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Disinfection of water and wastewater by TiO_2 photocatalysis, sonolysis and UV-C irradiation

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Abstract

The efficacy of various advanced oxidation processes based on ultraviolet and ultrasound irradiation to inactivate *Escherichia coli* in sterile water and total coliforms (TCs) in biologically treated municipal wastewater was evaluated. H_2O_2-assisted UV-A/TiO_2 photocatalysis (9 W lamp) could generally lead to nearly complete *E. coli* destruction in 20 min contact time with the extent of inactivation depending on the photocatalyst type and loading (in the range 0–0.75 g/L) and oxidant concentration (in the range 0–100 mg/L). Low frequency (in the range 24–80 kHz), high power (in the range 150–450 W) ultrasound irradiation provided by a horn-type sonicator was less effective than photocatalysis requiring longer contact times (i.e. 120 min) for *E. coli* inactivation. TiO_2 photocatalysis, UV-C irradiation (11 W lamp), ultrasound irradiation, chlorination (in the range 1–5 mg/L chorine) and various combinations of them were tested concerning their ability to disinfect municipal effluents already subject to activated sludge treatment. Of these, UV-C irradiation was more efficient than the rest in achieving full and permanent (i.e. without bacteria regeneration) inactivation after short periods of contact time.

Keywords: Disinfection; Photocatalysis; Ultrasound; UV-C; Water; Wastewater

1. Introduction

The disinfection agents commonly used both at drinking water and wastewater treatment plants are chlorine and its related compounds, such as sodium and calcium hypochlorite and chlorine dioxide, with chlorine being by far the most widely used disinfectant. However, in the early 1970s, it was found that chlorine reacts with the natural organic matter present in water and wastewater to produce various undesirable chlorinated disinfection by-products (DBPs) [1,2]. Of the wide variety of chlorinated DBPs formed, trihalomethanes and haloacetic acids are of primary concern since many of them have been found to be carcinogenic and/or mutagenic. In addition, chlorination of water has been associated with taste and odor problems caused not only by chlorine itself but also from odorous disinfection by-products [3]. Moreover, wastewater disinfection by chlorine requires subsequent dechlorination of the treated effluent to minimize the potential toxic effects of low level chlorine residuals on aquatic organisms as well as to prevent the formation of DBPs in the receiving water bodies [2].

Because of the concerns over the formation of DBPs, ongoing research focuses on the development of alternative disinfection methods. In recent years, advanced oxidation processes have received considerable attention for the degradation of organic pollutants as well as the disinfection of waters and wastewaters [4]. Regarding water and wastewater disinfection, semiconductor photocatalysis has received considerable attention over the past few years with emphasis given on the inactivation of bacteria [5–23] and, to a lesser extent, of viruses [9,20,23–25] and protozoan parasites [13,20,26]. TiO_2 is commonly used as the photocatalyst since it is inexpensive,

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commercially available at various crystalline forms and particle characteristics, non-toxic and photochemically stable.

Other than photocatalysis, ultrasound irradiation has also been used for water disinfection. Sonochemisty involves the use of ultrasound waves to produce an oxidative environment via cavitation that yields localized microbubbles and super-critical regions in the aqueous phase [27]. The collapse of these bubbles leads to extremely high local temperatures and pressures. These conditions are very short-lived but have shown to result in the generation of highly reactive radicals which are responsible for the oxidative destruction of organics found in waters as well as bacteria inactivation [28–30].

The aim of this work was to investigate the efficiency of TiO_2 photocatalytic inactivation of *Escherichia coli* bacteria suspensions in sterile distilled water as a function of photocatalyst type and concentration, hydrogen peroxide addition and aeration. Moreover, process efficiency to disinfect biologically treated municipal effluents was evaluated and also compared to other methods such as ultrasound irradiation, chlorination, UV-C irradiation and their combinations.

2. Experimental and analytical

2.1. Chemicals

The inorganic salts used in the present study, namely NaCl, KCl, Na_2HPO_4, K_2HPO_4, KH_2PO_4, as well as agar and the catalase solution (273,780 units/mL) were purchased from Fluka. Peptone, meat extract and hydrogen peroxide as a 30 wt% solution were supplied by Merck, while NaOCl used as a chlorination agent was provided by the Municipal Wastewater Treatment Plant (WWTP) of Chania, Western Crete, Greece.

Three commercially available titanium dioxide TiO_2 samples were employed in this study, namely: (a) Aeroxide P 25 (Degussa P 25) supplied by Degussa AG (anatase:rutile 75:25, 21 nm particle size, 50 m^2/g BET area); (b) Hombicat UV 100 supplied by Sachtleben Chemie GmbH (anatase, 5 nm particle size, >250 m^2/g BET area); (c) Tronox A-K-1 supplied by Kerr-McGee Chemicals LLC (anatase, 20 nm particle size, 90 m^2/g BET area).

2.2. Bacterial strain

The bacterial strain used in the present study was *E. coli* K 12 (ATCC 23716, DSM 498) (DSMZ, German Collection of Microorganisms and Cell Cultures). *E. coli*, a model microorganism widely used as an indicator of faecal contamination, was inoculated in 50 mL of the appropriate nutrient broth according to DSMZ catalogue (i.e. 5 g/L peptone, 3 g/L meat extract, 4 g/L K_2HPO_4, 1.5 g/L KH_2PO_4 and 5 g/L NaCl) and grown overnight at 37 °C by constant agitation under aerobic conditions. The bacterial cells were collected by centrifugation, washed two times with sterile phosphate buffered saline (8 g/L NaCl, 0.2 g/L KCl, 1.15 g/L Na_2HPO_4 and 0.2 g/L KH_2PO_4 at pH 7.3). Finally, the bacterial pellet was suspended in sterile deionized water and diluted to the required cell density corresponding to 10^4–10^5 CFUs/mL. Deionized water (18.2 MΩ cm at 25 °C) used for solution preparation was prepared on a water purification system (EASYpureRF) supplied by Barnstead/Thermolyne (USA).

Disinfection experiments were also conducted with effluents taken from the activated sludge process of Chania WWTP. The effluents had 30–40 mg/L total solids, up to 35 mg/L chemical oxygen demand, neutral pH and 10^3–10^4 CFUs/mL concentration of TCs.

2.3. Photocatalytic and ultrasound disinfection of deionized sterile water spiked with E. coli

UV-A irradiation was provided by a 9 W lamp (Radium Ralutec, 9W/78, 350–400 nm). The photon flux of the lamp was determined actinometrically using the potassium ferrioxalate method and it was found 4.69×10^{-6} einstein/s. Ultrasound (US) irradiation was provided by two horn-type sonicators operating at 24 kHz and a variable electric power output up to 450 W (Dr Hielscher UP400S, Germany) and at 80 kHz and a variable electric power output up to 150 W (LabPlant Ultrason 250, UK). Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor, purchased from Ace Glass (Vineland, NJ, USA) which is described in detail elsewhere [31].

In a typical photocatalytic run, an *E. coli* suspension in sterile deionized water was introduced in the reaction vessel and the appropriate amount of TiO_2 was added to achieve the desirable catalyst loading in the range 0.25–0.75 g/L. The resulting suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of *E. coli* bacteria onto the catalyst surface. After that period of time, the UV-A lamp was turned on, while at the same time a measured volume of a diluted H_2O_2 solution was added dropwise with a peristaltic pump (slow addition of H_2O_2 was done over several minutes to avoid high local concentrations) to yield 25–100 mg/L H_2O_2 concentrations in the final solution. Unless otherwise stated, when the UV-A lamp was turned on, pure O_2 was continuously sparged in the liquid and the reaction mixture was continuously stirred. The temperature was maintained at 25 ± 1 °C with a temperature control unit (Crioterm, Italy). The external reaction vessel was covered with aluminum foil to reflect irradiation exerting the outer wall of the reaction vessel. Similar procedures were followed for the sonochemical disinfection experiments.

At specific time intervals about 2 mL of the reaction solution were withdrawn and were immediately quenched adding 20 μL of a catalase solution. Prior to analysis, samples were not filtered to remove TiO_2 particles to avoid losses of bacteria during filtration. Following quenching, samples were analyzed with respect to viable *E. coli* cells employing the serial dilution-agar plate technique. One hundred microliters of diluted samples were spread over the surface of the appropriate solid agar medium (5 g/L peptone, 3 g/L meat extract, 15 g/L agar, 4 g/L K_2HPO_4, 1.5 g/L KH_2PO_4 and 5 g/L NaCl) in 90 mm Petri dishes and then incubated for 24 h at 37 °C. The method

detection limit was 10 CFUs/mL. For the undiluted samples, 1 mL of sample was spread over the surface of four 90 mm Petri dishes (i.e. 250 μL of sample per Petri dish) and the *E. coli* colonies present were added after incubation for 24 h at 37 °C. Following this experimental procedure, the detection limit was reduced to 1 CFUs/mL for the undiluted samples [8]. Finally, *E. coli* colonies were counted with an IUL Colony Counter (Spain).

2.4. Disinfection of biologically treated wastewater

The efficiency of the UV-A/TiO_2 photocatalytic process to disinfect effluents taken from the activated sludge process of a municipal treatment plant was also evaluated. In addition, other disinfection methods were also tested namely chlorination, UV-C irradiation and ultrasound irradiation. For chlorination tests, different dosages of NaOCl were added in the effluent to yield 1–5 mg/L free chlorine concentration in the solution. UV-C irradiation was provided by an 11 W low pressure mercury lamp (Phillips, TUV PL-S). The photon flux of the lamp was determined actinometrically using the potassium ferrioxalate method and it was found 7.15×10^{-6} einstein/s. Ultrasound irradiation was provided by two horn-type sonicators as described earlier. Disinfection efficiency was evaluated measuring TCs inactivation over time. This was done according to the standard TCs membrane filter technique [32].

3. Results and discussion

3.1. Photocatalytic disinfection of E. coli suspensions in sterile deionized water

3.1.1. Efficiency of photocatalysis in E. coli inactivation

In a preliminary control experiment, a 10^4 CFUs/mL *E. coli* suspension in sterile deionized water was stirred for prolonged time in the dark at 25 °C. It was found that *E. coli* population remained practically unchanged after 120 min, thus showing that the bacteria were stable at the conditions employed in the present study and cell damage due to osmotic effects was negligible. In addition, another control experiment was performed stirring an 8.75×10^4 CFUs/mL *E. coli* suspension in sterile deionized water in the presence of 0.5 g/L Degussa TiO_2 for prolonged time in the dark. It was found that cultivable *E. coli* population decreased to 3.45×10^4 CFUs/mL (i.e. 61% decrease) over the first 15 min and further decreased to 2.30×10^4 CFUs/mL (i.e. 75% decrease) over the first 30 min beyond which the residual *E. coli* concentration remained stable. This result is in contrast with previous literature reports stating that *E. coli* population remained constant after stirring in the presence of Degussa TiO_2 for prolonged time in the dark [5,6,8,10]. The above result implies that *E. coli* bacteria interacted with the catalyst surface and this interaction resulted in loss of cultivability. It also implies that equilibrium between adsorption/desorption was achieved within 30 min. Recently, it has been reported that *E. coli* bacteria adsorb onto the surface of TiO_2 and this adsorption alters cell membrane integrity without affecting bacteria cultivability [33]. However, in our case it can be speculated that aggregation of titania clusters and their interactions with *E. coli* are responsible for reduced bacteria viability as expressed by the 75% reduction of cultivable *E. coli* population. If TiO_2 was actually toxic in the dark to all *E. coli* bacteria present in the solution, then a continuous decrease of *E. coli* population would be expected throughout the experiment.

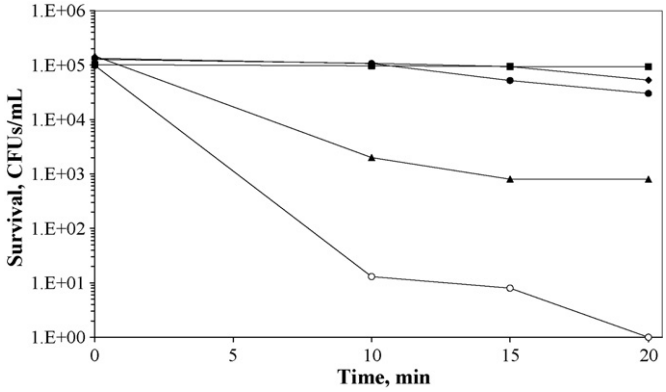

Fig. 1. *E. coli* inactivation in water by ultraviolet irradiation. (◆) UV-A alone; (▲) UV-A/TiO_2; (●) UV-A/H_2O_2; (○) UV-A/TiO_2/H_2O_2; (■) H_2O_2 (in the dark). [H_2O_2] = 25 mg/L; [Degussa TiO_2] = 0.5 g/L.

Fig. 1 shows the effect of UV-A irradiation on water disinfection as a function of contact time. UV-A irradiation alone resulted in only about 40% bacteria reduction after 20 min; however, coupling UV-A irradiation with 25 mg/L H_2O_2 enhanced *E. coli* inactivation leading to 77% bacteria reduction after 20 min. An additional dark run was performed with 25 mg/L H_2O_2 showing that, at the conditions in question, no inactivation occurred. The experiments were repeated in the presence of 0.5 g/L Degussa TiO_2 and bacteria reduction after 20 min of treatment was 99.5 and 99.999%, respectively, for the UV-A/TiO_2 and UV-A/TiO_2/H_2O_2 systems. In summary, disinfection efficiency follows the order: UV-A/TiO_2/H_2O_2 > UV-A/TiO_2 > UV-A/H_2O_2 > UV-A.

3.1.2. Mechanism of the photocatalytic inactivation of E. coli

In the literature there exists some controversy regarding which are the oxidative species actually responsible for the bactericidal action of TiO_2 photocatalysis. It is generally accepted that hydroxyl radicals $HO^{\bullet}$ are the main oxidative species responsible for the photocatalytic inactivation of *E. coli* bacteria [9,14]. However, there is also some evidence that other reactive oxygen species (ROS) generated photocatalytically, such as superoxide radicals $O_2^{\bullet -}$, perhydroxyl radicals $HO_2^{\bullet}$ and hydrogen peroxide H_2O_2 also contribute to the photocatalytic inactivation of *E. coli* [5,8,9].

Upon irradiation of TiO_2 with light energy greater than the band gap energy of the semiconductor ($h\nu > E_g = 3.2$ eV) conduction band electrons (e_{cb}^-) and valence band holes (h_{vb}^+) are generated and they may either undesirably recombine liberating heat or make their separate ways onto

the catalyst surface and induce several reactions as follows [34,35]:

$$h_{vb}^{+} + H_2O \rightarrow HO^{\bullet} + H^{+} \quad (1)$$

$$h_{vb}^{+} + OH^{-} \rightarrow HO^{\bullet} \quad (2)$$

$$e_{cb}^{-} + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$O_2^{\bullet -} + H^{+} \rightleftharpoons HO_2^{\bullet} \quad (4)$$

$$O_2^{\bullet -} + 2H^{+} + e_{cb}^{-} \rightleftharpoons H_2O_2 \quad (5)$$

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (6)$$

$$H_2O_2 + e_{cb}^{-} \rightarrow HO^{\bullet} + HO^{-} \quad (7)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^{\bullet} + HO^{-} + O_2 \quad (8)$$

$$H_2O_2 + h_{vb}^{+} \rightarrow HO_2^{\bullet} + H^{+} \quad (9)$$

$$H_2O_2 + HO^{\bullet} \rightleftharpoons H_2O + HO_2^{\bullet} \quad (10)$$

Addition of hydrogen peroxide in the solution leads to the production of extra hydroxyl radicals as well as other ROS according to reactions (7)–(10), thus enhancing bacteria inactivation. Hydrogen peroxide is a stronger electron acceptor than oxygen and reacts, therefore, more efficiently with conduction band electrons. In addition, hydrogen peroxide may be formed photocatalytically (reactions (5) and (6)) and subsequently be degraded to radicals.

In the absence of photocatalyst, hydroxyl radicals as well as other ROS are generated, thus causing bacteria inactivation [5]. Furthermore, H_2O_2 direct photolysis may also occur and this would also generate hydroxyl radicals. However, the degree of hydroxyl radicals formation from H_2O_2 direct photolysis is expected to be relatively low since it is well known [4] that hydrogen peroxide is effectively photolyzed by UV-C ($200\ nm < \lambda < 280\ nm$) rather than UV-A irradiation due to its low molar extinction coefficient in the UV-A region of the electromagnetic spectrum.

Previous studies have shown that H_2O_2 and UV-A irradiation may act synergistically in weakening cell membranes, thus making bacteria more sensitive to oxidative inactivation [5,8]. Cell membrane is the crucial site of attack for effective inactivation regardless the oxidative species involved in the process. It has been proposed that the cell wall is initially damaged, followed by a progressive damage of the cytoplasmic membrane and intracellular components [17,19]. Hydroxyl radicals as well as other oxidizing species attack the polyunsaturated phospholipids components of the lipid membrane, therefore inducing major disorder in the cell membrane. Oxidation of the lipid membrane results in loss of essential cell functions that rely on the integrity of the cell membrane, such as respiration, ultimately leading to cell death [21].

3.1.3. Screening of catalysts and effect of aeration

In further experiments, the photocatalytic performance of various commercially available TiO_2 samples was evaluated, namely Degussa P 25, Hombicat UV 100 and Tronox A-K-1 and the results are shown in Fig. 2. As clearly seen, Degussa P 25, one of the most commonly employed and effective TiO_2 photocatalysts [4,6], was appreciably more active than the other two TiO_2 samples. An additional run without O_2 sparging was performed and the results are also shown in Fig. 2; lack of O_2 only marginally decreased the extent of final (i.e. after 20 min) *E. coli* inactivation which was 99.98 and 99.999% without and with O_2 sparging, respectively. The presence of molecular oxygen positively influences photocatalytic inactivation since the photogenerated conduction band electrons reduce adsorbed molecular oxygen on the TiO_2 surface leading to the formation of hydroxyl radicals as well as other reactive species.

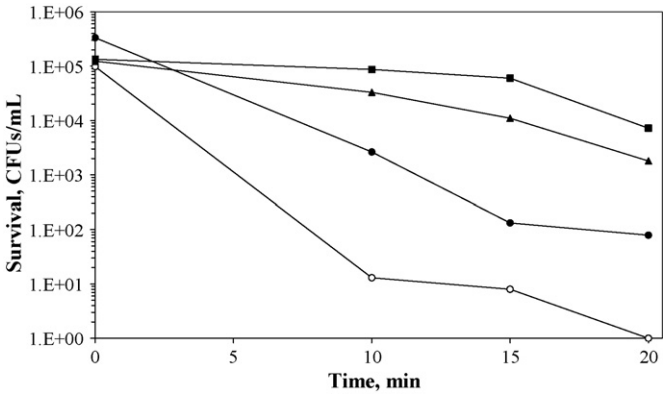

Fig. 2. Effect of catalyst type and oxygen sparging on *E. coli* inactivation in water during UV-A/TiO_2/H_2O_2 treatment. (○) Degussa P 25, oxygen; (▲) Tronox A-K-1, oxygen; (■) Hombicat UV 100, oxygen; (●) Degussa P 25, without oxygen. [H_2O_2] = 25 mg/L; [TiO_2] = 0.5 g/L.

3.1.4. Effect of catalyst loading

TiO_2 loading in slurry photocatalytic processes is an important factor that can influence strongly the efficiency of the process. Experiments were performed using Degussa P 25 loadings in the range 0.1–0.75 g/L and the results are shown in Fig. 3. As seen, *E. coli* inactivation was sufficiently high after 20 min contact time (99.99%) even for the lower TiO_2 loading tested (0.1 g/L); increasing TiO_2 concentration to 0.75 g/L led to over 99.999% inactivation after 15 min contact time and this

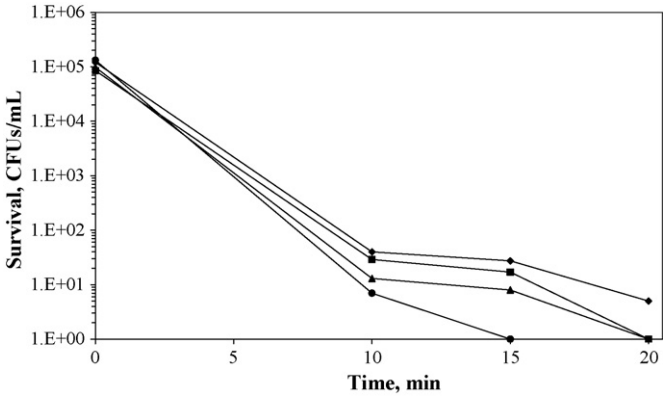

Fig. 3. Effect of Degussa P 25 loading on *E. coli* inactivation in water during UV-A/TiO_2/H_2O_2 treatment. (◆) 0.1 g/L; (■) 0.25 g/L; (▲) 0.5 g/L; (●) 0.75 g/L. [H_2O_2] = 25 mg/L.

became 100% after 20 min contact time (data not shown in Fig. 3 since the ordinate is in logarithmic scale). It should be borne in mind that according to current EU regulations *E. coli* population in water must be equal to zero. The above results are in agreement with previous literature reports stating that *E. coli* inactivation increased by increasing Degussa TiO_2 loadings in the range 0.025–1 g/L under solar simulated light in a batch photocatalytic reactor [36]. It was also found that above 1 g/L catalyst loading, *E. coli* inactivation reached a plateau attributed to weak light penetration into the bulk of the solution at these high catalyst loadings [36]. Such an effect was not observed in our experiments probably due to the fact that relatively low catalyst loadings were tested. However, even at these low catalysts loadings tested, *E. coli* photocatalytic inactivation was appreciably high.

3.1.5. Effect of hydrogen peroxide concentration

In further experiments, the effect of hydrogen peroxide concentration was also studied in the range 25–100 mg/L and the results are shown in Fig. 4. Increasing H_2O_2 concentration from 25 to 50 and finally to 100 mg/L had practically no effect on inactivation since, in all cases, destruction was 99.999% after 20 min contact time. Blank runs were also performed with H_2O_2 in the dark without catalyst showing no bacteria inactivation after 20 min contact time even at the higher hydrogen peroxide concentration employed.

3.2. Ultrasound disinfection of E. coli suspensions in sterile deionized water

In a final set of experiments, bacteria inactivation by means of US irradiation without and with H_2O_2 in the range 25–100 mg/L was investigated and the results are shown in Fig. 5. As can be seen, 92.3% inactivation was achieved after 120 min of irradiation at 24 kHz frequency and 160 W power without H_2O_2. Addition of 25–50 mg/L H_2O_2 positively influenced ultrasound-assisted *E. coli* inactivation leading to about 99.99% destruction after 120 min, with the corresponding blank runs without ultrasound yielding only 15–40% inactivation, respectively (data not shown).

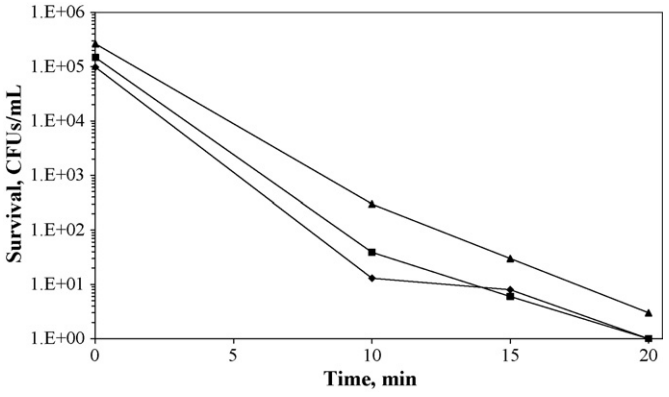

Fig. 4. Effect of H_2O_2 concentration on *E. coli* inactivation in water during UV-A/TiO_2/H_2O_2 treatment. (◆) 25 mg/L; (▲) 50 mg/L; (■) 100 mg/L. [Degussa TiO_2] = 0.5 g/L.

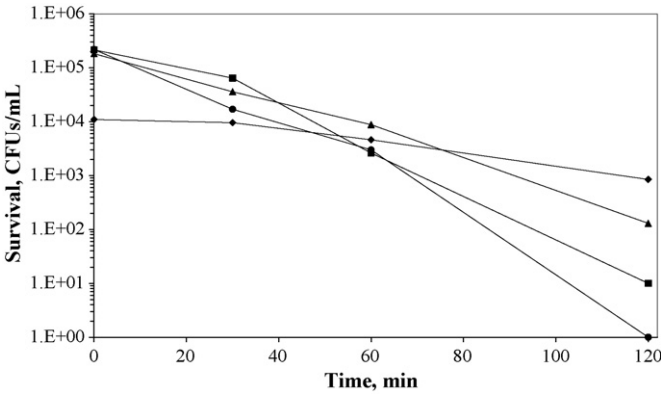

Fig. 5. *E. coli* inactivation in water by ultrasound irradiation (24 kHz, 160 W) at various H_2O_2 concentration. (◆) 0 mg/L; (■) 25 mg/L; (▲) 50 mg/L; (●) 100 mg/L.

At 100 mg/L H_2O_2 concentration, bacteria inactivation after 120 min contact time was 99.999% regardless whether ultrasound was used or not (data for the blank run not shown). Therefore, it may be concluded that ultrasound irradiation for prolonged periods of time and in the presence of high H_2O_2 dosages has practically no influence on H_2O_2 disinfection capacity.

Ultrasound is able to inactivate bacteria and de-agglomerate bacterial clusters through a number of physical, mechanical and chemical effects arising from acoustic cavitation, namely [29]: (i) chemical attack by the sonogenerated hydroxyl radicals, (ii) pressure and pressure gradients resulting from bubble collapse causing cell damage due to mechanical fatigue and (iii) shear forces induced by microstreaming occur within and consequently damage bacterial cells.

Nonetheless, as seen from Figs. 4 and 5 US/H_2O_2 is significantly less efficient than UV-A/TiO_2/H_2O_2 for *E. coli* destruction requiring far longer contact times for sufficient disinfection.

3.2.1. Wastewater disinfection

Ultraviolet irradiation (UV-A alone, UV-C alone and UV-A/TiO_2) was also employed to disinfect biologically treated effluents and the results, in terms of TCs inactivation over time, are shown in Fig. 6. UV-A irradiation for 60 min with and

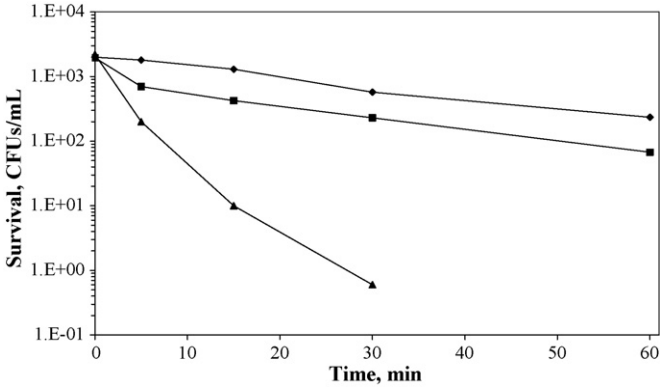

Fig. 6. TCs inactivation in wastewater by ultraviolet irradiation. (◆) UV-A alone; (■) UV-A/TiO_2; [TiO_2] = 0.25 g/L; (▲) UV-C alone.

Table 1
Extent of TCs destruction and 24 h regeneration following disinfection with various methods

Disinfection process	TCs destruction (%)	Regeneration[a] (%)
60 min UV-A	87.7	27.3
60 min UV-C	100	0
60 min UV-A/TiO_2	96.6	20.5
240 min UV-A/TiO_2	100	1.7
15 min (3 mg/L) chlorination + 5 min UV-C	99.7	2.4
5 min UV-C + 15 min (3 mg/L) chlorination	99.8	1.9
15 min (150 W, 80 kHz) US + 5 min UV-C	100	0
5 min UV-C + 15 min (150 W, 80 kHz) US	99.9	2.8
15 min (150 W, 80 kHz) US + 15 min (5 mg/L) chlorination	97.4	0.3
30 min (150 W, 80 kHz) US + 30 min (5 mg/L) chlorination	98.5	0.2

[a] Defined as number of surviving bacteria over their initial population.

without 0.25 g/L TiO_2 resulted in 96.6 and 87.7% inactivation, respectively; the experiment with the catalyst was repeated for prolonged periods of time leading to 99.99 and 100% bacteria kill after 120 and 240 min, respectively (data not shown in Fig. 6). Disinfection by UV-C proved to be substantially effective yielding 99.99 and 100% inactivation after 30 and 60 min contact time (data for 100% removal not shown in Fig. 6 since the ordinate is in logarithmic scale). Successful disinfection technologies should be capable of both inactivating rapidly bacterial populations and inflicting permanent damage, thus avoiding possible regeneration. In this view, samples taken 24 h after the end of the disinfection were re-analyzed with respect to the bacterial population that might have been regenerated and the results are summarized in Table 1.

UV-C irradiation imposed permanent damage as no bacteria regrowth was monitored after 24 h. On the other hand, UV-A irradiation for a short period of time (60 min with or without catalyst) led to partial reactivation; at prolonged treatment times though, practically no regeneration occurred.

In Chania WWTP (and elsewhere indeed), effluent disinfection is accomplished by means of chlorination. Typical operating conditions involve chlorination with NaOCl at a chlorine concentration of 5 mg/L for 30 min. To compare the efficiency of the aforementioned UV-based processes to that of chlorination, experiments were conducted at various chlorine concentrations and the results are shown in Fig. 7. Chlorination strongly depends on chlorine concentration yielding 62, 85, 91.2, 93.5 and 97.1% bacteria kill after 60 min at 1, 2, 3, 4 and 5 mg/L chlorine concentration, respectively. These results show that, at the conditions employed in this study, UV-based disinfection is at least equally effective to standard chlorination.

Coupling UV-C irradiation with chlorination may be beneficial in reducing treatment times needed for inactivation. As seen in Table 1, irradiation for 5 min followed or preceded by 15 min chlorination at a moderate chlorine concentration is capable of destroying bacteria completely and also minimizing regeneration.

In a final series of experiments it was decided to test ultrasound irradiation as a means of disinfection. Fig. 8 shows the effect of low frequency, high power ultrasound on TCs inactivation over time. US irradiation for 60 min resulted in 94.5 and 97.6% inactivation at 80 and 24 kHz frequency, respectively, and a constant power of 150 W. Increasing power to 450 W at 24 kHz led to 99.7% inactivation after 60 min.

Interestingly, at the conditions employed in this study, complete regeneration occurred 24 h after the ultrasound disinfection, thus implying that cell inactivation was temporary. In light of this, it appears that US irradiation has to be coupled to another process capable of inflicting permanent cell damage. As seen in Table 1, US irradiation alongside UV-C irradiation or chlorination can effectively inactivate TCs at short treatment times eliminating the chance for significant inactivation. In the

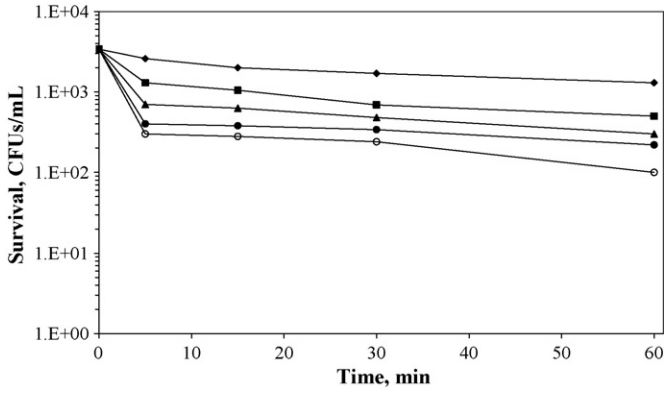

Fig. 7. Effect of chlorine concentration on TCs inactivation in wastewater. (◆) 1 mg/L; (■) 2 mg/L; (▲) 3 mg/L; (●) 4 mg/L; (○) 5 mg/L.

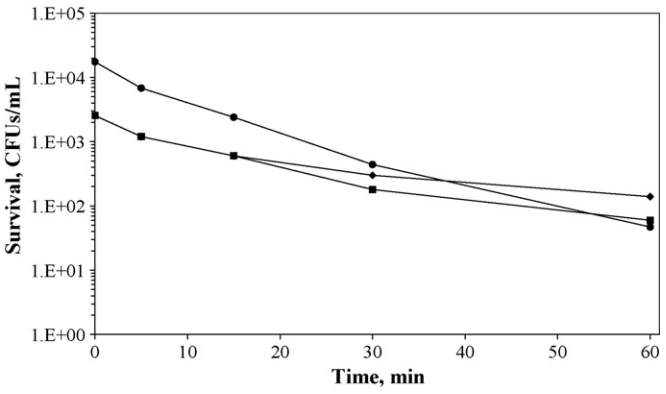

Fig. 8. TCs inactivation in wastewater by ultrasound irradiation. (◆) 80 kHz, 150 W; (■) 24 kHz, 150 W; (●) 24 kHz, 450 W.

case of combined US irradiation and chlorination (at 5 mg/L chlorine concentration), bacteria population still decreases 24 h after disinfection and this is presumably due to residual chlorine's ongoing action.

4. Conclusions

The conclusions drawn from this study can be summarized as follows:

(1) TiO_2 photocatalysis is capable of inactivating *E. coli* water suspensions at relatively short contact times. Photocatalytic inactivation in the presence of 0.5 g/L Degussa P 25 TiO_2 was 99.5% after 20 min contact time. Moreover, addition of H_2O_2 is beneficial to the photocatalytic inactivation of *E. coli*. In the presence of 0.5 g/L Degussa P 25 TiO_2 and 25 mg/L H_2O_2 inactivation was 99.999% after 20 min contact time.
(2) Increasing TiO_2 loading in the range 0.1–0.75 g/L results in increased *E. coli* inactivation. At 0.75 g/L TiO_2 complete removal of *E. coli* is observed at 20 min contact time. On the other hand, increasing H_2O_2 concentration in the range 25–100 mg/L has practically no effect on *E. coli* inactivation.
(3) Ultrasound irradiation is capable of inactivating *E. coli* bacteria but at longer contact times relative to TiO_2 photocatalysis. H_2O_2 positively influences sonolytic inactivation of *E. coli*.
(4) TiO_2 photocatalysis and sonolysis can inactivate TCs in a real wastewater but at long contact times. Photocatalysis in the presence of 0.25 g/L TiO_2 results in complete removal of TCs after 240 min contact time and insignificant regeneration after 24 h, while ultrasound irradiation (24 kHz, 450 W) leads to 99.7% inactivation after 60 min and almost complete regeneration after 24 h.
(5) Disinfection by UV-C is very effective yielding 100% inactivation after 60 min contact time and no regeneration of TCs after 24 h.
(6) Coupling ultrasound with UV-C irradiation results in complete removal of TCs after 30 min contact time and no regeneration after 24 h.

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