

TiO₂, WO₃, AND V₂O₅, SUPPORTED ON ACTIVATED CARBON: PREPARATION, STRUCTURAL AND CATALYTIC BEHAVIOUR IN PHOTOCATALYTIC TREATMENT OF PHENOL AND LIGNIN FROM OLIVE MILL WASTEWATER

Ali Imran Vaizogullar¹, Mehmet Ugurlu^{1*}, Aylin Ayyildiz², Selman Ilteris Yilmaz², Abdul J Chaudhary³

¹Vocational School of Healthcare, Med Lab Program, Mugla Sitki Kocman University 48000 Mugla, Turkey

²Department of Chemistry, Faculty of Science, Mugla Sitki Kocman University, 48000 Mugla, Turkey

³Institute for the Environment, Brunel University, London, UB8 3PH, UK

ABSTRACT

The photocatalytic degradation of olive mill wastewater (OMW) of TiO₂/V₂O₅/AC and TiO₂/WO₃/AC (activated carbon) catalysts, prepared by a sol-gel method in aqueous solution was investigated. Initially, the TiO₂/V₂O₅/AC and TiO₂/WO₃/AC nanoparticles were obtained using a sufficient thermal treatment by gradually increasing the temperature from 300, 400 and 500°C with 1 h intervals for a total of 3 h. Then, the characterizations of these materials were carried out using (SEM), (TEM), (EDX), (FTIR) and X- (XRD). Secondly; the photocatalytic degradation of these materials has been investigated in OMW using ultraviolet (UV), hydrogen peroxide (H₂O₂) and nanoparticles. Initially, chemical coagulation experiments with lime and alum have been carried out to obtain more treatment. In the photolytic degradation, the effect of catalysis, times, pH, H₂O₂ and temperature were selected as parameters. The results show that the removal percentage of color, phenol and lignin increased with the use of H₂O₂ and O₃ together. The percentage removals of color for TiO₂/WO₃/AC, TiO₂/V₂O₅/AC were 89.55 and 86.30% respectively. In addition, the percentage removals for phenol were 94.30, 96.26% and for lignin 51.96 and 48.08%, respectively. Optimum values for the degradation of color and phenol were found at pH 7.0 using TiO₂/WO₃/AC, and TiO₂/V₂O₅/AC, whereas, the optimum degradation for lignin was achieved when the solution was pH<5.0 and pH>9.0 for the same nanocomposite materials. The optimum time and temperature were found 24 h at 308K. The pseudo-first order model was applied and R² values were from 0.90 to 0.99.

KEYWORDS:

Activated carbon, Phenols, Waste water treatment, TiO₂, O₃, V₂O₅

INTRODUCTION

Olive mill wastewater (OMW) generated by the olive oil extracting industry is a major pollutant due to its phytotoxic high organic load and antibacterial phenolic compounds which are not biodegradable in the environment. Mediterranean countries are mostly affected by this serious environmental problem, since they are responsible for 95% of the worldwide olive-oil production [1-4].

There are many methods used for OMW treatment, as proposed by Kestioglu et al. [5]. The advanced oxidation processes are physico-chemical treatment methods which commonly use either ozone or Fenton's reagent in the presence and absence of UV radiation. In this study, advanced oxidation processes were used under different conditions to remove both COD and phenol. The data obtained show that above 99% removal for both COD and total phenol was achieved with both H₂O₂/UV and O₃/UV combinations. Another treatment of OMW consisting the application of an integrated centrifugation-ultra filtration system allows an efficient reduction of pollution and a selective separation of some useful product [6]. Traditional physical and chemical techniques, such as flocculation, coagulation, filtration, evaporation, the electrochemical treatment of OMW and burning systems also partially solve the problem [7-10]. In addition, Oukili et al.[11] have investigated activated clay as adsorbents for removal of organic compounds from OMW, the removal of phenolic compounds have also effectively been investigated using lime.

OMW been tested with a mixture of aluminium sulfate and ferric chloride, calcium hydroxide solution and also acidifying of the waste with hydrochloric acid solution [10]. They have determined the clarifying percent of the wastewater. Calcium hydroxide and aluminum sulphate have also been used besides magnesium sulphate COD value dropped to 20-30% with calcium hydroxide, when added until the pH of the waste reached [10-14]. The organic content of OMW was oxidized using monopersulfuric acid in several biological studies to

eliminate the pollution effect of OMW [15,16]. The biodegradation of phenolic compounds have been investigated by using aerobic microbial cultures too [5, 17]. Kai and co-workers [18] have studied for the degradation of Dimethyl Phthalate using photo-fenton process. Aref and co-workers [19] have performed the degradation of 2-Nitrophenol from Petrochemical Wastewater. As a result, there is no such economical and easy solution for the removal of organic compounds from OMW.

A commonly applied method for removal of COD, colour, phenol and organic compounds from industrial effluents is Advanced Oxidation Processes (AOPs). AOPs are related to the formation of OH radicals, accelerating oxidative degradation of numerous organic compounds dissolved in wastewater. AOPs include several processes such as ultraviolet/ozone (UV/O₃), ultraviolet/hydrogen peroxide (UV/H₂O₂), and ozone/hydrogen peroxide [20, 21]. In the present study, decolourization and removal of some organic compounds from OMW were aimed by using TiO₂/V₂O₅/AC and TiO₂/WO₃/AC nanoparticles. In addition, there is no study reported in the literature related to use of O₃, UV, TiO₂, WO₃, V₂O₅ and AC together in the OMW treatment.

MATERIALS AND METHODS

Characterization of OMW. OMW samples were collected from an olive-oil producing plant (Mugla) using a modern production process. No chemical additives have been used during the olive oil production.

The pre-treatment experiments. Pre-refining process was carried out to obtain the more removal from OMW. In this process, the chemical coagulation technique and the mixture of lime and alum (Aluminum sulfate) in certain proportions were used. In this step, 1g of lime and 4g of alum were added in 1L of crude OMW and stirred for 15 minutes at 100 rpm/min then for 30 minutes at 30 rpm/min slowly. The mixture was set aside for 24 hours to have formation of flocks and precipitation [22]. Then, filtrated wastewater was maintained in appropriate medium for photocatalytic experiments.

TiO₂/V₂O₅/AC and TiO₂/WO₃/AC nanoparticles preparation. In this study, 120 mL ethanol and 20 mL tetra-n-butyl titanate were mixed, then 10 mL acetic acid, 2 mL distilled water few drops of acetone were added and stirred for 3 hours (solution A). After that, 8-20 mesh AC was activated with nitric acid, washed with distilled water and left for drying. Acid activated was stirred for three hours with the previously prepared solution (solution A). After completion of the reaction, (NH₄)₁₀H₂(W₃O₇)₆ solution was added drop-wise and kept under constant temperature to get TiO₂/W₂O₅/AC particles.

Prepared particles were filtered and dried at 100°C for 3 hours. Dried samples were thermally activated at 300, 400 and 500°C each for one hour. Same procedure was repeated to prepare TiO₂/V₂O₅/AC particles but NH₄VO₃ solution was used instead of (NH₄)₁₀H₂(W₃O₇)₆. Both type of particles were characterized. The crystalline phase structure of the sample was examined by XRD (Rigaku-Smart Lab) using copper K radiation ($\lambda = 0.154056$ nm). The FT-IR spectra these particles were recorded on Thermo-Scientific, (Nicolet IS10-ATR) spectrophotometers. The size and shape of the particles were investigated by SEM (JEOL JSM-7600F) and TEM (JEOL JEM 2100F HRTEM). Elemental analysis was carried out using (JEOL JSM-7600F) EDAX analyzer with SEM.

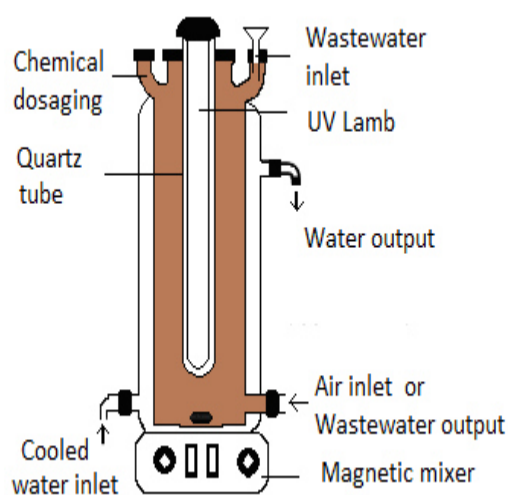


FIGURE 1
Appearance schematic of UV reactor used at the experimental study

Photolytic experiments. In photolytic experiments, the effects of reaction temperature, catalysis amount, OMW concentration, solution pH and addition of H₂O₂ were investigated. In all the experiments, color, phenol and lignin concentration changes taking place in OMW were analysed through spectroscopic methods. OMW samples carried out the pre-treatment were directly treated using the specially designed UV reactor (Height: 60cm, volume: 1.0 L). This reactor consists of a closed system having an UV lamp (GPH846TL, 17W, 254 nm), properties of fixed mixing and cooling and oxygen entry (Fig 1). The pH of (the) solution was adjusted using diluted HCl and NaOH solutions. All experiments were run at least twice.

Determination of color changes. Maximum wavelength in the visible region and absorbance intensity were 420 nm and 4.0, respectively on OMW using Dr. Lange spectro-photometer. Color changes were investigated at this wavelength and the color

removal (%) was calculated using the following expression.

$$\text{Color removal (\%)} = \frac{A_x^0(\text{crudeOMW}) - A_x(\text{treated})}{A_x^0(\text{crudeOMW})} \times 100$$

Lignin and phenol measurement. APHA Standard Methods were used for the measurements of lignin and phenol in OMW (APHA 2005). The concentration of lignin and lignin degradation compounds were calculated of developing color resulting from the reaction of phenol with 4-aminoantipyrine and reaction of lignin with folin phenol reagent (tungstophosphoric and molybdophosphoric acid) at λ_{max} 700 nm, respectively. The concentrations of phenol were determined analyzing the developed colour resulting from the reaction of phenol with 4-aminoantipyrine at λ_{max} 500 nm [22].

RESULTS AND DISCUSSION

SEM analyses. The surface morpholog of all samples was investigated using a SEM and images are given in Figure 2(a, b, c and d). Figure 2a shows the typical SEM micrograph at the lower magnification of the AC. As seen in the Figure 2a, AC structure has porous morphology. Figure b shows also AC

structure that obtained with at the higher magnification. The SEM images of $\text{TiO}_2/\text{V}_2\text{O}_5$ and $\text{TiO}_2/\text{W}_2\text{O}_5$ doped AC samples were given in Figure 2c and 2d. As seen in the Figure 2c and 2d, $\text{TiO}_2/\text{V}_2\text{O}_5$ and $\text{TiO}_2/\text{W}_2\text{O}_5$ were attached to the AC surface. The proof of this adhesion was demonstrated by EDS and Compositional element rates obtained (Energy Dispersive X-ray Spectroscopy (EDS)) were given in Table 1.

TEM images of the nanocomposites. The samples were also put under TEM investigation for the determination of structure. Figure 3 (a, b, c) shows the images with increasing magnifications from the samples. Figure 3a shows the typical TEM micrograph of the amorphous AC. The TEM images of $\text{TiO}_2/\text{V}_2\text{O}_5$ and $\text{TiO}_2/\text{W}_2\text{O}_5$ doped AC samples were given in Figure 3b and 3c. As seen in the Figure 3b and 3c, $\text{TiO}_2/\text{V}_2\text{O}_5$ and $\text{TiO}_2/\text{W}_2\text{O}_5$ were at-tached to the AC as with SEM results.

Figure 4 shows the XRD patterns of AC (a), $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b) and $\text{TiO}_2/\text{WO}_3/\text{AC}$ (c) amorphous and crystal structures. According to Figure 4, the X-ray patterns confirm that activated carbon samples were amorphous and $\text{TiO}_2/\text{V}_2\text{O}_5$ and $\text{TiO}_2/\text{W}_2\text{O}_5$ doped samples have crystal diffractions peaks.

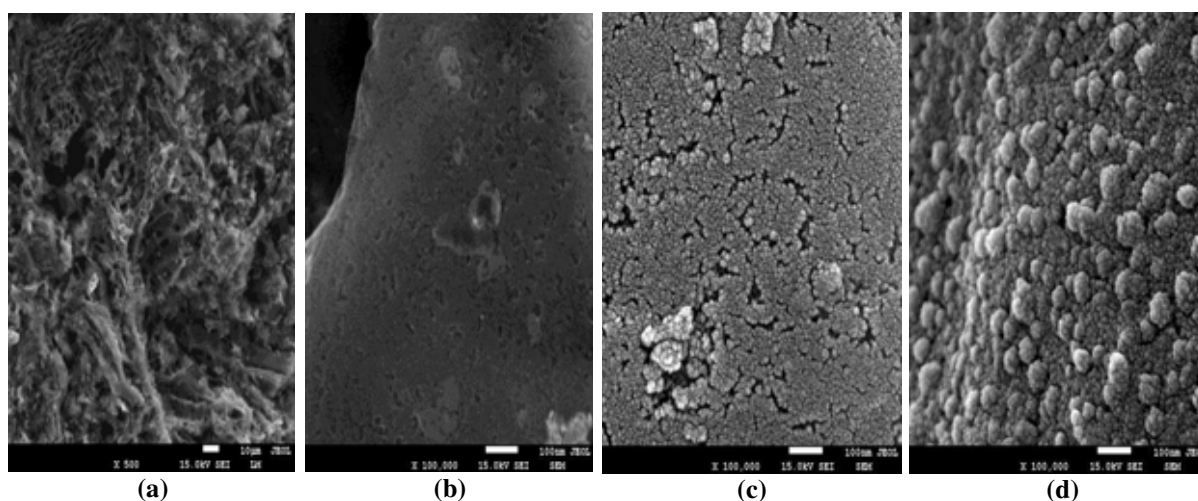


FIGURE 2
SEM images belonging to Activated carbone (a) (b), $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (c) and $\text{TiO}_2/\text{WO}_3/\text{AC}$ (d).

TABLE 1
EDS results belonging to all samples

Element (Weight %)	C	O	Ti	V	W	Mg	Ca	Si	P	Totals
AC	86.71	11.00	-	-	-	0.84	0.82	0.46	0.32	100.00
$\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$	65.47	21.37	12.10	1.07	-	-	-	-	-	100.00
$\text{TiO}_2/\text{WO}_3/\text{AC}$	71.66	20.75	6.39	-	1.21	-	-	-	-	100.00

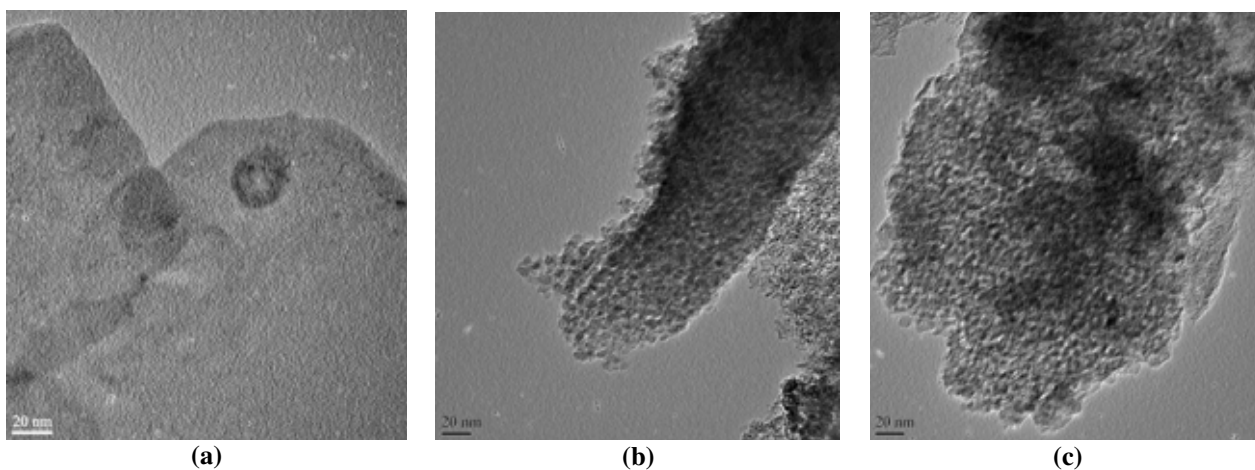


FIGURE 3
TEM images belonging to AC(a), TiO₂/V₂O₅/AC (b) and TiO₂/WO₃/AC(c) XRD analysis

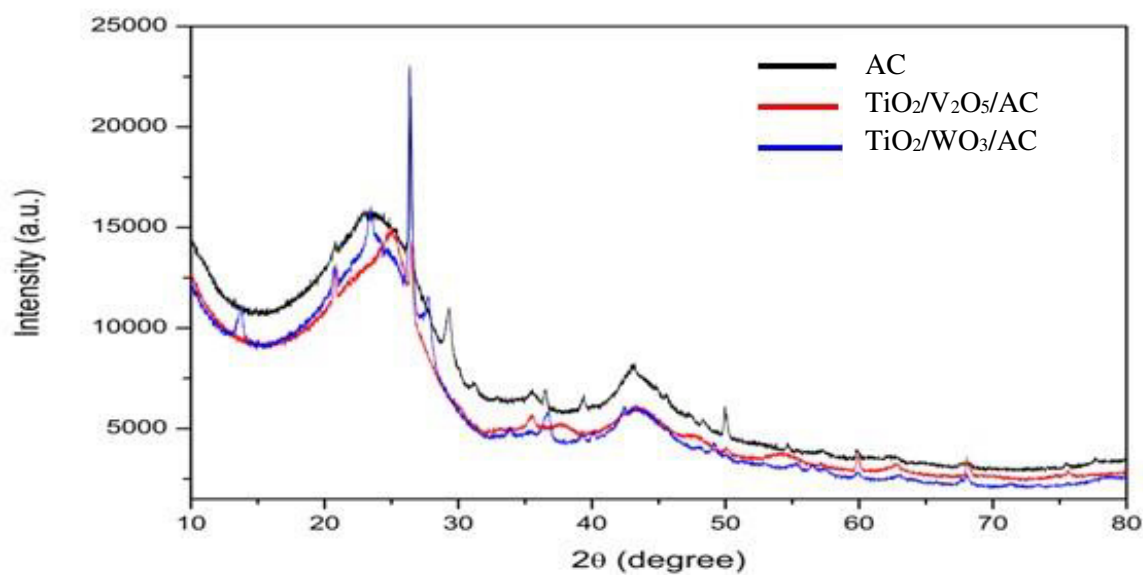


FIGURE 4
XRD spectra belonging to TiO₂/AC, TiO₂/V₂O₅/AC and TiO₂/WO₃/AC

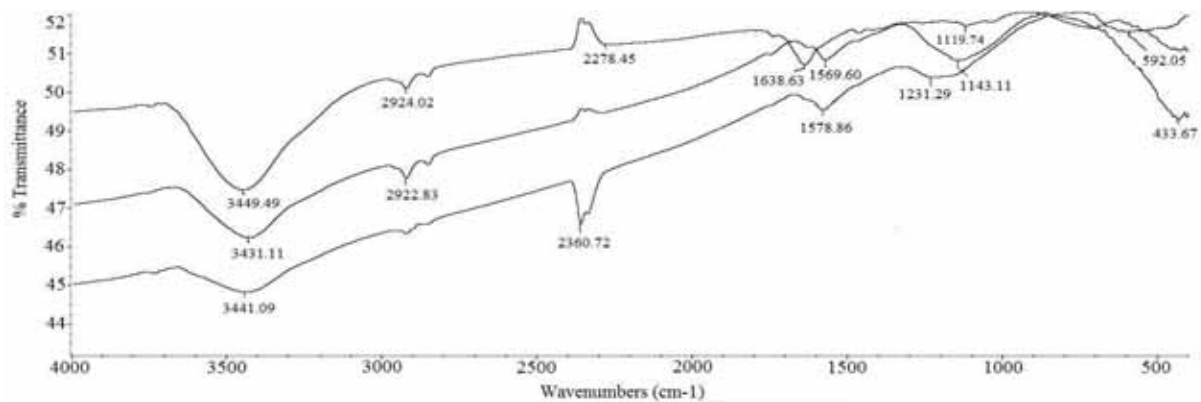


FIGURE 5
FTIR spectra belonging to TiO₂/AC (a), TiO₂/V₂O₅/AC (b) and TiO₂/WO₃/AC (c)

FTIR analysis. When compared, both AC and TiO₂/AC spectra showed stretching vibration at 3440 cm⁻¹ related to -OH. C-H stretching were also observed at 2923 cm⁻¹ related to -CH₂. Band height and broadness reflects that these groups did not change after the application of TiO₂. The band at 1575 cm⁻¹ disappeared that was related to aromatic C=C and a new band appeared at 1638 cm⁻¹ related to titanium carboxylate. Disappearance of C=C related band and appearance of TiO₂ bands proves the impregnation of TiO₂ particles on the surface of AC (Figure 5a). Hydroxyl band on the surface of TiO₂/V₂O₅/AC decreased and shifted to 3431 cm⁻¹ was also observed. It was different from WO₃ as -CH₂ bands did not disappear that means they were unaffected, only -OH groups did reaction. Similar to WO₃ connectivity, bands at 1638 cm⁻¹ related to titanium carboxylate disappeared. Similarly, the C=C band at 1575 cm⁻¹ shifted to 1569 cm⁻¹ after reaction with V₂O₅. The C-O band at 1156 cm⁻¹ in pure AC also shifted to 1143 cm⁻¹ after the removal of titanium carboxylate and reaction with V₂O₅ (Figure 5b). After comparing the spectrum of TiO₂/WO₃/AC, the band of -OH shifted from 3440 cm⁻¹ to 3441 cm⁻¹ and area under the peak is also decreased in addition to the disappearance of -CH₂ band at 2924 cm⁻¹ after the addition of WO₃ (Figure 5c). Therefore, it can be believed that WO₃ affected these groups. Separately, the band related to titanium carboxylate after the addition of TiO₂ disappeared after heating and a small peak was observed at 1578 cm⁻¹. Another band appeared at 1231 cm⁻¹ that is related to W=O. It proved the addition of WO₃.

Effect of oxidant concentration, time and catalyst type. The photocatalytic degradation of OMW was significantly improved and O₃, H₂O₂, O₃/H₂O₂, TiO₂/WO₃/AC and TiO₂/V₂O₅/AC materials were used together and separately. Then the obtained results for color, phenol and lignin were plotted in Figure 6a, 6b and 6c, respectively. The data in Figure 6 (a) showed that almost 80% of colour was removed from the OMW effluent streams with both catalysts at the end of 24 hours. Especially proportion of discoloration was significant when O₃ and H₂O₂ were used. Under the same experimental conditions, the removal of phenol was above 90% using the combined O₃/H₂O₂ system. However, the same removal percentage was almost obtained TiO₂/V₂O₅/AC and TiO₂/WO₃/AC for phenol (100, 95 %). However, the percentage removal was very low when ozone or H₂O₂ was used alone. Under the same experimental conditions, the lignin removal rate was overall 50% usually for both catalysts at the end of 48 hours (Figure 6c). The coloured components of OMW are normally related to lignin, tannin and the other high amount of organic compounds. All commercial OMW streams contain non-biodegradable products and are dark red to black in colour [2]. The effluent colour is primarily due to lignin and its degraded products, which are chemically stable, resistant to biological degradation and are intractable to separation by conventional treatment methods [23, 24]. However, the treatment systems that we have used in this study can be used successfully to remove not only the colored components but other hazardous organic compounds as well.

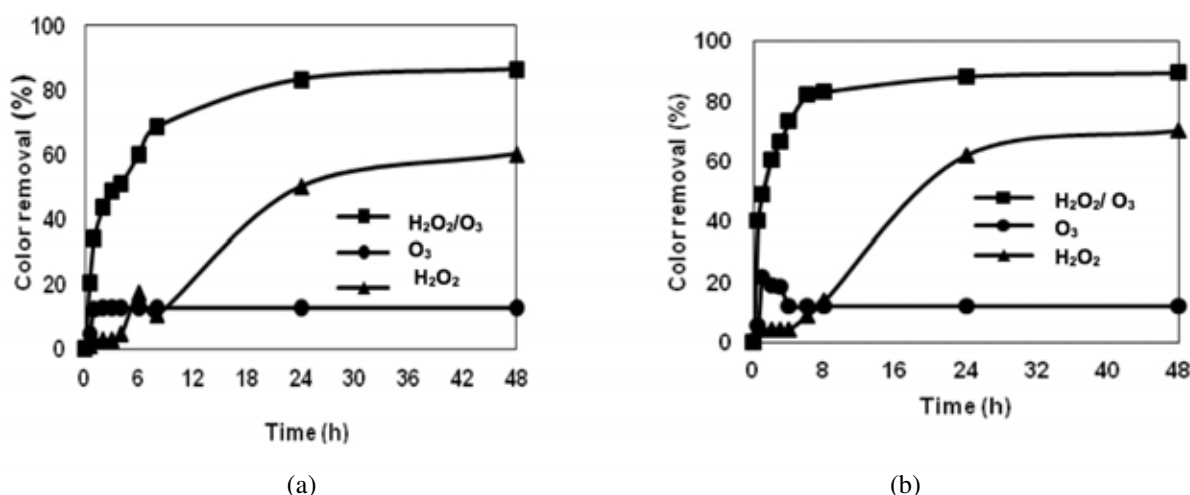


FIGURE 6a

The changes of color removal due to times and different parameters for both catalysis' TiO₂/V₂O₅/AC (a) and TiO₂/WO₃/AC(b)(pH:5.0, 298K, Solid/ liquid: 0.5g L⁻¹, O₃:1.5Lmin⁻¹, H₂O₂ :15 mL⁻¹ and UV:17 Watt)

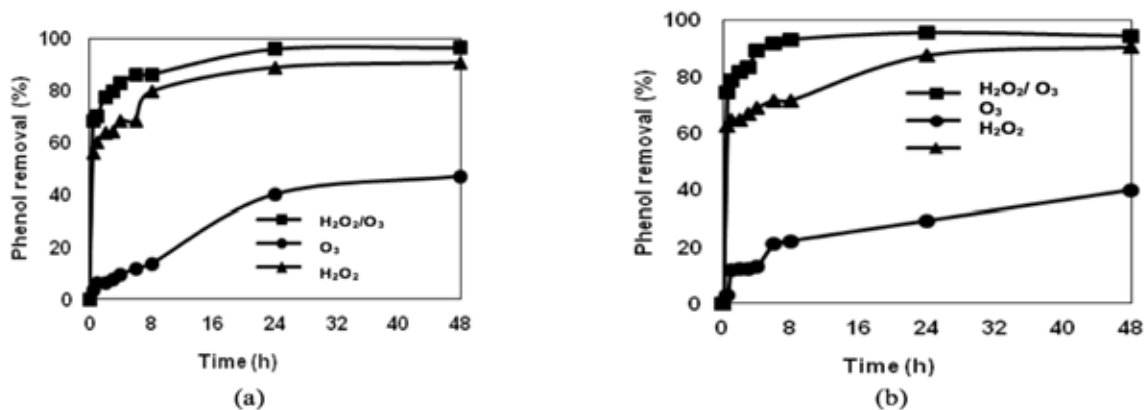


FIGURE 6b

The changes of phenol removal due to times and different parameters for both catalysis $TiO_2/V_2O_5/AC$ (a), $TiO_2/WO_3/AC$ (b) (pH:5.0, 298K, Solid/liquid: $0.5g L^{-1}$, O_3 : $1.5Lmin^{-1}$, H_2O_2 : $15 mL^{-1}$ and UV: 17 Watt)

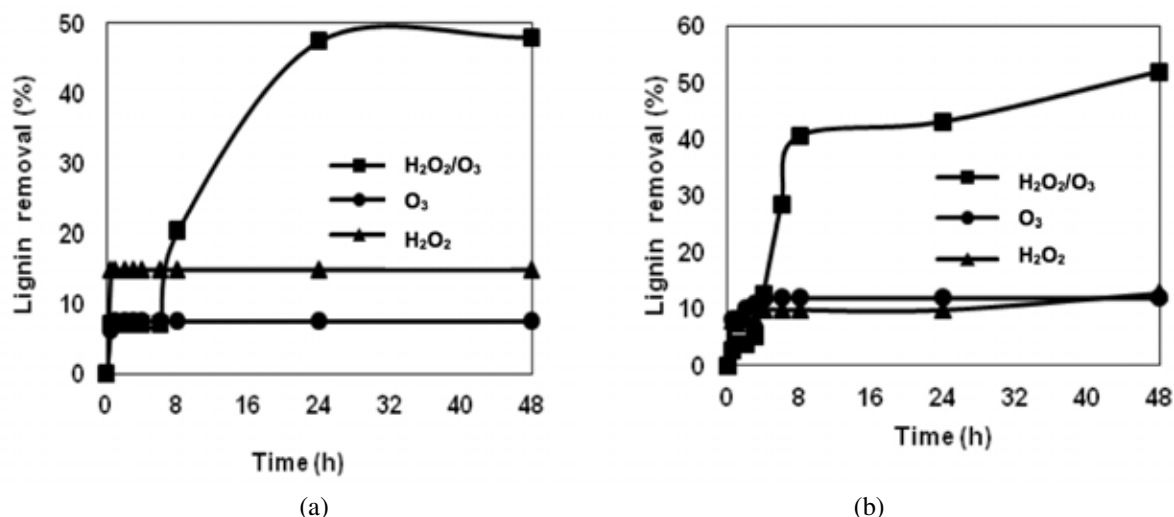


FIGURE 6c

The changes of lignin removal due to times and different parameters for both catalysis $TiO_2/V_2O_5/AC$ (a), $TiO_2/WO_3/AC$ (b) (pH:5.0, 298K, Solid/liquid: $0.5g L^{-1}$, O_3 : $1.5Lmin^{-1}$, H_2O_2 : $15 mL^{-1}$ and UV: 17 Watt)

The effect of Temperature. The change in temperature normally affects the rate of reaction in most chemical reactions, so the photolytic reactions for both catalysts were carried out at 298K, 308K and 318K in this experimental. The effects of temperature on the removal of colour, phenol and lignin are presented in Figure 7a, 7b and 7c, respectively.

The changes in color of OMW were also examined related to the changes in temperature and times. The data obtained show that an increase in the percentage of removal was achieved when the temperature was decreased from 308K to 298K for the two catalysts systems (Figure 7a). The rates of color removal after 8 hours were 84.18% and 79.76% for the $TiO_2/WO_3/AC$ and $TiO_2/V_2O_5/AC$ catalytic systems, respectively. The decrease in the

percentage removal of color at higher temperature may be associated with the solubility of colored components present in the effluent streams or the effect of quantum yield for the photochemical yield [25]. The higher dissolution of the particulate coloured matter and other polyphenolic compounds in OMW such as tannins colored components at high temperatures may be responsible for the decrease in the overall color removal at higher temperature. OMW was strongly colored related to lignin, tannin and at high amount of organic compounds.

Lignin is a biopolymer synthesized and stored in plant cell walls together with cellulose and hemicelluloses serving the function of making the root and stem mechanically strong and hard. Its main function is to act as a physical and chemical barrier

against biodegrading systems. The high extent of the change taking place in color indicates that the above-mentioned compounds have been considerably degraded and dissolved into different compounds [29]. The changes taking place in phenol and lignin

concentrations under the same conditions were analysed to examine this better, and to see the changes taking place in lignin and phenolic compounds. The results for phenol and lignin are plotted in Figs 7b and 7c, respectively.

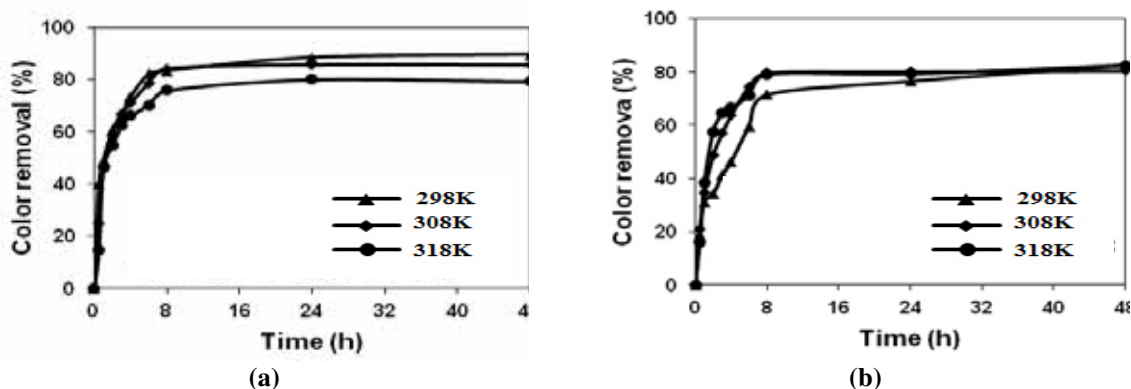


FIGURE 7a

The changes of color removal due to temperature and times for both catalysis. TiO₂/WO₃/AC (a) TiO₂/V₂O₅/AC (b) (pH:5.0. 298K. Solid/Liquid: 0.5g L⁻¹. O₃:1.5Lmin⁻¹. H₂O₂:1515 mL⁻¹and UV:17 Watt.

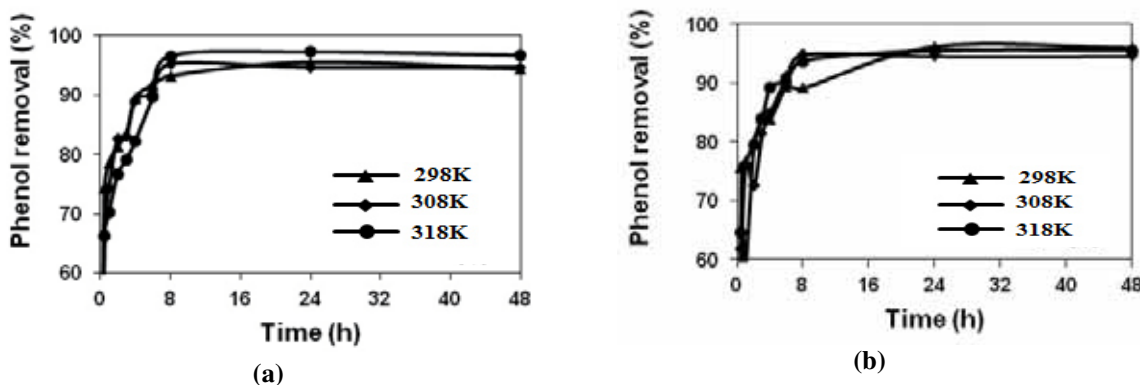


FIGURE 7b

The changes of phenol removal due to temperature and times for both catalysis TiO₂/WO₃/AC(a), TiO₂/WO₃/AC (b) (pH:5.0. 298K. Solid/Liquid:0.5g L⁻¹. O₃:1.5Lmin⁻¹. H₂O₂:15 mL⁻¹and UV:17 Watt.

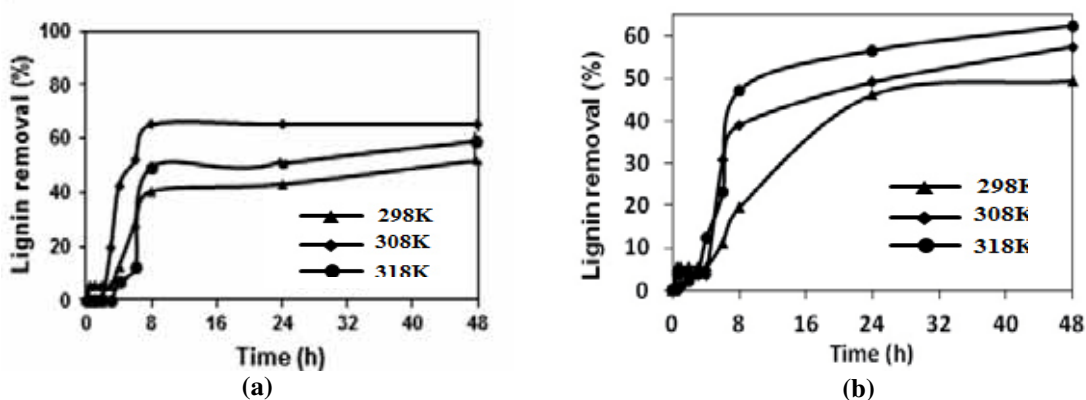


FIGURE 7c

The changes of lignin removal due to temperature and times for both catalysis, TiO₂/V₂O₅/AC (a), TiO₂/WO₃/AC(b) (pH:5.0. 298K. Solid/Liquid: 0.5g L⁻¹. O₃:1.5Lmin⁻¹. H₂O₂:15 mL⁻¹ and UV:17 Watt)

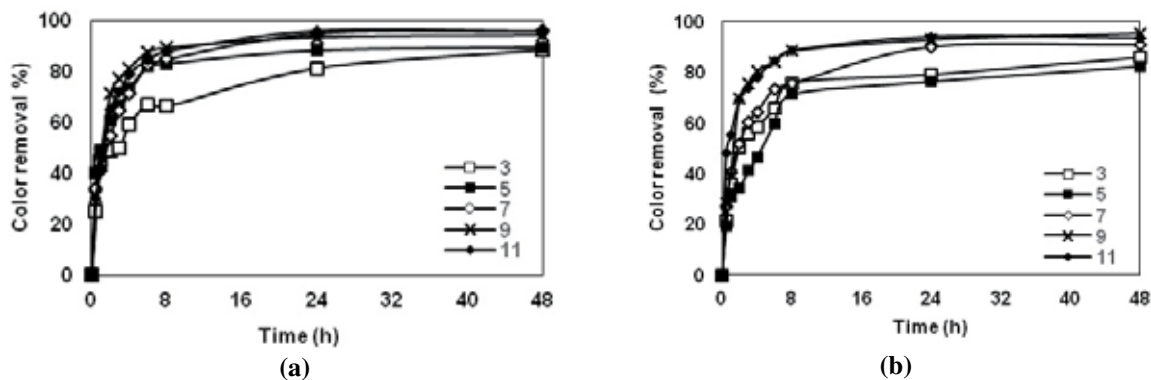


FIGURE 8a

The changes of color removal due to different pH and times for both catalysis $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a) and $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b) (298K, Solid/Liquid: 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV: 17 Watt)

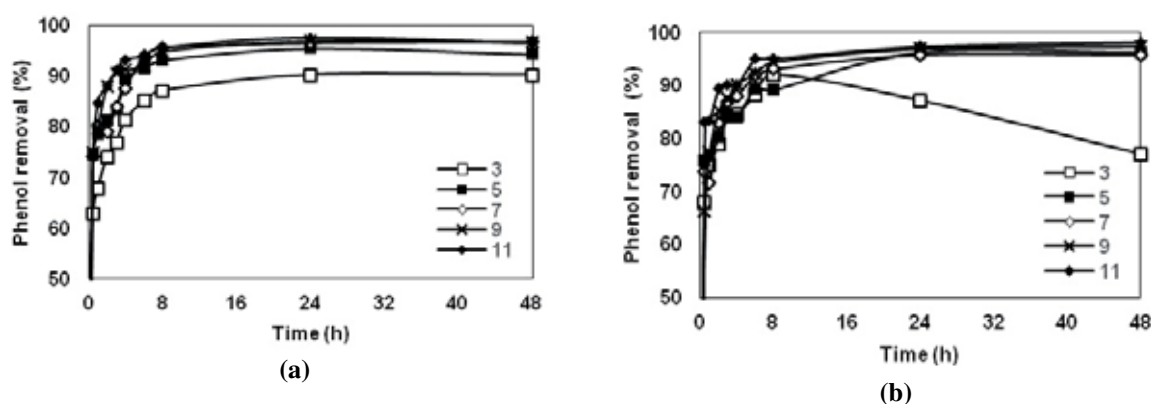


FIGURE 8b

The changes of phenol removal due to different pH and times for both catalysis $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a) and $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b) (298K, Solid/Liquid: 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV: 17 Watt)

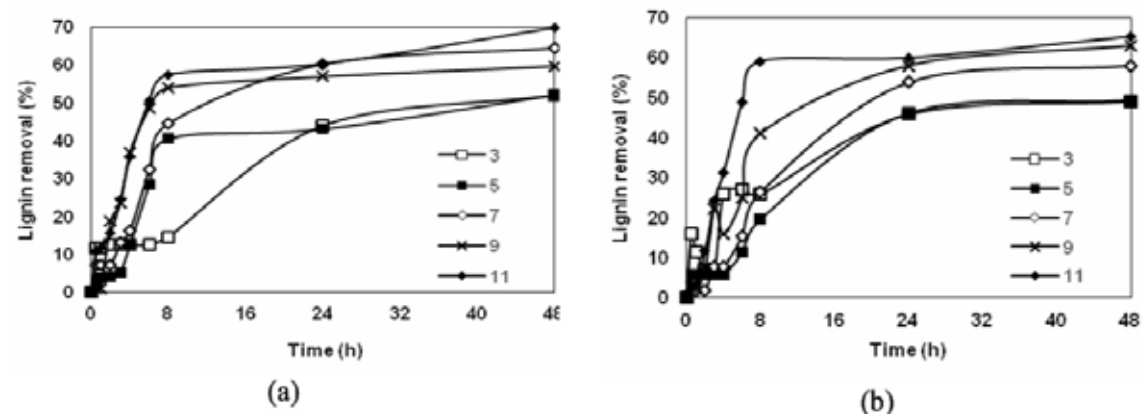


FIGURE 8c

The changes of lignin removal due to different pH and times for both catalysis $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a), $\text{TiO}_2/\text{V}_2\text{O}_5/\text{WO}_3/\text{AC}$ (b) (298K, Solid/Liquid: 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV: 17 Watt)

The effects of temperature and time on the percentage degradation of phenol were investigated for $\text{TiO}_2/\text{WO}_3/\text{AC}$ and $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ systems. The data obtained show that the percentage degradation values were 95.17% and 94.88% at the 318K,

respectively. The rate constants for the two catalysts were $25.62 \times 10^{-2} \text{ h}^{-1}$ and $16.14 \times 10^{-2} \text{ h}^{-1}$, respectively at the same temperature (Table 1). Lignin is a three dimensional, optically active phenylpropanoid polymer and it does not dissolve in water as a high-

weighted hydrophobic polymer. It is more resistant to biodegradation than other polymers because of its heterogeneous character and its inconvenience for hydrolytic degradation [10, 27-29]. The lignin removal percentages for both catalysts are shown in Figure 7c. As seen from these Figures while temperature increases, removal of lignin was observed increasing about 8 hours; fixation was observed at the rate of removal. Maximum percentage removal of lignin was 65.34 % at 308K.

The effect of pH. The pH of solution in the photocatalytic reactions taking place on the particulate surface is an important parameter [29]. Depending on the initial pH for both catalyses, removal of colour, phenol and lignin are presented in Figure. 8a, 8b and 8c, respectively. As seen from these Figures maximum colour and phenol removals were obtained at between pH 7.00 and 11.0 (100.0 and 80%) respectively. Lignin removal was obtained 70 and 50 % at the same pH values.

The data in Figure 8a show that colour removal is associated with the pH of the solution. The lowest

colour removal was at pH 3.0 using $\text{TiO}_2/\text{WO}_3/\text{AC}$ catalyst (70%). Except for this pH values there was a significant colour removal depending at all other pH values studies in this work. Particularly colour removal up to 100% occurred at pH 11:0 for both catalyses.

The effect of pH on the percentage removal of phenolic compounds using different photolytic processes was also investigated. The data in Figure 8b shows that the percentage removal of phenol was highest (95-96%) after pH 9.00 for both catalyses. This case can be explained due to the availability of abundant OH^- ions at high pH values. Formation of radicals during photolytic reactions and existence of multiway interactions such as substrate, solvent molecules and other electrostatic interactions can be related to the changes in pH values. When changes in removals of lignin depending on pH and time of photolytic reactions was observed at the end of reaction. The highest removal was at 8 h. and showed constant stability after this period approximately (60-70 %) (Fig 8c).

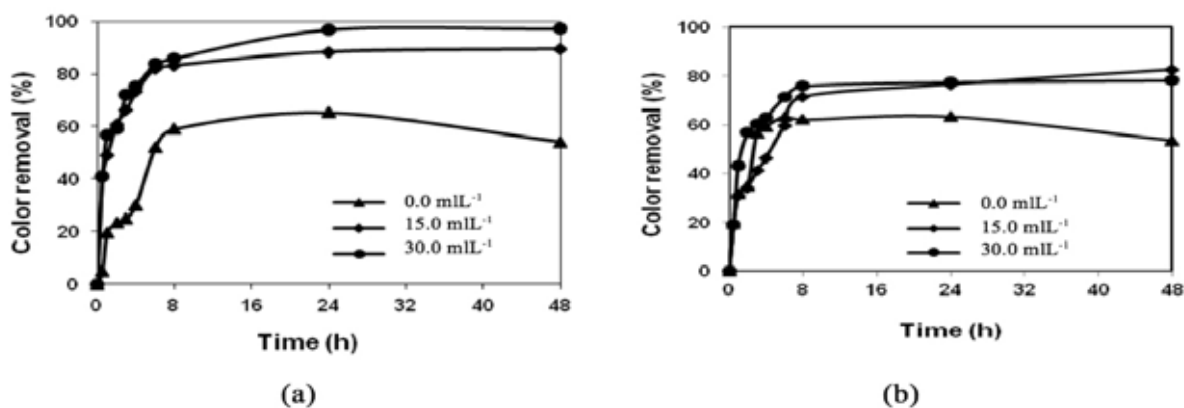


FIGURE 9a

The changes of color removal due to amount of different H_2O_2 and times for both catalysis, $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a) and $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b), (298K, Solid/Liquid: 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV: 17 Watt)

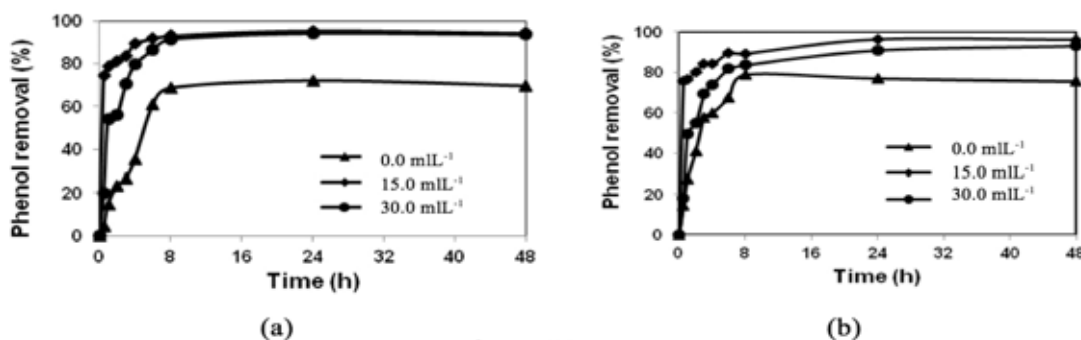


FIGURE 9b

The changes of phenol removal due to amount of different H_2O_2 and times for both catalysis $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a) $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b) (298K, Solid/Liquid: 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV:17 Watt)

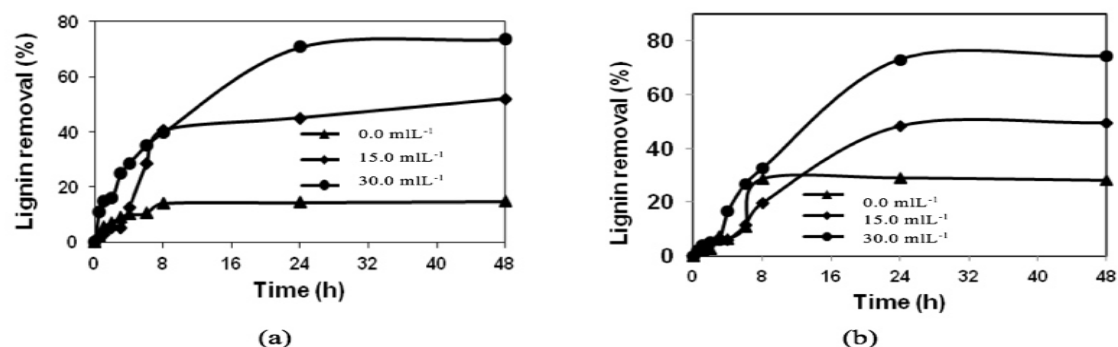


FIGURE 9c

The changes of lignin removal due to amount of different H_2O_2 and times for both catalysis, $\text{TiO}_2/\text{WO}_3/\text{AC}$ (a) $\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$ (b) (298K, 0.5g L^{-1} , O_3 : 1.5Lmin^{-1} , H_2O_2 : 15 mL^{-1} and UV: 17Watt)

TABLE 2

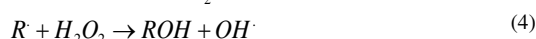
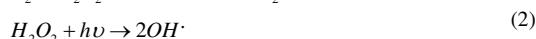
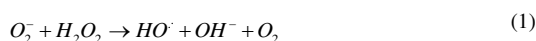
Effect of pH, catalyst and temperature on the kinetics of color, phenol and lignin removal

Parameter	$\text{TiO}_2/\text{V}_2\text{O}_5/\text{AC}$						$\text{TiO}_2/\text{WO}_3/\text{AC}$					
	Color		Phenol		Lignin		Color		Phenol		Lignin	
	$k \times 10^{-2} (\text{h}^{-2})$	r^2	$k \times 10^{-2} (\text{h}^{-1})$	r^2	$k \times 10^{-2} (\text{h}^{-1})$	r^2	$k \times 10^{-2} (\text{h}^{-1})$	r^2	$k \times 10^{-2} (\text{h}^{-1})$	r^2	$k \times 10^{-2} (\text{h}^{-1})$	r^2
The Effect of Temperature (K)												
298	14.25	0.88	12.14	0.89	4.12	0.95	27.31	0.93	18.11	0.94	4.15	0.91
308	18.54	0.97	15.11	0.93	11.98	0.84	22.91	0.98	24.62	0.97	13.08	0.97
318	20.15	0.91	16.14	0.88	7.14	0.91	14.15	0.90	25.62	0.93	6.14	0.89
The Effect of pH												
3.00	20.02	0.97	19.36	0.97	8.82	0.94	21.26	0.93	18.81	0.99	10.61	0.97
5.00	18.54	0.97	15.11	0.93	11.98	0.84	22.91	0.98	24.62	0.97	13.08	0.97
7.00	26.31	0.96	25.63	0.97	12.51	0.87	40.19	0.96	29.16	0.94	15.52	0.92
9.00	28.02	0.98	30.69	0.98	14.03	0.96	33.74	0.97	24.87	0.96	13.54	0.97
11.0	30.12	0.90	16.14	0.91	15.12	0.92	30.14	0.92	18.41	0.87	8.21	0.90
The Effect of H_2O_2												
0.00	4.11	0.91	10.12	0.83	2.10	0.90	4.12	0.86	5.02	0.86	2.14	0.87
15.00	18.54	0.97	15.11	0.93	11.98	0.84	22.91	0.98	24.62	0.97	13.08	0.97
30.00	17.31	0.96	29.21	0.98	10.31	0.97	24.21	0.98	36.41	0.99	19.61	0.92
The Effect of UV, O_3 , H_2O_2 , $\text{O}_3/\text{H}_2\text{O}_2$												
UV	1.12	0.95	3.15	0.82	0.14	0.91	1.10	0.70	0.01	0.87	0.14	0.92
O_3	4.11	0.91	10.12	0.83	2.10	0.90	4.12	0.86	5.02	0.86	2.14	0.87
H_2O_2	17.10	0.87	26.14	0.84	5.12	0.87	8.11	0.90	12.6	0.94	5.14	0.93
$\text{O}_3/\text{H}_2\text{O}_2$	20.54	0.97	36.11	0.93	11.98	0.84	22.91	0.98	24.62	0.97	13.08	0.97

The Effect of H_2O_2 . The rate of photocatalytic degradation of the organic compounds was significantly improved by the addition of H_2O_2 as an additional oxidant. Figure 9a, 9b and 9c show the percentage degradation when H_2O_2 was added as an oxidant in the concentration range of $0.00\text{--}30\text{ mL}^{-1}$. The percentage removals of colour, phenol and lignin after 24 hours were 100 %, 95 % and 75 % using the $\text{TiO}_2/\text{WO}_3/\text{AC}$ catalytic system respectively. As a result, higher percentage removal is obtained with increasing the concentration of oxidizing matter. The presence of UV, H_2O_2 , and $\text{TiO}_2/\text{WO}_3/\text{AC}$ can

decrease the concentration of organic compounds in the photocatalytic process. This can be explained as follows; the recombination of valence-band holes ($\text{h}^{\text{VB}+}$) and conduction-band electrons (e^{CB}) have been regarded as an unfavourable or limiting process in photocatalysis. The electron will combine with oxygen molecule to produce superoxide radical anions (O_2^-), meanwhile the hole in the valence band may react with water (H_2O) or hydroxyl ions (OH^-) to generate the hydroxyl radicals (OH^\cdot). The OH^\cdot and O_2^- are the primary oxidizing species in the photocatalytic processes [23,29].

An indirect interaction of organic compounds with OH[•] radicals and direct with H₂O₂ in degradation has been suggested [8]. In another study, catalytic reactions using UV and H₂O₂ have been reported to have significant removal of organic substances on particular pesticides derivations [29, 31]. It has been reported that the combination of O₃ and UV can significantly increase the formation of radicals at high temperatures which ultimately increases the degradation of various organic compounds [32-34]. The data obtained in this study are in accordance with the previous studies since the removal of colour, phenol and lignin increases with the combined use of different oxidants under different conditions. It is well known that hydroxyl free radicals are highly reactive, they can abstract hydrogen from hydrocarbons and can perform oxidation (E=2,80 V). These radicals can easily get into reaction with any organic compound and are highly reactive under the UV light.



Using UV- TiO₂ is highly reactive and reported in advanced oxidation reactions with high yields. Reactions shown in equation 1 and 4 are very effectively reported [35].

Photodegradation kinetics. The degradation kinetics of wastewater by using TiO₂/V₂O₅/AC, TiO₂/WO₃/AC and without catalyst in the presence of UV light was evaluated using the linearised form of pseudo first- order rate

$$\ln (C_t/C_0) = -kt \quad (5)$$

where C₀ is the initial concentration (mg/l), C_t is the concentration (mg/l) at time t, t is the UV light exposure time and k₁ is the first-order rate kinetics. Table 2 shows that the degradation process follows the pseudo first-order rate kinetics as evidenced from the regression (r²) analysis that is greater than 0.80. The higher rate constant achieved using TiO₂/V₂O₅/AC can be attributed to the combined effects of adsorption of organic molecule over catalyst surface followed by oxidation using the generated hydroxyl radical and direct attack of photogenerated holes [36].

CONCLUSIONS

In this study various photocatalytic systems have been optimized for the treatment of wastewater originating from olive oil production industries un-

der different condition. The nanocomposite materials were prepared and their efficiencies were examined using various photolytic and photocatalytic systems. As a result of this study, all pollutants could be removed (80-100%) from solution after 2 hour containing 30 ml L⁻¹ H₂O₂ at higher pH (9.00-11.00) values. The results indicated that TiO₂/WO₃/AC is significantly more active than TiO₂/V₂O₅/AC. H₂O₂ plays a crucial role in catalytic activity in the reaction. Moreover, the necessity to analyse the products with further techniques while the reactions in black water purification continue emerges. It is concluded that it is important to investigate the structure analyses of substances formed during the reaction process and reaction mechanisms during photocatalyst process through HPLC, gas chromatography, NMR and other techniques in further studies.

ACKNOWLEDGEMENTS

This study was financially supported as a project (12/110) by Research Project Coordination Unit, Mugla Sitki Kocman University. The authors wish to thank to the central research laboratory of Muğla Sitki Koçman University for XRD, BET, FTIR, SEM and TEM analyses

REFERENCES

- [1] Israilised, C.J. Vlyssides, A.G. Mourafeti, V.N. and Karvouni, G. (1997) Olive oil waste water treatment with the use of an electrolysis system. *Bioresource Technology*, 61,163-170.
- [2] Adhoum, N. and Monser, L. (2004) Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chemical Engineering and Process*, 433,1281-1287.
- [3] Ugurlu, M. and Karaoglu M.H. (2011) Photocatalytic removal of olive mill waste water by TiO₂ loaded on sepiolite and under natural solar irradiation. *Environmental Progress & Sustainable Energy*, 2011.30.3. 326-336.
- [4] Aref, S., Mahmoud, S. and Tayeb, A. (2017) Employing Photo Fenton and UV/ZnO Processes for Removing Reactive Red 195 From Aqueous Environment, *Fresen. Environ. Bull.*, 26, 1560-1565
- [5] Kestioglu, K., Yonar, T. and Azbar, N. (2004) Feasibility of physico-chemical treatment and advanced oxidation processes (AOPs) as a means of pre-treatment of olive mill effluent (OME). *Process Biochemistry*, 40, 2409-2416.
- [6] Turano, E., Curcio, S., De Paola, M.G., Calabro, V. and Iorio G. (2002) An integrated centrifugation-ultrafiltration system in the treatment of olive mill wastewater. *Journal of Membrane*

- Science, 209, 519-531.
- [7] Haiyan, J., Jing, X., Yuanguo, X., Jia, Y., Yeping, L., Liying, H., Qi, Z., Hui, X. and Huaming, L. (2016) Synthesis of Magnetic BiOBr-NiFe₂O₄ Hybrids and The Efficient Photocatalytic Activity, 25, 3083-3091.
- [8] Schwitzguebel, J.P., Aubert, S., Grosse, W. and Laturnus, F. (2002) Sulphonated Aromatic Pollutants: Limits of Microbial Degradability and Potential of Phytoremediation. Environmental Science Pollution Research 9(1), 62-72.
- [9] Qin, L., Han, J., Deng, Y., He, C. and Chen, W. (2016) The Preparation of Ag/Cu₂O Hollow Nanospheres For Enhanced Photocatalytic Activity. Fresen. Environ. Bull., 25, 391-400.
- [10] Ugurlu, M. and Hazirbulan, A.S. (2007) The removal of some organic compounds from Pretreated olive mill wastewater by sepiolite. Fresen. Environ. Bull. 6(8), 887-895.
- [11] Oukili, O., Chaouch, M., Rafiq, M., Hamdi, M. and Benlemlih, M. (2001). Bleaching of olive mill wastewater by clay in the presence of hydrogen peroxide, Angewandte Chemie Science Material, 26, 45-53..
- [12] Aktas, E.S., Imre, S. and Ersoy, L. (2001) Characterization and lime treatment of olive mill wastewater. Water Research. 35, 2336-2340.
- [13] Curi, K., Velioglu, S.G. and Diyamandoglu, V. (1980) Treatment of olive oil production wastes. In: Treatment and Disposal Liquid and Solid Industrial Wastes. 189-205. Pergamon Press. Oxford.
- [14] Tsonis, S.P., Tsola, V.P. and Grigoropoulos, S.G. (1989) Systematic characterization and chemical treatment of olive oil mill wastewater. Toxicological and Environmental Chemistry. 20-21, 437-457.
- [15] Hamdi, M., Garcia, J.L. and Elluoz, R. (1992) Integrated biological process for olive mill wastewater treatment. Bioprocess Engineering. 8, 79-84.
- [16] Brunetti, G., Senesi, N. and Plaza, C. (2008), Organic matter humification in olive oil mill wastewater by abiotic catalysis with manganese(IV)oxide, Bioresource Technology, 99, 17, 8528-8531
- [17] Lallai, A., Mura, G., Palmas, S., Polcaro, A.M. and Baraccani, L. (2003) Degradation of Para-Hydroxybenzoic Acid by Means of Mixed Microbial Cultures. Environmental Science and Pollution Research. 10(4), 221-224.
- [18] Kai, Y., Jianwei, G., Yang, L., Hong, L. and Yi, W. (2017) Optimization of Photo-Fenton Process with Diatomite-6833257(I-Fe₂O₃ For Treatment of Dimethyl Phthalate Using Response Surface Methodology. Fresen. Environ. Bull., 26, 1477-1484
- [19] Aref, S., Kazem, M. and Davood, S. (2016) Degradation of 2-Nitrophenol From Petrochemical Wastewater By UV/NiFe₂O₄/Clinoptilolite Process. Fresen. Environ. Bull., 25, 500-508.
- [20] Han, D.H., Cha, S.Y. and Yang, H.Y. (2004) Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H₂O₂ process and kinetic study. Water Research, 38, 2782-2790.
- [21] Hung-Yee, S. (2006) Degradation of dye house effluent containing C.I. Direct Blue 199 by processes of ozonation. UV/H₂O₂ and in sequence of ozonation with UV/H₂O₂. Journal of Hazardous Materials B, 133, 92-98
- [22] APHA-AWWA-WPCF (2005) Standard methods for the examination of water and wastewater. 21th.ed.-Washington DC.
- [23] Shu, H.Y. and Chang, M.C. (2005) Pre-ozonation coupled with UV/H₂O₂ process for the decolorization and mineralization of cotton dyeing effluent and synthesized C.I. Direct Black 22 wastewater. Journal of Hazardous Material, 121, 127-133.
- [24] Ksibi, M.S.B. Amor, S. Cherif, E. Elaloui, A. and Houas, M. (2003) Photodegradation of lignin from black liquor using a UV/TiO₂ system. Journal of Photochemistry and Photobiology A: Chemistry, 154, 211-218.
- [25] Parlar, H. and Korte, F. (1979) The significance of quantum yield during determination of environmental photochemical degradability of organic compounds, 8, 797-807.
- [26] Ugurlu, M. and Kula, I. (2007) Decolourization and Removal of Some Organic Compounds from Olive Mill Wastewater by Advanced Oxidation Processes and Lime Treatment. Environmental Science Pollution Research, 14(5), 319-325.
- [27] Ugurlu, M. and Karaoglu, M.H. (2011) TiO₂ supported on sepiolite: Preparation. structural and thermal characterization and catalytic behaviour in photocatalytic treatment of phenol and lignin from olive mill wastewater. Chemical Engineering Journal, 166, 859-867.
- [28] Qamar, M. and Muneer, M. (2005) Comparative photocatalytic study of two selected pesticide derivatives. Indole-3-acetic acid and indole-3-butyric acid in aqueous suspensions of titanium dioxide. Journal of Hazardous Materials, 120 (1-3), 219-227.
- [29] Ghalya, Y., Faraha, J.Y. and Fathyb, A.M. (2007) Enhancement of decolourization rate and COD removal from dyes containing wastewater by the addition of hydrogen peroxide under solar photocatalytic oxidation. Desalination. 217, 74-84.
- [30] Kus, M., Gernjak, W., Ibanez, P.F., Rodriguez, S.M., Galvez, J.B. and Icli S. (2006) A comparative study of supported TiO₂ as photocatalyst in water decontamination at solar pilot plant scale. Journal of Solar Energy Engineering. 128, 331-337.

- [31] David, R.H., Ke, L.R. and Rhodes, T.C. (2016) A photolysis coefficient for characterizing the response of aqueous constituents to photolysis. *Frontiers of Environmental Science Engineering*, 10, 428–437.
- [32] Min, Z., Jian, L., Yiliang, H. and Wilson P.C. Photocatalytic degradation of polybrominated diphenyl ethers in pure water system. *Frontiers of Environmental Science Engineering*, 10, 229–235
- [33] Eunsung, K., Chang, K., Kyunghyuk, L. and Joonwun, K. (2015) Decomposition of aqueous chlorinated contaminants by UV irradiation with H₂O₂. *Frontiers of Environmental Science Engineering*, 9(3), 429- 435.
- [34] Yunrui, Z., Wanpeng, Z. and Xun, C. (2008) Catalytic activity of cerium-doped Ru/Al₂O₃ during ozonation of dimethyl phthalate. *Frontiers of Environmental Science Engineering*, 2(3), 354-357.
- [35] Esplugas, S., Gimenez, J., Contreras, S., Pascual, E. and Rodriguez, M. (2002) Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 36(4), 1034-42.
- [36] Ahmed, S. Rasul, M.G. Martens, W.N. Brown, R. and Hashib, M.A. (2010) Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments. *Desalination*, 261, 3-18.

Received: 13.12.2016

Accepted: 24.03.2017

CORRESPONDING AUTHOR

Mehmet Ugurlu

Department of Chemistry

Faculty of Science

Mugla Sitki Kocman University

48000 Mugla – TURKEY

E-mail: mnazlican@hotmail.com, tr
mehmetu@mu.edu.tr