Evaluation of an alternative method for wastewater treatment containing pesticides using photocatalytic oxidation and constructed wetlands

V. Kitsiou[1], C. Berberidou[1], A. Antoniadis[2], E. Ntonou[2], D. Lambropoulou[1], 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: vasso_k3@hotmail.com

INTRODUCTION

Modern agriculture is supported by the use of pesticides to control a variety of agricultural pests that can damage crops and livestock and reduce farm productivity. However, agrochemical wastewater from intensive agriculture is polluting water with pesticides. 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)*. Tap water was used throughout the study. Experiments were conducted at pilot scale and took place 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 final effluent was channeled into surface flow constructed wetlands for the final purification. The photocatalytic treatment was tested in a pilot-scale unit able to treat 15 L of wastewater and constitutes of three parts:
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, in parallel order (Fig. 4).

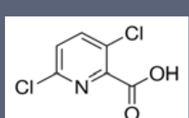

Figure 1: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, M_r: 192 g mol^{-1}) is the active ingredient of the commercial pesticide Lontrel 100 AS (Dow Agrosciences).

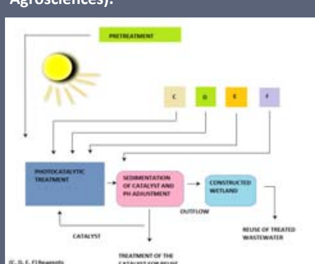

Figure 2: Graph of the wastewater treatment system using the combined action of photocatalytic oxidation and constructed wetlands.

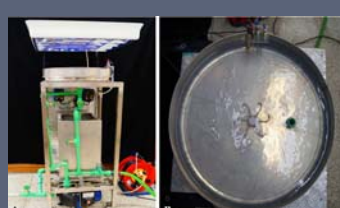

Figure 3: Pilot photocatalytic unit for the treatment of wastewater containing pesticides.

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

RESULTS AND DISCUSSION

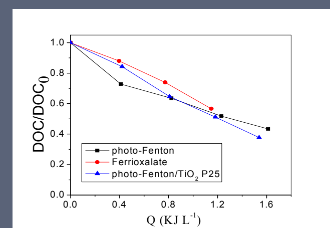

Figure 5: Mineralization of simulated wastewater containing CLPR vs. solar energy density in the presence of three different photocatalytic systems within 1h of illumination: photo-Fenton (■); Ferrioxalate (●); TiO_2/photo-Fenton (▲). [CLPR]=40 mgL^{-1}; H_2O_2=100 mg L^{-1}; [Fe^{3+}]=7 mg L^{-1}; [$C_2O_4^{2-}$]=33 mg L^{-1}; pH_o =3.2.

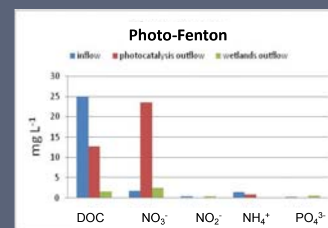

Figure 6: Variation of DOC and inorganic ions prior to and after solar photocatalysis with the photo-Fenton reagent and sequential treatment with constructed wetlands of simulated wastewater containing 40 mg L^{-1} CLPR: [Fe^{3+}]=7 mg L^{-1}; [H_2O_2]=100 mg L^{-1}.

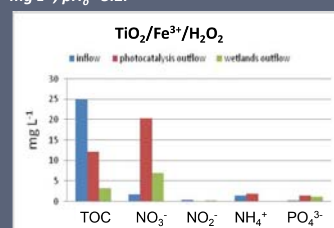

Figure 7: Variation of DOC and inorganic ions prior to and after solar photocatalysis with photo-Fenton/TiO_2 and sequential treatment with constructed wetlands of simulated wastewater containing 40 mg L^{-1} CLPR: [TiO_2 P25]=0.5 g L^{-1}; [Fe^{3+}]=7 mg L^{-1}; [H_2O_2]=100 mg L^{-1}.

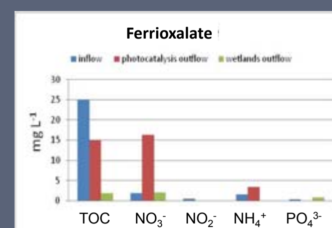

Figure 8: Variation of DOC and inorganic ions prior to and after solar photocatalysis with the Ferrioxalate reagent and sequential treatment with constructed wetlands of simulated wastewater containing 40 mg L^{-1} CLPR: [Fe^{3+}]=7 mg L^{-1}; [$C_2O_4^{2-}$]=33 mg L^{-1}; [H_2O_2]=100 mg L^{-1}.

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 photocatalyis and constructed wetlands provides several advantages to each other, resulting in a flexible and operational system of wastewater treatment.
- Photocatalysis as pre-treatment, 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 degradatiion.
- The 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 under the outflow required limits.

ACKNOWLEDGEMENTS

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