as 90%, 97% and 94% at 3 g/L Nano-GO/M concentration (Fig. 5). With increasing Nano-GO/M composite concentration from 1 g/L to 2 g/L and to 3 g/L, more surface area of the composite is generated and more OH⁻ radicals are formed, therefore removal efficiencies were increased. However, as the concentration of Nano-GO/M composite was increased from 3 to 5 g/L, the total removal yields remained almost the same. In order to avoid using too much catalyst, 2 g/L Nano-GO/M concentration was selected as optimum dosage.
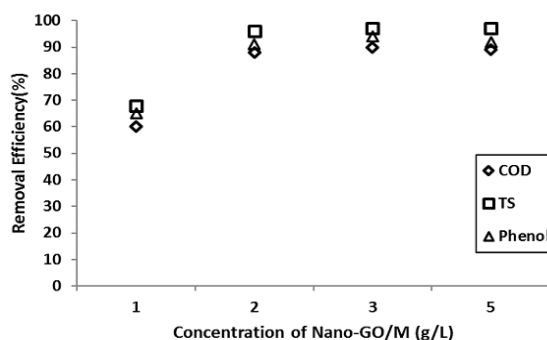

Figure 5. Removal yields of all pollutant parameters (pH 4, T: 20°C, irradiation time: 45 min UV power: 300 W)

J. Effects of Irradiation Time on the Treatment of OMW under UV Light

With increasing of irradiation times under UV light from 15 up to 60 min, COD, TS and total phenol removal efficiencies were increased. The removal efficiencies were varying between 63-89% for COD, 70-96% for TS and 68-92% for total phenol after adding 2 g/L Nano-GO/M composite at room temperature and at original pH of OMW under 300 Watt (Fig. 6). 45 min irradiation time was selected as optimum irradiation time. Further increase in irradiation time (60 min) did not increase the removal efficiencies significantly.
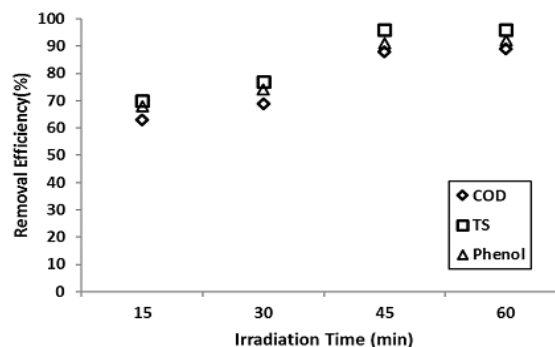

Figure 6. Removal yields of all pollutant parameters at increasing irradiation times (pH 4, T: 20°C, UV power: 300 W)

K. Effects of pH Levels on the Treatment of OMW under UV Light

The initial pH value of wastewater plays an important role in the photocatalytic degradation of organic compounds. Fig. 7 demonstrates the effect of pH on the photocatalytic degradation of organic pollutants in OMW on the surface of Nano-GO/M composite. Original pH of OMW (pH=4), pH 7 and pH 10 were studied to investigate the optimum pH for removal of COD, TS and total phenol from OMW. All experiments realized with 2 g/L Nano-GO/M composite, under 300 Watt 45 min irradiation time at room temperature (Fig. 7). Increasing the pH levels decreased removal efficiencies of all pollutants. The maximum removal efficiencies were obtained as 88%, 96% and 91% at pH 4.
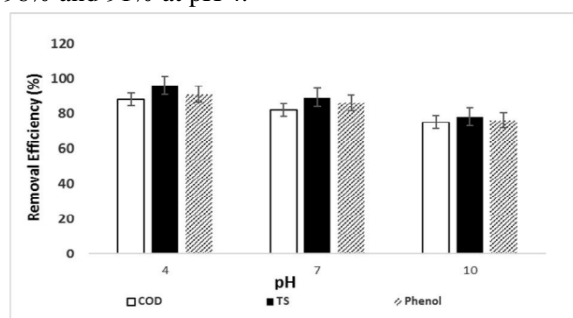

Figure 7. Removal yields of all pollutant parameters at increasing pH levels (T: 20°C, irradiation time: 45 min UV power: 300 W)

L. Measurement of the Concentration of Phenolic Compounds by HPLC in Treated OMW with Nano-GO/M Composite Under UV Irradiation

Raw OMW and treated OMW with 2 g/L Nano-GO/M composite under 45 min UV irradiation (300 Watt) at original pH of OMW (pH 4) and a temperature of 20 ^{0}C, gallic acid and p-coumaric acid polyphenols measured with HPLC. Gallic acid and p-coumaric acid acid amounts were measured as 65.51821 mg/L and 43.85360, respectively, in raw OMW. After treatment of OMW with UV, whole of gallic acid in OMW was removed. The yield was 100% after photooxidation. On the other hand, after treatment under UV, p-coumaric acid was measured as 30.1684 mg/L. Removal efficiency of, p-coumaric acid calculated as 31.20% (Table II).

Table II. Removal Efficiencies of polyphenols (gallic acid, p-coumaric acid) in OMW.

Polyphenols	Raw OMW (mg/L)	Treated OMW (mg/L)	Removal Efficiency (%)
Gallic acid	65.51821	0	100
p-coumaric acid	43.85360	30.1684	31.20

M. Reusability Studies of Nano-GO/M Composite

Recovery of Nano-GO/M composite is a key factor of decreasing the cost of treatment of OMW and an eco-friendly treatment approach. In this study, Nano-GO/M composite were regenerated and reused after first use.

Table III. Calculation of COD, TS and total phenol yields by recovery of Nano-GO/M composite (T: room temperature, Nano-GO/M composite concentration: 2 g/L, UV irradiation time: 45 min, UV power: 300 Watt, pH: 4 (original pH of OMW).

Pollutant/Treatment Step		1.	2.	3.	4.	5.	6.
COD	Initial Concentration (mg/L)	117000	14040	1825,2	292,032	58,4064	15,76973
	Final Concentration (mg/L)	14040	1825,2	292,032	58,4064	15,76973	5,046313
	Removal Yield (%)	88	87	84	80	73	68
TS	Initial Concentration (mg/L)	84250	11795	1887,2	358,568	82,47064	24,74119
	Final Concentration (mg/L)	11795	1887,2	358,568	82,4706	24,74119	9,401653
	Removal Yield (%)	86	84	81	77	70	62
Total Phenol	Initial Concentration (mg/L)	660	59,4	5,94	0,7128	0,128304	0,032076
	Final Concentration (mg/L)	59,4	5,94	0,7128	0,1283	0,032076	0,009944
	Removal Yield (%)	91	90	88	82	75	69

2 g/L Nano-GO/M composite were used for six times under 45 min UV irradiation (300 Watt) for 1 liter OMW at original pH of OMW (4), at room temperature. COD, TS and total phenol parameters measured to determine the removal of OMW wastewater after six sequential with the same Nano-GO/M composite. All results were shown in Table III for COD, TS and total phenol, respectively.

Considering the final concentrations of COD, total phenol and TS, in the treated OMW after six times, this treated wastewater can be discharged to the sewage systems according to discharge limits illustrated in Regulation of Water Pollution Control, The Official Newspaper dated 31.12.2004' 'The

Official Newspaper Numbered 25687 (2004), (discharge limits of COD and total phenol; 4000 mg/L and 20 mg/L, respectively) (Table IV).

Table IV. Discharge limits according to Regulation of Control of Water Pollution (2004) a; not considering these parameters for wastewater assessment

Parameter	Sewer systems, in the infrastructure systems ending with ultimate treatment
Temperature (°C)	40
pH	6.5-10.0
COD (mg/L)	4000
Total Phenol (mg/L)	20
Total Nitrogen (mg/L)	- [a]
Total Phosphorous (mg/L)	- [a]

Treated OMW can be used for irrigation water, (according to COD and total phenol parameters) however pH, salt, conductivity, ions (Ca^{+2} and Mg^{+2}), oil and grease, pathogen microorganism, heavy metal concentration in OMW must be measured before using for irrigation water 'Regulation of Wastewater Treatment Plant Technical Methods,' Table E7.2, (2010) for irrigation of treated wastewater (Table V), pH of OMW must be 6-9.

Table V. Limits for irrigation of treated wastewater according to Wastewater Treatment Plant Technical Methods Notification' Table E7.2., (2010)

Parameters	Units	The degree of damage in use		
		None (I.class water)	Less-Middle (II.class water)	Dangerous (III.class water)
Salinity				
Conductivity	µS/cm	< 700	700-3000	>3000
Total Dissolved Solids	mg/L	< 500	500-2000	>2000
Permeability				
SAR$_{Tad}$ 0-3		EC ≥0.7	0.7-0.2	< 0.2
3-6		≥ 1.2	1.2-0.3	< 0.3
6-12		≥ 1.9	1.9-0.5	< 0.5
12-20		≥ 2.9	2.9-1.3	< 1.3
20-40		≥ 5.0	5.0-2.9	< 2.9
Specific ion toxicity				
Sodium (Na)				
Surface Irrigation	mg/L	< 3	3-9	> 9
Trickling Irrigation	mg/L	< 70	> 70	
Chloride (Cl)				
Surface Irrigation	mg/L	< 140	140 −350	> 350
Trickling Irrigation	mg/L	< 100	> 100	
Boron (B)	mg/L	< 0.7	0.7-3.0	> 3.0

CONCLUSSIONS

OMW treatment was studied with photooxidation mechanism using Nano-GO/M composite. According to the characterization analysis of the Nano-GO/M composite, it was synthesized successfully. The effects of Nano-GO/M dosage, irradiation time and pH levels on the OMW treatment efficiencies were investigated. Among the Nano-GO/M concentrations (1, 2, 3 and 5 g/L) and irradiation times (15, 30, 45 and 60 min),

optimum Nano-GO/M concentration and irradiation time were selected as 2 g/L and 45 min, respectively. For maximum removals of COD, TS and total phenol (86%, 94% and 96% under 300 W UV irradiation). the optimum pH was found at pH: 4 is the original pH of OMW. This decrease the cost of the chemical utilized in both photocatalytic studies. In addition, removal of polyphenols (gallic acid and p-coumeric acid) were investigated.

According to the results, gallic acid and p-coumeric acid removal efficiencies were found as 100% and 31.20%. Reusability studies of Nano-GO/M composite showed that the composite can be used after six times for removals of COD, TS and total phenol. The treated wastewater quality indicates the first class.

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