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Municipal wastewater treatment by sequential combination of photocatalytic oxidation with constructed wetlands

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ABSTRACT

Aim of the present work is the study and the experimental evaluation of an alternative and innovative wastewater treatment system, which combines the action of photocatalytic oxidation with the surface flow constructed wetlands. This low cost and environmental friendly system is based on the utilization of solar irradiation and natural processes for wastewater treatment purposes. 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, the nutrients, as well as the pathogenic bacteria of wastewater, even in cases of great inflow variability, in terms of hydraulic and organic load, and thus may be proven a promising solution for municipal wastewater treatment in the near future.

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. During the last decades centralized conventional wastewater treatment systems were typically provided to large cities and secondary towns. They involve large capital investments and operating costs, resulting in systems which are considered as not proper solutions for small villages that cannot afford such expensive treatment facilities [1,2]. 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 is of interest to regulating authorities everywhere.

The so-called advanced oxidation technologies (AOTs) are among the most effective chemical oxidation processes [3,4], and are currently gaining significant importance in water treatment applications. 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 final conversion to CO_2, H_2O and inorganic salts. The increased concern for the use of the AOTs may be explained by the need for seeking of new, alternative to the conventional ones and environmentally friendly technologies.

Among these, heterogeneous and homogeneous solar photocatalytic detoxification methods (TiO_2/H_2O_2, Fe^{3+}/H_2O_2) have shown recently great promise for the treatment of industrial wastewater, groundwater and contaminated air [5,6], allowing the contribution of the renewable sources of energy (solar energy) to the process of cleaning and restoring the environment.

Our group is trying to develop a simple and effective solar heterogeneous or homogeneous photocatalytic method for the treatment and reuse of municipal wastewater of small communities and villages in small islands in the area of the Aegean Sea, where there is a wide variation of the population between the winter and summer season, due to touristic activities. This variation leads, during the year, to wastewater effluents with very different hydraulic and organic load, thus causing problems to conventional-biological treatment plants and leading to effluents of low quality.

The system combines the action of photocatalytic oxidation with the 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 treated wastewater capable of being reused, e.g. for irrigation. More specifically, as can be seen in Fig. 1, the method consists of the combination of a common physicochemical precipitation, a solar photocatalytic reduction of the organic content of wastewater by the use of a heterogeneous or homogeneous solar photocatalytic method, and finally passage of the wastewater through a constructed wetland, for the final purification of the wastewater to make its reuse possible.

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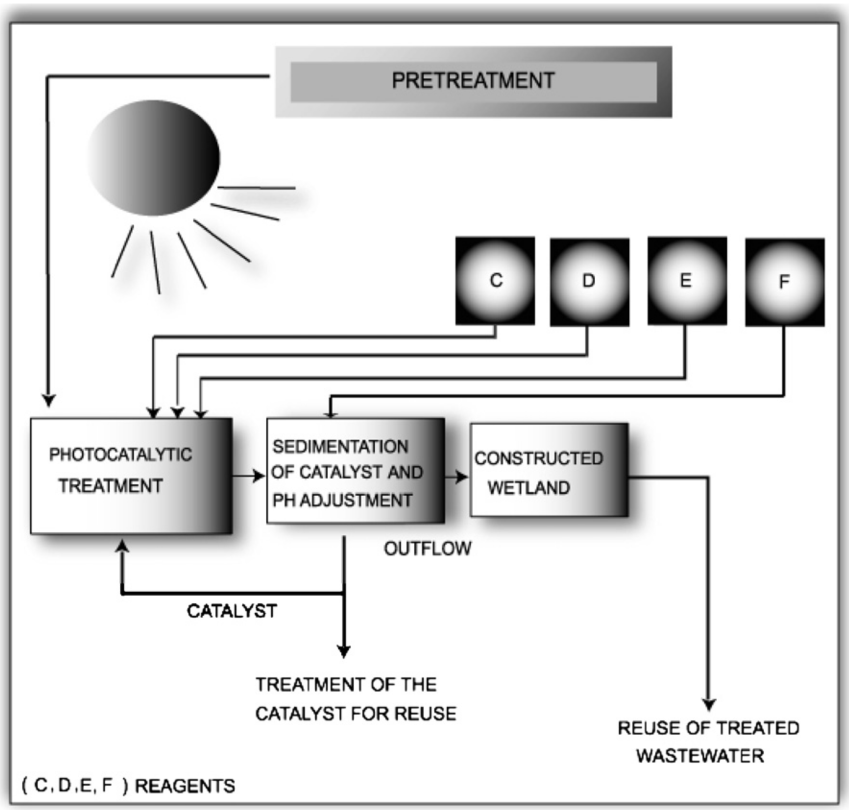

Fig. 1. Conceptual flowchart of the proposed municipal wastewater treatment system using the combined action of photocatalytic oxidation and constructed wetlands.

This combination gives an integrated system for treating municipal wastewater, that has a lower investment cost in comparison to conventional-biological treatment plants, has the ability of treating wastewater with different hydraulic and organic load and it makes the reuse of effluents possible.

The aim of this work is to present the preliminary results from the experimental evaluation of the sequential heterogeneous photocatalytic and wetland treatment of a simulated municipal wastewater and a real cesspool wastewater in the presence of artificial and solar light. According to the literature, the photocatalytic treatment of wastewater from different industrial sectors has been examined previously in laboratory experiments and in field studies, but only lately have a few studies been made on the organic content reduction of municipal wastewater by using the above mentioned methods [7,8].

2. Experimental

2.1. Materials

The synthetic municipal wastewater (SMW) (Table 1) was prepared according to OECD Guidelines [9]. This synthetic sewage gives a mean dissolved organic carbon (DOC) concentration in the influent of about 100 mg L^{-1} (250 mg L^{-1} COD).

Table 1
Composition of the synthetic municipal wastewater (SMW).

Substances	Concentration (mg L^{-1})
Peptone	160
Meat extract	110
Urea	30
K_2HPO_4	28
NaCl	7
$CaCl_2{\cdot}2H_2O$	4

For the experiments conducted in this paper a synthetic sewage was used with four times higher initial organic content concentration (400 mg L^{-1} DOC), which is more representative for the COD values of the real cesspool wastewater influents.

TiO_2 P-25 Degussa (anatase/rutile = 3.6/1, surface area 56 $m^2\,g^{-1}$, nonporous) was used for all the heterogeneous photocatalytic experiments. All other chemicals, such as $FeCl_3{\cdot}6H_2O$, H_2O_2, $HClO_4$, were purchased through commercial companies and were used without further purification.

Experiments were conducted at laboratory scale using both synthetic and cesspool wastewater. Each experiment consisted of two phases. In the first phase the wastewater was treated by using heterogeneous photocatalysis, for the reduction of the organic load, and the final effluent was channelled 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 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 3.38 mW cm^{-2}, as determined by the PMA 2100 pyranometer of the Solar Light Company, equipped with a UV-A sensor S/N 8773. All photocatalytic experiments in the presence of solar light have been contacted in Thessaloniki (latitude 40°62′, longitude 22°95′), Greece, during the months July and August. The UV-A light intensity in this time period ranged between 2.6 and 4.5 mW cm^{-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 ∼6 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 above mentioned pH value of 6 was found to be the optimum one for the sedimentation of the catalyst and its separation. 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. The dimensions of each wetland were 60 cm × 30 cm × 50 cm. The water level was 10 cm above the soil surface, the hydraulic residence time of each wetland was 6 days and the hydraulic loading rate was 1.5 L d^{-1}. As wetland substrate a mixture of sandyloam soil and zeolite (5:1) was used. All wetlands were planted with *Typha* spp.

The raw cesspool wastewater was obtained from the wastewater treatment plant (WWTP) of Angelochori village in the Prefecture of Thessaloniki.

2.2. Analysis

Dissolved organic carbon (TOC) analysis was performed using a TOC analyzer (Shimadzu, model 5000A). Chemical oxygen demand (COD) and phosphates were measured according to APHA-AWWA-WEF [10]. 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, while the consumption of H_2O_2 during the reaction was followed by iodometry.

3. Results and discussion

3.1. Combination of heterogeneous photocatalytic oxidation with constructed wetlands for the treatment of SMW under artificial irradiation

A general description of heterogeneous photocatalysis under artificial or solar irradiation is presented in several excellent review articles [11,12]. A brief summary is presented here only for the sake of completeness.

It is well established that by irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor (E_g > 3.2 eV) conduction band electrons (e^-) and valence band holes (h^+) are generated. Part of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons, act as powerful oxidants and reductants respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti(III)-sites, reducing it to superoxide radical anion $O_2{}^{-}$, while the photogenerated holes can oxidize either the organic molecules directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $OH^\bullet$ radicals. These radicals together with other highly oxidant species (e.g. peroxide radicals) are reported to be responsible for the primary oxidizing step in photocatalysis. The $OH^\bullet$ radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with a standard reduction potential of 2.8 V. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, leading finally to their complete mineralisation.

Fenton reagent, a mixture of Fe^{2+} salts and H_2O_2, produces in a very simple way $OH^\bullet$ radicals (Eq. (1)) and can easily oxidize organic compounds. This reagent is an attractive oxidative system 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 can be enhanced by UV-A/vis light (artificial or natural), producing additional $OH^\bullet$ radicals and leading to the regeneration of the catalyst (Eq. (2), Photo-Fenton reaction) [13,14]. The illumination results in the formation of more $^\bullet OH$ radicals, reduction of the amount of the sludge, due to the reuse of the catalyst, and complete oxidation of most of the organic compounds, while it makes possible the application of the method at large scale facilities [6].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \quad (1)$$

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

These reactions are known to be the primary forces of the photochemical self-cleaning of atmospheric and aquatic environment [15].

Constructed wetlands on the other hand are attractive ecological systems for municipal, industrial, and agricultural wastewater treatment [16–18]. 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. Since these systems 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 [19,20].

At first, some preliminary experiments were performed, concerning the photocatalytic organic content reduction of the simulated municipal wastewater. It should be noted that, as blank experiments had shown, by illumination of the TiO_2/SMW suspension in the absence of H_2O_2, a very small decrease in the concentration of SMW was observed, while the dark adsorption of the organics onto the TiO_2 surface, expressed as carbon, under the given experimental conditions removes ∼15% of its content.

Fig. 2 shows the concentration–time profiles during the 400 mg L^{-1} SME photocatalytic oxidation under three different experimental conditions. As seen, in the absence of Fe^{3+}, the maximum decrease of the dissolved organic content after 6 h illumination at pH 3 is about 10% in the presence of 0.5 g L^{-1} TiO_2 and 1.5 g L^{-1} H_2O_2. The poor result can be proved furthermore

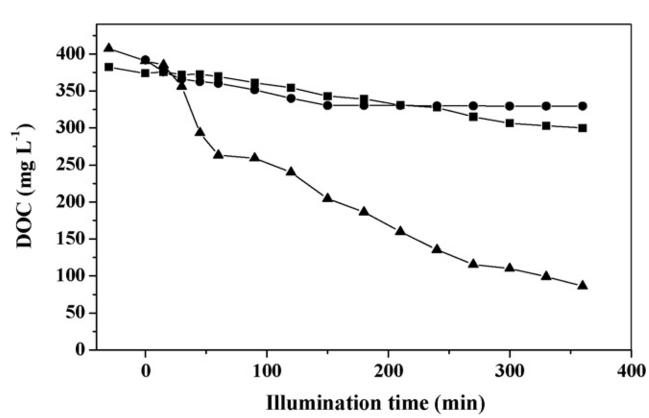

Fig. 2. Organic load reduction of 400 mg L^{-1} synthetic wastewater in the presence of (■) 0.5 g L^{-1} TiO_2 + 1500 mg L^{-1} H_2O_2, (●) 28 mg L^{-1} Fe^{3+} + 2125 mg L^{-1} H_2O_2 and (▲) 0.5 g L^{-1} TiO_2 + 28 mg L^{-1} Fe^{3+} + 2125 mg L^{-1} H_2O_2. pH = 3, light intensity I = 3.38 mW cm^{-2}:.

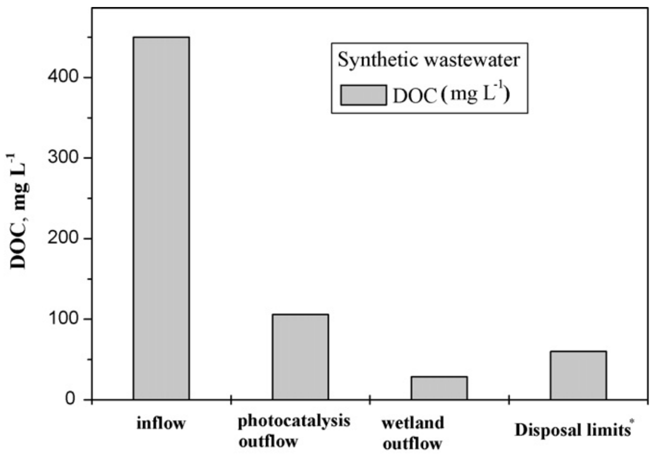

Fig. 3. Organic load reduction of synthetic wastewater during the treatment phases of the combined system. (*Limits set by Greek legislation PD/22374/91/94 for the disposal of the treated wastewater at Thermaikos Gulf.)

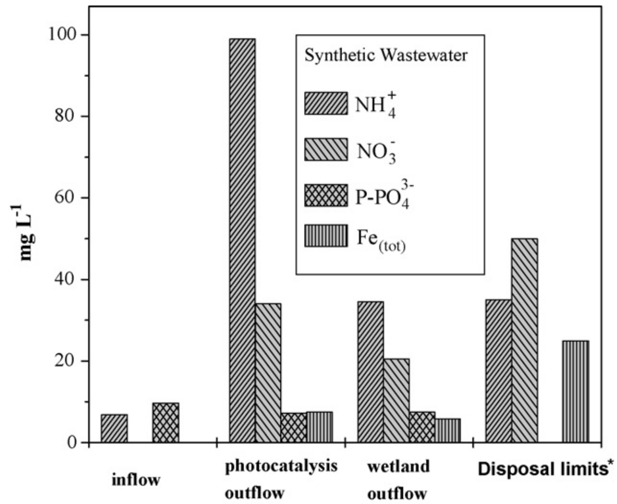

Fig. 4. Concentration of the mineralization products of synthetic wastewater during the treatment phases of the combined system.

by the fact that the hydrogen peroxide has not been consumed at the end of the experiment, since the catalyst is blocked by the concentrated wastewater. Similar results have been obtained also in the case of the Photo-Fenton reagent, when the starting concentration of Fe^{3+} and H_2O_2 is low. The homogeneous photocatalytic oxidation in the presence of 28 mg L^{-1} Fe^{3+} and 2125 mg L^{-1} H_2O_2 leads also to a ∼10% reduction of the organic content after 6 h of illumination, while by using an initial concentration of Fe^{3+} and H_2O_2 of 112 and 3200 mg L^{-1} respectively (data not shown in the figure), the TOC reduction value was increased to 62%. In the contrary, the addition of 28 mg L^{-1} Fe^{3+} to the TiO_2–H_2O_2/SMW suspension increases significantly the photocatalytic efficiency, leading after 6 h of illumination to a 78% reduction of the DOC content. Furthermore, the rate of consumption of H_2O_2 increases rapidly, proving that oxidation takes place.

The superiority of the combined system can be explained by the reduction of Fe^{3+} ions to Fe^{2+} from the photogenerated electrons in TiO_2. These Fe^{2+} ions with hydrogen peroxide via the Fenton reaction represent a supplementary source of hydroxyl radicals in the photocatalytic system. Thus, in the irradiated aqueous TiO_2 suspension in the presence of Fe^{3+} ions, two sources of hydroxyl radical generation are present [21].

In the following experiments where the simulated wastewater was used, the initial DOC concentration was 400 mg L^{-1}, which corresponds to a COD concentration of 1 g L^{-1}, while the optimum concentration of the catalyst and the reagents, as it was found from the previous experiments at an initial pH value 3, was 0.5 g L^{-1} TiO_2, 28 mg L^{-1} Fe^{3+} and 2125 mg L^{-1} H_2O_2.

As it is shown at Fig. 3 the sequential photocatalytic-constructed wetland treatment of the simulated municipal wastewater under artificial irradiation revealed a 94% decrease of the organic load in total: more specifically, the photocatalytic oxidation after 6 h of illumination led to a 77% reduction, while the respective one after passing the constructed wetlands was 17%. Concerning the ammonium and nitrate ions, as can be seen in Fig. 4, their concentration was increased during the photocatalytic oxidation, due to the mineralization of the organic nitrogen, from 6.88 to 99 mg L^{-1} and from 0 to 34 mg L^{-1}, respectively. The followed treatment by the constructed wetlands decreased their concentration to 34 for the NH_4^+ and to 20 mg L^{-1}, for the NO_3^- ions, a reduction of 65% and 42% respectively, compared to the outflow of the photocatalytic oxidation.

Concerning the phosphate ions, a 25% reduction at the photocatalytic treatment was observed, without any difference in the outflow of the wetland, while the total iron concentration, as can be seen in Fig. 4, was 7.28 mg L^{-1} at the outflow of the photocatalytic reactor, after its precipitation due to the augmentation of the pH value, and 5.82 mg L^{-1} at the final outflow.

3.2. Combination of photocatalytic oxidation with constructed wetlands for the treatment of raw cesspool wastewater under solar illumination

In the experiments where raw cesspool wastewater was used, the initial COD concentration was about 1200 mg L^{-1}, depending on the inflow of the wastewater treatment plant.

Experiments using real cesspool wastewater under solar irradiation, as can be seen in Fig. 5, revealed a 98.6% decrease of the organic load in total: more specifically, the photocatalytic oxidation after 6 h exposure to solar light followed by the sedimentation led to 85.9% reduction, while the respective one after passing the treated cesspool wastewater through the wetlands was 12.7%.

Concerning the ammonium and nitrate ions, as can be seen in Fig. 6, their concentration was increased during the photocatalytic oxidation due to the mineralization of the organic nitrogen from

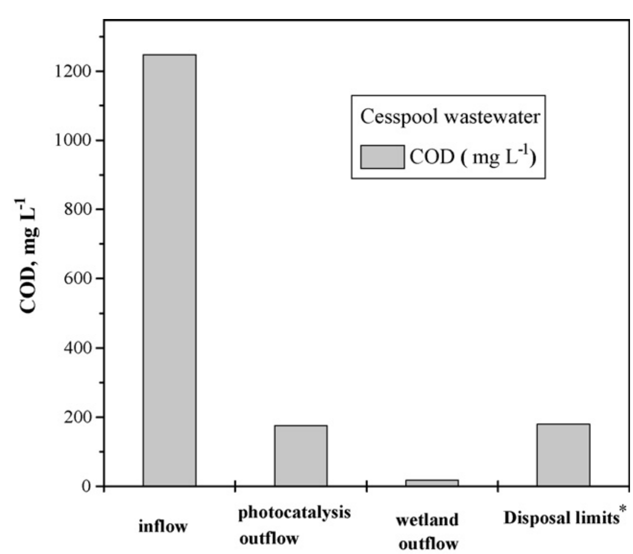

Fig. 5. Organic load reduction of cesspool wastewater during the treatment phases of the combined system. (*Limits set by Greek legislation PD/22374/91/94 for the disposal of the treated wastewater at Thermaikos Gulf.)

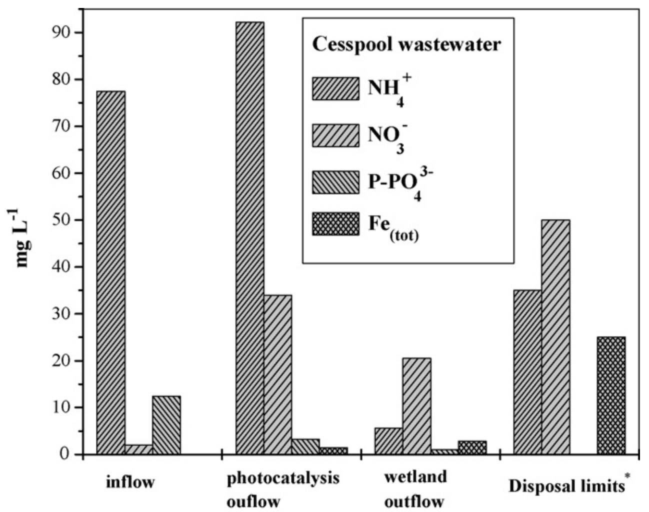

Fig. 6. Concentration of the mineralization products of the cesspool wastewater during the treatment phases of the combined system.

77.5 to 92.3 mg L^{-1} and from 2 to 34 mg L^{-1}, respectively. The followed treatment by the wetlands decreased their concentration to 5.65 and 20.5 mg L^{-1}. Concerning 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, after its precipitation due to the augmentation of the pH value, and 2.82 mg L^{-1} at the final outflow.

The determination of the pathogenic bacteria, expressed as total *E. coli* colonies, showed that their population decreased significantly during the photocatalytic oxidation from 7.6×10^9 to 1.2×10^2 CFU mL^{-1}. At the final outflow of the integrated system, after the passage from the constructed wetland, no population of *E. coli* was observed, revealing the disinfection of the wastewater.

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.

The combination of photocatalytic oxidation and constructed wetlands provides several advantages to each other, resulting in a flexible and operational system of wastewater treatment. More specifically, the post-treatment at the constructed wetlands reduces the cost and the required amounts of chemical reagents, as well as the reaction time during the photocatalytic oxidation and permits the reduction of nitrogen and phosphorous concentrations under the outflow required limits. On the other hand, the photocatalytic oxidation used as a pre-treatment, reduces the required area (~50%) and therefore the establishment cost of the constructed wetland. Additionally, the photocatalytic oxidation leads to the extension of operational lifetime of the wetland since it eliminates clogging and other problems related to hard degradable substances.

The preliminary results revealed that heterogeneous photocatalysis and constructed wetlands are compatible methods and their combination results in an innovative, effective wastewater treatment system. One of its main advantages is the ability of effectively coping with peaks of hydraulic and pollutants load. The use of solar light, combined with the simple technology required for this method, can offer economically reasonable and practical solutions to the processing of this liquid waste. However further research is needed for the strengthening of the results and the optimization of the system's performance.

Concerning the heterogeneous photocatalytic oxidation, the presence of iron ions increases the photocatalytic efficacy of the TiO_2/H_2O_2 system, allowing the reduction of the necessary catalyst concentration needed. Consequently, the photocatalytic $TiO_2/Fe^{3+}/H_2O_2$ system could be considered as an innovative and efficient system for the treatment of concentrated municipal wastewater.

Acknowledgements

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