Integration Of Photocatalytic Oxidation And Constructed Wetlands For The Purification Of Wastewater Containing Pesticides

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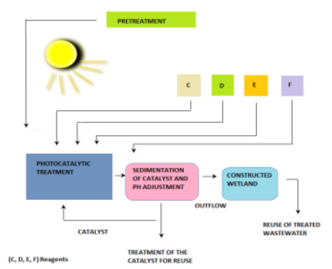

Flow diagram of the wastewater treatment system using the combined action of photocatalytic oxidation and constructed wetlands.

Aim of the present work is the study and the experimental evaluation of an alternative wastewater treatment system, which combines the action of photocatalytic oxidation with surface flow constructed wetlands. This low cost and environmentally friendly system is based on the utilization of solar irradiation and natural processes for wastewater treatment purposes. Experiments were conducted in pilot scale using solar irradiation, for the treatment of simulated wastewater containing the pesticide clopyralid. The data evaluation revealed that the combined system may effectively mineralize and reduce the phytotoxicity of the wastewater, providing a promising solution for the treatment of wastewater containing pesticides in the near future.

Agrochemical wastewater from widespread intensive agriculture in the Mediterranean Region is polluting water with pesticides. Although they play an important role in agriculture, pesticide compounds could cause significant environmental problems upon their release to the environment [1]. Their widespread application is an important concern due to their high toxicity, their ability to accumulate, as well as their tendency for mobility and the long-term effects on living organisms. Advanced oxidation processes (AOPs) have been recognized as an efficient approach to pesticide degradation [2-4]. AOPs are chemical oxidation processes characterized by the production of extremely reactive and unselective species such as hydroxyl radicals ($OH^•$), which are able to degrade even the most recalcitrant molecules into CO_2, H_2O and inorganic ions [3, 5].

The need for alternative methods of treatment of wastewater containing pesticides, resulted in the evaluation of a low cost treatment system that is based on solar photocatalytic oxidation and natural processes. The system combines the synergetic action of photocatalytic oxidation with surface flow constructed wetlands, in order to utilize the high solar irradiation in the Mediterranean region and the ability of the constructed wetlands to improve water quality through natural processes, providing wastewater capable of being reused.

Aim of this work is to present results from the experimental evaluation of this combined system on the purification of simulated wastewater containing clopyralid, (3,6-dichloro-2-pyridine-carboxylic acid), a systemic herbicide from the chemical class of pyridine compounds, often detected in drinking water [6]. Clopyralid may be persistent in soil under anaerobic conditions, it presents high solubility in water and is particularly stable against hydrolysis and photolysis. Its chemical stability along with its mobility enables this herbicide to penetrate through soil, causing a long term contamination of ground water and surface water supplies [7, 8].

Experiments were conducted at pilot scale and consisted of two phases. In the first one, the wastewater was treated by photocatalytic oxidation, aiming to the reduction of the organic load, while the final effluent was channeled into surface flow constructed wetlands for the final purification. The photocatalytic treatment was tested using solar irradiation in a pilot-scale unit able to treat 20 L of wastewater. The unit constitutes of three parts: a) A photocatalytic, fountain type, reactor. The main idea is based on the design of six nozzles, through which the waste to be processed, enters the tank from the bottom of the unit, to the reactor. The nozzles create parallel, turbulent flow and vigorous stirring of the wastewater. Excess of the wastewater overflows and leads back to the tank, from which is recirculated to the reactor by a pump. The irradiation source (solar or artificial) is located above the reactor, illuminating the suspension. b) A reservoir located at the lower part of the reactor, for storing wastewater, and c) an Imhoff type tank for separation of the treated effluent from the catalyst. For the needs of the second phase, three surface flow wetlands were constructed in parallel order. The design of the wetlands was based on the suggested by EPA method [9].

Figure 1 shows that the decrease of the organic load in total reaches 93, 92 and 87%, while photocatalytic oxidation itself leads to a 49, 40 and 52% DOC reduction in the case of photo-Fenton, Ferrioxalate and TiO_2 P25/photo-Fenton, respectively, within 1 h of solar illumination. Subsequently, constructed wetlands lead to an additional DOC reduction in all three cases, proving its beneficial contribution to the removal of the organic content of the simulated wastewater. The concentration of the inorganic ions (nitric, nitrate, ammonium, phosphate) at the outlet of the wetlands were in all cases below the acceptable levels according the Greek legislation concerning the disposal of wastewater at Thermaikos gulf (prefectural order 22374/91/94), as well as than the limits defined by the European directive concerning drinking water quality.

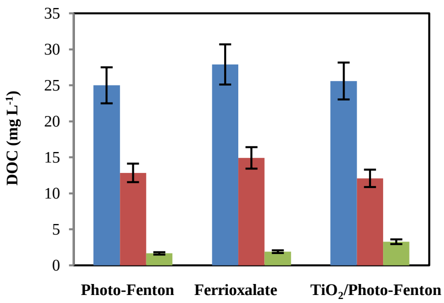

Fig. 1: Organic load reduction of wastewater containing 40 mg L^{-1} clopyralid in the presence of solar irradiation and photo-Fenton, Ferrioxalate or TiO_2/photo-Fenton (7 mg L^{-1} Fe^{3+}, 100 mg L^{-1} H_2O_2, 33 mg L^{-1} $C_2O_4^{-2}$, 0.5 g L^{-1} TiO_2 P25) after 1 h of treatment with the combined system: (■) photocatalysis inflow, *(*■) photocatalysis outflow and *(*■*)* wetland outflow.

The evaluation of potential phytotoxicity of the samples during the various stages of treatment with the integrated system solar photocatalysis (Ferrioxalate: 7 mg L^{-1} Fe^{3+}, 33 mg L^{-1} $C_2O_4^{2-}$, 100 mg L^{-1} H_2O_2)/constructed wetlands *(Typha spp)*, was conducted by employing three higher plant species (*Sinapis alba*, *Lepidium sativum*, *Sorghum saccharatum*).

The root inhibition (RI) of the initial simulated wastewater containing 40 mg L^{-1} clopyralid displayed a negligible variation between the three types of plants (*Sorghum saccharatum:* 50.90%, *Sinapis alba:* 52.42 and *Lepidium sativum:* 57.59). At photocatalysis outflow, the RI value demonstrated for all three types of plants, a significant decrease in comparison to the initial clopyralid solution (63.7, 75.2 and 82.1% for *Sorghum saccharatum*, *Sinapis alba* and *Lepidium sativum*, respectively), followed by a subsequent reduction of RI at the outflow of the wetland, possibly due to further degradation of intermediate products that exist in the wastewater after photocatalysis. These findings demonstrate that phytotoxicity decreases remarkably after the use of the combined solar photocatalysis/constructed wetlands system.

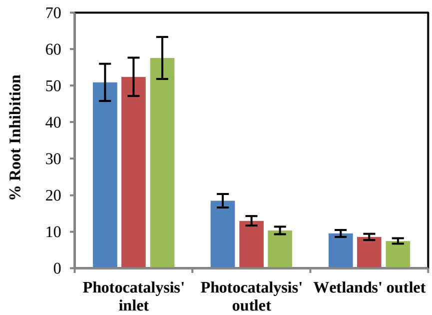

Fig. 2: Effect of simulated wastewater containing 40 mg L^{-1} clopyralid to the length of the root system of the plants: (■) *Sorghum saccharatum*, (■) *Sinapis alba* and (■) *Lepidium sativum, during treatment employing the integrated system photocatalysis (*Ferrioxalate*:* 7 mg L^{-1} Fe^{3+}, 33 mg L^{-1} $C_2O_4^{2-}$, 100 mg L^{-1} H_2O_2*)*/constructed wetlands *(Typha spp)*, in the presence of solar irradiation.

In conclusion, the integrated system solar photocatalysis/constructed wetlands may effectively mineralize and reduce phytotoxicity of simulated wastewater containing clopyralid and may be proven a promising solution for the treatment of wastewater containing pesticides in the near future.

Acknowledgements
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