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Development and evaluation of an alternative method for municipal wastewater treatment using homogeneous photocatalysis and constructed wetlands

A. Antoniadis [a], V. Takavakoglou [b], G. Zalidis [b], I. Poulios [a,*]

[a] Department of Chemistry, Laboratory of Physical Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[b] School of Agriculture, Laboratory of Applied Soil Science, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

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Abstract

Wastewater collection and treatment is an important parameter of sustainable development. In Mediterranean region especially, the design and operation of competitive wastewater treatment systems for small communities and touristic facilities is a challenge to wastewater engineers. Within this context an alternative method of wastewater treatment has been developed that is based on solar photocatalytic oxidation and natural processes. The system combines the synergetic action of the homogeneous photocatalytic oxidation with the surface flow constructed wetlands in order to utilize the high solar irradiation and the ability of the constructed wetlands to improve water quality through natural processes. Aim of this work is to present the design, development, and experimental evaluation of the combined system. Experiments were conducted at laboratory scale using artificial as well as solar irradiation, for the treatment of both synthetic and cesspool wastewater. The data evaluation revealed that the combined system may effectively reduce the organic load and nutrients of wastewater, even in cases of great inflow variability, in terms of hydraulic and organic load, and thus may be proven a promising, competitive and environmental friendly solution for wastewater treatment in the near future.

Keywords: Photo-Fenton reagent; Constructed wetlands; Solar energy; Municipal wastewater

1. Introduction

Wastewater treatment systems have been designed to minimize the environmental impacts of discharging untreated wastewater. Different options for wastewater treatment have different performance characteristics and also different direct impacts on the environment [1]. The last decades centralized conventional wastewater treatment systems were typically provided to large cities and secondary towns. However, the establishment and operation of theses systems in the Mediterranean region have been costly and problematic. Conventional wastewater treatment plants involve large capital investments and operating costs, resulting to treatment systems which are considered as not proper solutions for small villages that cannot afford such expensive conventional treatment systems [2,3]. Money and water are not available to meet the regions needs for such services. In addition, low water use rates and several operational problems have been encountered with such systems in rural and especially in touristic areas where the population size varies seasonally.

The need for alternative methods of wastewater treatment well established in the environmental and socioeconomic status of Mediterranean region resulted in the development of a low cost treatment system that is based on solar photocatalytic oxidation and natural processes. The system combines the synergetic action of the homogeneous photocatalytic oxidation with the surface flow constructed wetlands (see Fig. 1) 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 treated wastewater capable of being reused, e.g. for irrigation. Aim of this work is to present the design and the preliminary results from the experimental evaluation of this innovative municipal wastewater system.

* Corresponding author. Tel.: +30 2310 997785; fax: +30 2310 997784.
E-mail address: poulios@chem.auth.gr (I. Poulios).

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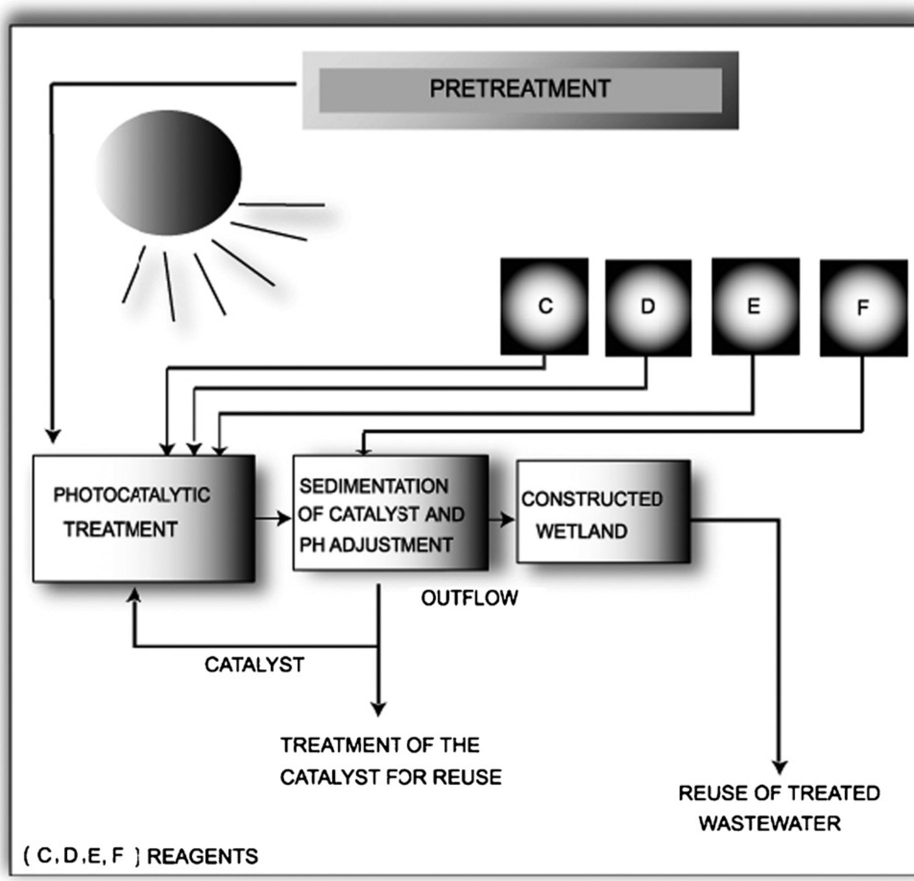

Fig. 1. Conceptual flowchart of the proposed municipal wastewater treatment system using the combined action of Photo-Fenton reagent and constructed wetlands.

2. Materials and methods

Experiments were conducted at laboratory scale using of both synthetic and cesspool wastewater. Each experiment consisted of two phases. In the first one, the wastewater was treated by using the Photo-Fenton reagent, for the reduction of the organic load, and the final effluent was channeled into surface flow constructed wetlands for the final purification.

The photocatalytic treatment was tested using both artificial and natural irradiation in a lab-scale reactor able to treat 12 L of wastewater. The photocatalytic reactor constitutes of four parts: a stabilization tank (30 cm in height and 24 cm in diameter), a round shape tank (12 cm in height and 38 cm in diameter), a magnetic stirrer and a sedimentation column. Wastewater was collected in the stabilization tank and by natural flow an amount of 12 L was channelled into the round shaped tank, where the photocatalytic oxidation took place under continuous stirring and application of solar or artificial irradiation.

For the experiments conducted under artificial light, 4 UV-A lamps (Philips TLD 15W/80) were situated above the photocatalytic reactor, providing light intensity of 3.175 mW/cm^2, as determined by the PMA 2100 pyranometer of the Solar Light Company, equipped with a UV-A sensor S/N 8773. The conducted experiments under solar irradiation took place in the region of Thessaloniki (latitude 40°62′, longitude 22°95′) Greece, during August 2005, where the solar light intensity varied between 2.5 and 4.5 mW/cm^2. The duration of the photocatalytic treatment was 5 h under solar irradiation and 11 h under artificial irradiation in order to reduce the organic load of the wastewater to less than 120 mg L^{-1} TOC, which was the desirable inflow concentration for the constructed wetlands according to the design of the system.

The necessary minimum concentration of iron ions and H_2O_2, as determined by previous experiments, was 112 mg L^{-1} Fe^{3+} and 3500 mg L^{-1} H_2O_2. Hydrogen peroxide was added in three doses, when the previous added concentration had been consumed. After the end of the treatment, the pH value was adjusted to 7 and the treated wastewater was channelled into the sedimentation column for the separation of the catalyst and the solid waste from the liquid phase. The overflow from the sedimentation column was used as inflow for the constructed wetlands where the final stage of treatment took place.

For the needs of the experiment 9 surface flow wetlands were constructed in parallel order. The design of the wetlands was based on the suggested by EPA [17] method. The design calculations were made using first-order kinetics model in which the inflow concentration, in terms of BOD_5, was 120 mg L^{-1} and the desired outflow concentration was 25 mg L^{-1}. Inlets of one point discharge were used to initiate flow into the wetland treatment area and inlet flow was distributed by gravity flow. The dimensions of each wetland were 60 cm × 30 cm × 50 cm. The water level was 10 cm

Table 1
Chemical composition of the synthetic municipal wastewater

Substances	Concentration (mg L^{-1})
Peptone	640
Meat extract	440
Urea	120
K_2HPO_4	112
NaCl	28
$CaCl_2{\cdot}2\ H_2O$	16
$MgSO_4\ 7\ H_2O$	8

above soil surface, the hydraulic residence time (HRT) of each wetland was 6 days and the hydraulic loading rate was 1.35 L day^{-1}. As wetland substrate a mixture (5:1) of sandyloam soil and zeolite (clinoptilolite) was used. All wetlands were planted with *Typha* spp. (six plants per wetland). Wetland outflow was based on single outlet weir designed to maintain the desired water level in the system as well as to sustain the functional capacity of the wetland.

The synthetic municipal wastewater (Table 1) was prepared according to OECD [18]. This synthetic sewage gives a mean dissolved organic carbon (DOC) concentration in the influent of about 400 mg L^{-1} (1000 mg L^{-1} COD), which is a representative COD value of the real cesspool wastewater influents. All other chemicals, such as $FeCl_3{\cdot}6\ H_2O$, H_2O_2, $HClO_4$, KOH were purchased through commercial companies and were used without further purification. The raw cesspool wastewater was obtained from the wastewater treatment plant (WWTP) of Aggelochori village in the Prefecture of Thessaloniki.

Dissolved organic carbon (TOC) analysis was performed using a TOC analyser (Shimadzu, model 5000A). Chemical oxygen demand (COD) and phosphates were measured according to APHA-AWWA-WEF [19]. COD was determined by the COD micromethod, while phosphates by the use of a spectrophotometer Perkin-Elmer Lambda 3. Nitrates and ammonium were measured using a Merck RQ Plus Reflectometer.

3. Results and discussion

The increased concern for the use of the *Advanced Oxidation Processes*, *AOPs*, may be explained by the need for seeking of new, alternative to the conventional ones and environmentally friendly technologies. Under this term the scientific community refers to the technologies whose effectiveness is based on the production of the $^{\bullet}OH$ radicals, one of the most powerful oxidant reagents. They can easily attack the organic molecules leading to the production of organic peroxide-radicals and their finally conversion to CO_2, H_2O and inorganic salts (reactions (1)–(3)).

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2{}^{\bullet} \quad (2)$$

$$R \rightarrow RO_2{}^{\bullet} \rightarrow CO_2 + \text{inorganic salts} \quad (3)$$

Among these, heterogeneous and homogeneous solar photocatalytic detoxification methods (TiO_2/H_2O_2, Fe^{3+}/H_2O_2) have shown recently great attention for the treatment of industrial wastewater, groundwater and contaminated air [4,5], allowing the contribution of the renewable sources of energy (solar energy) to the process of cleaning and restoring the environment.

Although it is well known for some time that Fenton reagent can easily oxidize organic compounds, it has been applied for water and soil treatment only during the last years [6–8]. Fenton reagent is an attractive oxidative system, which produces in a very simple way OH radicals (reaction (4)) for wastewater treatment, due to the fact that iron is a very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally safe. Furthermore, it was found that the reaction could be enhanced by UV/VIS light, artificial or natural, producing additional $^{\bullet}OH$ radicals and leading to the regeneration of the catalyst (reaction (5)) (Photo-Fenton reagent) [9,10]. The illumination results in the formation of more $^{\bullet}OH$ radicals, the reduction of the amount of the sludge, due to the reuse of the catalyst and the complete oxidation of most of the organic compounds, while it makes possible the application of the method at large scale facilities.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (4)$$

$$Fe^{3+} + H_2O + h\nu(\lambda < 450\,\text{nm}) \rightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \quad (5)$$

$$\text{R-H} + {}^{\bullet}OH \rightarrow ROO^{\bullet} \rightarrow CO_2 + \text{inorganic salts} \quad (6)$$

Reaction (5) closes a catalytic cycle, which produces 2 $OH^{\bullet}$ for every reacting molecule of peroxide. The steps of oxidation through the Photo-Fenton reagent are: adjustment of pH value below 4, due to the fact that iron precipitates as hydroxide at higher values of pH, activation of the photocatalytic system by illumination with solar or artificial light, oxidation of the pollutants present in the wastewater, neutralization of pH, clogging and sedimentation. Consequently, the reduction of the organic content takes place at the stages of oxidation and clogging.

Advantages of the photocatalytic processes are their simplicity, the mild operation conditions and the fact that they can be powered by sunlight, thus reducing significantly the electric power required and therefore reducing the operating costs.

Constructed wetlands on the other hand are attractive ecological systems for municipal, industrial, and agricultural wastewater treatment [11–13]. Constructed wetlands have the ability to efficiently treat a variety of wastewaters, removing organics, suspended solids, pathogens, nutrients and heavy metals. The water treatment mechanisms and pathways occurring in constructed wetlands are similar to those that occur in natural ecosystems. In general, the nature and magnitude of the organic load determines the balance between the treatment mechanisms and the dominant removal pathways in a constructed wetland used to treat wastewater. The main wastewater treatment processes occurring in constructed wetlands [11,14] are presented in Table 2. Since these systems

Table 2
Wastewater treatment processes occurring in constructed wetlands

Physical	Chemical	Biological
Sedimentation of denser particle fractions	Precipitation	Microbial decomposition and mineralization of organic material
Filtration of lighter particle fractions by macrophytes and biofilms	Adsorption onto wetland substratum and detritus	Microbial nutrient transformation (nitrification/denitrification)
Aggregation of particles leading to removal by either sedimentation or filtration	Volatilisation	Direct biological uptake from the water column (algal and bacterial biofilms)
Exposure of influent to UV-A radiation via sunlight	Oxidation–reduction	In-direct biological uptake from within the rootzone (benthic biofilms and emergent aquatic macrophytes)
		Microbial competition resulting in the die-off of pathogens
		Direct animal grazing of influent organic material

are practically self-sufficient, the cost to build and maintain them is relatively low. Adapting wetland design to wastewater treatment needs, involves a trade-off between efficiency and sizing of constructed wetlands [15,16].

Experiments using synthetic municipal wastewater under artificial irradiation revealed a 94% decrease of the organic load in total. The photocatalytic oxidation led to a 77% DOC reduction, while the constructed wetlands led to an additional 17% reduction (Fig. 2). Concerning the ammonium and nitrate ions, their concentration was increased during the photocatalytic oxidation from 6.88 to 99 mg L^{-1} and from 0 to 34 mg L^{-1}, respectively, due to the mineralization of the organic nitrogen. The followed treatment by the constructed wetlands decreased their concentration to 34 and 20 mg L^{-1}, a 65 and 42% reduction, respectively, compared to the outflow of the photocatalytic oxidation.

As far as the phosphate ions, a 25% reduction at the photocatalytic treatment was observed, without any difference in the outflow of the wetland. The use of iron resulted the presence of 7.28 mg L^{-1} at the outflow of the photocatalytic reactor, which was reduced to 5.82 mg L^{-1} by the wetland (Fig. 3).

Experiments using real cesspool wastewater under solar irradiation revealed a 98.6% decrease of the organic load in total. More specifically, the photocatalytic oxidation followed by the sedimentation led to a 85.9% DOC reduction, while the constructed wetlands led to a 12.7% DOC reduction (Fig. 4). Concerning the ammonium and nitrate ions, their concentration was increased during the photocatalytic oxidation due to the mineralization of the organic nitrogen from 77.5 to

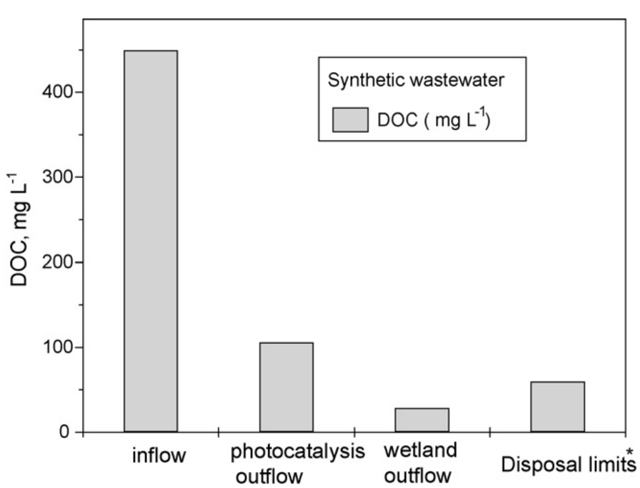

Fig. 2. Organic load reduction of synthetic wastewater during the treatment phases of the combined system (*limits set by Greek legislation PD/22374/91/94 for the disposal of the treated wastewater at Thermaikos Gulf).

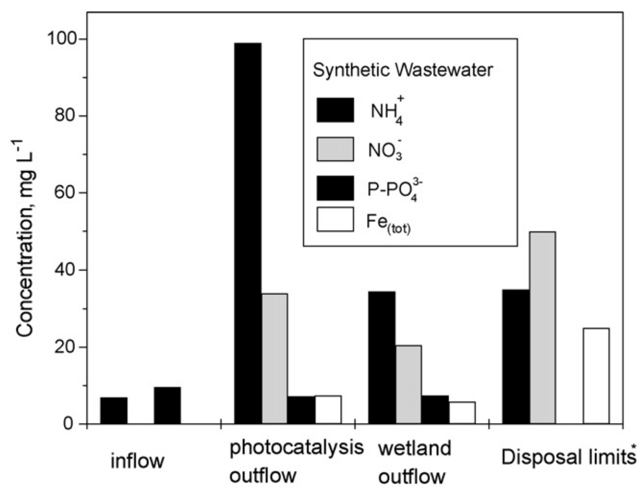

Fig. 3. Nutrients concentration of synthetic wastewater during the treatment phases of the combined system.

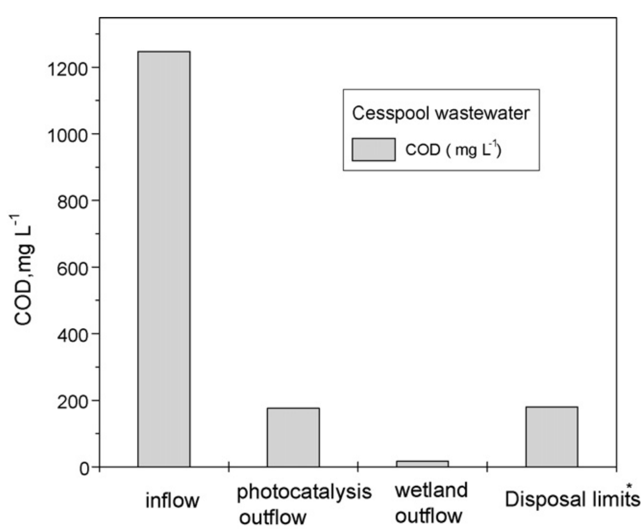

Fig. 4. Organic load reduction of cesspool wastewater during the treatment phases of the combined system.

Table 3
Positive interactions between photocatalysis and constructed wetlands in a combined system

Positive effects of constructed wetlands on photocatalysis	Positive effects of Photocatalysis on constructed wetlands
Reduction of treatment time	Reduction of the required area (about 50%)
Reduction of the required amounts of chemical additives	Lower cost of establishment
Lower cost of operation	Elimination of clogging problems
Seasonal operation in touristic areas may effectively cope with peaks of hydraulic and pollutants load	Extension of operational lifetime
Reduction of nitrogen and phosphorous concentrations	Elimination of problems related to hard degradable substances (e.g. dyes, pesticides)

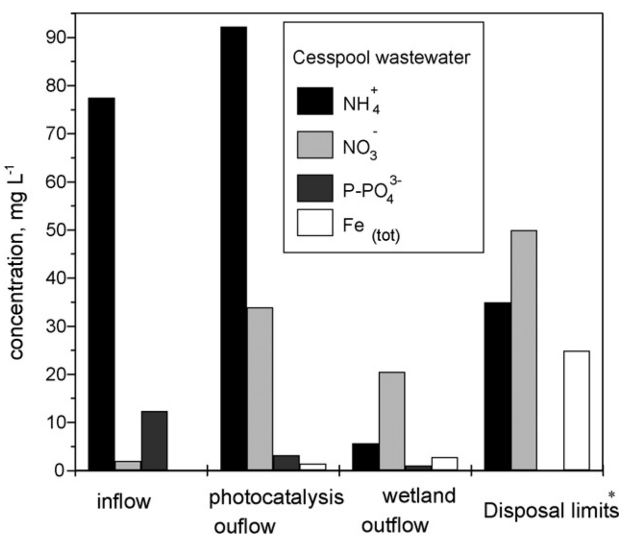

Fig. 5. Nutrients concentration of cesspool wastewater during the treatment phases of the combined system.

92.3 mg L^{-1} and from 2 to 34 mg L^{-1}, respectively. The followed treatment by the constructed wetlands decreased their concentration to 5.65 and 20.5 mg L^{-1}. As far as the phosphate ions, a reduction of 73% at the photocatalytic treatment and of 17.9% at the wetland was observed. The total iron concentration was 1.47 mg L^{-1} at the outflow of the photocatalytic reactor, and 2.82 mg L^{-1} at the final outflow (Fig. 5).

The combination of homogeneous photocatalysis and constructed wetlands provides several advantages to each other as can be seen in Table 3 resulting in a flexible and operational system of municipal wastewater treatment.

4. Conclusions

The combined system, which was tested under natural and artificial irradiation, effectively reduces the organic load and nutrients of both synthetic and cesspool wastewater. In all cases the quality of the outflows fulfilled the environmental legislative requirements (Prefectural Decision 22374/91/94) in the region of Thessaloniki (Greece), where the system was tested. Photocatalytic oxidation found to be very effective in the reduction of the organic load (77–86%), although a considerable amount of nitrates and ammonium ions were produced during the process. However, the additional wastewater treatment in the constructed wetlands reduced the concentration of the above-mentioned ions to acceptable levels according to the legislation requirements.

Comparing to conventional systems of wastewater treatment, the main advantages of the combined system are:

- Low cost of establishment and operation.
- Ability to treat wastewater with great variability of hydraulic and pollutants load.
- No need for additional disinfection method.
- Utilization of solar energy and natural processes.
- Wastewater reuse opportunities.

From the results of the present work one could claim that in small communities and villages, where there is a wide variation of the population between the winter and the touristic season and where the biological treatment of wastewater has a lot of disadvantages, the solar photocatalytic treatment of municipal wastewaters in combination with a natural process such as the constructed wetlands could be employed as a powerful alternative tool for the reduction of the organic content and reuse of this liquid waste. The use of solar light, combined with the simple technology required for the combined system can offer economically reasonable and practical solutions to the processing of this liquid waste.

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