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

V.Kitsiou[1], C. Berberidou[1], D. A. Lambropoulou[1], A. Antoniadis[1], E. Ntonou [2], G. C. Zalidis[2], I. Poulios[1*]

(1) Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

(2) Laboratory of Applied Soil Science, Department of Geology, Aristotle University of Thessaloniki, Thessaloniki, Greece

*Correspondence: poulios@chem.auth.gr

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INTRODUCTION

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.

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

MATERIALS AND METHODS

Simulated wastewater containing the pesticide clopyralid were prepared using the commercial product *Lontrel 100 AS (Fig. 1)*. Experiments were conducted at pilot scale in two phases (Fig. 2). In the first one, the wastewater was treated by photocatalytic oxidation in the presence of solar irradiation, aiming to the reduction of the organic load, while the treated effluent was channeled into surface flow constructed wetlands for final purification. Photocatalytic treatment took place in a pilot-scale unit able to treat 20 L of wastewater consisting of:

1) A photocatalytic, fountain type, reactor (Fig. 3). The main idea is based on the design of six nozzles, through which the waste enters the tank from the bottom of the unit, to the reactor. The nozzles create vigorous stirring of the wastewater, which is exposed to a light source (solar or artificial) located above the reactor. Excess of the wastewater overflows and leads back to the tank, from which is recirculated to the reactor by a pump;
2) A reservoir located at the lower part of the reactor, for storing wastewater, and
3) 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 based on the suggested by EPA method (Fig. 4).

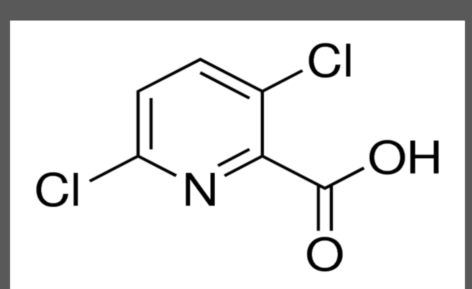

Figure 1: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, M_r: 192 g mol^{-1}) is the active ingredient of the commercial pesticide Lontrel 100 AS (Dow Agrosciences).

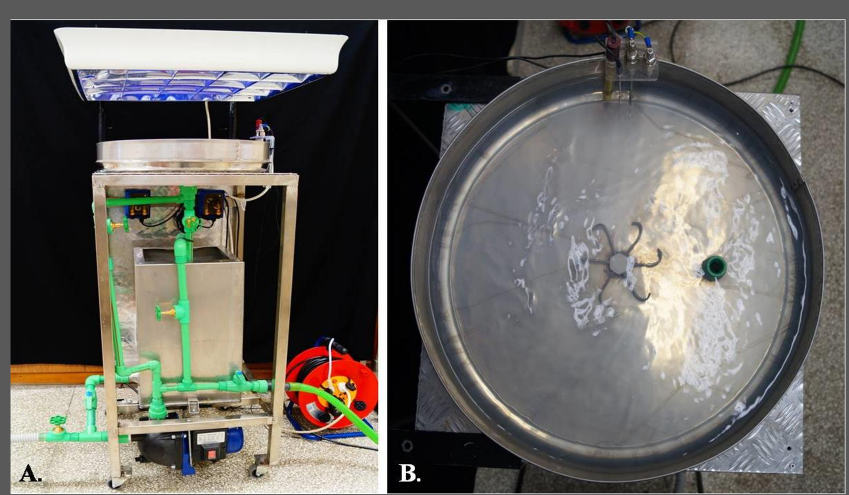

Figure 3: Pilot photocatalytic unit for the treatment of wastewater containing pesticides.

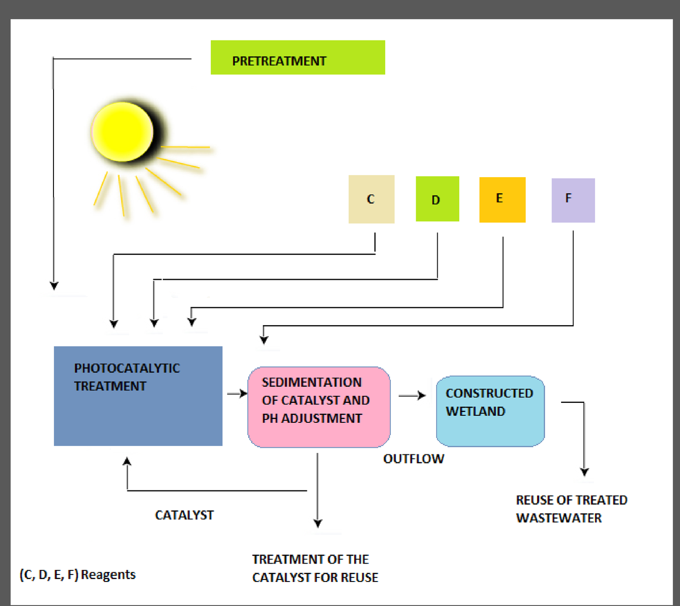

Figure 2: Graph of the wastewater treatment system using the combined action of photocatalytic oxidation and constructed wetlands.

Figure 4: Surface flow constructed wetlands using the plant species Typha spp.

RESULTS AND DISCUSSION

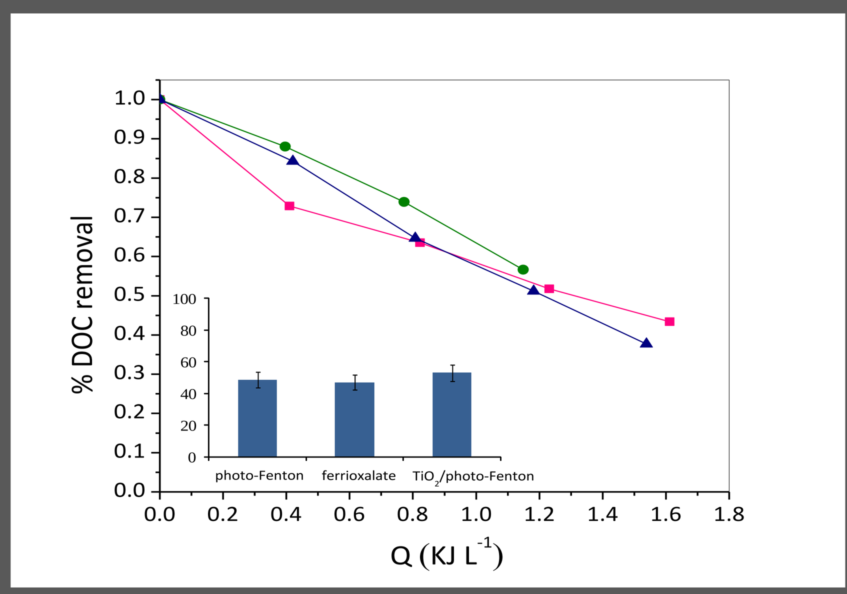

Figure 5: DOC reduction of the simulated wastewater containing clopyralid vs solar energy density, Q, employing: (■) photo-Fenton, (●) ferrioxalate and (▲) TiO_2/photo-Fenton (7 mg L^{-1} Fe^{3+}, 100 mg L^{-1} H_2O_2, 33 mg L^{-1} $C_2O_4^{-2}$, 0.5 g L^{-1} TiO_2 P25). Inset: % DOC reduction within 60 min of solar illumination employing the three photocatalytic systems. Initial clopyralid concentration: 40 mg L^{-1}.

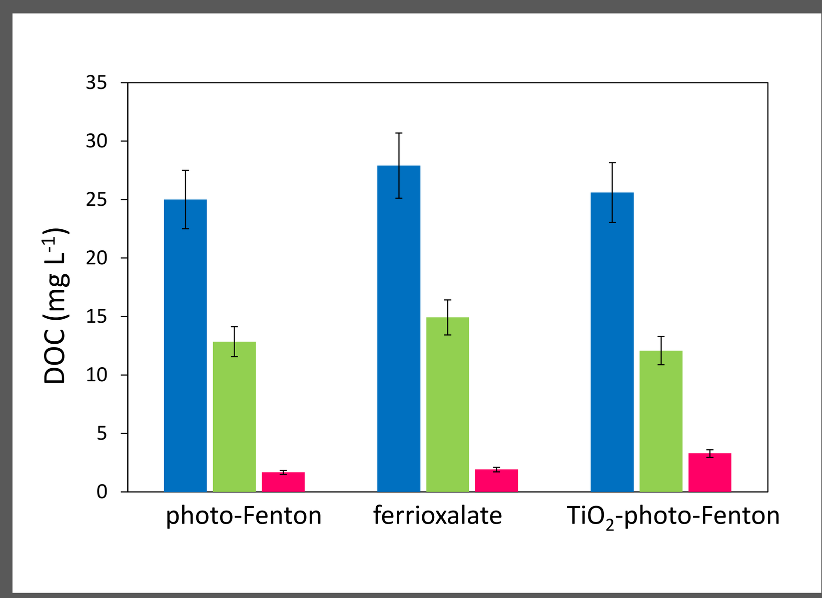

Figure 6: DOC of the wastewater containing clopyralid in the presence of solar irradiation and photo-Fenton, ferrioxalate or TiO_2-photo-Fenton (7 mg L^{-1} Fe^{3+}, 100 mg L^{-1} H_2O_2, 33 mg L^{-1} $C_2O_4^{-2}$, 0.5 g L^{-1} TiO_2 P25) during the treatment phases of the combined system: (blue) photocatalysis inflow, (green) photocatalysis outflow and (red) wetlands outflow. Initial clopyralid concentration: 40 mg L^{-1}.

Photocatalytic method / treatment stage	NO_3^- (mg L^{-1})	NO_2^- (mg L^{-1})	NH_4^+ (mg L^{-1})	PO_4^{3-} (mg L^{-1})
photo-Fenton / photocatalysis inflow	1.80	0.46	1.49	0.36
photo-Fenton / photocatalysis outflow	23.47	n.d.	1.86	0.15
photo-Fenton / wetlands outflow	2.58	0.43	n.d.	0.61
ferrioxalate / photocatalysis inflow	1.91	0.38	1.72	0.41
ferrioxalate / photocatalysis outflow	16.39	0.07	3.37	n.d.
ferrioxalate /wetlands outflow	2.10	0.04	n.d.	0.74
TiO_2-photo-Fenton / photocatalysis inflow	1.73	0.48	1.66	0.32
TiO_2-photo-Fenton / photocatalysis outflow	20.37	0.03	1.95	1.32
TiO_2-photo-Fenton / wetlands outflow	6.93	0.34	n.d.	1.13

Table 1: Concentrations of inorganic nitrogen species and phosphate ions of the simulated wastewater containing clopyralid during the treatment phases of the combined system in the presence of photo-Fenton, ferrioxalate and 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). Initial clopyralid concentration: 40 mg L^{-1}.

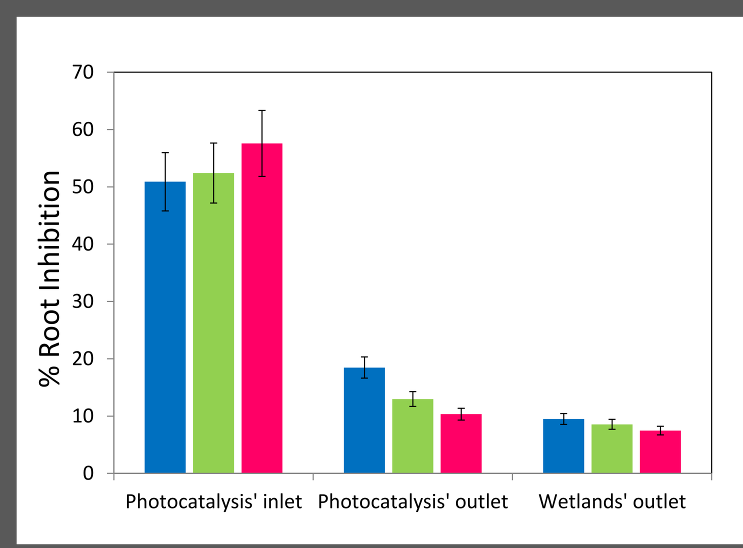

Figure 7: Effect of *simulated wastewater containing clopyralid* to the root length of the eukaryotic plants: (blue) *Sorghum saccharatum,* (green) *Sinapis alba* and (red) *Lepidium sativum, employing the integrated system solar photocatalysis (ferrioxalate: 7 mg L^{-1} Fe^{3+}, 33 mg L^{-1} $C_2O_4^{2-}$, 100 mg L^{-1} H_2O_2)/constructed wetlands (Typha spp).* Initial clopyralid concentration: 40 mg L^{-1}.

CONCLUSIONS

✓ The combined system, tested under natural irradiation, effectively reduces the organic load and nutrients of synthetic wastewater, providing outflows in agreement with the Greek environmental legislative requirements .

✓ Combination of photocatalysis and constructed wetlands reduces the required area (~50%) thus, the establishment cost of constructed wetlands. It also extends the operational lifetime of wetlands, eliminating clogging and other problems related to substances resistant to degradation.

✓ Post-treatment in constructed wetlands reduces operational costs, amounts of required chemicals, reaction time during photocatalytic oxidation and results to the reduction of nitrogen and phosphorous concentrations below the outflow required limits.

✓ Phytotoxicity of the wastewater after treatment with the ferrioxalate/wetlands process, evaluated by the calculation of the root inhibition of eukaryotic plants, was significantly reduced.

ACKNOWLEDGEMENTS

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