Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 4106-4110

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19106

Treatment of Olive Mill Wastewater by Catalytic Ozonation Using Activated Carbon Prepared from Olive Stone by KOH

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Received: 17 February 2015; *Accepted*: 5 April 2015; *Published online*: 16 July 2015; AJC-17413

Olive stone and olive mill wastewater generated by the olive oil extracting industry were major pollutants not only in Turkey but also in other Mediterranean countries for thousands of years. Physical and chemical techniques, such as adsorption, biological degradation, advanced oxidation processes, chemical coagulation, flocculation, filtration, lagoons of evaporation and the electrochemical treatment of olive mill wastewater and burning olive stone partially solve the problem. The aim of the present study was to investigate the potential uses of KOH impregnated olive stone as a catalyst and reduce the pollution level of olive mill wastewater to discharge standards. In addition by the removal of polluting waste materials, the preparation of activated carbon from such agricultural by-products would also include economic gains for products manufactured from the abundant waste source.

Keywords: Catalytic ozonation, Olive mill wastewater, Olive stone, Activated carbon.

INTRODUCTION

The extraction and manufacturing of olive oil in Mediterranean countries produces industrial wastewater, which is commonly named olive mill wastewater (OMW). Ironically, while consumption of the olive oil itself provides benefits to human health, its resulting by-products (olive mill wastes during olive processing) represent a serious environmental threat, especially in the Mediterranean, Aegean and Marmara regions that account for approximately 95 % of worldwide olive oil production[1]. Due to their high load of organic matter, acid pH and polyphenols olive mill wastewater may have adverse impacts on soil, surface water and groundwater and their disposal still represents an unsolved environmental problem. The organic matter mainly consists of polysaccharides, sugars, phenols, polyalcohols, proteins, organic acids and oil[2]. The phenolic and aromatic compounds have been considered as the important contributors to the toxicity of olive mill wastewater[3,4]. Since the olive oil industries are responsible for a high quantity of pollution, it has become imperative to solve this problem by developing optimized systems for the treatment of olive oil wastes.

Olive stone is also a significant waste product of the olive oil industry. A better way to generate added value from this by-product is to use it as inexpensive precursor for the preparation of activated carbon (AC)[5]. The resulting products from carbonization of olive stones have been successfully used as sorbents for a wide variety of pollutants in aqueous solutions[6-9]. In addition to its excellent adsorption capacity, activated carbon also exhibits catalytic activity due its high surface area and surface chemical properties[10].

Ozone, in particular, has many oxidizing properties desirable for use in water treatment. It is a powerful oxidant capable of oxidative degradation of many organic compounds, is readily available, soluble in water and leaves by-products more biodegradable[11]. Ozone (O_3)/activated carbon coupling is a recent wastewater treatment that combines different actions: direct or indirect ozonation in the bulk liquid, adsorption on activated carbon and direct or indirect oxidation of compounds on the activated carbon surface[12-14]. For this study, activated carbon was produced by using physical and chemical activation method and characterized its pore structure. In chemical activation, KOH was used to prepare the activated carbon with high porosity by treatment and impregnation of the olive stone. Prepared activated carbon was used catalytic ozonation as catalyst.

In this study, the degradation of the pollutant organic matter present in olive mill wastewater was carried out by a single lime treatment, a single ozonation, a single catalytic ozonation and combinations of two steps: a lime treatment followed by ozonation and a lime treatment followed by catalytic ozonation. With lime treatment the aim was to reduce pollution effect of olive mill wastewater.

EXPERIMENTAL

The original wastewater was obtained from an olive oil production plant, located in the Adana area of Turkey, which uses the traditional mill and pressing process. No chemical additives are used during the olive oil production. The characteristics of olive mill wastewater used in this work are presented in Table-1. The absorption band at 410 nm was chosen to measure the colour parameter, whereas the absorption bands at 280 nm and 254 nm were indicative of aromatic ring and double bonds, respectively[15].

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF OLIVE MILL WASTEWATER SAMPLE

Parameters	Value
Colour	Black
pH	4.71
Conductivity (µS cm^{-1})	7010
Total suspended solid (mg L^{-1})	16.75
Oil and grease (mg L^{-1})	5690
COD (mg L^{-1})	33133
TOC (mg L^{-1})	8967
Total phenol (mg L^{-1})	1715
A_{254} (cm^{-1})	1.2050
A_{280} (cm^{-1})	1.1920
A_{410} (cm^{-1})	0.2050

Prior to degradation experiments, the olive mill wastewater was filtered on Whatman filters No. 131 to remove suspended solids, then diluted 1:8 with distilled water. The samples were stored at 4 °C and shaken each time before being used for experiments. A total suspended solid gravimetric method 2540D and oil and grease Soxhlet extraction method 5520D were carried out at according to validated standard methodologies from APHA-AWWA-WPCF[16]. Total phenolic content was determined with the Folin-Ciocalteu method by using gallic acid as a reference phenolic compound[17]. COD and TOC analyses were performed by using HACH COD tests (100-2000 ppm) and HACH TOC tests (60-735 ppm) on samples diluted 1:8.

Before starting ozonation experiments, 1 L of olive mill wastewater was treated by adding lime up to a pH of 12. The aim of the pre-treatment with lime was to remove total suspended solids in order to improve the efficiency of the subsequent treatment by ozonation processes. Almost 10 g L^{-1} of lime was added to reach a pH of 12[18]. Olive mill wastewater and the lime mixture was rapidly mixed at 100 rpm for 60 min and then flocculated at 30 rpm for 60 min. After 12 h, the mixture was filtered through a 'tricotton' cloth under a vacuum. Following this, 125 mL was taken from the filtered mixture and diluted with distilled water to one liter. The pH (by adding hydrochloric acid and sodium hydroxide) of the diluted olive mill wastewater was adjusted to the desired values.

Preparation of activated carbon samples: The catalyst was prepared from waste olive stone by chemical activation with KOH. In the first step of activation, olive stone was mixed with KOH at the KOH/OS ratio of 0.70:1 and the mixture was mixed continuously for 24 h. The mixture was then dried at 110 °C to prepare the impregnated sample. In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). The impregnated sample was heated up to activation temperature (800 °C) under N_2 flow (100 mL/min) at the rate of 10 °C/min and held at the activation temperature for 1 h. After activation, the sample was cooled under N_2 flow and washed several times with hot distilled water until a neutral residue was obtained. The washed sample was dried at 110 °C to prepare activated carbon[19].

Instrumentation: Ozone was provided by a generator (TOG C2B) capable of producing up to 8 g/h ozone, when fed with oxygen. In our experiments, production of ozone was 6.24 g/h and the resulting ozone-oxygen gas stream was fed to the reacting medium through a bubble gas sparger with constant flow rate of 116 L/h at room temperature. The ozonation experiments were made in a glass reactor (Fig. 1) which had approximately 1200 cm^3 capacity, with a cover containing inlets for bubbling the gas feed and stirring and outlets for sampling and venting. For all the experiments, the reactor was charged with 1 L of olive mill wastewater solution. Sample contact times were 10-60 min. Samples (about 5 mL) were withdrawn at regular times for analysis.

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10–6 to 1. Before measurement, the sample was degassed at 300 °C for 2 h. The BET surface area (S_{BET}), total pore volume (V_{total}), micropore area (S_{micro}), mesopore area (S_{meso}), average pore diameter (D_p) results were obtained from the adsorption isotherms. Mesopore volume was determined by subtracting the micropore volume from the total pore volume. The morphological analysis of prepared and treated active carbons were carried out on a Philips SEM 505 electron microscope equipped with EDX analyzer. The removal efficiency of the samples was determined with the absorbance value of the samples by monitoring UV-visible spectrum using a Shimadzu UV-2101 PC double beam spectrophotometer. The intermediates produced during ozonation of olive mill wastewater were determined by GC-MS (Shimadzu QP2010) with a TRB-WAX (100 % polyethylene glycol) column (0.2 µm, 30 m × 0.30 mm) and electron impact (EI) detector (70 eV). The run temperature was 50 °C (5 min) – 10 °C min^{-1} – 270 °C (10 min) and the temperatures of the inlet, interface and ion sources were 270, 270 and 230 °C, respectively. The IR spectra was obtained in the 4000–400 cm^{-1} region using KBr pellets on a Perkin–Elmer RX-1 FTIR spectrometer.

RESULTS AND DISCUSSION

Characterization of activated carbon samples: The BET analysis results of the activated carbon prepared from olive stone was given in Table-2.

TABLE-2
POROUS STRUCTURE PARAMETERS OF THE ACTIVATED CARBON

S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Dp (nm)
1275	185	1091	0.73	0.094	0.064	2.29

Table-2 shows that the specific surface area of activated carbon is 1,275 m^2/g. The highly active surface properties of

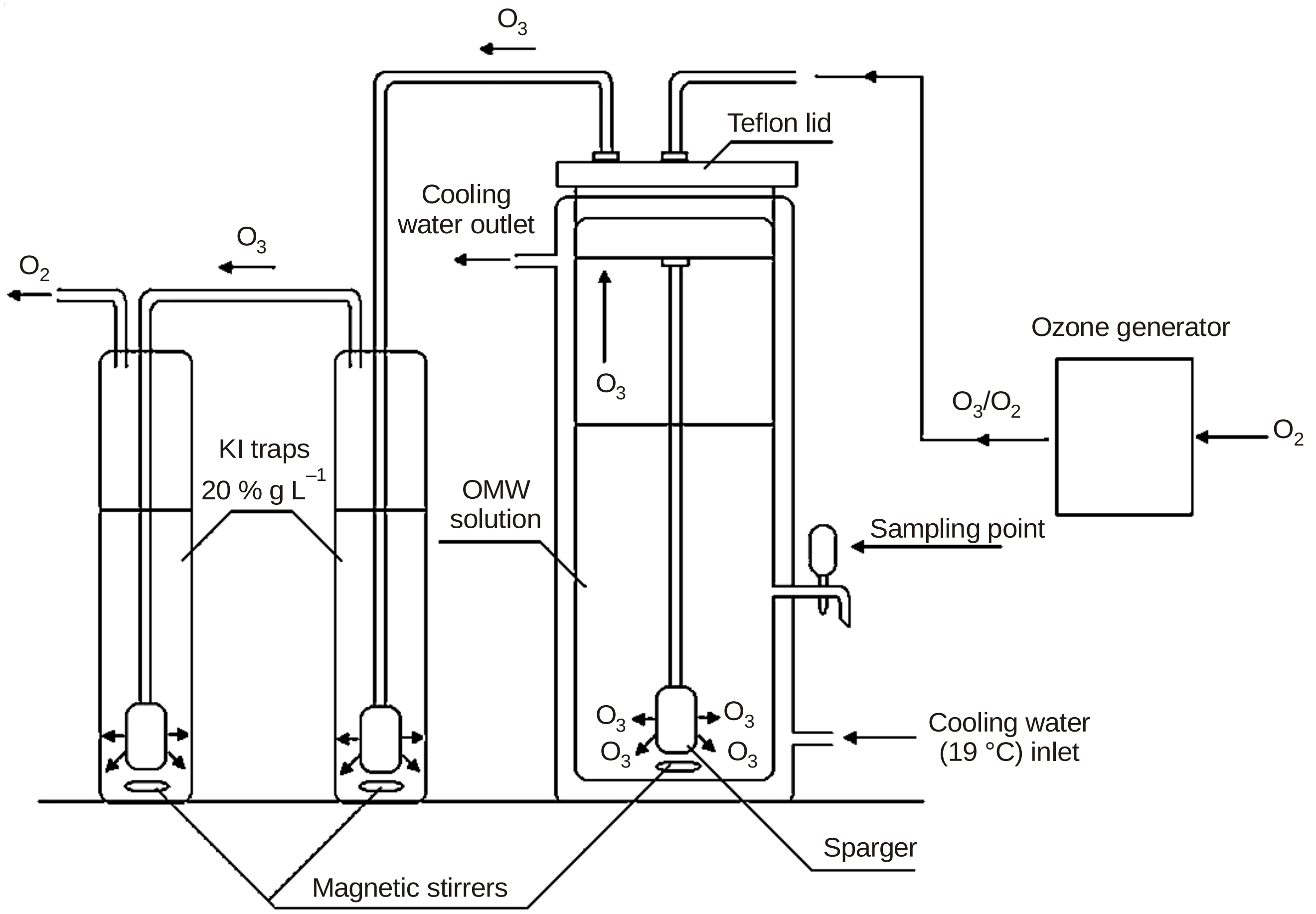

Fig. 1. Experimental setup for ozonation process [Ref. 20]

activated carbon was attributed to their chemically modified surfaces. The porosity is dependent on the starting material[21,22]. Pore volume analysis showed that during KOH activation of activated carbon pore volumes evolve by generation of micropores (13 %) and the originally narrow micropores collapse to mesopores (87 %).

Surface morphology plays a significant role in determining the surface availability. The SEM image presented in Fig. 2 shows a highly porous morphology of the KOH treated activated carbon with pores. The micrographs reveal that the external surfaces are full of cavities and large holes which suggest that activated carbon exhibits a high surface area.

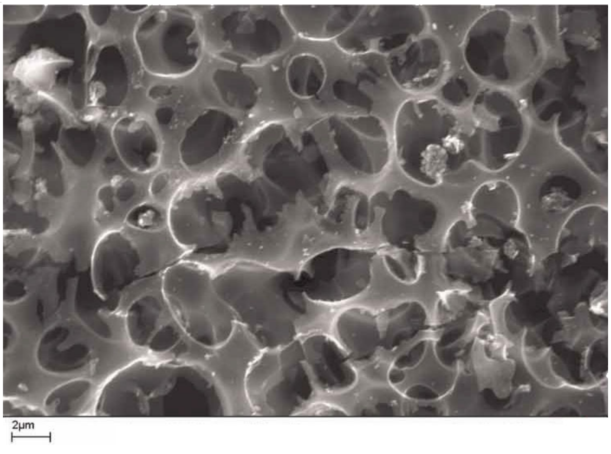

Fig. 2. SEM micrograph of activated carbon

Effect of pH on ozonation of olive mill wastewater: To determine the optimum pH value, pH of the olive mill wastewater solutions were adjusted to 5, 7 and 11 and each subjected to ozonation for 60 min. In particular, double bonds, aromatic compounds and decolourization were determined by measuring the absorbance of the samples at 254, 280 and 410 nm, which corresponds to the absorbance of some organic compounds occurring in olive mill wastewater, respectively. According to the results of UV-visible absorbance measurement optimum pH was found to be 7. The effect of the pH in the removal rates is displayed in Fig. 3.

Effect of double bond, aromaticity and colour removal on samples of olive mill wastewater ozonation: Using only Whatman filters, samples of olive mill wastewater and pretreated with lime samples of olive mill wastewater were adjusted to pH 7. Single ozonation and in presence of activated carbon ozonation for 60 min in diluted olive mill wastewater solutions were carried out. UV-visible measurements of the samples were taken 254, 280 and 410 nm at regular intervals. The removal rate at the three wavelengths are given in Fig. 4. According to the figures, the best method is lime treatment/O_3 with removal efficiency at UV_{254} 70.47 %, UV_{280} 78.57 % and UV_{410} 96.24 %.

Removal of total phenolics: The pH of the olive mill wastewater solutions was adjusted to pH 7. Ozonation experiments with activated carbon and without activated carbon were carried out in these olive mill wastewater solutions. The reduction rate of total phenolics is shown in Fig. 5. As can be observed,

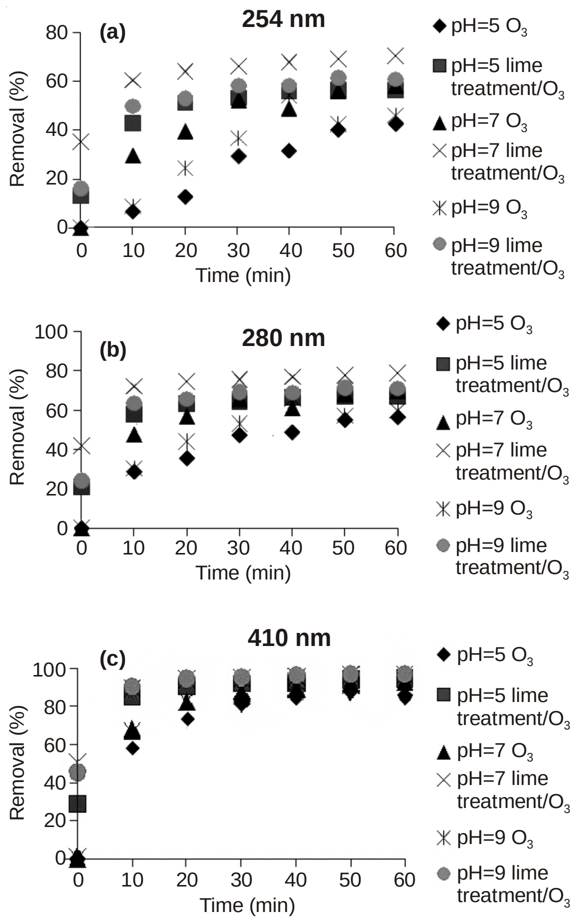

Fig. 3. (a) UV_{254}, (b) UV_{280} and (c) UV_{410} removal *versus* time by ozonation, lime treatment/ozonation at varying pHs

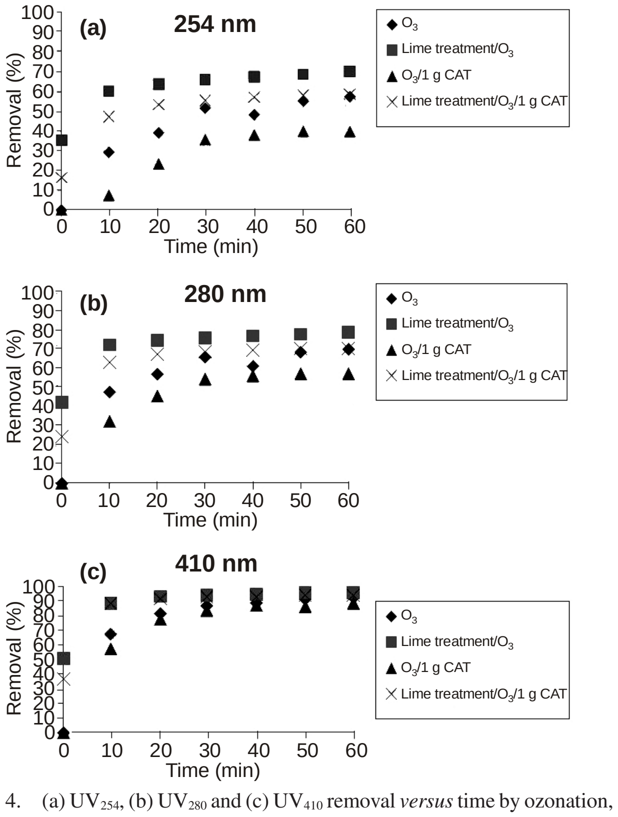

Fig. 4. (a) UV_{254}, (b) UV_{280} and (c) UV_{410} removal *versus* time by ozonation, lime treatment/ozonation, ozonation/1 g CAT, lime treatment/ozonation/1 g CAT at the pH = 7

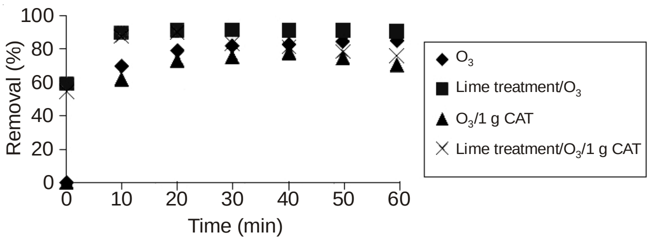

Fig. 5. Total phenolics removal *versus* time by ozonation, lime treatment/ ozonation, ozonation/1 g CAT, lime treatment/ozonation/1 g CAT at pH = 7.0

a significantly higher removal than 90 % is reached after 10 min of ozonation in lime treatment/ozonation experiments. Similarly, important dephenolization (around 90 %) was achieved by using activated carbon lime treatment/ozonation experiments but, the rate of phenol removal was decreased after 30 min ozonation time. This decreasing rate of phenol removal may have resulted in degradation of the occurring phenolics with process of ozonation.

Effect of ozonation and lime treatment/ozonation methods on the COD and TOC reduction efficiency: Ozonation and lime treatment/ozonation methods for olive mill wastewater according to the results were compared to both the COD and the TOC after 60 min ozonation time. Lime treatment/ozonation with removal of COD (39 %) and TOC (40 %) was found to be the optimal method. Fig. 6 shows the experimental COD and TOC results.

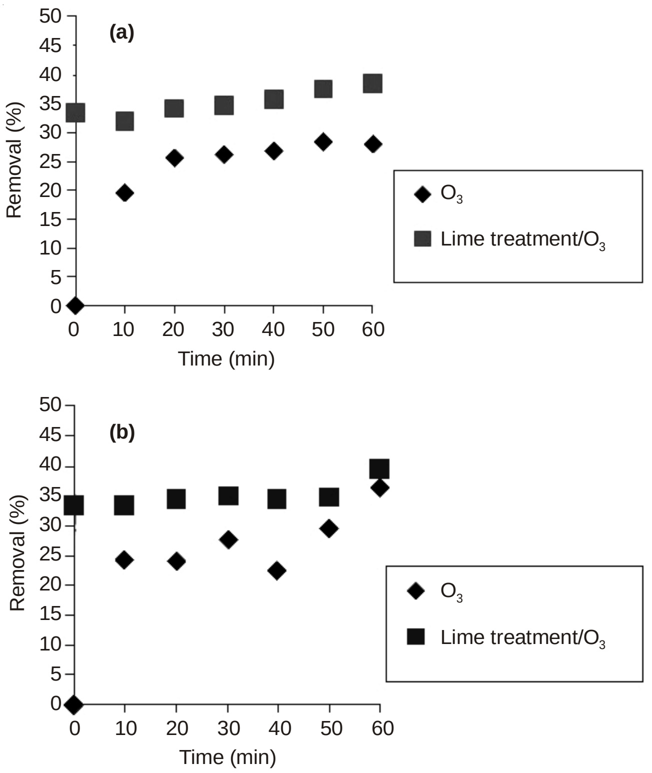

Fig. 6. (a) COD and (b) TOC removal *versus* time by ozonation, lime treatment/ozonation

GC-MS analysis of olive mill wastewater before and after ozonation: Fig. 7 shows GC-MS results of before and after treatment at pH 7. Ozonation at optimum pH 7 was capable of substantially reducing the concentration of the majority of

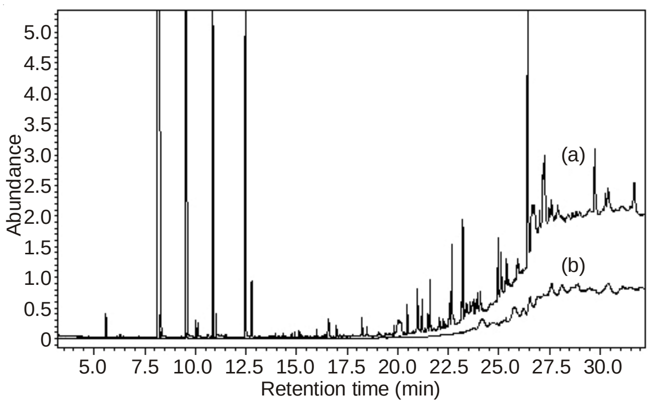

Fig. 7. GC-MS chromatograms of samples taken before and after ozonation treatment: (a) original sample; (b) after 60 min (pH = 7)

identified compounds (phenol, 4-propyl phenol, hydro-*p*-coumaric acid, vannilic acid, 2,3-dihydrobenzohydrofuran, *etc*.) present in the untreated olive mill wastewater sample, while they have nearly disappeared after 60 min treatment.

FTIR analysis of activated carbon prepared from olive stone before and after ozonation: Activated carbon has exhibited competitive effect on reacting $OH^\bullet$ radicals which are formed by ozone decomposition. Therefore, degradation of olive mill wastewater in the presence of activated carbon decreased significantly compared with lime treatment/ozonation. This assumption was supported by taking IR spectra of activated carbon before and after reaction with $OH^\bullet$ radicals in large excess.

The absorption band 3326 cm^{-1} appears after reaction with hydroxyl radicals. The absorption band 1571 cm^{-1} of carbonyl groups are considered as higher, while the absorption band 1713 cm^{-1} disappears after reaction with hydroxyl radicals.

Conclusion

The lime pre-treatment proposed to reduce the polluting effect of olive mill wastewater is an applicable method in practice, since lime can easily be purchased anywhere and it is cheaper than other chemicals. In the present study, it was aimed to investigate the potential uses of activated carbon as a catalyst and reduce the pollution level of olive mill wastewater to discharge standards. When the effect of pH on the removal was tested on ozonation processes, the lime treatment/ozonation combine process was found to be the best method. In the presence of activated carbon, ozonation on samples of olive mill wastewater showed less activity towards the removal of double bond, aromaticity and colour, TOC, COD and total phenol concentration. Phenyl groups in activated carbon structure reacted with $OH^\bullet$ radicals and caused a decrease in degradation levels of olive mill wastewater of parameters. The lime treatment/ozonation of olive mill wastewater at pH 7.0 reduced the values of COD, TOC and total phenol concentration 39, 40 and 90 % respectively.

The use of activated carbon prepared from olive stone provides attractive opportunities for improving the economic and environmental impact of the olive oil industry's technologies. The combination of the catalysts as activated carbon with ozonation in this study did not give very effective results compared with the lime treatment/ozone process. Activated carbon may be used after lime pretreatment as an adsorbent before the ozonation process instead of a catalyst. Indeed, using activated carbon as an adsorbent may increase removal of COD, TOC and total phenol before the ozonation process. It may also reduce contact time with ozone during the oxidation process.

ACKNOWLEDGEMENTS

This work was financially supported by Academic and Research Projects Unit of Çukurova University (BAPB) (Project No: 2007YL31).

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