Start-up of a free water surface constructed wetland for treating olive mill wastewater

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Abstract
An olive mill's existing evaporation pond was separated into five cells and transformed into a free water surface constructed wetland. The constructed wetland was used as a post-treatment stage for olive mill wastewater (OMW). Wastewater was previously treated by an aerobic trickling filter. The influent concentrations in the constructed wetland were 27400, 4800, 105 and 770 mg.L^{-1} for COD, phenols, ortho-phosphate and TKN, respectively. Despite the rather high influent concentrations, the performance of the constructed wetland was very good since after the 60-day start-up operation period it achieved removal rates of about 94, 95, 95 and 98% for COD, phenols, ortho-phosphate and TKN, respectively. The major pollutant removal processes can be attributed to both biological processes occurring in the wetland and photo-oxidation. Laboratory-scale experiments with OMW from fifth cell of the wetland revealed that the net contribution of photo-oxidation after 112 h of simulated solar radiation at 765 W/m^2 (*i.e.*, about 38 days of sunlight irradiation) was 18 and 31% removal for COD and phenols, respectively. In the constructed wetland, the total removal reached 81 and 86% for COD and phenols, respectively, for the same time period (38 days).

Keywords: Constructed wetlands, free water surface flow, olive mill wastewater.

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Although olive oil extraction is rather important for Mediterranean countries, as almost all worldwide production (95%) is produced there [1], the olive mills are also major environmental pollutants. Olive mill wastewater (OMW) is produced from three-phase olive mills and is characterized by its high organic (110–220 kg COD/m^3) and phenolic load [1]. Therefore OMW treatment is imperative in order to protect the environment. As olive mills are usually small family enterprises they cannot handle the cost of a conventional treatment facility.

Although CWs have been used to treat a variety of wastewaters, only few attempts to treat OMW have been presented previously [2–6]. In these studies all three CWs types were used to treat OMW, although the majority of these applications used VF systems [2,4,6], while HSF [7] and FWS [3] systems have only been used once. To minimize the pollutant load and reduce phytotoxicity [8], the majority of these applications used various pre-treatment stages including coagulation [2], electrochemical oxidation [4], and biological trickling filters [6]. In the studies in [3] and [5] no pre-treatment stage was used, however the OMW was strongly diluted with tap water until it reached a dilution factor of 10 [3].

The present study presents the results of the start-up period of a full-scale FWS CW treating pre-treated OMW in a Mediterranean climate. OMW is first treated in a trickling filter and is then introduced into the FWS CW. Laboratory-scale photo-oxidation experiments were performed to estimate the quantitative contribution of photo-oxidation to the total pollutant removal. To the best of our knowledge, this is the first study on the effectiveness of a full-scale CW in treating OMW.

MATERIALS AND METHODS

Trickling filter

The olive mill plant is located near Amfilochia city in Aitoloakarnania Prefecture (Western Greece). OMW produced in the olive mill is initially treated by a trickling filter. The trickling filter is a metallic cylindrical tank 1.8 m in diameter and 3 m in height. It is filled with random-type high-density polyethylene (HDPE) media, with a specific area of 188 m^2 m^{-3}, a specific weight of 47 kg m^{-3}, and filter porosity 95%. To achieve natural aeration the filter has twelve ventilation valves

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at its base and its top is open to the air. OMW enters the filter through a rotating distributor, thus ensuring uniform distribution of the wastewater and then is drained to the filter's base. The treated OMW is led into the bottom of a plastic cylindrical recirculation tank of 30 m^3 total volume, where it is mixed with the raw wastewater from the olive mill plant. This diluted wastewater from the plastic tank is continuously recirculated to the top of the filter at a flow rate of 160 L min^{-1}, using a pump. Influent concentrations ranged from 34000 to 46000 mg L^{-1} for COD, from 4000 to 10000 mg L^{-1} for phenol, from 700 to 1100 mg L^{-1} for TKN, and from 100 to 180 mg L^{-1} for ortho-phosphate. Effluent concentrations ranged from 11500 to 27500 mg L^{-1} for COD and from 2600 to 4900 mg L^{-1} for phenols, from 600 to 1000 mg L^{-1} for TKN, and from 70 to 110 mg L^{-1} for ortho-phosphate. The treatment system removes about half of the organic and phenol loads, while nutrients (nitrogen and phosphorus) are also removed at lower percentages [9]. Treated wastewater overflows from the recirculation tank into the FW CW.

Description of the full-scale constructed wetland

The full-scale CW is an FWS divided into five cells by soil barriers (Fig. 1). To avoid OMW leakage, the base of the CW was lined with clay. The CW has an incline of 2% and the five cells cover a surface area of 400, 350, 700, 350 and 250 m^2 for cells 1–5, respectively (total area 2050 m^2). The first two cells, the closest to the influent entry point, were kept unplanted due to the high pollutant concentrations present in these cells that are toxic for plant growth, while the three last cells were planted with common reeds (*Phragmites australis*) in March 2011. Reed growth was rapid in the following two months. At the end of April, pre-treated OMW was introduced into the first cell for one day until all the cells were flooded. From this point in time, OMW did not flow in or out of the CW or between the cells until the end of June. The CW operated under batch conditions for 60 days (a hydraulic residence time (HRT) of 60 days). The CW had an initial mean depth of 0.5 m, thus initial OMW volumes in the FWS CW were 200, 175, 350, 175 and 125 m^3 for cells 1–5, respectively (total OMW volume 1025 m^3). In real operation conditions the CW will receive a maximum flow rate of 30 m^3/d, while the maximum hydraulic loading rate (HLR) and organic loading rate (OLR) will be 14.6 L m^{-2} d^{-1} and 285 g COD m^{-2} d^{-1}, respectively. The CW's minimum HRT under continuous flow will be 35 d. Due to high evapotranspiration (ET) rates, the depth of the CW reduced to 20 cm after 60 days. Liquid samples (38 samples per campaign) were collected in six monitoring campaigns from April to June from the influent, effluent, and various other points of each cell, in order to cover the whole CW area. The CW operated for only 60 days, as during this period the OMW level in the CW was minimal due to high ET rates. In each monitoring campaign the CW depth was also measured in order to estimate ET values and correct measured pollutant concentrations. To calculate these removal efficiencies the pollutant concentration in cell 1 at day 0 was used as the influent value and the concentration in cell 5 at day 60 was used as the effluent value.

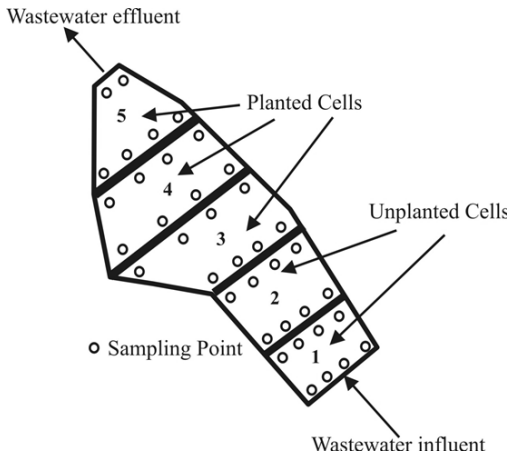

Figure 1. Full-scale free water surface flow constructed wetland layout (scale 1:600).

Photo-oxidation experiments

Photo-oxidation of centrifuged (4000 rpm for 20 min) wastewater samples taken from the fifth cell at day 0, was performed using a Suntest XLS+ solar light simulator from Atlas (Germany) equipped with a xenon arc lamp (2.2 kW) and special glass filters restricting the transmission of wavelengths below 290 nm. An average irradiation intensity of 765 W m^{-2} (range between 300 and 800 nm) was maintained throughout the experiments and was measured by an internal radiometer. Chamber and black panel temperatures were regulated by the pressurized air cooling circuit and monitored using thermocouples supplied by the manufacturer. Irradiation experiments were performed using a cylindrical 250 mL Duran® glass UV-reactor with a flat flange lid with three necks (Lenz, Germany; light absorbance λ < 300 nm) with a thermostatic jacket. A tap water cooling circuit was used to prevent any heating of the solution and keep the temperature at 24±1 °C. Aliquots (10 mL) were collected at different time intervals, and the concentration of total phenols and COD was analyzed according to the procedures described below. To assess biological activity, a control experiment was also carried out under dark conditions. In this experiment the same OMW was placed in a vessel and aliquots were collected at the same time intervals with the ones from the photo-oxidation experiment. During this experiment (data not shown) no alterations in COD or phenol concentrations were observed, leading to the con-

clusion that no significant microbial activity took place. Equivalent days of sunlight were determining according to the following equation based on the OECD guidelines [10,11] for the testing of chemicals:

$$\text{Days of sunlight} = \frac{h \times r}{0.75 \times 12}$$

where *h* represents hours of irradiation by the Xenon lamp of Suntest simulator, *r* is the ratio of intensity of the xenon radiation to that of the sunlight in the studied period, 0.75 is the correction factor for diurnal variation of natural sunlight, and 12 is the conversion of hours to days.

Water sample analysis

The water samples were analyzed for COD, TKN, orthophosphate (OP), and phenols. The open reflux method was employed to measure COD, the titrimetric method was used to measure TKN, and the stannous chloride method was used to measure phosphorus [12]. Phenol (with respect to syringic acid) concentrations were determined spectrophotometrically according to the Folin–Ciocalteu method [13] using a JASCO V-530 UV/Vis spectrophotometer. Meteorological data (air temperature, atmospheric pressure, air humidity, wind velocity and direction, and total precipitation) were collected from the closest meteorological station in Kompoti (www.meteo.gr). Figure 2 presents time series charts for mean air temperature and total rainfall. During the CW operation the mean air temperature was 24.7 °C and the total precipitation was 90 mm, while the OMW temperature in the CW varied from 14 to 23 °C.

Meteorological parameters significantly affect pollutant removal efficiency in CW systems [14]. For example, high amounts of precipitation tend to dilute wastewater, thus effluent concentrations appear to be

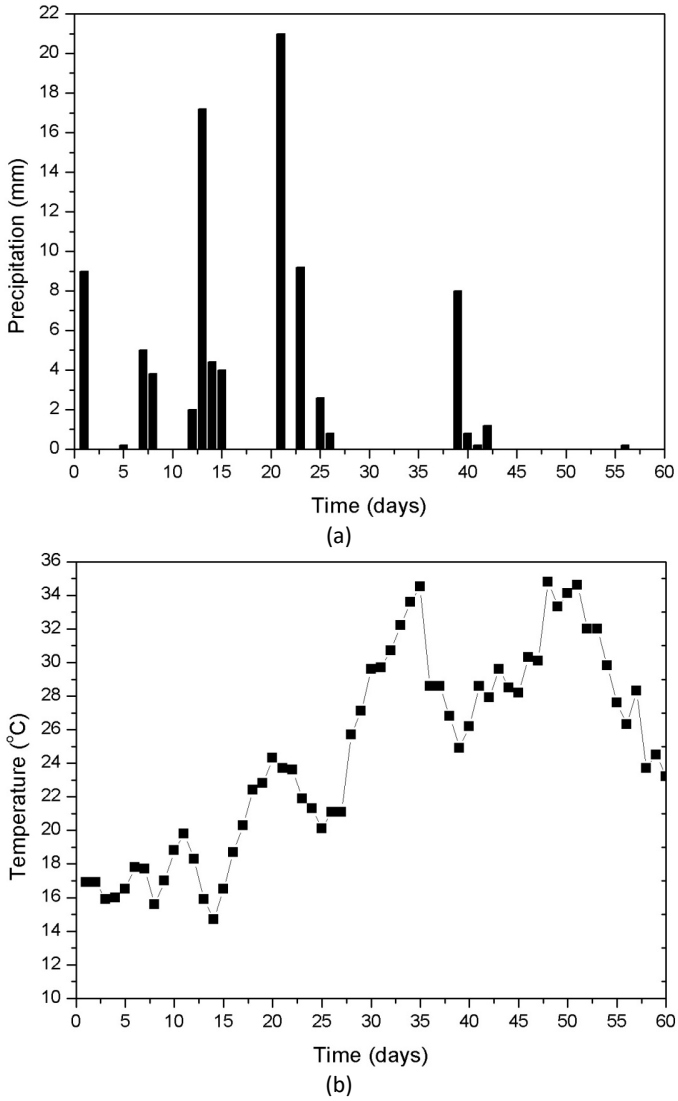

Figure 2. Time series charts for: a) air temperature and b) precipitation during the study period.

lower than expected and removal efficiencies higher. On the contrary, during periods of high temperature and solar radiation, water levels can decrease due to increased ET values, leading to underestimation of removal efficiency. In order to avoid over – or under – estimation of pollutant concentrations, the measured values were corrected by estimating OMW volumes in each cell in each sampling campaign. During the study period, the total precipitation was 90 mm, which added 185 m^3 of water into the whole CW. At the end of the 60-day study period, the final depth of the CW was 0.2 m, resulting in an average ET value of 6.5 mm d^{-1} (×60 *d* = 39 cm over 50 cm initial depth).

RESULTS AND DISCUSSION

The mean concentrations of COD and phenols in the raw OMW were 45000 and 9500 mg L^{-1}, respectively. The filter effluent concentrations, when OMW was introduced into the CW, were 27400 and 4800 mg L^{-1} for COD and phenols, respectively.

Figure 3 presents time series charts for COD, phenols, TKN and TP from samples of OMW taken from the FWS CW (mean values of concentrations are presented with a relative standard deviation not exceeding 5%). Mean pollutant concentrations of all the wastewater samples taken from each cell were used for the time series charts. Pollutant concentrations at the different sampling points in each cell did not show great variations (standard deviations were 801, 961, 1.3 and 2.5 for COD, phenols, TP and TKN, respectively), thus implying that OMW was homogenized in all cells. These homogenized pollutant concentrations in each cell occur due to the fact that CW was operated under batch conditions and OMW did not flow among the cells. At the beginning of the experiment (day 0) influent concentrations were 27400, 4800, 191 and 770 mg L^{-1} for COD, phenols, TP and TKN, respectively. At day 0, when the entire CW was flooded, all pollutant concentrations in cells 2–5 were lower than in cell 1, indicating that the soil barriers acted to reduce the pollutant loads, possibly due to suspended solids reten-

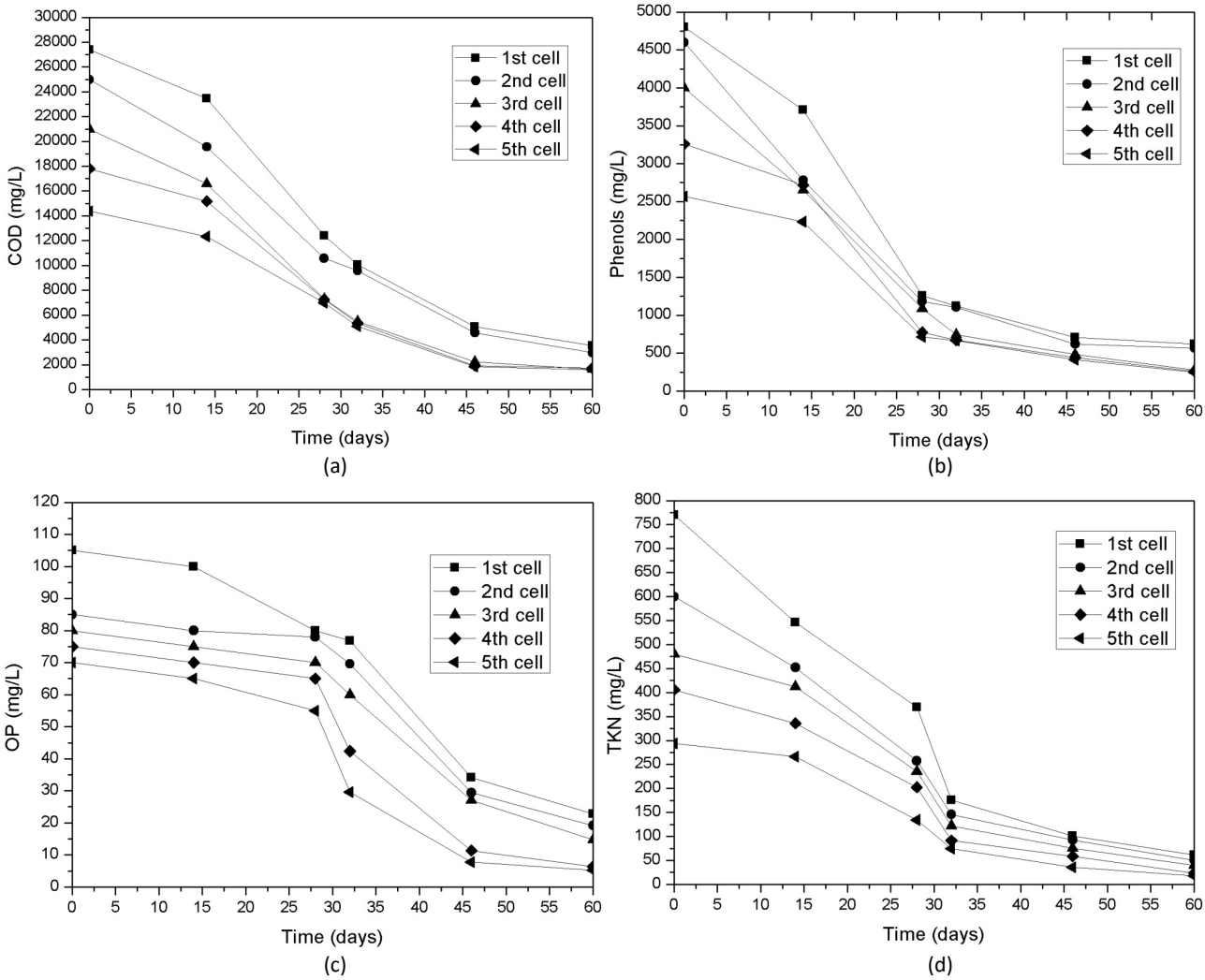

Figure 3. Time series charts of corrected pollutant concentration in the FWS CW for: (a) COD, (b) phenols, (c) OP and (d) TKN.

tion. Pollutant concentrations decreased with time in all cells and followed similar trends. After 60 days of operation significant removal of all pollutants was achieved, as total removal efficiencies were recorded as 94, 95, 95 and 98% for COD, phenols, OP and TKN, respectively.

COD, phenols and TKN show similar trends of concentration decrease, as organic matter and nitrogen are mainly removed by microbial activity, which is enhanced in periods with high air temperatures [14]. Although OMW temperature values were higher (23 °C) at the end of the 60-day study period, the observed decrease in concentrations of COD, phenol and TKN was limited, possibly because the remaining pollutants are not easily bio-degradable. On the other hand, OP concentrations showed a more gradual decrease with time, as OP is mainly removed through precipitation in FWS CWs.

Although the monitoring program lasted only 60 days, the FWS CW achieved high pollutant removal rates in this short operation period. However, the measured final effluent concentrations were 3960 mg L^{-1} for COD (corrected value 1584 mg L^{-1}, Fig. 3a), 656 mg L^{-1} for phenols (corrected value 248 mg L^{-1}, Fig. 3b), 13 mg L^{-1} for OP (corrected value 5.2 mg L^{-1}, Fig. 3c), and 45 mg L^{-1} for TKN (corrected value 18 mg L^{-1}, Fig. 3d). These measured concentrations remain above legislation limits, as according to the EU Directive 1991/ /271/EEC, COD, total nitrogen and total phosphorus limits are 120, 10 and 2 mg L^{-1}, respectively. Therefore, further treatment should be achieved by modifying the treatment facility in two ways: a) by introducing flocculation and sedimentation prior to the trickling filter treatment in order to reduce organic load and b) by recalculating the CW's effluent in order to increase HRT and lead to lower pollutant concentrations. Another issue for the operation of this treatment system is the sludge that accumulates mainly at the bottom of the first two unplanted compartments. This sludge can be easily removed periodically and treated. Co-composting of this sludge with other agro-industrial by-products is a viable and low cost solution, as many composting applications have used olive mill wastes as co-composting materials [15].

In previous studies the main CW types used for OMW treatment were HSF [7] and VF [2,4,6]. Results of only one FWS application have been published [3]. While for all CW types COD removal efficiencies present similar values (subsurface flow CWs ranged from 69 [7] to 73% [6] and FWS was 86% [3], subsurface CWs treated higher organic matter surface loads (ranging from 15 [2] to 6589 g m^{-2} d^{-1} [6], compared to the FWS (5-15 g m^{-2} d^{-1} [3]). The FWS CW of the present study appears to perform better than the other CW's as the organic matter surface load was significantly higher (57 g m^{-2} d^{-1}). VF CWs are more efficient in OMW treatment, as their organic matter and phenol removal efficiencies were higher compared with the other CW types. However, they do have one major drawback in OMW treatment and that is pore clogging due to the high concentration of suspended solids [5]. CWs appear to be extremely efficient in OMW treatment. Additionally, they have low construction and operational costs, and therefore could be an attractive treatment method for owners of small olive mills.

The photo-oxidation experiment lasted 112 h and samples were taken every hour for the first 6 hours and then twice a day. The 112-h duration of the experiment was chosen as it corresponds to approximately thirty--eight days of sun radiation in this part of Greece, according to data from the local meteorological station. Figure 4 presents the photo-oxidation kinetic profiles for COD and phenols, respectively. COD and phenol concentrations gradually decreased with time and at the end of the experiment their removal rates were 18 and 31%, respectively. In comparison, effluent concentrations in the CW at day 38 were 5200 mg L^{-1} for COD and 672 mg L^{-1} for phenols resulting in removal rates of 81 and 86%, respectively. These rates indicate that photo-oxidation is an important pollutant degradation process that is also costless as it only requires solar energy. The differences between the removal efficiencies of FWs CW and the photo-oxidation experiment were very high, and appear to prove that biological oxidation is the dominant mechanism of organic matter and phenol degradation.

In the photo-oxidation experiment phenol concentrations increased during the first hours of the experiment. This could be attributed to the split of multiphenolic substances to phenols. According to [1], in the first phase of phenol photo-oxidation, aromatic intermediates are formed which increase the total phenol concentration. Figure 4 also presents the exponential fit for COD and phenol degradation during the photo-oxidation experiment. It appears that for both phenols (R^2 = 0.945) and COD (R^2= 0.944), second order decay was satisfactory. This second order decay is expressed by FOCUS [16] as a bi-phasic pattern of degradation, where a fast initial decrease in pollutant concentrations is often followed by a slower decline.

CONCLUSIONS

This study examined: a) the pollutant removal efficiency of a FWS CW receiving pre-treated OMW and b) the contribution of photo-oxidation to the pollutant removal process. The photo-oxidation contribution appeared to be limited, since following 112 h of laboratory simulated solar radiation at 765 W m^{-2} (corresponding approximately to thirty-eight days of sun radiation) removal rates of COD and phenols were 18 and

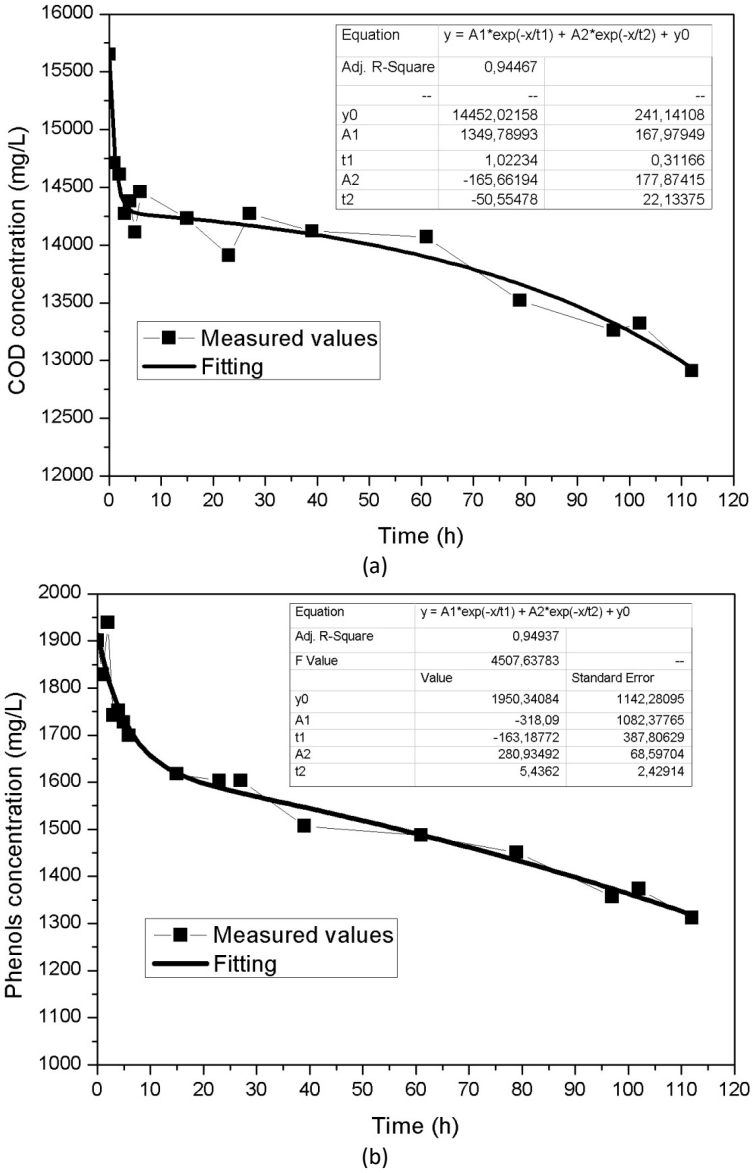

Figure 4. Time series charts and fitting of the photo-oxidation experiment for: a) COD and b) phenols.

31%, respectively, while for the same period, the total removal rates in the full-scale CW reached 81 and 86% for COD and phenols, respectively. The 60-day operating period of the full-scale FWS CW showed that:

- The full-scale FWS CW was quite efficient in treating pre-treated OMW, as it managed to reduce COD from 27400 to 3960 mg L^{-1}, phenols from 4800 to 656 mg L^{-1}, TKN from 770 to 45 mg L^{-1}, and OP contents from 191 to 13 mg L^{-1}.
- The pollutant surface loads applied in this study were significantly higher than those applied in other FWS CWs reported in the literature.
- Despite the high removal efficiencies, the final effluent concentrations still exceed legislation limits for irrigation use or environmental disposal.

Results from the present and previous studies indicated that CWs are extremely effective in treating OMW, which, in combination with their extremely low construction and operation costs, make them a very attractive treatment method for owners of small olive mills.

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IZVOD

IZGRADNJA VESTACKE MOCVARE U CILJU TRETIRANJA OTPADNE VODE NASTALE USLED RADA MLINA ZA MASLINE

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(Naučni rad)

Postojeći evaporacioni bazen koji se nalazi u sklopu mlina za masline je podeljen u pet ćelija i transformisan u sistem mokrih polja. Ovako koncipiran sistem korišćen je kao faza tretmana otpadnoh vodu koje nastaju u procesu prerade maslina. Otpadna voda je prethodno tretirana u aerisanom kapajućem filteru, a potom uvođena u mokra polja. U influentu mokrih polja, koncentracija hemijske potrošnje kiseonika, *COD*, je bila 27400 mg L^{-1}, fenola 4800 mg L^{-1}, ortofosfata 105 mg L^{-1} i ukupnog Kjeldal azota, TKN, 770 mg L^{-1}. Uprkos velikoj koncentraciji zagađujućih materija u influentu, učinak mokrih polja je bio veoma dobar s obzirom na to da je nakon 60 dana od početka rada sistema dostigao uklanjanje zagađenja od 94% za COD, 95% fenola, 95% orto-fosfata i 98% TKN. Najveći deo uklanjanja polutanata iz vode se može pripisati biološkim procesima u mokrim poljima i foto-oksidaciji. Eksperimenti na laboratorijskom nivou u pet ćelija sa predmetnom otpadnom vodom su pokazali da je neto doprinos foto-oksidacije posle 112 sati simulirane solarne radijacije na 765 W/m² (što odgovara ukupnom zračenju od oko 38 dana sunčevog zračenja) bio 18% za COD i 31% fenola. U konstruisanim mokrim poljima, za isti period od 38 dana, stepen uklanjanja zagađenja je bio 81% za COD i 86% za fenol.

Ključne reči: Mokra polja • Optadna voda • Prerada maslina